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Isotopes: From Earth to the Solar System

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INTRODUCTION

I was born into a working-class family in the industrial city of Hamilton, Canada, in 1930 (although there was no work to be had at that time). Except for one distant uncle, none of my many contemporary relatives had attended college. My parents, both Canadian-born, provided unlimited encouragement during my school years and willingly agreed with my wish to get a university education, as long as they did not have to pay for it. Following the good advice of my high school teachers, I applied to Queen's University in Kingston, Ontario, and was awarded enough scholarship support to make attendance possible. My classmates were an interesting group, in that about half were veterans of World War II and were about 10 years older than I was. This created a serious, studious environment that suited me well.

From the beginning, I assumed that I would work in industry, the only income-producing environment I knew of, so I enrolled in the program in chemical engineering. I found the chemical part much more interesting than the engineering part, and switched to the program in pure chemistry. Because the Canadian economy depends strongly on natural resources, the program in chemistry included required courses in geology (taught by Willis Ambrose) and mineralogy (taught by Leonard Berry). These courses were influential in later career decisions.

My M.Sc. at Queen's was done with physical chemist Grenville B. Frost, a colorful character who chain-smoked roll-your-own cigarettes. He had studied at Berkeley with William F. Giaque, Canadian-born discoverer of ^{18}O and ^{17}O . My master's thesis involved calorimetric measurement of low-temperature heat capacities of vacuum-dehydrated $\text{CuSO}_4 \cdot \text{H}_2\text{O}$ and $\text{MgSO}_4 \cdot \text{H}_2\text{O}$. The crystalline form of the latter is the mineral kieserite, now believed to be abundant on the surface of Mars.

In the early 1950s, the only Canadian universities with Ph.D. programs in the physical sciences were at the University of Toronto and at McGill University, and most Canadian students wishing doctoral studies went abroad, either to England or the United States. Of the four American universities to which I applied, only Caltech and MIT offered enough financial support for survival, and I chose Caltech as the more distant and unknown (except for the internationally famous chemist, Linus Pauling).

Linus Pauling was chairman of the Division of Chemistry and Chemical Engineering, and his emphasis on molecular structure and chemical bonding pervaded the Division. It was his policy that all new graduate students should begin research within the first two weeks of their enrollment, so we all shopped around for a research project. Many chose X-ray crystallography, an exceptionally tedious subject in those days when the only "computers" were mechanical Frieden and Marchand desk calculators (one crystal structure = one Ph.D.). Inorganic chemistry professor Don M. Yost suggested that I walk across campus to talk to a new group of geochemists, most of whom had joined Professor Harrison Brown in a move from the University of Chicago to Caltech. Brown was considered a rising star in geochemistry and was hired by Robert P. Sharp (Chairman of the Division of Geological Sciences) to put Caltech on the map in this new (in 1952) field. Harrison Brown welcomed me and suggested that I talk to two of his younger associates: Clair Patterson about "the strontium problem" and Samuel Epstein about "the oxygen problem." I had no idea how these

two elements had gotten into trouble, but was quickly won over by Sam's outgoing enthusiasm. Sam Epstein (Epstein 1997) had been a post-doc at Chicago with Harold Urey, whose ground-breaking paper on "the thermodynamics of isotopic substances" was only five years old in 1952. Sam's papers on carbonate paleothermometry were just coming out (Urey et al. 1951, Epstein et al. 1953, Epstein & Lowenstam 1953). Sam apparently had a plan to extend oxygen isotope geochemistry to all of Earth science: After dealing with the oceans and meteoric waters (Epstein & Mayeda 1953), he set me, as his first graduate student, the task of extending the principles of mineral/water isotopic thermometry to the higher-temperature range of hydrothermal processes (Clayton & Epstein 1961). His next student, Hugh P. Taylor, then took care of igneous rocks (Taylor & Epstein 1962a,b). G. Donald Garlick, the third student, did metamorphic rocks (Garlick & Epstein 1967), followed by Samuel M. Savin, who covered sedimentary rocks (Savin & Epstein 1970a, 1970b, 1970c). For all of us who were students at that time, it was a golden opportunity to enter a rich field with a powerful new set of techniques. Of course, using geochemical tools on real rocks rekindled my interest in geology that was first awakened in my undergraduate courses at Queen's.

I was never very comfortable with the southern California environment and was happy to leave Pasadena after four years. I had fully expected to return to Canada, but no job opportunities appeared. The best available option was an assistant professorship in the Department of Geophysics and Geochemistry at the Pennsylvania State University. Penn State, with its close connection to the Geophysical Laboratory, was a major center for experimental petrology and I learned the use of high-pressure hydrothermal apparatus. I shared a lab with Leonard Herzog, a recent MIT Ph.D. in geochronology, who was also an assistant professor, while he simultaneously founded a new company, Nuclide Corporation, to build mass spectrometers. My two years at Penn State were mostly uneventful, and I was very grateful for an opportunity to move to the University of Chicago in 1958.

