

### TITANIUM ISOTOPE MASS-DEPENDENT FRACTIONATION DURING EVAPORATION OF $\text{CaTiO}_3$ .

J. Zhang<sup>1,2</sup>, A. M. Davis<sup>1,2,3</sup>, N. Dauphas<sup>1,2</sup>, and A. Hashimoto<sup>4</sup>. <sup>1</sup>Chicago Center for Cosmochemistry, <sup>2</sup>Department of the Geophysical Sciences, <sup>3</sup>Enrico Fermi Institute, The University of Chicago, Chicago, USA; <sup>4</sup>Department of Cosmochemistry, Hokkaido University, Sapporo, Japan. E-mail: junjunzhang@uchicago.edu

**Introduction:** High temperature evaporation can produce mass-dependent fractionation (MDF) of isotopes, and it plays an important role in determining chemical properties of solar materials. Previous experiments have focused on evaporation effects on moderately volatile (*e.g.*, Mg, Si) [1–4], volatile (Cd) [5], and highly volatile elements (Hg) [6]. From these studies, an interesting finding is that the experimentally determined fractionation law for Mg, Cd, or Hg during evaporation is different from the theoretical exponential law. This finding has received little attention, although it may cause serious concerns especially in the studies of non-mass-dependent fractionation (non-MDF). Small deviations from the exponential law would cause inadequate MDF corrections by assuming the exponential law. Any inadequate MDF corrections would then introduce artifact non-MDF.

Here we investigated Ti isotopic mass fractionation law during evaporation of  $\text{CaTiO}_3$  for three reasons. First of all, titanium is highly refractory and it has five stable isotopes. Secondly, titanium MDFs were found in some bulk meteorites and calcium-, and aluminum-rich refractory inclusions (CAIs), up to ten ‰ per a.m.u. [7]. Thirdly, high precision Ti non-MDFs (*e.g.*,  $\epsilon^{46}\text{Ti}$  and  $\epsilon^{50}\text{Ti}$ ) have been published for CAIs and bulk meteorites [8], but it is uncertain whether there is any artifact Ti non-MDF resulted from the evaporation. We aim to answer two questions: (1) Is the fractionation law during evaporation always different from the exponential law, irrespective of elemental volatility? (2) What mechanism causes the discrepancy?

**Experimental evaporation procedure:** Details of the procedure were provided elsewhere [9]. Briefly, the starting material was  $\text{CaTiO}_3$ , which was synthesized by mixing constituent oxides and by sintering in air at 1425°C and later at 1550°C (CT-1425 and CT-1550, respectively). Five evaporation runs CT-2, CT-3, CT-4, CT-5, and CT-1 were performed in the vacuum furnace at 2005°C, with evaporated fractions of 3.0%, 23.0%, 47.5%, 68.7%, and 83.4%, respectively.

**Titanium separation procedure:** After sample dissolution, titanium was separated via a two-stage procedure using TODGA and AG1-X8 resins, respectively [10]. Samples were loaded onto a 2-mL TODGA cartridge, rinsed with 10 mL 12M  $\text{HNO}_3$  to remove major matrix elements [11], and titanium was collected with Mo and minor Nb, Ta and W in 10 mL 12M  $\text{HNO}_3$  + 1 wt%  $\text{H}_2\text{O}_2$ . The second separation stage is a modified version of a previously used procedure [12],

using a 0.8-mL column (AG1-X8). It removed major matrix with 10 mL 4M HF independently from the first column and separated Ti from Mo, Nb, Ta, and W with 9M HCl + 0.01M HF. The total yields for both columns exceed 95%.

