

DUAL SI AND O ISOTOPE MEASUREMENT OF METEORITIC SAMPLES USING IRMS.

P. J. A. Hill¹, N. R. Banerjee¹ and G. R. Osinski^{1,2}, ¹Department of Earth Science, Centre for Planetary Science and Exploration (CPSX) and ²Department of Physics and Astronomy, University of Western Ontario, London, ON, Canada.

Introduction: Theoretical models and isotopic systems have become an increasingly sophisticated tool to investigate the accretionary history and origin of planetary bodies in the solar system. In addition to the stable isotopes of oxygen, the stable isotopes of silicon in terrestrial and extraterrestrial samples have been used to further understand planetary processes [1–5] and have been used to argue against an enstatite chondrite Earth [6]. In respect to the Moon, silicon isotopes have been utilized to constrain both the element ratios within the bulk silicate Moon and the timing of the Giant Impact relative to the Earth's core formation [7].

Analytical Techniques for Silicon Isotope Determination: The analysis of the Si isotope ratios in terrestrial and extraterrestrial material has historically been measured through three main techniques: isotope ratio mass spectrometry (IRMS), secondary ion mass spectrometry (SIMS), and multi-collector inductively coupled plasma mass spectrometry (MC-ICPMS). Each technique has its own strength and weakness. IRMS allows the analysis of many types of sample (bulk rock, mineral separates, water, etc.) with high precision, though requires fluorination [8, 9]. Similarly MC-ICPMS is capable of measuring many types of material with high precision [10, 11] however, interference on ³⁰Si by ¹⁴N¹⁶O means that $\delta^{30}\text{Si}$ is commonly calculated empirically from $\delta^{29}\text{Si}$. Using a high-resolution MC-ICPMS it is possible to resolve polyatomic interference and measure all three stable isotopes [12]. SIMS analysis cannot measure isotopic ratios in bulk samples but provides exceptional spatial resolution on individual grains, not capable using IRMS or MC-ICPMS. Despite this advantage, the precision using SIMS is generally lower than IRMS or MC-ICPMS [13, 14].

Dual Si and O Isotope Measurement using IRMS: A unique laser line system has been developed in the Laboratory for Stable Isotope Science at Western University, Canada, that simultaneously extracts Si and O from the same 1–2 mg aliquot of sample. The stable isotopes of Si and O are then measured on specially configured MAT253 and Delta V Plus isotope mass ratio spectrometers, respectively.

Detailed Technique: This laser line utilizes a 25W CO₂ laser to heat the sample in the presence of BrF₅ to release SiF₄ and O₂ gas from bulk sample and grain separates for measurement on the isotope ratio mass spectrometers. Prior to reaction, BrF₅ is purified to ensure the best possible precision in determining the silicon stable isotope ratio. The sample chamber is pre-fluorinated overnight to ensure the removal of any adsorbed water. The sample is heated with the laser in a stepwise pattern by carefully controlling the power as the beam is focused until the reaction is complete. The liberated gas is first purified through a cryogenic metal trap (cooled with liquid nitrogen) and is left for sufficient time so that SiF₄, along with other fluorination products are condensed out. The O₂ gas is then purified and transferred for analysis on a Delta V Plus isotope ratio mass spectrometer in dual inlet mode as described by [15]. Once the O₂ gas is collected, the SiF₄ gas in the first metal trap is warmed with an ethanol-liquid nitrogen mixture (-100°C) and condensed onto the next metal trap using liquid nitrogen. Repeating this heating-freezing from trap to trap purifies the SiF₄ gas. This stepwise process uses two metal cryogenic traps and one cryogenic glass trap with the gas passing through a heated Ni bead trap to remove any residual fluorine compounds. Once purified the SiF₄ is condensed onto a Pyrex glass sample tube and transferred to a custom built MAT 253 isotope ratio mass spectrometer with collectors for mass 28, 29, and 30 in dual inlet mode.

Summary: Most literature focuses on the measurement of oxygen or silicon isotopes. However, the implementation of this IRMS technique allows for the precise analysis of Si and O isotopes from the same aliquot of bulk sample, which cannot be done with SIMS or ICP-MS analysis. Although simultaneous measurement of Si and O using IRMS has been conducted on biogenic silica [16], there has been no investigation of extraterrestrial material. This study explores the application of this unique technique to Apollo, meteoritic, and terrestrial samples.

References: [1] Armytage R. M. G et al. 2011. *Geochimica et Cosmochimica Acta* 75:3662-3676. [2] Fitoussi C. et al. 2009. *Earth and Planetary Science Letters* 287:77-85. [3] Savage P. S. et al. 2010. *Earth and Planetary Science Letters* 295:139-146. [4] Savage P. S. et al. 2011. *Geochimica et Cosmochimica Acta* 75:6124-6139. [5] Chakrabarti R. and Jacobsen S. B. 2010. *Geochimica et Cosmochimica Acta* 74:6921-6933. [6] Fitoussi C. and Bourdon B. 2012. *Science* 335:1477-1480. [7] Armytage R. M. G. et al. 2012. *Geochimica et Cosmochimica Acta* 77:504-514. [8] Molini-Velsko C. et al. 1986. *Geochimica et Cosmochimica Acta* 50: 2719-2726. [9] De La Rocha C. L. et al. 1996. *Analytical Chemistry* 68: 3746-3750. [10] De La Rocha C. L. 2002. *Geochemistry, Geophysics, Geosystems* 3: art. No.-1045. [11] Cardinal D. et al. 2003. *Journal of Analytical Atomic Spectrometry* 18: 213-218. [12] Georg R. B. et al. 2006. *Chemical Geology* 235: 95-104. [13] Stone J. et al. 1991. *The Geochemical Society, Special Publication No. 3*: 487-504. [14] Zinner E. et al. 2003. *Meteoritics & Planetary Science* 38: A60. [15] Ali A. et al. 2016. *Meteoritics & Planetary Science* 51: 981-995. [16] Leng M. J. and Sloane H. J. 2008. *Journal of Quaternary Science* 23:313-319.