Research plans for the postdoctoral fellowship at Carnegie Institution for Science
Investigation of volatile element depletion in Vesta

Scientific background

A striking feature of the rocky planetary bodies (e.g., Earth, Moon, Mars and Vesta) is that they are all depleted in volatile elements compared with chondrites, which are their building blocks. As shown in Fig. 1, using alkali elements K and Rb as a representative of volatile elements, their ratios relative to the refractory elements U and Sr, respectively, show a depletion trend of volatiles among the planetary bodies [1]. Under what conditions these planetary objects acquired this signature is still an enigma.

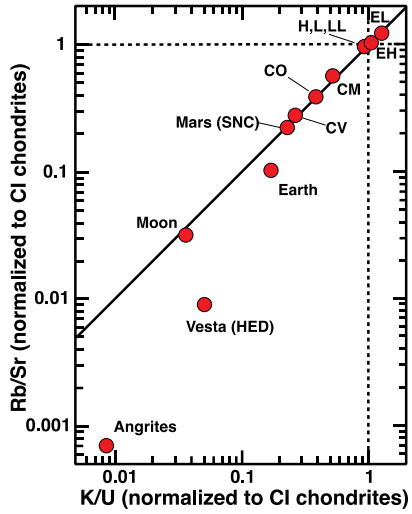

Fig. 1. CI chondrite normalized Rb/Sr vs. K/U ratios showing volatile depletion in planetary bodies. Modified from [1].

The asteroid Vesta is probably the best place to investigate the phenomenon. It has been considered to be the best representative of a rocky proto-planet (e.g., [2]). It accreted and differentiated at the very beginning of the solar system formation. Age constrains from short-lived isotopic systems ^{26}Al–^{26}Mg [3]-[5], ^{60}Fe–^{60}Ni [6], ^{53}Mn–^{53}Cr [7] and ^{182}Hf–^{182}W [8]-[10] suggest that Vesta formed and differentiated within the first several million years after CAI formation (the time zero of solar system). Differentiated bodies like Vesta are considered to be the components that larger terrestrial planets predominantly accreted from (e.g., [11], [12]). Vesta is also one of the most volatile depleted objects, more depleted than Mars and the Earth-Moon system (Fig. 1). The antiquity and the highly volatile depletion feature of Vesta allow one to probe the origin and the evolution of volatile elements in planetary bodies (Angrites are a very good candidate, as shown in Fig.1, but their volatile depletion is too extreme to be studied using the proposed method below. Besides, they are very rare compared to meteorites from Vesta, which are ~60 % of all achondrites [13]).

For my postdoctoral research, I intend to investigate the volatile depletion processes that occurred on Vesta, to allow better understanding of the reasons for the volatile depletion feature of rocky planetary bodies. To tackle this, I propose to use isotope tracers to assess the conditions that could have potentially led to the volatile depletion. Isotope tracers are very powerful in reconstructing geological processes, and there are more and more emerging isotopic systems showing great potential [14]. I will focus on two most recent and novel isotopic systems, K and Rb, to measure their isotopic compositions in HED (Howardite–Eucrite–Diogenite) meteorites, which are thought to be sourced from Vesta [15]-[18]. The reasoning behind choosing to investigate these two elements are that they are both volatile, and are therefore the most suitable for studying volatilization processes. In addition, they are both alkali metals and have very similar chemical behaviors (i.e., following each other closely in many processes), but are contrasting in mass. During volatilization, this mass difference would translate to different extents of isotope fractionation, and the slope of the two isotope fractionations would be very diagnostic in differentiating evaporation kinetics (e.g., equilibrium vs. kinetic processes). Combining the two elements together would present a unique and powerful tool in examining the volatilization conditions in fine detail, which would be difficult by looking at just one isotopic system.

Another intriguing feature of Vesta is that in addition to the depletion in K and Rb, the ratio of the two elements (K/Rb) is quite different from that of other planetary bodies. It can be seen from Fig. 1 that Vesta deviates a lot from the 1:1 line that other planetary bodies follow (U/Sr ratio is more or less constant for these bodies here, and it is the change in K/Rb ratio that causes the deviation from the line). This is quite surprising, because theoretically, the two elements should track each other closely in magmatic processes, since they have quite similar chemical behaviors. Volatility difference between K and Rb would not likely cause such a large fractionation (note that the Moon is depleted to a similar extent but its K/Rb ratio is not much fractionated). One possibility is that the ratio is controlled by mineral crystallization during magmatic differentiation (i.e., the measured K/Rb ratios in HEDs are not fully representative of bulk Vesta). Fractionation of K from Rb have been observed in plagioclase (e.g., [19]), which is a major phase in HED meteorites. Therefore, in addition to K and Rb isotope measurements, I intend to also perform lab petrology experiments to investigate the elemental partition and isotope fractionation of K and Rb during magmatic differentiation of mafic compositions relevant to Vesta. This experimental study will tease out the contribution of magmatic differentiation to the volatile depletion signature of Vesta.

