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A Special Issue dedicated to Robert N. Clayton

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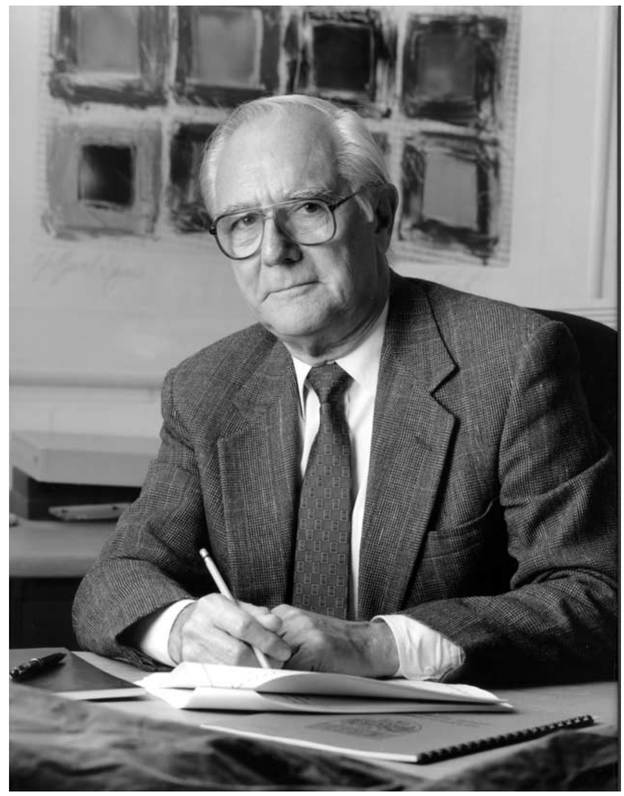
On June 30, 2001, Robert N. Clayton formally retired after 43 years of service at The University of Chicago. The papers presented in this special issue of *Geochimica et Cosmochimica Acta* are an outgrowth of the Hudnall Symposium that was held in his honor on June 7–8, 2001 in the Department of the Geophysical Sciences at The University of Chicago. The symposium was attended by his present and former students, postdoctoral fellows, and colleagues.

Bob Clayton was born in Hamilton, Ontario, in 1930 and received B.S. and M.S. degrees from Queen's University in Kingston, Ontario. In 1955 he received his Ph.D. at Caltech under the mentorship of the late Samuel Epstein in the exciting new field of stable isotope geochemistry. He then moved to Penn State University as an assistant professor (1956–1957) where, in addition to his professorial duties, he blew glass for commercial stable isotope mass spectrometers being constructed there by Len Herzog. Bob can still be seen repairing a leak or adding a new piece to an extraction line as he continues to include laboratory work in his daily routine.

In 1958, Bob joined the faculty of the Chemistry department and the Enrico Fermi Institute of Nuclear Studies at The University of Chicago, where he inherited the laboratory of Nobelist Harold C. Urey as well as Urey's able chemist Toshiko Mayeda. Bob has acquired additional laboratory space with the passage of time, but the hub of activity and meeting place for his daily coffee klatch with students and colleagues remains that original laboratory, whose appearance today is not markedly different from its appearance in the late 1950s. The first paper by the formidable and prolific team of Clayton and Mayeda was published in 1963 and described a method of extraction of oxygen from oxides and silicates by BrF_5. It remains their most highly cited publication! In the first twelve years of Bob's career at Chicago, he made only one foray into meteoritics, reporting on his discovery of unusually high $^{13}C/^{12}C$ ratios of certain meteoritic carbonates.

Retaining his positions in the Department of Chemistry and The Enrico Fermi Institute of Nuclear Studies, Bob joined the Department of the Geophysical Sciences when it was founded in 1961. He maintained these joint appointments until he retired, and also served as Chairman of the Department of Geophysical Sciences (1973–1976) and Director of the Enrico Fermi Institute (1998–2001).

Bob's first students Jim O'Neil, Tarkesh Sharma, and Dave Northrop were chemists who conducted some of the first laboratory experiments on oxygen isotope relations in mineral–fluid systems. Henry Schwarcz joined the group in those early days as Bob's first postdoctoral fellow and studied oxygen isotope variations in metamorphic rocks. Soon after, Ty Coplen laboriously upgraded an old cycloidal mass spectrometer on which H_3^+ and HD^+ ions could be resolved. Development of methods and theory, stable isotope thermometry, oxygen isotope variations in hard rocks, the formation of basinal brines, and the use of oxygen isotope measurements in determining the provenance of aeolian dust were part of the intellectual agenda during those early times. Some of these themes are timeless and are represented by papers in this volume, including O'Neil et al. on oxygen isotope equilibrium fractionation between phosphate and water; the calculation of Cl stable isotope fractionation factors by Schauble et al.; the exploration of the "salt effect" on mineral–water fractionation factors by Hu and Clayton; oxygen isotope variations in metamorphic rocks from the Greek Isles by Matthews et al.; the empirical calibration of oxygen isotope thermometry in zircons by Valley et al.; and the



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use of stable isotope ratios as paleoclimate proxies by Bar-Matthews et al.

