DIFFERENTIATION OF THE HED PARENT BODY AND AN EVALUATION OF THE MELTS COMPUTATIONAL PROGRAM.

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Summary: Melting experiments were performed on the Righter-Drake [1] HED parent-body bulk composition at temperatures and pressure appropriate for eucrite formation, and run products were analyzed by Mössbauer spectroscopy to derive modes. MELTS calculations were performed using experimental conditions. Comparison of these three data sets lends insight into the accuracy of MELTS for modeling the thermodynamic conditions of these extraterrestrial materials.

Introduction: The HED meteorites (howardites, eucrites and diogenites) are a group of meteorites thought to originate from the same parent body, probably 4 Vesta, which has a eucrite-like surface composition [2]. The two most prevalent ideas for the origin of eucrites are fractional crystallization and partial melting. The former suggests that eucrites are residual liquids; the latter assumes that different degrees of partial melting formed various eucrites [3].

Righter and Drake proposed a model that they believe reconciles issues of timing and other physical conditions that previous models have failed to address. They envision a scenario in which eucrites and diogenites form after the equilibrium crystallization of a magma ocean present on the HED parent body [1]. Accordingly, they have modeled this crystallization history using MELTS and MAGPOX/MAGFOX, two thermodynamic modeling programs.

Our primary focus was to perform experiments that were comparable to those of Righter and Drake's model. The experimental data can then be used to evaluate the ability of MELTS to reproduce the results of experiments run at the same conditions.

Experiments: The composition used was that specified by Righter and Drake as their chosen bulk composition for the HED parent body — 70% L and 30% CV chondrites [1], to which we added 0.5 wt.% Sc_2O_3. Experiments were run for 3-8 days (varied so as to approach equilibrium), two charges per run, in a 1-atm Deltech gas-mixing furnace at iron-wüstite oxygen fugacity. Experiments were hung on Re loops to prevent iron-loss, and were rapidly drop-quenched to minimize quench effects. Temperature steps used were 1180°C, 1200°C, 1225°C, 1250°C. The 1180°C temperature is Stolper's original proposed eucrite liquidus [3], and 1250°C is the Righter-Drake model temperature at which equilibrium crystallization gives way to fractional crystallization [1]. The two intermediate temperature steps (1200, 1225°C) were chosen to provide a continual dataset.

Two minor but important differences distinguish our experiments from the calculations of [1]: our experiments were at 1 bar, while the calculations of [1] are at 500 bar; and we took the calculations of [1] literally, so our starting composition has 1 wt.% Na_2O. The HED parent body probably has 10X less Na.

MELTS calculations were also conducted to compare to the experimental data [4]. These calculations were run using the same temperatures, pressure, and oxygen fugacity as used above. The bulk composition was that of Righter-Drake, but adjusted for estimated Na-loss that occurred during the experiment.

Analysis: Experiments were imaged in backscatter on a JEOL 5910LV SEM to locate viable melt-pockets for analysis. Melt-pockets were no larger than 50 microns at the highest melting temperatures, and no melt-pockets smaller than 10 microns were analyzed at the lowest temperatures. Experiments were analyzed using the JSC Cameca SX100 electron microprobe with a 5 micron beam at 15 kV. For each analysis of a melt pocket, analyses were also performed on adjacent olivine and pyroxene crystals.

Microprobe data were used to check the stoichiometry of olivine, as well as to calculate the average compositions of all phases, partition coefficients, and Fe/Mg K_DS. Modes were calculated using Ca-Mg-Al-Si (CMAS) mass balance. These modes were then used to confirm that had been no Fe loss. Mössbauer analyses of 20-30 mg of each run were undertaken at MHC using procedures described in [5].

Results and Discussion: Calculations for olivine stoichiometry were extremely good, indicating that the microprobe analyses were well-calibrated. K_DS for Fe/Mg were also as expected (~0.33 for olivine and ~0.29 for pyroxene), indicating that equilibrium had been closely approached. Phases were generally homogeneous and showed little variation from grain to grain.

Comparison to MELTS. The compositions of the experimental phases were compared to MELTS calculations; this revealed consistent agreement between the two methods at each temperature. To illustrate this, delta (Δ) values were calculated for major oxides of the three major phases at each temperature step:

$$\Delta = ({}^{i}C_{meas} - {}^{i}C_{MELTS}) / {}^{i}C_{meas} * 100$$

where i is the major oxide (MgO, SiO_2, FeO, CaO or Al_2O_3), and C is the concentration of that oxide in wt. %, either as measured or calculated by MELTS. Figure 1 is a representative graph for the 1180°C run. As can be seen in Figure 1, the agreement between experimental results and MELTS calculations is quite good for the elements Mg, Si and Fe, with $\Delta \leq 5\%$ relative. Aluminum, a major constituent of the melt phase, also shows this level of agreement between experimental and MELTS results. The only significant discrepancy is with CaO. Underestimation of the pyroxene (and olivine) CaO content results in an overestimation of CaO in the melt. These observations are generally true of all four temperature steps.

