

DEVELOPMENT OF SUBMICRON OXYGEN-THREE ISOTOPES ANALYTICAL PROTOCOL FOR ~1 μm WILD 2 PARTICLES. M. Zhang¹, K. Kitajima¹, and N. T. Kita¹, ¹WiscSIMS, Department of Geoscience, University of Wisconsin–Madison, Madison, WI 53706, USA (mzhang467@wisc.edu).

Introduction: Wild 2 particles returned by the “Stardust” mission have been providing us with new understandings of materials accreted to outer solar system comets since 2006. The major surprise is the findings of crystalline silicate particles similar to CAIs and chondrules in primitive chondrites, which provided strong evidence of large-scale transport of solids across the full dimension of the solar nebula [1]. The conclusion is mainly based on mineralogy and chemistry of the “terminal particles” at the end of stardust tracks in space-exposed aerogels, which are coarse-grained ($> 1 \mu\text{m}$, up to $\sim 30 \mu\text{m}$) and have been better preserved during the high-speed ($\sim 6.1 \text{ km/s}$) capture processes [2, 3]. Oxygen isotope studies of terminal particles with sizes typically $> 2 \mu\text{m}$ have identified both solar-like ^{16}O -rich materials (CAI, LIME olivine, and pyroxene) and chondrule-like ^{16}O -poor materials [3-11].

There are many more smaller (1-2 μm) Wild 2 crystalline silicate particles that were recovered as terminal particles of short carrot-shaped tracks and those smaller tracks located near the bulbous part of aerogel tracks. Systematic survey of a large number of these smaller crystalline silicate particles will allow for a more comprehensive view of the stardust particles, such as abundances of ^{16}O -rich particles ($\delta^{18}\text{O}$, $\delta^{17}\text{O} \sim -50\%$) similar to those studied by [4, 8] and very ^{16}O -poor particles ($\delta^{18}\text{O}$, $\delta^{17}\text{O} > +100\%$) that have been only observed among these smaller particles [7].

However, these 1-2 μm particles are too small for high precision ($\leq 2\%$, 2SD) oxygen isotope analyses with a typically $2 \times 1.5 \mu\text{m}^2$ ion beam [3-6, 8]. NanoSIMS studies have determined the oxygen isotope ratios of those particles with relatively large analytical uncertainties ($\geq 10\%$, 2SD) using the ion imaging model [9, 10, 12]. Besides, the ion imaging model of SIMS has also been used for this purpose [7]. In contrast, we developed a submicron analytical protocol for oxygen-three isotopes by spot analysis using CAMECA IMS 1280 at the University of Wisconsin-Madison. The analytical settings are generally same to previous high-precision SIMS analyses with 2 μm spot size [4, 8].

Analytical methods: A Cs^+ primary beam was focused to $\sim 1 \times 0.8 \mu\text{m}^2$ and intensity of $\sim 0.4 \text{ pA}$. The beam size and shape were optimized by inspecting the $^{16}\text{O}^-$ ion image of a SIMS pit after 5 min sputtering, with a $10 \times 10 \mu\text{m}^2$ primary beam rastering.

This method was established for 2 μm spot for 30 min analyses by [8]. The primary beam intensity is significantly lower than previous $\sim 1 \mu\text{m}$ oxygen-three isotopes analytical protocol ($\sim 8 \text{ pA}$) developed for Wild 2 particles [3]. Secondary ion intensities of $^{16}\text{O}^-$, $^{17}\text{O}^-$, and $^{18}\text{O}^-$ are $3\text{--}4 \times 10^5 \text{ cps}$, $1\text{--}2 \times 10^2 \text{ cps}$, and $7\text{--}9 \times 10^2 \text{ cps}$, which were detected simultaneously by a Faraday cup (FC) and two electron multipliers (EM), respectively. Due to low intensity of $^{16}\text{O}^-$ ($< 10^6 \text{ cps}$), we use 10^{12} ohm feedback resistor for the FC amplifier. The contribution of tailing $^{16}\text{O}^1\text{H}^-$ ions on the $^{17}\text{O}^-$ signal was corrected by the method described in [13]. A single analysis takes $\sim 10 \text{ min}$ that includes 60 s for presputtering, 60 s for centering secondary ions (DTFA scan once), and 200 s for signal integration ($10 \text{ s} \times 20 \text{ cycles}$). The measurement time is much shorter than the previous submicron oxygen-two isotopes analytical protocol (24 min) developed in WiscSIMS lab [14], in order to reduce the pit depth and avoid penetrating tiny Wild 2 particles.