In the 1940s and 1950s, the Enrico Fermi Institute of the University of Chicago had been the birthplace of modern isotope geochemistry, under the leadership of Harold Urey (Nobel Prize in 1934 for the discovery of deuterium) and Willard F. Libby (Nobel Prize in 1960 for carbon-14 dating). The Institute had been the home of most of the Caltech geochemistry group with whom I had worked. Harold Urey reached the (then) mandatory retirement age of 65 in 1958, and moved to UCSD, where he had 20 more scientifically productive years. He had worked on isotope separation as part of the nuclear bomb project in World War II, and moved to Chicago in 1945. Since his scientific career had been interrupted by the war work, he set off in a new direction: application of chemistry to the study of the Moon and planets. A part of this work was the development of oxygen isotope paleothermometry, mentioned above. With Harold Urey's retirement from Chicago in 1958, the Department of Chemistry and the Institute for Nuclear Studies (later the Enrico Fermi Institute) sought to continue their activity in geochemistry, which led to my move to Chicago just after Urey departed. In 1962, the previous Departments of Geology and of Meteorology were merged into the Department of the Geophysical Sciences, which I was invited to join. The joint departmental appointments were very beneficial to me, both as

a stimulus to maintain intellectual breadth and as a source of graduate students of diverse backgrounds.

In 1951, with the participation of his post-doc, Sam Epstein, Urey hired a laboratory technician with a Chicago bachelor's degree in chemistry named Toshiko Mayeda. When Urey left Chicago, I inherited much of his laboratory, and persuaded Tosh Mayeda to stay. She became the mainstay of our laboratory studies and student education for the next 45 years until her death at age 81. She played an essential role in almost everything that follows in this report.

In attempting to organize material for this paper, I was struck by the observation that two or three central themes can be parlayed into a lifetime career. One of these themes came directly from my graduate work: laboratory measurements of isotopic equilibrium fractionation factors for materials of geologic interest. Closely related to that theme is the study of mineral/fluid interactions in natural materials. Another theme has been the study of isotopic variations in extraterrestrial materials, in which chemical and physical processes may have occurred that are not known in terrestrial environments. This theme, in turn, has led to laboratory studies of evaporation of rocks and minerals. In the descriptions that follow, it is clear that the studies based on these themes have involved a large number of graduate students, post-docs, and other collaborators, to whom I express my thanks. By focusing this review on these two themes, I have omitted direct reference to the research of many other excellent graduate students and research associates whose work contributed to the strength of our program.

ISOTOPIC THERMOMETRY

Fortunately, much of terrestrial inorganic geochemistry occurs close to thermodynamic equilibrium. This simplification may be less common in biogeochemical processes. The original calibrations of the calcium-carbonate/water oxygen isotope geothermometers were done by analysis of either inorganic precipitates (McCrea 1950) or tests of living marine organisms grown at known temperatures (Epstein et al. 1951, 1953). My first hydrothermal experiments (Clayton 1961) confirmed the earlier results at low temperature and extended the experimental range to 700°C by an exchange reaction, which allowed a test for equilibrium by approaching that state from opposite directions. Further laboratory studies of carbonate-water systems were carried out by graduate students Jim O'Neil and Dave Northrop (O'Neil et al. 1969, Northrop & Clayton 1966). A key piece of the carbonate puzzle was provided by Taleshwar Sharma, who determined the fractionation factor for the standard phosphoric acid technique for carbonate analysis (Sharma & Clayton 1965). Jim O'Neil also measured oxygen isotope exchange equilibrium in quartz-water and magnetite-water (O'Neil & Clayton 1964, Clayton et al. 1972), providing a calibration for a geothermometer widely used for igneous and metamorphic rocks. Beginning with the mineral/water exchange experiments of Matsuhisa et al. (1978), we moved from cold-seal bombs at one kilobar to piston-cylinder apparatus at 10–20 kbar, to take advantage of the more rapid exchange rate at higher pressure. These experiments also demonstrated that the use of $^{17}\text{O}/^{16}\text{O}$ ratios along with $^{18}\text{O}/^{16}\text{O}$ ratios permitted the

classical equilibration from opposite directions to be carried out in one experiment, rather than two. Alan Matthews, visiting from Israel, did hydrothermal exchange measurements with pyroxenes and zoisite (Matthews et al. 1983a, 1983b). Further hydrothermal experiments carried out by Matsuhisa et al. (1979) revealed discrepancies among various laboratory experiments and between laboratory and rock data. These were identified much later as due to the use of water as a common exchange medium (Hu & Clayton 2003).

