Final Report: NAGW-4112 PI: Kevin D. McKeegan

Development of a high resolution-high sensitivity ion microprobe facility for cosmochemical applications

NASA NAGW-4112 has supported development of the CAMECA ims 1270 ion microprobe at UCLA for applications in cosmochemistry. This instrument is the nation's first high-resolution, high-sensitivity ion microprobe and offers unique analytical capabilities that enable us to attack cosmochemical problems which have proved difficult to address with previous generation secondary ion mass spectrometers. Although we had originally proposed to operate the CAMECA ims 1270 as a *NASA Investigator Facility Instrument* that would be made available to the PM&G community, the Lunar and Planetary Geosciences Review Panel judged that this plan was premature. Therefore, funding ($80k/yr) was approved to help bring the instrument to an operational status and test its capabilities, as well as to develop a technique for accurate, precise microbeam analysis of oxygen isotope ratios in polished thin-sections. The grant has been renewed as NAG5-4704 administered through NASA's Goddard Space Flight Center.

The first 2 years of support were largely devoted to solving numerous hardware and software problems with the prototype ims 1270 that required modifications to the ion optics, vacuum system, ion counter, computer control systems, and electronics. Many improvements (too numerous to mention here) in electronics and the reliability of the microprocessor controls have been made by our electrical engineer, George Jarzebinski, who was partially supported by this grant. A major advance was the construction of a UCLA-designed ion counting system that replaces the CAMECA supplied system for quantitative measurements (the CAMECA system is still used for ion imaging). This system, which utilizes a directly coupled electron multiplier, fast amplifiers and discriminator combined with CAMAC-based counting modules, is characterized by a constant deadtime of ~18 to 20 nsec and low noise (<0.01 cps background). We have also implemented a computer-controlled adjustment to the discriminator threshold and software for automated acquisition of the pulse-height distribution, a capability that has proved critical for obtaining reliable isotope data with the electron multiplier operated at high count rates.

In addition to instrumental improvements, during the second and third years of support our research efforts focussed on measurements of the isotopic abundances of oxygen on a small spatial scale in materials from primitive meteorites with a view toward better elucidating the compositions of, and the nature of the mixing processes occurring between, various oxygen isotope reservoirs in the solar nebula and on meteorite parent bodies. As part of this work, we have continued to improve measurement techniques for precise and accurate determination of $\delta^{18}O$ and $\delta^{17}O$ in silicate, oxide, and carbonate minerals. Our applications may be divided along two lines of inquiry: the first concerns the origin and distribution of oxygen isotope anomalies in the nebula, high temperature gas-solid interactions, and the formation and thermal processing of refractory inclusions, while the second may be broadly defined as looking for tracers of volatile reservoirs and fluid interactions on meteorite parent bodies.

Substantial progress was made in both research areas during the last two years of this grant resulting in publication of five manuscripts and eleven abstracts (listed below). These results are briefly summarized here under the same general research headings as reported in last the full proposal.

Oxygen isotopic composition of CI olivine and pyroxene

We completed a study of the first oxygen isotopic ($\delta^{18}O$ and $\delta^{17}O$) measurements of rare mafic silicates in the most chemically primitive meteorites, the CI chondrites (Leshin *et al.*, 1997). The results have implications for both high temperature processing in the nebula and low-T aqueous alteration on the CI asteroid. The olivine data show a correlation of ^{16}O-enrichment with FeO content falling approximately along the ^{16}O (or CCAM) mixing line, but generally extend to higher values of $\Delta^{17}O$ than for similar phases in other carbonaceous chondrites. These data indicate that even prior to alteration and formation of secondary minerals, the CI chondrites were the most ^{16}O-depleted carbonaceous chondrites. The results fit well within the general framework of the two-stage models put forth by Clayton and Mayeda (1984) and Rowe *et al.* (1994) for the isotopic evolution of CI materials, but imply more complete gas-solid equilibration in the nebula and constrain the initial fluids on the CI parent body to have had lower $\Delta^{17}O$

values than previously postulated. Our refined model indicates that the temperature of aqueous alteration on the CI parent body was no more than ~50ºC and the fluid:rock ratio was less than previously estimated.

