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How to cite:

Rumble, D.; Miller, M. F.; Franchi, I.A. and Greenwood, R.C. (2006). Variations in the oxygen three-isotope terrestrial fractionation line revealed by an inter-laboratory comparison of silicate mineral analyses. In: 37th Lunar and Planetary Science Conference, 13-17 Mar 2006, Houston, Texas, USA.

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Version: [not recorded]

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## VARIATIONS IN THE OXYGEN THREE-ISOTOPE TERRESTRIAL FRACTIONATION LINE REVEALED BY AN INTER-LABORATORY COMPARISON OF SILICATE MINERAL ANALYSES.

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**Introduction:** The terrestrial fractionation line illustrating  $^{17}\text{O}/^{16}\text{O}$  variations as a function of  $^{18}\text{O}/^{16}\text{O}$  is a consequence of mass-dependent isotope fractionation that occurs during heterogeneous chemical reactions between minerals, waters and magmas. Different planetary bodies may be characterized by different linear fractionation data arrays because of differences in bulk oxygen isotope composition. The Lunar fractionation line is coincident with that of the Earth [1]; that of Mars lies parallel to the former but is offset by  $\approx +0.32\text{‰}$  [2] in  $\delta^{17}\text{O}$ . In contrast, that of Vesta is offset by  $\approx -0.23\text{‰}$  [3,4]. Theory predicts, however, that the slopes of these linear fractionation arrays, when reported in a format appropriate for direct comparison [5], will not necessarily be identical. Equilibrium isotope fractionation of oxygen is predicted, in general, to yield steeper slopes than kinetically controlled isotope exchange [e.g. 6]. The greater degree of precision given by improved analytical techniques has raised the question of whether or not differences in slope can be detected by defining accurately the  $^{17}\text{O}/^{16}\text{O}$  to  $^{18}\text{O}/^{16}\text{O}$  array slopes of minerals. A related question is whether chemically-specific effects can cause distinctive slopes of the fractionation array. We have performed an inter-laboratory comparison of the oxygen three-isotope composition of replicates of specific groups of silicate minerals in order to (a) validate the slope value obtained; (b) permit a quantitative distinction to be made between the attendant fractionation line slopes given by different sample groups.

**Samples:** The samples chosen for study were: (1) quartz, primarily of hydrothermal origin, together with a single sample of flint; (2) garnets from the diamond-eclogite and coesite-eclogite facies metamorphic belts of China [7,8] and Kazakhstan [9].

**Methods:** The samples were analyzed by laser fluorination as described in [7] for GL and [10] for PSSRI. The GL garnet data set ( $\approx 70$  analyses) was acquired over several years by a number of operators. The garnet analyses at PSSRI were performed in a single batch (8 samples, in replicate), as were the quartz analyses (7 samples, in replicate) in both laboratories. Oxygen gas generated from quartz at PSSRI was split and analyzed on two different mass spectrometers – a VG Micromass PRISM III and a

Thermo MAT 253. A Thermo MAT 252 was used at GL.

**Results and Discussion:** The results (Table 1) show good agreement between both laboratories for TFL slopes measured on each of the garnet and the quartz populations. There is a systematic difference in slope, however, between the quartz and garnet samples. Whereas the measured slopes of the two mineral groups overlap slightly at the 95% confidence level, the observation that both laboratories agree on the magnitude and sign of the differences in slope demonstrates that the ability to distinguish between these groups of samples, and possibly also between equilibrium vs. kinetic geochemical processes, is within reach.

**Table 1**

Reported uncertainties are 95% confidence limits. The  $\delta^{18}\text{O}_{\text{VSMOW}}$  values ranged from  $\sim -1$  to  $33\text{‰}$  for the quartz and flint, whereas the corresponding range for the garnets was  $\sim -10$  to  $+10\text{‰}$

Silicate	PSSRI slope ( $\lambda$ )		GL slope ( $\lambda$ )
	Prism III	MAT 253	MAT 252
Silica (quartz or flint)	0.5241 $\pm 0.0008$	0.5245 $\pm 0.0009$	0.5240 $\pm 0.0016$
Eclogitic garnets	0.5263 $\pm 0.0008$		0.5255 $\pm 0.0014$

**References:** [1]Wiechert U. et al. (2001) *Science*, 294, 345–348. [2]Franchi I. A. et al. (1999) *Met. Planet. Sci.*, 34, 357–661. [3]Wiechert U. et al. (2004) *Earth Planet. Sci. Lett.*, 221, 373–382. [4]Greenwood R. C. et al. (2005) *Nature*, 435, 916–918. [5]Miller M. F. (2002) *Geochim. Cosmochim. Acta*, 66, 1881–1889. [6]Young E. D. et al. (2002) *Geochim. Cosmochim. Acta*, 66, 1095–1104. [7]Rumble D. and Yui T. F. (1998) *Geochim. Cosmochim. Acta*, 62, 3307–3321. [8]Zhang Z. M. et al. (2005) *Amer. Mineral.*, 90, 857–863. [9]Masago H. et al. (2003) *J. Metamorphic Geol.*, 21, 579–587. [10]Miller M. F. et al. (1999) *Rapid Commun. Mass Spectrom.*, 13, 1211–1217.