

**STABLE ISOTOPE FACILITIES AT THE CENTER FOR STABLE ISOTOPES (CSI), UNIVERSITY OF NEW MEXICO.** K. Ziegler<sup>1,2</sup> and Z.D. Sharp<sup>1</sup>, <sup>1</sup>Dept. of Earth and Planetary Sciences, University of New Mexico, Albuquerque, NM, 87131, zsharp@unm.edu, and Center for Stable Isotopes, University of New Mexico, Albuquerque, NM 87131, <sup>2</sup>Institute of Meteoritics, University of New Mexico, Albuquerque, NM 87131, kziegler@unm.edu

**Introduction:** The Center for Stable Isotopes (CSI) at the University of New Mexico is particularly well situated for stable isotope analysis of meteorite and mission return samples (e.g., the Hababusa-2 sample returns). Over the last 15 years, and more recently with the University-supported conversion to a University-wide research center, our laboratory's analytical capabilities have been focused on addressing planetary-related research questions. In particular, we have worked to develop the best possible analytical precision combined with high spatial resolution for oxygen, hydrogen and chlorine isotope ratios of solid materials. CSI houses 7 mass spectrometers and custom peripheral devices, with most of these systems tailored for specific research tasks. A significant part of the mission of the new Center for Stable Isotopes is outreach across the University and greater scientific community. The University has committed funds for upgrading our facilities and provided the Center with additional technical support staff specifically with the goal of extending our collaborative research effort as defined by our research mission statement. Opening the facility to outside NASA-supported scientists is an important part of our plans. Both authors have NASA funded research projects and equipment, and already have worked with a large number of NASA-funded and other scientists from other institutions in collaborative research efforts.

**Instrumentation** In addition to conventional stable isotope analyses (CNOS analyses of solids using elemental analyzer (EA), TC-EA for H and O, and GC-IRMS), our specific NASA-related systems are outlined in the following subsection. The modifications and improvements made to these systems are directly tailored to improving analytical precision and reducing sample size, critical for rare extraterrestrial materials.

*Triple oxygen isotope analyses of silicates.* Combined  $\delta^{18}\text{O}$  and  $\delta^{17}\text{O}$  analyses of meteoritic materials is a fundamental geochemical parameter [1]. Displacements from the *Terrestrial Fractionation Line* (TFL), given by  $\Delta^{17}\text{O}$ , have long been used to classify extraterrestrial materials. Only recently, it has been recognized that with great care, precision of  $\Delta^{17}\text{O}$  values can be increased to better than 0.01‰ [2]. We have recently purchased a new Thermo Finnigan MAT 253 mass spectrometer (50% NASA funding) specifically configured for measuring the triple oxygen isotope compositions of  $\text{O}_2$  gas. We have also constructed a new

laser extraction system with a gas chromatographic system for purification of  $\text{O}_2$  gas from contaminating  $\text{NF}_3$  gas (Fig. 1). Our precision for  $\Delta^{17}\text{O}$  values is now 0.005‰ when extremely long counting times are used. These time-demanding analyses would normally limit the mass spectrometer time available for other research projects, but because we have a second, lower-precision laser extraction system/mass spectrometer, we can afford to have long counting times for our high precision system without compromising other research. Our immediate applications include determining dif-



Fig. 1. Photograph of our new high-sensitivity MAT 253 mass spectrometer with our new  $\text{CO}_2$  laser extraction line including a GC column required for the highest purity of molecular  $\text{O}_2$ .

ferences in the  $\Delta^{17}\text{O}$  values of terrestrial and lunar samples, inter-sample and inter-mineral variability in  $\Delta^{17}\text{O}$  values of Martian meteorites, and, exploring subtle differences or similarities between different meteorite groups (OCs vs. UOCs, HEDs vs. mesosiderites, PMG variability, etc.). A modified analytical set-up (including Ni-bombs for direct fluorination of  $\text{H}_2\text{O}$  and extraction of  $\text{O}_2$  gas) is also used to analyze waters. Currently, we are using this system analyzing waters evolved from stepwise dehydroxylation of a variety of Martian meteorites in order to explore the existence and nature of multiple oxygen isotope reservoirs on Mars.

*Micro extraction line.* The above-mentioned extraction system provides for the highest possible precision  $\Delta^{17}\text{O}$  analyses attainable by any method. It is, however, limited to a minimum sample size of  $\sim 0.7$  mg. In order to analyze smaller samples, we have constructed a continuous flow extraction system similar to the pioneering system described by E. Young and colleagues [3]. One critical difference is that our system is

not *in situ*, in which a UV laser ablates a sample in an  $F_2$  atmosphere. While the *in situ* system has the clear advantage of being a spot analysis, it suffers from complications including 'edge effects',  $O_2$  blanks from the  $F_2$  reagent, and passive fluorination of the sample chip. Our system uses  $BrF_5$  reagent and a  $CO_2$  laser for complete reaction of individual  $\mu g$ -sized samples. The purity of  $BrF_5$  is higher than  $F_2$ , edge effects are eliminated and passive fluorination is drastically reduced. The sample size is closer to that of the ion microprobe spatial resolution, while providing a significantly higher precision for  $\Delta^{17}O$  analysis. In order to extract physical samples while maintaining similar high spatial resolution, we use a UV laser to cut out  $\mu g$  blocks from thin wafers as described below.