Specific hypotheses to test

The low abundances of volatile, alkali elements K and Rb, and the very fractionated K/Rb ratio in HED meteorites were noticed very early, pointed out first in 1960 [20]. The hypotheses that have been proposed since then to explain the depletion can be classified as three types: (i) incomplete condensation of elements in Vesta's building blocks [21], (ii) core formation of Vesta leading to partition of volatile elements into the core [22]-[24], and (iii) partial vaporization processes through magma eruption [25], magma outgassing during crystallization [26], or Vesta's early magma ocean [27], [28].

The three hypotheses can be effectively differentiated using isotopic compositions of volatile elements such as K and Rb as outlined below. (i) For incomplete condensation, the theory of evaporation condensation predicts that the condensates would be enriched in light isotopes in a kinetic condensation regime [29]. Therefore, if incomplete condensation is primarily responsible for volatile element depletion, Vesta should have light bulk isotopic compositions compared with chondrites. (ii) Core formation in Vesta featured high temperatures (> 1500 K; [23], [24], [30]), under which the isotope fractionation theory predicts negligible equilibrium isotope fractionation between the core and the mantle. Therefore, core formation would not change much the isotopic composition of the silicate portion of Vesta, and Vesta should have similar isotopic compositions to the building block chondrites. (iii) Partial vaporization processes, based on evaporation theories [29], would most likely leave a heavy isotopic signature in Vesta since light isotopes are expected to be preferentially evaporated away due to kinetic isotope fractionation.

Potassium and Rb isotope data are still very rare, due to the analytic challenges associated with their measurement. Humayun and Clayton (1995) measured K isotopic compositions among planetary bodies but the precision was not high enough to distinguish any differences among them [31]. Tian et al. (2018) reported, in abstract form, some K isotope data with enough precision to observe heavy K isotopic compositions of HEDs compared with chondrites [28], and much larger K isotopic variation of HEDs (~0.6 ‰) compared with that of terrestrial igneous rocks (~0.1 ‰). For Rb isotopes, only two data points of HEDs have been reported [32]. The two values are both heavier than chondrites but are quite contrasting from each other (a difference of ~1 ‰). It is not clear which value is representative of the bulk Rb isotopic composition of Vesta and if the two values reflect the range of isotopic variations of HEDs.

Taken at face value, the reported heavy K and Rb isotopic compositions of HEDs are more consistent with the last scenario stated above, i.e., (iii) partial vaporization. However, it remains unknown, considering the large variation of reported K isotopic compositions among HEDs and very few Rb isotope data, the bulk K and Rb isotopic compositions of Vesta. More data is required, especially for Rb isotopes. Whether the reported large isotopic variation of K could be due to or partly due to magmatic differentiation and mineralogical control needs to be examined. It has been suggested that a high K/Rb elemental ratio in mafic rocks could be largely controlled by their plagioclase [19]. This could be the reason why HEDs have a fractionated, high K/Rb ratio (Fig. 1), considering abundant plagioclase in HEDs (especially in eucrites). It is also likely that some isotope fractionation could have occurred along with the elemental fractionation, causing isotopic variations in HEDs. To test this, I will perform lab experiments to check the effect of plagioclase crystallization on K and Rb contents and isotopic compositions in mafic rocks. The bulk isotopic compositions of Vesta will be established after teasing out the effect of plagioclase crystallization, and it will provide a baseline to differentiate the proposed scenarios. If partial vaporization is responsible for the volatile depletion, the further question would be to distinguish/disentangle the processes and conditions that could have caused the partial vaporization (i.e., large-scale magma ocean or relatively local-scale magma eruption/degassing). This will be done by examining the concentrations and correlated isotopic compositions of K and Rb in individual HEDs carefully, comparing them with that of the bulk Vesta and with evaporation theories.

Methods

Measuring K and Rb isotopes is still a major analytical challenge in the field, resulting in only a few isotope data. The main difficulty for K is in MC-ICPMS analysis, due to the isobaric interference of Ar, which is the main sample introduction gas. For Rb, it is a trace element, and a clean separation of it from matrix elements especially K is quite challenging due to the very similar chemical behaviors of the two elements. Nonetheless, my Ph.D. training at the University of Chicago has prepared me for the work. I spent three years developing a Rb purification and isotope measurement method, for investigating the formation of the Moon. The method allows separation of both clean Rb and K from a same sample (in comparison, a test on the Rb separation method in a recent paper [32] showed an insufficient separation of the two elements) and worked very well on terrestrial and lunar samples. For the period of my postdoctoral study, I would like to apply the newly developed method to Vesta, measuring Rb and K isotopic compositions of HED meteorites (measuring HEDs is more challenging than measuring the Earth-Moon system since they are more depleted, but is doable). For the study, only HED "falls" will be used because the "finds" experienced terrestrial weathering under which K and Rb isotopes could have been fractionated (the two elements are very sensitive to fractionation during weathering). There are 62 HED "falls" in total (35 Eucrites, 16 Howardites and 11 Diogenites), and 20 representative samples (12 Eucrites, 4 Howardites and 4 Diogenites) will be measured for the study. I currently have 10 Eucrites and 1 Diogenite, and the rests will be obtained by requesting from Field, Smithsonian and other museums.

