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NanoSIMS, Raman and Synchrotron FTIR Study of Interplanetary Dust Particles (IDPs).

*H. Busemann<sup>1</sup>, N. Spring<sup>1</sup>, P. Hoppe<sup>2</sup>, L. Nittler<sup>3</sup>, S. Bajt<sup>4</sup> (<sup>1</sup>University of Manchester, <sup>2</sup>MPI Mainz, <sup>3</sup>Carnegie Institution of Washington, <sup>4</sup>DESY Hamburg)*

Presolar Graphite: Its Abundance and Formation Conditions.

*S. Amari<sup>1</sup>, E. Zinner<sup>1</sup> and R. Gallino<sup>2</sup> (<sup>1</sup>Washington University, St. Louis, <sup>2</sup>Università di Torino)*

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*B. Jacobsen<sup>1</sup>, J. Matzel<sup>1</sup>, A.N. Krot<sup>2</sup>, I.D. Hutcheon<sup>1</sup>, M. Telus<sup>2</sup>, and K. Nagashima<sup>2</sup> (<sup>1</sup>Lawrence Livermore National Laboratory, <sup>2</sup>University of Hawai'i)*

Investigation of Garnet Formation and Evolution in Magmatic Rocks Using Zircon Chronology and Trace Element Chemistry.

*R. Economos<sup>1</sup>, A.K. Schmitt<sup>1</sup> and J. Wooden<sup>2</sup> (<sup>1</sup>University of California, Los Angeles, <sup>2</sup>Stanford University)*

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*G.R. Huss, R.C. Ogliore, K. Nagashima, M. Telus, and C.E. Jilly (University of Hawai'i)*

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## **6<sup>th</sup> Biennial Geochemical SIMS Workshop Poster Session**

### **New Ion Probe Facilities**

#### **The NanoSIMS50L at Arizona State University: An Update**

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On March 28, 2010 the Cameca Ametek NanoSIMS50L was delivered to Arizona State University. In January 2011 it was set up temporarily for prescribed performance tests and initial applications while renovations proceeded on its permanent home. The specifications of beam size, beam stability, stage reproducibility and so on were achieved. The instrument was transported to its permanent lab space in the basement of the Department of Chemistry and Biochemistry on October 3, 2011. This poster will show pictures of the initial installation and move to its permanent space. The NanoSIMS50L will be used to study a wide array of problems: investigations in soft (biological) materials and hard materials (minerals), and at the interface between the two (biosensors, antibiotic clays, nanoparticle toxicity). Some initial results will be shown at the meeting.

### **Measurement Techniques**

#### **Negative Secondary Ion Dating of Monazite Using Positive Metal (Cs<sup>+</sup>, Ga<sup>+</sup>) Primary Beams at High Spatial Resolution**

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SIMS analysis of monazite generally detects positive secondary ions (e.g., Pb<sup>+</sup>, Th<sup>+</sup>) generated by sputtering with negative oxygen primary ion beam species (O<sup>-</sup>, O<sub>2</sub><sup>-</sup>). Here, an alternative technique is presented of analyzing negative secondary ions which takes advantage of the intrinsically higher brightness of positive metal ion sources (Cs<sup>+</sup>, Ga<sup>+</sup>) compared to duoplasmatron sources. The limitations of extremely low secondary ion yields for Pb<sup>-</sup> and Th<sup>-</sup> are overcome by analyzing negatively charged molecular species (e.g., PbP<sup>-</sup>, ThP<sup>-</sup>). For monazite, lower useful yields of negative ion species are compensated by higher sputtering rates of Cs<sup>+</sup>, as well as Ga<sup>+</sup> on Cs<sup>+</sup> impregnated areas. A mass resolution power of  $M/\Delta M \sim 4000$  is required to resolve interferences if a conductive carbon coating is applied. This is similar to the transmission required for positive secondary ion analysis of monazite, so that the overall secondary ion yield per incoming primary ion is in fact higher for PbP<sup>-</sup> relative to Pb<sup>+</sup> by nearly a factor of two. By using a  $\sim 500$  nm Ga<sup>+</sup> beam, we have successfully tested the capability of ion imaging for detecting age heterogeneities in selected  $10 \times 10 \mu\text{m}^2$  areas of monazites from the Fosdick Migmatite Dome, West Antarctica (samples courtesy F. Korhonen and M. Grove). Such heterogeneities would not be resolvable by conventional SIMS monazite spot analysis at  $\sim 20$  mm lateral resolution.

