WATER IN NOMINALLY ANHYDROUS CRUSTAL MINERALS OF VESTA. A. Stephant[1], R. Hervig[1] and M. Wadhwa[1]. [1]School of Earth and Space Exploration, Arizona State University, Tempe, AZ 85287.

Introduction: Characterizing the abundance and distribution of water in the inner Solar System is essential for understanding the sources and timescales of water delivery to the terrestrial planets and planetesimals [1]. In this context, the Howardite-Eucrite-Diogenite (HED) meteorites are important to study since they are thought to originate from the asteroid Vesta [2]. These achondritic meteorites provide a record of processes occurring on differentiated planetesimals in the early Solar System [4]. Although the HEDs are typically thought to be volatile-depleted [2], recent analyses of apatites in eucrites demonstrate that water may have been present, at least locally in the Vestan interior [5-7]. These studies also showed that the hydrogen isotope composition of eucritic apatites was similar to that of Earth and carbonaceous chondrites. These findings place new limits on the timing of water accretion into planetesimals in the inner Solar System. Specifically, it is suggested that water and other volatiles were likely accreted to the early Earth within a few Ma of CAI formation rather than during a late delivery event [6].

Since eucrite minerals crystallized from basaltic magmas, their compositions can provide insights into the compositions of their parent melts and the processes that attended their solidification to form Vesta's crust [2]. However, recent studies have shown that there may be complications involved in inferring the water contents of parent magmas based on the water contents of igneous apatites [8-10]. In particular, apatites in eucrites are late-stage minerals crystallizing from the residual melt after a significant fraction of the parent melt had already crystallized. As such, to infer the water content of the parent magma based on the apatite composition, a significant correction is required for the large degree of crystallization of other phases before the apatites were formed.

Nominally anhydrous igneous minerals, such as pyroxenes, may be better suited to determining the water content of eucritic parent magmas. Several studies have shown recently that clinopyroxenes could be as good as olivine-hosted melt inclusions for quantifying the water content of the parent magma [11-14]. Moreover, clinopyroxene is a major phase in eucrites and is one of the first crystallizing minerals from the eucrite parent melt [2]. As such, this mineral may be more reliable than later-forming minor or trace minerals for constraining the hydrogen isotopic composition and the water content of magmas formed on Vesta.

In this study, we present δD values and H_2O abundances in clinopyroxenes of two eucritic meteorites.

Samples: Polished thick sections of two eucrites, Juvinas and Tirhert, were studied here. Both of these eucrites are observed falls (Juvinas fell in France in 1821, while Tirhert fell in Morocco in 2014). Juvinas is a basaltic eucrite, classified as part of the main group (MG) trend. It is a monomict, equilibrated eucrite of petrologic type 5. Tirhert is a cumulate eucrite, classified as an unbrecciated petrologic type 6 eucrite.

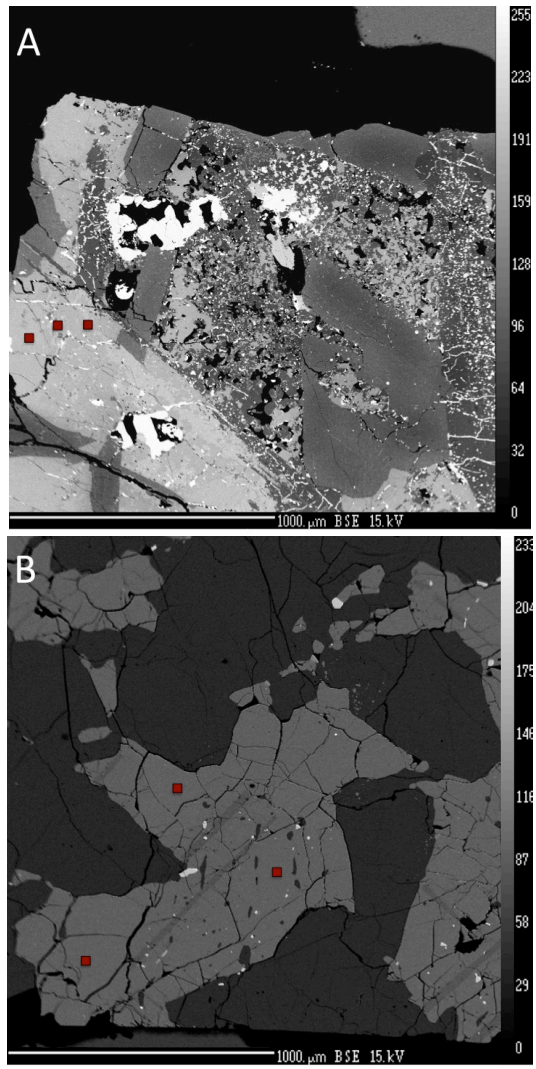

Figure 1 : Backscattered electron images of Juvinas (A) and Tirhert (B). Spots analyzed by SIMS (shown as red squares) in the large pyroxenes (light grey phase) were chosen to avoid cracks and inclusions.

