

**A MODEL OF OXYGEN ISOTOPE EXCHANGE BETWEEN MOLTEN SILICATE SPHERULES AND AMBIENT WATER VAPOR WITH NONZERO RELATIVE VELOCITY.** S. Arakawa<sup>1</sup>, D. Yamamoto<sup>2</sup>, T. Ushikubo<sup>3</sup>, H. Kaneko<sup>4</sup>, H. Tanaka<sup>5</sup>, S. Hirose<sup>1</sup>, and T. Nakamoto<sup>4</sup>, <sup>1</sup>Yokohama Institute for Earth Sciences, Japan Agency for Marine-Earth Science and Technology (3173-25 Showa-machi, Kanazawa-ku, Yokohama, 236-0001, Japan. arakawas@jamstec.go.jp), <sup>2</sup>Department of Earth and Planetary Sciences, Kyushu University (744, Motoooka, Nishi-ku, Fukuoka, 819-0395, Japan), <sup>3</sup>Kochi Institute for Core Sample Research, Japan Agency for Marine-Earth Science and Technology (200 Monobe-otsu, Nankoku, Kochi, 783-8502, Japan), <sup>4</sup>Department of Earth and Planetary Sciences, Tokyo Institute of Technology (2-12-1 Ookayama, Meguro, Tokyo, 152-8550, Japan), <sup>5</sup>Astronomical Institute, Graduate School of Science, Tohoku University (6-3 Aramaki, Aoba-ku, Sendai, 980-8578, Japan).

**Introduction:** Oxygen isotope compositions of chondrules have been evolved via isotope exchange reaction with ambient vapor, and those would reflect the chondrule-forming environment such as the dust-to-gas and water-to-rock ratios of the environment [1]. Ushikubo et al. [2] measured the oxygen isotope compositions of chondrules in Acfer 094, one of the least thermally metamorphosed and aqueously altered carbonaceous chondrites whose petrologic type is 3.00 [3], and they reported the following notable features: (i) phenocrysts and mesostasis in the same chondrule have similar oxygen isotope compositions, (ii) porphyritic chondrules frequently host relict olivine grains that are distinguished by the difference in oxygen isotope compositions, (iii) relict olivine grains in the same chondrule are either <sup>16</sup>O-enriched or <sup>16</sup>O-depleted compared to chondrule phenocrysts, i.e., <sup>16</sup>O-enriched and <sup>16</sup>O-depleted relict olivine grains are exclusively present in one chondrule, and (iv) oxygen isotope compositions of chondrule phenocrysts are correlated with their Mg# values (i.e., the molar percentage of MgO / (MgO + FeO)). These features are regarded as the evidence of the efficient oxygen isotopic exchange between (molten) chondrules and the ambient vapor [4].

The oxygen isotope compositions of chondrules are distributed along a line with slope  $\sim 1$ , which is called the primitive chondrule minerals (PCM) line, in the three-oxygen isotope diagram [2]. This trend cannot be explained by the mass-dependent isotopic fractionation that makes a variation along a line with slope  $\sim 0.52$  [5], and it is usually interpreted as the results of mixing between isotopically distinct reservoirs [1]. One of the possible reservoir of <sup>16</sup>O-depleted materials is H<sub>2</sub>O ice in the outer solar system as products of self-shielding of carbon monoxide in the protosolar molecular cloud [6] or the solar nebula [7]. Therefore, oxygen isotope exchange reaction between chondrule precursors and water vapor have a potential to explain the variation of oxygen isotope compositions of chondrules.

Yamamoto et al. [8] performed laboratory experiments to determine the oxygen isotope exchange

kinetics between silicate melt and water vapor. They found that the oxygen isotope exchange efficiency on the melt surface is  $\beta \sim 0.3$  in colliding water molecules. Using the  $\beta$  value obtained from laboratory experiments, we can calculate the temporal evolution of oxygen isotope ratios from the Hertz–Knudsen equation [8]. However, since the Hertz–Knudsen equation is only applicable when the relative velocity between silicate melt and the bulk motion of H<sub>2</sub>O vapor is zero. Here we introduced the relative velocity effect into the Hertz–Knudsen equation to investigate isotopic fractionation of chondrules formed by dynamic process such as shock waves in the protoplanetary disk.

**Model:** The oxygen isotope exchange reaction is controlled by the balance between the influx and efflux of water vapor. Figure 1 is the schematic of the influx and efflux of water molecules at the molten chondrule surface. Here we describe the theoretical model of the influx and efflux which can be applied to chondrules moving with finite velocity.

