HIGH-PRECISION SILICON ISOTOPE RATIO MEASUREMENTS OF EARTH AND ENSTATITIC METEORITES AND IMPLICATIONS FOR Si ISOTOPE FRACTIONATION DURING CORE FORMATION. K. Ziegler[1], E. D. Young[1,2], J. T. Wasson[1], [1]Institute of Geophysics and Planetary Physics, UCLA, Los Angeles, CA 90095 (eyoung@ess.ucla.edu). [2]Department of Earth and Space Sciences, University of California Los Angeles (UCLA), Los Angeles, CA 90095 (kziegler@ess.ucla.edu),

Introduction: Core formation processes in planets may impart stable isotope ratio signatures on the bulk silicate Earth due to partitioning between the metallic core and silicate [1]. Enstatite chondrites (E-chondrites) are the only primitive meteorite group with stable oxygen isotope compositions similar to Earth [2]. The E-chondrites also possess a metal phase with substantial amounts of Si. We have begun a program of analyses aimed at searching for Si isotope fractionation between metal and silicate in E-chondrites and related rocks with the goal of testing the suggestion that there is substantial Si isotope fractionation between these phases during planet formation.

Silicon has long been suggested as a probable light element in Earth's Fe-Ni core [3]. New studies of silicon isotopic compositions ($^{30}Si/^{28}Si$) of the silicate phases of Earth and E-chondrites [1, 4] produced conflicting results as to their similarity or dissimilarity. Differences observed in $^{30}Si/^{28}Si$ between mantle rocks and meteorites in general have been attributed to fractionation between core and mantle (metal and silicate) [1]. A recent experimental study of Si isotope fractionation between silicate and metal phases suggests a 2 ‰ $^{30}Si/^{28}Si$ fractionation between Si in silicate and Si in metal at high pressure and temperature [5]. If such a fractionation is generally applicable [1], even at lower pressures for example, then the E-chondrites, with their abundant Si in metal, provide the opportunity to test the assertion that there is a strong Si isotope fractionation between metal and silicate in rocks.

Our first Si isotopic data for Earth's mantle and E-meteorite silicate suggest that there is no substantial difference between them, contradicting the results of Georg *et al.* [1], but supporting those of Fitoussi *et al.* [4].

Samples and Methods:

Silicon Isotopes. To date we have Si-isotope data on San Carlos (SC) olivine and the silicate phase of the Mt. Egerton meteorite (USNM 3272). Mt. Egerton is an enstatitic meteorite formed from E-chondrites; it mainly consists of coarse enstatite and metal containing 2.06 wt.% Si.

Silicon was extracted from silicate using dilute HF [6], and from iron metal by dissolution in concentrated HCl to form a silica gel [7] that was then dissolved in dilute HF. These digestions were further diluted with MilliQ water by a factor of 250 prior to purification. Silicon was purified for isotopic analysis using a cation exchange resin [8]. Silicon isotope ratio measurements were made with a ThermoFinnigan Neptune multiple-collector inductively coupled plasma-source mass spectrometer (MC-ICPMS). Corrections for instrumental mass bias were performed by sample-standard bracketing. Internal precision for the measurements is ±0.06 ‰ (2se) or better based on replicate standard analyses. The external reproducibility of our in-house standard is similar to the internal precision. Silicon isotopic analyses of more meteorites, including the metal- and silicate phases of some chondrites, are in progress, and results will be reported at the conference.

Oxygen Isotopes. High-precision infrared laser-heating fluorination with an analytical precision of ~0.02 ‰ is essential for the differentiation of close or overlapping $\Delta^{17}O$ ranges. We obtained oxygen isotope data for 7 E-chondrites, for San Carlos (SC) olivine and other Earth materials by dual inlet gas-source mass spectrometry (ThermoFinnigan DeltaPlus).

All isotope results presented here are averages from duplicate and triplicate sample aliquots, and averages from multiple mass spectrometrical analyses.

