

INTERMINERAL OXYGEN THREE-ISOTOPE SYSTEMATICS OF SILICATE MINERALS IN EQUILIBRATED ORDINARY CHONDRITES. D. McDougal¹, N. T. Kita¹, D. Nakashima^{1,2}, T. J. Tenner¹, J. W. Valley¹, and T. Noguchi³ ¹WiscSIMS, Department of Geoscience University of Wisconsin-Madison, Madison, WI 53706, USA (djmc Doug@wisc.edu). ²Tohoku University, Miyagi 980-8578, Japan. ³Kyushu University, Fukuoka 819-0395, Japan.

Introduction: Clayton [1] indicated that O isotope thermometry of olivine (Ol), low-Ca pyroxene (Lpx), and plagioclase (Pl) in equilibrated ordinary chondrites (EOCs) provides metamorphic temperatures (600-1000°C) that generally increase with increasing petrologic type. In the study of Itokawa particles analyzed by a secondary ion mass spectrometer (SIMS), Nakashima et al. [2] reported O three-isotopes in Ol, Lpx, high-Ca pyroxene (Hpx), and Pl, in Guareña (H6) and St. Séverin (LL6) chondrites that are not equilibrated. While $\Delta^{18}\text{O}_{\text{Pl-Hpx}}$ ($= \delta^{18}\text{O}_{\text{Pl}} - \delta^{18}\text{O}_{\text{Hpx}}$) values are consistent with peak metamorphic temperatures of EOCs (800-1000°C), isotope fractionations between Lpx-Ol and Hpx-Ol are too small (<0.5‰) when compared to those expected from Pl-Hpx. Nakashima et al. [2] suggested O isotope diffusion in Ol and Lpx was too slow during sub-solidus heating and thermal metamorphism to reset $\delta^{18}\text{O}$. To follow up [2], we report O-isotope systematics of 11 EOCs that cover all groups (H, L, LL) and metamorphic types (4, 5, 6), including S1-S4 shock stages, as well as unbrecciated and brecciated meteorites.

Samples: The 11 EOCs investigated here are: Forest Vale (H4), Bjurböle (L4), Soko Banja (LL4), Allegan (H5), Mifflin (L5), Ausson (L5), Tuxtuac (LL5), Estacado (H6), Lorton (L6), Bruderheim (L6), and St. Mesmin (LL6). Some of these EOCs were studied by [1, 3]. Shock stages are low (S1-S2), except for Bruderheim (S4). Mifflin, St. Mesmin and Bruderheim are breccias. Small fragments (2-6 mm) of individual meteorites were mounted in epoxy with San Carlos olivine standard grains and polished.

Methods: Per sample, approximately 8 target areas, each with coexisting Ol, Lpx, Hpx, and Pl, were identified using a scanning electron microscope with EDX (SEM, Hitachi S3400). Silicate minerals were >20 μm in size, and were either in direct contact or were up to 100 μm apart. In type 4 chondrites only coexisting Ol and Lpx were selected for analyses, as Hpx and Pl grains were too small for SIMS spots (15 μm dia.). Chemical compositions were measured via electron microprobe (EMP, Cameca SX-51). SIMS O three-isotope analyses were performed with the WiscSIMS Cameca IMS 1280 as described by [2]. Typical spot-to-spot reproducibility of $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$ is 0.3 ‰ and 0.5‰ respectively (2SD). Post-

analysis, SIMS pits were inspected by SEM.

Results: Fig. 1 shows examples of individual spot data from types 5-6 chondrites. Individual mineral data from unbrecciated type 6 EOCs (Fig. 1b, 1c) are indistinguishable within analytical uncertainties. Isotope fractionations between Lpx-Ol and Hpx-Ol in these type 6 chondrites are small ($\leq 0.5\%$), and are comparable to those reported in other type 6 chondrites [2]. Data are more scattered in type 5 (Fig. 1a) and brecciated type 6 chondrites (Fig. 1d), relative to unbrecciated type 6 EOCs.

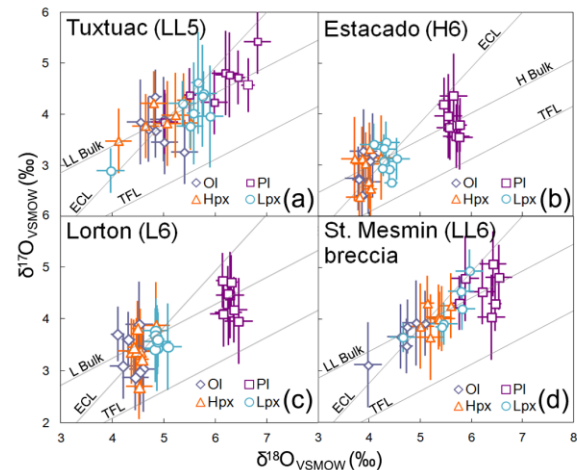


Fig. 1. O three-isotope ratios of mineral phases in types 5 & 6 chondrites. TFL: terrestrial fractionation line. ECL: equilibrated ordinary chondrite line [3]. Bulk H, L, LL chondrite mass-dependent fractionation lines [3] are also shown.

Ol and Lpx data from type 4 chondrites are shown in Fig. 2. They distribute widely above the TF line in $\delta^{18}\text{O}$, similar to those observed in LL3 chondrules [4]. Two Ol analyses from Soko Banja (LL4) plot below the TF line (Fig. 2) with the lowest $\Delta^{17}\text{O}$ value of $-8.1 \pm 0.3\%$, similar to relict olivine in LL3 chondrules [4].