The Apollo program launched an exciting new era of research at Chicago, and much of Bob's attention was now focused on extraterrestrial materials. With Naoki Onuma, the first attempts to apply oxygen isotope thermometry to nebular materials were reported. Their results agreed well with temperature estimates made on the basis of volatile element contents determined by Ed Anders and his group. Larry Grossman joined the Department of the Geophysical Sciences in 1972, and his thermodynamic calculations provided estimates of condensation temperatures of calcium–aluminum inclusions (CAIs) to which oxygen isotope temperatures could be compared. These comparisons, however, were more than a bit confusing at first, as the oxygen isotope thermometer gave some very odd temperature estimates for CAIs. Doggedly pursuing this problem, Bob unraveled anomalies in the 45/44 ratios of the CO_2 gas being analyzed and soon realized that they were caused by unexpectedly low $^{17}O/^{16}O$ ratios in the meteoritic materials. Recognizing the significance of this discovery, he quickly embarked on three-isotope measurements of oxygen liberated from meteoritic materials and published his famous slope–1 line in *Science* in 1973. The story of the moments of recognition was captured in Bob's own words by David Fisher in his book *Birth of the Earth*. Cosmochemistry was never the same again and became the dominant focus of the ensuing career of Bob Clayton. This amazing discovery of oxygen isotope anomalies in meteorites led to studies of isotopic anomalies in other elements. If isotopic anomalies were present in oxygen, the most abundant rock-forming element, what about silicon? A mass spectrometer constructed in-house using parts from the Argonne National Laboratory made Si-isotope measurements possible by Carol Molini-Velsko. The paper by Hu et al. is testament to the continued need for innovation in mass spectrometry to study "mass-independent fractionation" (MIF) in other isotopic systems. Hu et al. describe their laser fluorination technique for the analysis of all four sulfur isotopes, with applications to the remarkable discovery of MIF in sulfur isotopes in Archean sediments. This work can trace its origins to the Clayton laboratory (in more ways than one), beginning with Bob's discovery of MIF in oxygen isotopes. Mark Thiemens, while a postdoctoral fellow with Bob, embarked on a search for MIF in experimental systems. This interest later led him to the recognition of MIF in the $O_2 \rightarrow O_3$ reaction. He then looked at natural systems where he discovered MIF in oxygen from atmospheric gases, and in sulfur from Archean sediments (with James Farquhar).

The acquisition of an ion microprobe at the University of Chicago in 1977 ushered in yet another new era of research with Ian Hutcheon, Richard Hinton, Andy Davis, Debra Scatena-Wachel, Tim Vanderwood, and others that revealed nucleosynthetic isotopic anomalies (^{50}Ti) and evidence for extinct radionuclides (^{26}Al). The discovery of mass fractionated Mg and O anomalies in the Fractionated Unknown Nuclear (FUN) inclusions led to intense efforts to understand mass fractionation in heavy elements (with Jianhua Wang), and to searches for nucleosynthetic anomalies in elements other than oxygen. The discovery of oxygen isotope anomalies led others to search for isotope anomalies in heavy elements, particularly the Fe-peak elements. Here, Podosek et al. report on ubiquitous Cr isotope anomalies in primitive chondrites. Bob's interest in oxygen isotope distribution in meteorites resulted in his $\delta^{17}O$-$\delta^{18}O$ plots becoming one of the principal means of establishing genetic relations between meteorite classes. The paper by Rubin et al. is an example of the continuing value of oxygen isotope measurements to the discipline of meteoritics. If refractory and major elements exhibited mass fractionation in meteorites, it was possible that volatile elements would exhibit mass fractionation on the planetary scale. A K isotope study made of lunar, meteoritic, and terrestrial materials using the ion microprobe as a solid source mass spectrometer revealed the surprising absence of K isotopic fractionation in planetary materials (with Munir Humayun). As the samples with the lowest $\Delta^{17}O$, ubiquitous nucleosynthetic anomalies, and mass fractionation of heavy elements, CAIs are indeed special objects and remain the subject of much research. The papers by MacPherson et al. and Campbell et al. report on processes in CAIs deciphered by microanalysis.

Chondrites were not the only meteorites that received attention in the Clayton laboratory. Bob and Tosh made seminal contributions to the understanding of stable isotope variations in achondrites, and the SNC meteorites which are thought to come from Mars. In fact, it was their oxygen isotope measurements that helped drive an obscure orthopyroxenite, ALH 84001, on to its rendezvous with destiny. The study of Knauth et al. on C and O isotope variations in desert caliches provides a terrestrial analog for carbonate deposition on Mars, with implications for carbonate genesis in ALH 84001. Paul Knauth began his career in stable isotope geochemistry as an undergraduate intern in the Clayton laboratory, before proceeding on to Caltech where he received his Ph.D. under the mentorship of Sam Epstein. As the result of an error at the publishers, his contribution to this volume was published earlier (Knauth et al., *Geochim. Cosmochim. Acta* **67**, 185–195). That work ties in with the paper by Kopp and Humayun, who present a new model for the origin of magnetite–carbonate assemblages in ALH 84001, with a discussion of stable isotope variations on Mars.