Mode calculations took a departure from the expected trends, based on the results of Righter and Drake. Although it had been anticipated that the modal pyroxene would increase consistently with a decreasing temperature, this proved not to be the case. Pyroxene, olivine and melt have relatively constant proportions across the temperature gradient, possibly due to the increasing Na content as temperature decreased and less Na was volatilized.

Modes were calculated using three methods: in addition to the analytical CMAS mass balance and MELTS calculations, a least squares method was also employed. All three methods yielded similar melt fractions; however, the analytical method consistently underestimated pyroxene compared to the other two methods. These results are also being compared to modes calculated from the Mossbauer data, which quantify olivine well but may not distinguish between pyroxene and glass. Interpretation of these data is still being considered.
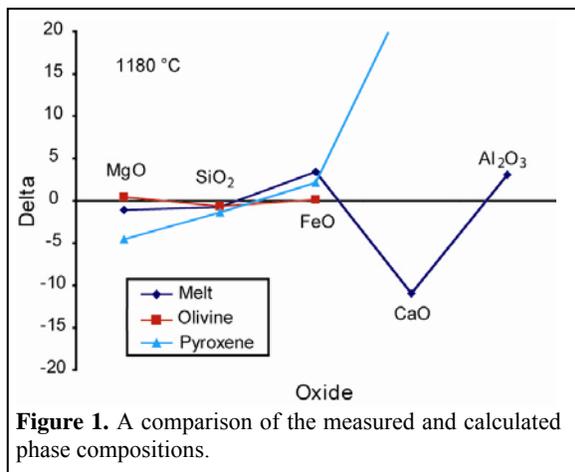

Figure 1. A comparison of the measured and calculated phase compositions.

Scandium Partitioning. Our Sc partition coefficients are similar to those of others and to unpublished work from JSC. $D(Sc)_{ol}$ ranged from 0.21 to 0.28; $D(Sc)_{px}$ ranged from 0.42 to 0.87.
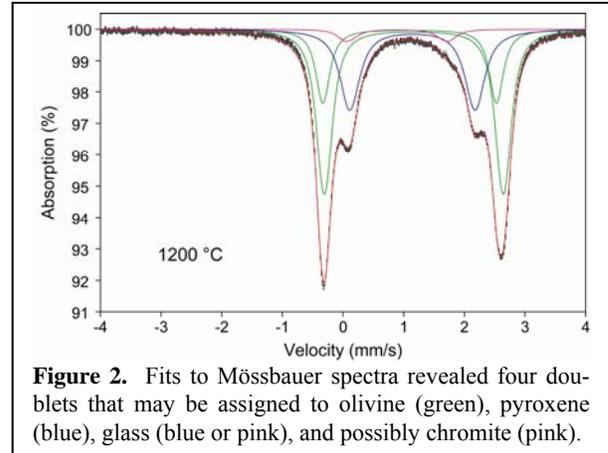

Figure 2. Fits to Mössbauer spectra revealed four doublets that may be assigned to olivine (green), pyroxene (blue), glass (blue or pink), and possibly chromite (pink).

Jones [6] emphasized the importance of the eucritic Sc/La ratio for the origin of eucrites [6]. Main Group eucrites have Sc/La ratios of about 0.6X CI, a significant fractionation. Using our measured D(Sc) values and modes, we calculate that the liquid of our 1250°C charge would also have a Sc/La ratio of about 0.6X CI. Crystallization from 1250°C to the liquidus temperature of eucrites would fractionate this ratio even further from chondritic.

Possibly this amount of fractionation is attributable to the enhanced Na in our experiments relative to eucrites. However, this type of Sc/La fractionation is to be expected in systems that have crystallized significant pyroxene. In fact, Jones [6] showed that the observed Sc/La of eucrites was possible with olivine fractionation alone. The larger values of D(Sc) for pyroxene exacerbates Sc/La fractionation and makes significant diogenite production difficult.

Conclusions: MELTS appears to approach equilibrium and does a good job of predicting phase compositions for this experimental composition. Phase proportions are less certain, and further research into this matter needs to be done. To this end, element maps have been made using the electron microprobe to get more absolute modal values for our experiments. These new data are in the process of being analyzed. Results from this may shed light on modal discrepancies. Overall, the data imply that Righter and Drake's conclusions based on MELTS seem to be corroborated. It remains to be seen if the Sc/La constraint can be met by the Righter-Drake model.

References: [1] Righter K. and Drake M.J. (1997) *MAPS,* 32, 929-944. [2] Grove T.L. and Bartels K.S. (1992) *LPSC XXII*, 437-445. [3] Stolper E.M. (1977) *GCA,* 41, 587-611. [4] Ghiorso M.S. and Sack R.O. (1995) *CMP,* 119, 197-212. [5] Dyar M.D. et al. (2007) *Amer. Mineral.*, 92, 424-428. [6] Jones J.H. (1984) *GCA,* 48, 641-648.