Meanwhile, our colleagues Julian Goldsmith and Robert Newton, experimental petrologists, were studying phase relations of the scapolite minerals and found that the silicate-carbonate meionite is unstable below about 900°C, and that the starting materials, feldspar plus calcite, recrystallize below this temperature (Goldsmith & Newton 1977). This observation suggested that we look for oxygen isotope exchange between silicates and carbonates in dry systems at high temperatures and pressures. We found that isotopic equilibration was rapid, so that calcite, rather than water, became the preferred common exchange medium for determining oxygen isotope fractionation factors among rock-forming minerals (Clayton et al. 1989, Chiba et al. 1989, Chacko et al. 1996, Hu et al. 2005).

All of the experimental measurements of isotopic fractionation factors cover only a limited range of temperatures, governed by practical considerations. Theoretical calculations, on the other hand, have no such limitations. The theory given by Urey (1947), and elaborated by Richet et al. (1977), works exceedingly well for gaseous molecules, but extension to solid phases requires additional approximations, which limit the accuracy of the results (Kieffer 1982). The best of both worlds can be achieved by using experimental data to fix the computational parameters and using the theory to extend the temperature range (Clayton & Kieffer 1991).

FLUID-ROCK INTERACTIONS

One of the early triumphs of stable isotope geochemistry was the demonstration by Craig et al. (1956) that water in geysers and hot springs is of predominantly local (meteoric) origin and is not derived from deep within the Earth. We applied the same strategy to oil-field brines (sometimes called connate waters) (Clayton et al. 1966) with a similar result: They are derived from local rain and are not trapped ancient seawater as was implied by the name connate. Craig's (1956) interpretation of the thermal water data was that water underwent isotopic exchange with the host rocks, leading to an increase in $\delta^{18}\text{O}$ of the water, with little or no change in δD . The rocks should, therefore, show a complementary decrease in $\delta^{18}\text{O}$, by an amount that is determined by the integrated water/rock ratio. We verified this prediction by analysis of drill cores and cuttings from geothermal areas in a water-rich system in New Zealand (Clayton & Steiner 1975) and a water-poor system from California (Clayton et al. 1968).

Rock-water interaction on a much larger scale occurs on the ocean floor, both at high temperature ($\sim 300^\circ\text{C}$ at spreading centers) and low temperature ($\sim 0^\circ\text{C}$). Oxygen isotope studies of these processes were carried out by graduate students Karlis Muehlenbachs (Muehlenbachs & Clayton 1972, 1976) and Emi Ito (Ito &

Clayton 1983). These studies showed the importance of hydrothermal circulation of seawater at spreading centers in maintaining a steady-state difference of about 6‰ in $\delta^{18}\text{O}$ between rocks of the sea floor and the overlying seawater. Another graduate student, Richard Becker, measured oxygen isotopes in the minerals of the banded-iron-formations (BIF) of the Hamersley Group in Western Australia as a test of the long-term variability of $\delta^{18}\text{O}$ of seawater preserved in these Archean chemical sediments (Becker & Clayton 1976). The approach was to use a mineral-pair (quartz-magnetite) for thermometry, then to use the mineral/water equilibrium to estimate the oxygen isotopic composition for the water. The same strategy was followed in meteoritic samples (Onuma et al. 1972b), with surprising results (Onuma et al. 1974).

Water-rock interaction is also important in regional metamorphism, as was shown by Engel et al. (1958) in carbonate rocks, by Schwarcz et al. (1970) in pelitic rocks, and by James & Clayton (1962) in BIF.

EXTRATERRESTRIAL ISOTOPES

With a thriving research program in terrestrial geochemistry, there was little incentive to venture into meteorite studies, where the samples are of unknown provenance without field relations, and even the problems were mostly unidentified. However, in 1963, my colleague, Edward Anders, a confirmed meteoriticist, prevailed upon me to do an oxygen isotope analysis of carbonate in the Orgueil carbonaceous chondrite, with the goal of comparing an “isotopic temperature” with his estimates of temperatures of formation based on volatile trace element abundances. We found the oxygen isotopic composition, $\delta^{18}\text{O}$, to be within the range of terrestrial carbonates, but the carbon isotopic composition, $\delta^{13}\text{C}$, was about 60‰ greater than that in terrestrial carbonates: A value beyond the range of any terrestrial materials (Clayton 1963). Among our conjectures concerning the origin of this $\delta^{13}\text{C}$ excess, we included the possibility of some unspecified nucleosynthetic origin. It was not until 24 years later that the source of the “heavy” carbon was discovered to be silicon carbide grains formed in presolar stellar interiors (Zinner et al. 1987). Strangely, although Ed Anders and I worked on overlapping subjects, occupied the same floor in the Enrico Fermi Institute for nearly 40 years, and were always on good terms, we never published a paper together.