For lab experiments, I will start with plagioclase crystallization experiments, analyzing K and Rb concentrations and isotopes in the experimental plagioclases and glasses to constrain the equilibrium fractionation between the two phases. The merits of performing lab experiments, rather than measuring natural plagioclase, are that crystallization conditions (composition, temperature, oxygen fugacity etc.) can be controlled, and one can also use elevated concentrations of K and Rb for starting materials to facilitate isotope measurements. More experiments (i.e., crystallization and investigation of the effects of other phases) can be conducted if the plagioclase experiments are successful.

References

[1] A. M. Davis, "Volatile evolution and loss," *Meteorites and the early solar system II*, vol. 1, pp. 295–307, 2006.

[2] C. T. Russell, C. A. Raymond, A. Coradini, H. Y. McSween, M. T. Zuber, A. Nathues, M. C. De Sanctis, R. Jaumann, A. S. Konopliv, F. Preusker, S. W. Asmar, R. S. Park, R. Gaskell, H. U. Keller, S. Mottola, T. Roatsch, J. E. C. Scully, D. E. Smith, P. Tricarico, M. J. Toplis, U. R. Christensen, W. C. Feldman, D. J. Lawrence, T. J. McCoy, T. H. Prettyman, R. C. Reedy, M. E. Sykes, and T. N. Titus, "Dawn at Vesta: Testing the Protoplanetary Paradigm," *Science*, vol. 336, no. 6082, pp. 684–686, May 2012.

[3] G. Srinivasan, J. N. Goswami, and N. Bhandari, "^{26}Al in Eucrite Piplia Kalan: Plausible Heat Source and Formation Chronology," *Science*, vol. 284, no. 5418, pp. 1348–1350, May 1999.

[4] J. Baker, M. Bizzarro, N. Wittig, J. Connelly, and H. Haack, "Early planetesimal melting from an age of 4.5662 Gyr for differentiated meteorites," *Nature*, vol. 436, no. 7054, pp. 1127–1131, Aug. 2005.

[5] M. Bizzarro, J. A. Baker, H. Haack, and K. L. Lundgaard, "Rapid Timescales for Accretion and Melting of Differentiated Planetesimals Inferred from ^{26}Al-^{26}Mg Chronometry," *ApJ*, vol. 632, no. 1, pp. L41–L44, Oct. 2005.

[6] A. Shukolyukov and G. W. Lugmair, "^{60}Fe in eucrites," *Earth and Planetary Science Letters*, vol. 119, no. 1, pp. 159–166, Aug. 1993.

[7] G. W. Lugmair and A. Shukolyukov, "Early solar system timescales according to ^{53}Mn-^{53}Cr systematics," *Geochimica et Cosmochimica Acta*, vol. 62, no. 16, pp. 2863–2886, Aug. 1998.

[8] Q. Yin, S. B. Jacobsen, K. Yamashita, J. Blichert-Toft, P. Télouk, and F. Albarède, "A short timescale for terrestrial planet formation from Hf–W chronometry of meteorites," *Nature*, vol. 418, no. 6901, pp. 949–952, Aug. 2002.

[9] T. Kleine, K. Mezger, C. Münker, H. Palme, and A. Bischoff, "^{182}Hf-^{182}W isotope systematics of chondrites, eucrites, and martian meteorites: Chronology of core formation and early mantle differentiation in Vesta and Mars," *Geochimica et Cosmochimica Acta*, vol. 68, no. 13, pp. 2935–2946, Jul. 2004.

[10] G. Quitté and J.-L. Birck, "Tungsten isotopes in eucrites revisited and the initial ^{182}Hf/^{180}Hf of the solar system based on iron meteorite data," *Earth and Planetary Science Letters*, vol. 219, no. 3, pp. 201–207, Mar. 2004.

[11] S. R. Taylor and M. D. Norman, "Accretion of differentiated planetesimals to the Earth," *Origin of the Earth*, pp. 29–43, 1990.

[12] R. W. Carlson and G. W. Lugmair, "Timescales of planetesimal formation and differentiation based on extinct and extant radioisotopes," *Origin of the Earth and Moon*, pp. 25–44, 2000.

