

Volatile concentrations and H-isotope composition of unequilibrated eucrites

Adam R. Sarafian¹, Sune G. Nielsen¹, Horst R. Marschall^{1,2}, Glenn A. Gaetani¹, Erik H. Hauri³, Kevin Righter⁴, Eve L. Berger⁵

¹Dept of Geology and Geophysics, WHOI, Woods Hole, MA 02540; ²Institut für Geowissenschaften, Goethe Universität Frankfurt, Altenhöferallee 1, 60438 Frankfurt am Main, Germany; ³Carnegie Institution for Science, DTM, Washington, DC 20015; ⁴NASA JSC, 2101 NASA Parkway, Houston, TX 77058; ⁵GCS– Jacobs JETS –NASA JSC, USA

Introduction: Eucrites are among the oldest and best studied asteroidal basalts (1). They represent magmatism that occurred on their parent asteroid, likely 4-Vesta, starting at ~ 4563 Ma and continuing for ~ 30 Myr (1). Two hypotheses are debated for the genesis of eucrites, a magma ocean model (2), and a mantle partial melting model (3). In general, volatiles (H, C, F, Cl) have been ignored for eucrites and 4-Vesta, but solubility of wt% levels of H₂O are possible at Vestan interior PT conditions (4). Targeted measurements on samples could aid our understanding considerably.

Recent studies have found evidence of volatile elements in eucrites (5), but quantifying the abundance of volatiles remains problematic (6). Volatile elements have a disproportionately large effect on melt properties and phase stability, relative to their low abundance. The source of volatile elements can be elucidated by examining the hydrogen isotope ratio (D/H), as different H reservoirs have drastically different H isotope compositions (7). Recent studies of apatite in eucrites have shown that the D/H of 4-Vesta matches that of Earth and carbonaceous chondrites (5, 6, 8), however, the D/H of apatites may not represent the D/H of a primitive 4-Vesta melt due to the possibility of degassing prior to the crystallization of apatite (6). Therefore, the D/H of early crystallizing phases must be measured to determine if the D/H of 4-Vesta is equal to that of the Earth and carbonaceous chondrites.

Eucrites consist of plagioclase and pigeonite (clinopyroxene), which are thought to have crystallized contemporaneously (3). Clinopyroxene, a nominally anhydrous mineral (NAM), contains H, C, F, and Cl in trace amounts, which allows for the use of partition coefficients to estimate the volatile content of the melt from which they crystallized (9, 10). In addition, the small amounts of hydrogen in pyroxene are sufficient for relatively high precision D/H measurements. Therefore, clinopyroxene may be an ideal recorder of primitive melt D/H and volatile contents if no post-crystallization alteration of the pyroxene occurred. Alas, the vast majority of eucrites are thermally altered, whereby magmatic Fe and Mg zoning in clinopyroxene has been erased. Since H diffusion rates are orders of magnitude faster than Mg and Fe, it follows that only samples with minimal thermal alteration may record magmatic D/H ratios and volatile concentrations. Therefore, for this study, we focus on the rare unequilibrated eucrites, Yamato 793548, 82210, 75011, and 74450.

Methods:

SEM. We used the JEOL 7600F at NASA-Johnson Space Center to BSE and EDS map all eucrites before SIMS analysis, minimizing beam exposure to phosphates to avoid alteration of the H-isotope ratios of phosphates by excessive electron beam exposure (11), to prevent this, we use low beam currents (~850 pA).

SIMS. We used the Cameca NanoSIMS 50L at the Carnegie Institution of Washington to measure H, C, F, Cl, and P concentrations and D/H in pyroxene. We also measured D/H in apatite. A 10 nA primary beam was rastered over a 15 x 15 μm² area, and the central 8 x 8 μm² of the secondary beam was collected using electronic gating.

Results: We measured EPMA and SIMS transects across large (100–1000 μm) pyroxenes from Yamato-793548, Y-822010, Y-75011, and Y-74450. Most pyroxenes have relatively Mg-rich cores and Fe-rich rims. Volatile element concentrations generally correlate with major elements, whereby pyroxene cores are MgO-rich and volatile-element poor and pyroxene rims are MgO poor and volatile-element rich (Figs. 1 & 2). D/H of pyroxene and apatite are within error of previously reported apatite measurements from eucrites (5, 8)

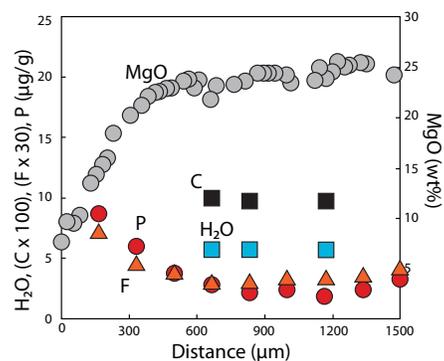


Fig 1. Data from SIMS and EPMA transect across large pyroxene grain in Yamato 74450. Uncertainty for volatile elements are ~5% relative and smaller than the symbol for MgO.