Analytical Methods: Backscattered electron images (e.g., Fig. 1) were obtained and chemical characterization of mineral phases in polished thick sections of

Tirhert and Juvinas was performed on the Cameca SX-100 electron microprobe at the University of Arizona.

Secondary ion mass spectrometry (SIMS) measurements of D/H ratios and H_2O concentrations were performed on the Cameca IMS 6f at Arizona State University. A Cs^+ primary beam of ~13 nA was rastered on a 30×30 μm^2 surface area. A field aperture set the analysed area to 15 µm diameter which reduced background associated with edge effects. Each measurement was comprised of 60 cycles of measuring H^- and D^- ions with a counting time of 1s and 10s, respectively. At the end of each measurement, $^{16}O^-$ was measured. The H_2O contents were estimated using a $H^-/^{16}O^-$ vs. H_2O calibration based on terrestrial standards. An estimation of the background for both $H^-/^{16}O^-$ and D^-/H^- ratios was made based on analyses of a dry clinopyroxene pressed in an indium amount. A total of 10 pyroxenes were analysed (5 on each of the two eucrites studied here).

Results: Pyroxenes in Juvinas show H_2O contents ranging from 20±5 to 40±10 ppm, while those in Tirhert range from 15±4 to 38±9 ppm. The δD values (where $\delta D=[(D/H_{sample})/(D/H_{SMOW})-1] \times 1000$) of pyroxenes in Juvinas range from -306±77 to 19±115 ‰, with a weighted average value of -157±200 ‰ (95% confidence interval; n=5). Similarly, the δD values of pyroxenes in Tirhert range from -342±68 to -30±97 ‰, with a weighted average value of -263±140 ‰ (95% confidence interval;, n=5). Figure 2 shows a plot of δD versus H_2O content in pyroxenes of Juvinas and Tirhert.

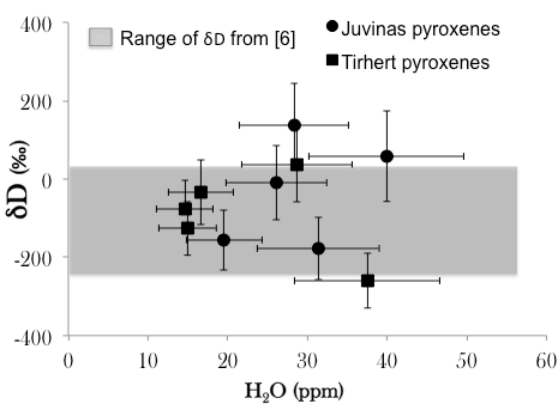

Figure 2 : δD (‰) vs. H_2O (ppm) of Juvinas (solid circles) and Tirhert pyroxenes (solid squares). Errors are 2 sigma, based on counting statistics. Grey band represents the range of δD values reported by [6] in eucrite apatites.

Discussion: The ranges of H_2O contents and δD values in pyroxenes of Juvinas and Tirhert are similar (Fig. 2). Thus, it seems likely that the H_2O contents and δD values were similar in the source reservoirs of the basaltic and cumulate eucrites on Vesta. Taken together, the weighted average δD value of all pyroxene analyses reported here is -220±100 ‰ (95% confidence interval; n=10). This value is indistinguishable from the weighted average of -162±127 ‰ reported for apatites from eucrites, which is in turn similar to that for Earth and carbonaceous chondrites [6].

We note, however, that we have not corrected the measured δD values for spallation effects. A maximum spallation contribution of 254‰ (with a 50% error) was estimated for lunar samples having an exposure age of ~28 Ma and H_2O content of 6.5 ppm [15]. We expect the correction for spallogenic D production in pyroxenes of the eucrite studied here to be lower because (i) Juvinas has a shorter exposure age of 11.9 Ma [16] (the exposure age of Tirhert is currently unknown, but is unlikely to be higher than that of other known eucrites), (ii) the H_2O contents of Juvinas and Tirhert pyroxenes are higher and (iii) Vesta is further from the Sun than the Moon. Nevertheless, considering that processes such as spallation by solar wind exposure and magmatic degassing may have resulted in increasing the original δD signature in the eucrite pyroxenes, the weighted average δD value of -220±100 ‰ must be considered an upper limit for Vesta.

In principle, measured H_2O abundances in eucritic pyroxenes can allow us to place limits on the H_2O content of the melts from which they crystallized. Several studies have noted a coupling between clinopyroxene H_2O content and the amount of Al^{3+} [11,12], leading to an equation for determining the H_2O partition coefficient between clinopyroxene and melt [13]. Using this equation and taking the H_2O abundances that we have measured in eucrite pyroxenes at face value, the H_2O content in the Juvinas and Tirhert parent melts is estimated to be 0.1-0.3 wt.%, However, there are substantial uncertainties in these estimates given that these samples could have been affected to a significant degree by processes such as magmatic degassing, crystal fractionation and/or terrestrial weathering.

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