**Titanium isotopic analysis:** Titanium isotopic analyses were performed by a Thermo Neptune MC-ICPMS in Origins Lab at the University of Chicago using sample-standard bracketing technique. Our bracketing standard, natural rutile from Kragerø, Norway, was also dissolved and chemically processed in the same way as the samples. The positions of Faraday cups correspond to the species  $^{44}\text{Ca}^+$ ,  $^{46}\text{Ti}^+$ ,  $^{47}\text{Ti}^+$ ,  $^{48}\text{Ti}^+$ ,  $^{49}\text{Ti}^+$  and  $^{50}\text{Ti}^+$  (sequence 1) and  $^{49}\text{Ti}^+$ ,  $^{51}\text{V}^+$ , and  $^{52}\text{Cr}^+$  (sequence 2). Titanium solutions were introduced in a 2%  $\text{HNO}_3$  + 0.005% HF mixture via two different desolvation inlet systems: an ESI SIS spray chamber and an Aridus II, with average sensitivities of ~ 15 and ~ 70 Volts/ppm for  $^{48}\text{Ti}$ , respectively. All measurements were made at high mass resolution. Ti mass-dependent fractionation (MDF) is expressed in  $\delta$  notation:

$$\delta^i\text{Ti}' = 1000 \times \ln \left[ \frac{({}^i\text{Ti}/{}^{47}\text{Ti})_{\text{sample}}}{({}^i\text{Ti}/{}^{47}\text{Ti})_{\text{rutile}}} \right], \quad (1)$$

where *i* represents 46, 48, 49, and 50. Titanium non-MDF is reported in  $\epsilon$  notation to reflect anomalies relative to the exponential law:

$$\epsilon^i\text{Ti} = 10,000 \times \left[ \frac{({}^i\text{Ti}/{}^{47}\text{Ti})_{\text{sample}}^*}{({}^i\text{Ti}/{}^{47}\text{Ti})_{\text{rutile}}^*} - 1 \right], \quad (2)$$

where the ratios marked with \* have been corrected for MDF by internal normalization to  $^{49}\text{Ti}/^{47}\text{Ti}$  using the exponential law. Analytical uncertainties are 95% confidence intervals and they were calculated from *n* replicate analyses during a single session.

**Results:** Our Ti MDF results using two different desolvation inlet systems are in good agreement within the uncertainties. The results using Aridus II are 2–10 times higher in precision than those from the spray chamber, so high-precision data from Aridus II are reported here (Fig. 1). Relative to natural rutile, the two starting materials CT-1425 and CT-1550 do not have any Ti MDF, with  $\delta^{50}\text{Ti}'$  values of  $0.00 \pm 0.04$  and  $-0.03 \pm 0.04$ , respectively, while five evaporation residues are all fractionated, with  $\delta^{50}\text{Ti}'$  values of  $0.14 \pm 0.04$ ,  $2.57 \pm 0.03$ ,  $8.48 \pm 0.07$ ,  $17.26 \pm 0.04$ ,  $27.62 \pm 0.03$  for CT-2, CT-3, CT-4, CT-5, and CT-1, respec-

tively. In all three-isotope plots shown in Fig. 1, titanium MDFs are well fitted by a linear function, with the slope and intercept given in each plot. We have plotted  $\delta^x\text{Ti}'$  value, where  $\delta^x\text{Ti}' = 1000\ln(\delta^x\text{Ti}/1000+1)$ , so that commonly used fractionation laws plot along straight lines. Interestingly, titanium isotopes all comply with the theoretical exponential fractionation law.