The year 1969 was a spectacular year for geochemists and cosmochemists: On February 8, the Allende meteorite fell in northern Mexico, yielding two tons of a very primitive meteorite; on July 24, the Apollo 11 astronauts returned to Earth with 20 kg of well-documented lunar samples (**Figure 1**); and on September 28, the Murchison meteorite fell in Australia, providing 100 kg of organic-rich carbonaceous chondrite. Laboratories around the world had prepared for the lunar samples, and were, therefore, ready to tackle the abundant new meteorites as well. Even a dyed-in-the-wool terrestrial geochemist could not resist the attraction of all these goodies. We first tackled the lunar samples, doing $^{18}\text{O}/^{16}\text{O}$ measurements on separated minerals (mostly plagioclase, pyroxene, and ilmenite) for isotopic thermometry, just as we had done with terrestrial rocks. The results were anticlimactic in that the $^{18}\text{O}/^{16}\text{O}$ fractionations among minerals are consistent with igneous crystallization temperatures and the $\delta^{18}\text{O}$ values of the rocks are very similar to those of terrestrial basalts (Onuma



Figure 1

Opening of our first lunar sample, Apollo 11 soil 10084, in September 1969. Surrounding R. Clayton (*seated*) are Toshiko Mayeda (*blue dress*), unidentified woman (*red dress*), R. Ganapathy (E. Anders post-doc), A.T. Anderson (faculty member), R. Becker (post-doc), T. Coplen (graduate student), and S. Mayeda (Tosh's daughter).

et al. 1970). The apparent identity in isotopic composition between Earth and Moon was not an issue at that time, but it became a major issue after general acceptance of the “giant impact” model for the origin of the Moon (Hartmann & Davis 1975).

My wife Cathy and I experienced the thrill of the midnight launch of Apollo 17 in December 1972 (with geologist H.H. Schmitt on board). On that occasion, I was urged by Caltech professor Jerry Wasserburg to be more active in lunar science. That led to our entry into nitrogen isotope studies of lunar rocks and especially lunar soils, which are collectors of all manner of materials from the space environment. The work of post-docs Richard Becker, Mark Thiemens, and Serge Fourcade showed huge variations ($>30\%$) in $^{15}\text{N}/^{14}\text{N}$ of nitrogen trapped in lunar soils. It was generally assumed at that time that this nitrogen was derived almost entirely from the solar wind (Becker et al. 1976, Thiemens & Clayton 1980, Fourcade & Clayton 1984), but there was no satisfactory explanation for such isotopic variability in the Sun itself (Geiss & Bochsler 1982). This problem has been resolved by novel analytical techniques (Hashizume et al. 2000), with the conclusion that the low- ^{15}N component ($\delta^{15}\text{N} < -240\text{‰}$) is of solar origin, and the high- ^{15}N component ($\delta^{15}\text{N} > +100\text{‰}$) has a nonsolar origin. An important conclusion is that there is a large isotopic difference between solar nitrogen and terrestrial nitrogen ($\delta^{15}\text{N} = 0\text{‰}$), an issue to which we will return later.

Following our lunar nitrogen studies, a series of graduate students measured nitrogen isotopes in increasingly difficult samples: stony meteorites (Kung & Clayton 1978), iron meteorites (Prombo & Clayton 1993), terrestrial crustal rocks (Zhang 1988), and terrestrial mantle rocks (Huang 1997). In all, the known variation in $^{15}\text{N}/^{14}\text{N}$ in Solar System materials exceeds a factor of three, a far greater range than

CAI:calcium-aluminum-rich
inclusions**NMD:**non-mass-dependent

can be accounted for by any known molecular chemistry. The terrestrial ratio lies near the middle of the range.

Participation in the Apollo lunar program had a profound and permanent influence on the direction of our research program. In preparation for isotopic analyses of lunar samples, the nature of which was unknown in advance, we undertook isotopic studies of ordinary chondrites (metamorphic rocks) and carbonaceous chondrites (aqueously altered sedimentary rocks). Most of this work was done by a wonderful colleague visiting from Japan, Naoki Onuma. Oxygen isotope fractionation among separated minerals in ordinary chondrites yielded good estimates of their maximum metamorphic temperatures (Onuma et al. 1972a). A second thermometric application was more speculative: an attempt to deduce temperatures at which minerals condensed from a nebular gas (Onuma et al. 1972b), based on mineral analyses from primitive carbonaceous chondrites. We assumed that $^{18}\text{O}/^{16}\text{O}$ variations were governed by chemical equilibrium, as was the case for known terrestrial processes. It was a year later, with the introduction of $^{17}\text{O}/^{16}\text{O}$ measurements, that we realized that our assumption of equilibrium was grossly incorrect.