*Influx.* When the relative velocity is  $v_{\text{rel}} = 0$ , the flux of colliding water molecules (per unit area) at the chondrule surface is given by the Hertz–Knudsen equation,  $J_0 = P / \sqrt{2\pi m k_B T}$ , where  $P$  is the partial pressure of ambient water vapor,  $m$  is the molecular weight of water,  $k_B$  is the Boltzmann constant, and  $T$  is the temperature of ambient water vapor. We found that, for  $v_{\text{rel}} \neq 0$ , the flux of colliding water molecules is given by  $J = J_0 (A + B)$ , where  $A = \sqrt{\pi}/2 \operatorname{erf}(s)/s$  and  $B = (s^2 - 1/2)A + \exp(-s^2)/2$ . Here  $s$  denotes the Mach number of water vapor.

The molecular weight of H<sub>2</sub><sup>*i*</sup>O,  $m_i$ , depends on the isotope species  $i$ . The sound velocity also differs among different isotopes. When the number density of H<sub>2</sub><sup>*i*</sup>O molecules in the ambient vapor is  $n_i$ , the flux ratio of H<sub>2</sub><sup>*i*</sup>O and H<sub>2</sub><sup>*j*</sup>O molecules,  $J_i / J_j$ , is not equal to the number density ratio,  $n_i / n_j$ . The influx of water molecules which can react with chondrules,  $J_i^{\text{in}}$ , is given by  $J_i^{\text{in}} = \beta_i J_i$ , where  $\beta_i$  is the isotope exchange efficiency of colliding H<sub>2</sub><sup>*i*</sup>O molecules [8].

**Efflux.** We also derive theoretical constraints on the efflux of water molecules (per unit area) at the chondrule surface from the point of view of isotope fractionation factors at equilibrium. We introduce the isotope ratio of the water vapor,  $R^{i/16}_{\text{vapor}} = n_i / n_{16}$ , and the isotope ratio of chondrules,  $R^{i/16}_{\text{chondrule}}$ , for  $i = 17$  and 18. Here we consider the case that the isotope exchange reaction is in steady state and  $v_{\text{rel}} = 0$ . The ratio of  $R^{i/16}_{\text{chondrule}}$  to  $R^{i/16}_{\text{vapor}}$  is equal to the isotope fractionation factor,  $\alpha^{i/16}$ ;  $R^{i/16}_{\text{chondrule}} / R^{i/16}_{\text{vapor}} = \alpha^{i/16}$ . The efflux of  $\text{H}_2^{i/16}\text{O}$  molecules after isotope exchange reaction,  $J_i^{\text{out}}$ , should be balanced with the influx:  $J_i^{\text{out}} = J_i^{\text{in}}$ , where  $J_i^{\text{in}}$  represents  $J_i^{\text{in}}$  for  $v_{\text{rel}} = 0$ . Assuming that  $\alpha^{i/16} \sim 1$  [9, 10] and  $\beta_i / \beta_{16} \sim 1$  [11] at high temperature, we obtained the following equation:  $J_i^{\text{out}} / J_{16}^{\text{out}} = \text{sqrt}(m_{16} / m_i) R^{i/16}_{\text{chondrule}}$ .

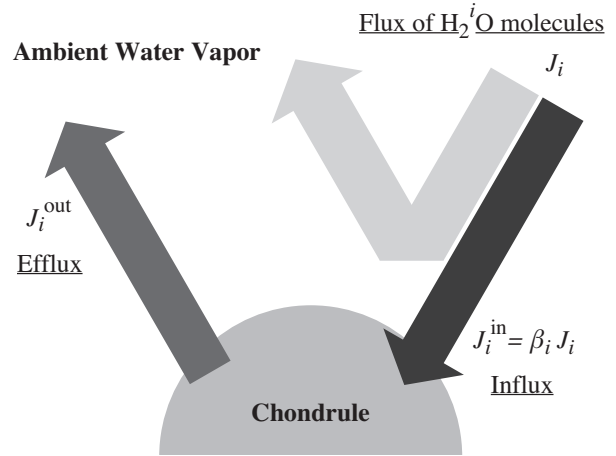
**Results:** Figure 2 shows the oxygen three-isotope plot for chondrules in steady state as a function of  $s_{16}$ , where  $s_{16}$  is the Mach number for  $\text{H}_2^{16}\text{O}$  molecules and  $s_{16} = 0.74$  ( $v_{\text{rel}} / 1 \text{ km/s}$ ) at  $T = 2000 \text{ K}$ . Here we assume that the oxygen isotope ratios of water vapor are  $\delta^{17}\text{O}_{\text{vapor}} = \delta^{18}\text{O}_{\text{vapor}} = 0$  in the  $\delta$  notation and those are constant over time.