In the different funding climate of that time, Gerry Wasserburg suggested to Bob that he apply for much larger grants from NASA and he did. Armed with an extra $100K or so, he decided to invest in an isotope ratio mass spectrometer dedicated to nitrogen isotope determinations. Richard Becker, Mark Thiemens, Serge Fourcade, and John Stone began investigations of N-isotope variations in lunar soils and breccias. Large secular changes in the $^{15}N/^{14}N$ ratio of lunar soils and breccias were inferred to reflect a change in solar wind composition through time. These studies were followed by determinations of nitrogen isotope ratios in chondrites and achondrites by C.-C. Kung, iron meteorites by Carol Prombo, and terrestrial rocks by Dachun Zhang and Lin Huang. The remarkable range of 120% observed in the nitrogen isotope composition of iron meteorites must have important implications to the origin of these bodies and is something that Bob still ponders creatively.

At the same time that all the action was happening in cosmochemistry, Richard Becker did his doctoral research on C and O isotopes in the Hamersley banded iron formation in an attempt to constrain the history of $\delta^{18}O$ in the oceans (Richard later returned to the Clayton laboratory to work on N-isotope variations in both terrestrial and extraterrestrial materials). Fred

Anderson worked on oxygen isotope distributions in mafic igneous rocks as a postdoctoral fellow, and Karlis Muehlenbachs did his doctoral research on $\delta^{18}O$ of dredged submarine basalts and gabbros. Karlis observed that, relative to oxygen in average mantle, oxygen in submarine basalts was isotopically heavier and oxygen in gabbros of oceanic crust was isotopically lighter. In a landmark paper published in 1976, Muehlenbachs and Clayton explained these observations as resulting from weathering reactions on the seafloor surface and hydrothermal alteration in the oceanic crust. An important implication of their model is that these reactions buffer $^{18}O/^{16}O$ ratios of the oceans to a relatively constant value for long geologic periods. But one had to know the depth to which the hydrothermal system penetrated to perform mass balance calculations. Emi Ito determined the oxygen isotope compositions of gabbros collected by the submersible *Alvin* from a depth profile along the Mid-Cayman Rise, and demonstrated that seawater penetrated only to the top of the plutonic layer. Bob's interest in hydrothermal systems began when he worked on oxygen isotope variations in a hydrothermal ore deposit as a graduate student. His continued interest in these systems brought him to places like New Zealand and Japan, where he established fruitful collaborations with local scientists.

In 1975 Bob joined forces with Julian Goldsmith and Bob Newton using the piston cylinder apparatus to investigate possible pressure effects on the partitioning of stable isotopes in reactions in the deep crust of Earth. From this followed studies of oxygen isotope exchange at high pressure (with postdoctoral fellows Yukihiro Matsuhisa, Alan Matthews, Hitoshi Chiba, and Tom Chacko). Bob's interest in equilibrium isotope exchange continues with the paper by Hu and Clayton in this volume.

The discovery of presolar grains in primitive chondrites by Ed Anders and Roy Lewis opened new possibilities for exploring the synthesis of the elements. Bob recognized very early on that a proper understanding of stellar nucleosynthetic processes from presolar grains required determinations of the isotopic compositions of specific elements in individual presolar grains. Bob and Andy Davis collaborated with Michael Pellin at Argonne National Laboratory using the resonance ionization mass spectrometric techniques developed there. This collaboration resulted in the development of a new mass spectrometer designed specifically for presolar grain analysis: CHARISMA (*CH*icago-*A*rgonne *R*esonance *I*onization *S*pectrometer for *M*ass *A*nalysis). New aspects of the experimental design and results on Ba isotopes in presolar SiC are reported in this volume by Savina et al.

Bob has been the recipient of many well-deserved awards during his career, including the prestigious Goldschmidt and Urey Medals. He is a Member of the National Academy of Sciences and a Fellow of both the Royal Society of London and the Royal Society of Canada. He is a recipient of the Bowie Medal, the highest honor bestowed by the American Geophysical Union.

In a 43-year career, Bob mentored 21 Ph.D. students and 22 postdoctoral fellows, and his mentorship of young scientists continues to the present day. He influenced numerous other colleagues directly and indirectly. The collection of papers presented in this volume covers some of the many aspects of isotopic geochemistry pioneered in the Clayton laboratory, and indicates the many directions that its present practitioners have developed. Our thanks go to each of the contributors for their efforts to make this special issue a success, to those whose contributions did not make it into this special issue, and to all who attended the Hudnall Symposium for making it the success that it was. Most of all we thank Bob Clayton and Tosh Mayeda for their contributions to our field. We warmly dedicate this special issue to Bob Clayton.