**UV laser micro sampling.** We are able to cut out  $\mu g$  samples from thin ( $\sim 100 \mu m$  or greater) plates of rock using a NewWave LUV 213 nm ultraviolet laser (Fig. 2). The laser is rastered back-and-forth along a predefined path with  $\sim 10 \mu m$  resolution until the sample is cut through. The high spatial resolution allows for individual phenocrysts, specific regions of chondrules or CAIs to be separated for analysis in the micro-system described above. We are currently applying this laser microsampling technique to NWA 7034 (aka "Black Beauty"), a basaltic breccia from Mars' crust that contains a large variety of clasts of different lithologies and minerals of different ages [4]

**Micro hydrogen isotope analysis.** Another analytical technique that we are pursuing is D/H determinations of nanoliter  $H_2O$  equivalent solid samples. We are miniaturizing our continuous flow analytical method for hydrogen isotope analysis of solid materials [5] by constructing a micro-reduction column and employing a high-efficiency open split system (Thermo Finnigan Gas Bench). This should allow us to reduce sample size by  $\sim 10^3$  to nanoliter  $H_2O$  equivalent range. We are pursuing this methodology as part of a Keck grant (P. Buseck, ASU, PI). Planned research will be centered on hydrous phases/minerals in unequilibrated chondrites and in differentiated meteorites. Understanding the role of water in the transition from planetesimals to rubble-pile asteroids to differentiated asteroid is crucial in understanding the origin of water on planets, and, therefore, in understanding the origin of life. For example, based on D/H ratios of comets, it is not plausible that they are the origin of Earth's water, but D/H ratios of CCs (similar to D/H of Earth's oceans) indicate that a large part of today's water could originate in protoplanets from the outer asteroid belt.

**Chlorine isotope analysis of solid materials.** A final analytical technique developed in our laboratory is pyrohydrolysis of solid samples for Cl isotope anal-

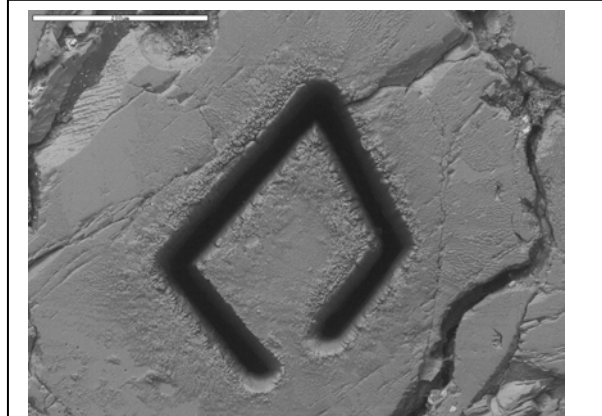


Fig. 2. SEM photomicrograph of a laser cut in a single crystal of olivine. The path is defined through the software. Samples are bathed in a stream of  $N_2$  gas during lasing to prevent possible reaction with atmospheric oxygen, and overheating. White bar is 200 microns.

yses. Our analyses are made in continuous flow using methyl chloride ( $CH_3Cl$ ) as an analyte. The gas source methyl chloride method provides the highest precision available. We recently modified our system to allow for a more efficient open split and have reduced the sample blank to bring the necessary size of analysis down to the sub- $\mu g$  Cl equivalent range. Immediate applications are to lunar and primitive chondrite samples. Initial research low petrologic type chondrites, Earth, Moon and Mars suggest that the low isotopic composition of primitive chondrites reflect the Cl isotope composition of the solar nebula.

**Summary:** The Center for Stable Isotopes at UNM is a laboratory uniquely situated and housed together with the Institute of Meteoritics and the Department of Earth and Planetary Sciences. Thus, CSI users have access to a range of microelectro and -ionbeam facilities, state of the art X-ray diffraction, spectroscopy, microscopy, chemistry laboratories, allowing for specific scientific collaborations within one building.

**References:** [1] Clayton, R.N., *Oxygen isotopes in meteorites*, in *Treatise on Geochemistry*, H.D. Holland and K.K. Turekian, Editors. 2003. p. 129-142. [2] Pack, A. and D. Herwartz, *The triple oxygen isotope composition of the Earth mantle and  $\Delta^{17}O$  variations in terrestrial rocks*. *Earth and Planetary Science Letters*, 2014. **390**: p. 138-145. [3] Young, E.D., et al., *Isotope-ratio-monitoring of  $O_2$  for microanalysis of  $^{18}O/^{16}O$  and  $^{17}O/^{16}O$  in geological materials*. *Geochimica et Cosmochimica Acta*, 1998. **62**: p. 3087-3094. [4] Santos, A.R. et al., *Petrology of igneous clasts in Northwest Africa 7034: Implications for the petrologic diversity of the martian crust*. *Geochimica et Cosmochimica Acta*, 2015. **157**: p. 56-85. [5] Sharp, Z.D., V. Atudorei, and T. Durakiewicz, *A rapid method for determination of hydrogen and oxygen isotope ratios from water and solid hydrous substances*. *Chemical Geology*, 2001. **178**: p. 197-210.