

CALCIUM AND TITANIUM MASS-DEPENDENT ISOTOPE FRACTIONATION DURING EVAPORATION OF CaTiO₃. J. Zhang^{1,2}, S. Huang³, A. M. Davis^{1,2,4}, N. Dauphas^{1,2,4}, S. B. Jacobsen³, and A. Hashimoto⁵. ¹Chicago Center for Cosmochemistry, ²Department of the Geophysical Sciences, Univ. of Chicago; ³Department of Earth and Planetary Sciences, Harvard Univ.; ⁴Enrico Fermi Institute, Univ. of Chicago; ⁵Department of Cosmochemistry, Hokkaido Univ. E-mail: junjunzhang@uchicago.edu

Introduction: High temperature evaporation can produce mass-dependent isotope fractionation (MDF) in solar system materials. Previous experiments have focused on evaporation effects on moderately to highly volatile elements [1–6]. However, evaporation effects on more refractory elements have only been explored in a preliminary way using ion probe [7]. Here we investigate two highly refractory elements, Ca and Ti, during evaporation of perovskite (CaTiO₃). We also compare our experimental results with Ca and Ti isotopic measurements of natural Ca-, Al-rich inclusions (CAIs) to constrain the conditions of CAI formation.

Evaporation experiments: Details of the free evaporation procedure were described in [7]. Briefly, the starting material CaTiO₃ (melting point: 1985 °C) was synthesized by mixing CaCO₃ and TiO₂ powders doped with REEs (<0.2 wt% total) and sintering in air at 1425 or 1550°C (CT-1425 or CT-1550, respectively). Five evaporation experiments, CT-2, CT-3, CT-4, CT-5, and CT-1, were carried out in a vacuum furnace at 2005°C, leading to evaporated Ca fractions of 3.7, 39.2, 64.5, 81.7, and 90.4 %, and evaporated Ti fractions of 2.9, 12.3, 36.8, 61.1, and 79.0 %, respectively.

Calcium and titanium isotopic analysis: After sample dissolution, two separate aliquots were taken from each sample solution for Ca isotopic measurements at Harvard University and Ti isotopic analysis at the Origins Lab of the University of Chicago, respectively. Separation of Ca was performed using AG50W-X12 resin [8], while Ti was separated via a two-stage procedure using TODGA and AG1-X8 resins [9].

Calcium isotopic ratios were measured with a GV Isoprobe-T TIMS using a ⁴³Ca-⁴⁸Ca double spike technique described in [8]. A two-step data acquisition sequence was used to measure: (1) ⁴⁰Ca⁺, ⁴¹K⁺, ⁴²Ca⁺, ⁴³Ca⁺ and ⁴⁴Ca⁺; and (2) ⁴⁴Ca⁺ and ⁴⁸Ca⁺. Calcium MDFs are reported relative to NIST SRM915a in δⁱ notation:

$$\delta^i Ca = 1000 \times \ln \left[\frac{({}^iCa/{}^{40}Ca)_{sample}}{({}^iCa/{}^{40}Ca)_{NIST\ SRM915a}} \right], \quad (1)$$

where *i* represents 44 or 42, so that commonly used fractionation laws plot along straight lines. Titanium isotopic compositions were measured on a Thermo Neptune MC-ICPMS using sample-standard bracketing technique following [9]. The bracketing standard, natural rutile from Kragerø, Norway, was also dissolved and chemically processed together with the samples. A two-step data acquisition sequence was used to measure: (1) ⁴⁴Ca⁺, ⁴⁶Ti⁺, ⁴⁷Ti⁺, ⁴⁸Ti⁺, ⁴⁹Ti⁺ and ⁵⁰Ti⁺; and (2) ⁴⁹Ti⁺,

⁵¹V⁺, and ⁵²Cr⁺. Titanium MDFs are expressed as follows:

$$\delta^j Ti = 1000 \times \ln \left[\frac{({}^jTi/{}^{47}Ti)_{sample}}{({}^jTi/{}^{47}Ti)_{rutile}} \right], \quad (2)$$

where *j* represents 46, 48, 49, or 50. Analytical uncertainties for both Ca and Ti isotopic compositions are 95% confidence intervals of replicate analyses.

Results and Discussion: Our results show that both Ca and Ti isotopes are highly fractionated during evaporation of CaTiO₃. Relative to NIST SRM915a, CT-1425 and CT-1550 show δ⁴⁴Ca_{SRM915a} values of 0.93±0.06 and 0.91±0.08 ‰, respectively, with a weighted average of 0.92±0.05 ‰. After standardization to this average value, evaporation residues CT-2, CT-3, CT-4, CT-5, and CT-1 have δ⁴⁴Ca values of 1.38±0.09, 20.32±0.06, 40.12±0.07, 71.64±0.09, and 99.29±0.06 ‰, respectively. For Ti MDFs, CT-1425 and CT-1550 do not have any fractionations relative to natural rutile, with δ⁵⁰Ti values of 0.00±0.04 and -0.03±0.04 ‰, respectively, while evaporation residues are all fractionated, with δ⁵⁰Ti values of 0.14±0.04, 2.57±0.03, 8.48±0.07, 17.26±0.04, and 27.62±0.03 ‰, respectively.