Oxygen isotopic measurements in magnetite nodules from type 3 chondrites

We have performed measurements of oxygen isotopic compositions of magnetite and co-existing olivine from carbonaceous (Choi et al., 1997) and unequilibrated ordinary chondrites (Choi *et al.*, in press). Although primarily funded through an NSF proposal to our UCLA collaborator Dr. John Wasson, without the partial support derived from this grant these measurements would not have gone forward. This work, which forms the major part of Ph.D. dissertation of Wasson's student, B.-G. Choi, has provided new data on aqueous alteration on asteroidal parent bodies of meteorites and has identified a significant new oxygen isotope reservoir in the early solar system: water characterized by a very high $\Delta^{17}O$ value of ~5‰.

In situ measurements of oxygen isotopic anomalies in refractory inclusions

Our major effort regards the determination of the spatial distributions of oxygen isotopic anomalies in CAIs. Such data can be used to constrain the formation and thermal evolution of individual inclusions, and ultimately has implications for understanding the origins of the premier isotopic anomaly in meteorites, a mystery that has only deepened in recent years with the apparent lack of ^{16}O-rich circumstellar dust grains in meteoritic acid residues. Our strategy has been to study several types of inclusions from different meteorites in an effort to contribute to the understanding of 'typical' inclusions as well as inclusions that are small or of rare types that have not been measured conventionally. In this effort, we have collaborated on a case-by-case basis with expert petrographers and cosmochemists who have made trace element and isotopic measurements of the inclusions. The idea is to work only on inclusions that have been well studied petrographically, chemically and isotopically so that through correlations of the O-isotopic data with detailed petrographic and chemical zoning information, we can definitively assess whether diffusion-controlled sub-solidus exchange of oxygen between a "normal" gaseous reservoir and ^{16}O-enriched dust can quantitatively explain the isotopic patterns and constrain CAI thermal histories. Correlations of oxygen isotope anomalies with ion microprobe measurements of the trace element abundances and other isotopic systems (especially Mg, Si, Ca, and Ti) in the same single crystals can also shed light on the ultimate origin(s) of the anomalous oxygen. In particular, the correlation of oxygen isotopes with initial $^{26}Al/^{27}Al$ abundances may help determine the timing of processes that caused oxygen isotopic exchange in CAIs.

<u>The microscopic distribution of ^{16}O excesses in a Type B1 Allende CAI</u>

McKeegan presented initial results of a survey of oxygen isotopes in all four major mineral phases of a Type B refractory inclusion from Allende at the 1996 Meteoritical Society meeting in Berlin. Since Berlin, many additional measurements have been made and a *Geochimica* manuscript is currently in preparation; only a brief description of the major results are provided here. The results of 86 oxygen isotopic analyses measured in 80 spots of USNM 3529-Z are summarized in Figure 1. The data fall along the mixing line (slope = 0.94) previously determined by gas-phase mass spectrometry measurements of whole CAI from Allende; the excellent agreement of the ion probe data for each mineral phase with the mixing line demonstrates that matrix effects on the instrumental mass fractionation between spinel and refractory silicate minerals are minor (< ~1-2‰/amu) under our measurement conditions. The data are also in general agreement with previous measurements on mineral separates from CAI by Clayton and colleagues in the sense that spinel and fassaite are ^{16}O-enriched relative to anorthite and melilite. Spinel is somewhat more anomalous than previously observed, possibly because we have analyzed only large grains from the interior of the inclusion. However, the most striking observation is that anorthite can have significant ^{16}O excesses of up to ~20‰ and, in each of 4 crystals analyzed in detail, the anorthite is strongly zoned in O isotopic composition. In only 1 case, however, is the zoning profile from core-to-rim as would be expected for simple volume diffusion. In the other cases, oxygen isotopic zoning is not readily modeled with reasonable diffusion geometries. An additional difficulty with *simple* diffusion models is presented by the lack of observable zoning within single melilite crystals even though isotopic exchange in melilite has *not* gone to completion (since some melilite has greater ^{16}O-enrichments than some anorthite). Inter-crystalline heterogeneity in melilite further complicates the picture: a large core melilite crystal is slightly more enriched in ^{16}O than melilite which crystallized from the rim of the inclusion. Recrystallized anorthites, which exhibit disturbed Al-Mg systematics, have apparently completely exchanged oxygen isotopes; the inference from ^{26}Al abundances is that this exchange happened within ~2 Ma of inclusion formation. We

are presently attempting to understand these data in terms of multistage thermal and chemical processing of this CAI.