A new chapter began with the arrival in Chicago of Larry Grossman, fresh from his ground-breaking study of the Allende meteorite at Yale University. The meteorite contains abundant calcium-aluminum-rich inclusions (CAIs), which he recognized as primordial high-temperature condensates from a solar nebular gas. Here was an ideal target for the “cosmothermometer” of Onuma et al. (1972b). Larry did sample selection and characterization, Tosh Mayeda did mineral separation and chemistry, and I did mass spectrometry. Like all oxygen isotope analysts at that time, we used carbon dioxide as the sample gas, and determined $\delta^{18}\text{O}$ using a double-collector to measure the ratio $\frac{46}{44+45}$ (m/e of ion beams). This required an additional measurement of $\frac{45}{44}$ on the same gas. Craig (1957) had shown how to correct the mass-45 signal (predominantly $^{13}\text{C}^{16}\text{O}^{16}\text{O}$) for a small contribution from $^{12}\text{C}^{16}\text{O}^{17}\text{O}$. For a series of carbon dioxide samples with identical $^{13}\text{C}/^{12}\text{C}$, Craig’s equations predicted a correlation between 45/44 variations and 46/44 variations, with a slope of about 0.034 ($^{17}\text{O}/^{13}\text{C}$). The expected relationship was found for a variety of terrestrial samples, but a slope twice as great was found for CAI minerals, which were interspersed with the terrestrial samples, using the same carbon source (graphite, used in the conversion of O_2 to CO_2) (**Figure 2**). The terrestrial samples follow a familiar mass-dependent isotope fractionation, of the sort discussed by Urey (1947), where $^{17}\text{O}/^{16}\text{O}$ variations, expressed as $\delta^{17}\text{O}$, are about one half as large as $^{18}\text{O}/^{16}\text{O}$ variations (as $\delta^{18}\text{O}$), whereas the meteorite data define a relationship in which variations in $\delta^{17}\text{O}$ are nearly equal to variations in $\delta^{18}\text{O}$ (Clayton et al. 1973). At that time, there were no known chemical processes that could produce such a “non-mass-dependent” (NMD) isotope effect, whereas it was known that ^{16}O (a “primary” nuclide) was synthesized in stars by processes different from those that produced ^{17}O and ^{18}O (“secondary” nuclides). It seemed obvious that the apparent ^{16}O excesses in some meteoritic minerals, referred to as isotopic anomalies, represented incomplete homogenization in the solar nebula, a proposal that had been advanced a year earlier for neon (Black 1972). Although a nucleosynthetic origin for the oxygen isotope anomaly was consistent with the meteorite data, it lacked testability and had little predictive power. It suggested that similar

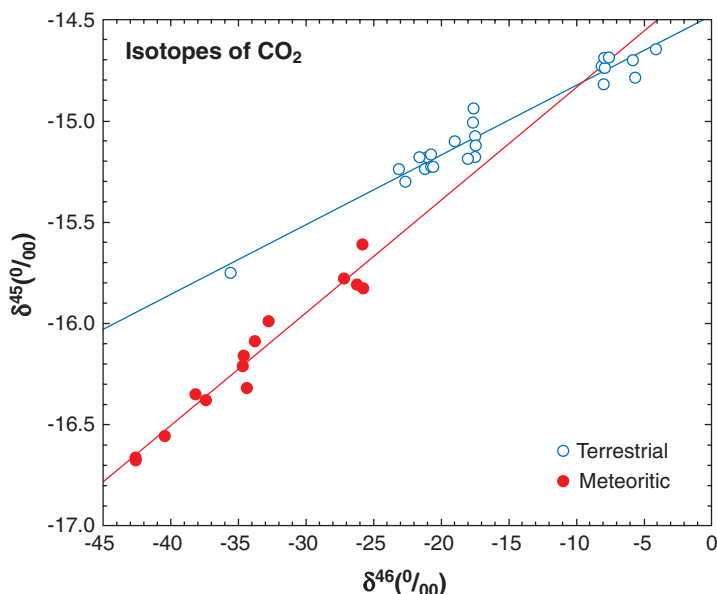


Figure 2

In May 1973, oxygen isotope analyses of terrestrial and meteoritic samples were interspersed. All mass spectrometer analyses used CO_2 as the sample gas, as was customary at that time. The data plotted are “raw” δ -values relative to the laboratory working standard, with no corrections applied. The ratio of scale factors is 15 : 1. Note that this is not a three-isotope graph because the ordinate is primarily a carbon isotope ratio and the abscissa is primarily an oxygen isotope ratio.

heterogeneity would be found for elements with similar nuclear and chemical histories, especially magnesium and silicon, but these have not been found (Clayton & Mayeda 1977, Mittlefehldt et al. in press). A purely chemical means to generate a slope-1 line in the oxygen three-isotope graph was found by Thiemens & Heidenreich (1983) in the laboratory synthesis of ozone (O_3) from oxygen (O_2). They attributed the effect to the phenomenon of isotopic self-shielding, as was known in one laboratory experiment (Sander et al. 1977) and in astrophysical settings (Bally & Langer 1982). More recently, Thiemens (2006) has favored a nonphotochemical mechanism based on kinetic effects of molecular symmetry (Gao & Marcus 2001).

