A Journey in Noble Gas Cosmochemistry and Geochemistry

Geochemical Perspectives

About the cover
Edwin Aldrin is setting up the aluminum foil of the Solar Wind Composition experiment (SWC) during the first manned lunar landing in 1969. The Genesis mission depicted on the top right later collected solar wind ions during more than two years. The Sun in the background was pictured by the Solar Dynamics Observatory in extreme UV light during a large solar flare. ALL IMAGES COURTESY OF NASA.

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DEDICATION

For Catherine

*with whom I share my life since my graduate student days
and whose love, inspiration and support I could not be without.*

PREFACE

A few years ago, Janne Blichert-Toft asked me to review a manuscript by Bernard Marty that became a volume of *Geochemical Perspectives,* describing his career and the contributions of his group at the CRPG in Nancy to the geochemistry of the "atmophile" elements H, C, N, and the noble gases (Marty, 2020). I very much enjoyed this reviewing task. It allowed me to get even better insight into the career and scientific life of a good friend, including all the facets that usually are not visible in normal scientific writings. When Janne then asked me if I would consider writing a similar account of my own scientific life, I was a bit hesitant at first, as this would already be the third contribution on noble gases in this series. In addition to Bernard Marty's *Geochemical Perspectives*, Manuel Moreira from the Institut de Physique du Globe in Paris had already given an account of his career in 2013 (Moreira, 2013). However, I soon convinced myself that all the personal aspects of our work indeed are too rarely reflected in our publications, including review articles and textbooks. *Geochemical Perspectives* provides an ideal venue for that and, in fact, has been conceived for exactly that purpose. So I set to work, knowing – but largely ignoring – that this would mean lots and lots of work. As it turned out, it was much more than I could possibly have imagined. One of my goals was to show how much of my life was not really planned but depended on luck and support from my mentors and many other people I came across during my career. I hope it becomes clear from these pages that trying to give back some of this guidance and support to my own students has been among the most rewarding aspects of my life and has led to often long lasting friendships, some of which are reflected in the pictures of this volume. Making new friends

has, of course, also been a most important aspect of my many collaborations all over the world, not least in competition with others or even in cases of scientific controversy. Probably this is one of the greatest privileges we have as scientists.

Looking back on the past almost half century, writing this memoir brought up many memories as well as surprises, which was one of the most gratifying aspects of this endeavour. Here is just one example among many that will become evident in the following pages: while I believed I was quite familiar with the history of studies of noble gases in "gas-rich" meteorites in the early 1960s, in this writing I was reminded, to my surprise, that when I began my doctoral work in the mid-1970s, the conviction that noble gases in gas-rich meteorites originate from the solar wind was by then only about 10 years old.

I have tried to avoid too much technical jargon. A list of acronyms is given at the end, prior to the index.

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ACKNOWLEDGEMENTS

As is probably the case with almost every scientist, my path has been shaped by numerous colleagues, mentors and students. First I would like to highlight six persons who have been particularly important to me along the way.

Peter Signer was by far the most important and influential person in my scientific life. His attitude as my supervisor during my graduate studies is aptly described with the German word "Doktorvater": guidance when necessary, always with the goals in mind, but with plenty freedom to achieve these goals. He also shaped my later scientific life, as postdoc, as permanent staff member and finally as his successor to lead the noble gas group at ETH. He was a scientist in the best sense, with fairness and honesty being very important, certainly influenced by his mentor Alfred O. Nier in Minneapolis, whom he deeply admired.

Alex Halliday brought the "Think Big" spirit to our group. When one morning in 1998 he presented us with the extremely ambitious proposal he was about to submit to the President of ETH for his endowment as the new professor of Isotope Geology at ETH, we only hoped that his disappointment after the meeting would be contained. When we met again for lunch, he had negotiated about ninety percent of what he had requested and he seemed much less surprised by this than I was. This allowed, among other things, a large increase of the noble gas laboratory and a significant expansion of our operations. All the new people Alex hired also helped me to significantly broaden my own scientific interests as explained in the main text.

With *Heinrich Baur* I have worked for longer than I did with anyone else. Heiri was a doctoral student in Peter Signer's group when I started in 1976, and we remained in the same team until Heiri's retirement in 2010. To this day we meet more or less regularly in the lab or the office. From Heiri I learned more about everything related to noble gas mass spectrometry than from anyone else, from ion optics to data reduction, from vacuum pumps to noble gas purification, from gas calibration to mass fractionation, and much more. "Ask Heiri" was common advice whenever one of us had a problem that his or her colleague could not answer. With his great modesty but always clear opinions, Heiri was the soul of our laboratory.

Christian Schlüchter has been instrumental in expanding our team's science agenda from cosmochemistry to geomorphology. Christian is what he looks like, a role model of a field geologist. He is a premier expert in glacial geology, with a great ability to recognise first order problems in geomorphology and palaeoclimate research that can be studied with cosmogenic nuclides. This has led to five doctoral theses that I had the privilege to supervise with Christian. His enthusiasm is contagious, and I am pleased that he refers to surface exposure dating with cosmogenic nuclides as the highlight of his career. Christian was also an important link between the noble gas group and the AMS laboratory at ETH.

Rolf Kipfer (RoKi) is leading research activities on noble gases in waters at Eawag/ETH since more than 20 years. After his doctoral thesis in the late 1980's in our group, he moved to Eawag, a few kilometres away, but his and his group's noble gas analytical activities remain in our lab. RoKi is a character you will not easily forget, outspoken, hardly ever shy to let you know his opinion and very dedicated to his science. His group's activities have become an important additional pillar of our laboratory. Here I focus only on projects in which I had the pleasure of being scientifically involved, which included co-supervision of several doctoral students.

Henner Busemann became my first doctoral student as principal supervisor in 1994. After his graduation, he embarked on a scientific journey halfway around the world before returning to ETH in 2014, but throughout all these years we continued to collaborate. Henner's expertise in meteoritic organic matter acquired at the Carnegie Institution in Washington DC became particularly important, a subject in which I'm not at all an expert. In 2014, when I retired, Henner took over the leadership of the noble gas group at ETH, continuing what Peter Signer had started almost 50 years earlier.

Among all the many other colleagues and friends who have shaped my path, let me mention first those external to our own research team at ETH, before – last, but of course by far not least – I would like to thank all colleagues and friends from ETH, many of which, of course, also participated in the studies with external colleagues.

Being a member of Don Burnett's Genesis Science Team for more than two decades has been one of the best and most important facets of my scientific activities. Don's enthusiasm and phenomenal knowledge of the opportunities

and problems of each group in the science team, as well as the incredible composure with which he accepted the hard landing of the sample capsule impressed us all greatly. Among the more than 100 members of (or related to) the Genesis science team I can only name a few who were particularly important for the work of our own group: Judy Allton, Richard Becker, Peter Bochsler, Fritz Bühler, Sarah Crowther, Johannes Geiss, Jamie Gilmour, Yunbin Guan, Amy Jurewicz, Bernard Marty, Kevin McKeegan, Martin Laming, Alex Meshik, Chad Olinger, Bob Pepin, Dan Reisenfeld, Karen Rieck, Roger Wiens, and Robert Wimmer-Schweingruber.

The numerous projects on cosmogenic nuclides in extraterrestrial and terrestrial samples particularly relied on collaborative efforts, as they often crucially depended on radionuclide measurements and other expertise not readily available in our group, like modelling, field expertise, *etc.* First I would like to thank Uli Herpers, Rolf Michel, and Rolf Sarafin who triggered my interest in cosmogenic nuclides. The AMS team at ETH Zürich also was crucial for our cosmogenic nuclide studies, in particular Vasily Alfimov, Georges Bonani, Marcus Christl, Susan Ivy-Ochs, Peter Kubik, Martin Suter, Arno Synal, Lukas Wacker, and Willy Wölfli. The many others with whom I worked on cosmogenic nuclides include Carlo Baroni, Jürg Beer, Marc Caffee, Luigia Di Nicola, Tibor Dunai, Gregory Herzog, Tim Jull, Nat Lifton, Kurt Marti, Jozef Masarik, Kuni Nishiizumi, Gérard Poupeau, Bob Reedy, Fritz Schlunegger, Reto Trappitsch, and Kees Welten.

I much enjoyed the hospitality in Charles Hohenberg's lab and the great atmosphere on the fourth floor in Bob Walker's McDonnell Center during my visits at Washington University in St. Louis. Karl (Charly) Kehm and Alex Meshik provided great assistance for my noble gas analyses on single grains. I also much enjoyed the long standing friendly controversy with Charles and Marc Caffee about evidence, or not, for an early active Sun found, or not, in the noble gas records in meteorites.

Birger Schmitz introduced us to the world of fossil meteorites and micro-meteorites. He never hesitated to express unconventional ideas and I am very happy that he approached us with the seemingly rather crazy idea to search for cosmogenic noble gases in tiny chromite grains from otherwise diagenetically altered meteorites. Mario Tassinari and the owners and workers at the Thorsberg quarry also were crucial for the success of this long lasting collaboration.

Bernard Marty kindly offered me the opportunity to measure nitrogen isotopes in single lunar regolith grains in Nancy, data that became key in the discussion about the lunar nitrogen conundrum. I very much enjoyed assistance in the lab by Frank Humbert and Laurent Zimmermann and many discussions with Pete Burnard and Marc Chaussidon. I also much appreciated later discussions and collaborations with the CRPG team, in particular with Guillaume Avice, Evelyn Füri, Ko Hashizume, Yves Marrocchi, and Reika Yokochi.

With Philipp Heck in Chicago and his team, in particular Levke Kööp and Jennika Greer, I have much enjoyed many fruitful collaborations long after Philipp's graduation in Zürich, mainly on single presolar grains, early solar system condensates, and lunar grains. I also greatly profited from the many joint projects with Addi Bischoff, Christoph Burkhardt, Thorsten Kleine, Thomas Kruijer and Knut Metzler at the University of Münster.

Paul Steinhardt and Luca Bindi taught us that no material is too exotic to be extraterrestrial, and that every effort is warranted to find more of it.

Jürgen Nauber is a constant source of interesting meteorite samples for research and also generously lends some of his most beautiful meteorites for the Focus Terra exhibition at ETH.

Thanks to the efforts by Colin Pillinger, Georg Delisle, and Mario Zucchelli I could share a unique adventure in Antarctica with my colleagues in the field Ian Franchi, Luigi Pedrolini and Antonio Rossi. Ali Al-Kathiri, Edwin Gnos, and Beda Hofmann gave me the opportunity to also search for meteorites in a hot desert, in the framework of the Omani-Swiss meteorite search programme.

With Editors Tim Jull, Frank Podosek and Derek Sears I had the great pleasure to work as Associate Editor of the two journals *Meteoritics/Meteoritics and Planetary Science* and *Geochimica et Cosmochimica Acta*. I also appreciate the efforts by Agnieszka Baier in the MAPS office and the numerous reviewers that helped me in this task. With Don Porcelli and Chris Ballentine I shared the adventure of editing the book *Noble Gases in Geochemistry and Cosmochemistry* in the series *Reviews in Mineralogy and Geochemistry*. Many thanks also to the authors who contributed to this book as well as Series editors Paul Ribbe and Jodi Rosso.

Paul Beattie of Cambridge Publications, Valentina Müller-Weckerle and very dedicated teams from ETH and other institutions were essential for the success of the 2002 Goldschmidt Meeting in Davos and the 2006 Annual Meeting of the Meteoritical Society in Zürich, respectively.

I greatly enjoyed the hospitality of the research teams of He Huaiyu during several visits at the Institute of Geology and Geophysics at the Chinese Academy of Sciences in Beijing and Miao Bingkui at the University of Technology in Guilin.

Throughout my career I profited much from the expertise and numerous discussions with Sachiko Amari, Edward Anders, Eric Asphaug, Richard Becker, Friedrich Begemann, Willy Benz, Peter Bochsler, Eric Feigelson, Dominik Fleitmann, Frank Gyngard, Tony Irving, John Kerridge, Bernard Lavielle, Roy Lewis, Bernard Marty, Richard Mewaldt, Larry Nyquist, Uli Ott, Minoru Ozima, Herbert Palme, Paul Pellas, Bob Pepin, Frank Podosek, Jim Ray, Andreas Reufer, Ludolf Schultz, Finley Stuart, Igor Tolstikhin, Igor Villa, Hisayoshi Yurimoto, and Ernst Zinner. My apologies to the many others not mentioned explicitly.

Most important for my career were all my colleagues and friends in Zürich. I had a good start back in 1976 thanks to my peers Heiri Baur, Philippe Etique, Herbert Funk, Hajo Knab, and Peter Horn.

A JOURNEY IN NOBLE GAS COSMOCHEMISTRY AND GEOCHEMISTRY

ABSTRACT

I started my journey in science by studying noble gases implanted by the solar wind in dust grains on the surface of the Moon, and with many colleagues I have studied solar wind implanted noble gases in natural and artificial samples throughout my career, the latter exposed primarily by the Genesis space mission. Major questions are what noble gases in the solar wind can tell us about the present and the past Sun, and how they can contribute to understanding the formation and history of the planets and their building blocks, represented, for example, by meteorites. Since my early years as a postdoc, I have also been interested in noble gases (and radioactive nuclides) produced in meteorites and other extraterrestrial samples by interactions with energetic elementary particles from galactic cosmic radiation (and the Sun). These so called "cosmogenic" nuclides allow us to study the transport of meteorites to Earth, and the dynamics of the top surface layers ("regoliths") on the Moon, asteroids, and comets. Cosmogenic noble gases are also crucial for studying even more exotic topics such as the history of tiny presolar grains that formed in the cooling envelopes of earlier generations of stars towards the end of their lives and were eventually incorporated into the meteoritic matter where they are found today. Cosmogenic noble

gases in some tiny phases in meteorites are also likely tracers of our highly active Sun at a very early stage in its history. A few years later, I started my third major research topic in cosmochemistry, the study of primordial noble gases in meteorites and other extraterrestrial samples. These noble gases were incorporated into meteorites or their precursors in the early solar system or even in a presolar environment. I also participated in studies by colleagues of isotopic anomalies of other elements important in cosmochemistry, my expertise being mainly in aspects of the influence of cosmic rays on these elements.

Although working in an Earth Science institution, it took quite a while before I started to also study noble gases (and radionuclides) in terrestrial samples. This is described in the second part of this contribution. A major focus was on cosmogenic noble gases and radionuclides produced in samples near the Earth's surface. Although production rates of cosmogenic nuclides on Earth are several orders of magnitude lower than in space, making their analysis more challenging, they have become an important tool in geomorphology. Because stable noble gas nuclides are particularly well suited to the study of ancient landscapes, much of our work focused on areas with arid climates, such as Antarctica and the Andes in Chile, in collaboration with geoscience colleagues. We also participated in the large multinational CRONUS collaboration, funded by the European Union, a community effort to improve our knowledge of nuclide production rates at the Earth's surface. In another major collaboration with external colleagues we are involved in noble gas analyses of water samples, ranging from lakes to aquifers to tiny inclusions in stalagmites. This research focuses on studying lake and groundwater dynamics, including contributions of mantle-derived noble gases such as in volcanic lakes. Atmospheric noble gases dissolved in suitable samples are also palaeotemperature indicators, supplementing information from other proxies such as oxygen isotopes.

PART I: RESEARCH IN COSMOCHEMISTRY

1. HOW – RATHER FORTUITOUSLY – I BECAME A NOBLE GAS COSMOCHEMIST

On January 3rd, 1976, I returned to Switzerland after a 15 month sojourn in South America, mostly spent in Guayaquil, Ecuador, but also by traveling around the continent, including an unforgettable trip to the Galapagos Islands. Two and a half years earlier, I had obtained my diploma in Physics (today we would call this a Master's degree) at the Swiss Federal Institute of Technology in Zürich (known to everybody as ETH Zürich). My diploma thesis was on a topic in infrared spectroscopy. After that, I felt the need to broaden my horizons, so I took a two semester *Interdisciplinary Postgraduate Course on Problems in Developing Countries*, again at ETH. This included a work experience in Ecuador, where I did programming work in a company planning a dam for irrigation and hydroelectric power generation. I was always a bit sceptical whether what I did made much sense, but the engineers in Guayaquil seemed happy with my work and asked me to continue a few months beyond the official internship.

Back in Switzerland, I had to start thinking about my future, which thus far I never had done really seriously. I first requested documentation from the International Committee of the Red Cross in Geneva for possible positions abroad, but did not apply. I also looked at the Institute of Photography at ETH, which offered a position for a doctoral student, but I did not apply there either. Yet, less than a month after my return, on February 1st, 1976, I began the work that I do to this day and that has shaped my life: I became a doctoral student

in Peter Signer's noble gas laboratory at the Earth Science Department at ETH. How did this happen so quickly?

In the gymnasium (more or less the equivalent to high school level in the UK or the US) I had developed a fairly serious interest in physics, quite different from chemistry, which I never really liked. My decision to study physics was therefore pretty straightforward, and it was also clear to me that I should do this in Zürich, close to the place where I grew up and continued to live with my parents. At ETH I developed a certain interest in astronomy, though without being able to claim that this shaped my path to the exploration of the solar system with meteorites.

This path I encountered much more fortuitously. Christoph Schuler, a friend from my student days, was about to finish his diploma thesis at the isotope laboratories of the ETH Earth Sciences. He informed me that in Peter Signer's group a graduate student named Urs Frick had just finished his dissertation and joined John Reynolds' team at the University of California in Berkeley. I imme-diately called Peter (Professor Signer at the time, of course) and was invited to visit a day or two later. My soon colleagues to be, Heiri Baur, Herbert Funk, and Philippe Etique, first showed me the lab, which left me terribly impressed. In particular, the mass spectrometers and gas extraction lines with all their piping looked so confusing that I became hesitant about ever being able to operate any of them myself. But Peter Signer's competent and friendly manner convinced me. YES, I would want to study noble gases in lunar samples. A few days later Peter informed me that I would be accepted, and so it was that I became a doctoral student in his group (note that ETH does not award PhD degrees but Doctoral degrees, so there are no PhD students at ETH).

Apart from the obviously good ambiance in Peter Signer's group, there was another even more compelling reason for my choice. Peter had explained to me the group's programme of studying noble gases from the solar wind implanted in lunar samples. *Wow*, to work with real matter from the Moon, brought back just a few years earlier between 1969 and 1972 by the Apollo 11 astronauts and their later colleagues! And, "solar wind" meant something special to me. Neil Armstrong and Buzz Aldrin had not only collected lunar dust and rocks, but, more importantly for a young Swiss scientist, had also exposed a piece of aluminum foil to the solar wind for 77 minutes to collect noble gases (Geiss *et al.*, 2004). Johannes Geiss at the University of Bern had convinced NASA to carry this foil on board the Apollo 11 as one of only three scientific experiments! This made Johannes the most famous scientist in Switzerland at the time and was the reason why I knew that something called solar wind existed. Seven years later the prospect of being able to work on precisely this topic made it clear: YES, this is what I want to do. Only later did I learn that Peter Signer actually had been the first to propose an experiment to trap solar wind noble gases in a foil exposed in space beyond Earth's magnetosphere. He and his colleagues in Bern suggested

that this might be done on a mission in preparation of the lunar landings or on the Moon itself (Signer *et al.*, 1965), an idea eventually realised by Geiss and his team (see Section 2.2).

So, less than a month after my return from South America, I started my life as a doctoral student in Peter Signer's noble gas laboratory among my fellow scientists Heiri Baur, Uwe Derksen, Philippe Etique, Herbert Funk, and
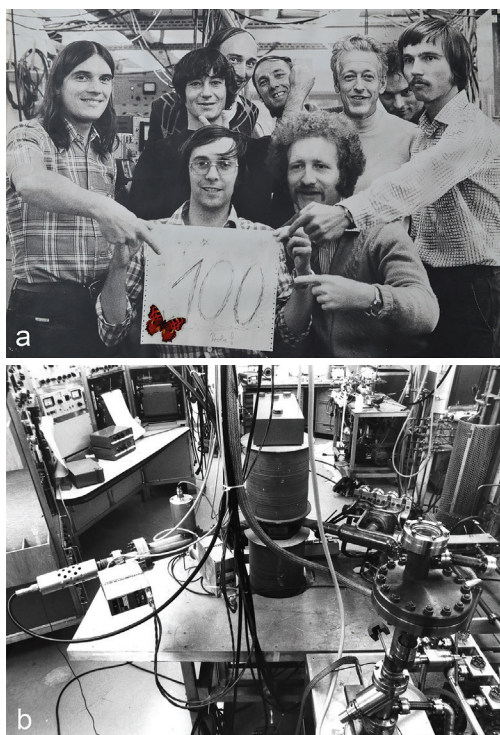
Peter Horn. Figure 1.1 shows us celebrating the analysis of the 100th lunar sample with the then new noble gas extraction line conceived by Urs Frick. The figure also shows one of the two mass spectrometers we used back in the 1970s. They had been brought to Zürich by Peter Signer from Al Nier's laboratory in Minneapolis, where Peter had spent seven years. The sector field mass spectrometers designed by Alfred O. C. Nier, the "father of modern mass spectrometry", enabled new fields of science such as geochronology, isotope geochemistry, and many more (De Laeter and Kurz, 2006). I remember a visit of Al Nier in Zürich on his way to a ski holiday in the Alps. Like probably everyone else who was fortunate enough to meet Al, I was very impressed by his kindness and the genuine interest he showed in my work as a young graduate student. As do really great scientists, he made me feel as if we were speaking at eye level.

Section 2 is devoted to studies of "solar" noble gases, mainly those implanted by the solar wind in lunar and meteorite samples and artificial targets exposed by the Genesis space mission between 2002 and 2004. My own work and that of many of my closest collaborators, including students and postdocs, spans a long period of time, from the start of my doctoral thesis in 1976 until well after my formal retirement in 2014. I will start with some solar noble gas basics and a few historical reminiscences.

2. NOBLE GASES FROM THE SUN

2.1 Fundamentals of Noble Gas Cosmochemistry – The Sun

The importance of noble gases in the Earth and Planetary sciences has been excellently explained in two previous volumes of the *Geochemical Perspectives* series by Manuel Moreira and Bernard Marty (Moreira, 2013; Marty, 2020). As Manuel explains, they are geochemical tracers *par excellence* because they are chemically (almost) inert and thus unaltered by chemical and biological reactions. They are also exceedingly rare in planetary environments, hence tiny additions from a wide variety of processes can be recognised much more easily than for other elements. As Bernard explains, noble gases are also important for understanding the geochemical cycles of other volatiles, including nitrogen and carbon, making them excellent tools to study geological and geochemical processes throughout the history of the Earth and the Solar system. I will come back to some of these topics. To begin with, I will focus on our home star, sketching the early history of analyses of samples containing noble gases from the Sun.

Knowing the abundances of the elements in the Sun is of paramount importance for geo- and cosmochemistry (Palme, 2018). The Sun contains more than 99.8 % of the mass of the solar system and is therefore representative of the composition of the material from which the planets and their building blocks formed. Today, the abundances of most elements in the Sun can be determined by the strength of characteristic absorption lines in the spectrum of the solar photosphere, *i.e.* the thin surface layer from which we receive the Sun's light (Asplund *et al.*, 2021). However, already in the 1920s and 1930s, Victor Moritz Goldschmidt used stony meteorite data to tabulate "cosmic" abundances of the elements, recognising that – unlike the Earth – many meteorites were not affected by melting and crystallisation. Indeed, it is one of the most remarkable facts in cosmochemistry that, for most elements, the abundances in one particular and extremely rare class of meteorites, the CI chondrites, agree spectacularly well with modern spectroscopically-derived photospheric values (Lodders, 2020; Fig. 2.1). CI chondrites are very friable and therefore only very rarely survive passage through the Earth's atmosphere, but their parent bodies are not rare in the (outer) asteroid belt, as indicated by reflectance spectroscopy (DeMeo and Carry, 2013) and recently also by the Hayabusa 2 and Osiris Rex missions to the asteroids Ryugu and Bennu. Therefore, the asteroid belt hosts material which has conserved the elemental composition of the solar nebula, the disk of gas and dust from which the Sun and planets of our solar system formed.
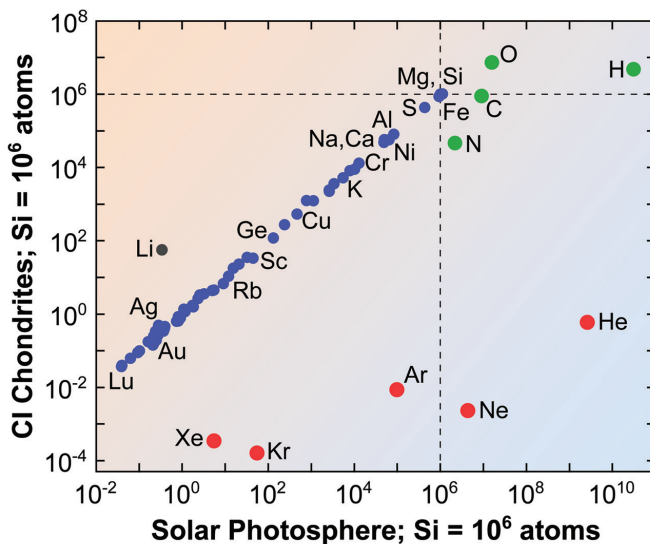
Element abundances in CI chondrites *versus* those measured (or in a few cases inferred) in the solar photosphere. On both axes, element abundances are normalised to $Si = 10^6$ atoms. For elements falling on the array between Lu and Mg (blue dots, only selected elements labelled), the CI and photospheric abundances agree mostly to within better than 10 – 20 %. Lithium is rare in the Sun because it has been consumed by nuclear burning. The noble gases and a few other highly volatile elements (H, C, N, O) are depleted in CI chondrites as well as in all other meteorite classes. Figure adapted from Lodders (2020).

While ultimately our preferred values for solar element abundances should be based on measurements relating directly to the Sun, the CI abundances are often used as a proxy by cosmochemists because for many elements they are more precise than the spectroscopic abundances. However, for a few elements this does not work, as is shown in Figure 2.1. Notably, noble gas abundances in CI chondrites (as well as in any other meteorite class) are many orders of magnitude below their values in the Sun. Also the abundances of H, C, N, and O, which occur mainly in highly volatile forms in the nebula, are depleted in CI chondrites relative to solar values. Actually, Figure 2.1 is slightly deceptive, since the solar noble gas abundances on the abscissa are not actual measured values in the photosphere. Noble gases do not produce absorption lines in the solar photospheric spectrum because energies of the relevant atomic transitions are not reached at the temperature of the photosphere (He was discovered in the Sun, but in the spectrum of the hotter chromosphere during an eclipse). Therefore, other means are required to estimate the noble gas abundances in the Sun. Knowing the isotopic composition of the noble gases in the Sun is also crucial for geo- and cosmochemistry, because – unlike most other elements – the

tiny amounts of noble gases in meteorites are not representative of the solar isotopic abundances. As we will see in Section 2.5.5, this also holds for oxygen and nitrogen, which became the two highest priority elements for the Genesis mission that collected solar wind atoms for analyses in terrestrial laboratories (Section 2.5.5).

What are the possibilities for determining noble gas elemental and isotopic abundances in the Sun? Helium is a special case. It is the second most abundant element in the Sun after hydrogen, accounting for almost a quarter of the Sun's mass (compared to ~74 % for H and a meager ~1.5 % for all elements heavier than He). Because the fusion of hydrogen to ^{4}He is the Sun's energy source, solar modelling allows for an accurate estimation of the Sun's He abundance by fitting the models to the Sun's luminosity. In addition, the Sun is an oscillating ball of gas, and these seismic oscillations provide an accurate He abundance in the Sun's outer convective zone (the outermost nearly 30 % of the solar radius, which is also relevant for the He abundance in the solar wind). The current best value for the He abundance in the outer convective zone provided by so called helioseismology is ~24.7 % (Basu and Antia, 1995). This is about 10 % less than the initial solar He abundance obtained from solar models, *i.e.* the abundance 4.6 Ga ago before the onset of fusion of hydrogen into helium in the Sun's core. This indicates a certain amount of gravitational settling of He (and heavier elements) from the solar surface region towards its interior.

The isotopic composition of the noble gases in the Sun can be reliably deduced by studying the solar wind, as discussed below. However, the solar wind is not a very good candidate for obtaining elemental abundances because the noble gas abundances in the solar wind do not perfectly represent the unaltered photospheric abundances. Understanding the relevant fractionation processes is a major topic in solar physics but requires independent estimates of the abundances in the solar wind source region. For Kr and Xe this can be done by interpolating between the CI chondritic abundances of elements and nuclides with neighbouring mass. The modern understanding of stellar nucleosynthesis (how elements are formed in stars) helps to select particularly well suited nuclides for such interpolations. Modern estimates for Kr and Xe often rely on models of the slow-neutron capture process ("s-process") that operates in evolved low to intermediate mass stars (Lodders, 2020). For Ne and Ar, interpolations are less reliable and their abundances in the Sun are therefore, *e.g.*, inferred from values obtained spectroscopically in much hotter stars, in particular B-type dwarfs whose abundances of other elements are similar to those of the Sun (Lodders, 2020).

2.2 The Solar Wind – a Cosmochemist's Perspective

The solar wind (SW) is a continuous stream of charged particles emitted from the Sun's outer atmosphere, the chromosphere and the corona. The solar wind as a concept was postulated by Ludwig Biermann in 1951 to explain why comet

tails always point away from the Sun (Biermann, 1951; Parker, 1958). It consists of electrons, protons (hydrogen nuclei), and ions of all other elements present in the Sun. Solar wind ions have speeds in the range of ~200–800 km/s, with an average flux near the Earth's orbit of about 2×10^8 protons/(cm$^2 \times$ s). The solar wind is intensively studied by solar physicists, often with *in situ* analyses by spacecraft, for example the Solar and Heliospheric Observatory (SOHO). An improved understanding of the solar wind is also a major goal of the Parker Solar Probe, named in honour of Eugene N. Parker, the visionary heliophysicist. In the years to come, this spacecraft will make multiple flybys much closer to the Sun than any previous mission (*e.g.*, Kasper *et al.*, 2021). Determining elemental and, in a few cases, isotopic compositions of the solar wind are only one of many goals of such missions. Mass spectrometers in space can distinguish compositional differences as a function of solar wind speed and other parameters such as different phases in the 11 year solar cycle. Some space missions also measure so called solar energetic particles, ions ejected from the Sun with much higher energies than the solar wind but with much lower fluxes (Reames, 2018). A few additional details of the physics of the solar wind are mentioned in Section 2.5.5 which is devoted to the Genesis mission. While data obtained *in situ* allow the solar physics community to obtain an ever better understanding of the Sun, even the newest generations of space borne mass spectrometers often do not provide elemental and isotopic composition data precise enough to be truly useful for cosmochemists. This is no wonder since the fluxes of heavier elements are much lower than the proton flux, scaling approximately with their abundance ratio to hydrogen. The Ar flux in the solar wind, for example, is about 300,000 times lower by number than the proton flux.

For cosmochemical purposes, a much larger number of solar wind atoms need to be analysed than is possible in space. The way to do this is by analysing in terrestrial laboratories samples that were directly exposed to the solar wind. Solar wind ions with energies on the order of one keV *per* nucleon are implanted several tens of nanometres deep into solid matter, sufficient to trap them securely. Suitable artificial samples are the aluminum foils exposed on the Moon by the Apollo astronauts and the ultraclean targets of the Genesis mission (Burnett and Genesis Science Team, 2011). The other possibility are natural samples exposed to the solar wind at the surface of atmosphere-less bodies like the lunar or asteroidal regoliths. With a few exceptions, from the solar wind only noble gases can be detected in natural samples, because for other elements the relative amounts added by the solar wind are too small. The ultrapure Genesis targets, on the other hand, allow for the analysis of a number of elements that is competitive with what mass spectrometers in space can provide but do so at higher accuracies.
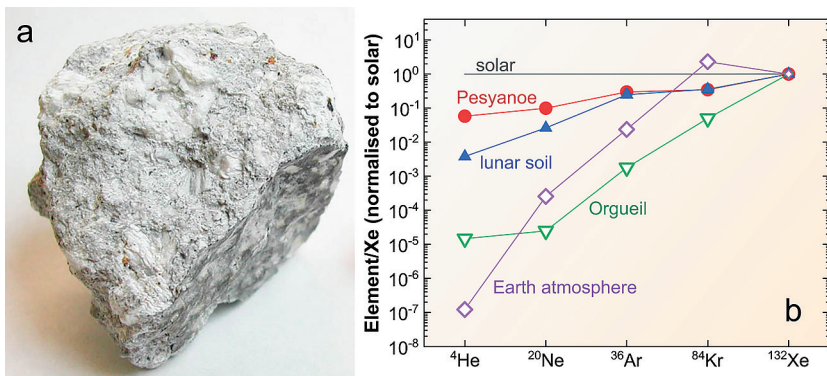
Figure 2.2 **(a)** The Pesyanoe enstatite achondrite (aubrite) fell in 1933 in the Soviet Union, a few hundred km east of Chelyabinsk. It is the first meteorite in which noble gases implanted by the solar wind were detected (Gerling and Levskii, 1956). Remarkably, Pesyanoe is to date the only solar gas-rich meteorite for which a solar wind contribution to the heaviest noble gas Xe can be reliably detected (Marti, 1969). In all other meteorites studied solar wind Xe is swamped by primordial Xe. Picture courtesy of Martin Horejsi. **(b)** Typical examples of noble gas abundances in meteorites and lunar regolith samples, normalised to Xe and solar abundances (Fig. 2.1). Note that for Ar the isotope ^{36}Ar is shown rather than the radiogenic ^{40}Ar. Signer and Suess (1963) distinguished between "solar" and "planetary" abundance patterns, represented here by the Pesyanoe meteorite and lunar soils on the one hand and the CI chondrite Orgueil on the other. Trapped solar wind noble gases in extraterrestrial samples are also depleted in the light noble gases relative to solar values, but the depletion is much less pronounced than for the "planetary" gases, whose abundances roughly compare to those in the terrestrial atmosphere. Although the term "planetary" gases is still used by some, it is now mostly avoided because the noble gas pattern of the terrestrial atmosphere (and those of Mars and Venus) and that of the primordial noble gases represented here by Orgueil are not directly related.

Around 1960, the first analyses of implanted solar wind noble gases in several meteorites were reported by laboratories in the Soviet Union and Germany (Gerling and Levskii, 1956; Zähringer and Gentner, 1960; Fig. 2.2). However, the exceptionally high concentrations, especially of the light noble gases He and Ne, were not immediately recognised as being of solar wind origin. They were initially referred to as "Uredelgase" or "primordial" noble gases. A first step towards the recognition of the solar wind origin of this component was made by Signer and Suess (1963), who distinguished two primordial noble gas components in different meteorites (Fig. 2.2b). One component has elemental abundances roughly similar to those expected for the Sun, while in the other the lighter gases are strongly depleted relative to Kr and Xe and expected solar abundances. Signer and Suess termed the first component "solar", and the meteorites with sometimes orders of magnitude higher concentrations of He, Ne, and Ar than their non-gas-rich counterparts became known as "gas-rich" meteorites.

Notably, Signer and Suess (1963) deliberately omitted the vague term "primordial noble gases" for the gas-rich component to avoid the appearance that it is necessarily associated with the early history of the solar system. Because the second component had abundance patterns somewhat resembling those of the terrestrial atmosphere, Signer and Suess called it "planetary". While this name was a perfectly reasonable choice at the time, it later caused confusion when it was realised that the noble gas abundance patterns of "planetary" gases in meteorites have no direct relevance to the Earth's atmosphere. As explained in Section 3.2, at least some "planetary" gas components are carried by presolar grains, hence predate the solar system.

In a next step, Suess *et al.* (1964) proposed that the "solar" component of Signer and Suess indeed represents noble gases from the Sun, implanted by the solar wind into grains on the surface of larger bodies. In particular, they speculated that cometary nuclei might be covered with chondritic material of a "sandbank-like" structure. The comets' interior ices would carry trapped noble gases in "planetary" proportions, whereas the grains in the sandy surface regions would have trapped the solar wind. Gas-rich meteorites often show a distinct dark-light pattern, with only the dark portions containing solar noble gases (Suess *et al.*, 1964). Eberhardt *et al.* (1965) provided further strong evidence for an origin of the solar component by ion implantation. Noble gas concentrations in the dark portions of the aubrite Khor Temiki negatively correlate with grain size, *i.e.* they are proportional to the surface-to-volume ratio of the grains, and gas concentrations in grain size separates etched to varying degrees progressively decrease. As an important detail, this did not hold for the isotopes ^{3}He and ^{21}Ne, which are mainly produced by cosmic ray interactions throughout the entire grain volumes. In an influential review paper, Pepin and Signer (1965) stated that the "planetary" component represents "a residue of primeval gases [occurring in the solar nebula very early in the history of the solar system] modified to varying degrees by diffusive loss", while the "solar" component represents a relatively late addition from the solar wind.

Hence, thanks to the noble gas pioneers, by 1965 it became accepted that meteorites would allow us to study matter from the Sun directly in our laboratories. Since the Sun constitutes the vast majority of matter in the solar system, this is obviously particularly important not only for noble gases but also for other elements, like O and N, whose elemental and/or isotopic abundances can neither be directly measured nor inferred from meteorites. Trapped solar wind in extraterrestrial samples also allows us, in principle, to study solar history, *e.g.*, potential variations in intensity and composition of the solar wind over time. However, the question of when gas-rich meteorites trapped their solar wind noble gases has remained partly controversial up to this day. Early on, it was often more or less tacitly assumed that all meteorites contain "ancient" solar wind from the early solar system, although evidence for this has never been clear. Yet, today, solar wind noble gases in extraterrestrial samples largely lost the attribute "primordial", as Signer and Suess (1963) and Pepin and Signer (1965) foresaw.
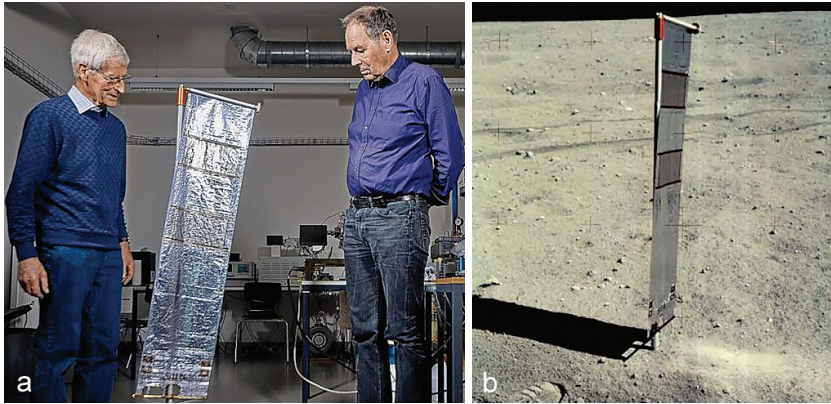
Figure 2.3 **(a)** Jürg Meister (left) and Peter Bochsler (right) looking back at a display piece of the Al foil that had been developed at the Physics Institute of the University of Bern for the Solar Wind Composition (SWC) experiment. Such foils were exposed to the solar wind on the first five lunar landings for between 77 minutes (Apollo 11) and 45 hours (Apollo 16). A strict NASA requirement was that the entire assembly had to weigh less than 1 pound (454 g). Picture courtesy of University of Bern, Physikalisches Institut. **(b)** The solar wind collector deployed by the Apollo 16 crew also included strips of platinum foils (dark areas). They provided the final Ne/Ar ratio in the solar wind as measured by the SWC experiment. Picture courtesy of NASA.

In any case, meteorites provided a means of measuring the elemental and isotopic composition of noble gases emitted by the Sun at a time when the first studies by space probes yielded parameters such as particle density and energy distribution of the solar wind but not yet much about its elemental or isotopic composition. Signer *et al.* (1965) proposed to collect solar wind ions in foils exposed on manned spacecraft missions planned in preparation for the Apollo lunar landings, or, alternatively, on the Moon itself. They pointed out that recent developments in noble gas analysis, driven at the time primarily by studies of meteorites, would certainly permit analyses of He, Ne, and Ar from the solar wind. This estimate was based on the flux of hydrogen in the solar wind measured by space missions and on the assumption of the then best estimates of element abundances in the Sun for the solar wind. As mentioned above, this idea of my doctoral thesis advisor-to-be Peter Signer eventually led to the very successful Apollo Solar Wind Composition (SWC) experiment by the University of Bern, led by Johannes Geiss (Fig. 2.3). Interestingly, Signer *et al.* (1965) also considered applying a high voltage to the foils, which would have greatly increased the amounts of ions collected and might have allowed the detection of Kr, Xe, and even H, N, and O. This idea was later realised in the Genesis mission (see Section 2.5.5).

2.3 My First Studies on Apollo Samples

The days and months after the first Apollo samples reached laboratories around the world must have been extremely thrilling for everyone involved. There they were, the first extraterrestrial samples ever brought back by humans, waiting to reveal the secrets of the Moon and more. Somewhat unfortunately for me, I missed that time by just a few years. Therefore, in my early years, I was sometimes a little envious when Herbert Funk and Heiri Baur told how, after degassing the first samples, they would stare at the chart recorder while waiting for signals on masses four or twenty, and how excited they were when the pen went off scale. Phone calls to other noble gas laboratories, for example in Bern or Mainz, confirmed their observations. The lunar regolith is indeed full of noble gases and the solar wind is obviously their main source (*e.g.*, Pepin *et al.*, 1970; Hohenberg *et al.*, 1970; Fig. 2.4a).

Already the first data from the aluminum foils exposed by the Apollo 11 astronauts showed that the experiment had been successful. It yielded a value for the ^{4}He flux in the solar wind (Bühler *et al.*, 1969), while foil data from later Apollo missions allowed the determination of precise elemental and isotopic compositions of He, Ne, and Ar in the solar wind (Eberhardt *et al.*, 1972; Geiss *et al.*, 2004; Fig. 2.3). Perhaps the most important result of the Apollo solar wind composition experiment was the reliable determination of the ^{3}He/^{4}He ratio in the solar wind. In the 1960s, the D/H ratio in terrestrial oceans of $\sim 1.6 \times 10^{-4}$ was thought to represent the "cosmic" or protosolar deuterium abundance. In this case, the ^{3}He/^{4}He ratio in the solar wind should have been higher than 10^{-3}, because deuterium had been converted to ^{3}He in the very young Sun. However, meteorites thought to contain implanted solar wind noble gases yielded lower ^{3}He/^{4}He values on the order of 4×10^{-4}. These lower values were confirmed by the Apollo foils, leading Geiss and Reeves (1972, 1981) to conclude that deuterium in Earth's water is enriched by almost an order of magnitude relative to the protosolar composition, due to low temperature reactions in interstellar clouds. This finding set new constraints on how the Earth acquired its water and other volatiles.

Analyses of samples from further lunar missions confirmed the Apollo 11 results and showed that the regolith is extremely rich in solar wind noble gases to a depth of at least 2.4 m but very likely further down (*e.g.*, Bogard *et al.*, 1973). However, these studies also made it clear that the noble gas record in the lunar regolith is not easy to read. Isotopic compositions of the solar wind component were similar but not identical to those measured in the Bern aluminum foils and elemental ratios in the regolith samples indicated losses of the lighter noble gases. Some minerals, such as ilmenite, are relatively retentive, while others, like plagioclase, are very leaky, especially for He and Ne. For me this meant that by the time I began to work on lunar samples in 1976, the initial excitement about the Apollo samples had already faded a bit. I could take the solar wind origin of the gases we extracted from bulk soil samples and mineral separates as an obvious fact, and it was only later that I realised that this finding had been a

major scientific break through only a decade earlier. Thus, I soon found myself on the sometimes winding road to an ever improved reading of the noble gas record conserved in the lunar regolith.
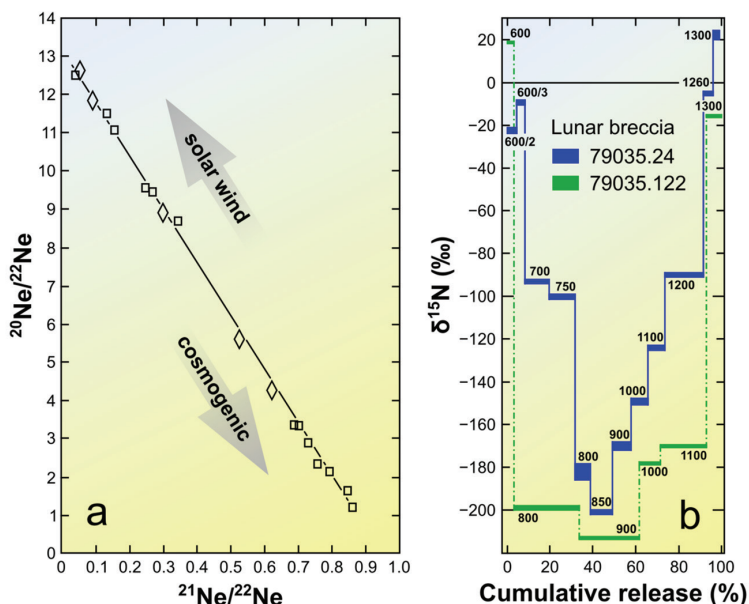
Figure 2.4 **(a)** A Ne three isotope diagram (^{20}Ne/^{22}Ne *vs.* ^{21}Ne/^{22}Ne) showing some of the first data reported for lunar regolith samples collected by Apollo 11 (Pepin *et al.*, 1970). In such diagrams, data points representing mixtures of two Ne components of different isotopic compositions fall on a straight line between the two end members. Data near the lower right are dominated by Ne produced by cosmic rays with all three isotopes having similar abundance. The upper left end of the mixing line defines a trapped Ne component with ^{20}Ne/^{22}Ne ~12.6, essentially identical to Ne found in gas-rich meteorites such as Pesyanoe, which in the days of Apollo was already widely accepted to be from the solar wind. The first lunar data such as shown here, together with the Apollo 11 SWC aluminum foil results, confirmed the solar wind origin of trapped Ne in some meteorites. Figure adapted from Pepin *et al.* (1970). **(b)** The nitrogen isotopic composition δ^{15}N (per mille deviation of ^{15}N/^{14}N from that of atmospheric nitrogen) as a function of the cumulative release of N in stepwise heating of lunar regolith breccia 79035. Release temperature of each step given in °C. Data from Frick *et al.* (1988, blue rectangles) and Thiemens and Clayton (1980, green rectangles). Low temperature steps with δ^{15}N close to terrestrial atmospheric values were interpreted at the time as recently implanted solar wind nitrogen, while intermediate steps with δ^{15}N ~ −200 ‰ were interpreted as ancient solar wind, depleted in ^{15}N relative to modern solar wind. The highest temperature steps release cosmogenic nitrogen produced by galactic cosmic rays near the lunar surface, for which the ^{15}N/^{14}N value is much higher than that of trapped nitrogen. Figure adapted from Frick *et al.* (1988).

The first scientific paper I was involved in discussed the mineral-specific retentivities of implanted solar noble gases in the major minerals in lunar soils. Unforgettable (on this and many later occasions) are the numerous discussions and editing sessions with the entire group in Peter's office, which was known as "The Smokehouse". At the end of a session, the ashtray was filled with the remnants of several loads of pipe tobacco, each actually only smoked to a minor extent. Perhaps the ambience was not really conducive to a pleasant smoking experience. In any case, it led to an important contribution (Signer *et al.*, 1977) that made it possible to better quantify elemental and isotopic fractionation processes of noble gases in the lunar regolith. However, to me this seemed a bit boring at the time. Also, a few years later at my first Lunar and Planetary Science Conference (LPSC, or "The Houston Meeting" to me) I had the impression that work on noble gases in Apollo samples was no longer considered to be at the scientific forefront, which by then was mainly represented by studies of noble gases in tiny acid resistant residues of bulk meteorites. This feeling was reinforced when the Zürich team visited the California Institute of Technology (Caltech) in Pasadena after the meeting, where Gerald (Jerry) Wasserburg was throwing a party for his Swiss friends. At that moment, I certainly did not realise what an honour it was to be invited to the home of the perhaps greatest geo- and cosmochemist of the time. The living room was decorated for the occasion by a three metre wide Bern flag, a reminder of Jerry's sabbatical in Bern a few years earlier. What I did realise, though, was that Jerry outright criticised Peter's current research as "pedestrian science". We did not like that, of course, but I believe this criticism helped spark my ambition to do more than pedestrian science. A dozen years later, at another Houston Meeting, I happened to be sitting next to Jerry, waiting to present our first direct analyses of primordial noble gases (the "Q-component") by *in vacuo* online etching of meteorite samples (Section 3.2.1). When I returned to my seat after my presentation, Jerry whispered: "A very good talk!". At that moment, I remembered the other evening in Pasadena. In retrospect, it gives me a really good feeling to note that noble gas research on lunar samples is thriving again to this day, in stark contrast to my impression in the late 1970s. Obviously, people who were not born in the days of Apollo still find the treasure trove filled with Apollo samples exciting.

My first LPSC talk in 1979 addressed a topic that I continue to work on up to this day: what can the lunar regolith (and perhaps gas-rich meteorites) tell us about possible long term variations in the Sun that would be reflected in the composition of the solar wind? In short, as summarised by Wieler (2016), I now believe that most of the claimed evidence for temporal changes in the solar wind composition has not withstood the test of time. Even the one temporal change I still defended in 2016, namely the about two fold increase in the Kr/Xe ratio in the solar wind over the past few billion years, may need to be reconsidered. I will in the following refer to such possible very long term variations as "secular" changes. But let's start at the beginning.

Three major problems we face in reading the lunar record are (i) how can we know when a sample acquired its share of solar noble gases, *i.e.* the "antiquity" of a sample, a term coined by John Kerridge (Kerridge, 1980), (ii) how can we be sure that noble gases (or nitrogen, see next section) residing at grain surfaces really came from the solar wind and not from some other source, and (iii) how can we be sure that differences in the composition of different samples reflect differences in solar wind properties and not modifications upon or after trapping. These problems will guide us in the following considerations.