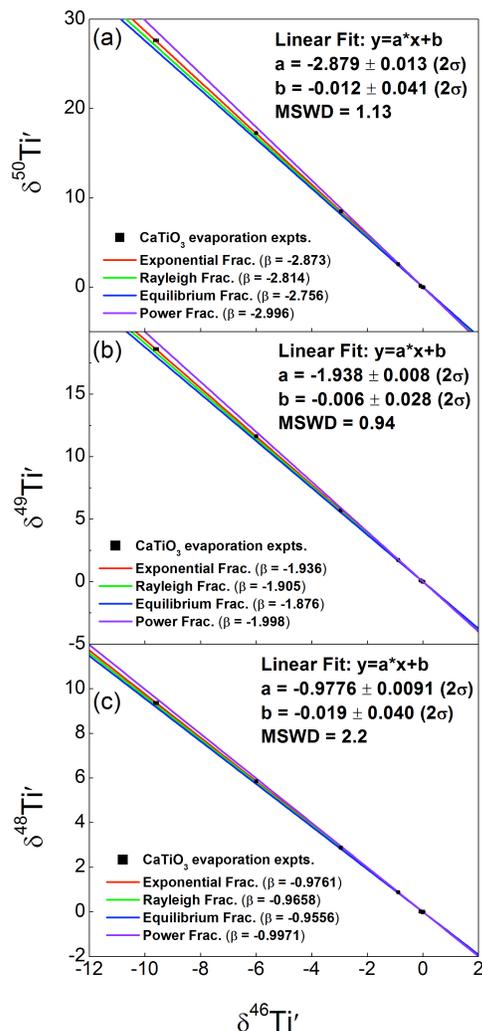


Fig. 1: Titanium MDFs of two evaporation starting materials and five evaporation residues (black squares), relative to the natural rutiles. The red, green, blue, and violet lines show the theoretical exponential, Rayleigh, equilibrium, and power laws, respectively.

**Discussions:** Evaporation of  $\text{CaTiO}_3$  produces residues that display a mass fractionation law for Ti, which we refer to as the experimental law. This experimental law is apparently off the equilibrium law and power law, and off the Rayleigh fractionation line, but indistinguishable from the exponential law (Fig. 1). It contrasts with the nonexponential fractionation law for

Mg, Cd, and Hg in previous evaporation studies. We will investigate the mechanism behind this difference in the next step.

Given that our experimental law for Ti is identical to the exponential law within uncertainties, there should be no apparent artifact Ti non-MDF introduced during MDF corrections by assuming the exponential law (Fig. 2). This is confirmed by the Ti non-MDF values for evaporation samples. For example, the  $\epsilon^{50}\text{Ti}$  values for CT-2, CT-3, CT-4, CT-5, and CT-1 are  $-0.08 \pm 0.14$ ,  $0.04 \pm 0.07$ ,  $0.02 \pm 0.08$ ,  $0.11 \pm 0.06$ , and  $0.26 \pm 0.23$ , respectively (Fig. 2). This suggests that the quantification of Ti non-MDF is accurate, even when Ti isotopes are highly mass fractionated during evaporation.

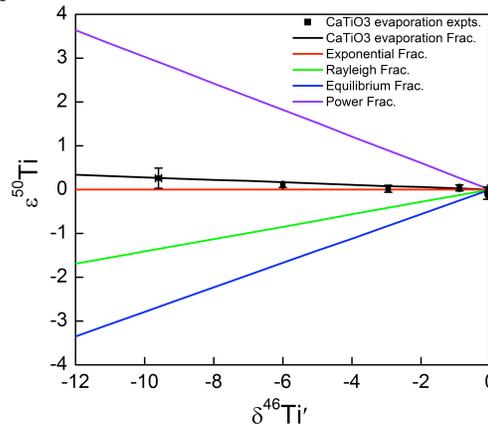


Fig. 2: Predicted artifact  $\epsilon^{50}\text{Ti}$  values introduced by inadequate MDF corrections assuming exponential law, if the chemical fractionation follows the the experimental law (black line), exponential law (red), Rayleigh law (green), or power law (violet). The black squares are measured Ti non-MDFs of evaporation samples.

**Conclusions:** The evaporation experiments of  $\text{CaTiO}_3$  show a fractionation law for Ti that is indistinguishable from the exponential law. No apparent artifact Ti non-MDFs are observed, even when Ti isotopes are highly mass fractionated during evaporation.

**References:** [1] Davis A. M. et al. (1990) *Nature*, 347, 655–658. [2] Davis A. M. et al. (1991) *GCA*, 55, 1151–1154. [3] Richter F. et al. (2007) *GCA*, 71, 5544–5564. [4] Knight K. B. et al. (2009) *GCA*, 73, 6390–6401. [5] Wombacher et al. (2004) *GCA*, 68, 2349–2357. [6] Estrade et al. (2009) *GCA*, 73, 2693–2711. [7] Clayton R. N. (1988) *PTRSL*, 325, 483–501. [8] Trinquier A. et al. (2009) *Science*, 324, 374–376. [9] Davis A. M. et al. (1995) *LPS XXVI*, 317–318. [10] Zhang J. et al. *JAAS*, in press. [11] Pourmand A. and Dauphas N. (2010) *Talanta*, 8, 741–753. [12] Schönbacher, M. et al. (2004) *Analyst*, 129, 32–37.