Rb and K isotopic variations in non-carbonaceous chondrites and Mars. N. X. Nie^{1,2}, X.-Y. Chen³, Z. Zhang¹, J. Hu¹, W. Liu², F. L. H. Tissot², F.-Z. Teng³, A. Shahar⁴, and N. Dauphas¹, ¹Origins Laboratory, Department of the Geophysical Sciences and Enrico Fermi Institute, The University of Chicago, Chicago, IL 60637 (nxnie@caltech.edu), ²The Isotoparium, Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, CA 91125, ³Isotope Laboratory, Department of Earth and Space Sciences, University of Washington, Seattle, WA 98195, ⁴Earth and Planets Laboratory, Carnegie Institution for Science, Washington, DC 20015, USA.

Introduction: Rb and K are two alkali metal elements with similar geochemical behaviors. Because they are both moderately volatile, their isotopes have been combined to investigate volatile depletion in planetary bodies, notably in the Moon and carbonaceous chondrites (CCs) [1, 2]. They are also lithophile and highly incompatible, so magmatic differentiation and core formation in planetary bodies would not fractionate them isotopically or decouple them from refractory lithophile incompatible elements.

While non-carbonaceous chondrites (NCs) have been measured for their K isotopic compositions (e.g., [3]), the origin of these K isotopic variations remains elusive and no coupled Rb isotopic data have been reported. In this study, we measured Rb and K isotopic compositions of various NCs and Martian meteorites, to shed light on the processes responsible for the isotopic variation of moderately volatile elements (MVEs).

Samples: Meteorite falls were selected for this study to avoid terrestrial contamination or weathering (Rb and K are highly fluid mobile). Seven ordinary chondrites (OCs) and six enstatite chondrites (ECs) with petrologic type ranging from 3–6 and 4 Martian meteorites were measured for their Rb and K isotopic compositions.

Methods: The procedure of sample digestion and Rb and K purification follows previously established method [4]. Sample powders of bulk meteorites, weighing from 50 to 120 mg (from bulk homogenized powders with masses of ≥ 200 mg), were dissolved and passed through four chromatography columns to extract Rb and K simultaneously. The Rb isotopic measurements (87Rb/85Rb ratio) were done using a ThermoScientific Neptune Plus MC-ICPMS at the Origins Lab of the University of Chicago. The K isotopic compositions (41K/39K ratio) were measured on a Nu Plasma II MC-ICPMS at the Isotope Laboratory of the University of Washington [5]. The data are reported using the conventional δ -notation against reference material NIST SRM984 for Rb and NIST SRM3141a for K.

Results: The NCs (OCs and ECs) display large isotopic variations from -1.02 to +0.29 ‰ for δ^{87} Rb and -0.91 to -0.15 ‰ for δ^{41} K. In contrast, Martian samples show limited isotopic variation of +0.06 to +0.14 for δ^{87} Rb and -0.36 to -0.08 for δ^{41} K. The isotopic

compositions of bulk Mars are estimated to be $+0.10\pm0.03$ % for Rb and -0.26 ± 0.05 % for K. For NCs, the bulk isotopic compositions are difficult to constrain because of the large isotopic variations.

The Rb and K elemental and isotopic compositions of the samples are plotted in Fig. 1, together with previously measured CC samples [2]. Elementally, K and Rb show a great correlation, with some NC samples of higher metamorphic grades falling off the correlation (Fig. 1A). Interestingly, the samples that fall off the K-Rb elemental correlation also plot off the isotopic trend between K and Rb (Fig. 1B). This suggests that thermal metamorphism on chondrite parent bodies has decoupled the two systems. The general trends between K and Rb reflect a more primordial signature of planetary accretion and formation, during which K and Rb behaved similarly, but parent body processes have caused the scattering of the data. For the OCs of lower metamorphic grades (types 3 and 4), the isotopic compositions show large scatter (Fig. 1B), which might reflect some initial heterogeneity on OC parent body.