## Coupled Fe and S Isotope Compositions in Individual Pyrite Nodules from Archean Shales

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Studies of Fe and S isotopic compositions of sedimentary pyrites have placed important constraints on the chemistry and the redox evolution of the ocean and the atmosphere over geological time [1-3]. Additionally, Fe isotopes have been proposed as a proxy of trace microbial metabolism [2, 4]. These studies have mostly been done by bulk analysis of the rocks or separated minerals, however individual pyrite nodules often show complex structures, with a fine crystalline nucleus surrounded by a coarse diagenetic rim. Whether there exists any isotopic variability within individual nodules is not known.

The aim of this study is to assess the formation of these pyrite nodules and to better understand the possible effect of microbial mediation on their isotopic compositions. We have performed in situ Fe and S isotope analyses in pyrite nodules hosted by shale from the late Archean (2.6 Ga, Zimbabwe). Fe isotopes were measured with ims 1270 ion probes at both UCLA and CRPG, Nancy following the method described by [5]. We also performed multiple S isotope measurements with the ion probe 1280 HR2 at CRPG. The measurements performed in CRPG and UCLA are perfectly in agreement with a reproducibility better than 0.2 ‰ (2 $\sigma$ ) in  $\delta^{56}\text{Fe}$ , which is similar to that achieved by bulk techniques. Reproducibility for  $\delta^{34}\text{S}$  reproducibility is  $\sim 0.2$  ‰ (2 $\sigma$ ) and  $\sim 0.1$  ‰ (2 $\sigma$ ) for  $\Delta^{33}\text{S}$ .

Two profiles have been performed in one nodule and show large variations in both  $\delta^{56}\text{Fe}$  ( $\sim 2.5$  ‰) and  $\delta^{34}\text{S}$  ( $\sim 5$  ‰). The  $\delta^{56}\text{Fe}$  profile shows that the rim of the nodules is enriched relative to the core. In contrast, the  $\delta^{34}\text{S}$  profile shows heavy isotope enrichment in the core and depleted rims. The core shows correlation between  $\delta^{34}\text{S}$  and  $\Delta^{33}\text{S}$  and between  $\Delta^{33}\text{S}$  and  $\delta^{56}\text{Fe}$ . Coupled S and Fe isotope analysis can assess the origin of the nodule pyrite and better constrain the biosignature potential of these isotopes.

[1] Rouxel et al. (2005) Science 307, 1088. [2] Johnson et al. (2008) Earth. Annu. Rev. Earth Planet. Sci. 36, 457. [3] Farquhar et al. (2000) Science 289, 756. [4] Archer and Vance (2006) Geology 34, 153. [5] Marin-Carbonne et al. (2011) Chemical Geology, 285, 50.

## Noble Gas Analysis by Laser Ionization Mass Nanoscope “LIMAS”

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Noble gas isotopic composition in submicron scale provides us new insights of the solar system. 3D profile of solar gas implantation of noble-gas-rich meteorites can establish a regolith formation process of asteroids. Secondary ion mass spectrometry could not measure noble gases. LIMAS is mainly consisted of Ga-FIB primary ion source, femto-second (fs) laser (Integra-C; 3.5 mJ, 40 fs, Quantronix), and multi-turn time of flight mass spectrometer “MULTUM II”, which is constructed by JEOL Ltd. (Ebata et al., this workshop). The fs laser can ionize noble gases spattered as neutral particles by Ga-FIB because the fs laser has high photon density ( $>10^{19}$  Wm<sup>-2</sup>). The fs laser ionized  $\sim 10\%$  of He in the focused area. We developed ion counting system for LIMAS because noble gases are depleted in solid materials. A time resolution of the system is 5 ns by using multi-channel scaler (SR430, Stanford Research Systems). Ultra-high vacuum chamber ( $2 \times 10^{-8}$  Pa) can reduce interferences of back ground gases of  $m/z = 4$  (e.g.,  $^{12}\text{C}^{3+}$ ,  $^{16}\text{O}^{4+}$ ). LIMAS could separate  $^4\text{He}$  from the interference ions ( $M/\Delta M < 1,600$ ) because a mass resolution was 7,000 ( $m/z = 4$ , FWHM) after 20 cycles. The sample used in this study was n-type Si wafer which was irradiated by  $^4\text{He}$  of  $8 \times 10^{16}$  atoms/cm<sup>2</sup>. Peak of  $^4\text{He}$  from He implanted in Si was obtained but the depth profile of  $^4\text{He}$  was not yet. In this workshop we will show a procedure of noble gas analysis for LIMAS and result of measurement of He-implanted Si wafer.