My first publication as first author was the abstract that accompanied the LPSC presentation just mentioned (Wieler *et al.*, 1979). Its title began with "*The solar wind half an aeon ago:…*". We studied mineral separates and bulk samples from about 2 m below the surface of the lunar regolith. Samples from the Apollo 15 deep drill core and other subsurface samples all contain solar wind noble gases, although the penetration depth of solar wind ions into solid matter is only a few tens of nanometres. The noble gases thus testify to the fact that the regolith is a very dynamic environment: almost every grain taken at any depth down to at least 2.4 m had once been at the immediate surface of the Moon. At the Apollo 15 site, this vigorous mixing must have taken place no later than about 500 Ma ago, since G. Price Russ, Donald Burnett, and Jerry Wasserburg (Russ *et al.*, 1972) had shown that the regolith at the Apollo 15 landing site had been undisturbed for at least almost 500 million years, except for the topmost few cm. The Caltech team had measured isotopes of Sm and Gd, whose abundances get modified by interactions with the galactic cosmic radiation (details in Section 3.1). Hence the samples we studied contained solar wind implanted at least half a billion years ago. The trapping could also have occurred earlier and not all grains of a sample were necessarily irradiated at the same time. However, no atom from the solar wind in these samples was implanted later than about 500 Ma ago, which is already a remarkable constraint (consult Box 2.1on the antiquity of lunar regolith samples for more details on the important problem of how old the solar wind in a given lunar sample may be). The conclusion of Wieler *et al.* (1979) was perhaps rather unspectacular: the relative He, Ne, and Ar abundances and the $^{20}Ne/^{22}Ne$ ratio in the solar wind half an aeon ago (or earlier) were not different from present day values outside the limits of uncertainty. Nevertheless, I felt that this conclusion of solar wind constancy deserved some attention because at the same time several other notable secular variations in solar wind composition were postulated (Kerridge, 1980). The most important of these will be discussed in the next section.

Text Box 2.1 – The Antiquity of Lunar Regolith Samples

Studies attempting to obtain information about possible long term variations in solar wind composition face the problem of how to determine when in the past a lunar regolith sample trapped its share of solar wind atoms. John Kerridge called this the "antiquity" of a sample (Kerridge,1980). This is a difficult problem. Kerridge *et al.* (1991) discuss several antiquity measures, most of which are semi-quantitative at best. In a few favourable cases, cosmic ray exposure ages (see Section 3.1) will provide

accurate upper bounds on the antiquity of a sample. This is the case when several samples from a rim of a relatively fresh crater have the same exposure age, which then very likely dates the formation age of the crater. Such samples were brought from larger depths to near the surface of the regolith upon crater formation, so all of their grains will have trapped their complement of solar wind between the time indicated by the cosmic ray exposure age and today. All such known samples have relatively young antiquities of ∼2–100 Ma. Many solar wind-bearing lunar samples are regolith breccias, that is, compacted soil. Many of these breccias were undoubtedly irradiated by the solar wind billions of years ago, as can be deduced with the semi-quantitative antiquity indicator $^{40}Ar/^{36}Ar$ discussed in the next paragraph.

"Parentless" ^{40}Ar is found in the surface layers of grains from every solar wind-bearing lunar soil. It is commonly believed to be radiogenic ^{40}Ar from the decay of ^{40}K ($T_{1/2} = 1.27$ Ga) that has been degassed from the lunar interior. Atmospheric ^{40}Ar atoms can become ionised and accelerated by the solar wind-induced electromagnetic field (Manka and Michel, 1970). Many of them will get lost from the atmosphere within a few months but some will be implanted into grains at the lunar surface along with solar wind ions, including ^{36}Ar. The ^{36}Ar serves as a measure of the time a sample was exposed at the lunar surface. So, if the ^{40}Ar concentration in the lunar atmosphere shows a secular variation, $^{40}Ar/^{36}Ar$ should vary with a sample's antiquity. Eugster *et al.* (2001) and Joy *et al.* (2011) present calibrations of the $^{40}Ar/^{36}Ar$ ratio as a function of solar wind antiquity based on a series of samples whose antiquity was inferred by various independent methods, including ^{39}Ar-^{40}Ar ages. Some remarkable samples also contain parentless xenon from the decay of the now extinct nuclides ^{129}I and ^{244}Pu and must have been irradiated very early. Quite remarkably, the trend described by the $^{40}Ar/^{36}Ar$ ratio roughly follows the curve describing the decay of ^{40}K, with values of around 20 for the samples with the highest antiquities, but only about 0.5 for the samples thought to have trapped solar wind within the last few or last few ten Ma. This may be more surprising than is often admitted, as I discuss in Wieler (2016). The more or less parallel decrease of the $^{40}Ar/^{36}Ar$ ratio and the ^{40}K decay curve seems to suggest that the ^{40}Ar in the lunar atmosphere comes entirely from the instantaneous complete degassing of some part of the Moon, and that the degassing volume has hardly changed over most of the Moon's history. At the same time, the flux of solar ^{36}Ar would have to have remained rather constant over the past several billion years. The latter requirement may not be too problematic. However, as far as ^{40}Ar is concerned, I believe that one might as well expect that – all other things being equal – the amount degassing from the lunar interior should to first order be proportional to the total ^{40}Ar produced (and thought to be still largely present) in the crust. If so, the $^{40}Ar/^{36}Ar$ ratio in regolith samples should be higher today than it was in the past. Obviously this expectation is not reflected in the data at all. It is thus questionable to me whether the observed secular decrease of $^{40}Ar/^{36}Ar$ does indeed reflect the decay of ^{40}K rather than a large temporal decrease of the degassing efficiency of the lunar crust, *e.g.*, due to a lower frequency of moonquakes or impacts today or decreasing diffusion in a secularly cooling crust. In my view, the evolution of the $^{40}Ar/^{36}Ar$ ratio in lunar samples of different antiquities is still poorly understood. Nonetheless, the $^{40}Ar/^{36}Ar$ ratio is a useful semi-quantitative antiquity indicator. It is also important to recognise that a sample's antiquity may be poorly defined due to multiple episodes of exposure at the surface.

2.4 The Lunar Nitrogen Saga

Spectacular variations in the nitrogen isotopic composition in lunar regolith samples have been reported since the mid-1970s. John Kerridge, then at the University of California in Los Angeles (UCLA), and Richard Becker and Robert Clayton at the University of Chicago observed that the $^{15}N/^{14}N$ ratios in different samples varied by some 15 % and correlated with the sample's cosmic ray exposure age (Kerridge, 1975; Becker and Clayton 1977). As it seemed reasonable to assume that the cosmic ray exposure age of a sample is a rough indicator of its antiquity – old exposure ages meaning old solar wind – it seemed that the proportion of the heavy isotope ^{15}N in nitrogen trapped in lunar samples increased dramatically over the past one or several billion years. Later analyses, in which the nitrogen was released in several steps by gradually increasing the extraction temperature, revealed two different trapped N components. The first, released at relatively low temperature, was high in ^{15}N, the second, released at higher temperature, was lower in ^{15}N. The difference in the $^{15}N/^{14}N$ ratios ($\delta^{15}N$) was as much as 30 % (Becker and Clayton 1977; Thiemens and Clayton, 1980). Figure 2.4b shows nitrogen isotope release patterns of regolith breccia 79035 obtained at the University of Minnesota by Urs Frick and co-workers together with data obtained earlier in Chicago by Mark Thiemens and Bob Clayton. These release patterns were not easily explained, but the leading hypothesis at the time – and later – was that the $^{15}N/^{14}N$ ratio in the solar wind had increased dramatically over time. One presumed mechanism was the break up (spallation) of oxygen atoms in the Sun's outer convective zone by energetic particles (Kerridge, 1975; Clayton and Thiemens, 1980). One of the main products would be nitrogen with a $^{15}N/^{14}N$ ratio much higher than the original solar value, leading to a secular increase of $\delta^{15}N$ in the solar wind (this should not be confused with cosmogenic nitrogen produced at the lunar surface and manifested in the highest temperature release fractions in Fig. 2.4b).

In Zürich we had always been sceptical of this interpretation. The idea that the variable $\delta^{15}N$ in lunar soils reflected a secular change in the solar wind seemed to contradict another observation: the proportion of nitrogen in lunar samples relative to that of Ar from the solar wind is about an order of magnitude higher than the ratio assumed for the Sun, *i.e.* $(N/Ar)_{Moon} \gg (N/Ar)_{Sun}$. If this problem was addressed at all, it was usually explained in terms of a much better "retentivity" of N compared to that of Ar, *i.e.* in lunar samples Ar from the solar wind was assumed to be much less tightly bound than solar wind nitrogen. However, while our work (Signer *et al.*, 1977, see above) had shown that the He and Ne retentivities are very mineral specific, Ar was retained equally well in all major minerals, and the Ar/Kr ratio was close to the accepted solar ratio. This would not have been expected if most of the solar wind Ar had been lost in a way that would have changed the N/Ar ratio so dramatically.

So, that same year, 1979, when I first attended the LPSC, Peter Signer encouraged me to visit the conference "The Ancient Sun – Fossil Record in the Earth, Moon, and Meteorites". This was the first time I attended one of these

small topical meetings which often are so rewarding, especially for young scientists. The meeting in Boulder, CO, allowed me for the first time to get in direct touch with many of the leading figures in N and noble gas research, such as John Kerridge, Robert (Bob) Pepin, Robert (Bob) Clayton, Kurt Marti, and many others. Nitrogen in lunar samples was one of the major topics. Kerridge and Clayton pointed out that the $^{15}N/^{14}N$ variations lacked a satisfactory explanation but again argued that spallation of oxygen in the solar surface region was the best bet (Kerridge, 1980; Clayton and Thiemens, 1980). If I remember correctly, I did not dare to contradict this view in the public discussion. After all, we had not performed any nitrogen analyses ourselves in Zürich (and have not done so to this day). However, in a private discussion with Bob Clayton, I mentioned our reservation, probably without impressing him too much. Nevertheless, he suggested that I ask NASA for a few grams of lunar regolith breccias 79035 and 79135, which he estimated to contain solar wind implanted perhaps 2.5 Ga ago (Clayton and Thiemens, 1980). These two samples have become cornerstones of my own work on lunar samples, although not primarily for N but for noble gases.

Nitrogen in lunar samples remained a controversial topic. Jim Ray was another young colleague I met in Boulder and hiked up to the Continental Divide with after the meeting. Unlike me, he had something to present on lunar nitrogen. He and his PhD thesis supervisor Dieter Heymann (Ray and Heymann, 1980) proposed that the young Sun might have been polluted by nitrogen from a planetary nebula. Geiss and Bochsler (1982) dismissed this idea, as well as a secular change of the N composition in the solar wind due to oxygen spallation or thermonuclear reactions. Instead, they proposed that an isotopically very light additional N component is added to the lunar regolith. At the 1989 "Sun in Time Conference" in Tucson, AZ, Geiss and Bochsler (1991) suggested that nitrogen from Earth's upper atmosphere might have reached the early Moon as an "Earth wind", a suggestion later also made by Ozima *et al.* (2005). The "Sun in Time Conference" was a meeting in the same spirit as "The Ancient Sun" ten years earlier, and in a paper published in the proceedings volume of this meeting, Kerridge *et al.* (1991) still had to conclude that lunar nitrogen remained a conundrum.

Such was the situation in 1998, when Bernard Marty kindly invited me to work for a while in his laboratory at the Centre de Recherches Pétrographiques et Géochimiques (CRPG) in Nancy. I proposed to attempt to measure argon and nitrogen concentrations and isotopic compositions in single ilmenite grains from an Apollo 17 soil. Franck Humbert and Bernard Marty had developed an analytical protocol that allowed the simultaneous analysis of tiny amounts of noble gases and nitrogen by static mass spectrometry. "Static" means that vacuum pump valves are closed before a sample's gas is introduced into the mass spectrometer. For noble gases this is routine because chemical "getter pumps" can be used to reduce the background of chemically active gases (H_2, CH_4, CO_2, *etc.*) to a level that does not compromise the analyses of minute amounts of noble gases. This is much more difficult with nitrogen which reacts with other elements and would therefore be taken up by the getter pumps before it could be measured.

But obviously, the very small amounts of N contained in single grains and the requirement to measure not only its isotopic composition but also its amount made static N analyses a necessity. In 1981, Urs Frick and Bob Pepin were the first to develop static N analysis for meteorite samples and later to apply this method also to lunar soils. The system developed a few years later by Humbert and Marty in Nancy remains one of the few facilities allowing static nitrogen analysis, and was ideally suited for the lunar grain studies I had in mind.

The lunar ilmenite measurements were not my first single grain analyses. As described in the next section, I had already analysed He, Ne, and Ar in single grains from two lunar soils for my doctoral thesis, and later in Charles Hohenberg's laboratory in St. Louis we measured all five noble gases in a further series of grains (Section 2.5.4.). But in 1998 in Nancy I made my first (and only) own nitrogen measurements, with great support from Franck Humbert and Laurent Zimmermann. I very much enjoyed the hospitality of Bernard and the whole team at CRPG, which was celebrated, among other things, with mirabelle plum liqueurs at Nancy's beautiful Place Stanislas. The data provided clear evidence in support of the suspicion that the overwhelming part of the nitrogen in lunar soils does not come from the solar wind (Wieler *et al.*, 1999). The $^{14}N/^{36}Ar$ ratios in the single grains varied by more than a factor of 400. Also the ^{36}Ar amounts varied by more than two orders of magnitude from grain to grain, reflecting their individual exposure histories to the solar wind. But in contrast to Ar, the N amounts in different grains varied by no more than a factor of six. Since the earlier analyses in St. Louis on single grains from the same samples had shown almost constant ratios of Ar/Kr/Xe from the solar wind (Wieler *et al.*, 1996), this indicated that most of the N in the grains must have come from some other source. Therefore, we concluded that the hypothesis that "the lunar regolith testifies to a secular variation of the N isotopic composition in the solar wind of ~30 % becomes thus highly questionable" (Wieler *et al.*, 1999). I was pleased to find that this conclusion soon became widely accepted. A few years later, the work in Nancy was continued with Ko Hashizume, who did detailed stepwise heating analyses of $^{14,15}N$ and Ar in single lunar grains and proposed a micrometeorite origin for the non-solar nitrogen component (Hashizume *et al.*, 2002). Previously, Ko – together with Marc Chaussidon – had performed nitrogen isotopic analyses by secondary ion mass spectrometry (SIMS) using the instrument in Nancy and had argued for a low abundance of ^{15}N in the solar wind, with a $\delta^{15}N$ value of less than -240 ‰ (Hashizume *et al.*, 2000). This conclusion was brilliantly confirmed a few years later by Genesis, as discussed in the next few paragraphs.

Given that it was becoming increasingly clear that most nitrogen in lunar soils had a source other than the solar wind, and the undisputed fact that even meteorites rich in solar wind noble gases were not suitable for measuring the solar $^{15}N/^{14}N$ ratio, the Genesis solar wind collection mission became a unique possibility to determine this ratio, a value of fundamental importance for cosmo-chemistry. I will discuss Genesis in detail in Section 2.5.5, but it is appropriate to emphasise here that – despite the crash landing of the sample return capsule

– among many other successes, the mission achieved its stated two main goals, the determination of the oxygen and nitrogen isotopic compositions in the solar wind. I had been involved in the preparation of Genesis since the late 1990s when Don Burnett, the mission's Principal Investigator, established the annual Genesis Science meetings on the Sundays prior to the LPSC. So I knew that determining the nitrogen isotopic composition of the solar wind was the second most important goal of the mission, and I suggested to Bernard Marty that he contact Don and join the team. So he did, which perhaps became one of my most important contributions to planetary sciences. I am quite proud of the fact that Bernard acknowledges that I was the one who introduced him to cosmochemistry, after exclusively studying terrestrial volatiles in his early scientific career.

In a first study, Marty and co-workers (Marty *et al.*, 2010) measured N isotopes in the gold plated steel cross used to mount the different collector materials in the Concentrator target of Genesis. As explained in Section 2.5.5, in this target the solar wind ion flux is enhanced several ten fold by electrostatic fields. Nevertheless, at best some 4 % of the measured nitrogen came from the solar wind; the rest was terrestrial contamination. However, Marty and co-workers could combine the N data with analyses of amounts and isotopic composition of solar wind Ne measured along arms of the "gold cross" in Nancy and by Veronika Heber in Zürich. This allowed them to extrapolate the measured N data to the solar wind N/Ne ratio and clearly showed that the $^{15}N/^{14}N$ ratio in the solar wind is considerably lower than in the terrestrial atmosphere. Instead, the best estimate of $(2.26 \pm 0.67) \times 10^{-3}$ was found to be consistent with the Jupiter value. In a second study, Marc Chaussidon, Bernard Marty, and colleagues (Marty *et al.*, 2011) used the Cameca 1280 SIMS instrument at CRPG in Nancy to analyse a SiC target from the Concentrator. This allowed them to obtain a much more precise value of $(^{15}N/^{14}N)_{SW} = (2.18 \pm 0.02) \times 10^{-3}$, which is about 40 % lower than the terrestrial atmospheric value. These beautiful data allowed Marty *et al.* (2011) to note that: "This result demonstrates the extreme nitrogen isotopic heterogeneity of the nascent solar system and accounts for the ^{15}N-depleted components observed in solar system reservoirs". This heterogeneity is reviewed by Füri and Marty (2015). Hence, the first part of the lunar N conundrum has been definitively solved: neither the $^{15}N/^{14}N$ ratios observed in some lunar samples which are higher than the terrestrial value, nor the low $\delta^{15}N$ values of around -200 ‰ found in other lunar samples represent the pure solar wind. However, what does or do the non-solar nitrogen component or components ubiquitous in lunar samples represent? This question is still being debated. Meteoritic or cometary contributions remain viable candidates (*e.g.*, Hashizume *et al.*, 2002; Mortimer *et al.*, 2016). Another possibility is a contribution from Earth's upper atmosphere, as proposed by Geiss and Bochsler (1991) and Ozima *et al.* (2005). It is almost a truism that documented samples from the far side of the Moon would be highly desirable for further progress, as noted in many papers in this and related contexts. Note that reviewer Bernard Marty informed me that Frank Podosek and he did not find any systematic variations between N/^{36}Ar and $\delta^{15}N$

values in a series of 12 lunar meteorites. As about half of those should originate from the backside, this does not support a substantial nitrogen contribution on the lunar near-side from an Earth Wind.

Did I just say that the conundrum of the lunar nitrogen is largely solved? While I believe that the overwhelming majority of the scientists in the field would agree, the person who collected some of the crucial samples for this discussion sees it differently. In 2019 – forty years after the Boulder meeting on the Ancient Sun – probably the largest crowd ever in the same lecture hall at an LPSC meeting was listening to NASA astronaut and geologist Harrison H. Schmitt's lecture celebrating the 50th anniversary of the Apollo 11 landing. Jack Schmitt is one of the two last humans (so far) to walk on the Moon and his talk was very entertaining. However, when he turned to the findings about the Sun obtained from nitrogen isotopes in lunar samples, I became uneasy. He repeated at length the old view that the isotopic composition of solar wind nitrogen has varied by 30 % and even suggested that the cause of this change may have triggered the Cambrian explosion of life on Earth some 550 Ma ago. He dismissed the Genesis data by Bernard Marty and co-workers as being irrelevant, since they disagreed with the lunar samples. Toward the end of the lecture I was getting pretty nervous, because probably not too many people in the lecture hall were as closely involved in the topic as I was. I was relieved when Don Burnett (who was sitting next to me) grabbed a microphone first and got things right, and in a much more elegant way than I could have done.
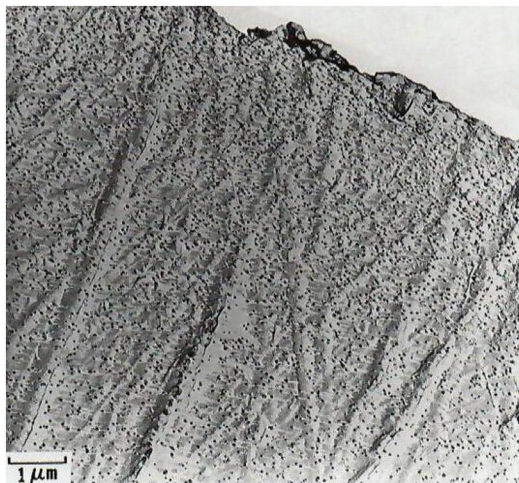
Figure 2.5 Solar flare tracks in a feldspar grain from the lunar regolith seen in a transmission electron microscope. The track density gradient from top to bottom is evidence of irradiation by solar flare particles at the immediate surface of the Moon. Photo from Fleischer *et al.* (1975), courtesy of R.S. Rajan.

2.5 The SEP Myth, the FIP Effect, and Genesis

Let me jump back to the days in 1980 when I was about to finish my doctoral thesis. The Sun emits not only solar wind ions with speeds of a few hundred km/s, corresponding to energies of ~1 keV/amu, but also so called solar energetic particles (SEP) with much higher energies of tens of MeV/amu. These are not emitted continuously like the solar wind, but as Coronal Mass Ejection events during solar flares. Solar energetic particles were observed as early as the late 1970s with mass spectrometers on space missions. In lunar samples and meteorites, the effects of these particles are known in the form of so called solar flare tracks, *i.e.* lattice damages created by SEPs mainly of iron group elements (Fig. 2.5) that can be made visible by chemical treatment in the laboratory. Solar energetic particles of these heavy elements penetrate hundreds of microns deep into solid matter, much deeper than solar wind ions, but the generation of latent solar flare tracks still requires grain exposure directly at the regolith surface. It therefore made sense to compare track densities and solar wind noble gas concentrations in the same samples. Gérard Poupeau, then at the Centre des Faibles Radioactivités in Gif sur Yvette (France), measured track densities, and I analysed noble gases in mineral separates from many samples as well as in single grains from two samples (Wieler *et al.*, 1980). Later, Gérard also taught me how to make tracks visible by etching and how to count their densities by light or electron microscopy (Wieler *et al.*, 1983). The comparison showed – at least on a whole grain scale – that solar wind Ar (and Kr and Xe) concentrations are not in saturation even in heavily irradiated lunar samples, *i.e.* do not reach an equilibrium value where for each newly implated atom from the solar wind another one is lost, for example by grain surface sputtering. I would not any longer put my money on another conclusion we reached in the 1980s. We claimed that the flux ratio of high energy solar particles to solar wind decreased by perhaps a factor of two over the past 1 – 3 billion years.

The first two publications on the Ne isotopic composition of SEP events by space missions reported nearly identical $^{20}Ne/^{22}Ne$ ratios of ~7.7 (Mewaldt *et al.*, 1979; Dietrich and Simpson, 1979), much lower than the solar wind value of 13.7 as measured in the Apollo SWC aluminum foils. Although the SEP data had large uncertainties, it seemed clear that the high and low energy solar corpuscular radiation differed in their isotopic composition. Already before the first space mission data became available, there was controversy about whether the noble gases trapped in lunar soils and gas-rich meteorites represent just the solar wind with its known energy of around 1 keV/amu, or – in addition – a second, higher energy component implanted at larger depth than the common solar wind ions. An early advocate of this view was David Black, then at the University of Minnesota and later director of the Lunar and Planetary Institute in Houston. He studied gas-rich meteorites and lunar samples by stepwise heating (Black and Pepin, 1969; Black, 1972). At relatively low temperatures, Ne with a $^{20}Ne/^{22}Ne$ ratio around 12.5 was released, which he labelled component Ne-B and identified it with solar wind Ne (Fig. 2.7). As we will see below, Ne-B eventually

turned out to be solar wind Ne isotopically fractionated upon implantation and grain surface sputtering. While it is thus not a pure component *sensu stricto*, Ne-B is still important, in particular in terrestrial noble gas studies (*e.g.*, Moreira, 2013). Higher temperature steps, however, fell on a straight line (marked as a light grey band in Fig. 2.7) between a point labelled by Black as Ne-C in the upper left hand and cosmogenic Ne in the lower right hand corner. In such three isotope diagrams, data points falling on a straight line are usually interpreted as a mixing line of two end member components at or somewhere beyond the two ends of the line. Hence, Black concluded that Ne-C with ^{20}Ne/^{22}Ne = 10.6 ± 0.3 must represent a true solar component isotopically different from solar wind Ne and implanted with higher energy than the solar wind. He assigned Ne-C to the low energy fraction (1–10 MeV/amu) of energetic particles emitted during solar flare events, and concluded that SF-Ne, as it was then called, has a lower ^{20}Ne/^{22}Ne ratio than the solar wind. When the first Ne isotopic data of SEPs directly measured in space indeed gave significantly lower ^{20}Ne/^{22}Ne ratios than the solar wind value, David Black's hypothesis that lunar samples and gas-rich meteorites contain measurable amounts of higher energy solar ions in addition to the solar wind became very popular. However, there was a serious problem with this. Ne-C accounted for up to several tens of percent of the total trapped Ne in the samples, which meant that the flux of SF-Ne would have to be orders of magnitude higher than what could be expected from extrapolations of the high energy SEP flux measured in space. Could this be the case?

Figure 2.6   Left to right: Bernard Marty playing the guitar at the 2016 EGU meeting in Vienna in the CRPG rock band Double Scotch (photo courtesy of Bernard Marty), Urs Frick at the 2010 meeting of former doctoral students of Peter Signer, and Rainer Wieler and Minoru Ozima discussing noble gas cosmochemistry at the 2002 Goldschmidt Conference in Davos.
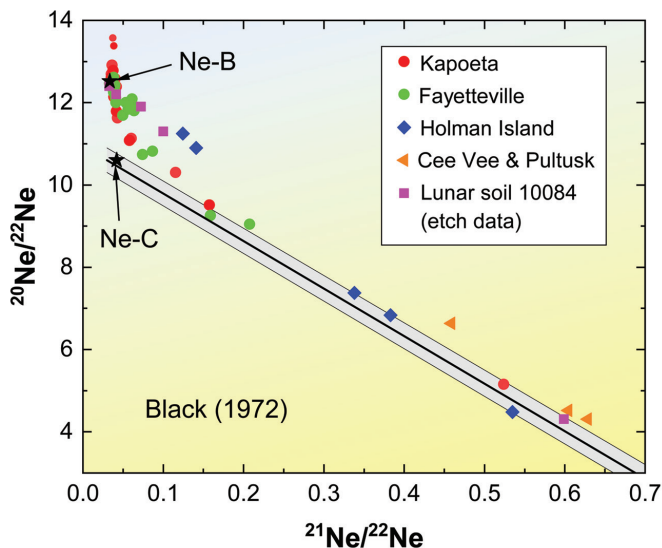
Figure 2.7   Neon three-isotope diagram ($^{20}Ne/^{22}Ne$ vs. $^{21}Ne/^{22}Ne$) with data published by Black (1972). Shown are data from gas-rich meteorites (gases extracted mostly by stepwise heating) and the first lunar soil 10084 (collected by the Apollo 11 crew) etched to various degrees (Hintenberger *et al.*, 1970). Low-temperature steps release Ne-B (upper left corner) identified by Black as solar wind Ne. Higher temperature steps fall near a straight line, apparently indicating a two-component mixture of cosmogenic Ne (lower right, off scale) and a second trapped component with $^{20}Ne/^{22}Ne$ ~10.6 in the upper left. Black called this component Ne-C and argued that it represents "low-energy (1-10 MeV/amu) solar flare Ne", which later became known as "SEP-Ne". Figure adapted from Black (1972).

2.5.1   Noble Gas Release by in Vacuo Etching

We decided that the most promising way to solve this puzzle would be to improve the quality and depth resolution of concentration profiles of trapped noble gases in lunar grains. So far, depth profiling had been attempted mostly by gas extraction in several temperature steps. In some cases also grain surface layers of different thickness were removed by etching multiple aliquots of the same sample. Information about gas concentrations and compositions in the etched layers had to be inferred by difference. We wanted to improve this by developing a device allowing stepwise etching of grain separates under "vacuum" in a gas extraction line connected directly to the mass spectrometer, as this would allow measuring separately the gases released in each etching step. This decision may have shaped my own research agenda more than any other of our technical developments. In short, for almost twenty years, our team gradually became perhaps the best

known advocates of the idea that the lunar and meteoritic regoliths testify to a very substantial contribution from a high energy solar noble gas component. And then, in 2006, all of a sudden we had to abandon our beloved idea, based on the initial analysis of a sample flown as part of the Genesis mission that had been specifically selected to study the high energy component. What was comforting was that we were able to do this in a paper in *Science*, actually the first article reporting scientific data from Genesis. How this all came about is described next. The *in vacuo* etching technique later also provided a unique way to study primordial noble gases in meteorites. This will be described in one of the later sections.
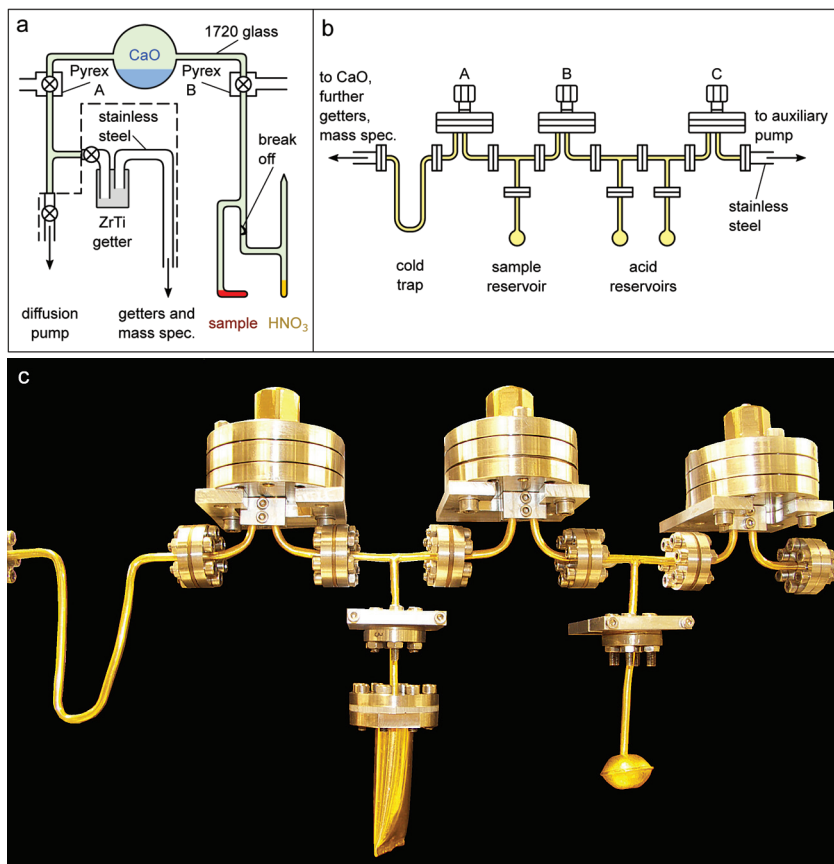
Figure 2.8   **(a)** Schematic representation of the glass and gold **(b)** lines used for *in vacuo* etching (CSSE) analyses. Figures adapted from Signer *et al.* (1993). **(c)** Image of the actual gold line (horizontal dimension ~30 cm). Picture courtesy of Ansgar Grimberg. The HNO$_3$ in the glass line was pre-degassed in an auxiliary vacuum system. Teflon stopcocks were used for valves A and B. Calcium oxide (CaO)

served as the first agent to remove acid vapour. The acid reservoir (only one was actually built, see bottom panel) of the gold line was degassed online. The gold line was fully bakeable. Acid exposed parts were made only of gold and some platinum. The parts of the valves visible in this image are made of stainless steel.

It may sound crazy to connect a noble gas extraction system containing strong acids to a mass spectrometer, with only a few valves and some cold traps and chemical getters in between. Perhaps it is indeed crazy, in particular because one of the acids we often use is HF, whose atomic mass of 20 equals that of the main Ne isotope. However, in all these years, we have had to deal with a serious increase of the background on mass 20 only once. This was after a rather silly mishap (if I remember correctly, we forgot refilling liquid nitrogen in a cold trap), but with no major consequences. Our first *in vacuo* etching line was made of glass and allowed etching of plagioclase and pyroxene with nitric acid. The first data obtained with this line were published by Wieler *et al.* (1986), and we often refer to this gas release and analysis technique as CSSE (for Closed System Stepped Etching). However, we also wanted to analyse ilmenite, the most noble gas retentive among the major minerals in lunar soil. This required a line allowing HF as the etching agent. Therefore, around 1990 we built the "gold line", which is still in use today. Both lines are described in a paper presented by Peter Signer in 1991 at a meeting in Durango, CO, honouring Alfred O. C. Nier, the "Father of Mass Spectrometry". As mentioned above, Peter had worked in Al's lab in Minneapolis for about seven years, and he greatly admired him. A Festschrift in his honour was therefore the right place to present the technical details of our CSSE lines (Signer *et al.*, 1993). The lines are shown in Figure 2.8. A typical reaction of dear friends of mine around the globe is: "Oh, only the Swiss can afford that, with all their bank vaults filled with gold". Of course, it's not quite like that. We had initially planned to use steel tubes, gold plated on the inside. But then Heiri Baur argued that pure gold tubes would not only allow for simpler construction and possibly lower blanks, but would probably also be more economical, since the gold from parts to be replaced could be recycled. Heiri was right. It turned out that the overall costs of the gold over all those years adds up to no more than what scientists spend for a few electronics parts of their instruments. The CSSE technique has also become a great success thanks to the excellent technical staff in our group, mainly Mathias Gerber and – more than anyone else – Urs Menet. The gold line even motivated Urs to become an amateur jeweler. Some of his friends received a gold wedding ring made by Urs.

Closed system stepped etching is not an analytical technique for the impatient scientist. The data shown in Figure 2.9 (left panel) were obtained using nitric acid as the etchant. Etch times *per* step ranged from less than an hour to several days, resulting in total run times of several weeks. Other analyses even took up to many months. The reward for this time consuming procedure is the fact that gases are released by dissolving the sample, so no elevated temperatures are needed that could lead to isotopic fractionation during gas release. Better

depth resolution compared to stepwise pyrolysis or stepwise combustion (the latter in the presence of small amounts of oxygen) can also be expected. Below we will also see that CSSE allows a carrier-selective gas extraction.

Figure 2.9 includes the data from two of several etch runs of plagioclase and pyroxene separates (Wieler *et al.*, 1986) and an ilmenite separate measured by Benkert *et al.* (1993). The first steps of the plagioclase analyses released Ne with a $^{20}Ne/^{22}Ne$ ratio somewhat below the value of 13.7 for solar wind Ne, known from the Apollo aluminum foils. Most remarkably, later steps always fell on a well defined straight line, pointing towards the composition of cosmogenic Ne in the lower right and extrapolating to a $^{20}Ne/^{22}Ne$ ratio of ~11.3 in the upper left. A pyroxene separate also etched by HNO_3 showed a different but closely related pattern. All data points aligned between a point only slightly below the Apollo solar wind composition and the 11.3 point seen in the plagioclase runs. Apparently, plagioclase was more or less completely dissolved by HNO_3, which in later steps led to large contributions of cosmogenic Ne sited in the grain volumes, while HNO_3 attacked only the surface layers of pyroxene grains containing implanted solar Ne.
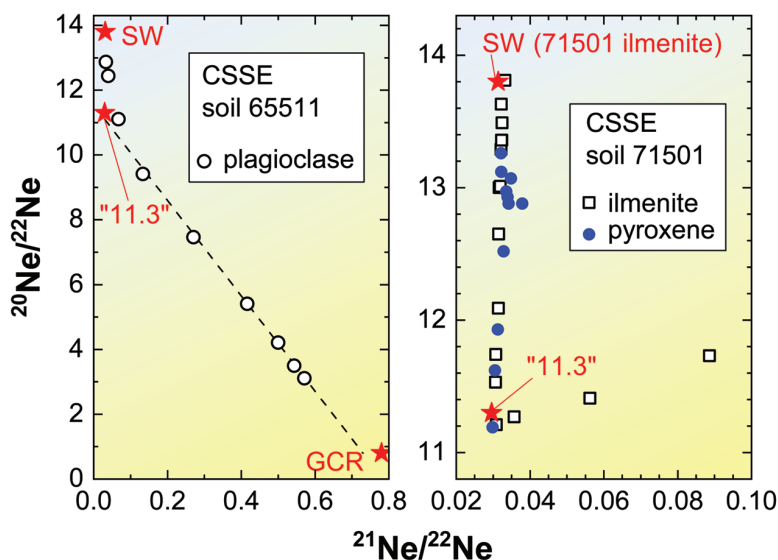
Figure 2.9   Ne three isotope diagrams of CSSE data (see text) of a plagioclase separate from lunar soil 65511 and an ilmenite and a pyroxene separate from lunar soil 71501 (Wieler *et al.*, 1986; Benkert *et al.*, 1993). The "SW" point represents solar wind Ne as derived with the 71501 ilmenite CSSE data, "11.3" represents the Ne component at the time thought to represent a second, higher energy component from the solar corpuscular radiation but later identified as "fractionated" solar wind (Grimberg *et al.*, 2006, Section 2.5.5). "GCR" represents cosmogenic Ne as measured in lunar plagioclase.

In 1984 Jean-Paul Benkert and Anselmo Pedroni contacted us for doctoral student positions and in 1990 Christoph Murer also joined the group as graduate student. This trio allowed us to expand the work on solar noble gases and was among the first of many doctoral students I was privileged to supervise, either as principal or co-supervisor, or – in the beginning – less formally as scientific advisor. Jean-Paul Benkert continued my own work on lunar samples, focusing on CSSE studies on ilmenite and pyroxene separates from two lunar samples, one relatively recently exposed to the solar wind and the other perhaps several billion years in the past (Benkert et al., 1993). He used the gold line to etch ilmenite grain separates from various lunar soils with hydrofluoric acid. Figure 2.9 shows that he obtained very similar Ne data patterns to those I had found for the pyroxene separate. All but the last few etch steps fell on a straight line, starting almost exactly at the $^{20}Ne^{22}Ne$ ratio observed in the Apollo foils (a fact discussed below), and ending close to the 11.3 value known from plagioclase and pyroxene. The last few steps trend slightly toward cosmogenic Ne produced by galactic cosmic rays (GCR Ne).

Anselmo Pedroni and Christoph Murer studied samples from solar gas-rich meteorites with CSSE. Christoph analysed iron-nickel separates in Acfer111, Fayetteville, and Noblesville, Anselmo bulk samples and mineral separates from Kapoeta and Fayetteville. The latter data showed a basically similar pattern as the lunar samples (Pedroni, 1989). Christoph Murer built a separate CSSE line consisting of pyrex glass that allowed him to use copper chloride ($CuCl_2$) as etchant, or more exactly as oxidising agent. This was based on previous work in Mainz by Else Vilczek and Heinrich Wänke who showed that copper-chloride selectively dissolves metallic Fe-Ni without affecting silicates. As expected, metallic Fe-Ni retains the light noble gases from the solar wind even better than lunar ilmenite, with He/Ar and Ne/Ar ratios being essentially identical to the solar wind values in the aluminum foils exposed on the Moon. He/Ar and Ne/Ar ratios were essentially constant throughout the entire CSSE runs, unlike what was observed in any of the lunar minerals studied (Murer et al., 1997).

All these studies convinced us that the "11.3-Ne" indeed represents a second solar Ne component, isotopically distinct from the known solar wind Ne, and essentially identical to David Black's Ne-C, albeit with a nominally slightly higher $^{20}Ne/^{22}Ne$ ratio. It seemed clear to us that the straight lines with correlation coefficients of up to 0.999 defined by the lunar plagioclase data could not mimic isotopically fractionated solar wind Ne that had diffused into the grain interiors. In addition, the "11.3-Ne" also showed up in pyroxene, ilmenite, and Fe-Ni metal, which all have much lower diffusivities for Ne than plagioclase. However, the problem which had already puzzled David Black in 1972 remained: this second solar component, thought to represent higher energy particles than the solar wind, appeared to be orders of magnitude too abundant to be consistent with the known fluxes of what was believed to be emitted during solar flares. We therefore concluded that the 11.3-Ne must represent particles with higher energies than the solar wind but nowhere close to those detected during

solar flares. We thus decided to call this component "SEP-Ne", for solar energetic particles, a somewhat unfortunate choice, since we did not pay enough attention to the fact that the acronym SEP had already been adopted by the space physics community for truly high energy particles. Probably the term "suprathermal solar ions" as suggested by Johannes Geiss would have been a better choice for the 11.3-Ne and would have avoided confusion. Yet, the "SEP component" was widely adopted by the cosmochemistry community, and the CSSE data of Benkert *et al.* (1993) seemed to show that SEP-He and SEP-Ar also existed, enriched in the heavy isotopes relative to the solar wind composition, just like SEP-Ne. Further analyses of the isotopic composition of solar energetic particles by space physicists partly revealed $^{20}Ne/^{22}Ne$ ratios similar to that of the SEP-Ne component in lunar samples, *i.e.* higher than the initial space mission value of ~7.7 (Mewaldt et al., 1979), which seemed to provide further support for the existence of that component, albeit it was later found that the isotopic compositions of the SEP of space physicists is highly variable, depending, *e.g.*, on charge state distributions (Leske *et al.*, 2007). Nevertheless, by the late 1990s I was almost completely convinced of the reality of our SEP component in lunar (and meteoritic) samples, and I think many colleagues shared this view. "Almost completely" refers to the lingering problem of the large fraction of SEP gases in the total solar noble gas inventory, up to 50 % in some cases. This was not easy to digest, even considering that the very surficial solar wind component might very well have been strongly depleted relative to the more deeply sited SEPs due to diffusive losses or surface sputtering. We suggested that the data indicate a periodic increase of solar activity in the past relative to present values. The Genesis mission, selected by NASA in 1997 to collect solar wind ions for about two years between 2002-2004, therefore provided a unique opportunity to test this hypothesis, as discussed next.

2.5.2   The End of the SEP Myth

Here I only recount how Genesis helped put the SEP component to rest; our overall involvement in this mission will be addressed in more detail in Section 2.5.5. Don Burnett of Caltech in Pasadena – the mission's Principal Investigator – proposed to fly a sample on Genesis that would allow very homogeneous etching with nitric acid over the entire analysed area and thus controlled depth profiling of the implanted solar noble gases. The selected sample was a Bulk Metallic Glass (BMG; Figure 2.10) which Veronika Heber in her doctoral thesis at ETH had shown to be etched very homogeneously. The BMG sample was mounted on the hinge holding the large Genesis sample panels, which is probably why it survived the crash landing of the Genesis sample return capsule essentially intact, the only sample that did so besides the concentrator target mentioned in Section 2.4 on nitrogen isotopes. In his doctoral thesis, Ansgar Grimberg measured He, Ne, and Ar in BMG using the CSSE technique. The Ne data published in *Science* (Grimberg *et al.*, 2006; Fig. 2.10) showed $^{20}Ne/^{22}Ne$ ratios in the first steps above

the solar wind value of 13.8, followed by a gradual decrease with increasing etching duration to a value very close to the "SEP-Ne" value of 11.3. This data pattern was in many ways strikingly similar to that previously observed in CSSE runs of lunar pyroxene and ilmenite separates. One obvious difference was that the data of the last steps did not deviate toward cosmogenic Ne with its high ^{21}Ne abundance, which is essentially not present in Genesis targets after only about two years of exposure to galactic cosmic rays. Another difference was that the $^{20}Ne/^{22}Ne$ ratio in the first steps was higher than the solar wind value, which, as we will see in Section 2.5.4, is explained by the fact that lunar soil grains, but not the Genesis samples, reach a steady state between solar wind ion implantation and grain surface sputtering. Indeed, the gas release pattern shown in Figure 2.9 (left diagram) was almost perfectly reproduced by that predicted by the SRIM ion implantation programme for a single solar wind Ne component, and the total Ne released had an isotopic composition almost identical to that measured for solar wind Ne in other Genesis targets, with $^{20}Ne/^{22}Ne = 13.8$. Ansgar also showed that the lunar data shown in Figure 2.9 (left diagram), including the straight line part between SEP and GCR, could be well reproduced by the single solar wind Ne component measured in the BMG onto which a simulated galactic cosmic ray produced (GCR) component was superposed. Furthermore, measurements carried out by the Advanced Composition Exporer (ACE) mission in parallel with Genesis made it clear that the latter had not collected large fluences of suprathermal ions above solar wind energy.

All this allowed us to conclude – in the first publication reporting scientific results from Genesis – that "no extra high energy component is required and that the solar neon isotopic composition of lunar samples can be explained as implantation fractionated solar wind". Such was the end of the SEP component, the characterisation of which I had for years considered one of my major contributions to noble gas cosmochemistry. At least I could take comfort in the fact that not everyone succeeds in retracting one of their favourite ideas in a prestigious journal like *Science*. Grimberg *et al.* (2008) additionally showed that the He and Ar data also measured in the BMG are compatible with a single implantation fractionated solar wind component and do not require higherenergy particles. In Wieler *et al.* (2007) we discuss some further consequences of the elimination of "SEP" from the "noble gas alphabet" of cosmochemistry.

While the investigation of the SEP conundrum had been the primary motivation for developing CSSE, I also started using that technique to investigate primordial noble gases in meteorites. In parallel I turned to other meteorite studies, including their cosmic ray exposure histories, and I continued to work on lunar samples, with an emphasis on the isotopic and elemental composition of the heavy noble gases Kr and Xe. To recount all these activities – all of which, of course, were done in collaboration with numerous colleagues – I dial back the clock once again.
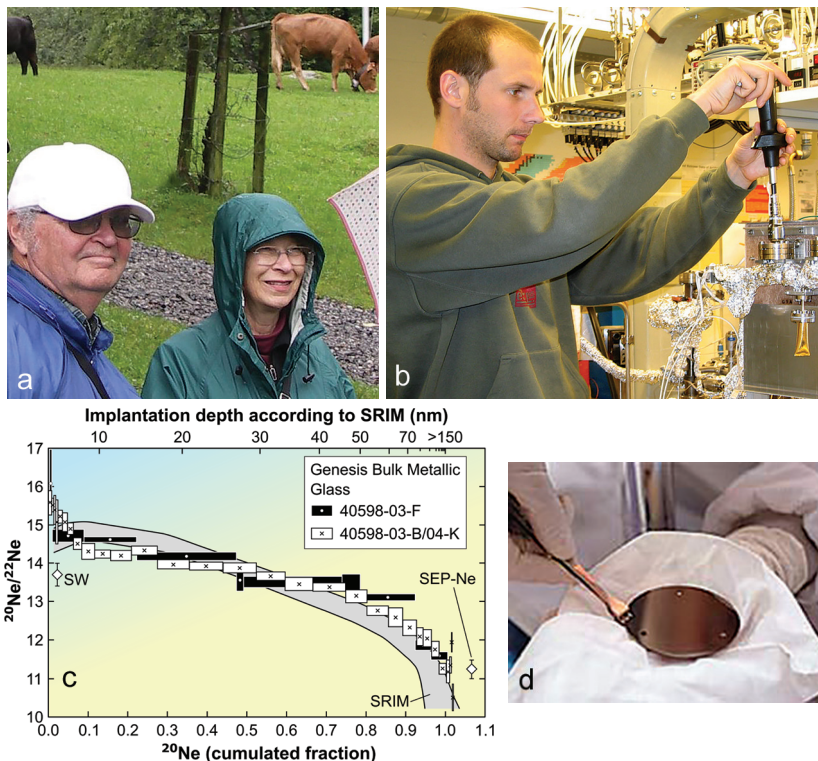
Figure 2.10 (a) The Principal Investigator of the Genesis mission Don Burnett and his wife Marie Louise on the Rütli meadow (a mythical place in Swiss history) during the excursion following the 2006 Meteoritical Society Meeting in Zürich. (b) Angar Grimberg operating a valve on the CSSE devise during the analysis of a bulk metallic glass (BMG) sample from the Genesis mission. (c) $^{20}Ne/^{22}Ne$ as a function of the cumulative fraction of ^{20}Ne released in two *in vacuo* etch runs of the Genesis BMG sample (rectangles). The grey-shaded area shows the depth dependence of a single solar wind Ne component with $^{20}Ne/^{22}Ne$ = 13.75 predicted by the SRIM ion implantation simulation code (www.srim.org). Uncertainties of measured data and SRIM calculations are 2σ. From Grimberg *et al. (2006)* with permission from AAAS. (d) The BMG platelet flown on Genesis to test the "SEP hypothesis". This sample survived the crash landing with but a few scratches. Picture courtesy of NASA.

2.5.3 Some Personal Reminiscences from the Days After my Doctoral Exam

It was during the early months of the Covid 19 pandemic, more precisely on April Fools' Day of 2020, that my partner Catherine Jakob and I celebrated the fortieth anniversary of our first beer together and our first kiss. In April 1980 I was about to submit my doctoral thesis and prepare its defense. My slightly stressful behaviour these days was a good test of our personal relationship. This was also the time when I submitted my only written scientific job application ever! It was for a postdoctoral position in the famous noble gas laboratory of John Reynolds in Berkeley. I would have succeeded Uli Ott, who was returning to Mainz. Probably my application was not convincing; in any case I did not get the job. And perhaps one reason for my unconvincing application was that I was not really keen to go to Berkeley, because Catherine was far too independent to easily give up – or even temporarily interrupt – her own professional life to follow me. So John Reynolds' negative answer was at least as much of a relief to me as it was – nevertheless – a disappointment. So I was all the more pleased when Peter Signer offered me an opportunity to stay in his group as a postdoc. In addition to other projects, this allowed me to continue the work on meteorites and lunar samples that I just alluded to above. A few years later, Peter asked me if I would consider becoming a permanent member of his group. This offer came with a rather large "IF" attached: IF our Department and the ETH administration would agree. Of course I did not think twice about Peter's offer and happily accepted. And ETH accepted too! Perhaps it was not as easy for Peter to push this promotion through as I imagined at the time. My contract stated that ETH would not guarantee my continued employment after Peter's retirement, but that seemed so far away that I hardly worried. So, in the mid-1980s I became a permanent staff member in the Department of Earth Sciences at ETH Zürich until my formal retirement in 2014, and I am still a guest scientist there today. When Peter retired in 1994, perhaps the administration had simply forgotten what they had written into the contract some 10 years earlier. It seems worthwhile telling this story, as such a smooth career path does not appear possible anymore. Remarkably, no substantial paperwork on my part nor any formal evaluations were necessary. Further down, I will talk about the years during which I – together with Heiri Baur – took over the management of the laboratory after Peter Signer's retirement.

