

THE STABILITY OF ZIRCONIA-SATURATED PEROVSKITE AND CONDITIONS IN THE EARLY SOLAR SYSTEM.

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Introduction: Perovskite and tazheranite (cubic zirconia) are among the most refractory oxides in nebular vapors [1] and important repositories for several refractory elements whose concentrations can potentially be used to constrain the environments of formation. There are numerous studies on the phase relations and thermodynamic properties of zirconias containing Al, Ca, Mg, Sc, Ti, and the REE [e.g., 2-4], but meteoritic zirconia is rare [5]. Meteoritic perovskite is much more common [e.g., 5-9], but there are few constraints on thermodynamic properties of the relevant solid solutions. Here, we describe experiments to determine the partitioning of minor elements between perovskite and zirconia of variable Zr/Ti; the results will be used to constrain thermodynamic modeling for the solid solutions represented by meteoritic perovskite.

Results and Discussion: We conducted synthesis experiments in air at 1550-1606°C for 6-18 days on oxide mixtures of ten bulk compositions within the zirconolite (CaZrTi₂O₇) - lakargiite (CaZrO₃) - ZrO₂ ternary, plus the same bulk compositions, but doped with one additional oxide (one of Al, Mg, Sc, Y, La, Nd, Gd, Yb) at concentrations ranging from 1-10 mole % (44 bulk compositions). At elevated temperatures, the lakargiite-zirconolite join, where most of the base compositions were placed, traverses a two-phase perovskite+cubic zirconia field and it is the partitioning of elements between these two phases that can potentially be used to constrain the thermodynamic properties of meteoritic perovskite. Most experiments produced two phases, but some crystallized zirconolite; others partially melted at or above 1600°C, especially those containing Al₂O₃>1 mole% or high TiO₂ (≥40%). Partition coefficients of Al, D_{Al} (wt% Al in perovskite / Al in zirconia) (0.4 to 2.9) increase with Zr in perovskite and, based on one experiment, with decreasing temperature. D_{Mg} (0.04-0.4) generally decreases with increasing Zr in perovskite. For a set of bulk compositions with constant Ca-, Zr-, and Ti-ratios, D_i for Y, Sc, and the REE vary smoothly as a function of ionic radius, with D_i for La(8) >Nd(2) >Gd(0.7) >Y(0.3) >Yb(0.2) >Sc(0.07). These experimental data will be used to constrain the thermodynamic properties of meteoritic perovskites but even without such modeling, there are some immediate constraints. For example, apparent partition coefficients of Al, Sc, and Y for tazheranite and perovskite in the Allende ultra-refractory inclusion ACM-1 [5] are in the range of those observed experimentally but, given 8 wt% ZrO₂ in the perovskite, it is likely that these phases equilibrated at <1600°C.

References: [1] Lodders, K. (2003) *Astrophys. J.* 591, 1220-1247. [2] Fabrichnaya, O. et al. (2013) *J. Eur. Ceramic Soc.* 33, 37-49. [3] Serena, S. et al. (2005) *J. Eur. Ceramic Soc.* 25, 681-693. [4] Jacobson, N.S. et al. (2001) *NASA Tech Mem.* #2001-210753. [5] Ma, C. et al. (2014) *Am. Mineral.* 99, 654-666. [6] Ivanova, M.A. et al. (2012) *MAPS* 47, 2107-2127. [7] El Goresy, A. (2002) *GCA* 66, 1459-1491. [8] Weber, D. and Bischoff, A. (1994) *GCA* 58, 3855-3877. [9] Fahey, A.J. et al. (1987) *GCA* 315-3229.