## Measuring 4 Isotope Sulfur on SHRIMP-SI

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**Introduction:** We have measured terrestrial sulfide grains with known  $\Delta^{33}\text{S}$  and  $\Delta^{36}\text{S}$  anomalies as well as troilite grains extracted from the Murchison meteorite firstly to test if SI can reproduce conventional data and secondly to test if early solar system photochemical reactions can be detected as non-mass dependent isotope fractionations in troilite S.

**Methods:** *In situ* isotopic analysis was performed using Sensitive High-mass Resolution Ion Microprobe – Stable Isotope (SHRIMP-SI). A 6 nA primary  $\text{Cs}^+$  ion beam (13 keV) was focused to ~20 microns with  $\text{S}^-$  secondary ions extracted at 10 keV. No electron gun was required for charge compensation. The sulfur isotopes were collected in multiple collection mode:  $^{32}\text{S}$  with 400  $\mu\text{m}$  collector slit and  $10^{10} \Omega$  current mode resistor,  $^{33}\text{S}$  with 150  $\mu\text{m}$  c.s. and  $10^{12} \Omega$ ,  $^{34}\text{S}$  200  $\mu\text{m}$  c.s. and  $10^{11} \Omega$ , and  $^{36}\text{S}$  with 200  $\mu\text{m}$  c.s. and  $10^{12} \Omega$ . Experiments substituting a 27pF capacitor for the  $10^{12} \Omega$  resistor and measuring  $^{36}\text{S}$  in charge-mode demonstrated superior reproducibility for latter. Overall SHRIMP SI is capable of measuring  $\delta^{34}\text{S}$  to ~0.3 ‰ (2s.d.)  $\Delta^{33}\text{S}$  to better than 0.3 ‰ (2s.d.) and  $\Delta^{36}\text{S}$  to better than 0.5 ‰ (2s.d.).

**Results:** Data for Archaean sulphides reproduce the known isotopic anomalies in  $\Delta^{33}\text{S}$  and  $\Delta^{36}\text{S}$ . Murchison troilite inclusions however are uniform within each inclusion but show differences between inclusions of up to several permil in terms of mass dependent fractionation. No non-linear effects have been detected at this stage in either  $\Delta^{33}\text{S}$  or  $\Delta^{36}\text{S}$ .

**Discussion:** SHRIMP analysis allows analysis of four-isotope S compositions with only a few nanograms of material. The external precision obtained for  $\Delta^{36}\text{S}$  is similar to that attained by conventional gas source mass spectrometry. Mass dependent fractionation in the Murchison inclusions is consistent with evaporation/condensation in the solar nebula.

## Precise and Accurate $^{18}\text{O}/^{16}\text{O}$ Measurements of Ca-Mg-Fe Garnet by SIMS

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We report high-precision measurements of  $^{18}\text{O}/^{16}\text{O}$  in garnet on the CCIM IMS1280 and develop a scheme for matrix correction of Ca-Mg-Fe garnet. The scheme is substantially similar to that described by [1]. Calcium occupancy on the dodecahedral site is strongly associated with IMF and there does not appear to be a significant matrix effect associated with Mg-Fe exchange. Neither Mn- nor Cr-rich garnet can be accurately corrected by this method. Improving upon previous work, we show that the uncertainty associated with the matrix correction can be quantified in a useful way, and furthermore show that the calibration is reproducible across different sample mounts, and under a range of instrument settings. Preliminary experiments with a low energy bandwidth suggest that this may be a useful technique, where matrix effects can be “enhanced” for the purposes of technique development. The spot-to-spot repeatability of the measurements is often better than  $\pm 0.2\%$  ( $2\sigma$ ), a precision that approaches (and sometimes exceeds) the repeatability of bulk silicate  $^{18}\text{O}/^{16}\text{O}$  by fluorination techniques. For these measurements SIMS-only uncertainties no longer dominate the uncertainty budget, and other sources of uncertainties – especially with respect to reference materials and matrix corrections – become important and must be addressed.