2.5.4 Light and Heavy Solar Noble Gases and the FIP Effect

In Section 2.5.2 we noted that although the hypothesis of a high energy solar noble gas component in lunar samples and gas-rich meteorites did not withstand the test of time, the work undertaken resulted in other important findings. Jean-Paul Benkert found that the first steps of mild etching (sometimes just a few minutes exposure to hydrofluoric acid vapour) always released Ne with an isotopic composition essentially identical to that of the Ne in the aluminum foils exposed on the Apollo missions (Benkert *et al.*, 1993). We concluded that ilmenite

grains at their top surface retained the true isotopic composition of noble gases in the solar wind. The value based on the initial etching steps of the ilmenite runs of $(^{20}Ne/^{22}Ne)_{SW} = 13.8 \pm 0.1$ has been adopted for many years by most workers, many primarily interested in noble gases from Earth's interior. It is perhaps somewhat ironic that for about 15 years, Benkert *et al.* (1993) was the most cited paper with my name on the author list mostly thanks to just this one number. Fortunately it has withstood the test of time, as we will see in the next section. That this should be so is far from straightforward, as we noted in the previous section that isotopic fractionation upon ion implantation into Genesis targets leads to isotopically lighter compositions at grain surfaces (Grimberg *et al.*, 2006, 2008). That the lunar samples do not show this effect has been explained by an equilibrium between ion implantation and grain surface removal by sputtering (Becker, 1998; Wieler, 1998; Vogel *et al.*, 2011). This idea was later confirmed, when the solar wind isotopic compositions of not only Ne, but also Ar, Kr, and Xe that had been derived largely with CSSE data from lunar soils (Benkert *et al.*, 1993; Wieler and Baur, 1994; Pepin *et al.*, 1995), were found to be essentially in agreement with those derived from Genesis (next section).
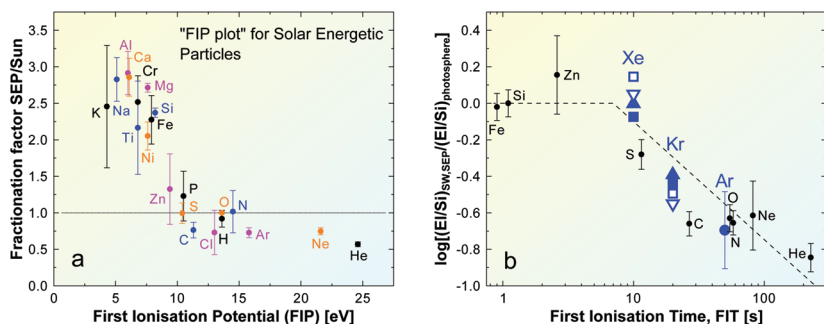
Figure 2.11 **(a)** "FIP-plot" showing elemental abundances in solar energetic particles measured by space missions relative to measured or inferred abundances in the solar photosphere as a function of their first ionisation potential. Element abundances are normalised to that of oxygen. Data from Reames (2018). **(b)** Element fractionation of noble gases and a few other elements in the solar wind or SEPs, relative to photospheric abundances, as a function of the element's First Ionisation Time (FIT). Element abundances are normalised to Si. Data for Xe, Kr, and Ar (blue symbols) are from the CSSE analyses of lunar soils given by Wieler and Baur (1995). Open symbols represent a high antiquity sample, closed symbols one of low antiquity; Kr and Xe are anchored to the inferred photospheric Ar value. The Xe fractionation is equal to that of low-FIP elements (FIP < 10–11 eV; here represented by Fe, Si, Zn), although Xe has a FIP of 12.2 eV. However, Xe has an exceptionally low FIT compared to other high FIP elements, which is consistent with the hypothesis that FIT is a relevant parameter governing element fractionation in the solar corpuscular radiation. Figure adapted from Wieler and Baur (1995).

In the 1990s, I focused my own solar wind studies mainly on the two heaviest noble gases Kr and Xe. Besides the solar wind isotopic composition of Kr and Xe obtained with CSSE (Wieler and Baur 1994), another long standing problem attracted my attention: to what extent can the elemental abundances of the heavy noble gases in the solar wind be derived from lunar (and meteorite) samples? Since about 1980, elements that are relatively easily ionised were known to be several times more abundant in the solar wind and in solar energetic particles relative to their known or assumed abundances in the solar photosphere (*e.g.*, Reames, 2018). These are the so called low FIP elements, with a First Ionisation Potential less than ~10-11 eV. Figure 2.11a shows a "FIP diagram" for solar energetic particles measured by space missions, but the FIP effect is also observed in the solar wind, as discussed below. The FIP effect is understood to arise upon separation of ions from neutrals when the particles expand from the solar chromosphere up into the corona (Reames, 2018). Krypton and xenon are of particular interest in understanding the FIP effect, as their first ionisation potentials are only slightly above the nominal low FIP threshold (Fig. 2.11b). Their abundances in the solar photosphere cannot be measured spectroscopically, but can still be derived with reasonable confidence (*e.g.*, Lodders, 2020). Therefore, the question was: can reliable abundance ratios of (Ar)/Kr/Xe in the solar wind be derived from lunar samples? And if so, are they similar or different from inferred solar values? First measurements had shown that the Xe/Kr ratio was several times higher than the value then assumed for the Sun (Eberhardt *et al.*, 1972; Bogard *et al.*, 1973). Because the N/Kr and N/Xe ratios were several times higher than the solar value – and N was widely considered at the time to be of solar wind origin – the prevailing view was that both Kr and Xe are not well retained in lunar samples, and that losses of Kr exceed those of Xe. Our online etching experiments on lunar mineral separates seemed to contradict this pessimistic view. The ratio Kr/Xe and essentially also Ar/Kr remained largely constant over several etch runs, unlike He/Ar and Ne/Ar which strongly increased with depth, as expected for diffusive loss of the two lightest noble gases. We therefore concluded that the relative abundances of the heavy noble gases in the solar wind are faithfully mirrored in lunar samples. Plotted on a FIP diagram, and anchored to Ar, this showed that Xe in the solar wind behaves almost like a low FIP element, although its first ionisation potential of 12.1 eV is above the low FIP threshold of ~10 eV observed for other elements (Wieler and Baur, 1995; Fig. 2.11b). Geiss and Bochsler (1985) had previously suggested that the *First Ionisation Time* (FIT) may be an important parameter governing FIP related fractionation. The FIT is a measure of how fast a sizeable fraction of the atoms ionise in the chromosphere, ranging between less than a second for Mg and up to several minutes for He (Geiss and Bochsler, 1985). FIT correlates well with FIP but is atypically short for Xe. Our data in Figure 2.11b therefore agreed well with Geiss and Bochsler's FIT hypothesis. Moreover, the FIP fractionation of Xe (especially relative to that of Kr) seemed to have been larger in high antiquity samples, suggesting a secular change in solar wind composition.

Figure 2.12 **(a)** Charles Hohenberg at the poster session during the 2006 Meteoritical Society meeting in Zürich. **(b)** Alex Meshik during the post conference excursion in Morocco after the 2014 Meteoritical Society Meeting in Casablanca, apparently unimpressed about the opportunity to search for shatter cones at a terrestrial impact site. **(c)** Rainer Wieler and Gregory Herzog at the Sonora Desert Museum near Tucson.

These findings required confirmation. The opportunity arose when Charles Hohenberg in St. Louis invited me to visit his laboratory in 1995 (Fig. 2.12). I proposed to analyse the elemental abundances of Ar, Kr, and Xe in individual grains of various mineral types from lunar regolith samples with different antiquities. So, during two months of St. Louis summer heat I was a guest on the famous "fourth floor" at the McDonnell Center for the Space Sciences at Washington University. Charles had been on sabbatical in Peter Signer's lab a couple of years before I started my doctoral work there. The two mass spectrometers in St. Louis reminded me in many ways of our two "Minneapolis machines", the instruments Peter Signer had brought to Zürich from Al Nier's'' laboratory (see above). The scientific life on the fourth floor was very inspiring, reflecting the spirit of Bob Walker, with Ernst Zinner, Tom Bernatowicz, Ghislaine Crozaz, Sachiko Amari, Frank Podosek, Larry Nittler and many more, of course not forgetting the many dogs that regularly accompanied their human friends to work. We worked hard, as many grains needed to be analysed. Not the least motivating for long working hours was the fact that it was simply too hot outside. Charles showed up in the lab almost every day, and few days went by that he did not modify at least one command in the machine control software that he had written himself. With a lot of help from Karl (Charly) Kehm and Alex Meshik, we produced a nice data set. Alex had just arrived from Russia and we lived next door to each other. I remember our first joint shopping trip. For Alex, a US style grocery store was even more overwhelming than it had been for me when I first visited the US. I couldn't convince him to buy just a small box with a few chicken wings for both of us, it had to be the largest size. So we ate chicken wings for four or five dinners in a row, and our initial supply of orange juice also lasted quite

a while. Alex, his wife Olga Pravdivtseva (who arrived later) and their daughter Xenia (guess why her parents chose that first name for her!) are still in St. Louis and have long since adapted to the American lifestyle.

The data obtained in St. Louis were published in *Nature* (Wieler *et al.*, 1996; Fig. 2.13). Within each sample, all grains showed essentially constant Ar/Kr/Xe ratios, regardless of mineral type and widely varying gas concentrations. This would not have been expected if the gas abundances had been altered by loss processes. And we also confirmed the difference in Xe/Kr of roughly a factor of two between high and low antiquity samples that had been observed in the *in vacuo* etch analyses. Hence, we concluded that the lunar regolith does indeed faithfully reflect abundances of the heavy noble gases implanted by the solar wind. This meant that the differences in Xe/Kr between samples that had captured their share of solar wind relatively recently, *i.e.* perhaps somewhere during the last 100 Ma or so, and samples with solar wind antiquities of billions of years, were not simply a result of element fractionation processes in the regolith after trapping that affected old and young samples differently.
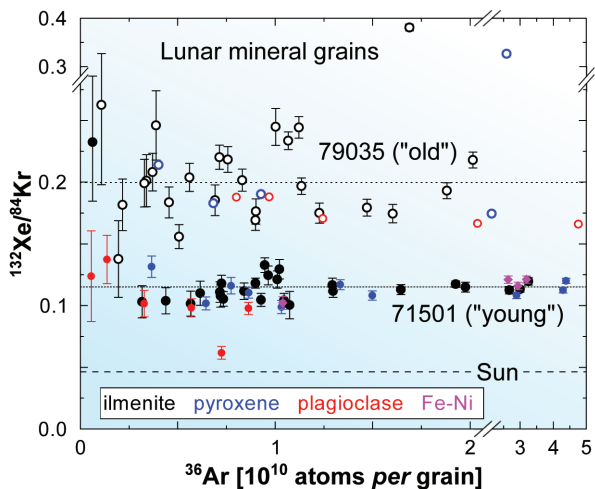
Figure 2.13 $^{132}Xe/^{84}Kr$ ratios *versus* amounts of ^{36}Ar (in 10^{10} atoms *per* grain) in individual mineral grains (mineral type is colour coded) of a low antiquity (71501, closed symbols) and a high antiquity (79035, open symbols) sample from the lunar regolith. Exact grain masses were not determined, but the spread in ^{36}Ar is much larger than the spread in grain surface area, indicating highly variable solar wind irradiation of different grains. Xe/Kr ratios in all grains from the same sample are similar, independent of mineralogy and solar wind Ar amounts. Solid lines indicate average $^{132}Xe/^{84}Kr$ ratios of the ilmenite grains of the two samples. These and similar single grain analyses carried out in Charles Hohenberg's laboratory in St. Louis provided further evidence that the Xe/Kr ratios in the lunar regolith reflect the true value in the solar wind. See text for further details. Figure adapted from Wieler *et al.* (1996).

Further confirmation that lunar regolith samples – or at least the clean mineral grains therein – correctly reflect the relative Kr and Xe abundances in the solar wind came with Genesis. As discussed in more detail in the next section, Xe/Kr ratios measured in various Genesis samples (Vogel *et al.*, 2011; Meshik *et al.*, 2014) are only marginally lower than the values in the low antiquity lunar samples, both when measured by *in vacuo* etching (CSSE) and single grain analyses. Vogel *et al.* (2011) and Wieler (2016) argued that this strengthened the conclusion for a secular decrease of Xe/Kr in the solar wind over the past several billion years. As I noted in my 2016 paper, this would – in my view – be the only remaining secular change in solar composition that had been proposed by John Kerridge in 1980. However, no clear explanation has been proposed as to how such a change could have happened, although I speculated in 2016 that it might be related to a hypothetical secular decrease in solar wind flux. Over the past few years, I have had many discussions with Peter Bochsler on this topic. If anything, Peter would rather expect Xe/Kr to have been lower in the early solar wind if ionisation in the chromosphere was dominated by EUV (extreme ultra-violet) photons. We discuss this in two LPSC contributions (Wieler and Bochsler, 2020; 2022). Does the lunar regolith perhaps tell us about processes unrelated to a secular change in solar wind composition?

We now explore the hypothesis that the high antiquity samples may contain Xe from the Earth's atmosphere carried to the Moon. The idea of an "Earth Wind" was mentioned earlier in Section 2.4., as Geiss and Bochsler (1982) and later Ozima *et al.* (2005) had suggested that the unexpectedly high nitrogen abundance in lunar soils may be due to a contribution from the terrestrial atmosphere. In the case of Xe, the idea has been fostered on the one hand by recent observations by the Nancy group led by Bernard Marty that Xe in the ancient terrestrial atmosphere has become isotopically heavier until about two billion years ago, suggesting a substantial loss of atmospheric Xe (*e.g.*, Avice *et al.*, 2018). On the other hand, Kevin Zahnle and co-workers (Zahnle *et al.*, 2019) proposed that Xe could be efficiently ionised in a hydrogen-rich early atmosphere by reso-nant charge exchange with protons, a process that would not work for any other noble gas with their higher first ionisation potentials. If some of these Xe ions reached the lunar surface, they could have been implanted into grain surface layers together with solar wind Xe. Wieler and Bochsler (2022) argue that this might explain the higher Xe/Kr ratios in high antiquity samples, but we also point out that the process must be modelled more realistically. For the time being, Earth Wind Xe on the Moon remains a hypothesis. As for many other open questions, samples from the far side of the Moon would be highly desirable for further tests.

2.5.5   The Genesis Mission

The Genesis mission collected solar wind ions in space at Lagrange point L1 (about 1.5 million km sunwards of Earth) for about two years and four months in various materials that were returned to Earth to be analysed by a large

number of laboratories. As such, it was a follow up of the Solar Wind Composition Experiment using aluminum foils exposed on the Moon by the Apollo astronauts (Section 2.2), though with a much broader scope. NASA selected Genesis in 1997 as the fifth of its low cost "Discovery" missions, with Donald Burnett from Caltech being the Principal Investigator. Perhaps Don (Fig. 2.10) should more aptly be called The Soul of Genesis, a role for which he received in 2012 the Leonard Medal, the Meteoritical Society's highest award. Like all space missions, Genesis was a huge team effort, but I allow myself to highlight two persons who certainly were among Don's most dedicated allies: Amy Jurewicz and Roger Wiens. For our group, Genesis provided much fresh motivation to extend our studies of noble gases (and other elements) in the solar wind, parts of which have been mentioned above. This work resulted in the doctoral thesis of Ansgar Grimberg and a multitude of projects by Veronika Heber and Nadia Vogel. Beyond this, Genesis has led to a large number of collaborations and much scientific exchange with colleagues around the world, far too many to mention them all here. The "Genesis Science Team Meetings" that Don organised on the Sundays before LPSC, and which still take place remotely since 2021, have brought together many old and new friends of mine for more than two decades and continue to be highlights in my personal agenda. The meetings confirm one of the main predictions in Don Burnett's mission proposal. As a sample return mission, Genesis has the advantage of enabling measurements using the best laboratory-based analysis techniques available for much of the 21st century (*e.g.*, Burnett and Genesis Science Team, 2011).

Veronika Heber was a particularly important person involved in Genesis in our team and later when working with Kevin McKeegan at UCLA. She started her work at ETH in 1998 as the third doctoral student for whom I acted as main supervisor after having succeeded Peter Signer as head of the noble gas cosmo- and geochemistry group (we will meet the first two of "my" graduate students, Henner Busemann and Jörg Schäfer, later). Before Veronika became involved in the preparatory studies to select the Bulk Metallic Glass sample to be flown on Genesis and eventually studied by Ansgar Grimberg (Section 2.5.2), she investigated another long standing problem with lunar samples. The question was whether the lunar regolith provided evidence for a (modest) secular increase in the ^{3}He/^{4}He ratio in the solar wind. I mentioned in Section 2.3 the perhaps most important result of the Apollo Solar Wind Composition experiment: definitive evidence that the D/H ratio in Earth's oceans is about an order of magnitude higher than the protosolar value before deuterium had been burned to ^{3}He in the very young Sun. Geiss and Reeves (1972) explained this in terms of equilibrium reactions between hydrogen and hydrogen compounds in the solar nebula and suggested that D/H values in the solar system could vary widely. There remained one open question, however: does the ^{3}He abundance in the outer convective zone of the Sun, the source region of the solar wind, correctly represent the protosolar (D + ^{3}He)/H ratio? It seemed possible that some ^{3}He, freshly synthesised in the solar interior as transient product in the reaction chain converting H into ^{4}He, was brought into the outer convective zone. Early lunar sample analyses had suggested this (Geiss, 1973). However, Veronika was able to disprove

this with a series of very high resolution stepwise etch analyses of both low and high antiquity samples (Heber *et al.*, 2003). Therefore, the ^{3}He/^{4}He ratio of the present day solar wind does not need to be corrected for a putative addition of freshly synthesised ^{3}He. Nevertheless, caution is still required, because the He isotopic fractionation between the Sun and the solar wind is still not perfectly known (see also later in this section), and also because different values are used for the protosolar ^{3}He/^{4}He ratio, the other important parameter for the calculation of protosolar D/H. Most workers adopt the value in Jupiter's atmosphere (Mahaffy *et al.*, 1998), which is also close to the value in the present day Local Interstellar Medium measured directly with foils exposed on the MIR space station (Busemann *et al.*, 2006; Section 3.3.4). Asplund *et al.* (2021) discuss these uncertainties in more detail.
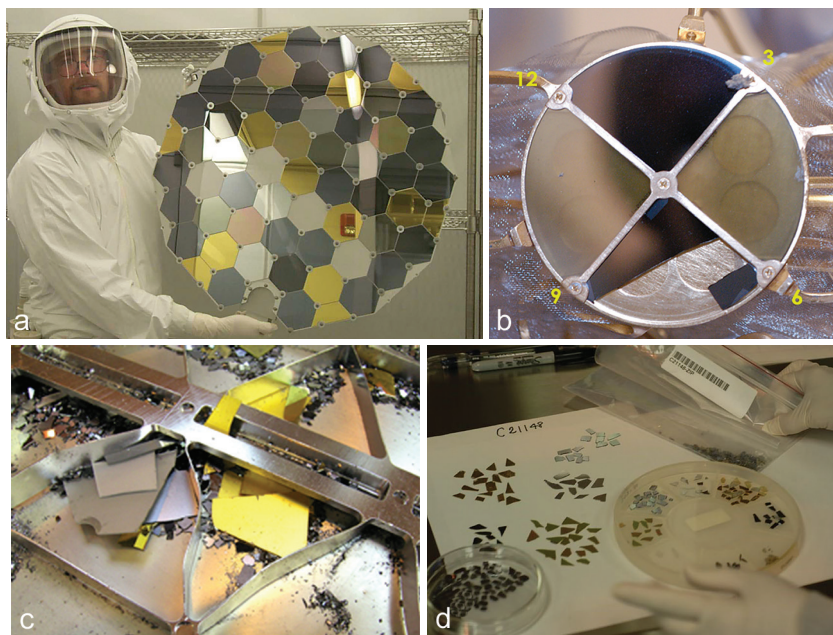
Figure 2.14 **(a)** One of four panels with hexagon collectors of either bulk solar wind or solar wind from one of three "regimes" (fast solar wind, slow wind, or solar wind from coronal mass ejections, Neugebauer *et al.*, 2003; Reisenfeld *et al.*, 2013). Collectors are made of different materials, such as silicon, aluminum on sapphire (AloS), *etc.* (Jurewicz *et al.*, 2003). Collectors of different regimes have different thicknesses, allowing regime identification after the crash. **(b)** The solar wind concentrator target survived the crash almost undamaged. This target was used to measure the O and N isotopic compositions in the solar wind. Neon data along a radial traverse of one of the SiC quadrants measured by Heber *et al.* (2011) were used to correct for isotopic fractionation of solar wind ions induced by the concentrator's electrostatic field (*cf.* Fig. 2.16). **(c, d)** Shards of collector materials after the crash. All pictures courtesy of NASA.

Veronika Heber's paper of 2003 in the *Astrophysical Journal* was the last major study of our group on solar noble gases based on analyses of lunar (or meteoritic) samples, as we now concentrated on the upcoming Genesis mission. Veronika and I became early members of the Genesis science team.

The history of Genesis has been told many times, including the crash landing in 2004 because a sensor which should have triggered the parachutes when the sample return capsule entered the atmosphere was installed upside down (*e.g.*, Burnett and Genesis Science Team, 2011). In Zürich on September 8, 2004, we had gathered in our coffee room to watch NASA's Live TV show from the landing site in the Utah desert, which was to culminate in helicopters catching the sample return capsule in mid-air. With us was a team from Swiss TV and I was quite well prepared to tell the public how happy we all were that we could finally soon start doing interesting science on matter returned from the Sun. Since at least the older generations in my country would still remember the days of the famous Apollo Solar Wind Composition experiment some 30 years ago, I also hoped to tell them that Genesis would allow a much wider range of measurements by a much larger community. But instead of helicopters and open parachutes, the NASA camera showed only a blurry image of something resembling a tumbling discus. And then nothing! Also the NASA commentator was unable to explain what he was seeing, but it was crystal clear that something had gone terribly wrong. I was shocked. We all were. My first worry was how to explain to Ansgar Grimberg that we now needed to activate plan B for his doctoral thesis, although I did not really have a plan B worthy of the name. Fortunately, as we saw above, we eventually did not have to rely on a contingency plan. My second problem that evening was what to say to the TV people and the public. I decided to hide my true feelings and play the optimist. I explained that, although we did not know any details at this moment, the precious samples were back on Earth, and even if they – most likely – were shattered to pieces, they might still allow for some analyses to be made. I added that although solar wind ions were implanted to only very shallow depths, they were not residing at the immediate surfaces of sample collectors, so it might just be a matter of selecting intact pieces and doing a thorough cleaning to be able to detect solar wind atoms. Although at the time I did not really believe what I was saying, it turned out to be very close to the truth, and I later learned that Don Burnett had made very similar statements to both the media and NASA officials. I am sure that, unlike me, Don was convinced about what he was saying already immediately after the crash. It took us a while to learn that the Bulk Metallic Glass – the target most important to us at the time – had remained essentially intact except for many scratches. Judy Allton and other members of NASA's Genesis sample curation team provided us with a part of the BMG sample so that Ansgar could produce a fine doctoral thesis and the first publications reporting Genesis data (Grimberg *et al.*, 2006; 2008), as explained in the Section 2.5.2. Figure 2.14 shows Genesis sample collectors pre-flight and broken upon the crash.

Our further work on Genesis was mainly carried out by Veronika Heber and Nadia Vogel (Fig. 2.15). Veronika's dissertation has already been mentioned, and Nadia's doctoral work in my group on primordial noble gases in meteorites is presented in Section 3.2.3. After postdoctoral positions at the Open University in Milton Keynes (Veronika), UC Berkeley (Nadia), and the University of Bern (Veronika and Nadia), they both returned to ETH. First, we focused on determining the elemental abundances and isotopic compositions of He, Ne, and Ar and the elemental abundances of Kr and Xe. The latter two are much rarer in the solar wind than the lighter gases He, Ne, and Ar, and therefore more difficult to measure. Our group was one of four teams analysing noble gases in Genesis targets. The others were led by Bob Pepin in Minneapolis, Alex Meshik in St. Louis, and Sarah Crowther and Jamie Gilmour in Manchester. Because of the controlled exposure conditions, Genesis data are less prone to unrecognised systematic errors than, for example, lunar sample analyses. In Zürich we used two different types of collector materials, DOS (Diamond-like carbon On a Silicon substrate, Fig. 2.15a) for He, Ne, and Ar and mainly silicon wafers for Kr and Xe (Heber *et al.*, 2009; 2012; Vogel *et al.*, 2011; 2019). The gases were extracted by UV laser ablation. DOS has the particular advantage that essentially no correction for losses of implanted solar wind ions by back scattering is required due to the low atomic mass of carbon.
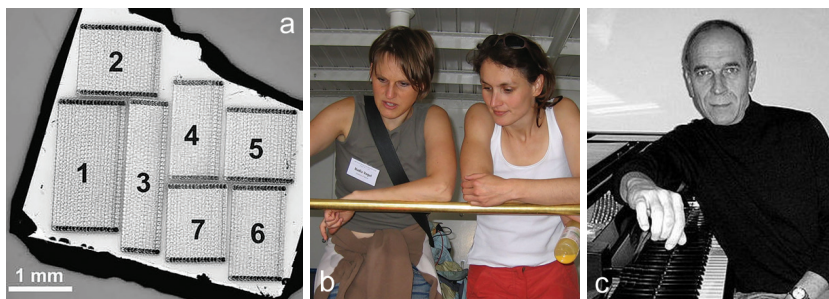
Figure 2.15   **(a)** A shard from a Diamond-like Carbon on Silicon (DOS) collector sampling bulk solar wind. Veronika Heber analysed seven different areas for He, Ne, and Ar by UV laser ablation (Heber *et al.*, 2009). Picture from Heber *et al.* (2009) with permission from Elsevier. **(b)** Nadia Vogel and Veronika Heber contemplating the engine of the boat "Stadt Zürich" on an excursion during the 2006 Meteoritical Society meeting in Zürich. **(c)** Jean-Paul Benkert at his piano. Jean-Paul is a dedicated Jazz Pianist.

A major goal was to establish if the solar wind noble gas compositions determined over many years on lunar samples could be confirmed. They were confirmed. For example, Veronika Heber's ^{20}Ne/^{22}Ne ratio of 13.78 ± 0.03 (Heber *et al.*, 2009) agrees perfectly with Jean-Paul Benkert's lunar value of 13.8 ± 0.1 (Benkert *et al.*, 1993). The backscatter-loss-corrected value of ~13.8 ± 0.2 determined with the Genesis Bulk Metallic Glass sample also agrees very well with

the DOS and lunar values, although this was not a primary goal of the BMG analyses (Grimberg *et al.*, 2008). As explained in the previous section, the excellent agreement of the isotopic composition of solar wind noble gases determined on lunar samples with the new Genesis values was far from trivial. The consistency confirmed the hypothesis (Becker, 1998, Wieler, 1998) that the outermost layers of lunar regolith mineral grains reflect the true isotopic composition of implanted solar wind. In the paragraph following the next one, this observation will again be important for the heavy gases Kr and Xe. Heber *et al.* (2009) also provided accurate isotopic compositions of solar wind He, Ne, and Ar as well as the elemental ratios He/Ne and Ne/Ar, which are now widely adopted by the scientific community.

Just as important as obtaining accurate values for the composition of the noble gases in the solar wind is obtaining reliable estimates of the isotopic and elemental fractionation between the Sun and the solar wind. For cosmochemists, the solar wind is often just a "proxy" for the composition of the Sun (or the solar nebula), which is their primary interest. For solar physicists, fractionation effects between the solar wind and its source region are of interest in understanding solar wind formation. Genesis therefore not only collected bulk solar wind during the entire 2.3 year collection period but also solar wind of three different "regimes", with the respective sample panels exposed according to an algorithm based on various parameters measured onboard (Neugebauer *et al.*, 2003; see Fig. 2.14). These were "Fast" or "coronal hole" solar wind, "Slow" or "interstream" solar wind and "CME", *i.e.* solar wind from so called Coronal Mass Ejections (*cf.* Reisenfeld *et al.*, 2013). These three regimes only allowed considerably less detailed studies of fractionation effects than data obtained by space-based instruments, but the Genesis regimes provided much higher accuracies, for elemental as well as isotopic abundances. Veronika Heber analysed isotopic fractionation of He, Ne, and Ar among the three Genesis regimes by carefully bracketing analyses of one regime with those of another regime (Heber *et al.*, 2012). The isotopic fractionation strongly decreases from He to Ne to Ar in all regimes, from about 6 %/amu for He to 0.25 %/amu for Ar. Roland Bodmer and Peter Bochsler in Bern had investigated the role of Coulomb collisions in the acceleration of minor species in the solar wind (Bodmer and Bochsler, 2000). Their predicted isotopic fractionation effects agreed well with the observed isotopic fractionation factors of He-Ar between the Fast and Slow Genesis regimes as measured by Heber *et al.* (2012). However, extrapolating the measured He isotope data to the solar H/He ratio as proposed by Gloeckler and Geiss (2000) yields a substantially different solar He isotopic composition than the value obtained according to the Inefficient Coulomb Drag hypothesis (ICD), a problem discussed by Asplund *et al.* (2021).

The observation that the ICD hypothesis well predicts noble gas isotope fractionations between Fast and Slow solar wind regimes also became important for correcting the measured oxygen isotopic composition in Genesis targets for fractionation between Sun and solar wind (McKeegan *et al.*, 2011). Because of its paramount importance to cosmochemistry, determining the isotopic composition

of oxygen in the solar wind was the most important goal of Genesis. The team led by Kevin McKeegan at UCLA brilliantly achieved this by combining the front part of a secondary ion mass spectrometer (SIMS) with an accelerator mass spectrometer, called the MegaSIMS instrument. When the measured solar wind data are corrected by the ICD formalism, the resulting solar oxygen isotope composition in a classical oxygen three isotope diagram falls almost exactly on the straight line defined by data from calcium-aluminum-rich inclusions (CAI), the first solar system condensates (McKeegan *et al.*, 2011). This is in line with a prediction explaining oxygen isotope compositions of CAIs to result from fractionation processes induced by isotope selective self-shielding during ultraviolet photolysis of CO in the solar nebula (Clayton, 2002). Veronika Heber and Nadia Vogel also provided noble gas data that were essential for correcting the oxygen isotope data for fractionation induced by the trapping process on board Genesis. Oxygen (as well as nitrogen, see Section 2.4) was measured in a circular "concentrator target" mounted at the centre of a focusing ion telescope in order to enhance the ion fluence by several ten times (Wiens *et al.*, 2003; Fig. 2.14). This led to an isotope fractionation dependent on the position of the analysed spots, which was corrected by Ne data measured in Zürich along a traverse of one of the SiC quadrants of the concentrator target (Heber *et al.*, 2011; Fig. 2.16). The corrected data define the isotopic composition of oxygen in the solar wind with high accuracy.
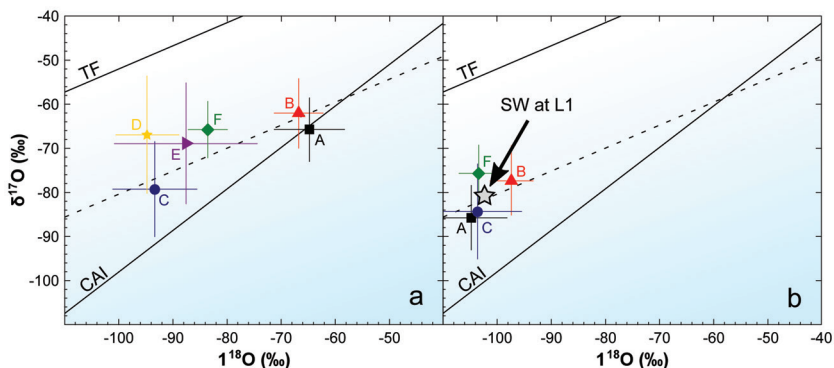
Figure 2.16 **(a)** Oxygen three isotope diagram showing data from different radial positions (*cf.* Fig. 2.14) of the Genesis concentrator target measured at UCLA with the MegaSims instrument (McKeegan *et al.*, 2011). The TF (Terrestrial Fractionation) line is the locus of isotopic compositions of terrestrial oxygen fractionated to various degrees, the line labelled CAI represents oxygen in Calcium-Aluminum-rich Inclusions in meteorites. **(b)** The data of the four most precisely measured spots (A,B,C,F) in panel (a) corrected for concentrator-induced isotopic fractionation along the dashed line defines the oxygen isotopic composition in the solar wind (SW) as measured by Genesis at Lagrange point L1. The isotopic fractionation along the radial position in the concentrator was determined with Ne isotopes by Heber *et al.* (2011). From McKeegan *et al.* (2011) with permission from AAAS.

Nadia Vogel investigated the elemental abundances of Ar, Kr, and Xe, first in bulk solar wind samples from Genesis (Vogel *et al.*, 2011). The very low concentrations of Kr and especially Xe required particularly careful analyses. As noted in Section 2.5.4, the Xe/Kr ratio measured in Si wafers sampling Genesis bulk solar wind was only marginally lower than the ratio determined in lunar samples of low antiquity. Also Ar/Kr in Genesis samples agreed with lunar values. This is an important confirmation that the lunar regolith correctly records the relative abundances of Ar, Kr, and Xe in the solar wind, implying that Xe is enhanced in the solar wind relative to Kr and Ar, presumably reflecting the lower first ionisation potential of Xe or its relatively short first ionisation time, as discussed in Section 2.5.4. That section also addressed the implications of this with respect to the observed secular decrease of Xe/Kr in lunar samples of different solar wind antiquities. After the bulk solar wind targets, Nadia analysed Ar, Kr, and Xe elemental abundances in regime targets, work that was eventually published after a "minor" delay of about eight years (Vogel *et al.*, 2019; Fig. 2.17). The enrichment of Xe relative to Ar and Kr and solar abundances is slightly more pronounced in the Slow solar wind (~12 %) than in the Fast solar wind, in accord with the idea that the first ionisation time of the heavy noble gases in the solar chromosphere at least partly governs their fractionation in the solar wind.
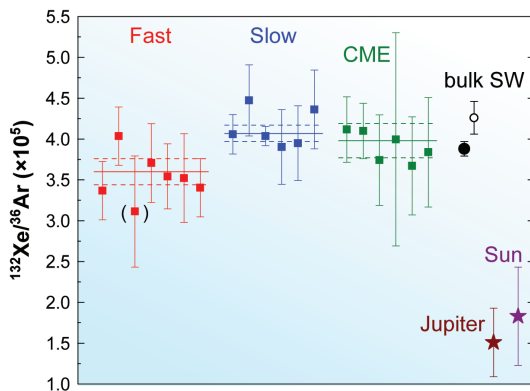
Figure 2.17 ^{132}Xe/^{36}Ar ratios in Si targets exposed to the three different regimes sampled by Genesis (Vogel *et al.*, 2019). The data confirm that Xe in the solar wind is enhanced relative to its abundances in the Sun (and Jupiter), with the Slow solar wind (and the CMEs) being slightly more fractionated that the Fast solar wind. Figure from Vogel *et al.* (2019) with permission from Elsevier.

Whereas we had focused on determining the *elemental* abundances of the very rare gases Kr and Xe in Genesis targets, Sarah Crowther and Jamie Gilmour in Manchester and – in a particularly heroic effort – Alex Meshik and his team in St. Louis, were able to measure the *isotopic* compositions of these two elements as well (Crowther and Gilmour, 2013; Meshik *et al.*, 2014; 2020). I was

very pleased to find that the Genesis data essentially confirmed the compositions deduced some 20 years earlier from lunar regolith data, to a large extent those we had obtained with closed system stepped etching analyses (Section 2.5.4.). As for the light noble gases He, Ne, and Ar, the agreement between lunar and Genesis data was not a trivial result.

Around the time of my official retirement in 2014 we performed a last set of analyses related to solar wind noble gases, but this time neither on lunar samples nor on Genesis targets. Together with our colleagues Peter Bochsler and Fritz Bühler from the University of Bern we reanalysed some of the aluminum foils exposed to the solar wind by the Apollo astronauts (Fig. 2.3). Fritz and Peter had been involved in the original measurements in Bern during the Apollo days (Geiss *et al.*, 1972; 2004). Forty years later, Nadia Vogel measured several pieces of the Apollo 15 foil in Zürich (Vogel *et al.*, 2015), after the samples had first been checked for dust contamination by Addi Bischoff and M. Horstmann in Münster. The major conclusion of this study was that mean isotopic and elemental compositions of He, Ne, and Ar in the solar wind have not significantly changed between the Apollo and Genesis mission periods. This conclusion was less trivial as it may sound, since short term variations in solar wind composition are well known from spacecraft data and, taken alone, also the different Apollo foil data could not rule out a minor temporal variability.

Genesis, however, has stuck with me to this day. In 2019, Don Burnett invited me as visiting scholar to Caltech in Pasadena. Don and I had received permission from Veronika Heber to finally publish another important data set of Genesis that she had produced between 2008 and 2013 while working at UCLA with Kevin McKeegan's group. With crucial contributions from Amy Jurewicz from Arizona State University and Yunbin Guan and Don Burnett at Caltech – among many others – Veronika had measured the abundances of several major elements in Genesis bulk solar wind and regime targets using SIMS at UCLA and Caltech. But after returning to Switzerland to the Paul Scherrer Institute, she had not found time to publish the results comprehensively. The abundances of major elements in Genesis targets are very important to understand element fractionation in the solar wind, both for low and high FIP elements, again because Genesis allows a much higher precision than spacecraft data. When I arrived in Pasadena on February 1st 2020, Covid 19 had already reached Europe (although it did not lock down the continent until around mid-March) but seemed very far from the US West Coast. Based on a first draft by Veronika, Don and I prepared a manuscript and we made good progress, until, almost overnight it seemed, Covid 19 also arrived at the West Coast and I had to return to Switzerland prematurely by mid-March. Barely two weeks earlier, Don and I had attended a hockey game between the LA Kings and the Toronto Maple Leafs, amidst perhaps 10,000 other hockey aficionados. On the day I left, the driver who took me to LAX airport said he had never made that trip so quickly. No traffic jams, obviously out of fear of the virus.

My early return led to a delay, but the paper was finally published in the *Astrophysical Journal* in early 2021 (Heber *et al.*, 2021). The FIP diagrams in Figure 2.18 display the abundances of the elements measured by SIMS, including the noble gas data from Vogel *et al.* (2019). The ordinate shows the fluence ratios of the elements with respect to that of Mg, normalised to the respective abundance ratios in the solar photosphere. The well known enhancement of low FIP elements is clearly visible in both the bulk solar wind and regimes, although the differences between regimes are remarkably small. As expected from solar physics and observations by space missions (*e.g.*, von Steiger *et al.*, 2000), the Fast regime is always less fractionated than the Slow and CME regimes. The differences in the Genesis regimes are remarkably small, however, which is new and potentially important and could only be recognised because of the high precision of Genesis data. In some cases, the data presented by Heber *et al.* (2021) approach the accuracy required to test the extent to which elemental abundances of CI chondrites approach solar abundances, although further analytical progress by the Genesis Science team is required to definitively answer some still lingering questions such as whether the data points in the left part of the diagram form a plateau, *i.e.* whether the low FIP elements (K – Fe) are unfractionated among themselves. The data in Figure 2.18 are consistent with this hypothesis within their uncertainties, but they are also consistent with an increase of fractionation with decreasing FIP.

Work on Genesis samples is ongoing, not only on this topic, as was again made clear at the 2021 and 2022 virtual Genesis science meetings. There is no question that Genesis was and is a success story, although it seems that some people only remember the images of the crashed landing capsule in Utah, and hence, erroneously, consider the mission a failure. This is one reason I felt it was important to write this section. Also for me personally, my long journey with solar noble gases, which started in 1976, is, I hope, not yet over. For example, I am following with great interest the work on new lunar samples brought back by the Chinese Chang'e 5 mission. Additionally, "Revealing the record of the ancient Sun and our astronomical environment" is one of the seven science objectives of NASA's Artemis programme, with the first crewed missions after Apollo planned to reach the surface of the Moon, hopefully around 2025.
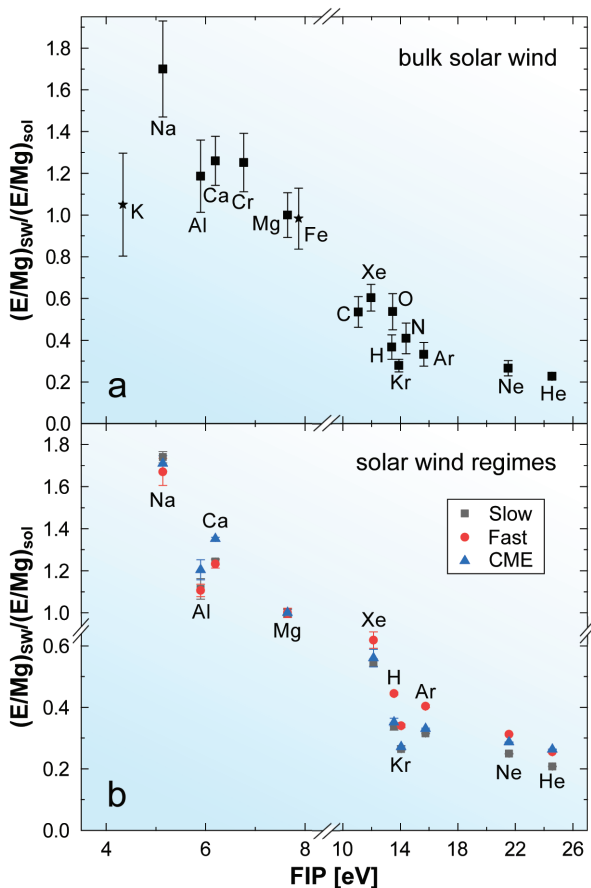
Figure 2.18 **(a)** Fluence ratios (element (E)/Mg) in Genesis bulk solar wind targets normalised to solar ratios as given by Heber *et al.* (2021). **(b)** Same for Genesis regime targets. Error bars in the upper panel include uncertainties on the solar abundances, while error bars in the lower panel only reflect analytical 1σ uncertainties. The FIP fractionations for the regimes are strikingly similar, with Fast SW being least fractionated, as expected (see text). The small differences between the individual regimes could only be detected thanks to the high precision of Genesis compared to spacecraft data. Figure from Heber *et al.* (2021).

3. NOBLE GAS (AND OTHER) STUDIES ON METEORITES AND OTHER SAMPLES FROM FAR AWAY

Let me come back one more time to my early days in science. As described in the previous section, my scientific focus during my doctoral studies was almost exclusively on lunar samples and their noble gases. Only in passing did I realise that nature also provides us with other interesting matter from beyond our Earth. My knowledge about meteorites and their noble gases in particular tended towards zero. In hindsight, it is hard for me to believe that this should really have been the case, since I had attended several cosmochemistry meetings, where of course I followed in particular the noble gas talks on meteorites. Probably I just had more than enough to do with understanding my own little niche in science without getting interested in the broader perspective. At the very least, I have learned from this that while the advice we usually give young people to also take an interest in the work of others is laudable, we should also actively promote this exchange.

Luckily, the wonderful book of meteorites – especially their noble gases – began to open after I graduated and was offered a postdoc position in Peter Signer's group. Gradually, the group's interests expanded to include noble gas geochemistry, from fissiogenic noble gases in uranium-rich minerals, to cosmogenic noble gases (and radionuclides) in terrestrial samples as a tool in geomorphology, to noble gas hydrology. Most of these activities have been in collaboration with other scientists and their complementary expertise. With the arrival of Alex Halliday at ETH in 1998, my personal interests further expanded to other isotope systems, with an emphasis on what noble gases could contribute to their understanding. While for the most part these activities have taken place in parallel, sometimes for decades, in what follows I will try to the extent possible to separate work on meteorites from work on terrestrial samples, the latter being addressed in Sections 4 and 5.

3.1 The (Extraterrestrial) Cosmogenic Noble Gas and Radionuclide Universe

In the early 1980s, Uli Herpers and Rolf Sarafin of the University of Cologne, together with Rolf Michel who just had moved from Cologne to the University of Hannover, presented us with their programme to study the production systematics of cosmogenic nuclides in meteorites. They proposed what eventually led to a broad collaboration between the groups in Hannover, Cologne, Mainz, and Zürich. These studies as well as our extensive further work on cosmogenic noble gases and radionuclides in meteorites will cover the first part of this section. Toward the end of the 1980s, I realised that our gas release technique by *in vacuo* etching (CSSE) might also be a powerful tool for studying the enigmatic

primordial noble gases in meteorites known as "phase Q" (for Quintessence). This and our other work on trapped noble gases in extraterrestrial samples form the second part of this section, which ends with a few – hopefully interesting – examples of projects somewhat off our main lines of research.

3.1.1　Cosmogenic Nuclides – a Very Short Historical Perspective

Cosmogenic nuclides are formed when primary or secondary particles of galactic cosmic rays (GCR), or in some cases solar cosmic rays (SCR, energetic particles emitted by the Sun), interact with atomic nuclei in extraterrestrial or terrestrial matter. The overwhelming part of primary cosmic ray particles are protons and – to a lesser extent – alpha particles, *i.e.* ^{4}He nuclei. When interacting with matter, these primary particles produce not only secondary protons, but also secondary neutrons, which in turn again produce cosmogenic nuclides. Cosmogenic nuclides are observable mainly in noble gas isotopes and radioactive nuclides, whose abundances in the target materials are otherwise extremely low. In solid matter, the cosmic ray flux has a mean attenuation length of roughly 50 cm. Therefore, cosmogenic nuclides in meteorites are mainly used to determine their exposure age, *i.e.* the time they spent as metre-sized or smaller bodies in inter-planetary space before falling to Earth, or in some cases their residence time in the uppermost metres of their larger parent body.

Research into cosmogenic nuclides started after World War II with the suggestion by Willard Libby that secondary cosmic ray neutrons should produce ^{14}C in the upper atmosphere of the Earth by interacting with ^{14}N. This idea led to radiocarbon dating. A few years later, Raymond Davis and Oliver Schaeffer suggested that cosmogenic nuclides produced in rocks at the Earth's surface could be used to study geological problems (Davis and Schaeffer, 1955). However, production rates of cosmogenic nuclides at the Earth's surface are several orders of magnitude below those outside the Earth's atmosphere and magnetic field, which act as an efficient shield for cosmic rays. Therefore, cosmogenic nuclides produced in rocks were routinely studied first in meteorites and lunar samples. The first successful application of cosmogenic isotopes to a meteorite was the determination of the cosmic ray exposure age of Norton County by Begemann *et al.* (1957). The most likely range reported for the tritium-helium-3 (^{3}H-^{3}He) age of 240–280 Ma is at least twice the modern value for Norton County (which is still one of the two highest exposure ages ever recorded for a stony meteorite; Miura *et al.*, 2007). Nevertheless, this pioneering study showed that meteorites have been broken off from a much larger parent object relatively late in the history of the solar system. Since then the question of how meteorites find their way to Earth has remained a major topic in cosmogenic nuclide research. Answering this question requires constant interplay between nuclide analyses and modelling efforts to improve our understanding of cosmogenic nuclide production mechanisms, production rates, and orbital dynamics (*e.g.*, Arnold *et al.*, 1961; Leya *et al.*, 2021; Gladman *et al.*, 1997). A more detailed introduction to cosmogenic nuclides is given by Wieler (2021).

3.1.2 My First Steps in Cosmogenic Nuclide Studies – New Science and Many New Friends

Peter Signer was a pioneer in cosmogenic noble gas research. While working in Minneapolis, he developed what has become known as the Signer-Nier model, which describes the production systematics of cosmogenic noble gases in iron meteorites, based on analyses of samples taken from cross sectional slabs of the two large meteorites Grant and Carbo. In Zürich, Peter continued to systematically study cosmogenic noble gases in meteorites together with Larry Nyquist, Jack Huneke, Herbert Funk, and Ludolf Schultz (see also next section). He therefore immediately accepted the proposal by Michel and Herpers to participate in their joint programme to study cosmogenic nuclide production. In Cologne, Uli Herpers (with Peter Englert and Wilfried Herr) analysed cosmogenic radionuclides (mainly ^{26}Al and ^{53}Mn) in meteorites by low level counting (for ^{53}Mn combined with neutron activation analysis) and planned to extend these studies by collaborating with the Accelerator Mass Spectrometry (AMS) team at ETH in Zürich (see below). Rolf Michel and his group in Hannover were modelling cosmogenic nuclide production in meteorites and were interested in experimental data as input to, and tests of, the models. Our contribution therefore consisted of measuring cosmogenic noble gases in meteorites, for which the Cologne group provided radionuclide data, and of noble gases in high purity artificial samples irradiated with high energy protons, as described in the next paragraph.

a   *R* = 15 cm   b
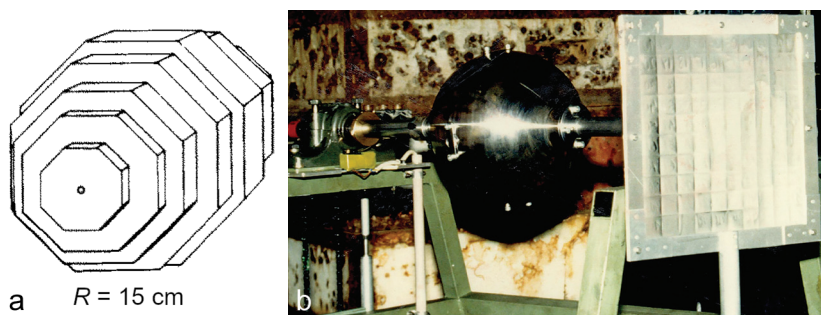
Figure 3.1 **(a)** Sketch of the model stony meteorite with a "radius" of 15 cm that was isotropically irradiated with 600 MeV protons at CERN (Michel *et al.*, 1989). The meteorite mockup was made of gabbro, which has a low water concentration (important because hydrogen efficiently moderates neutrons) and a density comparable to that of ordinary chondrites. A steel tube inserted along the central axis and a second one in a bore hole perpendicular to it (not shown) contained numerous foils of elements important for cosmogenic nuclide production, as well as degassed samples from the Jilin chondrite. Figure from Michel *et al.* (1989) with permission from Elsevier. **(b)** Picture of the iron sphere (r = 10cm) isotropically irradiated with 1.6 GeV protons at Laboratoire Nationale Saturne in Saclay (Leya *et al.*, 2004a). Rotational and translational movements of the sphere enabled an isotropic irradiation. The sphere contained high purity foils and chemical compounds of 28 different

target elements. The bright square on the right is an Al foil upstream of the proton beam whose 100 individual pieces were analysed for short lived ^{22}Na to determine the proton fluence and control beam homogeneity. Picture courtesy of Ingo Leya.