Discussion: The large isotopic variations in NCs are elusive. Several processes that could have induced large isotopic variations among NC samples are, i) chondrule nugget effect, ii) volatilization during parent-body metamorphism, and iii) thermal diffusion during parentbody metamorphism. The processes are discussed here.

i) Chondrule nugget effect. The large isotopic variations of NC samples could reflect that the sample masses used in this study are insufficient to be representative of the bulk composition. A possible cause in this respect is the presence of chondrules that have fractionated K (and Rb) isotopic compositions relative to bulk hand specimen; a phenomenon known as nugget



Fig. 1 The Rb and K elemental concentrations (A) and isotopic compositions (B) of meteorites. Data of CCs are from [2].

effect [6]. Using the K isotopic variation of chondrules in type 3 OCs measured by SIMS [7, 8], we calculate the chondrule nugget effect as a function of sample mass, shown in Fig. 2. For a sample size of ≥ 200 mg used in this study, chondrule nugget effect can only account for about ± 0.15 ‰ variation for Rb and ± 0.2 ‰ for K, too small to account for the observed variation.



Fig. 2 Modeled isotopic deviation from the bulk as a function of sampled mass due to chondrule "nugget effect". Blue line shows the 2 s.d..

ii) Volatilization during parent-body metamorphism. It has been postulated that chondrite parent bodies accreted homogeneously from type 3 materials, but subsequent metamorphism due to ²⁶Al decay led to some volatile loss. Vaporized volatile elements would presumably migrate from the hot center to the cold outer part of a body, causing isotopic fractionation. This has been used to explain the isotopic variations of MVEs in NCs (e.g., [9]). We modeled the effect of volatilization during OC parent body metamorphism on the Rb and K isotope fractionation. In the modeling, a body of 80 km radius was calculated for its thermal evolution due to ²⁶Al heating. The body was then divided into 2000 concentric layers, and the volatilization of Rb and K in each layer due to heating and the gas transport of them across layers were modeled using a numerical method. The result shows that the gas transport is rather inefficient compared to the volatilization. As a result, very limited volatile migration could occur, and no measurable isotope fractionation could be produced. Therefore, this process could not explain the observed large Rb and K isotopic variation in OCs.

iii) Thermal diffusion during parent-body metamorphism. During parent body metamorphism, alkalis could diffuse from high to low concentration regions at the hand specimen scale at elevated temperatures, causing large kinetic isotopic fractionation. Without metamorphic equilibration, regions with distinct K and Rb concentrations and similar isotopic compositions could coexist. As chondrite parent bodies experience heating during metamorphism, those chemical differences are gradually erased by diffusion, which could be accompanied by isotopic fractionation driven by the fact that light isotopes diffuse faster than heavier ones. We have used a simple 1D diffusion model to calculate how much diffusion and isotope fractionation of K could happen during this process (Rb is less well constrained because of the unknown bulk diffusivity). The model assumes a K-depleted area in the center of a K-enriched area (two areas are of the same size of 10 cm in width) and no-flux boundary conditions. The calculated isotope profile as a function of diffusion time is plotted in Fig. 3. The isotopic difference between the two areas is also plotted. The K isotopic variation calculated from the modeling ranges about 1 ‰ at bulk sample scale, which is comparable to the observed K isotopic variation. This suggests that thermal diffusion is a possible cause for the observed Rb and K isotopic variations in NCs.

Conclusion: NCs show large Rb and K isotopic variations. Quantitative modeling of i) chondrule nugget effect and ii) volatilization during parent-body metamorphism suggests that two processes are unlikely the cause of the isotopic variations. Modeling of iii) thermal diffusion during parent-body metamorphism suggest that this process could produce K isotopic variation comparable to the observed variation. Thus, thermal diffusion might have played an important role in causing the large isotopic variations of MVEs in NCs.



Fig. 3 Modeling of diffusion-induced K isotope fractionation during NC parent-body metamorphism. The center 0.1 m (top panel) is assumed to be K depleted. Temperature is assumed to be 1000 K.

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