The White Angel: an enigmatic F-inclusion from the Leoville chondrite

We performed O-isotope measurements of melilite, wollastonite, perovskite, and fassaite in a collaborative effort with Dr. E. Zinner and Dr. C. Caillet to understand the origins of the "White Angel" inclusion from the CV3 chondrite Leoville. The results were presented by Zinner and the Lunar and Planetary Science Conference (see attached abstract). This inclusion is highly unusual in that it is characterized by mass fractionated Mg and O isotopes, but the oxygen has apparently undergone an isotopic exchange event prior to the mass fractionation (unlike "normal" FUN inclusions). Two generations of wollastonite are seen in the O-isotope data: primary wollastonite has ^{16}O-excesses of 40-50‰, whereas wollastonite from re-melted

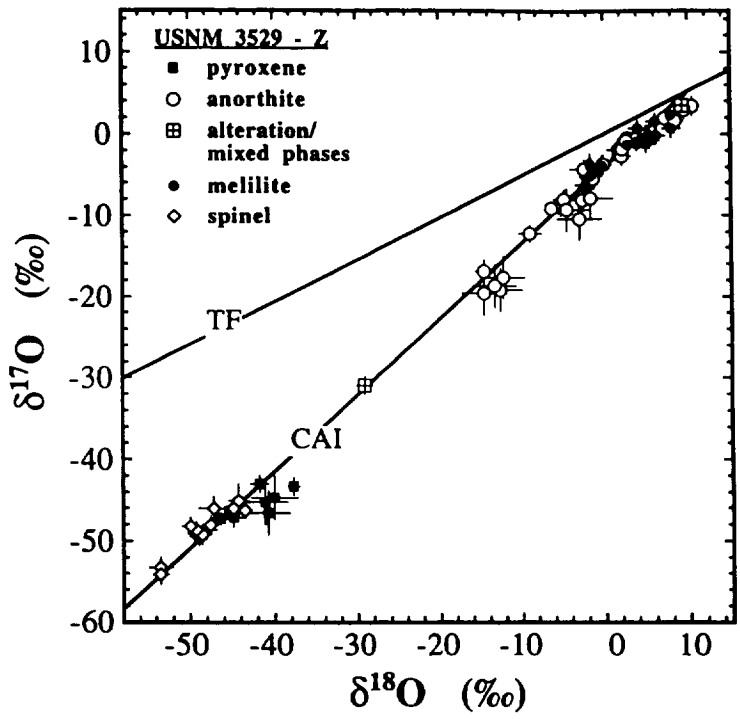

Figure 1. Oxygen isotopic composition of minerals in Allende CAI USNM 3529-Z.

regions of the inclusion has an O-isotopic composition similar to that of melilite. A manuscript describing these results is in preparation.

Refractory objects in Unequilibrated Ordinary Chondrites

In collaboration with Dr. Sara Russell and Dr. Glenn MacPherson of the Smithsonian Institution, we have measured δ^{18}O and δ^{17}O in a CAI from Semarkona finding that all phases (including melilite) are enriched in ^{16}O to a degree similar to what is typically seen in spinel and pyroxene of CAIs from carbonaceous chondrites. A CAI from the Quinyambie meteorite also exhibits ^{16}O-excess and lies far from the field of oxygen isotopic compositions for other phases in ordinary chondrite meteorites. These data and their implications for ^{26}Al distributions were discussed by McKeegan at the 1997 Meteoritical Society meeting in Hawaii. A manuscript (see below) is in press with *Science*. Additional O-isotopic measurements have been made on refractory chondrules from ordinary chondrites; the data indicate that these objects are more closely related to ordinary (ferromagnesian) chondrules than to CAIs.