Clayton (2002) sparked a revival of interest in photochemical self-shielding in the ultraviolet photolysis of gaseous CO in the solar nebula, based primarily on the great advances in spectroscopy (e.g., Ubachs et al. 2000), in astrophysical modeling (e.g., van Dishoeck & Black 1988), and in telescopic observations (e.g., Sheffer et al. 2002). When I first suggested the self-shielding mechanism to Larry Grossman, he replied: “That’s fine, except that it goes in the wrong direction,” i.e., it makes ^{16}O -poor minerals, not the ^{16}O -rich phases found in CAIs. The solution to that problem was simple, but not for the faint of heart: move the isotopic composition of the solar nebula (including the Sun) to the ^{16}O -rich end of the CAI array, rather than

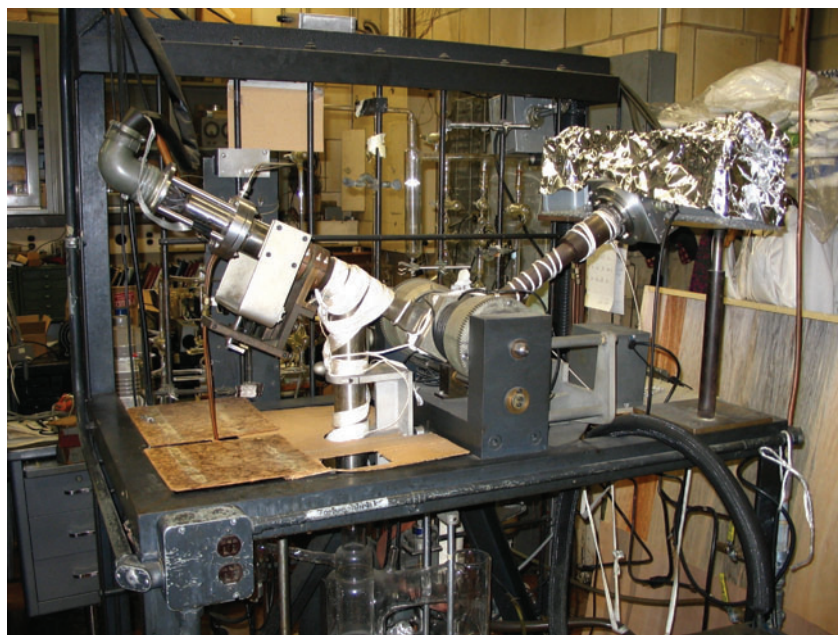
the ^{16}O -poor end, where Earth and the rest of the inner Solar System lie. Thus, this model makes a clear prediction of the solar composition, soon to be tested by isotopic analysis of the solar wind implanted in NASA's Genesis collectors.

Even without full knowledge of the underlying cause of oxygen isotope variability in meteorites, these variations have been very useful in classification of meteorites and in relating meteorites to their parent asteroids or planets (Clayton et al. 1976, Clayton 2004). This function has been especially valuable with the discovery of thousands of meteorites in Antarctica and the world's deserts. Oxygen isotope "fingerprints" have confirmed that eucrites, diogenites, and howardites are from a single parent body, as are shergottites, nakhlites, chassignites, and ALH 84001 (Clayton & Mayeda 1996). They also show genetic relationships between some stony and iron meteorites (Clayton & Mayeda 1978). From the middle 1970s until about 2000, Tosh Mayeda and I had a monopoly on the use of oxygen isotopes for meteorite classification. One result of this situation was the production of a large homogeneous database because we used the same analytical procedures and apparatus throughout. In particular, mass spectrometry was carried out on an instrument built in the University of Chicago machine shop (**Figure 3**), which was commissioned in 1959 and produced good data until 2004. Data were collected on a strip-chart recorder, and data reduction included calculation by abacus. Even meteorite dealers are aware that an oxygen isotope analysis may have a significant effect on the market value of their specimens. I am grateful to meteoritists and curators around the world for a generous supply of interesting meteorites.

During 2004 and 2005, NASA and the Lunar and Planetary Institute sponsored a series of workshops with the title "Oxygen in the Solar System." At the final workshop

Figure 3

McKinney-Nier design isotope ratio mass spectrometer, used for all Chicago oxygen-isotope measurements on meteorites.



in the series (Oxygen in the Earliest Solar System Materials and Processes), held in Gatlinburg, TN, in September 2005, I was presented with a poster purporting to show every oxygen isotope data point generated in our lab (see Frontispiece: the poster in the background shows oxygen isotopic compositions of all extraterrestrial materials, as compiled by A.M. Davis and G.J. MacPherson).