Linear relationships between measured isotopic fractionation and the degree of evaporation are found for both Ca and Ti (Fig. 1), indicating that the evaporation complies with Rayleigh distillation behavior. From the slopes of the linear regressions, experimental fractionation factors α_{Ca} and α_{Ti} (hereafter α_{Ca} and α_{Ti}, respectively) can be derived [3]. The experimental fractionation factors of α_{Ca}=0.9562±0.0039 and α_{Ti}=0.9823±0.0010 are in good agreement with theoretical factors assuming that Ca and Ti evaporate as Ca atoms and TiO₂ molecules, respectively. We also calculated equilibrium partial pressures of gas species at 2005°C using thermodynamic data [10]. The results show that the partial pressure of Ca is higher than that of CaO by a factor of two, while the partial pressure of TiO₂ is three and fourteen orders of magnitude higher than those of TiO and Ti, respectively. Taking our measurements and thermodynamic calculation together, Ca and TiO₂ appear to be the dominant evaporating species from molten CaTiO₃.

Given that Ca and TiO₂ are the dominant evaporating species, we further investigate their isotopic fractionation laws during the evaporation. Fig. 2 shows the relationships between δ⁴⁴Ca vs. δ⁴²Ca and δ⁵⁰Ti vs. δ⁴⁶Ti in evaporation residues. As expected, they follow the Rayleigh fractionation law for Ca and TiO₂, and lie

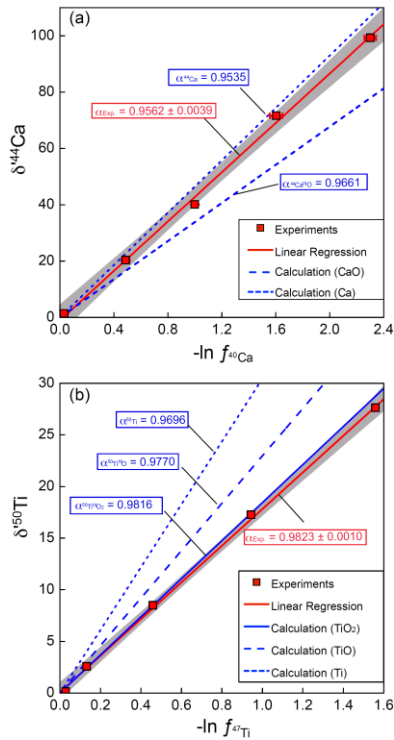


Fig. 1: Calcium and Ti isotopic compositions as a function of the isotope fraction remaining in the residue (red squares). A linear regression is shown (red line), with 95% confidence envelopes (gray areas). The blue lines are calculated fractionations of different evaporating species.

significantly off the power law, and slightly off the exponential and equilibrium fractionation laws (Fig. 2).

Our experimental results also have important implications for CAI formation in the early solar nebula. Fig. 3 shows MDFs of Ca and Ti per amu (F_{Ca} and F_{Ti}) in perovskite residues from our experiments and in natural CAIs [11]. The experimental data lie along a curve rather than a straight line because the Ti/Ca atomic ratio during evaporation changed from 1.0 to 1.9 with the extent of evaporation. Initially, more Ca was evaporated, and then the Ti/Ca ratio of the evaporating material increased, causing the curve in Fig. 3 to steepen. The CAIs lie along a steeper line. The positive relationships between F_{Ca} and F_{Ti} shown in both experimental and natural samples suggest that a non-equilibrium evaporation process affected some natural CAIs. The tendency of CAIs to have larger $F_{\text{Ti}}/F_{\text{Ca}}$ than the experimental data is likely due to differences in activity-composition relationships between Ca-Ti-O melt and CAI compositions.

Conclusions: Calcium and TiO_2 seem to be the dominant evaporating species during the evaporation of CaTiO_3 . The evaporation follows the Rayleigh fractionation law. The positive correlation between MDFs of Ca and Ti of some CAIs suggests that they experienced

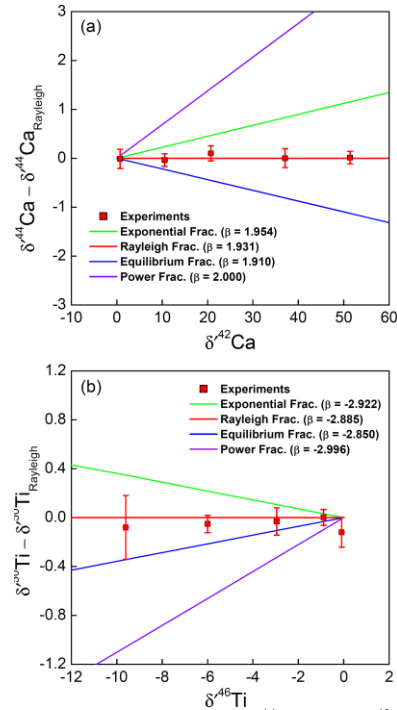


Fig. 2: Relationships between $\delta^{44}\text{Ca}$ vs. $\delta^{42}\text{Ca}$ (a) and $\delta^{50}\text{Ti}$ vs. $\delta^{46}\text{Ti}$ (b) measured in evaporation residues (red squares) compared with various fractionation laws.

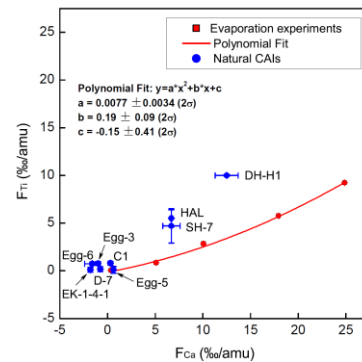


Fig. 3 Titanium and Ca MDFs in CAIs [11] (blue circles) and in perovskite evaporation residues (red squares). The red line is a polynomial fit of the evaporation residue data points.

evaporation at such high temperature that even highly refractory elements like Ca and Ti evaporated.

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