[1] Page et al. (2010) Chem Geol v270(1-4) 9-19 doi: 10.1016/j.chemgeo.2009.11.001.

## Oxygen Isotope Analysis on a 20 Year Old SHRIMP II: How Are We Doing?

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The development of in-situ O isotope measurements in geologic material to high precision by SIMS has generated significant interest from the geological community. We present here data from our 20 yr old SHRIMP II. Notwithstanding differing philosophies in data reduction, we find that these data are comparable to recently published data.

SHRIMP II operates with an energetic electron beam to neutralize charge build up and no energy slit is used during these measurements. Only minor down hole drift in the isotope ratio is observed, but this is the current limitation on precision at ca. 0.1 ‰. Within an analytical session, spot-to-spot reproducibility is better than 0.4 ‰ (95% confidence limits).

Kita et al. [1] have emphasised that sample flatness is of paramount importance for optimum data quality for instruments with high extraction field gradients. SHRIMP however, has a large extraction gap with a relatively small field gradient and as a consequence exhibits only minor sensitivity to topographic effects. This is further manifest in the relative insensitivity of SHRIMP to the location of the target with respect to its mount position.

We present as an example, zircon oxygen isotope data from mounts previously analysed by LA-ICPMS for their Hf isotopic composition. Data acquired adjacent to laser pits are indistinguishable from other reference zircons.

[1] Kita, N.T., Ushikubo, T Fu, B. and Valley J (2009) Chem Geol., 264, 43-47.

## Nano SIMS Study on Oxygen Isotopic Measurements of Silicate

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The Nano SIMS is characterized by a high lateral resolution and multi-collection capabilities [1]. This instrument has been used one of the major tools to study presolar grains and elemental imaging with submicron resolution [2]. We are now developing analytical protocols to measure the  $^{18}\text{O}/^{16}\text{O}$  and  $^{17}\text{O}/^{16}\text{O}$  ratios of silicate minerals using the Nano SIMS 50. A 16kV  $\text{Cs}^+$  primary beam, focused to less than 50nm, was used to sputter negative secondary ions from the sample surface. Oxygen isotope ions were collected on four detectors simultaneously. For the high precision oxygen isotopic measurements, a 5-micron raster of  $\sim 500\text{pA}$  focused  $\text{Cs}^+$  ion is used. For the charge compensation, a few  $\mu\text{A}$  of electrons was applied on the sample surface with zero energy. The high mass resolution achieved in the Nano SIMS allowed the accurate separation of the  $^{17}\text{O}^-$  and  $^{16}\text{O}^1\text{H}^-$  peaks. A pre-sputtering of the surface was performed before any measurement in order to remove the carbon coated layer. Secondary ions were collected for 100 cycles of 4s each. We will show that the Nano SIMS can be a very valuable tool to measure the oxygen isotopic compositions.

[1] P. Hoppe (2006), Applied Surface Science 252, 7102-7106. [2] A.N. Nguyen, E. Zinner (2004), Science 303, 1497-1499.

## Identifying the Unwanted: High Resolution Mass Scans of Geologic Materials

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Ion microprobe analyses rely on the production of secondary ions from solid target materials. In the material science community, complexity in ion production is noted for even simple targets comprised of only a few elements. In geological materials, complex mass spectra result from the large number of elements present and their propensity to form molecular ions. The analyses of molecular species is a cornerstone of zircon age determinations but resolution of unwanted interferences is also required.

We have developed a protocol to measure SIMS spectra under varying analytical conditions (mass resolution, energy filtering). These spectra can be stacked to allow identification of relevant species and custom built software allows individual peaks to be scrutinised. A reference lookup list means that isobars can be readily identified.

Preliminary spectra have been obtained on SHRIMP-RG, an instrument that allows mass resolution up to 20,000. A combined faraday – ion counter detection system is rapidly switched depending on count rates. Energy filtering can be changed to establish the nature of the molecular interferences based on the progressive exclusion of polyatomic interferences with energy offset.

Thus far we have applied this technique to NIST glasses as well as minerals used for geochronology – zircon, monazite, and xenotime. For monazite, unresolved interferences in the Pb spectrum could potentially affect some analyses.