Manuscripts supported by NAGW-4112:

1. Choi B.-G., McKeegan K. D., Leshin L. A., and Wasson J. T. (1997) Origin of magnetite in oxidized CV chondrites: in situ measurement of oxygen isotopic compositions of Allende magnetite and olivine. *Earth and Planetary Science Letters* 146, 337-349.
2. Leshin L. A., Rubin A. E., and McKeegan K. D. (1997) The oxygen isotopic composition of olivine and pyroxene from CI chondrites. *Geochimica et Cosmochimica Acta* 61, 835-845.
3. Leshin L. A., McKeegan K. D., Carpenter P. K., and Harvey R. P. (1998) Oxygen isotopic constraints on the genesis of carbonates from martian meteorite ALH84001. *Geochimica et Cosmochimica Acta*, in press.
4. Choi B.-G., McKeegan K. D., Krot A.N., and Wasson J. T. (1998) Extreme oxygen isotopic compositions in magnetite from unequilibrated ordinary chondrites. *Nature*, in press.
5. McKeegan K. D., Leshin L. A., Russell S. S., MacPherson G. J. (1998) Oxygen isotopic abundances in calcium-aluminum-rich inclusions from ordinary chondrites: Implications for nebular heterogeneity. *Science*, in press.

Abstracts:

1. Choi B.-G., Coath C. D., Leshin L., Wang J., McKeegan K. D., and Wasson J. T. (1995) In situ measurement of oxygen isotope compositions of magnetite in the Allende CV3 chondrite. *Meteoritics* 30, 498-499.
2. Leshin L. A., Rubin A. E., and McKeegan K. D. (1996) Oxygen isotopic compositions of olivine and pyroxene from CI Chondrites. *Lunar Planet. Sci.* XXVII, 745-746.
3. McKeegan K. D., Leshin L. A., Russell S. S., and MacPherson G. J. (1996) In situ measurement of oxygen isotopic anomalies in a Type B Allende CAI. *Meteoritics and Planetary Science* 31, A86-A87.
4. Leshin L. A., Harvey R. P., McCoy T. J., and McKeegan K. D. (1996) Water in apatite from shergottite QUE94201: Abundance and D/H. *Meteoritics and Planetary Science* 31, A79-A80.
5. Leshin L. A., McKeegan K. D., and Harvey R. P. (1997) Oxygen isotopic constraints on the genesis of carbonates from martian meteorite ALH84001. *Lunar Planet. Sci.* XXVIII, 805-806.
6. Caillet C., Zinner E., McKeegan K. D., and Hervig R. L. (1997) The White Angel: an enigmatic wollastonite-bearing F inclusion from the Leoville CV3 chondrite. *Lunar Planet. Sci.* XXVIII, 199-200.
7. Choi B.-G., McKeegan K. D., Krot A. N., and Wasson J. T. (1997) Magnetite in unequilibrated ordinary chondrites: evidence for an ^{17}O-rich reservoir in the solar nebula. *Lunar Planet. Sci.* XXVIII, 227-228.
8. Engrand C., McKeegan K. D., and Leshin L. A. (1997) *In situ* analysis of the oxygen isotopic composition of individual minerals in Antarctic micrometeorites. *Meteoritics and Planetary Science* 32, A39-A40.
9. McKeegan K. D., Leshin L. A., Coath C. D., Choi B.-G., and Engrand C. (1997) Oxygen isotopic measurements with the UCLA Cameca ims 1270 ion microprobe: applications in cosmochemistry. *International Conf. On Secondary Ion Mass Spectrometry: SIMS XI* (invited). Orlando, Fla.
10. McKeegan K. D., Leshin L. A., Russell S. S., and MacPherson G. J. (1997) Ion microprobe measurements reveal large oxygen-16 excesses in calcium-aluminum-rich inclusions of an ordinary chondrite. *Meteoritics and Planetary Science* 32, A88-A89.
11. Russell S. S., Leshin L. A., McKeegan K. D., and MacPherson G. J. (1997) Oxygen isotope composition of aluminum-rich chondrules: Clues to their origins. *Meteoritics and Planetary Science* 32, A111-A112.

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