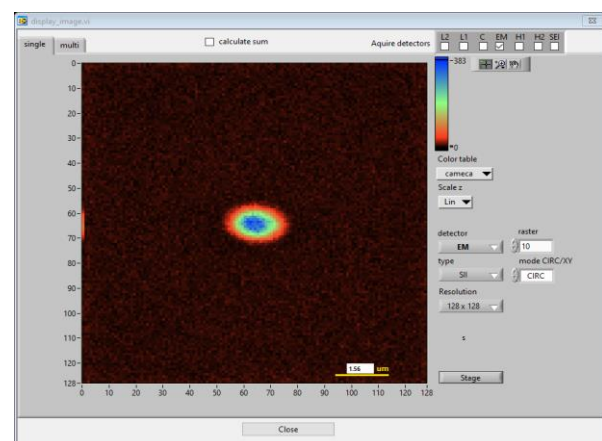


Fig. 1. $^{16}\text{O}^-$ ion image of a SIMS pit made by 5 min sputtering, showing the pit size (middle of the cyan circle) is $\sim 1 \times 0.8 \mu\text{m}^2$.

In order to evaluate the performance of the analytical protocol, we selected one AOA (G17) and two chondrules (G133 and G39) from the ungrouped Acfer 094 chondrite for SIMS analyses on olivine ($\text{Fo} > 90$). SIMS oxygen isotope analyses of the three objects were previously conducted by [15, 16] and resulted in homogeneous oxygen isotope ratios with mean $\Delta^{17}\text{O}$ values of -23% for G17, -6% and 0% for G133 and G39, respectively. San Carlos olivine standard (SC-OI;

[17]) was used as running standard to bracket the AOA and chondrules analyses. Instrumental bias of olivine analyses in AOA and chondrules were corrected solely using SC-OI, since the bias differences among forsteritic olivines are typically within 1 ‰ [17, 18]. After SIMS analyses, pits were checked using a field-emission SEM (Zeiss Auriga) at UW-Madison.

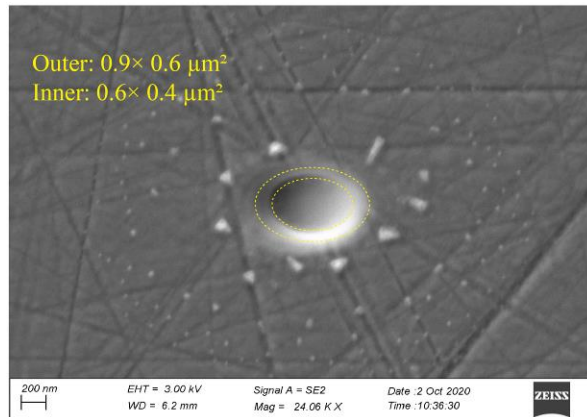


Fig. 2. SE image of a SIMS pit after 10 min analysis.

Results: Secondary electron (SE) image of AOA and chondrules show oval pits with a size of $0.9 \times 0.6 \mu\text{m}^2$ and a central size of $0.6 \times 0.4 \mu\text{m}^2$ (Fig. 2). This is smaller than our empirical estimate from ion image (Fig. 1). The pit depth was estimated to be $\sim 200 \text{ nm}$, by adopting a sputter rate of $0.21 \mu\text{m}^2/\text{s/nA}$ determined by [19], which are much shallower than those made by previous submicron oxygen-two isotopes analytical protocol ($\sim 1 \mu\text{m}$) [14] and $\sim 1 \mu\text{m}$ oxygen-three isotopes analytical protocol with a primary beam of 8 pA and a measurement time of $\sim 10 \text{ min}$ [3].

Spot-to-spot reproducibility (2SD) of bracketing SC-OI standard was $\sim 6\text{‰}$, $\sim 7\text{‰}$, and $\sim 9\text{‰}$ for $\delta^{18}\text{O}$, $\delta^{17}\text{O}$, and $\Delta^{17}\text{O}$, respectively. Reproducibility of $\delta^{18}\text{O}$, $\delta^{17}\text{O}$, and $\Delta^{17}\text{O}$ among four analyses of each AOA and chondrule were in a range of 1.0-3.6‰, 5.9-12.6‰, and 6.2-11.6‰, respectively (Fig. 3), which are comparable to that of SC-OI. While the analytical uncertainties of $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$ are slightly smaller than previous $\sim 1 \mu\text{m}$ oxygen-three isotopes analytical protocol ($\sim 4\text{‰}$) [3], they are lower than those obtained from ion imaging model of both NanoSIMS and SIMS (typically $\geq 10\text{‰}$) [7, 9, 10].