The objective is to produce a library of SIMS spectra for common geological materials for general usage which will aid in the development of new techniques by allowing the ready identification of unwanted isobars.

## Mn-Cr Sensitivity Dependence on FeO Content of Olivine

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$^{53}\text{Mn}$ - $^{53}\text{Cr}$  systematics of secondary ferroan olivines ( $Fa_{-70-100}$ ) in several CV chondrites revealed the presence of radiogenic  $^{53}\text{Cr}$  corresponding to initial  $^{53}\text{Mn}/^{55}\text{Mn}$  ratio of  $\sim(2.0-2.5)\times 10^{-6}$  (Hutcheon et al., 1998; Hua et al., 2005; Jogo et al., 2009). These results were interpreted as formation of ferroan olivine through aqueous activity on CV parental asteroid(s)  $\sim 7$  Myr after CV CAIs, assuming their initial ratio of  $\sim 9\times 10^{-6}$  (Moynier et al., 2007). In these studies, the measured  $^{55}\text{Mn}^+ / ^{52}\text{Cr}^+$  ratios in ferroan olivine were corrected using relative sensitivity factors (RSFs) estimated on San Carlos olivine ( $Fa_{-10}$ ). Sugiura et al. (2005), however, found a RSF from a synthetic glass having Fe- and Ca-rich olivine composition similar to angrite olivine is  $\sim 1.6$  (defined as measured/true) systematically different from those measured on San Carlos olivine (RSF  $\sim 0.6$  and  $0.9$  from Jogo et al., 2009 and Hutcheon et al., 1998, respectively). Similar results on ferroan olivines were obtained by McKibbin et al. (2011). Matzel et al. (2009) also reported the RSF is positively correlated with Fe and Si and negatively correlated with Na. If those RSFs are applied to Mn-Cr data of nearly pure fayalite, the inferred initial  $^{53}\text{Mn}/^{55}\text{Mn}$  would become more than twice higher than the reported values. In order to obtain more accurate initial  $^{53}\text{Mn}/^{55}\text{Mn}$  ratio in ferroan olivine, we started investigating sensitivity factors on a suite of terrestrial and extraterrestrial olivines with different FeO contents ( $Fa_{10-100}$ ). The preliminary results will be reported at the workshop.

## Development of SIMS Multicollection Fe and Ni Isotopic Measurements

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We have developed a reliable multicollection protocol for measuring the Fe and Ni isotopic composition of chondrules using the Cameca-ims 1280. These measurements are important for determining the initial solar system abundance of <sup>60</sup>Fe, a short-lived radionuclide that is considered essential for understanding the birth environment of the solar system. Nickel isotopes, <sup>60</sup>Ni, <sup>61</sup>Ni, and <sup>62</sup>Ni, are measured on electron multipliers (EMs) and <sup>56</sup>Fe is measured on a Faraday cup. We use a 6-7nA <sup>16</sup>O<sup>-</sup> beam. Each spot is presputtered using a 25μm raster, which is reduced to 15μm for the measurements. A MRP of ~4500 is achieved using multicollector exit slits of 250μm and is adequate for resolving the major interferences on the Ni isotopes (e.g. <sup>44</sup>Ca<sup>16</sup>O, <sup>45</sup>Sc<sup>16</sup>O, <sup>46</sup>Ca<sup>16</sup>O). The count rates of these interferences are measured at the end of each measurement to ensure that a tail correction is not required. We do not resolve the <sup>60</sup>Ni hydride on <sup>61</sup>Ni, but the contribution is significantly less than 1%. We initially had trouble with rapidly changing EM gains, but we have determined that the act of checking the gains using count rates of ~150k cps destabilizes the detectors for at least a day. We now set the multiplier high voltages once at the beginning of the run and then monitor EM gain changes through repeated measurements of standards. Drift corrections are applied to the data. Isotope ratios are calculated from time-interpolated total counts, following [1], and data are corrected for detector background, deadtime, and tails of interference peaks, when necessary. Internal mass-fractionation corrections are performed for each point. The main sources of uncertainty for these measurements come from the <sup>61</sup>Ni count rates, which can be as low as 6 counts per second and from the sensitivity factor (defined as (<sup>56</sup>Fe/<sup>62</sup>Ni<sub>true</sub>)/(<sup>56</sup>Fe<sup>+</sup>/<sup>62</sup>Ni<sub>measured</sub>)), which ranges from 0.4 to 0.9 and is strongly dependent on the Fe/Ni ratio of the sample.