Fig. 2. Unequilibrated clast in Yamato 74450. SIMS and EPMA transect labeled. Field of view is 2 mm across

Discussion: Measuring volatile element concentrations, especially H, at $<10 \mu\text{g/g}$ is inherently challenging due to the need of maintaining low analytical backgrounds. The measured eucrites were breccias, and the pyroxene grains were internally fractured, which further complicated analyses. It had to be ensured that no cracks were analyzed. Due to the cracks in pyroxene, no full rim-core-rim SIMS volatile transects could be obtained. Despite this, we were able to observe a correlation between volatile elements and major elements (Fig. 1). Generally, pyroxene grains have volatile-poor cores and volatile-rich rims (e.g., F), which lead us to conclude that primary magmatic zoning is present in the pyroxene grains. In addition, the cores of pyroxenes of varying sizes, $\sim 100\text{--}1000 \mu\text{m}$ in the long dimension, displayed similar H contents ($8 \pm 2 \mu\text{g/g H}_2\text{O}$), which argues that post-crystallization diffusion did not occur. Primitive melt volatile element contents can therefore be calculated, using previously determined pyroxene-melt partition coefficients (9, 10). Based on 48 analyses of the cores of pyroxenes from our four measured eucrites, we conclude that eucrite magmas contain $\sim 260 \pm 70 \mu\text{g/g H}_2\text{O}$ (2 SD) and $2.5 \pm 0.3 \mu\text{g/g F}$ (2 SD).

To determine the bulk H_2O content of the parent asteroid, 4-Vesta, one must take into account the petrogenesis of eucrites. The two competing hypothesis are partial melting of the mantle (3) and melts extracted from a magma ocean (2). Assuming the former, we calculate the mantle H_2O content of 4-Vesta assuming that melting occurred until just olivine (70%) and orthopyroxene (30%) remained with a degree of partial melting of 15%; we determine a H_2O abundance for 4-Vesta of $\sim 40 \mu\text{g/g}$. This value should be considered a minimum, because we do not account for degassing before clinopyroxene crystallization. If we assume

eucrites are melts extracted from a magma ocean, then this magma ocean must have had at least $260 \mu\text{g/g H}_2\text{O}$ at the time of melt extraction, and the primitive magma ocean would have had $130 \mu\text{g/g H}_2\text{O}$ if the magma ocean crystallized 50% prior to melt extraction. 4-Vesta likely crystallized phases, e.g., olivine, and also degassed during its magma ocean stage (6). Hence, if eucrites were directly derived from a magma ocean, our estimate for the H_2O content of 4-Vesta is a lower limit.

D/H. The hydrogen isotope composition of both early (pyroxene) and late (apatite) crystallizing phases were measured. Pyroxene and apatite *D/H* show little variation with an average δD of $-139 \pm 92 \text{‰}$ ($n=6$), which is well within the uncertainty of previously published eucrite apatite H-isotope analyses (5, 8). The observation that our unequilibrated eucrites match the *D/H* of eucrites with varying degrees of equilibration suggests that thermal alteration on 4-Vesta was relatively early (12), such that no H-bearing exotic material was able to overprint the equilibrated apatite *D/H* signature. Also, the observation that the early-crystallizing pyroxene *D/H* matches that of the late-crystallizing apatite implies that H_2 did not degas in large proportions during solidification of eucrites. Therefore, either H_2 and H_2O (and possibly CH_4) were degassing contemporaneously, or little to no H-species degassing occurred at all.

Conclusions: We measured major and volatile element concentrations, as well as *D/H* in four unequilibrated eucrite clasts. Assuming a partial melt model for eucrites, we obtain a minimum H_2O content of 4-Vesta of $\sim 40 \mu\text{g/g}$. If we assume a magma-ocean model for the genesis of eucrites, we obtain a minimum of H_2O content of 4-Vesta of $\sim 130 \mu\text{g/g}$. The H isotope signature of unequilibrated eucrite clasts matches that of eucrites with varying degrees of equilibration, which gives further confidence to the previously established δD of 4-Vesta of approximately -150‰ , which is similar to Earth and other inner solar system bodies.

References:

- [1] D. W. Mittlefehldt, (2014) *CdE-G*. **75**, 155–183.
- [2] B. E. Mandler, L. T. Elkins-Tanton, (2013) *MAPS*. **48**, 2333–2349. [3] E. Stolper, (1977) *GCA*. **41**, 587–611. [4] K. Righter, (2007) *CdEG*. **67**, 179–200. [5] A. R. Sarafian, et al., (2014) *Science*. **346**, 623–626. [6] A. R. Sarafian, T. John, J. Roszjar, M. J., (2016) *EPSL*. 1–9. [7] F. Robert, (2001) *Science*. **293**, 1056–1058.
- [8] T. J. Barrett *et al.*, (2016) *MAPS*. **51**, 110–1124. [9] E. H. Hauri, G. A. Gaetani, T. H. Green, (2006) *EPSL*. **248**, 715–734. [10] C. Dalou, et al., (2012) *CMP*. **163**, 591–609. [11] J. J. Barnes *et al.*, (2012) *Chem. Geol.* **337-338**, 48–55. [12] T. Iizuka *et al.*, (2015) *EPSL*. **409**, 182–192.