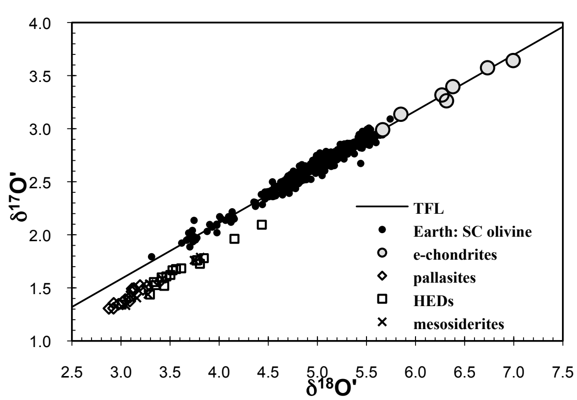

Figure 1. The correlation of the oxygen isotope composition ($\delta^{17}O'$ *vs.* $\delta^{18}O'$) of Earth material is expressed as the terrestrial fractionation line (TFL, slope 0.528), here defined by multiple analyses of SC olivine from our laboratory. Our E-chondrite oxygen data plot on the same line. Also shown, for comparison, are differentiated meteorite groups that do not fall onto the TFL [2]. Values are relative to V-SMOW.

Results: Oxygen isotope data clearly show that Earth ($\Delta^{17}O$ = 0.005‰, s.e. 0.002) and E-chondrites ($\Delta^{17}O$ =-0.007‰, s.e. 0.017) are very similar (Fig. 1).

$\Delta^{17}O$ values of all other meteorite groups deviate from the terrestrial fractionation line ($\Delta^{17}O$ larger or smaller than 0.0‰).

Our Si isotope data show that SC olivine has $^{30}Si/^{28}Si$ ($\delta^{30}Si$ values relative to NBS-28) of −0.24‰ that is within the range of values obtained in the two other recent studies [1, 4], and also in an earlier study of Si isotopes in Earth materials [9]. Our silicate (enstatite) from the Mt. Egerton meteorite has a $\delta^{30}Si_{NBS-28}$ value of −0.34‰, making the difference between Earth and Mt. Egerton silicate 0.1‰. However, we note that that these two numbers are from two different silicate phases: olivine in the case of Earth's mantle and enstatite in the E-chondrite. Theoretical calculations predict that equilibrium fractionation between these phases causes a small difference between pyroxene and olivine, with pyroxenes lower in $\delta^{30}Si$ than olivine by 0.1‰ at high T [10]; part of the difference we see between our E-chondrite silicate and terrestrial olivine is attributable to inter-mineral Si isotope fractionation.

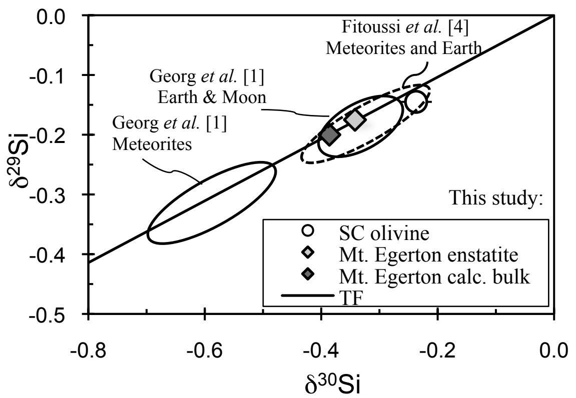

Figure 2. $\delta^{29}Si$ *vs.* $\delta^{30}Si$ diagram. Shown are the fields of published data for Earth and Moon and meteorites [1, 4], and the data points from this study. Analytical error bars (standard errors of multiple aliquots) are plotted but small. The slope of the silicon TF line is 0.5178. Values are relative to NBS-28.