[1] Ogliore R.C. et al. (2011). Nucl. Instrum. Methods. Phys. Res. B, 269, 1910-1918.

## Exciting New SIMS Results

### NanoSIMS, Raman and Synchrotron FTIR Study of Interplanetary Dust Particles (IDPs)

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IDPs are among the most primitive early solar system materials available for laboratory analysis. As >80 % may originate from comets, they allow the study of comets in the laboratory without sample return. The ultimate goal of our study will be the (destructive) examination of the heavy noble gases in IDPs to assess the volatile contents in comets. In order to identify the dust that is most likely of cometary origin, we performed correlated analyses of the organic matter (OM) in IDP fragments by Raman and Synchrotron-FTIR (ALS Berkeley) spectroscopy, and NanoSIMS (MPI Mainz).

The ALS study was performed in transmission on small IDP fragments transferred to KBr windows. The N isotopes were determined in bulk IDPs pressed into gold foil with the MPI NanoSIMS in mapping mode. Bulk IDPs spot and scanning Raman spectroscopy was performed prior to the SIMS examinations.

The analyses yield large spectral and isotopic variations in the OM. The <sup>15</sup>N/<sup>14</sup>N bulk ratios cover the typical range from terrestrial to large <sup>15</sup>N enrichments (up to >600 ‰), indicating pristine OM of possibly protosolar origin. Although the various fragments of a given IDP do not necessarily have to show comparable properties, FTIR, Raman and NanoSIMS examinations show some interesting rough patterns: The most primitive IDPs based on N isotopes and C Raman band parameters show aliphatic hydrocarbon and amine signatures, whereas non-chondritic IDPs (e.g., with dominant AlO, CaAl or FeS) show low δ<sup>15</sup>N values and no useful C Raman signals. Bulk δ<sup>15</sup>N values and C Raman band parameters roughly correlate. IDPs from different collections, including the comet Grigg-Skjellerup collection, do not show systematically distinct properties.

## Presolar Graphite: Its Abundance and Formation Conditions

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Presolar graphite grains are present only in primitive meteorites and those from Murchison (CM2) and Orgueil (CI) are essentially only ones that have been extensively studied [1-6]. These grains show that isotopic and morphological features depend on density.

There are four density fractions from Murchison: KE3 (1.65 – 1.72 g/cm<sup>3</sup>), KFA1 (2.05 – 2.10 g/cm<sup>3</sup>), KFB1 (2.10 – 2.15 g/cm<sup>3</sup>) and KFC1 (2.15 – 2.20 g/cm<sup>3</sup>) [7]. Although many grains are isotopically anomalous, the fractions also contain grains of solar origin. We estimated that, from relative proportions of grains of presolar and solar origins, the abundance of presolar grains in Murchison is 0.87 ppm.

Many KE3 grains and KFA1 grains are characterized by <sup>18</sup>O excesses, Si isotopic anomalies, high <sup>26</sup>Al/<sup>27</sup>Al ratios (up to ~ 0.1). A few grains show the initial presence of <sup>44</sup>Ti (T<sub>1/2</sub> = 60 a) in the form of <sup>44</sup>Ca excesses. These isotopic signatures indicate that the grains formed core-collapse supernovae. From these isotopic signatures, we calculated the abundance of supernova grains to be 0.21 ppm. In KFB1 and KFC1, grains with isotopically light C are dominant. Noble gas and ion probe analyses of KFC1 as well as TEM observations [8, 9] indicate that the grains formed in low-metallicity asymptotic giant branch (AGB) stars. Model calculations of AGB stars of 3M<sub>sun</sub> and 5M<sub>sun</sub> of a third of solar metallicity indicate that the envelope becomes C-rich when its <sup>12</sup>C/<sup>13</sup>C reaches ~100. From the C isotopic ratios of the grains from KFB1 and KFC1, we estimated the abundance of AGB star origin to be 0.40 ppm. These numbers underline differences between graphite and SiC. In SiC grains, those of AGB star origin comprise more than 90% of the grains, while those of supernova origin (X grains) comprise only 1%.

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## Dating Aqueous Alteration in Unequilibrated Ordinary Chondrites.

