

AN EXPERIMENTAL STUDY OF TRACE ELEMENT PARTITIONING BETWEEN PEROVSKITE, HIBONITE AND MELT: EQUILIBRIUM VALUES; A.K. Kennedy¹, G.E. Lofgren² and G.J. Wasserburg¹, ¹Lunatic Asylum, Div. of Geol. and Planet. Sci. 170-25, C.I.T., Pasadena, CA 91125, ²SN2 NASA, Johnson Space Center, Houston, TX 77058.

Introduction: The presence of perovskite (CaTiO₃) and hibonite (Ca Al₁₂O₁₉) within different regions of Calcium-, Aluminum-rich Inclusions (CAI) and the trace element concentrations of these minerals in each circumstance, constrain models of precursor formation [1], nebular condensation [2], the thermal history of inclusions with relict perovskite and hibonite [2,3] and the formation of the Wark-Lovering rim [4]. At present mineral/melt partition coefficient (D) data for hibonite are limited to a few elements in simple experimental systems [5], or to those derived from hibonite-glass pairs in hibonite/glass microspherules [6]. Similarly, there is only limited data on perovskite D that are applicable to meteorite compositions [7,8]. Apart from the importance of partitioning studies to meteorite research, D values also are invaluable in the development of thermodynamic models [9], especially when data is available for a large number of elements that have different ionic charge and radii. In addition, study of the effect of rapid cooling on partitioning is crucial to our understanding of meteorite inclusions [3,10]. To expand our knowledge of mineral/melt D for perovskite and hibonite, we have instituted a study similar to that of [10], where D values are obtained in both equilibrium and dynamic cooling experiments. As an initial phase of this study we have measured mineral/melt D for major elements (Ca, Mg, Al, Ti and Si), 15 rare earth elements (La-Lu) and 8 other elements (Ba, Sr, U, Th, Nb, Zr, Hf and Ge) in perovskite and hibonite grown under equilibrium conditions, in bulk compositions that are respectively similar to Compact Type A (CTA) CAI and to a hibonite/glass microspherule [6]. Experimental mixes (Table 1) were doped with REE at 20-50x chondritic (ch) abundances, Ba at 50 ppm, Sr, Hf, Nb and Zr at 100 ppm and, U and Th at 200 ppm. Trace element abundances were measured with the PANURGE ion microprobe using the techniques and standards of [11]. Major element compositions were obtained by electron microprobe analysis.

Experimental Technique: Experiments were performed in 1 atmosphere gas-mixing furnaces. The oxygen fugacity was fixed at -1.5 log units below the Iron-Wustite (IW) buffer curve. The temperature and cooling rate were controlled with a Eurotherm controller. Perovskite experiments were held at temperatures within the range 1525°C to 1545°C for 4 hours, then cooled at 2°C/hour to either 1500°C or 1450°C and then allowed to equilibrate at this temperature for 24 hours. Complex cooling and heating paths were used to reduce the number of crystal nuclei in the hibonite experiments. Experiments were held at a temperature of 1500°C for 8 hours, then cooled to, and held at, either, 1300°C or 1350°C for 24 to 36 hours, then heated to, and held at, 1450°C for 9 to 24 hours. The experiments were then either quenched, or cooled at 2°C/hour to either 1400°C or 1300°C and equilibrated at this temperature for 24 hours. In both perovskite and hibonite experiments large (up to 200 um wide) individual crystals adjacent to the main mass of melt were selected for analysis. Points from the core, rim and adjacent glass were analysed and for hibonite analyses were performed adjacent to the different crystal faces. Melt inclusions, which were common in experiments on olivine and orthopyroxene [10], were not observed in the analysed crystals.

Results: Figure 1 shows representative D patterns for perovskite and hibonite for the complete set of elements analysed, with the elements grouped by ionic charge and arranged in descending order from left to right according to ionic radii. The data shown is for hibonite equilibrated with the melt at 1350°C and 1400°C. Pattern #2 is from the 1400°C experiment and patterns #6 and #7 are from a single crystal in the 1350°C experiment. The pattern for perovskite is from an experiment with a final temperature of 1450°C. D range from 10⁻² to >10 for both minerals and there is a strong similarity between the patterns. Perovskite and hibonite D are almost identical for the divalent cations Ba (respectively 0.02 and 0.03) and Sr (respectively 1.1 and 0.8) in our

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experiments. D_{Ca} is as expected, with respective values of 1.2 and 0.32 in perovskite and hibonite. Our D are similar to those of other experimental studies [5,8]. D_{Mg} for perovskite is low, 0.03 when compared with the value for hibonite, 0.5. Mineral/melt D for the REE decrease continuously from $D_{La}=6$ to $D_{Lu}=0.03$ in hibonite. For perovskite, REE D s increase slightly from $D_{La}=10$ to $D_{Nd}=15$ and then decrease continuously to $D_{Lu}=1.0$, and D s for trivalent cations with smaller ionic radii than the REE are lower, with $D_{Al}=0.08$ and $D_{Sc}=0.15$ lower than $D_{Cr}=0.8$ and $D_V=1.0$. D values for Cr, Sc and V were not measured in hibonite due to interferences [1]. With the exception of D_{Th} and D_{Si} in perovskite and D_{Si} in hibonite, the D values for tetravalent cations and Nb, the only pentavalent element fall within the range of D s for the REE (Fig. 1). D_{Th}/D_U equals 3 in perovskite and approximately 15 in hibonite.