Over the years, Rolf Michel's group has isotropically irradiated five roughly spherical targets of different sizes (between 5 and 25 cm radius) with high energy protons of 600 MeV and 1600 MeV, respectively, comparable to the energy range of GCR particles (*e.g.*, Michel *et al.*,1989; Leya *et al.*, 2004a). Figure 3.1 shows a sketch of the r = 15 cm "stony meteorite" irradiated with 600 MeV protons at CERN in Geneva and the r = 10cm "iron meteorite" irradiated with 1.6 GeV protons in Saclay near Paris. The idea behind these "thick target" irradiations was to get a better handle on the development of the secondary particle cascade within a meteorite than is possible based only on measured or calculated "thin target" cross sections for nuclide production. Thin target irradiations measure the probability that a particular nuclide will be produced in a particular target element irradiated by a proton (or more often a neutron) with a particular energy. Thick target experiments are especially important to study the nuclide production by secondary neutrons. They often dominate the total production, and also only few thin target data for neutrons are available. Four of the meteorite mockups were made of granodiorite or gabbro rocks very low in water to simulate stone meteorites, while the r = 10 cm sphere consisted of iron. Tubes inserted in each meteorite dummy were filled with a large variety of targets relevant for cosmogenic nuclide production, such as high purity Mg, Al, Si foils, or, for the elements O, Na, S, K, and Ca, compounds such as FeS_2 or Na_2MoO_4 (*e.g.*, to irradiate elemental Na would have been too dangerous). In addition, the bores were filled with degassed samples from two meteorites. Irradiations were performed at CERN and at Laboratoire National Saturne in Saclay near Paris. Isotropic irradiation of the "meteorites" was achieved by a superposition of two rotational and two translational motions. In addition to the thick target experiments, foils were irradiated upstream of the dummy meteorites to determine thin target cross sections for many nuclides and target elements. Short lived and long lived radionuclides were analysed by gamma spectroscopy and AMS, respectively (*e.g.*, Englert *et al.*, 1984; Leya *et al.*, 2000a). Noble gases (He, Ne, and Ar) in the pure target elements were measured in Zürich, and the degassed meteorite samples and compounds were analysed in Mainz by Hartwig Weber and Friedrich Begemann. This entire huge data set (involving more people than I can list here) served as input to the nuclide production models developed in Hannover. I will come back to these modelling efforts below, where I will address the work of Ingo Leya, who came to Zürich after completing his doctoral thesis in Hannover with Rolf Michel.

The collaboration between the Hannover-Cologne team, our group in Zürich, and (as we soon will see), the Accelerator Mass Spectrometry group at ETH Zürich, led by Willy Wölfli, Martin Suter, and Georges Bonani was key to my education in cosmogenic nuclides in extraterrestrial samples. Two crucial events happened in 1984. The first was the "Third International Symposium on Accelerator Mass Spectrometry" in Zürich, organised by the AMS team at ETH, and the second the "Workshop on Cosmogenic Nuclides" in Los Alamos, organised by Robert (Bob) Reedy and Peter Englert. Only a few years earlier had it been recognised that tandem Van de Graaff accelerators, while becoming outdated in high energy physics research, could be used as very efficient detectors of radionuclides in Earth and environmental sciences. AMS systems count atoms rather than their decays, so much smaller samples are needed for nuclides with relatively long half-lives, such as ^{14}C, ^{10}Be, ^{26}Al, and others. In Switzerland, Hans Oeschger, the pioneer of climate science at the University of Bern, had motivated the group of Willy Wölfli to develop ^{14}C analyses by AMS. Figure 3.2 shows the 6 MV Tandem Accelerator used for these analyses and, a few years later, also for cosmogenic ^{10}Be, ^{26}Al, and other rare nuclides. The figure also shows one of the many later instruments developed by the Zürich AMS team. Most ^{14}C analyses today are done with much smaller accelerators that require considerably lower acceleration voltages to separate the rare nuclide of interest from a huge isobaric background. At the 1984 Zürich meeting, the Cologne-Zürich collaboration presented their first ^{10}Be analyses in meteorites by AMS (Sarafin *et al*. 1984). It was also at this meeting that I first met Kunihiko (Kuni) Nishiizumi, who became a very good friend and collaborator. Kuni was, and still is, keen to always using the latest technological developments, so he introduced

us to the then new world of e-mail. We immediately decided that we too needed this wonderful tool, but we also were convinced that one single e-mail address would do for the entire Signer group. Well, it didn't stay that way for long.

A few months later, the "Workshop on Cosmogenic Nuclides" became even more important to me. Arriving after midnight, I realised that Los Alamos is a somewhat special place. I had been a bit nervous about how I would find my hotel so late at night, but no problem, a US government limousine was waiting at the airport, offering a ride to everybody. The next day, Rolf Sarafin and I enjoyed the Los Alamos summer sun when we decided we desperately needed a cold beer. No bar or restaurant was open in mid-afternoon, but we found the solution in form of an army veterans club. We had to become club members, which was recorded in a very thick book, but helped us to finally get our much needed beer.

At the Los Alamos workshop I met for the first time many colleagues who since became good friends. Let me mention Jim Arnold, Marc Caffee, Jitendra Goswami, Gregory Herzog, Charles Hohenberg, Tim Jull, Kurt Marti, Kuni Nishiizumi, Bob Pepin, Bob Reedy, and Tim Swindle, among others. This two-day topical meeting helped me find my own place in the cosmogenic nuclide family. I guess my first presentation of noble gas and [10]Be data on the Knyahinya meteorite discussed next was well received.

Text Box 3.1 – Ringberg Meetings

Initially to promote the cosmogenic nuclide collaboration mentioned above, Friedrich Begemann of the Max Planck Institute für Chemie in Mainz gathered us every two to three years for a week at Ringberg Castle, the convention site of the Max Planck Society overlooking Lake Tegernsee at the foothills of the Bavarian Alps. While the first meetings in the late 1980s brought together exclusively the Hannover, Cologne, Mainz, and Zürich groups to discuss the irradiation experiments of the artificial meteorites and the nuclide production modelling, several later meetings had a broader scope and a more international audience, though still retaining a focus on noble gas geo- and cosmochemistry. Anyone who ever had the pleasure of attending a meeting at Ringberg will never forget this unique and stimulating place (Fig. 3.3). Herzog Luitpold in Bayern (Duke Luitpold in Bavaria) laid the castle's foundation stone in 1912 and devoted all his energy to its construction until his death in 1973. His friend Friedrich Attenhuber designed all the furniture and contributed every single painting. Instead of trying to describe the castle's bewildering architecture, which uniquely reflects the taste of the two men, I recommend a visit to the website: https://www.schloss-ringberg.de/

As I already remarked above about the Los Alamos meeting in 1984, such small topical gatherings are very useful not only scientifically but also for socialising. Unforgettable are the evening discussions with Bavarian beer. Most importantly, Friedrich Begemann insisted that NO abstracts were allowed to be handed in in advance! At least at one of the meetings, he set up a "Pants Down" session, where everybody was encouraged NOT to present all their wonderful findings and theories but rather their failures, unexplained issues, missing ideas and so on.

Figure 3.3 **(a)** A winter impression of Schloss Ringberg in Bavaria. **(b)** A guestroom. If you are assigned a room like this, you are probably considered a VIP. Pictures courtesy of Max Planck Society.

3.1.3 The Knyahinya Meteorite – a Benchmark for Cosmogenic Nuclide Systematics

In 1983, Peter Signer visited Gero Kurat at the Natural History Museum in Vienna, which hosts one of the world's most important meteorite collections. Peter was much impressed by Gero's office, which was perhaps ten times the size of his own modest office in Zürich and was overlooked by a large portrait painting of Emperor Franz Josef I. But Peter became even more thrilled when Gero showed him the largest stone meteorite in the Vienna collection. With more than 500 kg recovered mass, Knyahinya had been the largest known stone meteorite worldwide when it fell in 1866 in what is now Ukraine, but at that time belonged to the empire of Austria-Hungary.

Knyahinya is exhibited in a hall which was aptly described in a newspaper feature: "The meteorite hall of the Naturhistorische Museum in Vienna looks as if it had fallen out of the sky itself. It has been allowed to preserve its aura of timelessness. It has remained unchanged since 1889". Figure 3.4 shows a mural of the fall of Knyahinya and its two largest pieces. Most importantly, the main mass actually consists of three pieces that broke on impact and fit almost perfectly together. The two largest pieces expose a nearly perfectly planar cross section, which, as it turned out, includes the meteorite's pre-atmospheric centre! This reminded Peter of the cosmogenic noble gas profile that Ludolf Schultz and he had obtained from samples along a drill core through the St. Severin chondrite taken by Paul Pellas and co-workers at the Muséum National d'Histoire Naturelle in Paris (Schultz and Signer, 1976). With Knyahinya, it was now possible to sample not only a linear profile, but a complete, two dimensional cross section through a very large chondrite without having to drill a core. Peter convinced Gero Kurat to allow us to sample across the cross section on one of the two large pieces. So it was that I went to Vienna several times to take gram-sized samples with a small core drill. In all, I drilled about forty holes, each perhaps a centimetre deep, prompting Gero to remark that only a Swiss could

turn a meteorite into something resembling Emmental cheese (Wieler, 1997). After sampling, the two large pieces were arranged in such a way that museum visitors can barely see the holes.
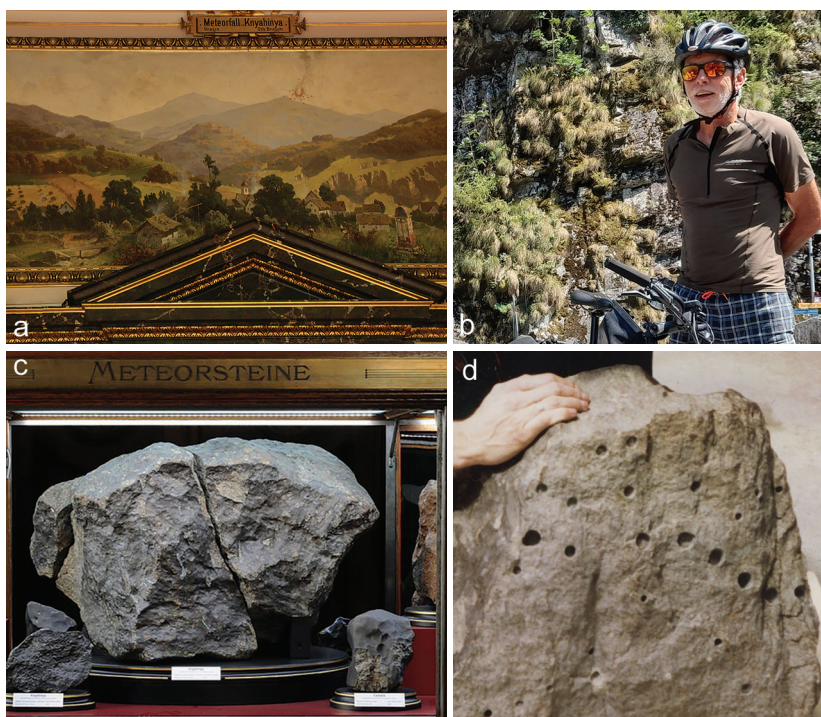
Figure 3.4 **(a)** Oil painting in the meteorite hall of the Natural History Museum in Vienna, depicting the fall of Knyahinya in western Ukraine in 1866. **(b)** Thomas Graf on a bike trip in Ticino in 2022. **(c)** Knyahinya split in three main pieces upon its fall, the two largest of which lie along an almost perfectly flat cross section passing close to the meteorite's pre-atmospheric centre. The pieces are arranged in such a way as to hide the holes produced in one of them during sampling for cosmogenic nuclide analyses. Photo courtesy of Natural History Museum, Vienna. **(d)** Many of these holes can be seen in this photo which was taken during a science fair in Zürich.

Knyahinya has probably become the most systematically studied meteorite for cosmogenic nuclides, and hence the Knyahinya data serve as benchmark for tests of cosmogenic nuclide production models. Our first data set was presented at the 1984 Los Alamos workshop, where I was able to show a correlation between the ^{10}Be activity in Knyahinya and the ^{22}Ne/^{21}Ne ratio. This ratio is a well known "shielding parameter", *i.e.* a somewhat loosely defined measure of the depth of a meteorite sample from the pre-atmospheric surface

of a "meteoroid" (the pre-atmospheric meteorite before it gets ablated upon its passage through the atmosphere) and also of the size of a meteoroid. Figure 3.5 shows the production rate of ^{21}Ne in H chondrites of different radii as a function of depth from the (pre-atmospheric) surface, calculated using a model of cosmogenic nuclide production by Ingo Leya and co-workers that will be discussed in detail in Section 3.1.5. Note that the production rate of most cosmogenic nuclides is not highest at the immediate surface of a meteoroid, where the flux and energy of the primary protons of the GCR are highest, but somewhat below this pre-atmospheric surface. This is because secondary cosmic ray protons and neutrons produce a large fraction of many nuclides, and the flux of secondaries increases from the surface down to a certain depth. Because the production of ^{21}Ne by secondary neutrons is higher than that of ^{22}Ne (the main process is ^{24}Mg(n,α)^{21}Ne), samples from deeper within a meteoroid have lower ^{22}Ne/^{21}Ne ratios than samples from near the surface, and samples from large meteoroids tend to have lower ^{22}Ne/^{21}Ne ratios than samples from small meteoroids, as shown in the next paragraph. The correlation of the ^{22}Ne/^{21}Ne shielding parameter with the ^{10}Be activity in Knyahinya implies that the production rate of ^{10}Be has a shielding dependency similar to those of Ne and other cosmogenic nuclides.
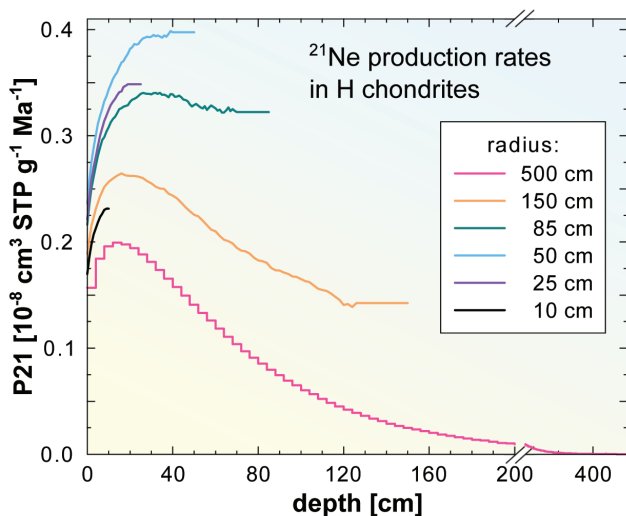
Figure 3.5 Production rate P21 of ^{21}Ne in spherical H chondrites of various radii as a function of pre-atmospheric depth, calculated with the nuclide production model by Leya and Masarik (2009, Section 3.1.5). Production rates increase from the surface to a certain depth; in larger objects they then decrease toward the centre of a meteorite. The increase reflects the build up of the cascade of secondary cosmic ray neutrons, and the subsequent decrease with depth reflects the overall slowing of cosmic ray particles and their reduced ability to produce cosmogenic nuclides.

In other words, the production of ^{10}Be (mostly from oxygen) by secondary cosmic ray particles increases from the surface up to a certain depth. The ^{10}Be data of Knyhinya that I showed in Los Alamos and the ^{10}Be measurements on a series of chondrites presented by Rolf Sarafin at the same meeting were the first data we obtained in our long and fruitful collaboration with the Zürich AMS group, later also on terrestrial cosmogenic nuclides, as discussed in Section 4.

Our work on Knyahinya received a new impetus in 1985 with the arrival of Thomas Graf as a doctoral student of Peter Signer. In the early 1960s, Peter and Al Nier had developed in Minneapolis a semi-empirical model that described the production of cosmogenic noble gases in iron meteorites. The Signer-Nier model, as it became known (Signer and Nier, 1962) was based on work by K. Ebert and H. Wänke in Mainz. Cosmogenic noble gas data from a cross section of the large iron meteorite Grant (see also Section 3.1.11) were used to fit two free parameters A and B in a semi-empirical production equation. Parameters A and B describe production by primary and secondary cosmic ray particles, respectively. This model was first extended to chondrites by Larry Nyquist. Thomas Graf now showed that the model also successfully reproduced measured concentrations of He, Ne, Ar, ^{10}Be, ^{26}Al, and ^{53}Mn as well as the ^{22}Ne/^{21}Ne ratio in Knyahinya (Graf *et al.*, 1990a;b). Figure 3.6 shows measured ^{22}Ne/^{21}Ne ratios in the Knyahinya cross section and – based on these data – modelled ^{22}Ne/^{21}Ne ratios as a function of shielding. This semi-empirical model allows the calculation of production rates in chondrites of variable sizes. Thomas also showed that an analysis of Ne and ^{10}Be in a single sample of a chondrite allows the derivation of a shielding-corrected exposure age.

Knyahinya turned out to be a remarkable stroke of luck. First, the centre of the meteoroid is preserved in the recovered meteorite, very close to the edge of the sampled cross section (Fig. 3.6). Second, from one edge of the meteorite only a few cm were lost by ablation upon atmospheric entry, as became evident by the ^{22}Ne/^{21}Ne shielding parameter. Third, Knyahinya was found to have experienced a one stage exposure history, avoiding complications in data interpretation in the event the meteoroid had broken apart during its journey to Earth. Such "complex" exposure histories will be discussed in the next section.

All these fortunate circumstances – together with Thomas Graf's excellent work – contributed to Knyahinya being studied for cosmogenic nuclides by many groups. For example, Bernard Lavielle and co-workers in Bordeaux and Tim Jull and co-workers at the University of Arizona analysed Kr, Xe, and ^{14}C, respectively, in cross section samples (Jull *et al.*, 1994; Lavielle *et al.*, 1997) and Ingo Leya used Knyahinya data to calibrate the GCR particle flux in the inner solar system, which he needed for his nuclide production model (Leya *et al.*, 2000b). Many other workers compared their meteorite data with those of Knyahinya. After his doctoral exam, Thomas Graf spent many years in Kurt Marti's group in La Jolla at the University of California, San Diego. Best known is his work on exposure age statistics of various chondrite classes (*e.g.*, Graf and Marti, 1995).
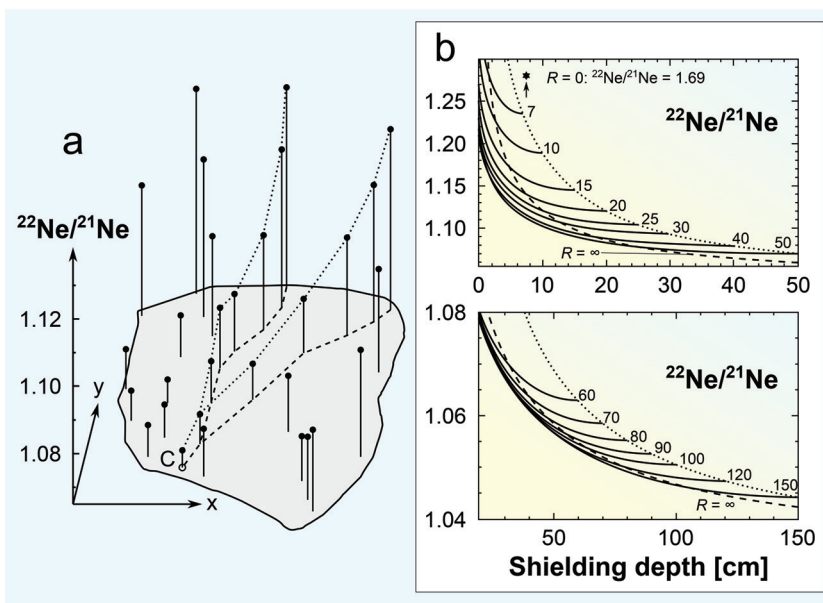
(a) The shielding parameter $^{22}Ne/^{21}Ne$ measured in the Knyahinya cross section (Graf *et al*., 1990a). C denotes the preatmospheric centre of the meteorite deduced from these and other data. Figure from Graf *et al*. (1990a) with permission from Elsevier. **(b)** $^{22}Ne/^{21}Ne$ as a function of meteoroid radius and sample depth in spherical chondrites predicted by the semiempirical model by Graf et al. (1990b). The modelled data are based on the measurements shown in the left panel. Figure from Graf *et al*. (1990b) with permission from Elsevier.

3.1.4 Other Collaborations on Cosmogenic Nuclides in Meteorites

Knyahinya was the first meteorite on which I was involved in a detailed cosmogenic nuclide study, but many others followed. Most of these studies were carried out in collaboration with one or more other teams, combining noble gas measurements with analyses of cosmogenic radionuclides and often also with modelling of nuclide production. The first such study was on the iron meteorite Grant (Section 3.1.3), using samples from the cross section already studied by Peter Signer in Minneapolis. In collaboration with Stephan Vogt in Cologne and the AMS group in Zürich we showed that the $^{10}Be/^{21}Ne$ ratio is independent of a sample's shielding and hence can be used to determine shielding-corrected ^{21}Ne cosmic ray exposure ages of iron meteorites (Graf *et al*., 1987). Grant and Carbo,

another large iron meteorite, were later used extensively to study very small but potentially important modifications of the isotopic composition of elements important to cosmochemistry by cosmic rays (Section 3.1.11).

Several studies were done on large pre-atmospheric meteorites with up to hundreds of recovered fragments, such as Bur Gheluai (Vogt *et al.*, 1993), Gold Basin (Welten *et al.*, 2003), or Almahata Sitta (Welten *et al.*, 2010; Riebe *et al.*, 2017c). Other large studies were done on groups of selected meteorites, for example from Mars (Wieler *et al.*, 2016) or the Frontier Mountain region in Antarctica (Welten *et al.*, 1999). The latter project was also a result of my wish to study some of the meteorites I had found myself. Some projects involved collaborations that went beyond the study of cosmogenic nuclides, such as the consortium formed by Derek Sears on the Fayetteville regolith breccia (Wieler *et al.*, 1989a,b), the work on Almahata Sitta (Riebe *et al.*, 2017c), a meteorite that had fallen in Sudan less than a day after the discovery of its immediate parent asteroid of a few metres size, and the work on meteorites containing cluster chondrite clasts (Müsing *et al.*, 2021). These clasts are characterised by deformed and indented, closely spaced chondrules thought to have accreted within hours or days after they had formed (Metzler, 2012). A special place in this list is reserved for the long standing controversy between my good friends Charles Hohenberg and Marc Caffee and myself over whether or not some samples in meteorites with very substantial excesses of cosmogenic noble gases testify to a very active early Sun (Section 3.1.7). Also the collaboration with Birger Schmitz and colleagues on fossil meteorites (Section 3.1.9) and the work with Philipp Heck and colleagues on presolar grains (Sections 3.1.7, 3.1.9 and 3.1.10) should be mentioned here.

Many of the projects mentioned in the previous paragraph address the broad topic of "complex exposure histories". An exposure history of a meteorite is said to be "complex" if not all of its cosmogenic nuclides were produced during a single stage of irradiation of the pre-atmospheric meteorite. For example, a meteorite may have broken up by a collision on its way to Earth, or part of its nuclide complement may have already been acquired near the surface of its parent body. Complex exposure histories may also reflect differential irradiation of certain components of a meteorite prior to its final compaction. This may happen, for example, in a parent body regolith (Section 3.1.6), or some grains may even "remember" early irradiation in the solar nebula or in presolar environments. If the last change of the irradiation geometry occurred earlier than a few half-lives of a radionuclide (*e.g.*, prior to some 3 Ma for ^{26}Al), essentially all the now detectable atoms of this nuclide will have been produced during the last irradiation stage. However, the same meteorite may inherit (stable) cosmogenic noble gas isotopes from (one or more) earlier irradiation stages. Perhaps some of the longer-lived cosmogenic radionuclides from an earlier stage also survived. To recognise complex exposure histories, it is therefore necessary to analyse several cosmogenic nuclides in the same sample or multiple samples from the same meteorite, or both (*e.g.*, Vogt *et al.*, 1993). Combinations of measurements of stable noble gases with suites of cosmogenic radionuclides with different

half-lives and different depth dependencies of their production rates are ideal. In addition, determinations of cosmic ray track densities are also desirable, but unfortunately have rarely been done in recent years. Such comprehensive studies require a large effort, which means that it remains a challenge to constrain the fraction of meteorites with a complex exposure history. Yet, it is important to obtain good estimates of the fraction of meteorites that suffered complex exposures in order to better understand the history of meteorites as they travel from the asteroid belt to Earth.

Perhaps the most important general finding of the above work – and many similar studies by others – is that it is difficult to unequivocally confirm or deny that a meteorite suffered a complex exposure history. However, it seems likely that complex histories are much more common than the few confirmed cases would suggest (*e.g.*, Herzog *et al.*, 1997). Wetherill (1980) had argued that fragmentation of meteorite-sized bodies on their way to Earth should be common. For a long time, this seemed to be in contrast to the small numbers of meteorites with well documented complex exposure histories, apart from those which clearly represent material from the regoliths of their parent-body asteroids. Among the well studied meteorites mentioned above, Bur Gheluai, Gold Basin, and Almahata Sitta likely suffered a complex history. George Wetherill's prediction may thus turn out to be correct.

One excellent result of working with others in the field of cosmogenic nuclides has been that it has allowed me to make many of my best and most lasting friendships within the scientific community. One of these good old friends is Kuni Nishiizumi (who showed me what e-mail is, see above). In the 1980s, Kuni invented the "Cosmogenic Dinner". He is a gourmet, and his main motivation probably was that he did not like the "chilli-cookoff and barbecue dinner" on Wednesday nights of the annual LPSC in Houston. The community of cosmogenic nuclide aficionados was (and is) quite small (usually we were crammed into the smallest available conference room at NASA's Gilruth Center). Kuni managed to convince many of us to skip the chilli-cookoff and gather at a good restaurant instead. Over the years Cosmogenic Dinners became a tradition and were later extended to the annual meetings of the Meteoritical Society. With the integration of colleagues from sample return missions such as Stardust and Genesis, the event was eventuelly renamed "Cosmogenic and Sample Return Dinner". Kuni always asked the older ones among us to bring their younger colleagues. For many early career scientists, this was a great opportunity to integrate into the community. There are too many good friends I have enjoyed Cosmogenic Dinners or worked closely with over the years to name them all. Marc Caffee, Goswami, Gregory Herzog, Charles Hohenberg, Tim Jull, Candace Kohl, Kurt Marti, Jozef Masarik, Kuni Nishiizumi, Larry Nyquist, Uli Ott, Paul Pellas, Bob Reedy, Ludolf Schultz, Tim Swindle, and Kees Welten are just a few of them. Particularly entertaining were good storytellers like Don Brownlee and Don Burnett, the Principal Investigators of the Stardust and Genesis missions, as well as Jim Arnold, one of the pioneers in cosmogenic nuclide research.

Text Box 3.2 – Searching for Meteorites in Antarctica and Oman

The Japanese and US meteorite search programmes were established in the 1970s and by the late 1980s had collected thousands of meteorites on Antarctic ice. These programmes had a tremendous impact on cosmochemistry research. They gave us the first recognised lunar meteorites and countless other highlights. European meteorite researchers benefitted from the extensive new collections as much as their colleagues overseas. Europeans were also regularly invited to join US collecting expeditions near the McMurdo station. But Europe itself had not set up its own meteorite collection programme in Antarctica. In the late 1980s, Colin Pillinger of the Open University in Milton Keynes decided to change that and formed a consortium to establish a European meteorite search programme for Antarctica, called EUROMET. With his charisma, Colin was the ideal person to convince the science programme of the European Economic Community (as the European Union was then called) to fund EUROMET. A few years later, he became highly popular in the UK as project leader of the (eventually failed) Beagle 2 mission, which was to search for life on Mars. Before it was launched, I invited him to present the mission at a colloquium at the Department of Earth Sciences at ETH. In my introduction, I showed a ranking of the then hundred most influential people in the UK according to TIMES. Colin was number 99, but among the scientists he was only beaten by Stephen Hawking (ranked around place 50, if I remember correctly). Colin replied that his colleagues in Milton Keynes had reacted with: "There is room for improvement, Colin!". Of course, the top position was reserved for Queen Elizabeth II.

Although there was no dedicated European meteorite search programme prior to EUROMET, Georg Delisle, a German glaciologist at the Bundesanstalt für Geowissenschaften und Rohstoffe in Hannover, had brought back a number of meteorites from the Frontier Mountain area in northern Victorialand in the 1980s. Georg had developed a keen interest in meteorites thanks to his first accidental meteorite finds in 1984 (Delisle *et al.*, 1993). The Frontier Mountain region is easily accessible from the small German Gondwana station in Terry Nova Bay and the larger Italian station opposite the same bay (now Stazione Mario Zucchelli). Colin Pillinger and Georg therefore decided that the Frontier Mountains would be the best place for a first EUROMET expedition. Colin persuaded Mario Zucchelli, head of the Italian Antarctic Program, to reserve two slots (out of about 140) for meteorite hunters. So it happened in the fall of 1990 that Ian Franchi from the Open University and myself joined the Italian expedition team in a preparatory camp in the Appenine mountains and on Monte Bianco, better known by many as Mont Blanc, the highest mountain in the Alps, shared by Italy and France. Falko Langenhorst and Stephan Weinbruch were the two unfortunate backup meteoriticists who also had to complete the preparation camp but would ultimately not make it to Antarctica. We practised how to extinguish a fire and a hundred other things, including how to safely board a helicopter. The latter lesson led to my first helicopter flight aboard a large Italian army helicopter over the beautiful glacier landscape high up at Monte Bianco. It may well be that I was selected for the first EUROMET expedition because, with my basic knowledge of Italian, I was able to convey the essence of the theoretical lessons to my British and German colleagues in a rudimentary way. Luckily, the hands on exercises such as extinguishing a fire or evacuating from a burning building did not require much translation. A few months later, Ian and I boarded the vessel Italica in Lyttelton, the port of Christchurch, New Zealand, bound for Terra Nova Bay. Also

with us was Italian geologist Antonio Rossi, who thankfully joined the meteorite search team for a few weeks before devoting the rest of his time in Antarctica to his own research.

Figure 3.7 **(a)** One of the first (capsized) icebergs encountered on our way from New Zealand to Antarctica. **(b)** Mt. Melbourne at Terry Nova Bay. **(c)** Adelie penguins at Terra Nova Bay in vigorous discussion. **(d)** A Weddell seal enjoying the Antarctic summer. **(e)** Ian Franchi and Antonio Rossi in front of the "Mela", our community room at Frontier Mountain, contemplating part of the equipment just downloaded from the helicopter. **(f)** Ian Franchi examining a meteorite on the blue ice.

The journey across the Southern Ocean was truly unforgettable (Fig. 3.7). The slow approach by boat to the most exotic place on Earth I ever have and ever will visit was a very different experience from an eight hour flight in a Hercules plane, the usual way to reach the US base in McMurdo. For many days we admired the wonderful spectacle of albatrosses dodging the high waves without noticeably flapping their wings. Later we enjoyed the first penguins on the first icebergs and drift ice floes. Once, as part of the on board entertainment programme, I was asked to give a lecture on the beauty and importance of meteorites. My first and only "scientific" talk in Italian, without any slides but supported by a lot of handwaving. Later we were trapped in the pack-ice for about two days, and I began to wonder whether we would ever reach the Antarctic continent, but the New Zealand helicopter pilots on board directed us back into open waters. Then, one morning, the beautiful volcanic cone of Mt. Melbourne showed up at the horizon and a few hours later we arrived at the Italian station at Terra Nova Bay. A very well organised and clean place, without any trace of the littering that seems to plague other Antarctic stations, reflecting the signature of Mario Zucchelli. Perhaps also not least to his credit, he had been able to secure a first class Chef for the team, the same who had been responsible for the well being of Bernardo Bertolucci's crew during the filming of "The Last Emperor" in China a few years earlier. We, the meteorite hunting team, not only enjoyed his excellent food while we were at the base, he also prepared a daily frozen meal for us to warm up at Frontier Mountain with our diesel powered microwave! A similar story which I like to tell my friends who are familiar with American Antarctic habits is about our daily bottle of wine. Ludolf Schultz once told me about the Antarctic wine experiment of his good friend Paul Pellas. Paul had bought a few bottles of wine at the grocery store in McMurdo, opened them and poured a small amount before safely freezing the resealed bottles. Paul then managed to bring around six bottles of the test winner to the field. Well, we brought well over six bottles to Frontier Mountain, as we had the opportunity to keep them unfrozen in our "mela", our apple-shaped "community room" in the field (Fig. 3.7).

Our field team consisted of Antonio, Ian, myself, and mountain guide Luigi "Pedro" Pedrolini, who was responsible for our safety but also had an excellent eye for spotting meteorites. Occasionally, Georg Delisle joined us from the Gondwana station. We were lucky with the weather, as we had to stay only one day in the mela or our tents due to very cold weather of some −30 °C and strong winds. All other days were pleasant with temperatures around −15 °C and quite often beautiful sunshine. The first certainty I had to forget is that meteorite hunting on Antarctic blue ice is easy, because almost every stone on the ice is a meteorite. The reality is completely different, at least at Frontier Mountain, where the blue ice in some places is literally covered with terrestrial pebbles. Yet, during the three weeks in the field, our party collected a total of 226 meteorites, labelled FRO90… , which are now stored at the Museo Nazionale dell Antartide in Siena: http://www.mna.it/collezioni/catalogo-meteoriti-sede-di-siena

No question, my trip to Antarctica is one of the most beautiful events of my life with many lasting memories, although I am not among those who would want to return to the icy continent every summer. On our way back, we again admired the albatrosses for hours. Then, on the approach to Lyttelton, I remember Ian Franchi and I watching other birds, mostly excellent flyers like seagulls. But we both had the same thought at the same moment: these birds cannot really fly, they are just struggling to stay in the air somehow. It is not easy to compete with the flying skills of an albatross!
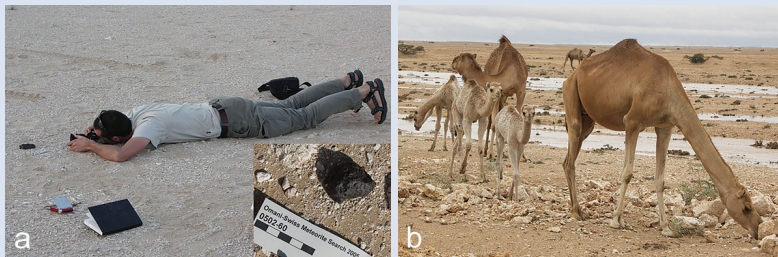
In later years, the Italian Antarctic programme continued the search for meteorites and micrometeorites in Antarctica under the auspices of Luigi Folco of the University of Pisa. Unfortunately, EUROMET did not have the long lasting influence of the US, Japanese, and more recently, Chinese search programmes. I myself almost made it to Lybia on a EUROMET search trip. I had already sent my passport to Ian Franchi in Milton Keyes, who would have organised the visa, but then Muammar Gaddafi felt badly treated by the British government and our trip had to be cancelled (which was probably the least of the problems related to this crisis). Fortunately, I got another chance to search for meteorites in a hot desert in 2005 when Beda Hofmann of the Natural History Museum in Bern and Edwin Gnos (now at the Natural History Museum in Geneva) invited me to join one of their collection expeditions in Oman (Fig. 3.8). To date (2017), the Omani-Swiss Meteorite Search Project has collected well over 6000 meteorites representing about 1000 individual falls, all well documented (https://www.nmbe.ch/de/forschung-und-sammlung/meteoritenforschung). To my knowledge, this is the largest collection of hot desert meteorites managed by academic and governmental organisations. It is certainly important not to leave this terrain exclusively to commercial meteorite hunters, who very often do not even document find locations.

3.1.5   Modelling Cosmogenic Nuclide Production

As a highly important outcome of the Hannover-Zürich collaboration, two persons that were to become among my most important collaborators and best friends found their way to Zürich from Rolf Michel's group in Hannover. Henner Busemann in 1994 became the very first doctoral student for whom I acted as the main supervisor. Two years later, Ingo Leya was to become my first postdoc (and later research associate) after completing his doctoral thesis in Michel's group. My long lasting collaborations with Henner – which continue to this day – are described below. Here is a good place to summarise Ingo's work in Zürich and later at the University of Bern.

Ingo's training in nuclear physics in Hannover enabled him to continue the modelling work on cosmogenic nuclide production in meteorites initiated by his mentor Rolf Michel, mentioned above. Here below a few more details about the physics and the modelling of nuclide production. More details can be found in, *e.g.*, Herzog and Caffee (2014), and David and Leya (2019).

Knowledge of nuclide production rates forms the basis for almost all applications of cosmogenic nuclides. Production rates of radioactive nuclides can to a first order be determined empirically, since their production rates equal their decay rates after some five half-lives of irradiation, and their concentrations therefore reach an equilibrium that will be approximately the same in all meteorites with identical major target element concentrations and a more or less "typical" size and sample depth. If the production rate of a radionuclide is known, its concentration in a meteorite that is not yet in equilibrium can then be used to determine the exposure age of that meteorite and, together with the concentration of a stable noble gas nuclide, also the production rate of that nuclide (Vogt *et al.*, 1990). However, this approach is limited to meteorites of "typical" size and will also fail for meteorites with a complex exposure history. Therefore, more sophisticated methods are needed, not only to obtain more reliable estimates of production rates, but also to better understand the physics of nuclide production and to compare the production systematics of different nuclides. The semi-empirical model used by Signer and Nier (1962) and Graf *et al.* (1990b) is one such approach. Models based on nuclear physics – in theory and experiment – are another. Such models were pioneered by Jim Arnold, Masatake Honda, Devendra Lal, Truman Kohman, and Bob Reedy (Arnold *et al.*, 1961; Kohman and Bender, 1968; Reedy and Arnold, 1972). On the one hand, these models are based on cross sections for the production of nuclides by protons and neutrons of different energies from relevant target elements. Cross sections are compiled in very large databases and are often values interpolated from rather few measured data points or based entirely on theory. On the other hand, the production of secondary protons and neutrons and their transport within a meteorite must also be modelled. Furthermore, the proton flux of the primary cosmic radiation in the inner solar system is a free parameter that can be fitted to measured radionuclide concentrations in meteorites, *e.g.*, Knyahinya, as explained above.

I mentioned above that Rolf Michel and his colleagues began developing their "Hannover" model of cosmogenic nuclide production in the mid-1980s. The noble gas and radionuclide data from the thick and thin target irradiations at CERN and Paris-Saclay allowed them to determine separately nuclide production in spherical meteorites by secondary protons and neutrons, respectively (*e.g.*, Michel *et al.*, 1989; 1996). Ingo Leya was involved in the latter of these two papers as part of his doctoral dissertation. In Zürich he used the Hannover model to calculate depth dependent production rates of cosmogenic He, Ne, and Ar as well as five radionuclides (^{10}Be, ^{14}C, ^{26}Al, ^{36}Cl, ^{53}Mn) from all major target elements in chondrites of various sizes (Leya *et al.*, 2000b). This paper also reported the correlation between the production rate of ^{21}Ne and the shielding parameter ^{22}Ne/^{21}Ne (see Fig. 3.9 for an updated version) as well as correlations among,

for example, [26]Al and [10]Be as a function of meteoroid size and sample depth. This widely used work allowed to calculate in an easy form shielding-corrected exposure ages of meteorites – within certain limits – for samples of different chemical composition. This work was done in friendly competition with others, notably Jozef Masarik and Bob Reedy at Los Alamos (Masarik *et al.* 2001b). Later, Ingo and Jozef (then at Comenius University in Bratislava) joined their efforts on modelling cosmogenic nuclide production in meteorites in another well known publication (Leya and Masarik, 2009). Figure 3.9 shows the dependence of the production rate of ^{21}Ne in H chondrites as a function of the ^{22}Ne/^{21}Ne shielding parameter modelled by these authors. While the model data for meteorites of modest size agree quite well with previously proposed empirical relationships (Nishiizumi *et al.*, 1980; Eugster, 1988), the latter fail for interior samples of large meteorites (r > 65cm) with ^{22}Ne/^{21}Ne ≤ 1.08.
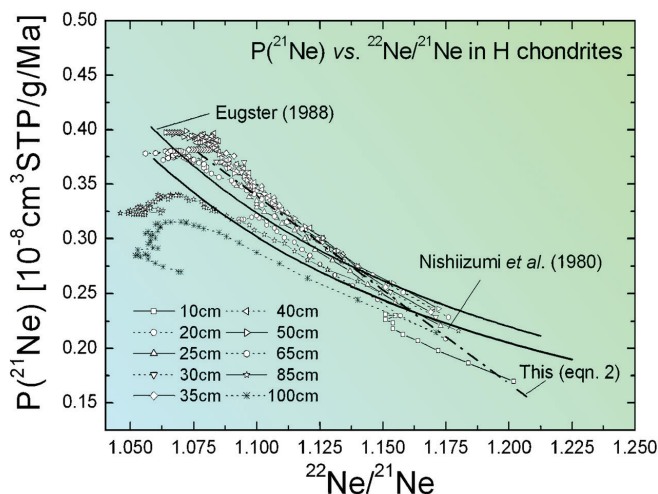
Figure 3.9 The production rate P(^{21}Ne) of ^{21}Ne in H chondrites of various radii as a function of shielding expressed by ^{22}Ne/^{21}Ne, according to model calculations by Leya and Masarik (2009). Also shown are correlation lines previously proposed by Nishiizumi *et al.* (1980) and Eugster (1988). The model calculations show that these correlations fail for interior regions of large meteorites with (^{22}Ne/^{21}Ne) ≤ 1.08. Figure from Leya and Masarik (2009) with permission from Wiley.

The latest update on Ingo Leya's work on modelling cosmogenic nuclide production in meteorites can be found in Leya *et al.* (2021). To summarise, the continuous development of new generations of physical models over the last decades has led to an ever improved understanding of cosmogenic nuclide production, but – as always – further progress is highly desirable and can be expected.

Ingo Leya also extensively models potential modifications of the isotopic composition of elements important for isotope cosmochemistry, such as tungsten. The motivation came when Alex Halliday arrived in Zürich in the late 1990s, and I will describe this work in Section 3.1.11.

Ingo continued to work with us in Zürich after he moved to Bern around 2004. One of the main projects from this time was to use the ^{36}Cl-^{36}Ar method to determine noble gas production rates in chondrites, including a re-evaluation of the ^{81}Kr-Kr exposure dating method. These studies were done in collaboration with Thomas Graf, Kuni Nishiizumi, Bernard Lavielle, Marc Caffee, Kees Welten, Natalie Dalcher, and others (Leya *et al.* 2004b, 2015; Dalcher *et al.*, 2013). The ^{36}Cl-^{36}Ar method is based on the fact that in Fe-Ni metal samples, more than 80 % of the cosmogenic ^{36}Ar is produced *via* its radioactive precursor ^{36}Cl. This means that the production rate of ^{36}Ar in metal samples can be determined directly by an analysis of ^{36}Cl in an aliquot or an adjacent metal sample. The ^{36}Cl-^{36}Ar technique is therefore an elegant way to determine cosmic ray exposure ages of samples without the need to know their pre-atmospheric shielding. The method was first applied to iron and stony iron meteorites (Schaeffer and Heymann, 1965; Begemann *et al.*, 1976; Lavielle *et al.* 1999). However, Kuni Nishiizumi and his collaborators managed to produce very clean metal separates from chondrites, requiring only minor corrections for trapped ^{36}Ar and cosmogenic ^{36}Ar produced from Ca in the remaining silicate impurities (Graf *et al.*, 2001).

The intrinsic accuracy of the ^{36}Cl-^{36}Ar technique encouraged Thomas Graf, Ingo Leya, and co-workers to further study the details of the most prominent peak in exposure age histograms of meteorites. It has been known for decades that exposure ages of meteorites are not evenly distributed, but show distinct clusters – different for each meteorite class – that indicate large collision events in the asteroid belt or on other parent bodies (Anders, 1964). The largest of these exposure age peaks accounts for about 45 % of all H chondrites, suggesting that the world's meteorite collections owe about 20 % of all their specimens from documented falls to a single collision in the asteroid belt about 7 Ma ago. However, in 1995, Thomas Graf and Kurt Marti had taken a closer look at the H chondrite histogram and suggested that the 7 Ma peak actually represents not one, but two different collisions (Graf and Marti, 1995; Fig. 3.10). Graf *et al.* (2001) and Leya *et al.* (2001) were able to provide further evidence for this double peak, perhaps some 700,000 years apart.

The ^{81}Kr-Kr technique allows one to directly derive the production rates of stable cosmogenic Kr isotopes in a sample of unknown shielding by a single noble gas analysis (Marti, 1967). The production rate of, *e.g.*, ^{83}Kr is deduced from the concentration of ^{81}Kr, which has a half-life of 229,000 a. However, to determine the production rate ratio P(^{83}Kr)/P(^{81}Kr) is less straightforward than for the ratio P(^{36}Cl)/P(^{36}Ar). Also, P(^{83}Kr)/P(^{81}Kr) likely depends on the concentration ratios of the major target elements for Kr production (Rb, Sr, Y, Zr). Leya *et al.* (2015) used ^{36}Cl-^{36}Ar ages of 14 chondrites to recalibrate the ^{81}Kr-Kr system

and concluded that ^{81}Kr-Kr exposure ages calculated according to Marti (1967) and Marti and Lugmair (1971) are too high by up to 30 %. Leya *et al.* (2015) also showed that the production rate ratio P81/P83 is indeed essentially constant for the entire shielding range covered by their chondrite samples, confirming the fundamentals of the technique. However, it must also be acknowledged that, as elegant as the ^{81}Kr-Kr method is in principle, it requires very precise analyses of very low ^{81}Kr amounts and sometimes also critical corrections for trapped Kr, which often limits the precision of ^{81}Kr-Kr ages.
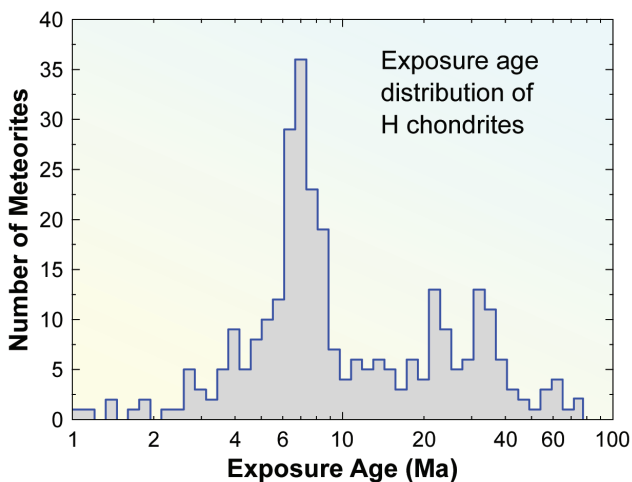
Figure 3.10 Exposure age histogram of H chondrite falls based on data compiled by Graf and Marti (1995). The prominent peak around 7 Ma comprises about 45 % of all H chondrite falls and is commonly considered evidence of one major collision in the asteroid belt. However, Graf and Marti (1995) argued that this peak is more likely the result of two different collisions. Graf *et al.* (2001) and Leya *et al.* (2001) provided further evidence for the double peak hypothesis based on ^{36}Ar-^{36}Ar cosmic ray exposure ages.

3.1.6   Regolith Dynamics Studied with Cosmogenic Nuclides

Cosmogenic nuclides, in particular cosmogenic noble gases, are also excellent for studying the mixing or exhumation history of the top few metres of a meteorite's parent body, especially regoliths on asteroids or the Moon, and the surface of Mars. Mixing of a planetary regolith by impacts leads to differences in concentrations of cosmogenic nuclides even in samples that ultimately arrive on Earth in the same meteorite. Obviously, such effects are expected in particular in gas-rich meteorites, *i. e.* meteorites that also contain solar wind implanted noble gases acquired at the surface of their parent body. One of the best known gas-rich meteorites is the H chondritic regolith breccia Fayetteville. We were therefore happy to
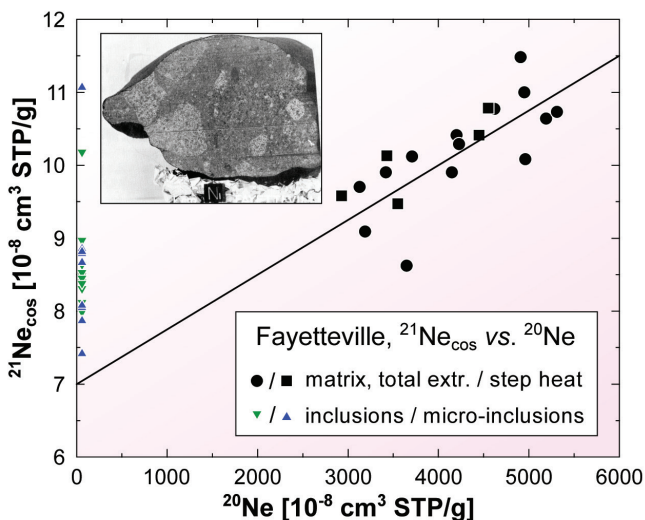
Cosmogenic ^{21}Ne *versus* solar wind-implanted ^{20}Ne in samples from the dark matrix (black squares and circles) and light inclusions (green and blue symbols near the ordinate) of the H3-6 chondritic regolith breccia Fayetteville shown in the inset. Samples from this slab were distributed among the Fayetteville consortium participants (Schwarz and Sears, 1988). Fayetteville exhibits a dark-light structure typical of chondritic regolith breccias. Dark portions are rich in noble gases implanted by the solar wind on the surface of the parent body, while the light inclusions represent pebbles on the parent body with sizes ranging from mm to several cm. In their interior, light inclusions are devoid of trapped solar wind gases. Cosmogenic Ne in the matrix samples correlates with solar Ne, indicating that part of the cosmogenic Ne was acquired on the Fayetteville parent body. The ordinate intercept of the best fit line through the matrix data points is an upper limit of the cosmogenic ^{21}Ne produced during Fayetteville's journey in space. The excess cosmogenic ^{21}Ne of each sample above the ordinate intercept value of ~7*10^{-8} cm^{3}STP/g is therefore a lower limit to its ^{21}Ne$_{cos}$ produced on the parent body. Figure adapted from Wieler *et al.* (1989a); inset from Schwarz and Sears (1988).

participate in the Fayetteville consortium set up by Derek Sears at the University of Arkansas in Fayetteville (Schwarz and Sears, 1988). Fayetteville is one of the meteorites with the highest concentrations of solar wind noble gases. It displays a dark-light structure typical for many gas-rich chondrites (Fig. 3.11), with solar noble gases being present only in the dark portions. These consist of compacted dust from the parent body, with many or most of the dust grains having once been at the immediate surface where they collected ions from the solar wind. The light inclusions were cm- or mm-sized pebbles in the regolith. Their interiors are free of solar wind particles which penetrate only a few tens of nanometres into solid matter. We analysed noble gases in samples from both, dark and light lithologies, and Paul Pellas at the Muséum d'Histoire Naturelle in Paris counted solar flare

tracks (Wieler *et al.*, 1989a;b; Pedroni, 1989). In the matrix samples, concentrations of cosmogenic ^{21}Ne correlate with those of solar wind-implanted Ne (Fig. 3.11). This correlation implies that not all cosmogenic ^{21}Ne in the fine grained matrix samples was produced during the Fayetteville meteoroid's journey to Earth but that a substantial fraction of it was already acquired on the parent body. Also many, if not all, of the solar wind-free light samples must have been irradiated by galactic cosmic rays on the parent body for at least several million years. We concluded that the distance of the Fayetteville parent body to the Sun was about 2-3 times that of the Moon, *i.e.* between 2 and 3 astronomical units, consistent with a main belt origin. Based on an argument developed by Ed Anders (Anders, 1975), we reached this conclusion by comparing solar and cosmogenic noble gases in gas-rich meteorites and lunar samples, respectively. Anselmo Pedroni, in his doctoral thesis came to a similar conclusion for the parent body of the gas-rich aubrite Kapoeta (Pedroni, 1989). Turning the argument around and assuming *a priori* that the Fayetteville and Kapoeta parent bodies both orbit in the main belt, the regolith dynamics on these bodies compare well with those on the Moon, in the sense that the ratio of residence time of grains at the top surface of the regolith to that in the top few metres is similar for all three bodies. This reasoning has subsequently been adopted in several other studies (*e.g.*, Obase *et al.*, 2020).

