

Mg AND Si ISOTOPE FRACTIONATION IN ALLENDE CAI SJ101 AS A RESULT OF

CONDENSATION. M. K. Jordan¹, E. D. Young¹, and S. B. Jacobsen², ¹Department of Earth and Space Sciences, University of California Los Angeles, Los Angeles, CA, USA, mjkjordan@ucla.edu, eyoung@ess.ucla.edu, ²Harvard University, Cambridge Mass, USA, Jacobsen@neodymium.harvard.edu.

Introduction: CAI isotopic compositions are monitors of volatility. The isotopic effects of evaporation are well understood through both theory and experimental work. Evaporation expresses itself as an enrichment in the heavy isotopes, due to the loss of lighter, more volatile isotopes. Less is known about the isotopic effects of condensation. Here, we present a model for condensation and explore its isotopic consequences.

Mg and Si isotope fractionation data were collected for a large type B CAI, SJ101 (provided by S. Jacobsen, Harvard). We find SJ101 to be depleted in the heavier isotopes of Mg and Si, apparently precluding evaporation as an important process in this object. Instead, the observed relative depletion in heavy isotopes is ruminant of condensation from a gas with roughly chondritic isotope ratios. Condensation generally occurs in response to oversaturation, or undercooling.

Sample Description: SJ101 is a large forsterite-bearing type B (FoB) CAI from Allende. The CAI predominately consists of large areas of Al-rich spinel-clinopyroxene (Sp-Cpx) lithology. Sinuous bands of Al-rich pyroxene with enclosed euhedral forsterite crystals occur throughout. The two major lithologies are separated by a transition zone of clinopyroxene enclosing both forsterite and spinel. The whole inclusion is surrounded by a Cpx-Sp-anorthite rim. Differing from other FoBs, SJ101 has no Wark-Lovering rim or Al-enriched mantle. [1]

SJ101 shows neither petrological nor isotopic evidence for evaporation. Instead, the negative $\delta^{25}\text{Mg}$ and $\delta^{29}\text{Si}$ values relative to chondrite, as well as Group II REE patterns, suggest formation by non-equilibrium condensation [3].

Analytical Methods: In-situ analyses were conducted using laser ablation multiple-collector inductively coupled plasma-source mass spectrometry (LA-MC-ICPMS, ThermoFinnegan NeptuneTM). We used a 193 nm eximer laser to extract Mg and Si from the sample. The laser was operated at a UV fluence of 20 J/cm². Material was ablated at a pulse repetition rate of 2 Hz, forming pits of 52 μm and 86 μm for Mg and Si respectively. Helium (0.17-0.51 l/min) carried ablated material from the sample chamber to a mixing chamber where it combines with Ar (0.69 l/min) before being introduced to the ICP torch.

Sample-standard bracketing was used to correct for instrumental mass bias. The standard used was a pol-

ished slice of San Carlos olivine. Analyses are reported as per mil deviations from the standard.

Data: $\delta^{25}\text{Mg}$ and $\delta^{29}\text{Si}$ values are reported relative to San Carlos olivine, which we take to be essentially chondritic. Figure 1 shows the $\delta^{25}\text{Mg}$ and $\delta^{29}\text{Si}$ values for each analysis and the distance of each analyses from the rim. Both $\delta^{25}\text{Mg}$ and $\delta^{29}\text{Si}$ values are consistently negative, indicating an enrichment in the lighter isotopes of the respective species. The average $\delta^{25}\text{Mg}$ value is $-1.6 \pm 0.5\%$ 1σ and the average $\delta^{29}\text{Si}$ value is $-0.2 \pm 0.1\%$ 1σ , implying condensation. There is evidence for an increase in $^{25}\text{Mg}/^{24}\text{Mg}$ toward the margin of the object.

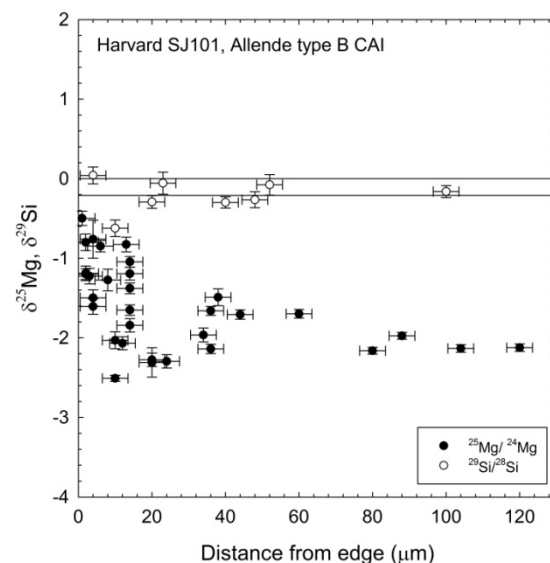


Figure 1. LA-MC-ICPMS Mg and Si isotope ratio data for CAI SJ101.