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Most chondrites are affected by varying degrees and types of alteration. The age of secondary minerals in unequilibrated ordinary chondrites (UOCs) has not previously been determined and the timescale for different episodes of fluid-assisted thermal metamorphism in various chondritic parent bodies is poorly constrained. <sup>53</sup>Mn-<sup>53</sup>Cr systematics, in secondary minerals, are an excellent clock to use for dating asteroidal parent body alteration. In order to constrain the timing of aqueous alteration on the UOC parent body, we studied the <sup>53</sup>Mn-<sup>53</sup>Cr systematics of fayalitic olivine in UOCs, Ngawi (LL3.0-3.6) and EET 90161 (L3.05). Due to the small grain size, the Cr isotopic compositions of fayalite grains in Ngawi and EET 90161 were measured with the NanoSIMS 50 at the Lawrence Livermore National Laboratory. A <sup>16</sup>O primary beam of ~35 pA was focused to ~300 nm spatial resolution and the mass resolving power was ~3500. The primary beam was rastered over areas between 4×4 μm<sup>2</sup> and 10×10 μm<sup>2</sup> to produce quantitative secondary ion images. Secondary negative ions were acquired by combined analysis, simultaneously measuring <sup>28</sup>Si<sup>+</sup>, <sup>44</sup>Ca<sup>+</sup>, and <sup>52</sup>Cr<sup>+</sup>, and subsequently stepping the magnetic field to measure <sup>53</sup>Cr<sup>+</sup> and <sup>55</sup>Mn<sup>+</sup>. Isotopic ratios were determined from the quantitative secondary ion images using L'Image (courtesy L. Nittler). Measured <sup>55</sup>Mn<sup>+</sup>/<sup>52</sup>Cr<sup>+</sup> ion ratios were converted to atom ratios using a relative sensitivity factor determined from measurements of San Carlos Olivine. Our data provide the first evidence for radiogenic <sup>53</sup>Cr in secondary phases in UOCs. Excesses of <sup>53</sup>Cr correlated with Mn/Cr ratios in the fayalitic olivine indicate an initial <sup>53</sup>Mn/<sup>55</sup>Mn ratio of ~2 × 10<sup>-6</sup>, suggesting that aqueous alteration occurred ~ 8 Ma after solar system formation on at least two ordinary chondrite parent bodies.

# Investigation of Garnet Formation and Evolution in Magmatic Rocks Using Zircon Chronology and Trace Element Chemistry

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Mesozoic plutons in the Transverse Ranges in southern California contain zircon grains that were inherited from their Proterozoic source rocks. These grains commonly occur as rounded, resorbed 20-40  $\mu\text{m}$  cores upon which Mesozoic magmatic zircon nucleated and grew. An investigation of ages and trace element compositions of these cores using the Stanford/USGS SHRIMP-RG yielded the interesting result that some of these cores were depleted in heavy REEs, a geochemical signature identified in metamorphic zircons that co-crystallized with garnet. However, these zircons yielded a range of Th/U compositions from 0.1 to 1, whereas Th/U compositions of  $< 0.1$  are a hallmark of metamorphic zircons. We hypothesized that these grains were generated in a magmatic environment in the lower crust. The behavior of garnet in the lower crust is of particular interest due to its indication of crystallization environment and role a potential driver of dynamic crustal behavior due to its high density. We have begun to investigate zircons from magmatic environments in which zircons and garnets are purported to co-crystallize in order to investigate the potential range of resulting geochemical behaviors.

Zircons were separated and analyzed from two garnet-bearing samples from the San Emigdio mountains, where deep Mesozoic arc crust is exposed. Separate U-Pb analyses and trace element analyses were conducted utilizing established analytical routines on the IMS Cameca 1270 at UCLA. Trace element analyses were conducted in monocollection with wide slit settings to maximize transmission and an energy offset of -100V to repress molecular interferences. REE oxide interferences were calculated using separate glasses doped with light and middle REEs. A quartz diorite sample, in which the chronology of garnet growth is controversial, yielded ambiguous age and REE results. We have therefore begun investigating these samples by identifying in-situ zircons within garnet separates, located for analysis using ion imaging. The analytical routine includes trace element analysis and U-Pb analysis together in a single cycle using variable energy offsets and a narrow slit setting required for an MRP of 4500 or greater necessary for the isolation of Pb peaks for geochronology. Initial analyses indicate that measurements of the more abundant heavy REEs are reproducible at this reduced transmission, but additional work is required to establish a standardization routine for concentration calculations.