SIMS: secondary ion mass spectrometer

MICROBEAM ANALYSIS

Joseph V. Smith, a professor of mineralogy at the University of Chicago for over 40 years, was a pioneer in the development of the electron microprobe for mineral analysis. In the early 1970s, he enlisted my collaboration in the acquisition and development of an ion microprobe secondary ion mass spectrometer (SIMS) for both trace element and isotopic analysis. The only other instrument of this type in the world at that time was in the laboratory of J.V.P. Long at Cambridge University. Our ion probe was made by using an existing, unused spark-source mass spectrograph (AEI-MS 702), to which was attached a primary ion-beam column. This instrument was particularly successful for measurements of radiogenic ^{26}Mg (e.g., Hutcheon 1982, Bar-Matthews et al. 1982) and for rare-earth abundances (e.g., Simon et al. 2002). It has also been used to measure mass-dependent fractionation of magnesium isotopes caused by evaporation of silicates in the laboratory (Davis et al. 1990, Wang et al. 1999). These laboratory studies showed that evaporation of solids and melts, even at very high temperatures, is accompanied by large kinetic isotope fractionation, so that isotopic measurement of elements such as magnesium, silicon, and iron in natural materials provides an excellent measure of the degree of evaporation. An example of such an application is the fractionation of iron and nickel isotopes during passage of metallic spherules through Earth's atmosphere (Davis & Brownlee 1993). Isotopic measurements of elements that are partially lost by evaporation during the melting of chondrules should shed light on conditions and timescales of formation of common chondrules. Such was the strategy that led to the doctoral research of Munir Humayun (Humayun & Clayton 1995). He used the ion microprobe for isotopic analysis of chemically separate potassium, an element that is depleted by factors of 5–10 in bodies ranging in size from chondrules to planets. Amazingly, no isotope effects were found. This observation has led to new constraints on the environment of chondrule formation (Cuzzi & Alexander 2006).

Reynolds & Turner (1964) reported finding a component of xenon in a carbonaceous chondrite that was enriched in heavy and light isotopes, later called Xe-HL. The research group of Edward Anders spent the next 20 years in an effort to isolate and identify the solid phase in which this xenon was implanted. The meteoritic world was surprised and delighted when this phase was identified as diamond (Lewis et al. 1987). This discovery opened the field of presolar (stardust) grains: samples of the atmospheres of stars that lived before our Sun was born (Anders & Zinner 1993). Our direct involvement in the study of presolar grains was made possible by collaboration with a brilliant group of materials scientists at the nearby Argonne National Laboratory, led initially by Dieter Gruen, and subsequently by Michael Pellin. Following the lead of Papanastassiou and others (e.g., Niederer et al. 1981), we had used

RIMS: resonant-ionization
mass spectrometer

SMOW: standard mean
ocean water

the Chicago SIMS to measure nucleosynthetic isotope variations in CAIs (Hinton et al. 1987). Our first joint ventures with the resonant-ionization mass spectrometer (RIMS) at Argonne had the same goals (Spiegel et al. 1992). It soon became clear that a much more fertile field lay in the measurement of heavier elements in presolar silicon carbide and graphite grains, revealing the details of *s*-process and *r*-process neutron-capture reactions in stars (e.g., Nicolussi et al. 1998).

WHAT DOES IT ALL MEAN?

With the discovery in 1973 of oxygen isotope heterogeneity in Solar System materials, I thought that the solar nebula had not been isotopically homogenized and that some residual nucleosynthetic variations had survived. Subsequent evidence has not supported this interpretation, and a local nonnuclear production of the effects is more likely. However, it is clear that some nucleosynthetic anomalies have survived, in the form of micrometer-sized presolar grains found in all primitive meteorites (Huss & Lewis 1995). Excesses or deficits of these grains can even have small manifestations on an asteroidal scale (Dauphas et al. 2004). A related major issue, not discussed in this review, is the extent of homogenization in the solar nebula of short-lived radionuclides. If they are of galactic origin, they may have been uniformly distributed; if they were locally produced, either by a nearby supernova (^{60}Fe) or by solar irradiation (^7Be), they are unlikely to have been uniformly distributed.

