HED PETROGENESIS: AN INSIGHT FROM LOW-CA PYROXENE – MELT REE PARTITIONING.
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Introduction: The Howardite-Eucrite-Diogenite (HED) achondrites are the basaltic and cumulate rocks which represent the crust, and possibly part of the mantle, of the asteroid 4 Vesta. Vesta is the only known intact differentiated protoplanet and the early formation and crystallization ages recorded [1] mean that the HED meteorites provide us with an invaluable snapshot of the early conditions and planet forming processes occurring in the early solar system. The genetic link between the diogenites and eucrites is currently debated, as the meteorites record a range of lithologies, major and trace element compositions.

There are two main models of vestan evolution to form the HEDs: partial melting and serial magmatism (e.g. [2], [3]) and the magma ocean model (e.g. [4], [5], [6]). Neither model can account for both the range of major and trace element compositions recorded in the HEDs. The serial magmatism hypothesis can produce the range of major and trace element compositions but requires more than one source of components to produce eucrites and diogenites, whereas the magma ocean model can produce the major element composition of the eucrites and diogenites from one source, but not the range in trace element compositions. In either model secondary processes are invoked. The depletion in highly siderophile elements in the HEDs [5] and the homogeneity in Oxygen isotopes [7] are more consistent with an extensive melting and magma ocean model for Vesta. Our previous work [8] tested the magma ocean model for major elements experimentally. This study builds on that work and investigates the mineral-melt trace element behavior for the most predominant minerals in the HED meteorites: low-Ca Pyroxenes.

The Rare Earth Elements (REE) are a particularly useful tool for modeling silicate planetary evolution as different magmatic processes have different effects on the abundances and fractionation of these elements. The Eucrites and Diogenites show a large range in REE abundance and fractionation, as seen on a Dy/Yb vs Yb plot (Figure 1). This variation is not correlated with major element composition. A range of processes have been suggested for the trace element variations in eucrites and diogenites including the crystallization of multiple sources (e.g. [9]) or remelting of early magma ocean cumulates (e.g. [10]).

In order to test and refine the current petrogenetic models, accurate mineral-melt partition coefficients are required. The partitioning of elements between phases varies as a function of mineral and melt composition, temperature, pressure and oxygen fugacity [12].

We performed a series of one atmosphere high temperature experiments on synthetic compositions believed to be representative of Vesta’s bulk composition and the composition of partial melts of Vesta (taken from [8]) in order to determine suitable REE partition coefficients between low Ca-pyroxene and basaltic melt over the temperature and composition range that the Eucrites and Diogenites were likely to have formed. The calculated partition coefficients were then used in petrogenetic models of the evolution of Vesta.

Experiments: Starting compositions representative of the Vesta mantle, and its derived basalts were synthesized from mechanical mixtures of high purity oxides and carbonates. The mixtures were de-carbonated at 900 °C for several hours. The mixtures were then reground and doped with 100-400 ppm of the REE elements before pelletisation and reduction overnight in a Gero vertical gas-mixing furnace. Experiments were performed between 1150-1350 °C at one atmosphere, and CO-CO₂ gas mixtures were used to buffer the experiments at just above the Iron-Wustite (IW) buffer. Major element analysis was performed on the experimental charges using the JEOL JXA-8600 Electron Probe in the Research Laboratory for Archeaoology and the History of Art (RLAHA) in the Department of Archeology, and trace element analyses were determined using the New Wave Research UP213 Nd:YAG laser
in the Department of Earth Sciences, both at the University of Oxford.

**Results:** As the temperature decreases from 1350 to 1150 °C, the melt and mineral compositions decrease in MgO, with increasing Al₂O₃ and CaO contents (Figure 2), as low Ca pyroxene (first orthopyroxene, then pigeonite below ~1200 °C) and then plagioclase crystallises. The trace element compositions were measured in both the pyroxene and the basaltic melt and pyroxene-melt partition coefficients (D) for each element were calculated using the formula: \( D = \frac{C_{\text{melt}}}{C_{\text{min}}} \).

![Figure 2. Major element composition of the low-Ca pyroxenes projected into the Wo-En-Fs Ternary Diagram, along with previous work [8] and diogenites [11].](image)

The Partition coefficients for the REE elements were found to increase as temperature decreased from 1350 – 1150 °C, and Wo content of the low-Ca pyroxene increased from 1.1 to 4.5, for example DLa from 0.004 to 0.0071, and DYb from 0.02866 to 0.2008. The Lattice Strain model was fitted to each experiment and Do, ro and E calculated for the 3+ ions in the M2 site. Ro increases and E decreases with increasing Wo content and decreasing temperature from 0.78 A and ~250 GPa at 1150 °C and Wo 6.5 to 0.75 A and ~360 GPa at 1350 °C and Wo 0.4. Above 1250 °C Do is around constant at ~0.1 but increases linearly between 1250 – 1150 °C by a factor of 3 to ~0.3 (Figure 3). This increase in Do over the crystallization temperatures of the Eucrites and Diogenites, is significant for petrogenetic modelling, leading to different results from previous studies which used fixed partition coefficients (e.g. [10]).

**Petrogenetic Models:** Petrogenetic models investigating partial melting, fractional crystallization, cumulate re-melting and intercumulate melt processes were set up in MATLAB, and combined the experimentally determined partition coefficients, with major element models calculated by the alphaMELTS [13] thermodynamic software, reported in [8].

![Figure 3. Do vs Temperature for the 3+ REE ions in the M2 site of the experimental low-Ca pyroxenes.](image)

**Results:** The range in REE abundances in the eucrites and diogenites can be explained by a combination of processes. The first is internal melting of Vesta (either partial or global) creating partial melts and cumulates which become progressively depleted with respect to trace elements as the fraction of melting increases. Then, fractional crystallization of these melts produces olivine, low-Ca pyroxene and feldspar depending on the start composition, with melt and mineral compositions becoming more enriched in trace elements as crystallization progresses.

Partial re-melting (either batch or fractional) of basalts and cumulates increases the REE fractionation (decreases Dy/Yb) in the residual lithology as melt is extracted. If intercumulate melt is trapped during cumulate formation then subsequent re-equilibration will decrease the REE fractionation (increase Dy/Yb).

**References:**