Discussion: O isotope ratios of individual mineral phases tend to homogenize with increasing petrographic types for unshocked and unbrecciated EOCs (Figs 1-2). The ^{16}O -rich relict olivine data clearly demonstrate incomplete O isotope exchange and disequilibrium in type 4 chondrites. Values for brecciated

ciated and shocked type 6 chondrite data are significantly scattered compared to unbrecciated type 6 data. These characteristics occur in H, L, and LL chondrite groups.

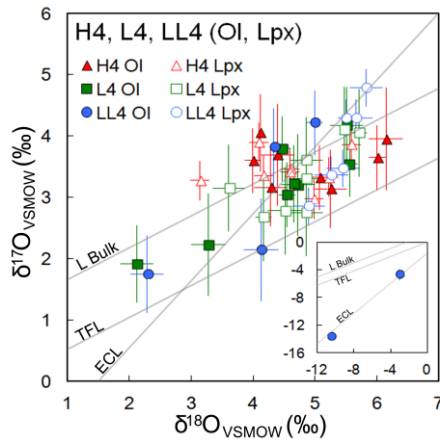


Fig. 2. O three-isotope ratios of Ol and Lpx in type 4 chondrites. Bulk L chondrite mass-dependent fractionation line [3] is shown as reference.

In Fig. 3, $\delta^{18}\text{O}$ data of coexisting Hpx and Pl are plotted from types 5 and 6 chondrites, which can be used to estimate temperatures of equilibrium isotope fractionation (T_{eq}). Unbrecciated type 6 data plot in a narrow range, corresponding to $T_{\text{eq}} = 700\text{--}800^\circ\text{C}$. In type 5 chondrites, multiple data pairs distribute along slope ~ 1 lines for each meteorite, consistent with equilibrium fractionation between Pl-Hpx, even though entire samples are not homogeneous. Estimated T_{eq} vary significantly, but suggest $\sim 1000^\circ\text{C}$ for Tuxtuac (LL5), $\sim 800^\circ\text{C}$ for Ausson (L5), and $600\text{--}700^\circ\text{C}$ for Allegan (H5). These temperatures may correspond to the closure temperatures of O isotope diffusion in Hpx [2], which increase with cooling rates after peak metamorphic temperatures. Tuxtuac (LL5) might have experienced faster cooling than other type 5 chondrites, based on nm scale exsolution in feldspar observed using transmission electron microscopy (TEM) [6].

Brecciated type 6 chondrite data are scattered (Fig. 3) and tend to show smaller fractionation in $\Delta^{18}\text{O}_{\text{Pl-Hpx}}$ than unbrecciated type 6 chondrite data, indicating higher temperatures. As such, individual mineral grains could have been homogenized by parent body metamorphism, and subsequently altered either by impact-generated heat, or by mixing of materials with different petrologic types as regolith breccia on the surface of parent bodies.

Homogeneous O isotope ratios within individual mineral phases in type 6 chondrites may suggest diffusional isotope exchange during thermal metamor-

phism, which would result in equilibrium fractionation. However, fractionations of Lpx-Ol ($\Delta^{18}\text{O}_{\text{Lpx-Ol}}$) in unshocked type 6 chondrites are much less than 1‰, which is expected for temperatures below 1000°C [2, 5, 7]. Even within target areas where all four minerals share grain boundaries, they do not show consistent equilibrium fractionations. This seemingly paradoxical result may indicate that the homogeneous isotope ratios in Ol were established by processes other than isotope diffusion during thermal metamorphism. Type 6 chondrites have a texture closer to equigranular, which implies significant recrystallization of original chondrule textures. Recrystallized minerals may have acquired homogeneous isotope ratios, while not being in equilibrium with each other.

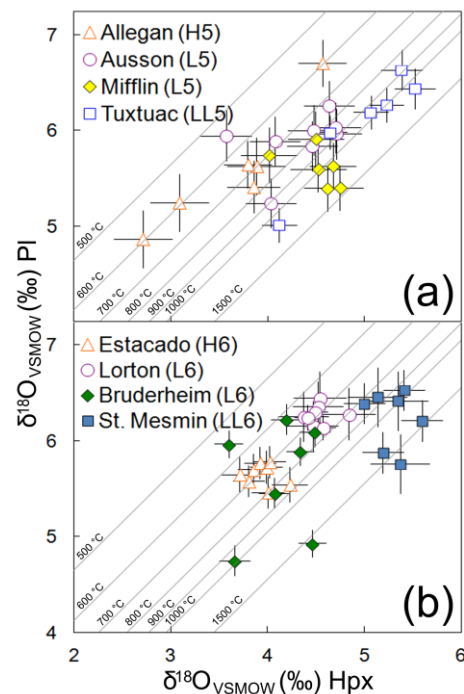


Fig. 3. Comparison of $\delta^{18}\text{O}$ values between Hpx and Pl within $100\ \mu\text{m}$ areas. (a) Type 5 chondrites, (b) Type 6 chondrites. Breccia data are shown with filled symbols. Equilibrium fractionation lines labeled with temperatures are calculated from [5].

References: [1] Clayton R. N. (1993) *Annu. Rev. Earth Planet. Sci.* 21, 115-149. [2] Nakashima D. et al. (2013) *EPSL*, 379, 127-136. [3] Clayton R. N. et al. (1991) *GCA*, 55, 2317-2337. [4] Kita N. T. et al. (2010) *GCA*, 74, 6610-6635. [5] Clayton R. N. and Kieffer, S. W. (1991) *Geochim. Soc. Spec. Publ.*, 3, pp.3-10. [6] Jones R. H. and Brearley A. J. (2011) *Meteoritics & Planet. Sci.*, 46, Abstract #5475. [7] Rosenbaum et al. (1994) *GCA*, 58, 2653-2660.