Further studies of asteroidal regoliths in Zürich included work on the Ghubara meteorite and on grains from asteroid Itokawa collected by the Japanese Hayabusa mission. Matthias Meier (Meier *et al.*, 2014b) showed that chromite grains in the Ghubara L5 chondrite were exposed to galactic cosmic rays for up to several 10 Ma, a result that is particularly relevant to studies on fossil meteorites which will be addressed in Section 3.1.9. Meier *et al.* (2014a) determined a ^{21}Ne exposure age of only about 1.5 Ma for one grain from Itokawa, but further grains analysed by Henner Busemann (personal communication, 2023) show exposure ages of up to some 20 Ma, exceeding the upper limit of a few Ma previously obtained by Nagao *et al.* (2011) for several other grains from Itokawa. These data indicate that the surface of this asteroid appears to be much younger than the lunar regolith. This may be due to either rapid loss of grains to space or rapid regolith turnover rates on Itokawa.

3.1.7   The T-Tauri Controversy

Young stars emit very high fluxes of energetic particles during their formation and early evolution (Feigelson, 2010). Figure 3.12 shows the intense X-ray emission of a five million year old young stellar cluster, which very likely is accompanied by a very intense energetic proton flux. From such observations, Eric Feigelson inferred that also the young Sun emitted a perhaps 10^5 times higher energetic proton flux than today. The very high activity of the early Sun likely left its mark in the form of several isotopic anomalies in meteorites. In particular, excesses of ^{10}B in early solar system condensates are thought to be due to the decay of ^{10}Be produced by spallation reactions induced by energetic particles from the early Sun (McKeegan *et al.*, 2000; Liu *et al.*, 2009). Perhaps some atypically high

initial abundances of ^{53}Mn and ^{26}Al in CAIs are also the result of high energetic proton fluxes from the early Sun (Nyquist *et al.*, 2009). It is therefore conceivable that early intense solar radiation also left its mark on the noble gas records of meteorites, perhaps even more conspicuously than on any other element. Can we really observe this?

This question has been the subject of intense debate since the pioneering work of Charles Hohenberg and his colleagues at Washington University in St. Louis in the 1980s. I have been involved in this controversy for many years. Marc Caffee and his co-workers observed that a small fraction of the individual grains of solar gas-rich chondrites and achondrites they studied contained much higher concentrations of cosmogenic ^{21}Ne and ^{38}Ar than the bulk meteorite (Caffee *et al.*, 1987). For the carbonaceous chondrites Murchison, Murray, and Cold Bokkeveld, the excess gas would correspond to exposure to galactic cosmic rays for as long as several ten and sometimes more than a hundred million years, if produced by GCR with present day flux. This would be much longer than the accepted exposure ages of the meteorites in space (their "4π age") of a few Ma (Woolum and Hohenberg, 1993). Prior to the noble gas analysis, groups of grains and later individual grains were first examined by Jitendra Goswami at the Physical Research Laboratory in Ahmedabad, India, for the presence or absence of crystal lattice damages caused by solar energetic particles (solar flare tracks, see Section 2.5). Very remarkably, only the track containing grains showed excesses of cosmogenic noble gases (Caffee *et al.*, 1987; Hohenberg *et al.*,

1990). The St. Louis collaboration therefore clearly favoured the view that excess cosmogenic noble gases (as well as the tracks) were the result of irradiation by the early active Sun.
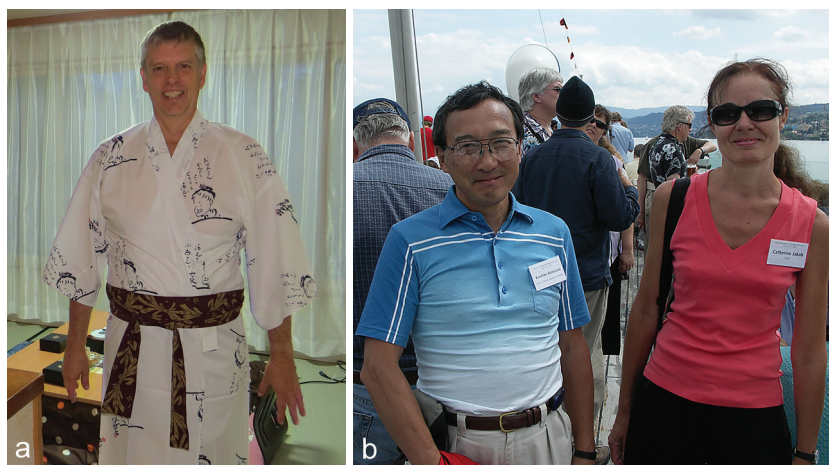
However, in our work on the gas-rich meteorite Fayetteville we expressed caution about this interpretation (Wieler *et al.*, 1989a). A correlation between solar flare tracks and excess cosmogenic noble gases in grains taken from a regolith should not be viewed as a strong argument that the cosmogenic gases also had been produced by solar – rather than galactic – energetic particles. Take a handful of well mixed soil from the lunar surface. If exposed to the solar and galactic cosmic radiation for a long time, most grains of this "mature" soil will contain solar wind noble gases and thus also solar flare tracks, as almost every grain was once at the immediate surface of the Moon (Wieler *et al.*, 1980). All grains will also contain cosmogenic noble gases, but in a well mixed regolith most of these gases will have been produced by the galactic cosmic radiation with its penetration depth of a few metres. Only a few percent of the cosmogenic gas will have been produced by solar cosmic rays, while the grains were in the top one or two centimetres of the regolith. Now consider another parcel of freshly produced regolith, perhaps from material recently brought to the surface by an impact. Such grains would be mostly free of solar wind noble gases, solar flare tracks, and cosmogenic noble gases. If you now add to this fresh material a few percent of "mature" regolith, you would find an almost one to one correlation between track-rich grains and grains with cosmogenic gases. However, the tracks would be the result of solar energetic particles, while the cosmogenic gases would have been mostly produced by galactic cosmic rays. Probably such

a clear cut case does not exist in the lunar sample collections, but in less mature asteroidal regoliths it is easy to imagine that intense mixing of immature with mature material happens. During the meteoroid stage, after ejection from the parent body, the now compacted soil would acquire further cosmogenic gases, as seen in the gas-poor and track-free grains and corresponding to the meteorite's 4π exposure age to GCR. Hohenberg *et al.* (1990) and Woolum and Hohenberg (1993) argued that carbonaceous chondrites are very unlikely to have experienced regolith exposures of hundreds of Ma. In contrast, Wieler *et al.* (2000) argued that the solar flare track densities in the meteorite grains were roughly two orders of magnitude lower than would be expected if the cosmogenic noble gas excesses had been predominantly produced by solar energetic particles.

Hence, in the early 2000s, the situation remained controversial. Many people endorsed the idea that meteoritic noble gases preserve a record of the early active Sun. Work began to focus on individual chondrules rather than individual mineral grains, and more or less clear evidence for cosmogenic noble gas excesses in some chondrules was reported, although by far not to the extent previously seen for track-rich single grains (Eugster *et al.*, 2007; Das and Murty, 2009). However, we remained sceptical that these excesses reflect an intense irradiation by energetic particles from the early Sun.

One major problem had always been that substantial excesses of cosmogenic noble gases were only found in samples from regolith breccias. Irradiation by an early active Sun should, however, also or predominantly have happened in a nebular environment rather than on a parent body surface. Chondrules, for example, should therefore show excesses whether they are now found in a solar noble gas-rich regolith breccia or in a meteorite without evidence of regolith origin. Therefore, in his Master's thesis at ETH, Antoine Roth (Roth *et al.*, 2011) compared the concentrations of cosmogenic He and Ne in single chondrules from the two carbonaceous chondrites Allende and Murchison, the former being free of solar noble gases and the latter representing a solar wind-rich regolith breccia. The samples from the latter meteorite were analysed with a high sensitivity mass spectrometer called Tom Dooley described in Section 3.1.8. All Allende chondrules contained very similar concentrations of cosmogenic ^{3}He and ^{21}Ne, consistent with the accepted meteoroid exposure age of Allende (Fig. 3.14a). Therefore, no Allende chondrule showed evidence for pre-exposure to either solar or galactic cosmic rays. In contrast, about one in five Murchison chondrules contained sizeable or even very large excesses, comparable to those reported for the individual Murchison grains studied by Hohenberg *et al.* (1990). The $(^{22}\text{Ne}/^{21}\text{Ne})_{cos}$ ratio in chondrules with excess Ne is also as expected for Ne produced by galactic cosmic rays but at odds with contemporary SCR-Ne.

Thus, while we did not definitively rule out that the excesses in Murchison chondrules were due to an early irradiation by SCR, we felt that Antoine Roth's data clearly argued for production in a parent body regolith by GCR, at any time in solar system history. This more mundane explanation required further evidence. We therefore decided to carefully discriminate between chondrules taken from the "clastic matrix" of Murchison and from lithic clasts, respectively,
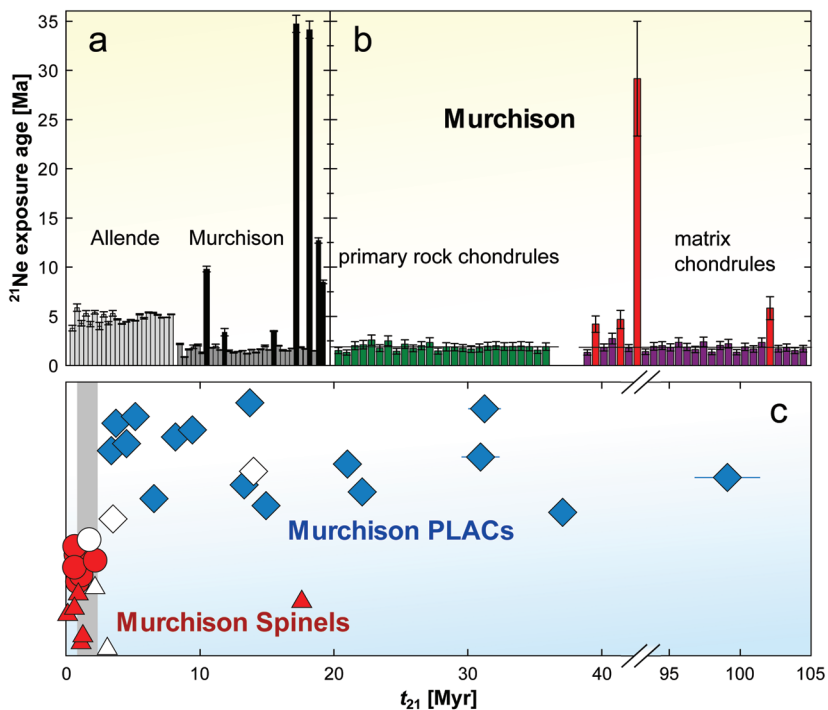
Figure 3.14   Data from three studies relevant to the question of whether noble gases in meteorites show evidence for intense irradiation by solar energetic particles from the early active Sun. **Panels (a) and (b)** show the nominal ^{21}Ne cosmic ray exposure ages of individual chondrules, assuming a 4π irradiation by GCR with present day flux in an average-sized meteorite. Figures adapted from Roth *et al.*, 2011 and Riebe *et al.*, 2017b. **Panel (c)** shows ^{21}Ne exposure ages of individual refractory grains from Murchison, also assuming 4π irradiation by present day GCR (Kööp *et al.*, 2018). The first two panels reveal that some chondrules from solar gas-rich portions of Murchison have excesses of cosmogenic ^{21}Ne over its true 4π exposure age, but that chondrules of the solar gas-free meteorite Allende and a solar gas-free primary rock fragment of Murchison do not have such excesses. In contrast, panel (c) shows that most of the platy hibonites in Murchison (blue diamonds; open symbols representing upper t_{21} limits) show ^{21}Ne excesses, while only one of 15 spinels (red and open triangles) has a such an excess. The spinels are also early solar system condensates, but formed slightly after PLACs (see text). While the chondrule data are readily explained by irradiation with GCR in the parent body regolith, the PLACs are evidence for irradiation by particles from the early active Sun. Figure adapted from Kööp *et al.* (2018).

the latter being fragments of "primary accretionary rocks" (PAR). Knut Metzler and co-workers at the University of Münster had distinguished these lithologies and concluded that PARs had accreted in the solar nebula (Metzler *et al.*, 1992). Important for our project was that the lithic clasts were single pebbles of a few centimetre size in the regolith and therefore all chondrules from one of these lithic clasts had experienced the same parent body mixing and irradiation history. On the other hand, chondrules from clastic matrix may all have had different mixing and irradiation histories in the regolith prior to the final compaction of Murchison. If all chondrules were exposed to an early active Sun, the lithic clasts (from the PARs) and the clastic matrix would be expected to contain a similar fraction of chondrules with (variable) cosmogenic noble gas excesses. Otherwise, if the chondrules did not record exposure to an early active Sun, all chondrules from a lithic clast would either be free of excess cosmogenic gas (if that clast never was near the parent body surface), or would contain the same concentration of excess gas, if the clast had been near the parent body surface for some time. In contrast, chondrules from the clastic matrix would contain variable excesses, as they would have independent regolith exposure histories.

In collaboration with Knut Metzler of the University of Münster, doctoral student My Riebe and postdoc Liliane Huber analysed Murchison chondrules from clastic matrix and a single lithic clast, respectively, with Tom Dooley (Riebe *et al.*, 2017b). All 26 chondrules from the lithic clast had essentially identical concentrations of cosmogenic He and Ne, corresponding to the 4π exposure age of Murchison (Fig. 3.14b). Also 23 of the 27 chondrules from the clastic matrix had the same concentrations as those from the pebble. The remaining four, however, displayed variable excesses of the same magnitude as previously reported by Antoine Roth (Roth *et al.*, 2011). We therefore concluded that the cosmogenic noble gas record of the Murchison CM chondrite does not provide evidence for irradiation by energetic particles from the early Sun, but can be readily explained by substantial irradiation of a portion of its chondrules by GCR in the parent regolith. The isotopic composition of the cosmogenic Ne in the pre-exposed chondrules – typical of production by GCR – is also readily expected in the regolith scenario but requires an *ad hoc* assumption in the early Sun scenario, since SCR from the early Sun would have to have had a much harder energy spectrum than present day SCR. While we explicitly proved the parent body scenario for only one meteorite, it seemed likely to us that it could be extended to other regolithic meteorites for which large excesses of cosmogenic noble gases have been reported.

That was the situation in 2017 from our perspective. Perhaps our view was not as spectacular as one might have hoped, given that it is incontrovertible that our early Sun emitted an enormously high flux of solar energetic particles, as young stars do today. After all, as seen above, the presence of [10]Be in early solar system condensates (McKeegan *et al.*, 2000; Liu *et al.*, 2009) is also widely accepted as evidence for a high SCR flux in the early solar system. Had we perhaps just missed the right samples? Yes, I think we did!

Philipp Heck of the Field Museum in Chicago, one of my former doctoral students, told me about the work of postdoctoral associate Levke Kööp at the University of Chicago on so called PLACs (Platy hibonite Crystals). PLACs display large nucleosynthetic isotope anomalies and are thought to have formed particularly early CAIs (Kööp *et al.*, 2016). As mentioned above, they also display ^{10}B excesses from the decay of early SCR produced ^{10}Be (Liu *et al.*, 2009), and were therefore primary candidates to search for early SCR derived noble gases. However, these grains are much smaller than typical chondrules and thus more difficult to analyse. The Tom Dooley mass spectrometer with its high sensitivity was therefore clearly the instrument of choice. Levke and her colleague Jennika Greer, also from the University of Chicago, came to Zürich to measure He and Ne in a series of PLACs from Murchison. To possibly distinguish effects from a hypothesised early SCR irradiation from regolith irradiation effects, they also measured spinel-bearing grains. These are also early solar system condensates but are somewhat younger than the PLACs. Spectacularly, Levke and Jennika found large excesses of cosmogenic ^{3}He and ^{21}Ne in a majority of the PLACs, while only one out of 15 spinel-bearing samples displayed such an excess (Fig. 3.14c). The latter could easily be explained by GCR irradiation in the Murchison parent regolith, but the contrasting much larger fraction of PLACs with excess gas clearly required another explanation. Obviously, the SCR produced ^{10}Be in these very early condensates is accompanied by noble gases which also testify to an irradiation by energetic particles from the early Sun (Kööp *et al.*, 2018).

To me this was a revelation. For almost three decades, I had repeatedly warned against interpreting excesses of cosmogenic noble gases in various meteorite samples as unequivocal evidence for irradiation by energetic particles from the "active early Sun". I had pointed out that in many cases irradiation with "ordinary" GCR particles is not only a simpler explanation but also fits better the available data. I remain convinced that this is true for most of the work referred to above. But now, with the platy hibonites, I became involved in the discovery of what I believe is convincing evidence that noble gases produced by early intense solar irradiation indeed are also present in meteorites. You just have to look at the right samples!

3.1.8   Tom Dooley

The work on early solar system condensates just described is a good example of how measurements of very small samples benefit from (or were made possible in the first place by) the unique noble gas mass spectrometer "Tom Dooley". Before presenting more studies based on "Tom", it is time to present this unique instrument and the person who built it.

Heinrich "Heiri" Baur (Fig. 1.1 and Fig. 3.15) is best known internationally for the Baur-Signer ion source for noble gas mass spectrometers. To this day, this source is used in many laboratories around the world because of its remarkable linearity. Two of the world's best known noble gas mass spectrometers at the

Institut de Physique du Globe in Paris are even partially named after Heiri, along with three other authorities: "ARESIBO I and II" stands for Claude Allègre, John Reynolds, Peter Signer and Heinrich Baur (Moreira, 2013; I suspect that ARESIBO instead of ARESIBA reflects the fact that "Baur" is pronounced more or less like "Booor" in French). Heiri arrived in Peter Signer's lab as a doctoral student a few years before I joined the group. After Peter's retirement in 1994, the two of us took over as co-leaders of the group until Heiri's retirement in 2010. The lab still benefits from his invaluable know how.

Figure 3.15 **(a)** The "compressor" ion source used in the Tom Dooley mass spectrometer. The vertically rotating cylinder compresses the gas along the grooves in the stator into a downscaled version of a Baur-Signer ion source (to the left of the centre section of the rotor). The rotation frequency of 1400 revolutions *per* second results in a velocity at the surface of the rotor comparable to the speed of He atoms at room temperature. This results in compression factors on the order of 100–200 for He and Ne atoms, respectively. The rotor is magnetically levitated with a precision of a few hundredths of a millimetre, requiring sophisticated control electronics. Figure courtesy of H. Baur. **(b)** Heiri Baur in 2022. **(c)** Colin Maden in 2011, critically inspecting the construction site of a new building next to our isotope lab building.

"Tom Dooley" is one of the mass spectrometers in our laboratory devised by Heiri. This instrument was primarily designed to measure terrestrial He with a very low ^{3}He/^{4}He ratio. This required high abundance sensitivity in the He region, *i.e.* the very small ^{3}He peak had to be well separated from the much larger ^{4}He peak. The flight tube therefore has an "appendix", hosting a Faraday collector exclusively for ^{4}He, whereas the other isotopes are measured by ion counting. To minimise vibrations, Heiri decided to mount the spectrometer on a heavy mass, and doctoral student Anselmo Pedroni organised a beautiful granite slab from a quarry in his home canton of Ticino. However, the ETH building department decided that 600 kg of stone was too heavy for our lab floor to carry. So we instead had to hang the slab with the mass spectrometer on it from the

ceiling, which could support more weight than the floor. This inspired Heiri to name the instrument after the unfortunate hero of a song that used to be very popular not only in the US but also in Germany and Switzerland:

> Hang down your head Tom Dooley
> Poor boy you're bound to die

Wikipedia knows that Tom Dula was hanged in 1868 for alleged murder of the mother of their unborn child, and his legend seems to have survived in North Carolina to this day. I guess we were not aware of the whole story in the 1980s (Wikipedia did not exist yet). The fact is that our Tom Dooley (today mostly just "Tom") is still alive and providing excellent data.

In its first life, Tom was used primarily to measure He (and tritium) in water samples and cosmogenic and mantle He and Ne in terrestrial rock samples, as will be discussed in the second part of this memoir below.

Later, Heiri Baur upgraded Tom into an essentially new and unique instrument. In a normal gas mass spectrometer, the gas to be analysed fills the entire flight tube plus (part of) the gas extraction and purification system. If the gas could be largely concentrated in the ionisation volume of the ion source, the sensitivity of the instrument could be greatly increased. Obviously, this would be of great benefit to the analysis of very small samples, in which we became increasingly interested, and would be particularly important for the lightest noble gases He and Ne, which have very low ionisation efficiencies due to their large ionisation potentials. One possibility was to concentrate the gas in the ion source region with a turbomolecular pump, placing the source at the high pressure end of the pump (Matsumoto *et al*., 2010). However, the achievable compression factor would not have been large enough to satify Heiri's ambitions. He hence designed a molecular pump that pushes the gas very efficiently into the small ionisation volume of the source, as shown in Figure 3.15. To avoid grease, the pump's rotor, which weighs several kilograms, needs magnetic bearings. This requirement had to be compatible with two other requirements to ensure sufficiently high compression efficiencies: the high thermal speed of He atoms implies a rotation frequency of 80,000 rotations *per* minute and a very small gap of about a tenth of a mm between rotor and stator. This required sophisticated control electronics to keep the magnetically levitated rotor in position with an accuracy of a few hundredths of a millimetre at 1400 rotations *per* second! Heiri achieved this in collaboration with a company led by a friend from his student days. Furthermore, to achieve the targeted compression factors, Heiri had to shrink his classical ion source by a factor of two in a linear dimension or a factor of eight in volume. Atoms lost through the source slit are efficiently recycled into the ionisation volume by differential pumping. All of this leads to very stable compression factors of about 200 and 100 for Ne and He, respectively, *i.e.* the gas pressure in the ion source becomes higher by about two orders of magnitude when the rotor is turned on. This allows sufficiently high count rates for gas amounts too small for precise analysis in conventional mass spectrometers, for example the single grain measurements presented in the previous section

or low level tritium analyses in water samples (*via* the decay product ^{3}He), as described in Section 5. The instrument is useful for He and Ne, for which a sizeable fraction of the atoms are ionised within an analysis time of typically 20 minutes. Krypton and xenon cannot be analysed in this instrument. Their half-lives against ionisation would only be on the order of one or two minutes, too short for analysis of even one isotope of these elements, let alone the determination of isotopic ratios, which requires (time consuming) mass-peak jumping.

Like many other instrumental developments in our laboratory, Tom Dooley could not have been accomplished without the excellent technical staff in our research team, mentioned in the acknowledgements section. Since Heiri's retirement, Colin Maden has been responsible as lab manager for technical developments and smooth functioning. Colin joined us after his dissertation in the AMS group at ETH.

3.1.9   The Fossil Meteorites

One particularly successful area of research largely based on Tom Dooley has been the work on fossil meteorites and micrometeorites with Birger Schmitz at Lund University in Sweden and colleagues. Birger and I already knew of each other from a book on the accretion of extraterrestrial material that he co-edited with Bernhard Peucker-Ehrenbrink (Peucker-Ehrenbrink and Schmitz, 2001), but I first met him in person at the Meteoritical Society meeting in Rome on September 11, 2001. Nadia Vogel had just delivered her talk on the microdistribution of noble gases in chondrules and their rims when the afternoon session was cut short because of the terrorist attacks in the United States. At first, we had no reliable information about what had happened, so Birger asked Nadia and me to talk about the many fossil meteorites that were being recovered from a quarry in southern Sweden (Fig. 3.16). He imagined that if we were able to measure noble gases in individual chondrules, we might also succeed to detect them in individual chromite grains extracted from otherwise fossilised meteorites. Birger knew that the chromites had survived the fossilisation process. Therefore they might have retained their cosmogenic noble gases during the ~470 Ma since their fall on Earth. As I recall, we were not convinced that this would be possible, but Birger is a person of great enthusiasm and persuasion. So we decided to give it a try, perhaps also just for fun. We agreed that Birger would send us some chromite grains from a number of fossilised meteorites from different sediment strata in the quarry were they were found. After dinner we headed for our hotels and when I turned on the TV to watch the collapse of Manhattan's Twin Towers, meteorites lost all interest for a while, for me and probably for everyone else at the meeting.

Yet, the first batch of chromite grains arrived in Zürich in 2002. Birger had handpicked them on many evenings, accompanied by his favourite opera recordings. The noble gas analyses of these grains marked the beginning of a long and fruitful collaboration. Besides Birger himself, Philipp Heck and Matthias Meier at our side were the two most important persons in this endeavour.
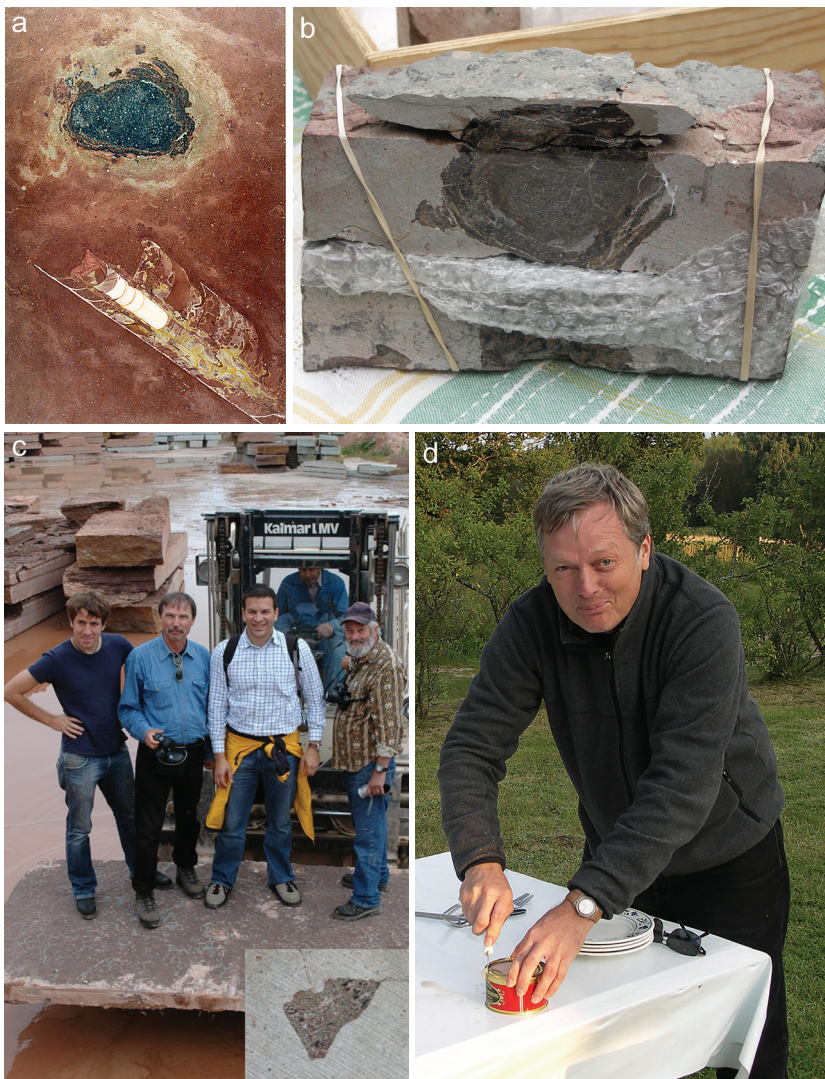
Figure 3.16 **(a)** A fossilised meteorite (~6 x 4 cm) next to a nautiloid shell. Picture courtesy of Birger Schmitz. **(b)** Another fossil meteorite of ~10 cm size. Many of these fossilised meteorites are found in a quarry in southern Sweden, indicating an unusually high flux of meteorites in the aftermath of the catastrophic break up of the L chondrite parent body about 470 million years ago. Fossilised chondrules are visible. These meteorites also preserve original meteoritic chromites and their cosmogenic He and Ne, from which we can infer that the first meteorites arrived on Earth very soon after the collision, within less

than a hundred thousand years. **(c)** Matthias Meier, Rainer Wieler, Philipp Heck, and Mario Tassinari are carried by a quarry worker to a 2 cm sized fossil meteorite still *in situ* at the Thorsberg quarry, shown in the inset at the lower right. **(d)** Birger Schmitz opening a box with surströmming to be served to his innocent foreign guests at his dacha. Initiates usually decline this "delicacy" of fermented herring with its terribly putrid smell and taste.

Both did their dissertations in my group and I have continued to work with both of them for many years after, as we will see below. Philipp now heads the famous meteorite collection at the Field Museum in Chicago, and is also affiliated with the University of Chicago, and Matthias has become director of the Natural History Museum in St. Gallen, Switzerland. Philipp's results for the first sets of chromite grains extracted from fossil meteorites were spectacular, but before I go into that, I must say a few words about the significance of the fossil meteorites from southern Sweden. The story has been told by Birger more than once (*e.g.*, Schmitz, 2013) and I am giving here only a much abridged and less authoritative version. It all started when Maurits Lindstöm found a fossil meteorite in a slab on a dump of a limestone quarry between Göteborg and Stockholm. Such meteorite-bearing slabs had been thrown away by the quarry workers because they were considered defective. However, once informed of the potential value of the fossil meteorites, the Thorsberg quarry owners and workers were very cooperative and, together with Mario Tassinari, carefully saved them. Mario (Fig. 3.16) was a collector of minerals, fossils, and almost anything else you can imagine, including old radios and corks from Italian and other wine bottles. His dedication to the search and preservation of the fossil meteorites was rewarded with a Doctor Honoris Causa from Lund University. Fossil meteorites were found in different strata within the quarried 3-4 metres, covering between one and two millions years of Mid-Ordovician geology. Birger concluded that the meteorites were not simply different pieces of a large fall, but represented many different falls, although all of them likely belong to the same class, the L chondrites. Large concentrations of extraterrestial chromite grains are also present in sediment strata in southern Sweden coeval to the fossil meteorite-rich beds at Thorsberg (Fig. 3.17; Schmitz *et al.*, 2001). These grains and the fossil meteorites indicate that the meteorite flux in the Mid-Ordovician was between one and two orders of magnitude higher than today. Given the stratigraphic age of the sampled limestone of around 466 Ma, this suggested a connection to the break up of the parent body of the L chondrites, which is reflected in the K-Ar and U-Th-He ages of around 500 Ma of many L chondrites (Bogard, 1995). This link became even clearer when the Heidelberg group determined high quality ^{40}Ar-^{39}Ar ages for a series of L chondrites (Korochantseva *et al.*, 2007), which dated the L chondrite parent break up (LCPB) at 470 ± 6 Ma, in agreement with the stratigraphic age of the meteorite-rich sediment layers. Therefore, the fossil meteorites represent a unique testimony of the largest known asteroid collision.

Could it be that noble gases in the chromites survived the meteorite fossilisation? If so, would noble gas analyses provide additional information about meteorite provenance and their journey to Earth? On the one hand, if we could show that all chromites contained cosmogenic noble gases, and in at least approximately similar concentrations for samples from one meteorite or from meteorites in the same stratum, this would indicate that potential gas losses must have been small. On the other hand, this would also be strong additional evidence that the individual meteorites were not just fragments of one very large fall, because, if so, inner pieces should have much lower concentrations of cosmogenic gases than samples from closer to the surface. When we started the project, we did not even dare to think of a third possibility: could it be that the

concentrations of cosmogenic noble gases correlate with the age of the layers in which the meteorites were embedded? But all this proved to be true. Heck *et al.* (2004) showed that all chromite batches (a few grains each) contained cosmogenic ^{21}Ne produced in space and that essentially none of it had been lost during the chromite's almost 500 Ma residence time on Earth, although the rest of each meteorite had been diagenetically altered. This allowed the determination of the cosmic ray exposure ages of the chromite's parent meteoroids (Fig. 3.17). The ages had considerable uncertainties because no shielding corrections could be applied and the Ne production rates from Cr were not very well constrained. But this was not a major problem. The main surprising observation was that the ages are very low for meteorite standards, ranging from about a hundred thousand to a million years. These unexpectedly low ages allowed us to document a trend with sediment age: meteorites from the lowest level in the quarry showed the shortest exposure ages, those higher up in the stratigraphic column, estimated to have been deposited 1-2 Ma later, had exposure ages about a million years higher than the ones at the bottom. This means that the first meteorites from the LCPB arrived on Earth within 100,000 years or even less, and that the high debris flow from this event lasted for at least a million years but probably longer. Such a short transfer time implies that the first debris from the break up was injected into an orbital resonance in the asteroid belt within a very short time.

Dynamical models of meteorite delivery from the asteroid belt to Earth predict that meteorites will first slowly drift into an orbital resonance and then possibly get ejected into an Earth crossing orbit and collide with our planet within a few million years at most (Gladman *et al.*, 1997). The best known orbital resonances manifest themselves in the "Kirkwood gaps", regions with low asteroid density. An example is the 3:1 Kirkwood gap at a semi-major axis of about 2.5 astronomical units, where an asteroid or meteorite orbits the Sun exactly three times in one Jovian year. The slow drift is the result of non-gravitational forces generated by asymmetric re-emission of thermal energy from solar illumination (the Yarkovsky effect; Bottke *et al.*, 2006). Once in a resonance, orbital motions of bodies become chaotic, with large swings in eccentricity leading to a rapid transit to the inner solar system (Wisdom, 1987). Overall, the exposure ages of meteorites (usually in the range of a few to tens of millions of years) are thus dominated by their drift phase in the asteroid belt. The very short exposure ages of the fossil meteorites provided evidence supporting Jack Wisdom's simulations of chaotic motions of particles in resonant orbits. They also showed that the LCPB occurred close enough to a strong resonance that collisional ejecta could directly reach a resonant orbit.

The trend of increasing exposure ages with decreasing statigraphic age must have convinced the sceptics who had doubted that the many fossil meteorites actually represent many different falls. I think that the 2004 paper by Philipp Heck and co-workers in *Nature* also has helped to establish the fossil meteorites in the minds of the planetary science community.

The LCPB has undoubtedly left its mark worldwide in the form of a global rain of meteorites. But a systematic search for macroscopic fossil meteorites (from the LCPB or other events) elsewhere on the planet will hardly ever succeed. The Thorsberg quarry is a remarkable stroke of luck, not only because it exploits exactly the right sediment layers, but also thanks to its team of exceptionally dedicated workers. However, even though a systematic search for macroscopic fossils is hopeless, sediment sequences on other locations on the globe coeval with those at Thorsberg may contain additional evidence of strong extraterrestrial influx from the LCPB. Extraterrestrial chromite grains dispersed in sediments might be good candidates, since in Sweden many such grains are also found in sediment strata of the same age as at Thorsberg. Meier *et al.* (2010) measured a suite of such grains from the Thorsberg quarry itself and to our surprise most of them contained solar wind noble gases. This implied that these grains were not remnants of macroscopic L chondrites, which rarely contain solar wind, but parts of micrometeorites that had been irradiated by the solar wind in space. Searching for sediment dispersed chromites from other places, Cronholm and Schmitz (2010) were successful at a location in central China deposited contemporaneously with the meteorite-rich strata in Sweden, and similar coeval chromite-rich sediments also are known near St. Petersburg in Russia. These grains as well have chemical compositions very similar to those of chromites from recent L chondrites. Matthias Meier, together with Carl Alwmark who joined our group as a postdoc after his PhD thesis with Birger in Lund, measured He and Ne in chromite grains from both sites (Alwmark *et al.*, 2012; Meier *et al.*, 2014c). Also these grains mostly contained solar wind noble gases and must, therefore, have arrived on Earth as micrometeorites. The solar noble gases overwhelmed cosmogenic noble gases in most grains, but a few of them allowed us to deduce cosmic ray exposure ages. Not so surprisingly any more, they were about as low as those of the chromites extracted from fossil meteorites (Meier *et al.*, 2014c). This clearly showed that the LCPB brought to Earth not only macroscopic bodies, but also large amounts of cosmic dust, on a global scale. What consequences could this have had for our planet?

Schmitz *et al.* (2008) proposed that the LCPB accelerated the process known as the Great Ordovician Biodiversification Event (GOBE) by showing that the onset of the main phase of biodiversification coincided with the arrival of LCPB material on Earth around 470 Ma ago. They argued that the LCPB produced not only a high meteorite and micrometeorite flux on Earth, but also frequent impacts of km-sized bodies. The latter would have accelerated biodiversification. This work was challenged by Lindskog *et al.* (2017), who argued that significant diversification in Baltoscandia began some 2 Ma before the asteroid break up. However, Schmitz *et al.* (2019) showed that the LCPB coincided with a significant eustatic sea level fall attributed to an Ordovician ice age. In contrast to the 2008 paper, Schmitz and colleagues now proposed that extraordinary amounts of fine dust in the entire inner solar system caused by the LCPB cooled

the Earth. This cooling could have been the tipping point that triggered the Ordivician icehouse conditions, which may have led to major faunal turnovers associated with the GOBE.

Birger Schmitz devotes much of his career to fossil meteorites and – more generally – to the effects of extraterrestrial matter accretion on our planet. I am pleased to be part of this endeavour, along with his many other friends and collaborators. Birger's frequent visits to Zürich are internally known as "Apfelstrudel meetings", as they usually end at a restaurant whose most important requirement is that it serves Birger's favourite dessert. I also greatly enjoyed several short research visits in the beautiful city of Lund, including a trip to the Thorsberg quarry, a few hundred km further north.

3.1.10 How Old are Presolar Grains?

Tom Dooley has extensively been used to measure He and Ne in individual presolar grains, which are certainly among the most fascinating objects in meteorites (Fig. 3.18). As their name implies, presolar – or circumstellar – grains predate the solar system. They condensed in the outflows of stars in the last stages of their evolution and found their way into the nascent solar system without having been melted or vapourised. Therefore, every presolar grain carries information about the evolution of its parent star, about galactic chemical evolution, and about dust formation in stellar environments (Zinner, 2014; Nittler and Ciesla, 2016). In particular, the very large isotopic anomalies displayed by almost every element studied in presolar grains contributes significantly to our understanding of element synthesis in stars, a line of research aptly named "astrophysics in the laboratory". Over the past nearly four decades, many different types of presolar grains have been identified. Besides the tiny, nanometre-sized diamonds discovered by Lewis *et al.* (1987), the most important are micrometre-sized silicon carbide (SiC) and graphite grains (Zinner, 2014). Individual grains are amenable to noble gas analyses, as is addressed next.

It is striking that presolar grains often contain a substantial fraction of the noble gas budget of bulk meteorites. Therefore, noble gases are ideal to trace enrichments or depletions of presolar grains in separated phases of meteorites. Much of the pioneering work on this subject was done at the University of Chicago and Washington University in St. Louis. Carbonaceous presolar phases (diamonds, SiC, and graphite) were identified by a series of acid dissolution steps undertaken to eliminate silicates and other acid-soluble phases (*e.g.*, Lewis *et al.*, 1987; Amari *et al.*, 1990; see review by Anders and Zinner, 1993). This technique, which has become known as "burning down the haystack to find the needle", was guided by noble gas analyses. In fact, the first ever isotopic anomalies in meteorites were reported for noble gases. These were radiogenic ^{129}Xe resulting from the decay of short lived ^{129}I in the early solar system (Reynolds, 1960) and primordial Xe-HL, which is enriched in the heaviest (H) as well as the lightest (L) isotopes (Reynolds and Turner, 1964).

However, while noble gases have been instrumental in detecting presolar grains, the minute concentrations of noble gases pose a serious challenge for single grain analyses, much more so than for elements that can be measured by SIMS and other techniques. Even so, we were able to detect nucleosynthetic ^{4}He and/or Ne isotopes in a minor fraction (typically 10–20 %) of the presolar graphite grains we studied (Heck *et al.*, 2009a; 2018; Meier *et al.*, 2012). For some of these grains we could assign a stellar source such as so called Asymptotic Giant Branch (AGB) stars or core collapse supernovae.
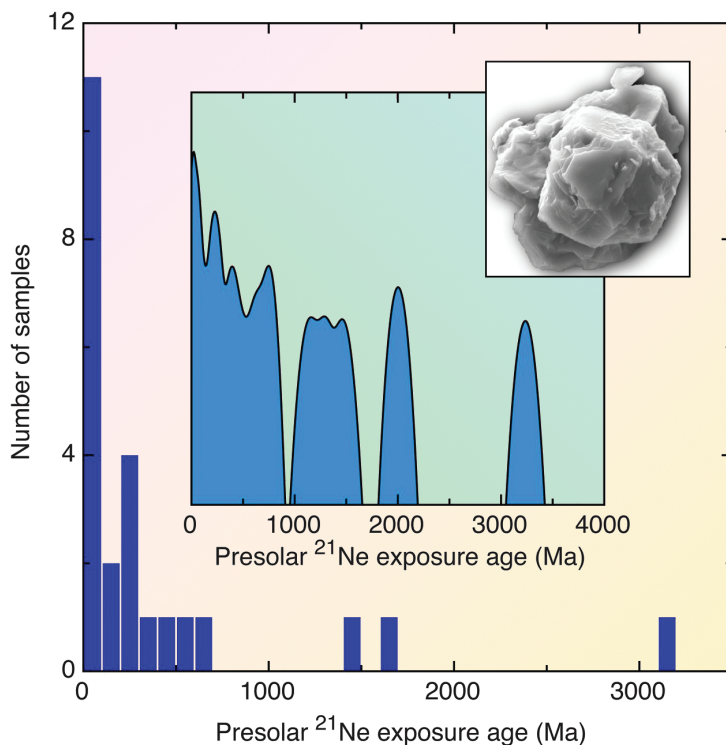
Figure 3.18 Histogram and diagram of kernel density estimation (inset) of presolar ^{21}Ne exposure ages of large presolar SiC grains reported by Heck *et al.* (2020). The picture on the upper right depicts a SiC grain of about 8 microns in size which has been shown in many reports worldwide addressing the study by Heck *et al.* (2020). Figure from Heck *et al.* (2020), SiC image courtesy of Janaina Àvila.

Perhaps the most rewarding aspect of our work on single presolar grains is that we have been able to detect cosmogenic noble gases in single SiC grains. Cosmogenic noble gases provide an estimate of the presolar ages of presolar grains, a task otherwise not (or not yet?) possible. Conventional radiometric

dating is hindered by the very small sample size and the highly anomalous isotopic composition of essentially every element in presolar SiC. The alternative is to determine the length of time the grains were exposed to galactic cosmic rays in the interstellar medium, which is best done with cosmogenic noble gas isotopes (Tang and Anders, 1988; Lewis *et al.*, 1994). The first ages provided by the Chicago group turned out to be unreliable because large fractions of the cosmogenic gases get immediately lost from the tiny grains by recoil (Ott and Begemann, 2000). We have therefore focused on some of the largest known presolar SiC grains where recoil corrections are smaller. Such grains, ranging in size from a few to tens of micrometres, had been separated from the Murchison meteorite by Sachiko Amari and co-workers at the University of Chicago. Most of the grains contained measureable amounts of cosmogenic ^{3}He and/or ^{21}Ne, corresponding to highly variable presolar exposure ages of between ~5 and 1000 Ma (Heck *et al.*, 2009b). These ages had large uncertainties due to inaccurate grain volume estimates, recoil corrections, and uncertain production rates of GCR nuclides in the interstellar medium outside the heliosphere. Gyngard *et al.* (2009) reported mostly considerably higher ages on other large SiC grains from Murchison, based on analyses of lithium isotopes with the Washington University NanoSIMS. So next we attempted a joint analysis of Li and noble gases on the same grains, again large SiC grains from Murchison. Philipp Heck, now at the Field Museum in Chicago, analysed He and Ne in Zürich with "Tom", along with his colleagues Jennika Greer and Levke Kööp. Reto Trappitsch of Lawrence Livermore National Laboratory calculated new values for interstellar production rates of noble gases, based on an interstellar GCR spectrum derived from data collected by NASA's Voyager 1 spacecraft at the edge of the heliosphere. As it turned out, these values differ only slightly from the old ones provided by Bob Reedy thirty years earlier (Reedy, 1989). Most grains have presolar exposure ages not exceeding some 300 Ma, with some values being as low as a few Ma. However, a few grains have exposure ages exceeding a billion years, with possible values as high as about 3 billion years (Heck *et al.*, 2020; Fig. 3.18). The uncertainties are substantial (see the inset in Fig. 3.18), but we nevertheless believe that these ages are reliable thanks to improved recoil corrections compared to those for the smaller grains in the pioneering Chicago studies. As already suggested by Heck *et al.* (2009b), we reiterated in our 2020 paper that the majority of the grains with a presolar age below 300 Ma may have originated from stars born during an episode of enhanced star formation roughly 7 Ga ago proposed by astrophysicists. Philipp Heck issued a press release about this work, in which he also noted that we had dated the so far oldest material ever. This statement immediately made headlines everywhere. It was in the news worldwide for at least a day or two, according to BBC attracting even more attention than the then latest gossip about Prince Harry and his wife Meghan. Even two years later, many internet sites still showed the picture of one of the SiC grains we analysed. Unfortunately, the lithium ages of the grains turned out to be too inaccurate to be useful because of the very large contributions of non-cosmogenic lithium.

3.1.11 Cosmogenic Nuclides as a Nuisance in Ultraprecise Isotope Analyses

Although cosmic ray produced nuclides are important tools in cosmochemistry, sometimes one would prefer to study samples whose isotopic composition has not been altered by cosmic ray interactions. Noble gas researchers have struggled with this problem for decades, since cosmogenic noble gases in meteorites often dominate or even completely overwhelm other noble gas components that may be of primary interest. As I will discuss in the next section on primordial noble gases, it is therefore common practice to separate cosmogenic noble gases from other components to the extent possible, either during sample preparation or during noble gas analysis. Examples include separation of presolar components by chemical means and gas extraction by stepwise heating. For most other elements, changes in isotopic composition caused by cosmic rays are so small that they could be largely ignored for a long time. This changed in recent decades, especially with the advent of multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS, even the acronym is a tongue twister), which has enabled ultrahigh precision isotope analyses for a large number of elements of cosmochemical interest (*e.g.,* Halliday *et al.*, 1998; Albarède *et al.*, 2004). Today, cosmogenic effects are considered for several elements of cosmochemical interest, particularly for iron meteorites with their very long cosmic ray exposure ages (Ek *et al.*, 2020) and some lunar samples. In some cases, noble gases play an important role in such corrections, as I will explain next on the example of tungsten, which I became involved with shortly after Alex Halliday joined ETH in 1998.

Alex and Der-Chuen Lee ("call me Albert") had made pioneering tungsten isotope measurements on lunar and meteorite samples at the University of Michigan in Ann Arbor (Lee and Halliday, 1997). These made it possible to date early metal silicate fractionation, *e.g.,* lunar and asteroidal core formation. However, it was recognised that in some samples the measured $^{182}W/^{184}W$ ratio reflected not only the decay of radioactive ^{182}Hf ($T_{1/2}$ = 8.9 Ma), but also a cosmogenic contribution, mainly from the capture of secondary cosmic ray neutrons by ^{181}Ta. This called for a reassessment of the timing of lunar core formation proposed by Lee and Halliday. Therefore, Ingo Leya modelled the production and "burnout" of W isotopes by cosmic ray interactions. Apart from the radiogenic isotope ^{182}W, the other tungsten isotopes also had to be considered, as they are used to correct for instrumental mass discrimination in MC-ICP-MS. Leya *et al.* (2000c) showed that, indeed, in many lunar samples neutron capture on Ta has caused a large part of the observed ^{182}W excess, since these samples were often exposed to cosmic rays for hundreds of Ma. However, for some lunar samples with much lower exposure ages (or perhaps much lower neutron fluences if they were mostly close to the surface of the regolith) only a minor or even negligible fraction of the ^{182}W excess was deduced to be cosmogenic. These results implied that the formation time of the Moon 50 Ma after CAI formation derived by Lee and Halliday (1997) did not need to be corrected due to cosmic ray effects. Leya *et al.* (2000c)

also concluded that the W isotopic composition of Martian meteorites was not substantially altered by cosmic rays because they have lower Ta/W ratios and much shorter exposure ages than lunar samples.

Ingo Leya also assessed cosmic ray induced variations on isotopic compositions of different extinct nuclide systems, including again ^{182}Hf-^{182}W (Leya *et al.*, 2003). In this paper he used Gd and Sm isotope shifts as proxies for the secondary cosmogenic neutron fluence in a sample. This approach improves the neutron dose estimate based on the noble gas derived cosmic ray exposure age which incompletely reflects the shielding of a sample during exposure. Although this allowed a better correction for ^{182}W, Ingo also showed that cosmic ray effects are negligible for ^{92}Zr and ^{98,99}Ru. Potentially detectable shifts on ^{53}Cr can be corrected *via* ^{54}Cr/^{52}Cr.

Apart from the work with Alex and Ingo, I was also involved in a number of studies on cosmogenic effects in iron meteorites, in collaborations with Ghylaine Quitté, Agnès Markowski, Peter Sprung, Thorsten Kleine, and Thomas Kruijer. Iron meteorites are well suited to date asteroidal core formation with the Hf-W system, as pioneered by Charles Harper (Harper *et al.*, 1991). Hafnium-tungsten ages indicated that many asteroids segregated their iron core very early, within one or a very few million years of CAI formation (Kleine *et al.*, 2005), a finding confirmed with very precise absolute Pb-Pb ages (Blichert-Toft *et al.*, 2010). It is therefore very important to date the core formation of differentiated asteroids very accurately and compare these dates with formation ages of chondritic parent bodies. However, the typically very old exposure ages of hundreds of Ma of iron meteorites require a reliable correction of the tungsten isotopic composition for cosmic ray effects. This is further complicated by the fact that knowing the

cosmic ray exposure age of an iron meteorite is often insufficient for an accurate correction. Many iron meteorites have large pre-atmospheric sizes and thus can exhibit large variations in their cosmogenic W concentrations from sample to sample, because cosmic ray neutron fluences first increase steeply with distance from the pre-atmospheric surface before they may decrease again towards the centres of very large meteoroids. The bars cut out of the slabs of the large meteorites Grant and Carbo which Peter Signer had studied in Minneapolis in the 1960s to develop his model of cosmogenic noble gas production in iron meteorites (Section 3.1.3) are still kept at ETH (Fig. 3.20). We used these samples to study to what extent the expected depth dependence of cosmogenic W production can be experimentally verified.
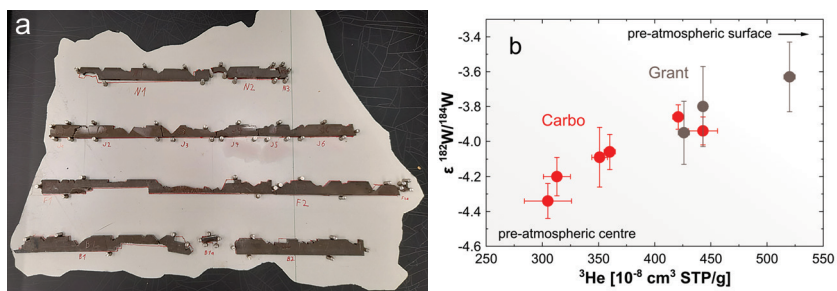
Figure 3.20 **(a)** Bars from the cross section slab of the Grant iron meteorite studied for cosmogenic noble gases and later for modifications of the isotopic composition of several other elements. As a result of the extensive sampling, the bars now resemble a mountain panorama. Long side of picture ~55 cm. **(b)** The ^{182}W/^{184}W ratio (expressed in ε-units relative to a terrestrial standard) in Grant and Carbo correlates with the distance from the meteorites' pre-atmospheric surface, indicating that the depletion of ^{182}W by neutron capture reactions was more important near the centre. Figure adapted from Markowski *et al.* (2006).