As for the oxygen isotope issue, two alternative mechanisms have been proposed for local generation of an ^{16}O -rich and an ^{16}O -poor reservoir from an initially homogeneous nebula: (*a*) a NMD chemical reaction, analogous to the ozone synthesis (Thiemens & Heidenreich 1983), but probably involving other oxygen-bearing molecules, and (*b*) a photochemical self-shielding process, probably involving carbon monoxide (Clayton 2002). The latter model explicitly predicts a solar isotopic abundance near that found in CAIs, i.e., $\delta^{18}\text{O} = \delta^{17}\text{O} \approx -50\%$ relative to standard mean ocean water (SMOW). The former model makes no specific prediction of the solar composition, but generally assumes a value near that of Earth. Both mechanisms necessarily imply formation by chemical disequilibrium. For example, formation of ozone in Earth's stratosphere requires input of solar energy for photodissociation of O_2 , and leads to steady-state concentrations of O_3 that are many orders of magnitude greater than the equilibrium value. Similarly, photodissociation of CO in the solar nebula leads to concentrations of atomic O and molecular OH that are far greater than equilibrium values (Sternberg & Dalgarno 1995), making the nebula more oxidizing than would be expected from the equilibrium oxygen fugacity.

Of the various scenarios that have been proposed for chemical processes in the solar nebula, leading to the formation of planets, satellites, asteroids, comets, and dust, one that I find most appealing is some version of the X-wind model of Frank Shu and colleagues (e.g., Shu et al. 1996). In the context of the observations discussed above, this model provides a natural setting for ultraviolet photolysis of gaseous CO: near the X-point, at a distance of only 0.05 AU from the young Sun. This environment is suitable for condensation of CAIs from a gas of solar oxygen isotopic

composition, and subsequent exchange with a gas that has been enriched in ^{17}O and ^{18}O by photochemistry. This environment is also suitable for chondrule formation, perhaps as liquid condensates, containing ferrous-iron-bearing silicates that are far from equilibrium. The model also provides extensive radial transport of materials, both inward and outward, providing a mechanism for formation of the rocky bodies of the inner Solar System, made from matter that was once much closer to the Sun.

Chondrule formation must have been a very common process in the early Solar System: Chondrules are the principal constituent of the most abundant meteorite group—the ordinary chondrites. Their shape and internal textures provide convincing evidence that they were, briefly, molten droplets in space. John Wood (1962) discussed the possibility that chondrules formed as molten condensates from a gas, but ruled out this possibility (Wood 1967) on the ground that equilibrium condensation of chondrule melts from a solar gas would require unreasonably high pressures. This view has been almost universally accepted in the meteoritical community, so that all current models of chondrule formation are based on melting of solid precursors, rather than direct condensation as liquids (Tachibana 2006). This approach, with the assumption that chondrule chemical compositions are determined by local thermodynamic equilibrium, leads to proposals of large dust/gas enrichments (to account for the oxidation state of iron) and large nebular volumes (to account for the lack of isotopic fractionation in sulfur and potassium).

The fact that the oxygen isotopic compositions of chondrules do not, in general, fall on mass-dependent fractionation trends implies that oxygen, the most abundant element in chondrules, is not in thermodynamic equilibrium with the surrounding gas. The arguments above, based on photochemistry (requiring an external energy source), suggest that disequilibrium chemical processes may be important, particularly those involving species such as atomic O and molecular OH, both kinetically rapid oxidizing agents. This disequilibrium could account for two enigmatic properties of chondrules: (*a*) the ferrous iron content of silicates, which is much higher than expected at equilibrium, and (*b*) the absence of evidence for volatile loss (Tsuchiyama et al. 1981), which also allows condensation above the melting temperature. The latter process would explain in a natural way why the maximum temperatures of chondrule melts fall in a narrow range, which would not be expected for transient heating of solid precursors.

As noted above, variability of nitrogen isotope ratios in the lunar soils and in meteorites is very large and unexplainable by known chemical or nuclear processes. The N_2 molecule is isobaric and isoelectronic with the CO molecule. The two molecules are photodissociated in the same part of the ultraviolet spectrum, so that photodissociation and isotopic self-shielding are expected for N_2 as well as CO. Unfortunately, nitrogen has only two stable isotopes, so NMD effects cannot be recognized. Furthermore, as a molecule with no dipole moment, N_2 is invisible by most astronomical methods. There is one interesting coincidence that may prove to be important: The $^{15}\text{N}/^{14}\text{N}$ ratio in Jupiter (Owen et al. 2001) may be the same as that in the Sun (Hashizume et al. 2000), whereas both are much lower than the ratio in inner Solar System samples.

FINAL NOTES

An important component in the life of our laboratory has been the morning coffee break, held in the mass spectrometer lab. For decades, we have gathered daily around a sturdy, well-worn table to discuss science or any other topic of general interest. This has provided a testing ground for new ideas, and a focal point for always welcome visitors.

When I was a boy, I was inspired by books on science, such as those written by George Gamow. It is now a great pleasure to be able to contribute to subjects he wrote about, such as “The Birth and Death of the Sun.”

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