[13] M. M. Lindstrom and R. Score, "Populations, pairing, and rare meteorites in the US Antarctic meteorite collection," p. 43, 1995.

[14] F.-Z. Teng, J. M. Watkins, N. Dauphas, and I. Swainson, "Non-traditional stable isotopes," 2017.

[15] T. B. McCord, J. B. Adams, and T. V. Johnson, "Asteroid Vesta: Spectral reflectivity and compositional implications," *Science*, vol. 168, no. 3938, pp. 1445–1447, 1970.

[16] R. P. Binzel, M. J. Gaffey, P. C. Thomas, B. H. Zellner, A. D. Storrs, and E. N. Wells, "Geologic mapping of Vesta from 1994 Hubble space telescope images," *Icarus*, vol. 128, no. 1, pp. 95–103, 1997.

[17] M. J. Gaffey, "Surface lithologic heterogeneity of asteroid 4 Vesta," *Icarus*, vol. 127, no. 1, pp. 130–157, 1997.

[18] H. Y. McSween, D. W. Mittlefehldt, A. W. Beck, R. G. Mayne, and T. J. McCoy, "HED meteorites and their relationship to the geology of Vesta and the Dawn mission," pp. 141–174, 2010.

[19] V. R. Murthy and W. L. Griffin, "K/Rb fractionation by plagioclase feldspars," *Chemical Geology*, vol. 6, pp. 265–271, Jan. 1970.

[20] P. W. Gast, "Alkali metals in stone meteorites," *Geochimica et Cosmochimica Acta*, vol. 19, no. 1, pp. 1–4, Mar. 1960.

[21] T. H. Prettyman, N. Yamashita, R. C. Reedy, H. Y. McSween Jr., D. W. Mittlefehldt, J. S. Hendricks, and M. J. Toplis, "Concentrations of potassium and thorium within Vesta's regolith," *Icarus*, vol. 259, pp. 39–52, Oct. 2015.

[22] E. A. Pringle, P. S. Savage, J. Badro, J.-A. Barrat, and F. Moynier, "Redox state during core formation on asteroid 4-Vesta," *Earth and Planetary Science Letters*, vol. 373, pp. 75–82, Jul. 2013.

[23] E. S. Steenstra, D. Dankers, J. Berndt, S. Klemme, S. Matveev, and W. van Westrenen, "Significant depletion of volatile elements in the mantle of asteroid Vesta due to core formation," *Icarus*, Sep. 2018.

[24] E. S. Steenstra, N. Agmon, J. Berndt, S. Klemme, S. Matveev, and W. van Westrenen, "Depletion of potassium and sodium in mantles of Mars, Moon and Vesta by core formation," *Scientific Reports*, vol. 8, no. 1, p. 2131, May 2018.

[25] E. Stolper, "Experimental petrology of eucritic meteorites," *Geochimica et Cosmochimica Acta*, vol. 41, no. 5, pp. 587–611, 1977.

[26] D. W. Mittlefehldt, "Volatile degassing of basaltic achondrite parent bodies: Evidence from alkali elements and phosphorus," *Geochimica et Cosmochimica Acta*, vol. 51, no. 2, pp. 267–278, Feb. 1987.

[27] A. R. Sarafian, T. John, J. Roszjar, and M. J. Whitehouse, "Chlorine and hydrogen degassing in Vesta's magma ocean," *Earth and Planetary Science Letters*, vol. 459, pp. 311–319, Feb. 2017.

[28] Z. Tian, H. Chen, B. Fegley, K. Lodders, J. A. Barrat, and K. Wang, "Potassium Isotope Differences Among Chondrites, Earth, Moon, Mars, and 4-Vesta --- Implication on the Planet Accretion Mechanisms," *Lunar and Planetary Science Conference*, vol. 49, Mar. 2018.

[29] F. M. RICHTER, "Timescales determining the degree of kinetic isotope fractionation by evaporation and condensation," *Geochimica et Cosmochimica Acta*, vol. 68, no. 23, pp. 4971–4992, Dec. 2004.

[30] K. Righter and M. J. Drake, "Core Formation in Earth's Moon, Mars, and Vesta," Icarus, vol. 124, no. 2, pp. 513–529, Dec. 1996.

[31] M. Humayun and R. N. Clayton, "Potassium isotope cosmochemistry: Genetic implications of volatile element depletion," *Geochimica et Cosmochimica Acta*, vol. 59, no. 10, pp. 2131–2148, 1995.

[32] E. A. Pringle and F. Moynier, "Rubidium isotopic composition of the Earth, meteorites, and the Moon: Evidence for the origin of volatile loss during planetary accretion," *Earth and Planetary Science Letters*, vol. 473, pp. 62–70, Sep. 2017.