## Magmatic Water in Martian Meteorites

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**Introduction:** Martian meteorites are primarily igneous rocks from basaltic lava flows or shallow-level sub-surface intrusions. Certain minerals within these rocks, for example amphibole (a calcium-aluminum silicate) and apatite (a phosphate), have water locked into their crystal structure. Providing these minerals have not been altered by weathering or shock processes, this water represents a direct sample of the water reservoir of Mars' mantle. As the planetary accretion process does not appear to fractionate hydrogen isotopes, the hydrogen isotope ratio of the water in these minerals represents the primordial ratio of the martian globe. Therefore, this ratio can be used to determine the origin of Mars' water.

**Methodology:** Thin-sections of the Nakhla martian meteorite were prepared without the use of water at the University of Hawaii (UH). D, H and Si isotopic compositions were analysed in situ with the UH Cameca ims 1280 ion microprobe, with a Cs+ primary beam. Prior to ion microprobe analysis all samples were stored in a vacuum oven at 60 °C to remove any terrestrial surface water.

**Results:** Apatite minerals in Nakhla show  $\delta\text{D}$  values between +150 to -105 ‰. These values are similar to those of the Earth's oceans, rocks and mantle, suggesting that the Earth and Mars, and possibly the other terrestrial planets, accreted water from the same source. The observed martian and terrestrial mantle  $\delta\text{D}$  values could be produced if the primordial water of Mars and the Earth originated purely from material with the composition of the carbonaceous chondrite meteorites.

## **Unusual Condensation in n-SN-Ia Ejecta the Key to Understand Ca Isotopic Variation Between Differentiated Asteroids**

*Typhoon Lee  
Academia Sinica, Taiwan*

We have achieved the world's highest intensity for the Ca mass peaks with Ca-40 ~ 2 nA in TIMS. At such high intensity even the smallest Ca peak (only account for 0.004% of Ca) at 46 amu can be measured using simple Faraday cups instead of the more troublesome multiplier. The largest anomaly is usually Ca-48 for which our 2 sigma precision is about 0.007%. This Ca-48 variation correlates with Ti-50 and Cr-54. Thus, they constitute a nuclear component that astrophysicists now believe can only come from a neutron-rich rare subset of Type Ia supernova. How to produce the variation of the order 0.01% over large bodies hundreds kilometers in size and AU in separation? Since SNI has only Fe and Ni but no H, C, N, O, S we speculate that Ca-48 has nothing to make oxide, sulfides etc. with thus must somehow be included in the Fe-Ni metallic grains. These chemically peculiar grains then carried the unusual nuclear component. The interaction between the magnetic dust and proto-solar magnetic field may produce a gradient over large distances. Alternatively, the variation may be caused by the sudden release of Ca from the FeNi and these very active Ca probably react with the surrounding gas. However, the data in literature indicate a max solubility for Ca in Fe metal is only 0.4% that is lower than the Ca/Fe production ratio in some SNIa. Will the extra Ca condense? If so, in which phase?

## **Data Reduction Issues**

### **Dangers of determining isotope ratios using means of individual ratios.**

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Traditionally in mass spectrometry, isotope ratios are determined by calculating the mean value of a set of ratios calculated from cycle data. Data are collected in cycles in order to monitor changes in the ion current with time and to identify noise spikes or other problems with the measurements. However, the mean of the individual ratios may be a badly biased estimator of the true ratio (Ogliore et al., 2011). The bias is always positive and if the number of counts in each ratio is low enough the bias can be quite significant. For those who study short-lived radionuclides, this bias is particularly insidious because it is inversely proportional to count rate in a way that looks very much like an isochron. This poster will illustrate several data sets that we have collected over the years, some of which are heavily biased and some of which are not. Fortunately, it is possible to use a much-less-biased estimator of the true ratios in cases of significant bias (Ogliore et al., 2011). Summing the total counts for each isotope and then calculating the ratio greatly reduces the bias in most cases. Other estimators are available for more extreme cases. One can still use the cycle data to check for problems with the data and to do time interpolation. But one should use the time-interpolated, edited total counts to calculate the final ratios, not the mean of the individual ratios. See also the oral presentation by Huss and Ogliore on Friday afternoon.

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