Figure 2 shows our data points in comparison to references [1] and [4]. Our SC olivine plots within the range, albeit at the more positive end, observed for Earth materials [primarily whole rock data; 1, 4]. Our Mt. Egerton silicate datum falls within the range of terrestrial rock as defined by our datum and previous work. Our value for the Mt. Egerton chondritic meteorite is consistent with chondritic values obtained by Fitoussi *et al.* [4], whereas Georg *et al.*'s [1] chondrite data are more negative ($\delta^{30}Si_{NBS-28}$ values of ~ −0.5 to −0.7‰). The Fitoussi *et al.* [4] dataset does show a small difference between Earth and carbonaceous chondrites of 0.08 ± 0.04‰ in $^{30}Si/^{28}Si$ (C. Fitoussi, pers. comm.). This agrees with our 0.1‰ difference between E-chondritic pyroxene and terrestrial olivine.

The metal phase of Mt. Egerton is, at the time of writing, in preparation for the extraction of Si and for isotopic analysis. In the meantime, we can use the results from the recent experimental study of Si isotope fractionation between silicate and metal that suggests a 2‰ $^{30}Si/^{28}Si$ fractionation at 1Gpa and 1800°C [5].

Discussion: Using petrographic and chemical data for the Mt. Egerton meteorite [11], and the following isotopic mass balance equation:

$$\delta^{30}Si_{silicate} * X_{Si} + \delta^{30}Si_{metal} * (1-X_{Si}) = \delta^{30}Si_{chondrite},$$

the bulk (silicate and metal phase) $\delta^{30}Si_{NBS-28}$ value of the E-chondrite can be calculated to be −0.39‰ , or 0.05‰ more negative than the silicate phase alone. Comparing this value to the whole rock values obtained by Georg *et al.* [1] for chondrites (Fig. 2) still creates a mismatch of the most positive values of their dataset with our single data point of >0.1‰. The implication is that our single meteorite datum is not in agreement with the data of Georg *et al.* [1]. Georg *et al.* [1] analyzed one E-chondrite (Abee), and obtained a $\delta^{30}Si_{NBS-28}$ value (−0.69‰) 0.34‰ more negative than our E-chondrite measurement. We are unclear as to whether the Georg *et al*. datum reflects the $^{30}Si/^{28}Si$ of the silicate phase or of the bulk (silicate plus metal) meteorite. We have separated the metal phase from the silicate phase from Abee and two more E-chondrites, and will present the results at the conference.

Our work underscores the importance of considering inter-mineral stable isotope fractionation when reconstructing planetary-scale isotope ratios. A thorough investigation of inter-mineral Si-isotopic fractionation is required in order to understand whole rock comparisons.

Conclusion: If our data prove correct, and if they turn out to be characteristic of chondrites in general, then the experimental data [5] place a limit on the amount of Si in the core of no more than ~ 3%.

References: [1] Georg, R.B. *et al*. (2007) *Nature, 447*, 1102-1106. [2] Ziegler, K. *et al. LPSC XXXVII*, Abstract #1894. [3] Allègre, C.J. *et al.* (1995) *EPSL, 134,* 515-526. [4] Fitoussi, C. *et al.* (2007) *Eos. Trans. AGU, 88*, U11A-0022. [5] Shahar, A. *et al*. (2008) *Geochim. Cosmochim. Acta, 72/12***,** Suppl. 1, p A848. [6] DeLaRocha, C.L. (1996) *Anal. Chem., 68*, 3746-3750. [7] Bauer, O. and Deiss, E. (1915) in Hall, W.T. and Williams, R.S. *The Sampling and Chemical Analysis of Iron and Steel* (McGraw Hill). [8] Georg, R.B. *et al.* (2006) *Chem. Geol., 235*, 95-104. [9] Douthitt, C.B. (1982) *Geochim. Cosmochim. Acta, 46,* 1449-1458. [10] Méheut, M. *et al*. (2009) *Chem. Geol., 258*, 28-37. [11] Watters, T.P. *et al*. (1980) *Meteoritics & Planet. Sci, 15*, p. 386.