The noble gas concentration data provide a good indication of the location of the pre-atmospheric centres of the two meteorites. Agnès Markowski, doctoral student of Alex Halliday, and her advisor Ghylaine Quitté showed that for both meteorites the ^{182}W/^{184}W ratio indeed correlates well with the inferred distance of the samples from the pre-atmospheric centre (Markowski *et al.*, 2006; Fig. 3.20). Unlike lunar samples, where ^{182}W is produced by neutron capture on ^{181}Ta, in iron meteorites neutron capture depletes ^{182}W by the reaction ^{182}W(n,γ)^{183}W. Hence, the ^{182}W/^{184}W ratio near the pre-atmospheric centres of Grant and Carbo is lower than near the surface by ~0.3-0.5 ε-units (1ε = 1 part in 10^4). Thus this work nicely demonstrated that the W isotopic composition in iron meteorites is affected by cosmic ray interactions and that the magnitude of the required correction varies with the pre-atmospheric shielding of the samples.

Since then, samples from the Grant and Carbo bars have been used to study effects of cosmic ray interactions on several other elements of interest in isotope cosmochemistry (*e.g.*, Qin *et al.*, 2015; Ek *et al.*, 2020). The bars therefore now resemble a mountain panorama (Fig. 3.20).

Unfortunately, in most cases the shielding is not as well constrained as in Grant and Carbo. Historically, ^{3,4}He/^{21}Ne ratios have been used for this purpose, but they are not very reliable proxies for the relevant cosmogenic neutron fluxes. Since ^{3}He is mainly produced by high energy protons, its production is highest near the pre-atmospheric surface, whereas the fluxes of (slow) secondary neutrons increase to a certain depth (leading to the anticorrelation of ^{3}He and burnout of ^{182}W indicated in Fig. 3.20). Thomas Kruijer tackled this problem by two different approaches. He had joined ETH in 2009 as doctoral student supervised by Thorsten Kleine and myself. First, Thomas analysed a series of the – unfortunately very rare – iron meteorites with known relatively low cosmic ray exposure ages. They could not only be expected to have (almost) negligible burnouts of ^{182}W but also marginal cosmogenic effects on other W isotopes used to correct for instrumental mass fractionation. Thomas showed that the Hf-W ages of those meteorites requiring essentially no corrections all postdated CAI formation, mostly by between 1-2 Ma (Kruijer *et al.*, 2012). This was a very important result because it ruled out earlier reports that some iron meteorites were even older than CAIs. The same conclusion had already been reached by Burkhardt *et al.* (2012), as will be discussed in Section 3.1.12. However, consistent with the earlier reports, Thomas concluded that the accretion and differentiation of many iron meteorite parent bodies preceded the accretion of most chondritic asteroids.

Figure 3.21 Thomas Kruijer (left) at the Paneth Colloquium 2012 in Nördlingen, Bavaria, and Thorsten Kleine at the "Researchers Night" outreach event in Zürich in 2007.

The second approach developed by Thomas Kruijer was to correct W isotopes by establishing a proxy for the fluences of cosmic ray neutrons in individual samples. Platinum isotopes capture neutrons efficiently, and Pt isotopic abundances are also modified by neutron capture reactions on Ir. As part of his doctoral thesis, Thomas measured Pt and W isotopes in many iron meteorites of various classes in Thorsten Kleine's laboratory at the University of Münster, after Thorsten moved from ETH to Münster. The variations in Pt isotopic compositions agreed very well with model calculations by Ingo Leya, which also take into account the Ir/Pt ratio of meteorites. Therefore, Pt isotopes are a very reliable tool for quantifying neutron capture effects on W isotopes (Kruijer *et al.*, 2013). This is shown in Figure 3.22, which displays Pt and W data of the two IID iron meteorites Carbo and Rodeo, which have almost identical Ir/Pt ratios. The correlation of Pt and W isotopic compositions defined by the Carbo data (which are affected by cosmogenic effects) extrapolate perfectly to the measured data of the weakly irradiated Rodeo (at ε^{192}Pt ~0). The model calculations also agree well with the measured correlation in Figure 3.22. This work was a major advance in dating asteroidal core formation by Hf-W. In principle, platinum (and Ir) data from a single sample of an iron meteorite allow a reliable correction of its W isotopic composition for cosmogenic effects without the need for independent shielding information. Kruijer *et al.* (2013) definitively showed that there was a time gap of at least ~1 Ma between CAI formation and metal segregation in the parent bodies of the iron meteorite groups they studied (IID, IVA, IVB). The study also confirmed earlier conclusions that the accretion of these differentiated bodies predates that of most chondrite parent bodies. Since then, Thomas Kruijer is contributing further notable studies on the dating of early solar system events.

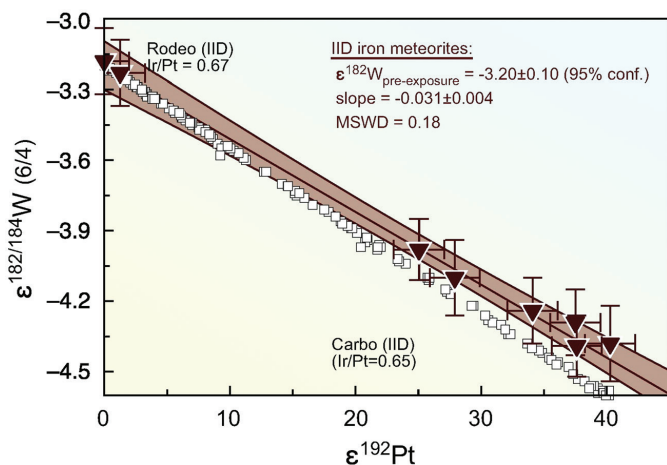Figure 3.22 Correlation of ^{182}W/^{184}W with the ^{192}Pt excess induced by reactions of cosmogenic thermal and epithermal neutrons on Pt and Ir isotopes for the two IID iron meteorites Rodeo and Carbo, which have nearly identical Ir/Pt ratios.

The correlation defined by the Carbo data (which are affected by cosmogenic effects) extrapolates perfectly to the measured data of the weakly irradiated Rodeo (at ε^{192}Pt ~0). The model calculations (open squares) also agree very well with the measured correlation. Data and figure from Kruijer *et al.* (2013) with permission from Elsevier.

3.1.12 More Cosmochemistry with Isotopes – and Theia the Impactor

Numerous discussions and several joint projects with colleagues and friends, mostly in the groups of Alex Halliday, Thorsten Kleine, Bernard Bourdon, and Maria Schönbächler, helped me broaden my horizon in isotope cosmochemistry of non-noble gas elements beyond the topic of correcting for cosmogenic effects.

Thomas Kruijer and colleagues studied nucleosynthetic tungsten isotope anomalies in CAIs. Fine grained inclusions have variable abundances of W isotopes from s- and r-process nucleosynthesis, whereas coarse grained CAIs have hardly any nucleosynthetic W anomalies (Kruijer *et al.*, 2014). Correcting the radiogenic ^{182}W abundances for nucleosynthetic isotope anomalies resulted in Hf-W ages of angrites in good agreement with their Al-Mg ages, which, contrary to other claims, argues against a heterogeneous distribution of ^{26}Al in the inner solar system regions where CAIs and angrites formed.

Mathieu Touboul measured tungsten isotopes in metal samples from the Moon that are essentially free of Ta derived cosmogenic W and therefore allow more reliable Hf-W ages than non-metal samples (Touboul *et al.*, 2007). In a second paper, Mathieu measured W in lunar ferroan anorthosites (Touboul *et al.*, 2009). In both papers he concluded that the Moon formed no earlier than some 60 Ma after CAI formation, later than previously thought. This work resolved a discrepancy with ^{147}Sm-^{143}Nd ages that had previously suggested late lunar formation.

Christoph Burkhardt and colleagues studied molybdenum and tungsten isotopes in detail in the Murchison carbonaceous chondrite and many other meteorites. Different leach fractions of Murchison indicated a heterogeneous distribution of W isotopes from s- and r-process nucleosynthesis, implying the presence of at least two different carriers of nucleosynthetic W (Burkhardt *et al.* 2012). These data allowed Christoph to propose an improved correction of the ^{182}W abundance for non-radiogenic anomalies, resulting in a decrease of the ages of iron meteorites by about two Ma, which solved the problem that iron meteorites had suggested that some planetesimals differentiated into core and mantle prior to CAI formation. As noted in the previous section, this puzzle has been further studied by Thomas Kruijer by correcting W isotopes for cosmogenic contributions. Burkhardt *et al.* (2011) reported Mo isotope data in a wide range of samples ranging from CAIs, chondrites, and differentiated meteorites to samples from Mars and the Earth. These data showed that the Earth must have accreted

from material different from any of the meteorites. As Burkhardt (2021) explains, this is also evident from isotope data of other elements such as Zr, Cr, Ti, *etc.*, and indicates that the Earth accreted from material belonging to the so called NC reservoir defined by non-carbonaceous meteorites, but most likely sunwards of the known NC representatives. Paul Warren (Warren, 2011) first pointed out the marked dichotomy between the two reservoirs typified on the one hand by carbonacous chondrites (CC), representing material accreted in the outer solar system, and the NC reservoir formed nearer the Sun on the other.

I very often discussed isotope cosmochemistry with Alex Halliday, although we never had any joint papers beyond those on cosmic ray effects discussed above. I remember particularly well the afternoon when Alex – apparently slightly stressed – told me that he needed my immediate help. That evening he had to submit a manuscript of a paper on the origin of the Moon (Halliday, 2000), but he was uncomfortable with having to repeatedly talk about "the Giant Impactor". He wanted a more catchy name for that body which would hopefully be embraced by the community but he did not have time to think about a suitable option. So he asked me to propose a name – preferably from mythology – that would evoke things like fire, impacts, thunder and the likes. I considered this an excellent idea and a good challenge for me and so I immediately set to work with the help of the internet which was still quite new at the time. The task turned out to be not that easy, however. Either I, or Alex, or both of us were unhappy with my first suggestions. Hawaiian gods or goddesses like Pele were taboo, since they were reserved for Jupiter's moon Io, and norse gods like Wotan or Thor did not appeal to Alex. Next I resorted to Greek mythology, but Hephaistos, the Greek god of forge and fire, again appealed neither to Alex nor me. So, already slightly embarrassed, I searched the family tree of Selene, the Moon goddess, and found her mother: Θεία or Theia, one of the twelve titans. I insisted, and Alex finally accepted that name, even though, according to Wikipedia, Theia is not associated with fire but rather with the bright blue sky, precious stones and precious metals. The name indeed stuck. Soon after Alex's paper was published, "Theia" became synonymous for the Giant Moon forming impactor. At the time we did not delve deeper into Selene's family tree, so only now, as I write this, do I realise that Theia is the daughter of Gaia. Hence our Moon seems to be both granddaughter and child of the Earth. Whether Alex and I would have been bothered by this if we had noticed it at the time, I cannot tell, but Greek mythology and the naming of planetary bodies is not perfectly plausible anyway. For example, Helios is another son of Theia, so a brother of Selene, which would not be very convincing in a planetary science context.

3.2 Primordial Noble Gases in Meteorites

3.2.1 The Quintessence Revealed by In Vacuo Etching

Once again, I take a leap back in time to my doctoral thesis and the years that followed. The 1970s were a wonderful time for noble gas geochemists, allowing us to explore the world of the many noble gas "components" trapped in meteorites that testify to the history of the early solar system and even presolar system processes. As early as 1964, Xe-HL was discovered by Reynolds and Turner as the first nucleosynthetic component in meteorites ever recognised (Fig. 3.23). A few years later, stepwise heating and physical separation techniques of bulk meteorites revealed a Ne component strongly enriched in ^{22}Ne compared to solar wind Ne and also compared to the major Ne component in bulk carbonaceous chondrites. This component was termed Ne-E at the time (Black and Pepin, 1969; Eberhardt, 1974). Such work provided clear evidence that presolar solids had survived in meteorites. In search of these, Roy Lewis and co-workers in Ed Anders' team at the University of Chicago realised that most of the primordial heavy gases Ar-Xe are concentrated in a minor phase that survived the dissolution of bulk meteorites by HF and HCl but lost its noble gases when attacked by oxidising acids such as HNO_3 (Lewis *et al.*, 1975). They named this component "Q" for "Quintessence" (Fig. 3.23) and the carrier Q was identified in 1981 as a carbonaceous phase by Uli Ott in Berkeley (Ott *et al.*, 1981). Xe-HL is a component substantially enriched in the heaviest ("H") as well the lightest ("L") isotopes and its carrier was identified as presolar nanodiamonds in Chicago in 1987 (Lewis *et al.*, 1987). The ^{22}Ne-rich gases eventually turned out to have more than one origin. In one of them, pure ^{22}Ne was brought to the solar system in presolar graphite grains as the decay product of extremely short lived ^{22}Na ($T_{1/2}$ = 2.6 a). In the other, presolar SiC grains carry a nucleosynthetic component with a ^{20}Ne/^{22}Ne ratio <0.1, *i.e.* about 100 times lower than atmospheric or solar wind Ne. The study of the multitude of primordial noble gas components in meteorites – of which there are many more than mentioned in this paragraph – is highly interesting for noble gas aficionados. But the field is also a nightmare for the uninitiated (and sometimes even for those of us who consider ourselves to be specialists). For comprehensive reviews on these issues I recommend Ott (2002; 2014), and Wieler *et al.* (2006). As Ott (2014) puts it succinctly: "The exact origin and the history for most of the trapped components … still present a puzzle". For example, it is unclear why in Xe-HL the lightest isotopes (^{124}Xe, ^{126}Xe), which are only produced by the p-process, and the heaviest isotopes (^{134}Xe, ^{136}Xe), which are only produced by the r-process, are so intimately mixed that a separation between the Xe-H and Xe-L branches has been at best only marginally achieved (Meshik *et al.*, 2001).

In the following, I will focus mainly on the Q component, on which we have concentrated much of our own work, in particular through CSSE. Component Q accounts for the vast majority of the primordial Ar, Kr, and Xe in primitive meteorites and for a minor but important fraction of their primordial He and

Ne. This does not, however, mean that the Q component is well understood, as we will see next. To quote Ott (2014) again: "[the puzzle] in particular holds for the Q component, ... although it is often thought to be derived from a gas of originally solar composition".

As noted at the beginning of Section 3, the exciting discoveries I mentioned in the previous paragraphs only marginally attracted my attention during my doctoral studies. As I recall, I did not take off my blinders until we started thinking about what else our unique CSSE line could be used for besides analysing noble gases from the solar wind. The answer seemed fairly obvious. The groundbreaking discovery of phase Q by Ed Anders' group in Chicago had relied on the difference between the gas concentrations in an "original" and an oxidised HF/HCl residue of a meteorite. Argon, Kr, and Xe concentrations of the oxidised (*e.g.*, HNO_3-treated) residues were much lower (and had a substantially different isotopic composition) than those of the original HF/HCl residues. In contrast, concentration differences for primordial He and Ne were much

smaller than those for Ar, Kr, and Xe, only 10 % or so. While the HF/HCl residues accounted for about one percent of the starting mass of the bulk meteorite sample, oxidation mostly resulted in very little further mass loss (but see also the paragraph after next). Therefore, component Q removed by oxidising acids was thought to represent very little mass with extremely high concentrations of mainly the heavy noble gases. Naturally, it was highly desirable to measure Q's noble gases directly, rather than deriving their concentrations and isotopic compositions by difference. This is perhaps less urgent for the heavy noble gases but is very important for He and Ne, whose concentrations and compositions in Q had to be calculated as the small difference between two almost equal numbers. We expected that we could characterise the Q component much better by oxidising HF/HCl residues *in vacuo* with HNO_3. If so, the CSSE line would not only allow stepwise analyses of noble gases implanted near grain surfaces, but would also be an excellent tool to selectively target phases of different susceptibilities to acid dissolution.
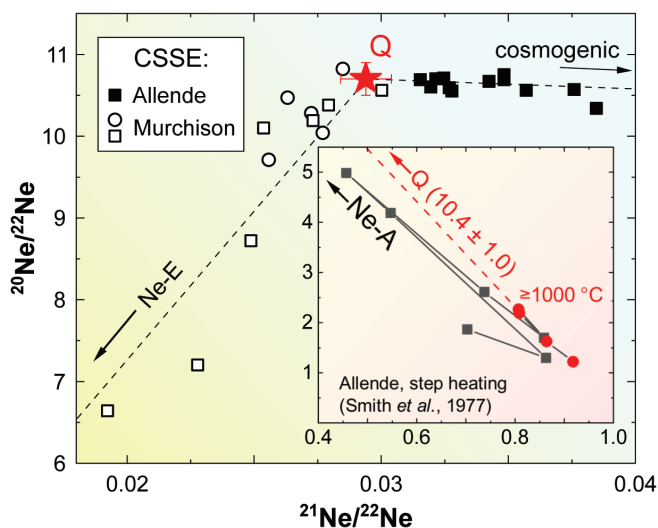
Figure 3.24 Ne three isotope diagram of CSSE data from HF/HCl residues of the meteorites Allende and Murchison (Wieler *et al.*, 1991; 1992). All etching steps (with oxidising HNO_3) of the Allende run released nearly pure Ne-Q plus minor amounts of GCR produced cosmogenic Ne. All steps of both Murchison runs also released Ne-Q but their final steps additionally released some Ne-E (almost pure ^{22}Ne). These data allowed a precise determination of the isotopic composition of Ne in phase Q (*e.g.*, $^{20}Ne/^{22}Ne = 10.7 \pm 0.2$; $^{21}Ne/^{22}Ne = 0.0294 \pm 0.010$). In contrast, stepwise heating data by Smith *et al.* (1977, inset) only showed a minor contribution of Ne-Q in the high temperature steps (1000–1200 °C, red dots), allowing for a less precise estimate for $(^{20}Ne/^{22}Ne)_Q$ of 10.4 ± 1.0.

I approached Ed Anders and he and Roy Lewis kindly provided us with HF/HCl-resistant residues from the two carbonaceous chondrites Allende and Murchison. We measured several aliquots of both meteorites in the two CSSE lines in use then, one made of HNO_3-resistant glass and the other a more sophisticated line whose acid exposed parts consisted of only gold and platinum (Section 2.5.1). We were immediately successful; the data were of better quality than we could ever have dreamed. We determined a precise value for the isotopic composition of Ne-Q and also He-Q (Wieler *et al.*, 1991). As shown in Figure 3.24, the CSSE data provided a much better separation of Ne-Q from other Ne components than had been obtained by stepwise heating at Caltech (Smith *et al.*, 1977). The CSSE data left no doubt that the Q component contains not only the three heavy noble gases but also some He and Ne. This had been disputed by Sabu and Manuel (1980), who used this putative absence as an argument in favour of their hypothesis that the solar system formed from the debris of a single supernova. Despite my confidence in the quality of our work, I was a little nervous when I first presented the Allende data at the 1989 LPSC. So all the more I was proud of the compliment by Jerry Wasserburg after my presentation, as described in Section 2.3. The next paper on Murchison (Wieler *et al.*, 1992) largely confirmed the Allende data but also showed that etching of HF/HCl residues by HNO_3 also released some Ne-E from presolar graphite and silicon carbide. This showed that the operational definition of phase Q (resistant to HF/HCl but not to HNO_3) is incomplete, although it remains of practical use. Murchison also provided a precise, directly measured isotopic composition of the Q-Xe component, which is slightly different from AVCC-Xe (AVerage Carbonaceous Chondrite), widely used at the time as representing primordial Xe in primitive meteorites. In fact, AVCC-Xe is not a pure component *sensu stricto*, but a mixture which in addition to Xe-Q also contains Xe-HL plus two additional minor components characterised first by Gary Huss and Roy Lewis (Huss and Lewis, 1994).

Henner Busemann's doctoral thesis work was the next major contribution of our group to noble gases in the Q component. Henner found his way to Zürich thanks to a flyer I had asked Rolf Michel in Hannover – his diploma thesis supervisor – to post on the bulletin board of his institute. After several postdoctoral and research scientist positions, first in the capital cities of Bern and Washington DC, then in Milton Keynes (narrowly missing the British capital) and Manchester, he found his way back to ETH in 2014, where he now leads the noble gas laboratory in its third generation. During all these years, we continued to work together, as we will see below.

In his dissertation, Henner studied HF/HCl-resistant residues of four carbonaceous and two unequilibrated ordinary chondrites using CSSE with nitric acid (Busemann *et al.*, 2000). Individual runs comprised up to 30 steps with *in vacuo* etch durations between a few hours and up to almost two weeks *per* step (Fig. 3.26)! With this huge data set, Henner presented a uniquely detailed characterisation of noble gases in Q. Among other findings, he noted a quite variable Ne isotopic composition of Q gases ($^{20}Ne/^{22}Ne$ varying between ~10.1–10.6; Allende and Murchison are thus at the upper end of this range, see Fig. 3.24).

In Mainz, Schelhaas *et al.* (1990) also had observed a relatively low $(^{20}Ne/^{22}Ne)_Q$ value based on stepwise combustion (heating in the presence of oxygen) of a HF/HCl residue from an unequilibrated ordinary chondrite. Henner further provided evidence that phase Q actually consists of two subphases Q1 and Q2 with affinities to different presolar carrier phases and he showed that variable elemental abundances of Q gases reflect both losses from an originally incorporated carrier by thermal metamorphism and aqueous alteration processes.

Figure 3.25   The first and last doctoral students, respectively, whom I had the pleasure to guide as responsible supervisor. Henner Busemann (left) is shown at his doctoral disseration celebration in 1998. Henner is a big fan of his hometown football club Hannover 96 but apparently that day he was supposed to put on a shirt of one of the Zürich teams. Henner co-supervised My Riebe (right), who is shown after her talk at the symposium celebrating my retirement in 2014. Picture (b) courtesy of Henner Busemann.

Many workers have studied phase Q – both the carrier and its associated noble gases – and many continue to do so. Although there has undoubtedly been much progress since the 1970s, almost 40 years after Lewis *et al.*'s discovery in 1975 most publications on the subject still refer to Q as "enigmatic" or include statements such as "the precise characterisation of phase Q has eluded decades of investigation". Unlike for presolar SiC, graphite, or nanodiamonds, there are no electron microscope images that unambiguously show phase Q. Lewis *et al.* (1975) had chosen the name "Quintessence", because they realised that a marginal loss of mass, together with an almost complete loss of Ar-Kr-Xe

upon oxidation of HF/HCl residues, imply an extremely gas-rich carrier which they could not further characterise at that time. Actually, the Chicago group had borrowed the Quintessence term from Papanastassiou and Wasserburg (1971) who used it to denote a minor glassy phase in an Apollo 12 rock highly enriched in trace elements such as K, Rb, and U, related to KREEP rocks later found at the Apollo 15 site (Hubbard *et al.*, 1971). "Quinta essentia" is latinised for the fifth element postulated by Aristoteles alongside the four traditional elements. He assumed that what he called "ether" was immutable and timeless, unlike the classic four elements which can transform into each other. While "Quintessence" seems to have fallen out of use in lunar science, the term – or at least the acronym Q – persists in noble gas cosmochemistry, although whether or to what extent the Q noble gases were derived from other noble gas components remains an open question. Today, it is widely accepted that phase Q in chondrites is carbonaceous (*e.g.*, Ott *et al.*, 1981), although sulfides have also been proposed as a second carrier (Marrocchi *et al.*, 2015). The most comprehensive recent characterisation of phase Q has been performed by Sachiko Amari at Washington University in St. Louis, Jun-ichi Matsuda at Osaka University, and colleagues. They studied in great detail the L4 chondrite Saratov, which is particularly well suited for this work because it contains Q noble gases but hardly any primordial gases from presolar SiC and nanodiamonds (*e.g.*, Amari *et al.*, 2013; Matsuda *et al.*, 2016). They reiterated that Q is likely only a minor part of the porous carbon of Saratov, a conclusion already made by Schelhaas *et al.* (1990) in Mainz. Amari, Matsuda, and colleagues note that Q apparently does not differ in structure and chemistry from the 99 % of other porous carbon phases. Q gases may be released simply by a restructuring, rather than by dissolution of the carbon during oxidation. This would imply that the (usually very minor) mass loss upon oxidation is not a measure of the mass of Q, as already suggested by Ott *et al.* (1981) and Busemann *et al.* (2000). Moreover, noble gases with isotopic compositions similar or identical to Q gases in carbonaceous and ordinary chondrites are also ubiquitous in carbon-rich phases in achondrites (ureilites, acapulcoites-lodranites) and even in carbon nodules in iron meteorites (Wieler *et al.*, 2006). Whether the Q gases in these meteorite types are transported in a carrier phase identical or similar to that in chondrites is unknown but doubtful.

The origin of Q gases is as enigmatic as their carrier. A first order observation is that they are highly fractionated in their elemental and isotopic compositions relative to solar noble gases, favouring the heavier elements and isotopes. Thus, there is most likely a connection between the noble gases in the Sun and the Q gases in meteorites. But where and by what process did the fractionation occur? In a presolar environment or later in the solar system? Wieler *et al.* (2006) review some of the many proposed environments and mechanisms. A presolar origin may more easily explain than a "local" solar system origin the fact that Q gases are so ubiquitous in all primitive and some differentiated meteorite classes. Also the apparent close association of Q gases with presolar dust seems to favour a presolar origin (Huss and Alexander, 1987). An example of a local origin was proposed by Bob Pepin (Pepin, 1991). He explored how the blow off of
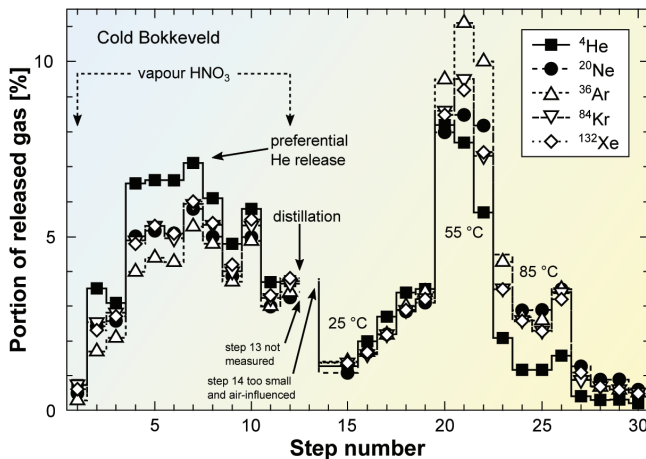
Noble gas release patterns of the CSSE etch run by HNO_3 of a HF/HCl residue of the carbonaceous chondrite Cold Bokkeveld (Busemann *et al.*, 2000). The fraction of gas released *per* step is indicated on the ordinate. The entire run took about 120 days, with individual steps lasting mostly between 2 and 8 days. During the first 12 steps, the sample was exposed to HNO_3 vapour. Prior to step 13, liquid acid was distilled onto the sample. From step 19 onward, acid temperature was gradually increased from room temperature to 85 °C. Figure from Busemann *et al.* (2000) with permission from Wiley.

transient atmospheres of early planetesimals may have fractionated an original solar type noble gas inventory toward Q composition. Also Ozima *et al.* (1998) suggested that Q gases may have formed in the solar nebula, as a result of some sort of Rayleigh distillation. Numerous laboratory experiments have attempted to simulate gas trapping by phase Q. Based on experiments in which material was deposited on fresh surfaces in the presence of noble gases, Hohenberg *et al.* (2002) suggested that such "active capture" of noble gases transiently adsorbed on the fresh surfaces might play a role in the trapping process of Q gases. In a series of experiments, Maïa Kuga, Yves Marrocchi, and co-workers at CRPG in Nancy simulated the trapping of noble gases on organic substances in a plasma (*e.g.*, Kuga *et al.*, 2017). The elemental and isotopic fractionation patterns of the trapped gases were consistent with those expected if the Q component is mass fractionated solar gas. However, Kuga and co-workers also note that trapping efficiency of Xe in laboratory experiments is orders of magnitude lower than would be necessary to trap Xe-Q in a canonical solar nebula environment. Jamie Gilmour at the University of Manchester (Gilmour, 2010) explains Q-Xe as mass fractionated solar Xe to which traces of components known to be present in presolar grains were added. It should be noted, however, that the (unknown)

isotopic composition of solar Xe might be significantly different from the known composition of Xe in the solar wind (Ott, 2014), such that Q-Xe might actually not be as different from Xe in the Sun as is usually assumed.

3.2.2 Etching Bulk Meteorites – and an Ar-Ar Study by In Vacuo Etching

Since Lewis *et al.* (1975) discovered that primordial noble gases in meteorites overwhelmingly reside in HF/HCl-resistant residues that represent only a very small fraction of a meteorite's total mass, primordial noble gas research had largely focused on such residues. This trend intensified when *bona-fide* presolar phases such as nanodiamonds, SiC, and graphite were separated from these residues (Lewis *et al.*, 1987; Tang *et al.*, 1988; Amari *et al.*, 1990). We also had used the CSSE technique to study meteoritic HF-HCl residues. However, the well known fact that the primordial noble gas budget is dominated by the acid resistant carriers did not preclude the existence of acid soluble presolar carriers that may yield important information about stellar nucleosynthesis or the history of meteorites and their parent bodies. This became evident when presolar silicates were found by ion imaging of bulk meteorite samples with a NanoSIMS instrument that allowed spatial resolution on a sub-micrometre scale (Nguyen and Zinner, 2004). A comprehensive characterisation of the primordial (and radiogenic) noble gas inventory of meteorites would need to include HF/HCl soluble phases.

Such a study using bulk meteorites would face the difficulty of clearly discerning primordial noble gases against a potentially overwhelming background of cosmogenic gases released from "normal" (primordial noble gas-free) silicates and oxides. We believed that the closed system stepwise etching technique should also be promising in this respect and probably superior to stepwise pyrolysis and combustion. Henner Busemann and colleagues had made pioneering CSSE studies on bulk enstatite chondrites (Busemann *et al.*, 2003; King *et al.*, 2013), so we decided to study next a bulk sample of Ivuna, one of the only five known CI chondrites (Riebe *et al.*, 2017a). My Riebe was the last doctoral student I had the pleasure to supervise, together with Henner. My had written her Master's thesis in Lund with Birger Schmitz on the possibility of detecting cosmic ray tracks in extraterrestrial chromite grains from terrestrial sediments (Section 3.1.9) and I first met her when Birger invited me for a research stay in Lund. After postdoctoral work at the Carnegie Institution of Washington DC, My is now back at ETH supervising her own first doctoral student.

A few percent of both primordial Ne and Xe were indeed released from HF soluble portions of Ivuna. Both this Ne and Xe have isotopic and elemental ratios that are readily explained as a mixture of the two most abundant primordial noble gas components in Ivuna bulk samples: HL and Q. Four percent of the Xe-Q may be derived from an HF soluble subfraction of phase Q, which again suggests that the operational definition of Q as a phase resistant to HF but attacked by strong oxidising acids is not entirely correct. On the other hand,

3 % of Ne-HL (the primordial Ne component whose bulk fraction is released in parallel with Xe-HL) may actually have resided in a different phase than the presolar nanodiamonds thought to be the carrier of Xe-HL. In another study, My Riebe investigated the effects of aqueous alteration on primordial noble gas carriers (Riebe *et al.*, 2020). She did this by combining CSSE and stepwise pyrolysis analyses on bulk samples of the Tagish Lake carbonaceous chondrite that had undergone varying degrees of aqueous alteration.

My Riebe's work demonstrated the potential of *in vacuo* etching to study primordial noble gases in bulk meteorites. Her work has been continued and extended by Daniela Krietsch in her doctoral thesis in Henner Busemann's group (Krietsch, 2020; Krietsch *et al.*, 2019). Daniela characterised the full noble gas inventory of a very primitive CR chondrite found in Antarctica using CSSE with five different etchants, starting with water, followed by acetic acid, HNO_3, HF, and HCl. Surprisingly, about one quarter to one third of the primordial He and Ne, the latter with a Ne-Q-like isotopic composition, were released in the first (water) step. Almost no Ar was released in this step, but acetic acid dissolved an Ar-rich carrier known to exist and to be lost by moderate parent-body aqueous alteration.

One further example of extending the reach of CSSE is the ^{39}Ar-^{40}Ar dating study initiated by Igor Villa at the University of Bern, which was inspired by discussions at one of the meetings at Ringberg Castle in Bavaria (see Box 3.1). I mention this example here, even though this work was done on a terrestrial sample, as it includes the first Ar-Ar analysis by CSSE ever done. Igor suggested that I participate in a consortium study aimed at investigating the mechanisms and pathways by which Ar diffuses through the McClure Mountains (MMhb) hornblende, a well known standard in ^{39}Ar-^{40}Ar dating (Villa *et al.*, 1996). Igor performed classical Ar-Ar analyses by stepwise heating on untreated and heated (~850 °C at 2 kbar) MMhb splits, Simon Kelley at the Open University in Milton Keyes performed IR laser traverses and UV laser depth profiling on single grains, and I analysed samples using CSSE with HF. There were minor but important differences in the Ar-Ar age spectra of the stepwise heating and CSSE runs. For example, the CSSE spectrum of the untreated sample provided evidence of a minor phase of low Ca/K in the first 5 % of Ar released that was not seen in stepwise heating. Gas release by acid attack at room temperature therefore provides information that may be blurred when gas is released by diffusion in the laboratory. Although promising in principle, Ar-Ar dating by CSSE has not become routine, mainly because it is too time consuming.

A similar caveat needs to be made for CSSE analyses in general. Almost every single *in vacuo* etch run represents a very major experimental effort, in most cases lasting between a few weeks up to several months, in any case much longer than typical stepwise pyrolysis runs (*e.g.*, Fig. 3.26). The technique thus is not expected to ever be used for routine analyses but must be limited to selected tasks.

3.2.3 Primordial Noble Gas Studies with High Spatial Resolution

The CSSE technique has been very efficient in distinguishing carriers of primordial noble gases with different chemical properties, especially with different susceptibilities to acid dissolution. The technique is not well suited, however, to study the location of primordial noble gases with high spatial resolution. This can instead be achieved by *in situ* extraction of noble gases from petrographically well characterised phases by laser heating, pioneered by Tomoki Nakamura and colleagues in Fukuoka, Japan (*e.g.*, Nakamura *et al.*, 1999; Okazaki *et al.*, 2001). Alternatively, small samples with a well characterised petrographic context and mineralogy can be mechanically extracted, with subsequent noble gas release by laser heating. This second approach was used by Nadia Vogel for her doctoral dissertation in my group (Vogel *et al.*, 2003; 2004a;b). We have already met Nadia in Section 2.5.5 on Genesis and will hear more about her in Section 5.2.2. which is devoted to our investigations of speleothems as palaeoclimate archives.
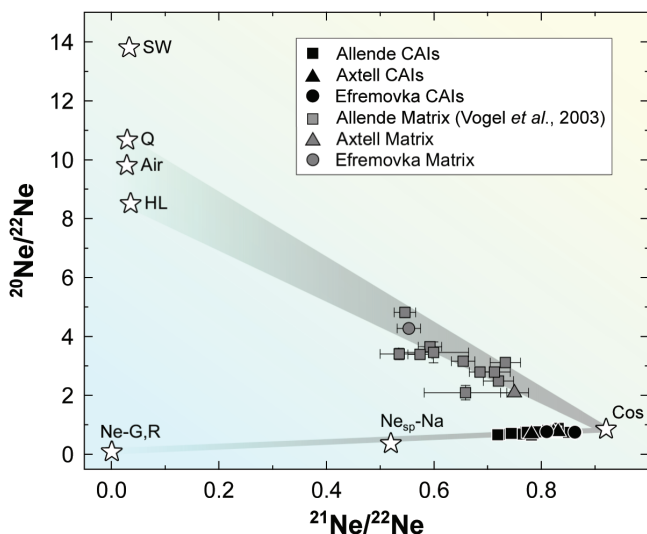
Figure 3.27   Ne data from CAIs and matrix samples of three carbonaceous chondrites (Vogel *et al.*, 2004a). All CAI data points (black symbols) fall on a mixing line between cosmogenic Ne typical for bulk chondrites and cosmogenic Ne expected for pure Na (or perhaps primordial near-poor ^{22}Ne, labelled Ne-G,R). Only matrix samples (grey dots) contain mixtures of cosmogenic and primordial trapped Ne (with compositions roughly between HL and Q). This work strongly suggests that earlier studies reporting occasional small amounts of trapped Ne in CAIs suffered from contamination of CAI samples with trace amounts of matrix material. Figure from Vogel *et al.* (2004b) with permission from Wiley.

One major goal of Nadia's dissertation was to study accretion and alteration histories of meteorite parent bodies based on the microdistribution of primordial noble gases in unequilibrated chondrites. All her studies benefitted significantly from the petrographic expertise of Addi Bischoff at the University of Münster. In her first paper, Nadia showed that in many meteorites noble gas concentrations were higher in fine grained rims around chondrules than in adjacent matrix portions of a meteorite (Vogel *et al.*, 2003). She concluded that this indicates accretion of nebular dust onto chondrules from regions whose noble gas concentrations decreased with time, which is incompatible with the formation of chondrule rims by aqueous alteration on a parent body as proposed by others. Her data imply a heterogeneous dust reservoir in terms of noble gas inventories in the accretion regions of meteorite parent bodies. In her next two publications, Nadia studied noble gases in CAIs and chondrules (Vogel *et al.*, 2004a;b). These high temperature components were known to be poor in, or even devoid of, primordial noble gases, but some workers had reported that in some cases chondrules and even CAIs appeared to have retained at least traces of noble gases carried to the solar nebula by presolar grains. If this were the case, it would have implications for CAI formation and early solar system evolution. Carefully avoiding potential cross contamination with matrix material, Nadia measured He, Ne, and Ar in her CAI study, with the Ne data being particularly revealing. She did not detect even traces of primordial Ne; all her data could be readily explained by cosmogenic Ne derived mainly from minerals rich in Na, Ca, and Cl (Fig. 3.27). In contrast to CAIs, some of the chondrules from the carbonaceous and LL chondrites she studied contain small amounts of primordial Ne and Ar, although the primordial Ar concentrations are much lower than the values reported by Okazaki *et al.* (2001) for chondrules in the enstatite chondrite Yamato 791790. Nadia concluded that – in contrast to CAIs – heating of chondrules and their precursor materials was not strong enough to quantitatively expel primordial noble gases. The very different primordial Ar concentrations between Nadia's chondrules on the one hand, and those in Yamato 791790 on the other, rule out for the former a scenario proposed by Okazaki and co-workers for the latter, which is that solar gases were implanted into the chondrule precursor material and later incompletely lost by diffusion. If the E chondrite data are confirmed by other meteorites, this could mean that different chondrule populations might have formed in fundamentally different environments or by different mechanisms.

3.3 Science Apart from Research Grant Applications

In a good team, ideas for promising research projects sometimes emerge that do not readily fit into the overall picture laid out in a research grant application. In some cases, such ideas may lead to stand alone projects, and in others to larger collaborations. In this section, I present some examples where such ideas led to what I think became interesting science.

3.3.1 May Half-Lives of Radioactive Nuclides Depend on Heliocentric Distance?

One day Matthias Meier approached me with some papers in which the authors claimed that the nuclear decay constants (λ) of several isotopes show an annual periodicity, being slightly higher in northern winter than in summer (*e.g.*, Jenkins *et al.*, 2012). For ^{36}Cl the reported variability of λ_{36} is of the order of ±1 %. Since the Earth is nearly 3.5 % closer to the Sun in early January than in early July, these authors and others proposed that the Sun influences nuclear decay rates in an unspecified way. They ruled out all other possible effects as cause for the observed variability in count rates, including environmental factors such as temperature or humidity. After further reading, we realised that there are two camps on this subject that are fiercely opposed to each other. One camp argues that there is increasing evidence for variable decay rates, while the other camp seriously doubts the quality of the experiments conducted by the former. Our gut feeling clearly leaned towards the latter view, but Matthias and I still discussed with an open mind what variable decay "constants" would mean for meteorite research. If decay rates already vary at the percent level for heliocentric distance variations covered by the Earth's orbit, the difference to the main asteroid belt could be dramatic. If so, cosmic ray exposure ages of meteorites based on radionuclide concentrations might be substantially off. Even more dramatically, radiometric ages of meteorites, *e.g.*, those determined by U-Pb dating, would be substantially in error if the decay constants determined on Earth do not apply for the asteroid belt. Hence, the isotope record in meteorites should provide a highly relevant test for the claim that nuclear decay rates depend on the distance from the Sun.

Matthias and I evaluated a large part of the relevant database on meteoritic, lunar and terrestrial samples, which includes both cosmogenic and radiogenic isotope systems (Meier and Wieler, 2014). The bottom line result of our study was – not at all to our surprise – that geo- and cosmochronological data provide no evidence for heliocentrically variable decay constants, whether for nuclides undergoing alpha-decay, beta-decay, or decay by electron capture. No explicit possible physical explanation for the radial dependency has been offered by the "variable decay" camp, but they compare the alleged variations of λ_{36} between Earth's perihelion and aphelion with a 1/R or $1/R^2$ dependence on heliocentric distance R. However, this would lead to larger semi-annual variations of decay rates than reported. Therefore to be compatible with reported data, Matthias and I assumed a proportionality of λ with $1/R^x$, x falling between 0.06 – 0.3. If such a dependence extended to the asteroid belt, the production rates and hence the saturation activities of cosmogenic ^{36}Cl would vary much more than is observed for meteorites with different orbital histories. Of particular interest is a comparison between absolute radiometric ages of meteorites of different classes based on the decay of uranium to lead and relative ages using (now extinct) short lived nuclides such as ^{182}Hf, ^{53}Mn, or ^{26}Al (Nyquist *et al.*, 2009). We concluded that these ages agree so well with each other that the parent bodies of angrites, CV and H chondrites would have had nearly identical orbits throughout solar system history. Moreover, solar physicists are able to derive an

age of the Sun from helioseismology combined with solar modelling. This age of 4.60 Ga (Houdek and Gough, 2011) is independent of meteorite ages based on radioactive nuclides and agrees with the U-Pb ages of the oldest meteorite samples to within its 1 % uncertainty. Last but not least, the U-Pb ages of Earth and meteorites agree much better than would be expected if uranium isotopes decayed much more slowly in meteorite parent bodies. We therefore concluded that none of the nuclides we had considered (including ^{36}Cl, which was extensively studied by Jenkins *et al.*, 2012) provide any hint for an influence of the Sun on their decay rates. We also noted in parentheses that our argument would not be relevant if the alleged seasonal variability were in fact not due to the variable Earth-Sun distance but, however unlikely this may seem, to the motion of the Earth with respect to the interstellar medium.

Matthias and I had a lot of fun when working on this paper, but once it was published we were a little worried whether we had now simply asserted something that no one in our own community would ever have doubted anyway. However, it turned out that our work was favourably received by one of the two camps among the nuclear particle physicists, those, of course, who strongly criticise the experimental expertise of the others with words like "poor metrology and incomplete uncertainty analysis" (Pommé and Pelczar, 2020).

3.3.2   Hypatia, a Sample from a Comet?

In 2013 I was asked to review a manuscript by Jan Kramers of the University of Johannesburg and his co-workers. They had examined a small piece of a very unusual rock of about 30 g found in the strewnfield of the enigmatic Libyan desert glass. The rock consists of almost pure carbon, is black, shiny and extremely hard. In the manuscript it was dubbed Hypatia, honouring the 4th century philosopher, mathematician, and astronomer who was the first woman to teach Platon's philosophy in Alexandria, which led to her execution by a Christian mob (Fig. 3. 28). Kramers and co-workers proposed that the Hypatia stone is a remnant of a comet nucleus that fell in Egypt, possibly the same impact that produced the Libyan desert glass. One argument for this provocative proposal was based on noble gas data. On the one hand, ^{40}Ar/^{36}Ar ratios as low as 40 (considerably below the terrestrial atmospheric value of ~300) proved that Hypatia is extraterrestrial. On the other hand, Kramers and co-workers argued that the Xe isotopic composition is consistent, albeit within large uncertainties, with a contribution from the exotic component Xe-G but not the more common Q component. In my opinion, the hypothesis put forward by Jan Kramers and his colleagues was highly interesting, although far from stringent. Therefore, I recommended accepting the manuscript, which was published in the journal *Earth and Planetary Science Letters* as Kramers *et al.* (2013). The rationale for my recommendation was that I felt that provocative or speculative ideas deserve to be published as long as they have a fundamentally sound basis that includes interesting experimental data. I point this out because some of my colleagues did not share my opinion and let me know.

Figure 3.28 **(a)** Part of the Hypatia rocklet studied by Kramers *et al.* (2013) and Avice *et al.* (2015). **(b)** A mural by Street artist MP5 honouring Hypatia of Alexandria in the Via Ipazia d'Alessandria in Naples. The Hypatia sample is clearly extraterrestrial but is not listed in the Meteoritical Society's meteorite database, because no additional sample is available for study. Picture courtesy of MP5.

Hypatia is not the only sample found on Earth proposed to derive from a comet. Matthieu Gounelle at the Muséum National d'Histoire Naturelle in Paris and colleagues, for example, suggested that the famous Orgueil meteorite derives from a body with cometary affinity (Gounelle and Zolensky, 2014) and Sara Russell and colleagues from the Natural History Museum in London suggested that comets are a likely source of much of the petrologic type 1 meteoritic material (Russell *et al.*, 2022). In any case, if a cometary connection of Hypatia could be confirmed, this would be of utmost importance. I therefore proposed to Jan Kramers that we repeat the noble gas (and nitrogen) measurements by more sophisticated analytical methods than those that had been available for the first study. In collaboration with Jan, this was done by a small consortium at CRPG in Nancy, the Institut de Physique du Globe Paris, and ETH Zürich. In addition, Falko Langenhorst in Jena characterised the sample by transmission electron microscopy. Guillaume Avice in Nancy was the principal investigator of the resulting paper (Avice *et al.*, 2015).

One of my tasks was to ask the Nomenclature Committee of the Meteoritical Society to formally approve Hypatia as a meteorite, as this is mandatory for publication in many journals, such as *Geochimica et Cosmochimica Acta* or *Meteoritics and Planetary Science.* However, this did not prove to be as straightforward as I had expected, despite the fact that Kramers *et al.* (2013) had provided clear evidence that Hypatia is extraterrestrial. The problem was that only about one gram of the original 30 g stone is still available, as the rest had somehow disappeared. This meant that we could not name an approved institution that would curate a type specimen. Therefore, according to the Meteoritical Society, Hypatia (or whatever name would have been accepted) cannot be called a

meteorite. Our solution was to publish the follow up study again in *Earth and Planetary Science Letters* (Avice *et al.*, 2015), which in 2015 had not yet enforced the rule of the Meteoritical Society (they do now). While we did not feel we had done anything illegal we were puzzled by the Nomenclature Committee's decision. It did seem to be a technicality though, and it is clear that the type specimen rule in general is crucial at a time when commercial interests in meteorites increasingly threaten scientific activity. It also helps ensure the overall integrity of the field by discouraging fraud.

Our data turned out to be broadly consistent with concentrations and isotopic compositions of noble gases and nitrogen in various types of carbon-rich meteoritic materials, including graphite nodules in iron meteorites. Hypatia may be different from all of these, but obviously sampled a similar cosmochemical reservoir. We did not confirm the presence of exotic noble gases (*e.g.*, Xe-G) but clearly detected noble gases with isotopic compositions close to the Q gases ubiquitous in meteorites (Section 3.2.1). We therefore did not confirm that Hypatia is a remnant of a comet nucleus. A relation between Hypatia and the Libyan Desert Glass is not warranted.

3.3.3 Quasicrystals in Khatyrka, Where and When Did they Form?

In 2012, Matthias Meier showed me a recently published paper entitled "Evidence for the extraterrestrial origin of a natural quasicrystal" by Luca Bindi of the University of Florence and co-authors (Bindi *et al.*, 2012). Thanks to Walter Steurer's inaugural lecture as Professor of Crystallography at ETH, which I had attended many years earlier, I had a vague idea of what quasicrystals are, although all I really remembered was that they had become an exotic but fascinating topic in modern crystallography. This was enough, however, to catch my attention as well, and in the following paragraph I attempt a rudimentary explanation of what quasicrystals are. Luca Bindi's paper presented evidence, mainly based on oxygen isotopes, that a mineral grain in which Bindi *et al.* (2009) previously had observed tiny quasicrystals is a small fragment of a meteorite. Matthias imagined that noble gas analyses of part of this grain might provide further clues as to the origin of quasicrystals formed in nature. He suggested that our Tom Dooley mass spectrometer would be an excellent argument to convince Bindi and co-workers to provide us with a tiny portion of what surely was an extremely precious sample. So our first idea was that such exotic matter in meteorites might also contain exotic noble gases, perhaps as interesting as, or even more so than, noble gases in known presolar grains like nanodiamonds or silicon carbide. A closer reading of Bindi *et al.* (2012) dampened our enthusiasm somewhat, as it seemed impossible to obtain enough quasicrystal material for a noble gas analysis. Nevertheless, Matthias got in touch with Luca, which was the beginning of our – small but nevertheless quite important – involvement in a truly fascinating story. The full story was presented by Paul Steinhardt in a book (Steinhardt, 2019) that makes as thrilling reading as any good detective story and which I will try to summarise in the following few paragraphs.