Conclusions: We developed a submicron oxygen-three isotopes analytical protocol, where the beam size is $0.9 \times 0.6 \mu\text{m}^2$, beam intensity is $\sim 0.4 \text{ pA}$, pit depth is $\sim 200 \text{ nm}$, and analytical errors (2SD) for $\delta^{18}\text{O}$, $\delta^{17}\text{O}$, and $\Delta^{17}\text{O}$ are $\sim 6\text{‰}$, $\sim 7\text{‰}$, and $\sim 9\text{‰}$, respectively. The analytical protocol meets the requirements for analyzing 1-2 μm Wild 2 particles and is capable of

distinguishing oxygen isotope ratios with differences greater than 10 ‰ in Wild 2 particles.

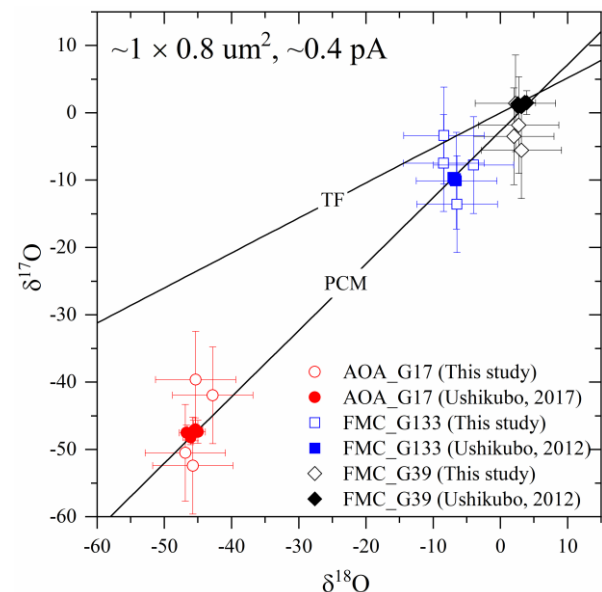


Fig. 3. Oxygen isotope ratios of an AOA and two chondrule fragments from the ungrouped Acfer 094 chondrite, which were determined by a $\sim 1 \times 0.8 \mu\text{m}^2$ beam. High-precision oxygen isotope data determined by $15 \mu\text{m}$ (G113 and G39) or $3 \mu\text{m}$ (G17) beams are plotted [15, 16].

References: [1] Brownlee D. E. (2014) *Annu. Rev. Earth Planet. Sci.*, 42, 179-205. [2] Brownlee D. et al. (2006) *Science*, 314, 1711-1716. [3] Nakamura T. et al. (2008) *Science*, 321, 1664-1667. [4] Nakashima D. et al. (2012) *EPSL*, 357-358, 355-365. [5] Joswiak D. J. et al. (2014) *GCA*, 144, 277-298. [6] Gainsforth Z. et al. (2015) *Meteoritics & Planet. Sci.*, 50, 976-1004. [7] Ogliore R. C. et al. (2015) *GCA*, 166, 74-91. [8] Defouilloy C. et al. (2017) *EPSL*, 465, 145-154. [9] Nakamura-Messenger K. et al. (2011) *Meteoritics & Planet. Sci.*, 46, 1033-1051. [10] Bridges J. C. et al. (2012) *EPSL*, 341-344, 186-194. [11] McKeegan K. D. et al. (2006) *Science*, 314, 1724-1728. [12] Stadermann F. J. et al. (2008) *Meteoritics & Planet. Sci.*, 43, 299-313. [13] Heck P. R. et al. (2010) *GCA*, 74, 497-509. [14] Page F. et al. (2007) *Am Min.*, 92, 1772-1775. [15] Ushikubo T. et al. (2017) *GCA*, 201, 103-122. [16] Ushikubo T. et al. (2012) *GCA*, 90, 242-264. [17] Kita N. T. et al. (2010) *GCA*, 74, 6610-6635. [18] Isa J. et al. (2017) *Chem. Geol.*, 458, 14-21. [19] Page F. Z. et al. (2010) *Chem. Geol.*, 270, 9-19.