

ISOTOPIC AND CHEMICAL FRACTIONATION DURING EVAPORATION OF CaTiO₃; Andrew M. Davis¹, Akihiko Hashimoto², Robert N. Clayton^{1,3,4} and Toshiko K. Mayeda¹; ¹Enrico Fermi Institute, ³Department of Chemistry, ⁴Department of the Geophysical Sciences, University of Chicago, Chicago, IL 60637; ²Department of Earth and Planets, Hokkaido University, Kita-ku, N10 W8, Sapporo 060, JAPAN.

Introduction. There is abundant evidence in refractory inclusions for high temperature isotopic and chemical fractionation events in the early solar system. Large enrichments in the heavy isotopes of oxygen, magnesium, silicon, calcium and titanium have been observed in some calcium-, aluminum-rich inclusions (CAIs). Rare earth element (REE) patterns of CAIs often show evidence for volatility fractionation. CAIs occasionally have negative cerium anomalies, but volatility fractionation of light REE (LREE) from heavy REE (HREE) is much more common. We have previously reported that residues with substantial enrichments in the heavy isotopes of oxygen, magnesium and silicon form from evaporation of liquids of forsterite composition [1] and of chondritic initial composition [2]. We have also shown that evaporation of a liquid of REE-doped chondritic initial composition forms residues whose REE patterns have large negative cerium anomalies [2,3]. In order to better understand the causes for these fractionations in nature, we have evaporated trace element-doped liquids of CaTiO₃ initial composition and measured oxygen, calcium and titanium isotopic compositions and trace element patterns in residues.

Experimental. The starting material was CaTiO₃, doped with ~100 ppm each of Sc, Sr, Zr, Nb, Ba, Hf, Ta and all 14 stable REE, and was synthesized by mixing constituent oxides and sintering in air for 2 hours at 1425°C. This material was suspended from an iridium loop and evaporated in a vacuum furnace at 2005°C for durations of 2 to 200 minutes, resulting in 3.0 to 83.4% mass loss. The melting point observed for this composition is 1985°C; all charges remained molten throughout the evaporation experiment. The bulk chemical compositions of residues were measured by electron microprobe; calcium and titanium isotopic and refractory trace element compositions were measured by ion microprobe; and oxygen isotopic compositions were measured by isotope ratio mass spectrometry of O₂ obtained from BrF₅ extraction of splits of each residue.

Major element fractionation. Liquids of initial CaTiO₃ composition preferentially evaporate calcium. The residues consist of perovskite and a titanium oxide, with the proportion of perovskite decreasing with increasing degree of evaporation. About half of the titanium in the titanium oxide is trivalent, based on high oxide totals in electron microprobe analyses and high backscattered electron albedo compared to TiO₂.

Isotopic fractionation. The residues are enriched in the heavy isotopes of oxygen, calcium and titanium. Mass fractionation during high temperature evaporation is caused by the kinetic isotope effect and can be described by the Rayleigh equation, $R/R_0 = f^{\alpha-1}$. f is the fraction remaining and, for the example of ¹⁸O/¹⁶O fractionation, $R = (^{18}\text{O}/^{16}\text{O})_{\text{residue}}$, $R_0 = (^{18}\text{O}/^{16}\text{O})_{\text{initial}}$, and $\alpha = (^{18}\text{O}/^{16}\text{O})_{\text{gas}} / (^{18}\text{O}/^{16}\text{O})_{\text{residue}}$. For the kinetic isotope effect, α is given by the square root of the masses of the evaporating species (e.g., for evaporation of O₂, α for ¹⁸O/¹⁶O fractionation is $\sqrt{32/34}$). α was calculated for each element from the slopes of $\ln(R/R_0)$ vs. $\ln f$ plots. When plotted on such plots, data for calcium and titanium fall along straight lines, as expected, but the oxygen data define a concave downward curve. This indicates that, as evaporation proceeded, the evaporating species remained the same for calcium and titanium, but changed from a lighter to a heavier species for oxygen. α 's determined in our experiment are given in Table 1 and compared with α 's calculated for various potential evaporating species. For oxygen, α 's calculated from the slope of the curve at $\ln f$ for the least and most evaporated residues are given. It is apparent from Table 1 that calcium evaporates as Ca atoms, titanium as TiO and TiO₂ molecules and oxygen initially as O₂ and later as species whose average molecular weight is heavier than that of TiO₂.

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Chemical fractionation. Elemental fractionations relative to the starting material are shown in Fig. 1. As in previous experiments [3], REE patterns are characterized by large negative cerium and smaller negative praseodymium anomalies in residues. However, unlike in previous experiments, we also observe depletions in europium in the more extreme residues.

The residues are also strongly depleted in barium. Thermodynamic calculations have shown that barium, like cerium, becomes volatile relative to other refractory elements under highly oxidizing conditions [4]. Europium and ytterbium are the most volatile of the REE under solar nebular oxygen fugacities, but becomes nearly as refractory as their neighbors under oxidizing conditions [4].

Conclusions. Since the evaporating species for calcium is lighter than that for titanium and calcium is more volatile than titanium in our experiment, one would expect evaporation residues to have larger enrichments in heavy isotopes of calcium relative to those of titanium. In fact, four refractory inclusions, HAL-type hibonite grains, tend to have more highly fractionated titanium than calcium [5]. Aluminum plays a major role in the relative volatilities of calcium and titanium. In the most extreme (95% mass loss) residues from evaporation of initial chondritic composition, about half of the titanium was lost, but little calcium and aluminum were lost [3]. Calcium may be more refractory than titanium during evaporation of materials whose residues form hibonite.

The fraction of titanium that is trivalent in the residues is similar to that expected in the solar nebula, yet these samples were evaporated in vacuum, not in a hydrogen-rich atmosphere. The formation of substantial fractions of trivalent titanium in material that initially contained only tetravalent titanium occurred because oxygen is more volatile than titanium. This result shows that equilibration with solar nebular gas may not be the only way to make a substantial fraction of the titanium in CAIs trivalent. Oxygen fugacity is not controlled in vacuum evaporation; indeed, the oxygen fugacity cannot be defined in the conventional sense. The apparent redox state of the residue is simply the result of the evaporation mechanisms of the different components. Kinetic evaporation in vacuum can lead to residues that equilibrium thermodynamic calculations would characterize as both oxidizing (Ce anomalies) and reducing (trivalent titanium).

It appears to be rather difficult to significantly fractionate the more refractory HREE from the more volatile LREE during evaporation (Fig. 1). We have conducted a second series of evaporation experiments on CaTiO_3 doped with 5 wt% refractory trace elements (in chondritic relative proportions) at 2150°C . Electron microprobe analyses of residues show no evidence for substantial HREE/LREE fractionation.

References. [1] Davis A.M. et al. (1990) *Nature* **347**, 655. [2] Wang J. et al. (1994) *LPS XXV*, 1457. [3] Wang J. et al. (1993) *Meteoritics* **28**, 454. [4] Davis A.M. et al. (1982) *GCA* **46**, 1627. [5] Ireland T.R. et al. (1992) *GCA* **56**, 2503.

Table 1. Gas/solid isotopic fractionation factors

<i>Measured</i>	
O (early)	0.98497
O (late)	0.99671
Ca	0.98833 ± 27
Ti	0.99272 ± 37
<i>Potential evaporating species</i>	
O	0.97014
O ₂	0.98473
Ca	0.98857
Ti	0.98953
CaO	0.98333
TiO	0.99216
TiO ₂	0.99373