Paul Steinhardt of Princeton University is a foremost expert in two seemingly disparate scientific fields, cosmology and crystallography. As theoretical cosmologist he studies the origin and fate of our universe (*e.g.*, Steinhardt and Turok, 2003). In crystallography, he was the first to propose the existence of a new form of matter with a quasiperiodic arrangements of atoms. In the 1980s, Paul began to think about the fact that properties of matter can be dramatically changed simply by reordering the atoms. Perhaps the best example is graphite and diamond. Both are made of carbon atoms only, but graphite is soft enough to be used in pencils, while diamond is among the hardest of all known materials. Ultimately, this led Paul to the idea of quasi-periodic crystals or simply quasicrystals. Simply put, you can cover a floor with regular hexagons without leaving empty space, but you cannot do this with pentagons, at least not in a periodic pattern. But Steinhardt and his student Dov Levine found a way to arrange pentagons in a nearly or quasiperiodic fashion without gaps, inspired by tilings in islamic art. They also demonstrated that the three dimensional equivalent, a quasiperiodic arrangement of atoms with five fold (icosahedral) symmetry, is possible and predicted that this should lead to an X-ray diffraction pattern as shown in Figure 3.29a (Levine and Steinhardt, 1984). Soon after, their hypothesis was verified when Dan Shechtman discovered the first compound with the predicted diffraction pattern in an artificially prepared Al-Mn alloy (Shechtman *et al.*, 1984; Fig. 3.29b), a discovery that earned Shechtman the Nobel Prize for chemistry in 2011. Thereafter many different types of quasicrystals were found, but all were produced under well defined laboratory conditions, usually by quenching metal alloys that often contain Al and Cu.

So, while quasicrystals soon became of interest to application oriented material scientists, Steinhardt's next burning question was: "can quasicrystals also form in nature, and if so, how"? The answer to the first part of the question seemed to come from Luca Bindi in Florence. Luca was meticulously searching for diffraction patterns with five fold symmetry in his museum's mineral collection. His Eureka moment came with a rather poorly documented sample a few millimetres in size, apparently collected in 1979 in far eastern Russia (Bindi *et al.*, 2009). Luca discovered a quasicrystal phase with five fold symmetry in this tiny sample, now known as icosahedrite (Fig. 3.29c). A first problem, however, was that most of the sample had been consumed during sample preparation. A second problem was that the sample consisted largely of alloys containing Al and Cu, and all experts consulted insisted that metallic Al does not occur in nature. However, Steinhardt and Bindi did not give up. In 2010, it turned out that the Florence sample was a tiny piece of a meteorite, likely of the type CV3 chondrite such as Allende. This became obvious when the oxygen isotopic composition of silicates was analysed at Caltech in Pasadena by John Eiler and Yunbin Guan (Bindi *et al.*, 2012). Hence, it seemed that Bindi and his co-workers had shown that nature could produce quasicrystals, at least in space. However, to be sure, a watertight proof was required that the quasicrystal-containing Al-Cu alloys were also part of the meteorite, notwithstanding the "impossibility" of the

existence of metallic Al in nature. But how was such a proof to be provided, given that almost no material was available for further investigations?
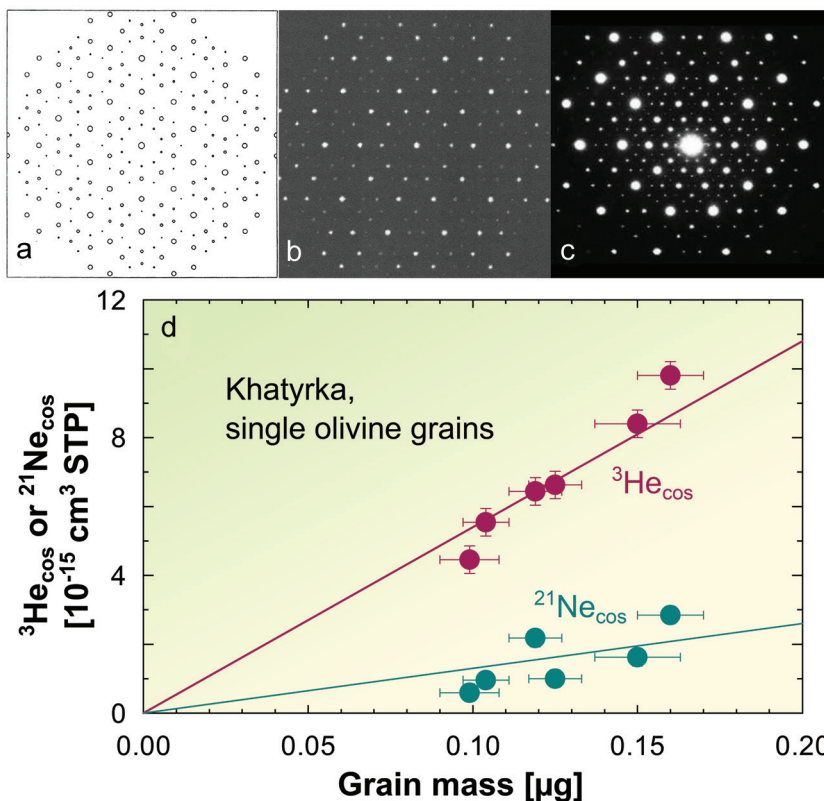

Figure 3.29 **(a)** Theoretical X-ray diffraction pattern of five fold symmetry predicted by Levine and Steinhardt (1984) for a crystal with a quasiperiodic arrangement of atoms. Figure from Levine and Steinhardt (1984). **(b)** X-ray diffraction pattern observed by Shechtman (1984) for an Al-Mn alloy. The two patterns are essentially identical, proving that quasicrystals exist, at least in artificial substances. **(c)** Diffraction pattern of five fold symmetry discovered by Bindi *et al.* (2009) in the "Florence sample" of the Khatyrka meteorite, demonstrating that quasicrystals also exist in nature. Pictures courtesy of P. Steinhardt. **(d)** The amounts of cosmogenic ^{3}He and ^{21}Ne in olivine grains of Khatyrka as a function of their mass provide independent evidence that Khatyrka is a meteorite, with an exposure age of 2-4 Ma. Figure adapted from Meier *et al.* (2018).

Detective work revealed that the Florence sample came from the Chukotka region in the far east of arctic Russia. Steinhardt was able to contact Valery Kryachko, the man who had found the sample back in 1979. Northeast Siberia

was certainly not the easiest place on Earth to search for additional meteoritic material more than 30 years later, but Steinhardt managed to set up an expedition of 13 people and a cat. The story of this expedition alone makes Paul's book exciting reading. Against all odds they found a few more grains of Khatyrka, as the meteorite was named. The new grains also contained Al-Cu alloys intimately intergrown with silicates, and indeed the quasi-crystalline phase icosahedrite was also found embedded in the Cu-Al alloys. Glenn MacPherson of the Smithsonian Institution in Washington had been among the most outspoken critics of the idea that the Al-Cu alloys in the Florence sample could be natural, but Steinhardt had nevertheless convinced him to join the expedition. In a detailed study of some new grains from the 2011 expedition, MacPherson *et al.* (2013) concluded that the Cu-Al alloys undoubtedly are natural and extraterrestrial. Khatyrka is described as a complex CV3 (ox) breccia. It appears that many in the meteorite community – including earlier critical voices – have by now largely accepted the natural origin of the Cu-Al alloys, and hence the fact that nature is capable of forming quasicrystals, although some remain sceptical. Alan Rubin and Chi Ma, for example, note that "At present, the origin of the weird assemblages in Khatyrka remains controversial, and Sherlock Holmes is unavailable" (Rubin and Ma, 2021, chapter 13). A leading hypothesis is that the quasicrystals in Khatyrka were formed under ultrahigh pressure, caused by impacts. Further evidence for this was found when Bindi *et al.* (2021) found a new type of quasicrystal in trinitite, the material formed by the first plutonium bomb test in New Mexico in 1945 (Bindi *et al.*, 2021).

What is our contribution to this story? After Matthias Meier and I had abandoned our original naive hope to possibly detect "superexotic" noble gases in the quasicrystals, we suggested to Luca and Paul that we study noble gases in silicates from Khatyrka. Luca sent us six olivine grains, likely fragments from a Khatyrka chondrule. We organised a small consortium that included Philipp Heck in Chicago (chemical composition and volume of grains) and Nicole Spring in Manchester (transferring the tiny and precious grains between different sample holders with her advanced micro-manipulation skills). Matthias measured He and Ne isotopes in Zürich with Tom Dooley (Meier *et al.*, 2018). All grains contained cosmogenic ^{3}He and ^{21}Ne in amounts well above what could reasonably have been produced near the Earth's surface (see Section 4.2). This provided independent evidence that Khatyrka is indeed a meteorite. Its cosmic ray exposure age is likely between 2 and 4 Ma (Fig. 3.29d). As we saw in Section 3.1, this is rather low for a meteorite, but falls within the range observed for a few other CV chondrites. However, the radiogenic ^{4}He concentration from the decay of uranium and thorium yields a U-Th-^{4}He gas retention age of only around 600 Ma, shorter than that of any other known CV chondrite. This implies that the Khatyrka parent body experienced a strong shock relatively late in its history, possibly the event that produced the second generation of quasicrystals in Khatyrka identified by Lin *et al.* (2017). Somewhat unfortunately, Khatyrka's unique combination of low exposure age and low ^{4}He retention age means that no other known CV chondrite lends itself to a detailed follow up search of native

Al-Cu alloys or even quasicrystals. For the time being, the few available grains of Khatyrka remain our only known source of extraterrestrial quasicrystals, with the possible exception of a micrometeorite from Antarctica hosting an exotic Al-Cu-Fe assemblage (Suttle *et al.*, 2019). On the other hand, Matthias has identified a possible parent body for Khatyrka. Asteroid 89 Julia has a matching reflectance spectrum, is the parent of a young asteroid family consistent with the ~600 Ma shock event recorded in Khatyrka, and is located near strong orbital resonances in the asteroid belt, which can explain its short cosmic ray exposure age (Meier *et al.*, 2018). This assignment is, of course, tentative. Yet, it inspired Phil Plait, a science fiction blogger calling himself "The Bad Astronomer", to suggest to the writers of a CBS series on life threatening asteroids a name for the material vital to the fictional engine needed to keep a dangerous asteroid away from Earth: Icosahedrite! Would that not be the ultimate example of how crucial "pure" science is to humanity's survival? (https://www.syfy.com/syfy-wire/cosmic-sleuthing-an-origin-story-for-a-really-weird-meteorite)

3.3.4 Helium Atoms from the Interstellar Medium

The next example is also from a long term and extensive collaboration, in this case between the Physics Institute of the University of Bern and the Institute for Space Research at the Russian Academy of Sciences. We at ETH were fortunate to become involved in this project at a late stage and yet to be able to provide some critical analyses for its success.

In 1991, Peter Bochsler contacted G. N. Zastenker at a meeting in Vienna with a proposal to capture neutral helium atoms from the interstellar medium in foils exposed on the Russian MIR space station. Zastenker was enthusiastic, and in 1996 the COLLISA experiment on MIR collected interstellar neutral atoms in a BeO layer on the surface of a Cu-Be foil. The helium in this foil was then analysed first at the University of Bern (Salerno *et al.*, 2003) and later in Zürich (Busemann *et al.*, 2006).

Knowledge of the ^{3}He/^{4}He ratio in the interstellar medium (ISM) is essential for models of galactic chemical evolution (GCE) and for predicting the overall abundance of ^{3}He (relative to H or ^{4}He) in the ISM. In particular, the present day interstellar ^{3}He abundance – compared to protosolar ^{3}He as inferred from Jupiter's atmosphere or from meteorites – allows us to track the GCE over the last 4.56 Ga. The COLLISA experiment provided a direct way to measure the helium isotopic ratio in the local interstellar cloud (LIC), the region of the local ISM currently traversed by the solar system. Neutral gas of the LIC reaching Earth's orbit before interacting with the solar EUV (extreme ultraviolet) photons retains its original isotopic abundances. COLLISA was obviously inspired by the Apollo Solar Wind Composition experiment, developed in Bern some three decades earlier, in which ions of the solar wind were trapped in aluminum foils on the lunar surface (Section 2.2). The additional main difficulty of COLLISA was the very low speed of the Earth relative to the neutral gas of the LIC, which

never exceeds about 80 km/s during northern spring (Zastenker *et al.*, 2002). This is considerably slower than the speed range of solar wind ions. Therefore, Al foils would not have trapped a sufficient fraction of the interstellar He. The problem was overcome with a CuBe foil covered with a thin BeO layer, resulting in a He trapping efficiency of the order of 10 % and a reasonably well defined He isotopic fractionation upon trapping. Over a period of several months in 1996, interstellar neutral atoms were collected for about 60 hours in ~140 time windows of a few minutes each, carefully avoiding, *e.g.*, neutral atoms from the Earth's upper atmosphere, while ions of various potential sources were electrostatically rejected (Zastenker *et al.*, 2002). This allowed Emma Salerno in Bern (Salerno *et al.*, 2003) to measure an interstellar ^{3}He/^{4}He ratio of $(1.7 \pm 0.8) \times 10^{-4}$. To my knowledge, this was the first laboratory-based direct analysis of interstellar matter. Salerno and co-workers concluded that their value is consistent with protosolar ratios obtained from meteorites and Jupiter's atmosphere, supporting the hypothesis that the abundance of ^{3}He in the Galaxy has not changed significantly over the past 4.5 Ga. However, the value has a substantial uncertainty, largely due to ^{3}He originating from the radioactive decay of tritium in the CuBe foil.
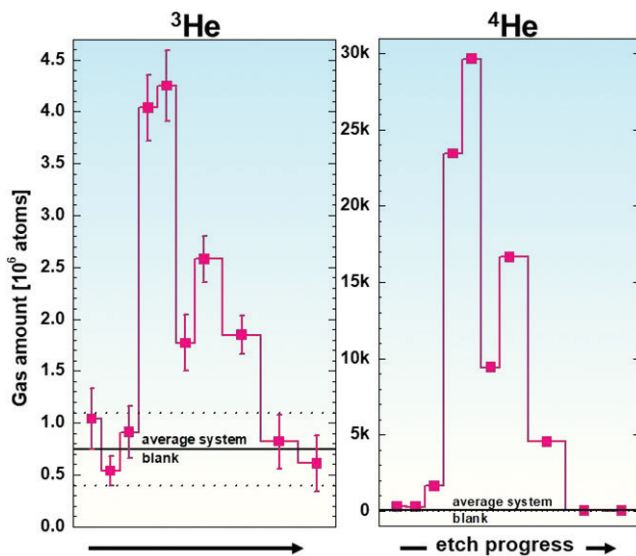
Figure 3.30   Release patterns of the two stable He isotopes in a BeO layer on a CuBe foil exposed to the flux of interstellar neutral atoms on the MIR space station (Busemann *et al.*, 2006). Gas release was by CSSE. Both isotopes were clearly above blank values determined with unflown foil pieces. The ^{3}He/^{4}He in the local interstellar medium determined by this experiment is identical within uncertainty to the protosolar value measured in Jupiter. Figure courtesy of Henner Busemann.

Henner Busemann was involved in the MIR foil analyses in Bern. A few years later, while he was working at the Carnegie Institution in Washington and occasionally as a guest at ETH, we decided to try to mitigate the ^{3}He blank problem by extracting the gas by CSSE (Section 2.5.1) instead of stepwise heating. Low extraction blanks for noble gas components of interest had previously proven to be a major advantage of gas release by selective acid dissolution of specific carriers *in vacuo*. For example, solar wind gases implanted at very shallow depths in lunar or asteroidal regolith grains were accompanied by much lower contributions of cosmogenic noble gases from the grain volumes than was possible by stepwise heating. Henner and I therefore proposed to dissolve only the very thin BeO layer of the foil by closed system etching. This would release the interstellar He, but hopefully leave in place much of the tritiogenic ^{3}He that had accumulated in the Cu-Be part of the foil, because no high temperatures would be needed in the gas release. Our plan worked well. Using HF, Henner etched about 50 cm^2 of a foil piece exposed on the MIR station in several steps and clearly observed interstellar ^{4}He as well as ^{3}He (Fig. 3.30; Busemann *et al.*, 2006). Several analyses of control foils showed that the helium blank was much lower than that achieved by Salerno *et al.* (2003) with stepwise pyrolysis. We obtained $(^3He/^4He)_{LIC} = (1.62 \pm 0.29) \times 10^{-4}$, the most precise determination of the He isotopic composition of the local interstellar cloud at that time, with an uncertainty almost three times lower than that reached by Salerno and co-workers. Since the ^{3}He/^{4}He ratio in the LIC is within uncertainty identical to the protosolar value of $(1.66 \pm 0.06) \times 10^{-4}$ measured in Jupiter's atmosphere, this reinforces the conclusion of Salerno *et al.* that during the last 4.6 Ga there has been no significant evolution of the ^{3}He abundance in the Galaxy.

3.3.5 What Kind of Giant Impact Formed the Moon?

My last example of science apart from research grants also relates to a major topic in planetary sciences: the origin of the Earth's Moon. As Giant Impact modelling is far from my core competences, it fits best in this section, as I would not have dared to include this project in one of my own research proposals.

A long standing conundrum in the Giant Impact hypothesis of lunar formation was – and perhaps still is – that "canonical" impact models predict that the Moon formed predominantly from material of the impactor Theia rather than the proto-Earth, which apparently contradicts the Moon's close geochemical similarity to Earth. It was again Matthias Meier who asked me one day what might possibly happen if Theia was modelled not as a body with silicate mantle and iron core, but as an object similar to Ganymed, Jupiter's largest Moon. Like other large moons in the solar system, Ganymed has a mantle of ice (and partially liquid water) overlying an inner region of silicates and iron. Probably rather naively, Matthias and I wondered whether Theia's evaporating water mantle might largely leave the system upon the collision with the proto-Earth. If so, this could result in a much larger fraction of the Moon deriving from the proto-Earth than in the case of a pure silicate/iron impactor. Matthias and

I knew of no study that modelled such a case, but we did not see why potential impactors in the early solar system should not possibly have been similar to Ganymed or other icy moons. So we approached Willy Benz at the University of Bern, one of the pioneers on Giant Impact modelling, and his graduate student Andreas Reufer.

As part of his dissertation, Andreas modelled impacts by relaxing the then canonical assumption that none or very little of the total mass of proto-Earth plus Theia is lost from the system (Reufer *et al.*, 2012). One consequence was that the collisional angular momentum no longer had to be tightly constrained, as escaping material could also carry angular momentum. "Hit and run" collisions, in which a significant fraction of the impactor and perhaps also the target escapes, were first studied by Asphaug *et al.* (2006). This approach allowed Andreas to expand the parameter space, permitting higher impact velocities and steeper (less grazing) impact angles. He modelled three types of impactors with different silicate and iron fractions and, in some cases, with a water ice mantle. While none of the model runs could reproduce the constraints of the actual Earth-Moon system, many of his runs resulted in moons that contained a considerably higher fraction of material from the proto-Earth than the canonical cases. In the "best" runs where Theia was a silicate-iron mix, a little more than 50 % of the disk mass from which the Moon would form came from the proto-Earth, and in the case of ice-rich impactors this fraction reached up to about 80 %. However, for ice-rich impactors, the efficiency with which material is brought into orbit is considerably lower than for Theias with higher densities, and the resulting disk mass was therefore not large enough to form a body the size of the actual Moon. Hence, the idea of ice-rich impactors does not seem to be able to easily explain the Giant Impact conundrum. Nevertheless, Andreas Reufer's work resulted in one of three papers published in 2012 which, I think, gave new impetus to Giant Impact research; the others were Canup (2012) and Ćuk and Stewart (2012). Today, more than ever, the Giant Impact origin of the Moon is a highly active research topic for both the modelling and cosmochemical communities.

PART II: RESEARCH IN GEOCHEMISTRY

4. NOBLE GASES IN TERRESTRIAL ROCKS

As noted in the introduction to Section 3, in the early- to mid-1980s I not only took my first steps away from solely studying lunar samples to becoming a meteoriticist, but also developed, more or less in parallel, an interest in noble gases (and radionuclides) in terrestrial samples. For a physicist with a meagre (to say the least) background in geology, this naturally required extensive collaboration with trained Earth scientists. The first of my two main terrestrial research areas were cosmogenic noble gases – largely in combination with cosmogenic radionuclides – as a tool in geomorphology. The second was the study of noble gases in water samples from lakes, groundwaters, and fluid inclusions in speleothems as a tool in limnology and climatology. These activities will be the topics of Sections 4 and 5. But first, in Section 4.1, I review the first two studies on noble gases in terrestrial samples in which I was involved.

4.1 My First Steps in Geology: Fissiogenic and Nucleogenic Noble Gases

For his doctoral thesis published in 1988, Jost Eikenberg proposed to Peter Signer a study of noble gases in uranium-rich minerals. The two long lived uranium isotopes ^{235}U and ^{238}U decay mostly along the well known α and β^- decay chains

to [207]Pb and [206]Pb, respectively, but they can also split into two roughly equal sized nuclides, including several xenon isotopes which are of interest here. Some of these fission reactions are triggered by fast or slow neutrons, but most importantly [238]U can also spontaneously fission. The half-life for spontaneous fission (sf) is much longer than the cumulative half-life of 4.47 Ga along the decay chain to [206]Pb. Nonetheless the spontaneous fission process can also be used to date U-rich minerals. For example, in zircon and monazite, Xe from spontaneous fission is often retained better than radiogenic [206,207]Pb. However, one problem has been that the fission half-life of [238]U has been controversial. The relevant quantity is $\lambda_{sf} \times {}^{136}Y_{sf}$, *i.e.* the decay constant λ for spontaneous fission of [238]U times the fractional yield *per* fission event of [136]Xe, the main fission Xe isotope. Values for this product determined with U oxides such as pitchblende were typically about 20 % lower than those measured with accessory U minerals such as zircon or monazite. Jost Eikenberg analysed a large series of carefully characterised uraninite and pitchblende samples with known, undisturbed geological histories and concordant U-Pb ages. In selecting the samples, Jost profited from the expertise of his thesis co-supervisor Victor Köppel. Jost's average $\lambda_{sf} \times {}^{136}Y_{sf}$ of $(5.7 \pm 0.4) \times 10^{-18}$/a was more robust than the U oxide-based values obtained by previous researchers, but essentially confirmed them (Eikenberg *et al.*, 1993). Hence, the discrepancy with the values based on U-rich accessory minerals remained. Therefore, in her doctoral thesis, Riccarda Ragettli did an equally careful study by combining U-Pb and U-Xe analyses of zircons and monazites, again with Victor as co-supervisor (Ragettli *et al.*, 1994; Fig. 4.1). She obtained $\lambda_{sf} \times {}^{136}Y_{sf} = (6.83 \pm 0.18) \times 10^{-18}$/a, again essentially confirming previous values obtained on accessory U minerals, but with improved precision. Ragettli *et al.* (1994) considered it very unlikely that diverse U-bearing oxides would lose more or less constant fractions of their fission Xe by diffusion, but noted that these minerals can readily regenerate their crystal structure after radiation induced lattice damage. We suggested that either this regeneration or changes in oxidation state could lead to a systematic loss of Xe. In a later paper, Jost Eikenberg and I investigated another possibility, namely that zircons and monazites might contain sizeable fractions of Xe from the spontaneous fission of [232]Th (Wieler and Eikenberg, 1999). However, with a series of very Th-rich monazites from China, we were able to establish an upper limit on λ_{sf} ([232]Th) that ruled out this possibility.

Jost Eikenberg also measured He, Ne, Ar, and Kr in many of the samples studied in his 1993 paper. One U-rich fluorite yielded essentially pure [22]Ne from the reaction [19]F(α,n)[22]Ne. To the best of our knowledge, the ratio [20]Ne/[22]Ne = 0.042 is the lowest value ever measured in a terrestrial sample. While this is not an Earth-shaking finding, it was quite remarkable for a meteorite noble gas person like me to learn that almost pure [22]Ne not only occurs in presolar grains in meteorites – remember the exotic Ne-E component in meteorites mentioned in Section 3.2.1 – but is also produced in natural samples on our own planet. Jost found in his samples also several noble gas components that were formed by so called Wetherill reactions, *e.g.*, [18]O(α,n)[21]Ne. He estimated that about 2.4 % of the [21]Ne in the Earth's atmosphere could be produced by such reactions. This

work inspired Ingo Leya and me to study the production of Ne by alpha particles from U and Th decay in the terrestrial crust and upper mantle (Leya and Wieler, 1999). These calculations relied on the same tools Ingo used to calculate cosmogenic nuclide production in meteorites and on planetary surfaces, as discussed above. Calculated production rates of Ne isotopes as functions of the concentrations of the major taget elements oxygen and fluorine and the number of alpha particles agree well with experimental data.
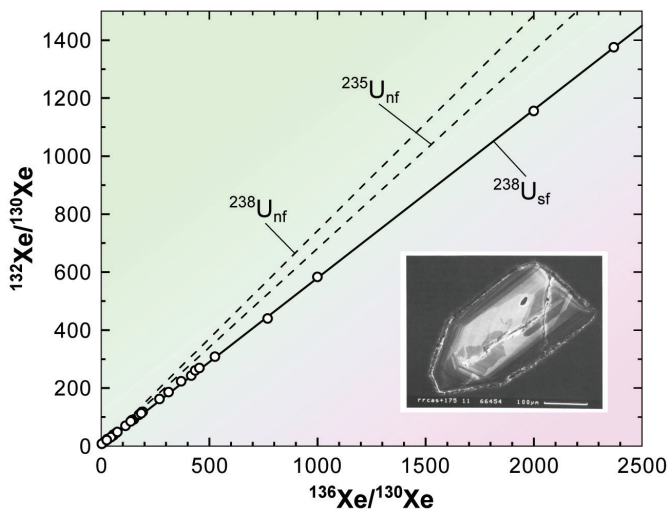

Xenon three isotope diagram of data from zircon and monazite separates studied by Ragettli *et al.* (1994). All data fall on a mixing line between atmospheric Xe and Xe from the spontaneous fission of ^{238}U. These data yielded a precise value for the product of the ^{238}U fission decay constant and the relative yield of ^{136}Xe of this process, *i.e.* for $\lambda_{sf} \times {}^{136}Y_{sf}$. The cathodoluminescence image of one of the analysed zircons shows that the crystal did not have an older generation core that could have compromised data interpretation. Figure adapted from Ragettli *et al.* (1994), inset with permission from Elsevier.

4.2 Cosmogenic Noble Gases and Radionuclides in Geomorphology

About a decade after Davis and Schaeffer (1955) had suggested that cosmogenic nuclides produced in rock samples near the Earth's surface through interactions with galactic cosmic rays could be used to study geologic problems (Section 3.1.1), Devendra Lal and Bernard Peters (Lal and Peters, 1967) provided a theoretical framework for such studies. However, analyses of *in situ* cosmogenic nuclides in terrestrial samples only became routine in the 1980s (*e.g.* Klein *et al.*, 1986;

Nishiizumi *et al.*, 1986; Kurz, 1986; see Gosse and Phillips, 2001; Niedermann, 2002; Granger *et al.*, 2013), although already twenty years earlier cosmogenic nuclides had become a widely used tool for studying the exposure history of meteorites and lunar samples, as mentioned in Section 3.1. The reason for this delay is the strong shielding by the Earth's atmosphere, which causes production rates at the Earth's surface to be several orders of magnitude lower than those on the lunar surface or in meteorites. The crucial break through in the early-1980s was the development of accelerator mass spectrometry (AMS), which had already revolutionised ^{14}C dating. AMS also allowed routine analyses of *in situ* cosmogenic radionuclides such as [10]Be, [26]Al, and [36]Cl in small samples (Section 3.1.2 and Fig. 3.2). Within a few years its use transformed quantitative geomorphology and quaternary geology (Gosse and Phillips, 2001; Dunai, 2010; Granger *et al.*, 2013). Landforms can now be dated and erosion rates measured over timescales relevant to soil-forming processes. Current radionuclide detection limits are low enough to allow the determination of surface exposure ages in some cases as low as <1000 years.
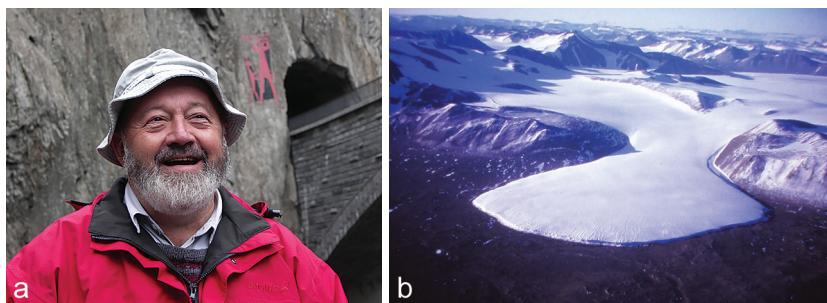

Figure 4.2 **(a)** Christian Schlüchter as Guide at the Teufelsbrücke (Devil's Bridge) near St. Gotthard Pass during the post conference excursion after the 2006 Meteoritical Society meeting in Zürich. **(b)** The Dry Valleys near McMurdo are a key area for studying Antarctic palaeoclimate. Shown is the Commonwealth Glacier and the entrance to Taylor Valley. Picture courtesy of Christian Schlüchter.

The first report of cosmogenic noble gases in terrestrial rocks was by Srinivasan (1976), who detected excesses of the lightest (and rarest) Xe isotopes in barites from South Africa and Australia. However, this remained the only report of cosmogenic heavy noble gases in terrestrial samples until Dunai *et al.* (2022) detected cosmogenic Kr in zircons from a suite of surface rocks. Much more convenient to analyse in terrestrial samples are the cosmogenic contributions to the two lightest noble gases He and Ne. This was pioneered by Mark Kurz at the Woods Hole Oceanographic Institution and by Harmon Craig, Kurt Marti, and co-workers at the University of California in San Diego, who reported cosmogenic [3]He and [21]Ne in high altitude samples from Hawaii (Kurz, 1986; Marti and Craig, 1987). Since then, analytical developments in noble gas mass spectrometry have enabled routine analysis of cosmogenic noble gases in a variety of

rocks on Earth (Niedermann, 2002; Blard, 2021). However, the detection limits for cosmogenic noble gases in terrestrial rocks have never reached the very low levels that are now routine for several radionuclides. Therefore, we decided to focus on the study of very old landscapes where the stable noble gases could have advantages over radionuclides or at least provide complementary information, as discussed in the following.

4.2.1 Antarctica

In 1991 we were contacted by Christian Schlüchter, then at ETH before he moved to the University of Bern two years later. Christian is a Quaternary Geologist who works almost everywhere on the planet and has a reputation as a globetrotter. Among his favourite terrains are the Dry Valleys in Victoria Land in East Antarctica. These ice-free valleys are among the oldest landscapes on Earth, with very little precipitation and very little erosion. For a geomorphologist like Christian, the prospect that all of a sudden age and erosion rates of such landscapes could be quantified with nuclides produced by cosmic rays must have been no less exciting than was the realisation by mid-20th century geologists that they could absolutely and reliably date the formation of rocks with radiogenic isotopes. Christian thus sought cooperation with the AMS group at the ETH Physics Department as well as with us at the Earth Science Department. As it just happened, we were looking for a dissertation project for Laura Bruno. So, because noble gases are ideal for investigating very old landscapes, as they do not decay like radionuclides, Laura set out to study the glacial history of Antarctica, or more exactly the history of Antarctica as reflected in the Dry Valleys. Laura's doctoral thesis was the first chapter of a very fruitful collaboration with Christian that led to several jointly supervised dissertations and many other projects. Laura's work also marked the beginning of our collaboration with the AMS group at ETH on terrestrial problems, extending our previous joint activities in cosmochemistry (Section 3.1). Our main partners in the AMS team were Susan Ivy-Ochs, Peter Kubik and later Lukas Wacker. For our cosmogenic nuclide studies in Antarctica, Carlo Baroni of the University of Pisa was also an important colleague. I already had met Carlo during my meteorite search at Frontier Mountain in the 1990/91 season at the Italian Antarctic Station at Terra Nova Bay (see Box 3.2).

The development and subsequent history of the Antarctic ice masses are major issues in palaeoclimatology. The most important question was the extent to which the Antarctic ice masses had been affected by the Pliocene climate oscillation. This was a global warming interval from 4.8 to 3.2 Ma ago with an increase in sea surface temperature of about 3 °C. Some workers argued that such warm conditions caused the ice sheet to collapse. Others proposed that the East Antarctic Ice sheet has remained stable since its formation perhaps 15 or 20 Ma ago and that the Antarctic climate had been cold and hyperarid ever since (Denton *et al.*, 1993). For Christian Schlüchter and colleagues, the Dry Valleys were a key area (Fig. 4.2). Had there been major erosional events indicating the

existence of running water in summer since the Dry Valley landscape formed? Cosmogenic nuclides – here primarily the stable noble gases – were the ideal (then new) tool to tackle this question.

Because the production rate of cosmogenic nuclides near a rock surface decreases with increasing depth and because even in the hyperarid Antarctic climate rocks slowly erode, concentrations of cosmogenic nuclides basically only provide minimum values for the time a sample was exposed to cosmic rays at the Earth's surface. The nominal age would equal the true exposure age only if no erosion had occurred (Fig. 4.3a). The analysis of two or more nuclides with different half-lives in the same sample allows, in principle, one to determine both the erosion rate and the exposure age (Fig. 4.3b), but for the moment we are concerned only with stable noble gases. More about cosmogenic nuclide systematics can be found in Section 4.3.1 about the CRONUS programmes.

Laura Bruno analysed ^{3}He and ^{21}Ne in pyroxene and quartz separates from boulders at two locations (Mt. Fleming and Table Mountain) in glacial deposits of the so called Sirius group. Pyroxenes were important because they retain cosmogenic helium much better than quartz and hence allow estimates of noble gas losses by diffusion. Christian Schlüchter had taken the samples with the eye of an experienced field geologist, allowing him to recognise boulders least disturbed since deposition. Laura's oldest minimum values of ~5 and 5.5 Ma for the two sites were among the oldest exposure ages of terrestrial samples ever measured until then (and also higher than the maximum values of about 4 Ma to be deduced from radioactive ^{10}Be). Laura's work (Bruno *et al.*, 1997) was thus the first unequivocal evidence based on cosmogenic nuclides that the East Antarctic Ice sheet had remained stable for at least the past 5 Ma, but likely even longer, presumably at least for 6-6.5 Ma. Bruno and co-workers also concluded that the maximum possible uplift rate of the Transantarctic Mountains was only ~170 m/Ma, much slower than necessary to explain the microfossils found in Sirius group sediments if these sediments were of much younger age, as argued by the proponents of an unstable ice sheet.

In his doctoral thesis, Jörg Schäfer extended the work of Laura Bruno to other locations in the Dry Valleys. His noble gas data, supplemented by ^{10}Be data provided by Susan Ivy-Ochs, gave minimum ages of up to 10 Ma (Schäfer *et al.*, 1999). As in other studies discussed here, samples were taken from erratic boulders (examples shown in Fig. 4.4) and/or bedrock surfaces. Jörg's data set confirmed Laura Bruno's conclusion as to the Pre-Pliocene age of the Sirius group sediments, which he estimated to be older than 20 million years. Maximum long term erosion rates were below 15 cm/Ma even at altitudes below 1000 m above sea level. Jörg concluded that this implies a permanently cold and hyperarid climate and thus a decoupling of the Antarctic climate from that of lower southern latitudes.
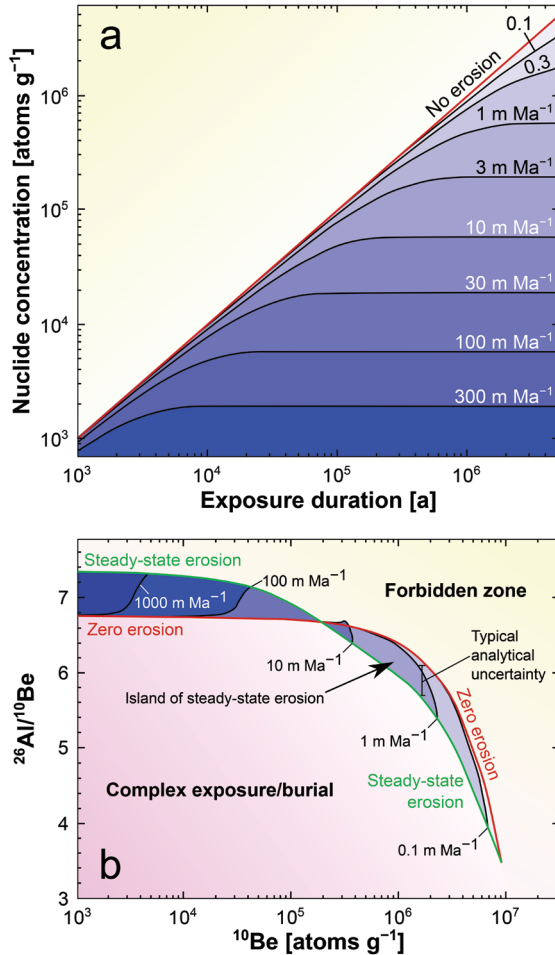
Figure 4.3 **(a)** Evolution of the concentration of a stable cosmogenic nuclide at the current surface of a terrestrial rock as a function of its exposure age and erosion rate, the latter assumed to be constant over the exposure period. The production rate is taken as 1 atom *per* gram per year. The nominal exposure age is equal to the true exposure age only in the absence of erosion. The higher the erosion rate, the sooner the nuclide concentration reaches erosional equilibrium. In these cases, the nuclide concentration yields the erosion rate. **(b)** "Banana plot" of cosmogenic nuclide concentrations, here with the two radionuclides ^{10}Be and ^{26}Al. Such diagrams are used to deduce – ideally – both the exposure age and erosion rate of a rock that has experienced a simple exposure history with constant erosion (Lal, 1991). Analytical uncertainties often prevent a unique solution, however. Data falling to the lower left of the "bananas" would indicate complex exposure or burial of the rock, i.e. part-time shielding from cosmic rays (*e.g.* Klein *et al.*, 1986). Diagrams adapted from Dunai (2010).

Jörg Schäfer provided additional evidence for a long term continuously arid climate in the Dry Valleys by measuring the age of a spectacular glacial remnant. This ice body in Beacon Valley is covered by a till layer with an $^{40}Ar/^{39}Ar$ age of ~8 Ma. As this age likely represents a lower limit on the age of the underlying ice, this implies exceedingly low ice sublimation rates, probably due to saturation of the till with moisture. This would also imply a constantly cold climate in Beacon Valley for at least 8 million years. Jörg measured cosmogenic ^{3}He and ^{21}Ne in erratic boulders from the till surface and from within the ice, respectively (Fig. 4.5). He derived a conservative lower limit of 2.3 Ma for the cosmic ray exposure age of the surface boulders, while the difference between the noble gas concentrations of the surface samples and one from the interior allowed him to derive an ice sublimation rate of no more than a few metres *per* million years (Schäfer *et al*., 2000). This and the high age (likely considerably older than the 2.3 Ma minimum age) support the conclusion from the Ar-Ar data that the ice in Beacon Valley was deposited many millions of years ago and has never been thinner than it is today.

The work of three further doctoral students confirmed the long term stability of a cold and hyperarid climate in East Antarctica. Peter Oberholzer and Stefan Strasky analysed noble gases in our laboratory. Luigia di Nicola from the Universities of Siena and Bern and later at the SUERC in East Kilbride, Scotland, measured the radionuclides ^{26}Al and ^{10}Be at the ETH AMS facility. These projects were carried out together with Carlo Baroni and Christian Schlüchter. The study area a few hundred km north of the Dry Valleys in North Victoria Land was chosen to address the objection of Van der Wateren *et al*. (1999) that landscape stability inferred from the Dry Valleys should not be generalised to the entire Transantarctic Mountains. The noble gas cosmic ray exposure ages showed that the long term stability and the very limited dynamics of the East Antarctic Ice Shield is also evidenced in northern Victoria Land (Oberholzer *et al*., 2003; 2008). Long term maximum erosion rates there are similarly low as

those in the Dry Valleys, testifying to a constantly cold and hyperarid climate also further north. Luigia and Stefan also found some very old exposure, again confirming long term hyperarid climates, but their data also showed that many samples had undergone a complex exposure history, reflecting, *e.g.*, ice level fluctuations (Strasky *et al.*, 2009a; Di Nicola *et al.*, 2012).

I should add here that I myself was not involved in the details of the project definitions of all these studies or the geological interpretation of the data. My contributions focused on the noble gas analyses and the more technical aspects of data interpretation.

4.2.2   Tibet and from there to the Indian Ocean

The Himalayas and adjacent high altitude regions in central Asia are sometimes referred to as Earth's third pole, and understanding the role of this vast region in shaping the global climate system is of paramount importance. The history of glaciations is of particular importance, since glacial cycles reflect broader climate changes. Himalayan glaciations may affect the global radiation budget and influence the Asian monsoon. Christian Schlüchter recognised the potential of cosmogenic nuclides for studying Tibet's glacial history and he invited three of the doctoral students who had worked with him on projects in Antarctica to join him for field work in Tibet. The acknowledgments in the dissertations of Jörg Schäfer, Peter Oberholzer, and Stefan Strasky not only testify to how much they benefitted from Christian's experience as a field geologist but also to how

deeply impressed they were by his empathy for foreign cultures. They studied noble gases and [10]Be in glacial moraine samples from different key areas in Tibet (Fig. 4.4). Beryllium-10 was again analysed in cooperation with Susan Ivy-Ochs and Peter Kubik from the AMS group at ETH. In short, these studies showed that glaciations in Tibet had had rather limited influence on global climate over the past ~170,000 years (Schäfer *et al.*, 2002; Schaefer *et al.*, 2008; Oberholzer, 2004; Strasky *et al.*, 2009b). A putative ice dome that once covered the entire plateau, as proposed by Kuhle (1998), was previously viewed with great scepticism and could now be rejected based on the cosmogenic nuclide data. The data also showed that increased moisture supply by an intensified summer monsoon had only limited influence on the Tibetan glaciations. Rather, these were influenced by the North Atlantic climate system (Oberholzer, 2004; Schaefer *et al.*, 2008). The latter paper by Joerg Schaefer (note the slight name change to avoid the pain with German Umlaut characters in citation records!) was published when he had already moved to the Lamont-Doherty Earth Observatory near New York, where he still works today.

Interactions between tectonics and climate make the Himalayas the world's largest sediment source to the oceans. The Tsangpo-Brahmaputra river system drains the Himalayan range and the Tibetan plateau, and this large catchment is ideal for studying how denudation processes are reflected in the sediment load. Maarten Lupker therefore decided to study the interplay between tectonic uplift, surface denudation processes, and sediment transport along the Tsango-Brahmaputra catchment (Lupker *et al.*, 2017). Maarten had been a Master's student at our institute under the supervision of Bernard Bourdon and Sarah Aciego. For his Master's thesis on the isotopic composition of Sr, Nd, and Hf in dust and ice from an ice core in Greenland, he received the inaugural Prix de Quervain of the Swiss Committee on Polar and High Altitude Research (in honour of Alfred de Quervain, the Swiss Geophysicist who crossed Greenland in 1912, the second traverse ever after Fridtjof Nansen's in 1888). I had been a member of the selection committee for the award and gladly agreed when Maarten expressed his wish to join our group as a postdoc after completing his PhD at CRPG in Nancy. He later moved to the Institute of Geology in our Department, but continued to work with us thanks to his interest in cosmogenic nuclides. These are an excellent tool for determining catchment-wide denudation rates over a wide range of spatial scales. Basically, the nuclide concentration in a sample of loose sediments from a river reflects how fast, on average, the river catchment is eroding upstream to the position of the sample (Brown *et al.*, 1995). Lupker *et al.* (2017) showed that denudation rates (measured with [10]Be in Zürich and at CEREGE in Aix-en-Provence) vary by two orders of magnitude between individual sub-catchments along the Tsangpo-Brahmaputra system. The sediment flux at the outlet in Bangladesh corresponds to a denudation rate on the order of one millimetre *per* year. Most importantly, Maarten Lupkers' study is an excellent example of the complications that can arise when attempting to derive catchment-wide denudation rates "from a bag of sand".

4.2.3 Northern Chile

The Western Central Andes constitute another area where the interplay of erosion, climate, and tectonics can be studied in an exemplary way. Fritz Schlunegger (now at the University of Bern) and our joint doctoral student Florian Kober combined analyses of ^{10}Be, ^{26}Al, and ^{21}Ne to determine erosion rates and cosmic ray exposure ages across a west-east transect in northern Chile. The transect spanned an elevation range from close to sea level to >4000 m above sea level and a climate range from hyperarid to semi-arid (Kober *et al.*, 2007). I had never joined my colleagues in Tibet, but this time I did not want to miss the opportunity to get at least a vague idea of how trained geologists like Fritz and Florian can assess a terrain to extract the most information from a minimum number of samples. To me, this remains both an art and a science, but there is definitely more to it than just walking on an Antarctic ice field or a hot desert surface in search of (dark) stones that might turn out to be meteorites. It was the first time I had been back to South America since my stay in Guayaquil and the subsequent long trip across the entire continent in 1974–75. I had been informed that in some parts of the Atacama desert not a single rainfall had been documented since the arrival of the Spanish conquistadores. Yet, during my two weeks in the port city of Arica we enjoyed half an hour of pleasant evening rain. On an unforgettable day trip we drove up to the Bolivian border at an altitude of over 4000 m, crossing the hot Atacama desert before finally passing Vicuna herds grazing in the freshly fallen snow. On several other trips along the Panamericana, we had seen a lone hiker heading north, and one day we met him at one of the small makeshift restaurants along the road. Yoshi had a good position in Japan that allowed him to take a break every few years to hike the world. He had crossed Asia in two legs from Western China to Istanbul, and once he participated in a deca-ultratriathlon in Mexico (38 km swim, 1800 km bike, and 421.95 km run, the latter on a 400 m track!). The present trip would eventually take him from Buenos Aires to Cuzco. He relied on the smallest backpack one can possibly imagine, with two half-litre bottles of water, a thin blanket for the night, and some stuff to periodically repair his sneakers. He often ate what others dumped out of their cars and when in need of water, he would simply signal to the truck drivers, who often politely stopped. Apparently this is one way to survive in one of the driest places on Earth. But when we met him, he was suffering quite a bit, perhaps from an upset stomach. So he accepted our offer of a ride to Arica, albeit with a bit of guilty conscience. After having recovered a few days later, he insisted that we take him back to where we had picked him up some 50 km south of Arica. A few months later I received a letter from him posted in Cuzco. No doubt he finished the journey without leaving a gap. I wonder if he has now also fulfilled his lifelong dream of hiking from Alaska to Tierra del Fuego.

As expected, Florian Kober showed that erosion rates and exposure ages along the transect correlate with altitude and present day rainfall. In the hyperarid Coastal Cordillera, erosion rates are extremely low, in the range of 10-100 cm/Ma, resulting in nominal minimum exposure ages between 1-6 Ma. In the semi-arid Western Cordillera, erosion rates are much higher, up to 46 m/Ma,

corresponding to nominal minimum exposure ages of 20,000–100,000 years. The erosion rates in the hyperarid zones are as extremely low as those in Antarctica and therefore can also be studied particularly well by stable cosmogenic noble gas isotopes. Dunai *et al.* (2005) reported exposure ages of up to 37 Ma measured by cosmogenic ^{21}Ne in quartz clasts from an area south of Arica. These authors concluded that their data require predominantly hyperarid conditions for several tens of million years, consistent with the hypothesis that the onset of aridity in the Atacama Desert may be the cause – rather than the consequence – of the uplift of the high Andes. The combination of cosmogenic noble gases and radionuclides allowed Kober *et al.* (2007) to study erosion in more detail than would have been possible with noble gases alone. When only one nuclide is analysed, one usually assumes nuclide saturation in a constant erosion regime, but this is not the rule in the study area. The data require more complicated exposure scenarios, such as episodic erosion by spalling of larger slabs. Kober *et al.* (2009) further showed for a river system in northern Chile that catchment-wide denudation rates determined by only one nuclide would not have been correct for most sub-catchments because sediments sometimes are buried for long periods of time. This study again demonstrated the usefulness of combined cosmogenic nuclide analyses.

4.3 Method Development on Terrestrial Cosmogenic Nuclides

As much as I enjoy working with geologists on field studies, I have never come close to being an expert in the field. Since the beginning of my cooperation on terrestrial cosmogenic nuclides, I have therefore instead tried to contribute to method developments in terrestrial cosmogenic nuclide research with my students, postdocs, and other colleagues. On the one hand, we have attempted to improve values for nuclide production rates and scaling factors, including exploring the use of less common minerals. On the other hand, we developed one of the first successful extraction lines for *in situ* produced cosmogenic ^{14}C, a very important cosmogenic nuclide, albeit one rather difficult to analyse. Much of this work was carried out in the framework of the CRONUS collaboration. So, before we go into the details of our work, let me introduce the CRONUS programmes.

4.3.1 CRONUS

We have seen in Section 3.1 that the production rate of a cosmogenic nuclide in a given meteorite is a fundamental quantity whose uncertainty often dominates the total error of a stated exposure age. Production rates are an even greater problem in terrestrial cosmogenic nuclide research. For a meteorite we can assume that the production rate at a given pre-atmospheric depth depends essentially only on the target element abundances (neglecting, for example, the small radial gradient of the galactic cosmic ray flux in the inner solar system). The main

uncertainties are therefore the pre-atmospheric size of the meteorite and the sample depth. In contrast, the main factors that govern production rates in terrestrial samples – apart from major target element abundances, *i.e.* mineral type – are the geographic location of a sample and its exhumation/erosion history. Location is important for two reasons (*e.g.*, Gosse and Phillips, 2001). First, the Earth's magnetic field allows only primary cosmic ray protons above a certain energy to reach the upper atmosphere, where they will induce nuclear reactions that produce the secondary cosmic ray neutrons that eventually reach the surface. This threshold energy depends on the geomagnetic latitude. Fortunately, the average position of the magnetic pole coincides with the geographic pole over timescales of about 10,000 years or more. Therefore, in most cases, the latitude correction can simply be based on the geographic latitude of a sample. Second, and even more importantly, the Earth's atmosphere efficiently shields the surface of our planet from cosmic rays. To illustrate this, the atmospheric load of ~1 kg/cm^2 at sea level is equivalent to about 4-5 m of concrete. As an example, nuclide production rates at 3000 m altitude and latitudes higher than about 60° are almost 20 times larger than values near sea level in regions close to the equator. A reliable "scaling" of production rates for altitude and latitude is therefore required. Devendra Lal (Lal, 1991) provided an early method based on cosmic ray flux data obtained by exposing photographic emulsions at different altitudes in the atmosphere. The "Lal scaling" became very popular and widely used for many years (Fig. 4.6a). However, scaling methods needed further testing and improvements. For example, there was an urgent need for a much larger database of directly measured production rates at different locations and for different mineral types. Production anomalies in certain regions of the world needed further investigation, the most striking being an approximately 20 % lower than expected value in Antarctica (Stone, 2000). In addition, possible fluctuations of production rates over time needed to be considered.