Example applications: (1) Low Ba relative to other refractory elements, such as Hf, Zr, La etc, in hibonite has been explained by increased volatility of Ba under oxidising conditions during condensation [2]. $D_{Ba} \ll D_{Hf}$, D_{Zr} and D_{La} in our experiments suggests an alternate explanation; that low Ba results from the incompatibility of Ba in hibonite. (2) High REE abundances (500-1000xch) and Th/U ratios of 3-4 in perovskite from the outer region of Type B1 CAI [3,12] are inconsistent with equilibrium partitioning between perovskite and a melt that contains ~20xch REE and that probably has Th/U >3 [13], and the perovskite is a relict. (3) Since D_{LREE}/D_{HREE} is ~200 for hibonite, LREE/HREE ratios of 1 indicate that in hibonite in L575, a Leoville CTA CAI, and 2 in hibonite in Linus Jr., an Allende CTA CAI, [14] are inconsistent with hibonite equilibrating with the melts that formed these inclusions, and hibonite is a relict.

Summary: We have measured mineral/melt D for 31 elements in perovskite and hibonite in equilibrium crystallization experiments on compositions that are applicable to meteorite inclusions. Our data includes elements not previously studied and provide a self consistent set of D . Use of these D will provide additional constraints for CAI research and for crystal fractionation models and partial melting in terrestrial igneous systems that contain perovskite.

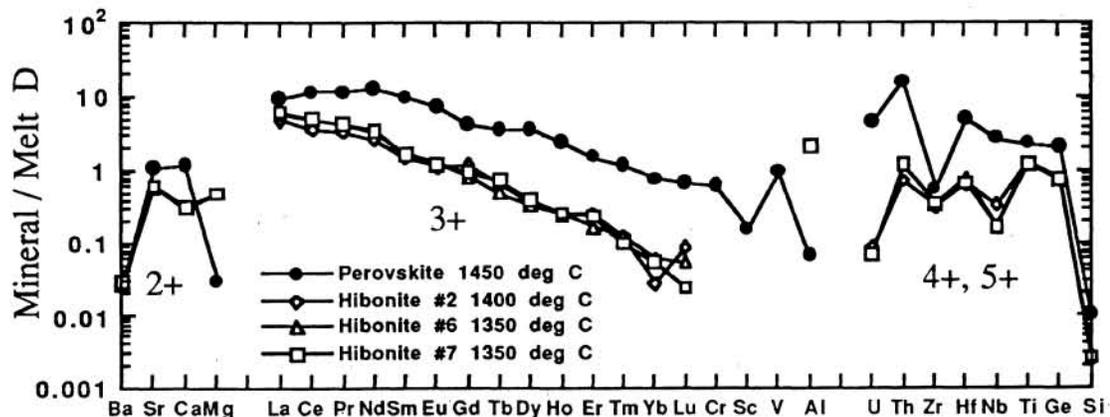


Table 1 Composition of starting mixes

	SiO ₂	Al ₂ O ₃	MgO	CaO	TiO ₂	FeO	Total
Perovskite	25.61	14.27	6.26	31.55	20.72	0.01	98.41
Hibonite	28.23	38.22	1.99	26.94	4.94	0.01	100.32

References: [1] Hinton et al. (1988) GCA 52 p2573; [2] Ireland et al. (1992) GCA 56 p2503; [3] Kennedy et al. (1990) LPSXXI p621; [4] Wark (1986) EPSL 77 p129; [5] Drake and Boynton (1988) Meteoritics 23 p75; [6] Ireland et al. (1991) GCA 55 p367; [7] Nagasawa et al. (1980) EPSL 46 p431; [8] Simon et al. (1993) submitted; [9] Colson et al. (1988) GCA 52 p539; [10] Kennedy et al. (1993) EPSL in press; [11] Kennedy and Hutcheon (1992) Meteoritics 27 p ; [12] Ireland et al. EPSL 101 p379; [13] Chen and Wasserburg (1981) EPSL 52 p1; [14] Kennedy et al. (1991) LPSXXII p 709. [Div. Contib. 5235 (799)].