For  $v_{\text{rel}} = 0$ , it is clear that the following equation,  $R^{i/16}_{\text{chondrule}} = R^{i/16}_{\text{vapor}}$ , is satisfied in steady state. In contrast, we found that  $R^{i/16}_{\text{chondrule}}$  deviates from  $R^{i/16}_{\text{vapor}}$  when  $v_{\text{rel}} \neq 0$ . For the supersonic limit ( $v_{\text{rel}} \rightarrow \infty$ ),  $R^{i/16}_{\text{chondrule}}$  becomes  $R^{i/16}_{\text{chondrule}} = \text{sqrt}(m_i / m_{16}) R^{i/16}_{\text{vapor}}$ , and mass-dependent isotope fractionation occurs in this case. The oxygen isotopic deviation of chondrule from vapor is approximately 27‰ for  $\delta^{17}\text{O}$  and 54‰ for  $\delta^{18}\text{O}$ .

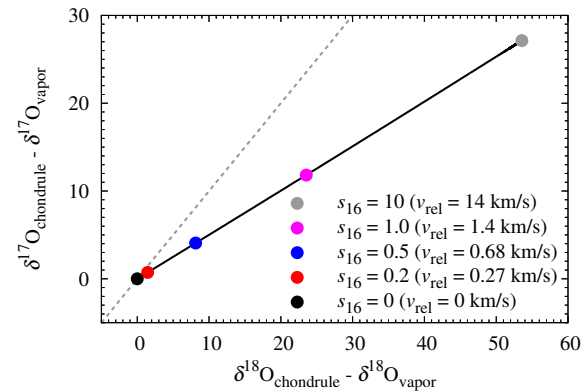
**Conclusion:** We found that large mass-dependent fractionation would be caused by isotope exchange with ambient vapor unless the relative velocity is sufficiently smaller than the sound speed of reacting molecules. As the oxygen isotope compositions of chondrules are plotted on the mass-independent mixing line with small deviation ( $\pm 1$  in the  $\delta$  notation; [1, 2]), our findings indicate that the relative velocity between chondrules and ambient vapor would be lower than a few hundred m/s ( $s_{16} < 0.2$ ) when chondrules crystallized.

**References:** [1] Tenner T. J. et al. (2018) in *Chondrules: Records of Protoplanetary Disk Processes* (ed. Russell S. S., Connolly, H. C. J., and Krot A. N.), 196–246. [2] Ushikubo T. et al. (2012) *GCA*, 90, 242. [3] Kimura M. et al. (2008) *M&PS*, 43, 1161. [4] Kita N. T. et al. (2010) *GCA*, 74, 6610. [5] Clayton R. N. and Mayeda T. K. (1983) *EPSL*, 62, 1. [6] Yurimoto H. and Kuramoto K. (2004) *Science*, 305, 1763. [7] Lyons J. R. and Young E. D. (2005) *Nature*, 435, 317. [8] Yamamoto D. et al. (2021) *GCA*, 314, 108. [9] Appora I, et al. (2003) *GCA*, 67, 459. [10] Di

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**Figure 1.** Schematic of the influx and efflux of water molecules at the molten chondrule surface. The influx of  $\text{H}_2^{i/16}\text{O}$  molecules which can react with a chondrule,  $J_i^{\text{in}}$ , is given by  $J_i^{\text{in}} = \beta_i J_i$ , where  $J_i$  is the flux of  $\text{H}_2^{i/16}\text{O}$  molecules and  $\beta_i$  is the isotope exchange efficiency. We note that  $J_i$  depends on relative velocity of the chondrule and the ambient vapor,  $v_{\text{rel}}$ . The efflux of  $\text{H}_2^{i/16}\text{O}$  molecules after isotope exchange reaction is  $J_i^{\text{out}}$ . We assumed that  $J_i^{\text{out}} / J_{16}^{\text{out}}$  is a function of the oxygen isotope composition of the chondrule.



**Figure 2.** Oxygen three-isotope plot for chondrules in steady state as a function of the Mach number for  $\text{H}_2^{16}\text{O}$  molecules,  $s_{16}$ . Here we assume that the oxygen isotope ratios of water vapor are  $\delta^{17}\text{O}_{\text{vapor}} = \delta^{18}\text{O}_{\text{vapor}} = 0$  and those are constant over time. The dashed line represents a mixing trend between  $^{16}\text{O}$ -rich and  $^{16}\text{O}$ -poor materials (e.g., PCM line [2]).