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Chlorine isotope fractionation during sublimation of metal chloride and implication for degassing of the lunar magma ocean

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The Moon is depleted in volatiles, while lunar samples exhibit a wide range of Cl isotopic composition ($\delta^{37}Cl$) (-4‰ to +81‰) relative to terrestrial materials (-14‰ to +16‰). The large Cl isotope fractionation in lunar sample has been interpreted as volatilization of metal chloride[1]. However, the behaviour of Cl isotope fractionation in volatilization is not well constrained. We conducted experiments to study Cl isotope fractionation during NaCl sublimation at temperature range from 923 K to 1061 K and pressures of 6×10^{-5} bar to 1 bar in the N_2 atmosphere.

The fractionation factor of Cl between gas and solid NaCl during sublimation can be described by the Rayleigh fractionation model. The fractionation factors are determined to be 0.9987±0.0001, 0.9956±0.0003, and 0.9981±0.00002 at 1, 1×10^{-2}, and 6×10^{-5} bar respectively. The measured $\alpha_{gas\text{-}solid}$ values are larger than the calculated ones using Graham's law ($\alpha_{gas\text{-}solid}$ values of 0.9826 for NaCl and 0.9914 for Na_2Cl_2), and are similar to the experimental results of NaCl melting ($\alpha_{gas\text{-}solid}$ of 0.9955 to 0.997 at vacuum to 1 bar)[2]. Compared with the sublimation rate in free evaporation experiments [3], the partial pressure is more than 98% of saturation vapor pressure even at 6×10^{-5} bar in our experiments. The Cl isotope fractionation is therefore controlled by diffusion in the gas and the condensed phases. Our experiments suggest that the Cl isotope fractionation is relatively smaller at low vacuum than that in high vacuum. It has been shown that the high $\delta^{37}Cl$ in lunar samples can be attributed to degassing of the lunar magma ocean with $\alpha_{gas\text{-}melt}\sim$ 0.996[4], which is similar to our result. The studies of halite sublimation from this work and evaporation of aqueous HCl solution at 1bar ($\alpha_{gas\text{-}liquid}$ = 0.996[5]) consistently indicate that degassing of the lunar magma ocean may have occurred at a certain pressure rather than in vacuum condition ($<1\times10^{-9}$ bar).

Reference:[1] Sharp et al. Science, 2010; [2] Sharp et al. LPSC, 2013; [3] Zimm et al., J. Chem. Phys., 1944; [4] Boyce et al. EPSL, 2018; [5] Sharp et al. GCA, 2010.