Condensation Theory: We consider the isotopic consequences of condensation from a nebular gas in terms of the kinetics of condensation, the degree of undercooling, and potential reservoir effects. Unlike evaporation fractionation factors (α_{evap}), we are unable to directly measure condensation fractionation factors (α_{cond}). A condensation model is needed to indirectly elicit α_{cond} . Invoking the law of mass action, we have [5]:

$$\alpha_{\text{eq}} = \frac{\alpha_{\text{cond}}}{\alpha_{\text{evap}}}$$

Equilibrium fractionation (α_{eq}) factors can be calculated and evaporation fractionation factors can be measured in the laboratory allowing us to solve for α_{cond} [5].

Kinetic fractionation associated with condensation depends upon collisional frequency and the ability of a molecule to incorporate into the structure of the condensed phase [5]. Collisional frequency favors the lighter isotopes to the condensate.

The degree of saturation controls the balance between equilibrium and kinetic isotope fractionation [4]. The saturation index $S_i = P_i/P_{i,\text{eq}}$ quantifies the degree of saturation with $S_i > 1$ implying condensation. S_i can be equated with a temperature difference from the equilibrium condensation temperature if the reaction pathway is known. Therefore, S_i corresponds to the degree of undercooling. The situation is analogous to production of snow in clouds [2].

Combining these parameters we arrive at a complete model for fractionation associated with condensation [2,4,5]:

$$\alpha_{\text{cond}} = \frac{\alpha_{\text{eq}}\alpha_{\text{kin}}S_i}{\alpha_{\text{eq}}(S_i - 1) + \alpha_{\text{kin}}}$$

where,

$$\alpha_{\text{kin}} = \alpha_{\text{evap}}\alpha_{\text{eq}}\sqrt{\frac{m_i}{m'_i}}$$

with m_i being the lighter isotope of the species of interest and m'_i being the heavier isotope.

In addition to the kinetic isotope effects, there are also reservoir effects. For condensation, the gas becomes progressively enriched in the heavy isotopes relative to the light isotopes as the condensate is extracted. Because the gas is likely to be well mixed, we can apply the concept of Rayleigh fractionation to this scenario. Using Rayleigh fractionation, we can calculate the isotopic composition of the condensed phase (liquid or solid) in terms of the fraction of the element of interest remaining in the vapor as

$$\delta_{\text{solid}} = (\delta_{\text{vapor}}^0 + 10^3)\alpha^{s/v}f^{\alpha-1} - 1000.$$

We are left with two competing effects, the reservoir effect that progressively enriches the condensate in heavier isotopes relative to light isotopes, and the kinetic effects of condensation that favor light isotopes in the condensate.

Discussion: Using this model we can calculate the expected fractionation as a function of the fraction of the element of interest remaining in the gas phase and the degree of oversaturation S_i . The Mg and Si isotopic data from SJ101 are plotted against the calculated curves as functions of S_i and F in Figure 2.

Because Mg and Si have similar volatilities, the simplest case suggests that the two elements would also have similar degrees of undercooling. We assess the data under this assumption and the assumption that the gas is initially chondritic in $^{25}\text{Mg}/^{24}\text{Mg}$ and $^{29}\text{Si}/^{28}\text{Si}$. Silicon isotope ratios are essentially chondritic while Mg ratios are lower than chondritic by ~1-2%. In order to produce the observed fractionation at the same fraction of remaining Mg and Si in the gas (consistent with similar volatilities and condensation temperatures), we find that Si requires undercooling of about 0.3 K and Mg requires about 0.5 K. This occurs with negligible losses from the gas (i.e., F is near unity). The degrees of undercooling required to explain the Si and Mg isotope data are very similar at F near 1. Therefore, we conclude that the most robust explanation for the data is that condensation to form this CAI occurred within one degree or less of the equilibrium temperature for these elements and that reservoir effects were not important.

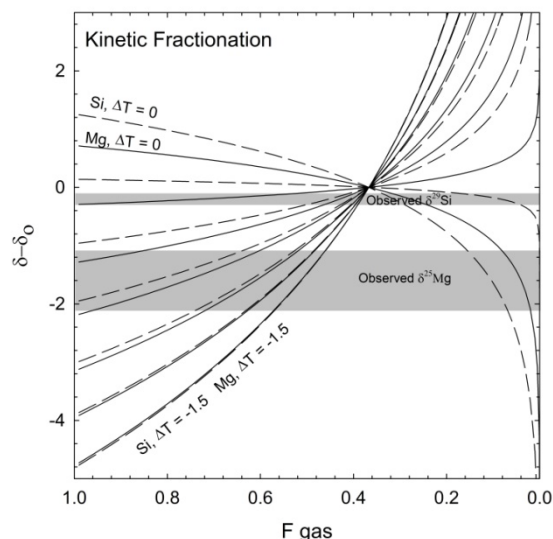


Figure 2. Calculated shifts in $\delta^{29}\text{Si}$ and $\delta^{25}\text{Mg}$ with condensation as a function of saturation S_i and fraction of Si and Mg remaining in the gas phase.

References:[1] Jacobsen S. B. et al. (2008) LPS XXXIX, Abstract #1999 [2] Jouzel J. and Merlivat L. (1984) JGR, 89, 1749-1757. [3] Petaev M. I. and Jacobsen S. B. (2009) LPS XXXI, Abstract #1388. [4] Simon J. I. and DePaolo D.J. (2010) EPSL, 289, 457-466. [5] Young E.D. and Schauble E.A. (2012) MetSoc, Abstract #5382