A large community effort was therefore launched in 2004–2005 under the name CRONUS (Cosmic Ray Produced Nuclide Systematics on Earth). The North American branch (CRONUS-Earth) was coordinated by Fred Phillips and colleagues (Phillips *et al.*, 2016a) and the European branch (CRONUS-EU) by Tibor Dunai, with regular advice (more than once over a beer) provided by Finlay Stuart (Stuart and Dunai, 2009). Tibor set up CRONUS-EU while working in Amsterdam, but soon afterwards moved to Edinburgh and later to the University of Cologne. I had known him since his time as doctoral student at ETH. We were very impressed when – within a few days after Peter Signer had offered him the position – without previous experience in noble gas geochemistry Tibor presented a proposal to study noble gas signatures in the sub-continental mantle, a region that hitherto had received much less attention than the mid-ocean ridge and ocean island basalt sources (Dunai and Baur, 1995).

The main goals of CRONUS included (i) testing scaling procedures by experiments with artificial targets, (ii) geological calibration of production rates using samples with independently known exposure ages, (iii) development
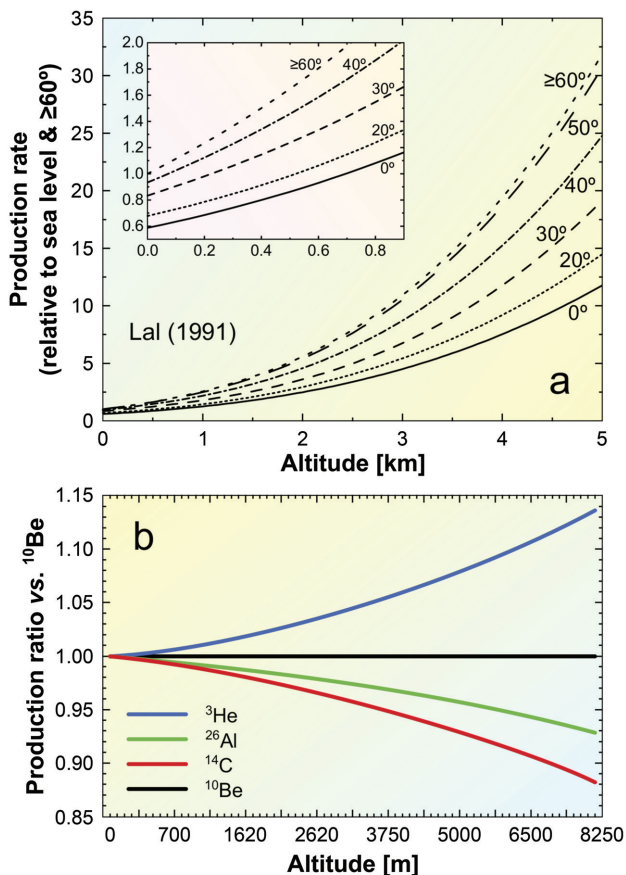
Figure 4.6 **(a)** Scaling factors of production rates of cosmogenic nuclides relative to values P_0 at sea level and geomagnetic latitudes ≥60° as published by Lal (1991). These classic Lal-scaling factors were widely used for many years. **(b)** A modern scaling procedure developed in the framework of CRONUS, known by the acronym LSD (Lifton, Sano, and Dunai, 2014), predicts minor differences in the altitude scaling factors for different nuclides. The figure shows how production rate ratios of (^{3}He, ^{26}Al, ^{14}C)/^{10}Be vary with atmospheric depth or altitude, compared to the ratio at sea level. Panel (b) adapted from Lifton *et al.*, 2014.

of improved numerical nuclide production models, and (iv) improvement of sample processing and analysis programmes, including inter-laboratory standard comparisons.

Both the AMS group and the noble gas group at ETH participated in CRONUS-EU, which was funded by the European Union as a "Marie Curie Research Training Network". As the name implies, the funding agency placed great emphasis on training young scientists in multinational cooperations. All students and postdocs funded by CRONUS-EU thus worked in institutions abroad. The programme started with a meeting in Amsterdam, where all the group leaders met all candidates for doctoral or postdoctoral positions. The group leaders presented their projects, the candidates their previous research, and then both sides expressed their preferences. My favourite postdoc candidate was Pieter Vermeesch, who had just completed his PhD on fission track dating at Stanford. Pieter was also the favourite of several of my colleagues. So imagine how happy I was when Pieter actually expressed his wish to join our team in Zürich, to work on an experiment with artifical quartz targets in vacuum containers exposed at different altitudes in the Swiss Alps (Vermeesch *et al.*, 2009; see below). At Stanford, Pieter had developed a deep interest in scientific statistics and today, as a service to the community, he is contributing several widely used tools. One of these is the Excel add-in "Cosmocalc", allowing cosmogenic nuclide calculations, which Pieter developed in Zürich. Later at Birkbeck and the University College, London, he provided a tool to visualise ages of detrital zircon populations ("Density Plotter"; Vermeesch, 2012), and a programme facilitating many different geochronological applications ("IsoplotR"; Vermeesch, 2018). After Pieter left for London, I was able to hire Kristina Hippe as a doctoral student with CRONUS-EU funds. Kristina's work will be discussed in the section on *in situ* ^{14}C below.

CRONUS-EU has undoubtedly fulfilled its goals, in particular as a starting point to motivate young scientists to become interested in cosmogenic nuclide research. One of several training weeks, during which students and postdocs met many of the senior scientists, took place on Mt. Etna in Sicily. As a particular highlight, I remember a lecture in the field by the late Pete Burnard, in which he vividly explained good sampling strategies. In his honour, the Pete Burnard award is now presented to a young scientist every second year at the small but highly successful DINGUE noble gas meetings that Pete initiated. DINGUE here stands for "Developments In Noble Gas Understanding and Expertise", but if you speak French, you will understand its other meaning as well!

CRONUS was a success story but work continues on cosmogenic nuclide production rates and their scaling factors. In their "Reflections on future directions for cosmogenic nuclide research" Fred Phillips and co-workers (Phillips *et al.*, 2016b) make several first order recommendations, including continuing efforts to understand the sources of the remaining discrepancies between models and data, and to devise consistent ways of calculating and reporting exposure ages benchmarked against reference ages. They further recommend efforts to facilitate the use of intercomparison materials and integrate the work of ongoing calibration campaigns. Many of these efforts are currently underway.

4.3.2 Work on Cosmogenic Nuclide Production Rates – in Zürich and Elsewhere

As noted above, production rates of cosmogenic nuclides on Earth depend critically on the altitude and latitude of the sampling site and thus are "scaled" almost universally to sea level and high latitudes. After the pioneering work by Lal (1991), scaling procedures were provided, *e.g.*, by Argento *et al.*, (2013) and Lifton, Sato, and Dunai (2014), the latter work also known as "LSD" (Fig. 4.6b). Artificial targets serve as input data and ground truth tests of scaling procedures. Ideally, a series of such targets are exposed simultaneously at different altitudes and, if possible, also at substantially differing latitudes. Given that production rates are very low and exposure durations limited by, for example, the duration of a PhD thesis, targets must be very large, in the range of kilograms or tens of kilograms, rather than on the order of tens of milligrams as is typical for natural samples. A first successful experiment was performed by Kuni Nishiizumi at the UC Berkeley Space Sciences Laboratory and co-workers (Nishiizumi *et al.*, 1996). They exposed several hundred kilograms of water (stored in waterbeds) for five years at one high and one low altitude site in California and then quantitatively extracted the cosmogenic ^{10}Be accumulated in this large amount of water. Brown *et al.* (2000) repeated the ^{10}Be experiment with 20 litres of water per sample exposed at three different elevations in the French Alps. These workers also determined cosmogenic ^{3}He in a second set of ten litre water samples.

These experiments motivated us to perform our own irradiations, in which several generations of graduate students became engaged. Some of the experiments were very successful, but I will also have to admit failures. In a first round, we used (artificial) quartz as the target, enclosed in ultrahigh vacuum stainless steel containers. In quartz, spallation of Si produces ^{21}Ne, unlike water, for which ^{3}He is the only detectable stable cosmogenic noble gas nuclide. This was deemed important as it should help to decide whether the production of ^{3}He, ^{21}Ne, and radionuclides such as ^{10}Be all follow the same altitude dependence (Fig. 4.6b). On heating, quartz releases ^{21}Ne at fairly low temperatures of about 600 °C, which we thought should be easy to achieve even for multi-kg samples in steel containers. Although quartz may partly lose ^{3}He over short periods of time, this could be controlled by analysing the headspace of the containers before heating.

Our initial plans were very ambitious and included at least two altitude profiles, one in the Alps, the other in North America (if possible at a high latitude). A complete latitude transect from 60 °N to close to the equator was also envisaged. In the end, the published project only covered one altitude profile in the Switzerland, with five targets exposed at elevations ranging from 550 metres (in Zürich) to 4550 metres at Monte Rosa, the second highest mountain in the Alps, on the Swiss-Italian border (Vermeesch *et al.*, 2009). Even this down-scaled project kept busy several generations of doctoral students, postdocs, and their supervisors, as documented in four different dissertations by Jörg Schäfer, Florian Kober, Peter Oberholzer and Stefan Strasky. We first had to learn how to make suitable quartz target samples (artificial quartz slabs ground to small

grains), and build containers and furnaces to ensure quantitative degassing of one kg of quartz at a temperature of 800 °C, which was less easy than initially imagined (Strasky 2008; Fig. 4.7). We also had to make sure that Ne blanks were low enough, and we had to evaluate ultrahigh vacuum valves that remain tight even at the low winter temperatures at high altitudes. Finally, the five targets in Switzerland were exposed for a year and analysed after recovery for cosmogenic ^{3}He and ^{21}Ne in the ultrahigh sensitivity Tom Dooley mass spectrometer. Two other samples exposed at different altitudes in Antarctica, deployed and recovered by Christian Schlüchter on two of his trips, were also analysed but unfortunately the results were not precise enough to be useful (Strasky, 2008). Two additional samples, also deployed by Christian in Tibet, unfortunately never made it back to Switzerland. I wonder whether they still languish on a rooftop awaiting recovery.
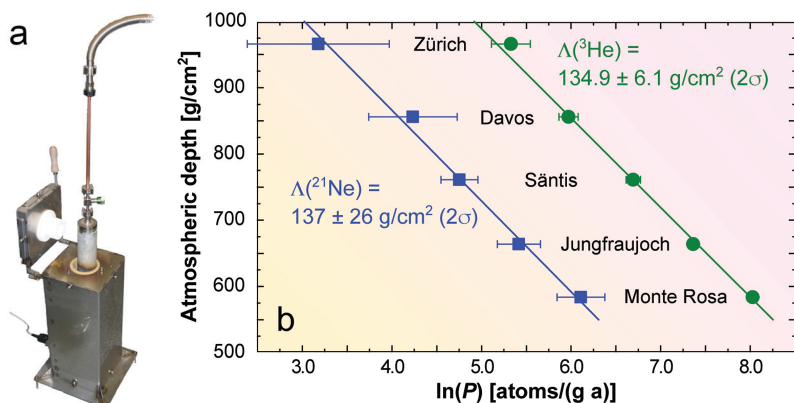

Figure 4.7 **(a)** Steel container holding 1 kg of quartz grains, enclosed in a furnace. The quartz grains are in the lowermost part of the steel tube, and thus can be heated to ≥800 °C. Five such quartz targets were exposed to cosmic ray neutrons at different altitudes (550- 4550 m). Picture from Strasky (2008). **(b)** Production rates of ^{3}He and ^{21}Ne (atoms/(g*a), log scale) in quartz as a function of altitude determined with these targets. Attenuation lengths Λ deduced for ^{21}Ne and ^{3}He are identical. Figure adapted from Vermeesch *et al.* (2009).

Pieter Vermeesch performed the data analysis of the targets from the Alps (Vermeesch *et al.*, 2009; Fig. 4.7). Attenuation lengths for ^{3}He and ^{21}Ne agreed within uncertainties. Basically as expected, production rates of both nuclides were proportional to neutron monitor count rates and followed the same scaling relationship as radionuclides. However, the uncertainties of our data and the limited altitude range covered did not allow us to test the slight differences in the modelled altitude scaling for different nuclides as predicted by Lifton *et al.* (2014) shown in Figure 4.6. The ^{3}He and ^{21}Ne production rates derived from the artificial targets agree – albeit with considerable uncertainties – with values obtained

from natural samples. Hence, this first experiment found a mostly successful end more than 10 years after its start. Unfortunately, the same cannot be said for a second experiment, an altitude profile again in the Swiss Alps, but this time with water as the target. We aimed to improve the accuracy by increasing the exposure durations by an order of magnitude to about ten years, and chose water because one of the main goals was to measure the branching ratio of directly produced ^{3}He and ^{3}He that "grew in" by decay of its radioactive precursor ^{3}H. Targets were deployed around 2005 and retrieved and analysed in 2015, but unfortunately the data did not allow a consistent interpretation. The reasons for this failure are unclear, but I suspect that such a long term project would have required better monitoring by the ultimately responsible person – me!

Figure 4.8 **(a)** Tibor Dunai and Riccarda Ragettli at a meeting of former doctoral students of Peter Signer in 2010. **(b)** Fin Stuart at an excursion to the Ming Tombs near Beijing during a noble gas meeting in 2010 at the Chinese Academy of Sciences. **(c)** Pete Burnard explaining sampling stategies during a CRONUS-EU workshop and field trip in 2010 at Mt. Etna in Sicily. **(d)** Florian Kober in Catania at the same workshop.

Determining the production rate of cosmogenic noble gases in various minerals has been a side issue in several of our papers, and two of them have been devoted specifically to this topic. Kober *et al.* (2005) measured cosmogenic ^{10}Be and noble gases in sanidine and Fe oxide minerals in silicic volcanic rocks from Chile that also contained quartz. The well known ^{10}Be and ^{21}Ne production rates in the latter mineral allowed us to determine $P(^{10}Be)$ and $P(^{21}Ne)$ in sanidine and $P(^3He)$ in Fe oxides. Such minerals are useful in exposure age studies in volcanic regions where the rocks lack quartz and pyroxene. With Vasily Alfimov and co-workers, Florian Kober also re-determined $P(^{21}Ne)$ in quartz using a large data set from samples with known ^{21}Ne and ^{10}Be concentrations, assuming that $P(^{10}Be)$ in quartz is known (Kober *et al.*, 2011). The approach we used minimised the influence of samples with a complex exposure history.

Martin Frank, now at GEOMAR in Kiel, is an isotope geochemist mainly interested in palaeooceanography. He joined Alex Halliday's team at ETH in the late 1990s. In an in house seminar we realised that Martin's expertise matched Jörg Schäfer's and my interests in the systematics of cosmogenic nuclide production. As mentioned earlier, production rates on Earth are influenced by the modulation of the cosmic ray intensity by the Earth's magnetic field. It is well known that the geomagnetic field intensity varies with time, but this is usually ignored in exposure age calculations, *i.e.* production rates are assumed to be constant at a given location regardless of when and how long a sample was exposed to cosmic rays. Shortly before his arrival in Zürich, Martin Frank had produced a field intensity curve over the last 200,000 years based on ^{10}Be data in a global series of deep-sea sediments (Frank *et al.*, 1997). To progress further we contacted Jozef Masarik at Comenius University in Bratislava. Jozef is not only an expert in physical models describing cosmogenic nuclide production in meteorites (as we saw above) but also simulates particle fluxes and cosmogenic nuclide production in the Earth's atmosphere and solid surface. Martin supplied

Jozef with the then best palaeomagnetic field reconstructions over the past 800,000 years and – during several visits to Zürich – Jozef modelled the effects of variable field intensity on the nuclide concentrations of samples taken today (Masarik *et al.*, 2001a). As I recall, we were quite relieved when it turned out that corrections are small (Fig. 4.10). At latitudes >40°, field intensity variations hardly influence production rates, and even at the equator integrated production rates for exposure ages between 40,000 to 800,000 years are only 10 to 12 % higher than the present day values, and for ages below 40,000 years the difference is even smaller. Perhaps somewhat counter intuitively, correction factors for stable nuclides and radionuclides with half-lives longer than a few hundred thousand years are almost identical. An early excursion of the magnetic field has less of an impact on the present day radionuclide concentration than a more recent field excursion of the same magnitude and duration, but for practical purposes this is negligible. For ^{14}C, with its comparably very short half-live of 5730 a, corrections are always smaller than ~2 % because the magnetic field intensity has remained fairly constant during the past ~10 ka, when most of the ^{14}C extant today was produced.

Later Jozef and I showed that effective production rates also depend to some extent on the shape and size of a sampled boulder, because cosmic ray neutrons are more easily lost back to the atmosphere from a non-flat sample than from a flat surface (Masarik and Wieler, 2003).
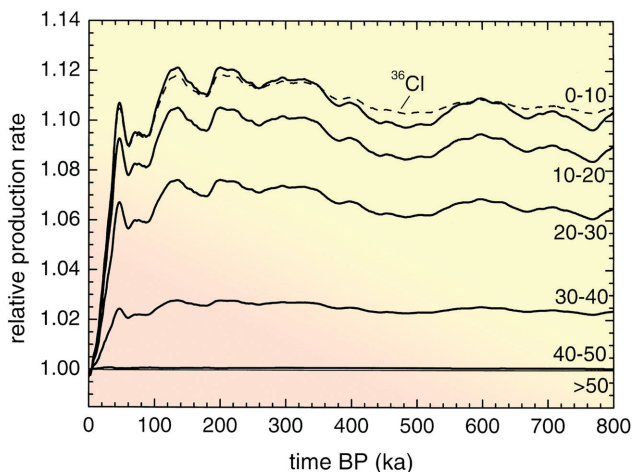

Figure 4.10   Effective integrated cosmogenic nuclide production rates, corrected for variations in geomagnetic field intensity for samples exposed at the Earth's surface during the past 800,000 years, calculated by Masarik *et al.* (2001a). The different curves are for different latitude ranges (marked at right, in degrees). Differences from present day values are negligible for latitudes >40° and hardly exceed 10 % even at the equator. Figure from Masarik *et al.* (2001a) with permission from Elsevier.

4.4 *In situ* [14]C in Terrestrial Samples

To a scientifically interested public, carbon-14 is without doubt the best known radioactive nuclide used for dating purposes. When I tell someone that we measure ages of rocks with radioactive nuclides, the response is often: "Oh I know, carbon-14". This refers to the classical ^{14}C dating of organic material, in which the cosmogenic radionuclide ^{14}C is produced in the atmosphere and subsequently incorporated into trees and other plants. In fact, organic ^{14}C dating is by far the most widely used method for isotopic age determination, today overwhelmingly by using Accelerator Mass Spectrometry. However, ^{14}C is also produced as a cosmogenic nuclide in solid matter, mostly by spallation of oxygen atoms by fast neutrons. But this *in situ* produced ^{14}C is rather rarely used in terrestrial applications. A seemingly good reason for this could be viewed in the short half-life of ^{14}C, which limits the time frame available for study to about 20,000 years at best, much less than the up to several million years covered by other radionuclides such as [10]Be. However, it is precisely the much shorter half-life of ^{14}C which makes *in situ* [14]C an attractive addition to the cosmogenic radionuclide toolkit. Not only is ^{14}C well suited for dating very young surfaces, but in combination with a long lived nuclide, it also allows the detection of complex exposure histories caused by interruptions in surface exposure over timescales ranging from the latest Pleistocene to the Holocene. Examples are interruptions caused by glacier re-advances, sediment transport, changes in surface erosion rates, and mass removal events (Hippe, 2017).

In situ ^{14}C in terrestrial samples so far is mostly studied only in niche applications because the analyses are difficult and time consuming. The difficulties include the needs for quantitative extraction of very low amounts, separation from atmospherically-produced ^{14}C, and ultralow blanks. Pioneering work was done at the University of Arizona by Tim Jull and Nathaniel (Nat) Lifton (Lal and Jull, 1994; Lifton *et al.* 2001). For his PhD thesis, Nat built a ^{14}C extraction line for quartz samples whose main features were a lower blank than obtained in previous systems, and – most importantly – the ability to extract ^{14}C as CO_2 only (preventing potential losses of CO) and to quantitatively separate the *in situ* [14]C from atmospheric or organic contamination. We therefore decided to build our own ^{14}C extraction line by essentially following the procedure developed in Tucson. Nat Lifton welcomed Florian Kober to visit his lab and kindly introduced him to his philosophy of ^{14}C extraction and its intricacies. Nat remained a constant source of support and inspiration during the construction of our facility in Zürich.

We copied much of the procedure developed by Nat Lifton, but added some important modifications. First, our extraction line is made of stainless steel tubing, not glass. All of our noble gas extraction and purification lines are stainless steel, and our workshop has extensive expertise in building metal-based ultrahigh vacuum systems. We therefore relied on this experience also for ^{14}C extraction, although common wisdom at the time seemed to be that only a glass line would guarantee a sufficiently low carbon blank. This turned out not

to be true. Second, we heated the quartz samples to about 1600 °C instead of the 1200 °C used in Tucson. This allowed us to omit the need for lithium metaborate ($LiBO_2$) as fluxing agent, eliminating one source of blank carbon. Third, the MICADAS 200 kV AMS system at ETH/PSI in Zürich (Fig. 3.2b) can be fed with CO_2, avoiding the sample graphitisation step, another potential source of blank carbon.

Our system as of 2009 (Fig 4.11) is described by Hippe *et al.* (2009). One day, Tibor Dunai offered to finance a doctoral student for two years with remaining funds of the CRONUS-EU programme if I could guarantee follow up support. Christian Schlüchter gave this guarantee, and so Florian Kober and I could happily welcome Kristina Hippe in our team in 2008. Kristina had completed her Master's thesis at the Freie Universität Berlin and arrived in Zürich when Florian and our workshop were working on the completion of the ^{14}C line. Kristina's first task was to set up analytical protocols and carry out an extensive test programme, consisting of blank, standard, and sample reproducibility tests and much more, all with great support from the AMS team at ETH, especially Lukas Wacker. When the line became operational around 2010 it was one of the very few systems that allowed routine analyses of *in situ* terrestrial ^{14}C. Kristina and her colleagues used ^{14}C in conjunction with other cosmogenic radionuclides to study denudation rates and sediment storage in the Bolivian Altiplano and the
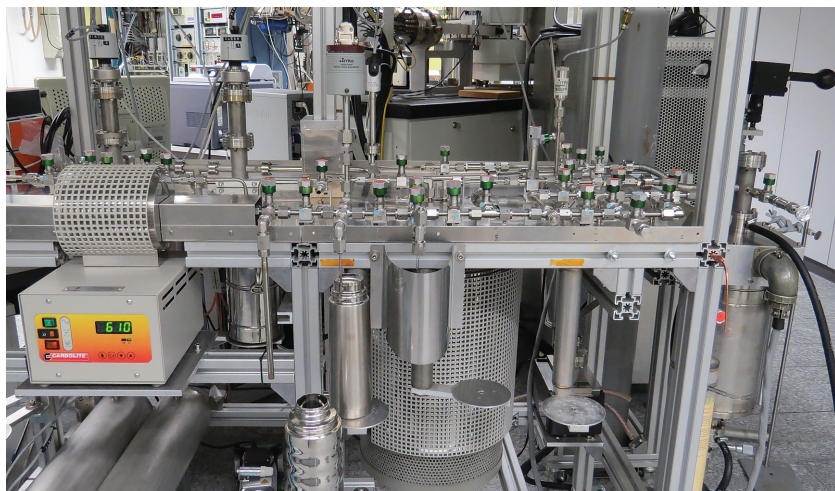

Figure 4.11   Extraction line for *in situ* cosmogenic ^{14}C in quartz at ETH, built in 2009 (Hippe *et al.* 2009). This is an essentially metal only line based on technologies used for noble gas extraction lines. Carbon is extracted from quartz at temperatures of ~1600 °C in the presence of oxygen. This circumvents the use of a flux agent. The CO_2 samples can be directly analysed with the 200 kV Micadas AMS instrument at ETH shown in Figure 3.2, bypassing graphitisation of the sample gas.

deglacation history in the Gotthard region in the Swiss Alps after the last ice age (Hippe *et al.*, 2012; 2014). An overview of scientific problems to be addressed with ^{14}C is given in her review paper (Hippe, 2017). A remarkable example is the ^{14}C depth profile presented by Lupker *et al.* (2015) along a quartzite core in Spain from the surface down to about 15 m. These data allowed Maarten Lupker to constrain the fraction of ^{14}C produced by secondary cosmic ray muons. Muons have a considerably larger depth range than neutrons and thus become the dominant producer of ^{14}C below a few meters depth, but their contribution should already be taken into account also in near-surface samples.

While ^{14}C is by now well integrated into the cosmogenic nuclide tool box, its measurement remains very time consuming, which results in a very small number of analyses overall, *e.g.,* compared to the workhorse ^{10}Be. Fortunately, sometimes even very few ^{14}C data provide important additional information. For example, Fogwill *et al.* (2014) complemented ^{10}Be analyses and ice sheet modelling with two ^{14}C analyses to reconstruct the evolution of two major ice streams entering the Weddell Sea in West Antarctica over the past 20,000 years. Nevertheless, more efficient ^{14}C analysis protocols and further reductions of blank values are highly desirable. An important step in this direction is the new ^{14}C extraction line that Maarten Lupker, Kristina Hippe, Lukas Wacker, and colleagues set up at the ETH AMS facility (Lupker *et al.*, 2019). Paul Muzikar discusses recent progress in combining ^{14}C and ^{10}Be analyses and gives an overview of operating *in situ* ^{14}C facilities (Muzikar, 2020).

5. NOBLE GASES IN WATER – THE COLLABORATION WITH EAWAG

Let me turn back the clock one last time, to the year 1986. Rolf Kipfer, better known to many as RoKi, with his fresh ETH Diploma in Geophysics, was about to start his doctoral thesis in Peter Signer's group. We had some good ideas for Rolf, but no mature project yet. Coincidentally, around that time, Thomas (Tommy) Gold at Cornell University approached Peter with his theory of an abiogenic origin of much of Earth's methane (Gold, 1987). Gold hypothesised that the Devonian Siljan Crater in Sweden, Europe's largest impact structure, might be a suitable source of abiogenic methane from the Earth's deep mantle. He suggested that we test this by measuring the isotopic composition of helium collected from boreholes at Siljan. As many will remember, Tommy Gold was a very charismatic person and we were quite intrigued by his idea. We were thinking that maybe we could help solve the world's energy problem (at that time global warming was still less of an issue than a possible global oil and gas shortage!). So we all – including RoKi – thought for a while that he had found his doctoral project. However, the work never got off the ground, most likely fortunately so, since Gold's hypothesis fell completely out of favour.

5.1 On a Wrong Track to Cold Fusion

But once again we wondered for a short while whether RoKi and the rest of us might contribute to solve the world's energy problem. On my way back from the 1989 LPSC, Otto Eugster of the University of Bern told me about a potentially sensational discovery. Fleischmann and Pons (1989) claimed to have observed nuclear fusion of deuterium atoms in an electrochemical reaction on a palladium electrode at room temperature. Although probably pretty much the entire scientific community was sceptical, the ensuing Cold Fusion hype was overwhelming, something I had never experienced before and have never experienced since. Reprints of their article were circulated worldwide by fax machines. The fax that I received after returning to Zürich was barely decipherable, so must have been a perhaps fifth or tenth generation copy. The idea of fusing hydrogen atoms at low temperature was not new. So called muon-catalysed fusion works well, although so far it is not a useful energy source because the energy required to produce muons exceeds the fusion output. At the Paul Scherrer Institute (PSI) near Zürich, muon-catalysed cold fusion had been studied for about ten years. Therefore, the group of Claude Petitjean decided to repeat the Fleischmann and Pons experiment, as did many other groups worldwide. We were asked to measure the ^{3}He and ^{4}He supposedly produced in the palladium electrode. To ensure that any ^{3}He present resulted from fusion reactions and not simply from the decay of tritium originally present in the heavy (deuterium-enriched) water, we had insisted that the experiment be performed with tritium-free heavy water. This was not an easy requirement, since deuterium enrichment most likely also leads to even stronger

tritium enrichment, unless one had started with "old" water, such as from glacial ice. Well, obviously this was not done, as the palladium sample analysed by RoKi showed a huge ^{3}He signal, clearly from tritium which must have been highly enriched in the heavy water. Our extraction line subsequently delivered for months a very high ^{3}He blank left over from that unfortunate sample, preventing many critical analyses. In any case, the PSI experiment gave no indications of fusion reactions *à la* Fleischmann and Pons (Blaser *et al.*, 1989). The upper limit of ^{4}He was at least six orders of magnitude below expectations for a neutron-free fusion rate as proposed by Fleischmann and Pons (1989). So, for a second time, we failed to do our part to solve the world's energy problem.

5.2 On the Right Track: Noble Gases in Lakes, Groundwaters and More

In the late 1980s, Friedrich Begemann brought together researchers working in different fields of noble gas cosmo- and geochemistry at one of the meetings at Ringberg Castle in Bavaria (see Box 3.1). Peter Schlosser from the University of Heidelberg introduced us to noble gas hydrology. He told us about his passion shared with Dieter Imboden in using physics to solve environmental problems. Dieter was setting up his research group at the Swiss Federal Institute of Aquatic Science and Technology near Zürich (better known as Eawag) and the newly formed Department of Environmental Science at ETH. However, a close collaboration between Peter Schlosser and Dieter Imboden was not possible at that moment, since Peter was about to move to the Lamont-Doherty Earth Observatory of Columbia University in New York to establish a research team for noble gas hydrology with focus on oceanography. Peter therefore recommended that we contact Dieter. This proved to be an excellent and remarkably fruitful idea, which led to our group's involvement in noble gas hydrology for more than 30 years, until this day. The most important person in this story is Rolf Kipfer who, thanks to Peter Schlosser's advice and Dieter Imboden's commitment, finally found his dissertation topic and his lifelong passion for noble gases in all kinds of waters.

Together with Heiri Baur, Markus Hofer and Urs Menet, RoKi set up the analysis techniques for determining noble gas concentrations and isotopic compositions in water samples. First, RoKi and his fellow doctoral student Werner Aeschbach-Hertig, together with their supervisor Dieter Imboden, investigated water dynamics in lakes. Over the years, RoKi's research group at Eawag broadened their interests to include groundwater dynamics, palaeoclimate reconstructions using groundwater aquifers and speleothems, contamination of groundwater with arsenic, gas monitoring in the field with portable mass spectrometers, and other topics, many of which have direct impact on society. From this large research programme I will discuss a few select studies in the following, mostly projects done in collaboration with our group and biased towards work where I was personally involved.
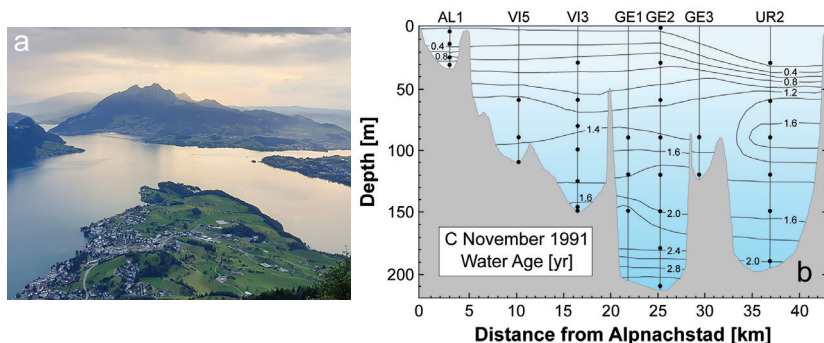
Figure 5.1 **(a)** Part of Lake Lucerne in central Switzerland. **(b)** Tritium-^{3}He ages (in years) along a transect of the lake at the beginning of winter. Using these data, Aeschbach-Hertig *et al.* (1996a) were able to study mixing of water in the different basins of the lake. Figure from Aeschbach-Hertig *et al.* (1996a) with permission from the American Society of Limnology and Oceanography.

5.2.1 A Noble Gas Perspective on Lakes

The dynamics of water bodies in lakes can be studied by tritium-helium dating, based on the radioactive decay of ^{3}H to ^{3}He with a half-life of 12.3 years. Atmospheric nuclear bomb tests in the 1950s and early 1960s delivered large amounts of tritium to the atmosphere, oceans, and lakes such that until today T concentrations are above their natural (pre-bomb) levels. Analysis of the ^{3}H and ^{3}He concentrations in a water sample allows one to determine its "tritium-^{3}He (T-^{3}He) age", which in the simplest case represents the time elapsed since the respective water parcel was separated from gas exchange with the atmosphere. Igor Tolstikhin developed the method in 1969 in Russia (Tolstikhin and Kamenskiy, 1969). Tritium concentrations in water are often measured by two successive ^{3}He analyses. A sample that has been completely degassed for a first analysis of ^{3}He is stored for a few months to build up tritiogenic ^{3}He in the laboratory and is then analysed a second time, which yields the tritium concentration of the water. In our laboratory, the high sensitivity Tom Dooley mass spectrometer (Section 3.1.8) is very well suited to measure even low concentrations of tritium in relatively small water samples. Actually, nominal T-^{3}He ages often do not represent true times when one water parcel got isolated from the atmosphere, but rather reflect mixing of multiple water masses with different histories. The T-^{3}He dating technique is very powerful precisely for studying such mixing processes. A fine example is provided in the dissertation of Werner Aeschbach-Hertig, who with his colleagues studied the water mixing dynamics in Lake Lucerne, one of the most beautiful lakes in the Alps (Fig. 5.1; Aeschbach-Hertig *et al.*, 1996a). It has a remarkably complex topography, consisting of six distinct basins divided by sills. In winter, significant density differences between individual basins drive

deep water exchange between them. Werner dubbed Lake Lucerne the "Swiss Miniature Ocean", alluding to work by others who study ocean mixing processes by T-^{3}He dating. Tritium-He dating also allowed Roland Hohmann in his dissertation to determine the renewal rates of deep water in Lake Baikal, the deepest and by volume largest lake on Earth (Hohmann *et al.*, 1998). In several further studies, RoKi, Werner Aeschbach-Hertig, and colleagues determined the fluxes of mantle-derived noble gases, *e.g.*, in Lake Van in Anatolia, and Laacher See in the Eifel in Germany (Kipfer *et al.*, 1994; Aeschbach-Hertig *et al.*, 1996b). A contribution from mantle gas is most conspicuous in helium, since the ^{3}He/^{4}He ratio in the mantle differs strongly from the atmospheric value.
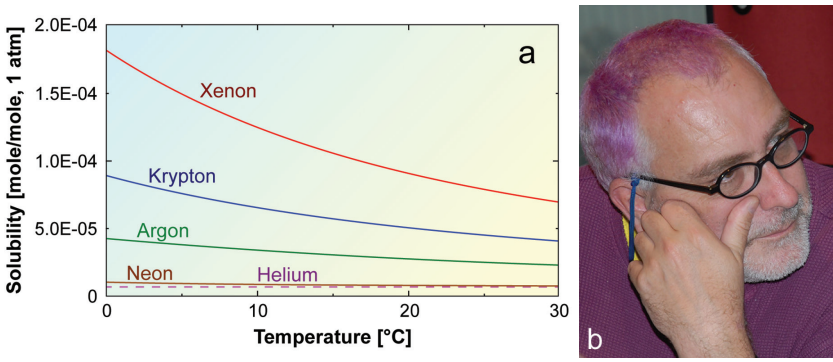
Figure 5.2 **(a)** The solubility of noble gases in water decreases with increasing temperature. The decrease is more pronounced for the heavier noble gases. **(b)** Rolf Kipfer (RoKi) in 2010.

5.2.2 Noble Gases in Groundwater and Speleothems as Palaeotemperature Archives

Noble gases in suitable aquifers provide information on palaeotemperature, because their solubilities are temperature dependent, especially for Ar, Kr, and Xe (Fig. 5.2). A precise determination of the concentration ratios of noble gases in groundwater samples with known infiltration ages therefore allows one, for example, to determine mean annual temperature differences between the Last Glacial Maximum (LGM) and the Holocene. Dissolved noble gases are particularly useful palaeotemperature recorders because they are insensitive to chemical and biological processes. After completing his doctoral thesis at ETH/Eawag, Werner Aeschbach-Hertig worked on this topic as a postdoc in Peter Schlosser's group at Lamont, before he returned to Europe, first to Eawag and then to the University of Heidelberg. Werner developed an improved scheme to correct for noble gases often present in water in excess of concentrations in equilibrium with the atmosphere (Aeschbach-Hertig *et al.*, 2000). Urs Beyerle and co-workers applied a similar correction for such "excess air" to data from an aquifer in

Switzerland and concluded that the mean annual air temperature in central Europe during the last ice age was at least 5 °C below the Holocene average (Beyerle *et al.*, 1998). By compiling data from many aquifers, Seltzer *et al.* (2021) reported similar temperature differences between the LGM and the Holocene for mid-latitudes and tropical regions, arguing against earlier claims that mean air temperatures near the equator were barely cooler during the LGM than today.

I had so far participated in only a few groundwater studies, but I became involved in the decoding of an even more spectacular palaeoclimate archive: speleothems (Fig. 5.3). When visiting caves we are fascinated by the long calcite structures that grow slowly due to precipitation of $CaCO_3$ from meteoric water. Especially the stalagmites that grow from the cave floor are excellent palaeo-climate recorders (McDermott *et al.*, 2005). Oxygen isotopes measured along a profile parallel to the growth axis of a stalagmite are used to reconstruct the mean annual temperature during its growth phase (Fleitmann *et al.*, 2004). However, the interpretation of the oxygen record is not easy, because the O isotopic composition of the calcite is not determined by the cave temperature alone. Therefore, an independent temperature recorder in stalagmites is highly desirable. RoKi's hope was that noble gases could provide such a thermometer, based on the same physical principle that has proven so successful in aquifers, with the caveat, of course, that the amounts of water available in a stalagmite sample are very much smaller than those in a groundwater sample. Regardless, RoKi approached Dominik Fleitmann, a speleothem researcher then at the University of Bern. The resulting collaboration yielded two doctoral theses, by Yvonne Scheidegger and Elaheh Ghadiri, and also Nadia Vogel was heavily involved in this work. Nadia had found her way back to ETH and Eawag after postdoctoral positions in Paul Renne's group at UC Berkeley and the University of Bern.

The development of analytical capabilities to use stalagmites as reliable noble gas palaeothermometers truly deserves the word "challenging". There were two big problems. First, a typical calcite sample of a few hundred milli-grams contains no more than a few mg of water in fluid inclusions, compared to the typical 45 grams we use in groundwater studies. Second, and even more challenging, stalagmites not only contain water-filled inclusions but also inclusions of air (see Fig. 5.3). The noble gases in the latter have atmospheric element ratios and, if included in the gas inventory, severely disturb the temperature signal represented by the noble gases dissolved in the water inclusions. Also problematic are atmospheric noble gases adsorbed during crushing of the calcite sample cubes. To some extent, atmospheric contamination can be corrected for by the same methods as "excess air" in groundwater. However, a substantial reduction of atmospheric noble gases during sample preparation was first required. Yvonne Scheidegger developed an analysis protocol that largely achieved this (Scheidegger *et al.*, 2011). She first crushed the calcite cubes in a noble gas-free atmosphere and then selected only grains of a certain size range. Because air inclusions tend to be larger than water inclusions, this reduced contamination

by the former. In favourable cases this allowed her to correct for the remaining atmospheric noble gases and determine the cave temperature at the time the water-filled inclusions formed.
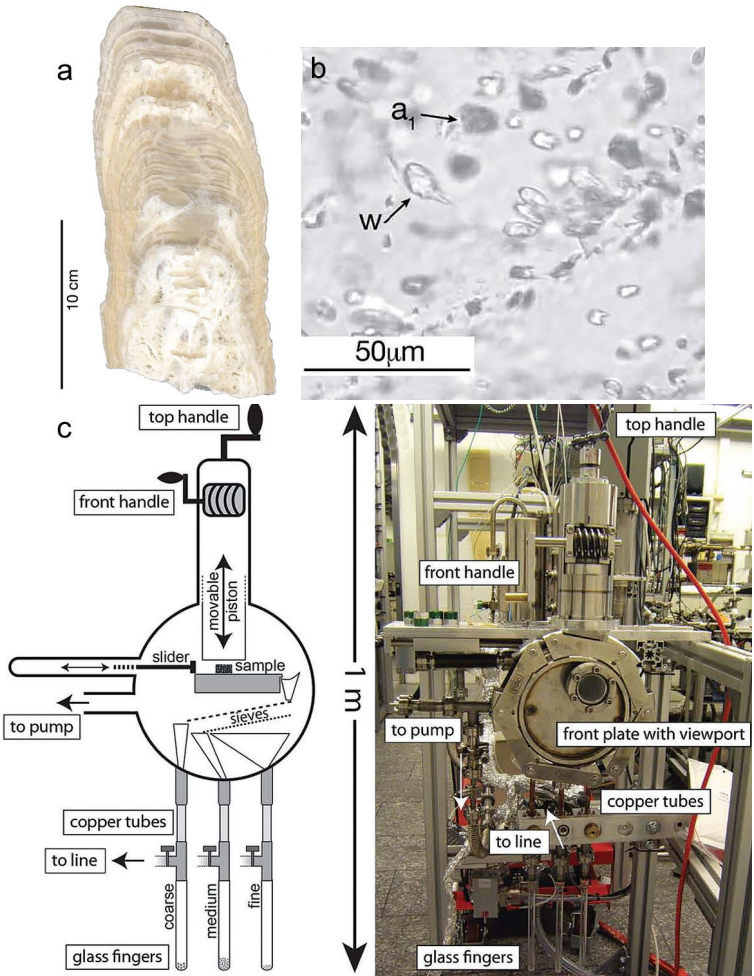

Figure 5.3　**(a)** A stalagmite sampled by Scheidegger *et al.* (2011) for palaeotemperature determinations with noble gases. **(b)** Inclusions in a stalagmite, with inclusions filled with water (w) and air (a), respectively. Image courtesy of Yvonne Scheidegger. **(c)** Combined vacuum crushing and sieving system for calcite samples from stalagmites, allowing a considerable reduction of atmospheric noble gas contamination in one of the fractions sieved *in vacuo* and hence improved noble gas palaeotemperature reconstructions. Figure from *Vogel et al.* (2013) with permission from the AGU and the Geochemical Society.

However, Yvonne's work also showed that an improved way to reduce contributions from noble gases from air inclusions was called for. We therefore approached our workshop technician Andreas Süsli with a truly difficult request: could Andreas build a device with which we could crush calcite cubes of a few mm in size and at the same time sort the crushed material into three different grain size fractions. This would all have to be done in ultrahigh vacuum and in such a way that the noble gases in the different fractions could be released and analysed without breaking the vacuum. It turned out that we had not overestimated Andreas' ingenuity. The device he constructed is shown in Figure 5.3c. The "combined vacuum crushing and sieving system" allowed Nadia Vogel to reduce atmospheric contamination in the best sieve fraction by up to two orders of magnitude, and the noble gas temperatures she derived reliably reproduced known growth temperatures of several stalagmite test samples (Vogel *et al.*, 2013). Elaheh Ghadiri then used the technique to determine the temperature reconstruction of the last glacial-interglacial transition (Younger Dryas) and the altitude gradient of this temperature with stalagmites in the Swiss Jura (Ghadiri *et al.*, 2018, 2020).

The vacuum crusher and siever once again demonstrated the enormous advantage of having highly qualified and well trained technical personnel fully integrated into the research group, enabling close daily interaction with the scientists. This is a big asset offered by ETH. Other examples already mentioned include the Closed System Stepped Etching devices, especially the "gold and platinum line", and the "Compressor ion source" in the Tom Dooley mass spectrometer.

5.2.3 Mass Spectrometry in the Field

The last topic I would like to raise is unrelated to my own work, but I mention it because noble gas analysis directly in the field has a promising future. The classic way isotope geochemists and environmental scientists analyse noble gases in fluid or gaseous samples is to collect them in the field in some type of vessel. The samples – usually in very limited numbers – are then transported to a laboratory to be analysed there with more or less sophisticated equipment. In many cases direct on site analysis of gas concentrations and perhaps also key isotopic ratios would be highly beneficial, as this would reduce logistics such as sample storage and transport, and, most importantly, allow on line monitoring or preliminary investigations that would help select the most appropriate samples for subsequent detailed laboratory analysis. The dynamics of gases or fluids in environmental systems often can only be adequately studied with a large number of samples taken at multiple points in space and time. A promising path toward this goal is to bring the analysis system into the field. Around 1980, John Reynolds and co-workers in Berkeley had developed a movable mass spectrometry system that was self-contained except for electrical power. The system was hosted in a truck and was applied, *e.g.*, to study noble gases in fluids at Yellowstone (Kennedy *et al.*, 1985). However, continued progress in the miniaturisation of mass spectrometers

is now leading to the development of much smaller portable systems, which allow field analyses of noble gases but also of biogeochemically active gases (Mielczarek *et al.*, 2020). Matthias Brennwald, Lars Mächler, Rolf Kipfer, and colleagues at Eawag have developed a commercialised portable mass spectrometry system the size of a large suitcase (Brennwald *et al.*, 2016). It measures the partial pressure of noble gases, N_2, O_2, CO_2, and CH_4 in gaseous and aqueous matrices in environmental systems. The system allows essentially maintenance-free and autonomous operation, with power supplied by, *e.g.*, two conventional car batteries. Yama Tomonaga and co-workers used this device to monitor the free gas phase in an underground rock laboratory in Switzerland in the context of a large scale radioactive waste management test (Tomonaga *et al.*, 2019). The system has also been applied, for example, at a CO_2 capture facility in Norway (Weber *et al.*, 2021), to analyse noble gases, CO_2, and N_2 at the East African Rift system in Tanzania within a few hours of sampling (Mtili *et al.*, 2021), and to study geogenic arsenic contamination of groundwaters with noble gases (Lightfoot *et al.*, 2022).

6. CONCLUDING REMARKS

Looking at programmes of geo- and cosmochemistry meetings, I am always impressed by how much science can be illuminated by a single group of elements – the noble gases. I have covered a very small part of this in these pages, but especially at dedicated noble gas meetings like the DINGUE series, I am always amazed at what colleagues are working on that I had no idea about. This fascinating aspect is not unique to noble gases, but at least from my point of view, noble gas geo- and cosmochemistry represents a particularly striking example. Alex Halliday notes in his preface to the book about noble gas geo- and cosmochemistry I co-edited with my colleagues Don Porcelli and Chris Ballentine (Porcelli *et al*., 2002) that "discoveries that have been made with noble gas geochemistry are of such a profound and fundamental nature that earth science textbooks should be full of examples …. [and] noble gas geochemistry is a broader and more versatile field than almost any other area of geochemistry". However, Alex also points out that noble gases are not as popular in textbooks and earth science teaching as they deserve to be. This is a problem reflecting the complexities that come along with the particular advantages of noble gases. Their rarity in most environments leads to detectability of a multitude of "components" produced by specific processes that would go unnoticed for most other elements. Minoru Ozima and Frank Podosek noted in the first edition of their classic book on noble gas geochemistry that "noble gas geochemistry often seems to non-practitioners to have much the air of the secret society and its dark art". I would add that even practitioners can quite easily get lost in the component jungle of the "noble gas alphabet". In the preceeding pages, I hope to have dispelled some of the darkness from the art of our beautiful area of science.

I also hope that this article reflects how much I enjoyed and continue to enjoy being part of a community whose activities range from studying the Sun, the early solar system and its later history, cosmic rays, meteorite delivery, and interstellar processes, to the history of and processes in the Earth, from its interior to its surface.

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LIST OF ACRONYMS

AMS	Accelerator Mass Spectrometry
BMG	Bulk Metallic Glass (Genesis target material)
CAI	Calcium-Aluminum rich Inclusions (in meteorites)
CME	(solar) Coronal Mass Ejections
CSSE	Closed System Stepped Etching (in vacuo)
CRONUS	Cosmic Ray Produced Nuclide Systematics on Earth
DINGUE	Developments in Noble Gas Understanding and Expertise (scientific meeting series, "dingue" = crazy in French)
DOS	Diamond-like Carbon on Silicon (Genesis target material)
ETH	Eidgenössische Technische Hochschule Zürich
EUROMET	European Programme to search for meteorites in Antarctica and hot deserts
EUV	Extreme Ultraviolet radiation
FIP	First Ionisation Potential
FIT	First Ionisation Time
GCR	Galactic Cosmic Rays/Radiation
ICD	Inefficient Coulomb Drag hypothesis
ISM	Interstellar Medium
LCPB	L Chondrite Parent Body break-up event

LGM	Last Glacial Maximum
LPSC	Lunar and Planetary Science Conferences (Houston TX)
PLAC	Platy Hibonite Crystals (in meteorites)
Q	Noble gas component in meteorites (from lat. Quintessence)
SCR	Solar Cosmic Rays (energetic particles)
SEP	Solar Energetic Particles
SIMS	Secondary Ion Mass Spectrometry
SRIM	Stopping and Range of Ions in Matter (software package)
SW	Solar Wind
SWC	Apollo Solar Wind Composition experiment
UV	Ultraviolet radiation

INDEX

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RAINER WIELER studied physics at ETH Zürich. After post-diploma studies on problems of developing countries at ETH with a one-year practical stay in Ecuador, he returned to science and in 1981 received his doctoral degree from the Department of Earth Sciences at ETH with a thesis on noble gases in lunar samples. He remained at ETH and habilitated in 1991 with a thesis on noble gases in primitive meteorites. In 1994, he became head of the Laboratory for Noble Gas Cosmochemistry and Geochemistry at ETH, where he was promoted to Professor in 2000. After his retirement in 2014, he remains a visiting scientist at ETH.

Rainer Wieler's scientific interests include the formation and history of the solar system, particularly as reflected in noble gases in extraterrestrial samples, the elemental and isotopic composition of the Sun, particularly as reflected in the solar wind, and the history of extraterrestrial matter as reflected in "cosmogenic" noble gases and radionuclides produced by interactions with galactic cosmic radiation. He also evaluates how cosmogenic nuclides can affect the isotopic composition of elements of cosmochemical interest. In collaboration with geoscientists, he uses cosmogenic noble gases and radionuclides as tools in quantitative geomorphology by determining ages and erosion rates of landscapes. He has also been involved in the analysis of noble gases in water samples ranging from lakes to tiny water inclusions in speleothems.

Rainer Wieler is a Fellow of the Meteoritical Society and asteroid (6366) Rainerwieler was named after him by the International Astronomical Union.