

**Ultra-refractory metal grains in hibonite-bearing inclusions with highly fractionated Mg isotopes.** K. Fukuda<sup>1</sup>, H. Hiyagon<sup>1</sup>, S. Sasaki<sup>1</sup>, W. Fujiya<sup>1,4</sup>, N. Takahata<sup>2</sup>, Y. Sano<sup>2</sup> and Y. Morishita<sup>3</sup>, <sup>1</sup>Department of Earth and Planetary Science, The University of Tokyo, Bunkyo-ku, Tokyo 113-0033, Japan; <sup>2</sup>Atmosphere and Ocean Research Institute, The University of Tokyo, Chiba 277-8564, Japan; <sup>3</sup>National Institute of Advanced Science and Technology, Tsukuba, Ibaraki 305-8567, Japan; <sup>4</sup>Max-Planck Institute for Chemistry, Particle Chemistry Department, 55128 Mainz, Germany.

### Introduction:

Hibonite ( $\text{CaMg}_x\text{Ti}_x\text{Al}_{12-2x}\text{O}_{19}$ ) is one of the first condensates from the solar nebula and would retain information about the high temperature processes in the earliest stages of the solar system evolution. Despite their highly refractory nature, some hibonite-bearing inclusions have little or no <sup>26</sup>Mg excess (the decay product of <sup>26</sup>Al), but do show wide variation of isotopic anomalies (e.g., Ca and Ti) [1, 2].

In the present study, we conducted ion microprobe analyses of Mg isotopes for 14 hibonite-bearing inclusions separated from the Murchison CM2 chondrite. Preliminary data were presented in the last meeting [3]. Among them, we found two unique inclusions, which exhibit highly mass-dependent Mg isotopic fractionation of up to ~50‰/amu (Fig. 1). If the process is governed by Rayleigh fractionation, the two inclusions must have experienced a severe evaporation event, in which more than 95% of Mg was lost from the molten precursors. Lack of excess <sup>26</sup>Mg and large mass fractionation of Mg isotopes suggest their possible relations to so-called FUN inclusions [4].

To further understand this fractionation process (e.g., temperature and heating duration), we measured elemental compositions of ultra refractory metal grains found in these inclusions and simulated the time variation of the metal composition during evaporation at various temperatures (1500-2500K) to see if we can reproduce the observed compositions.

### Samples:

Two inclusions (MC037 and MC040) contain abundant hibonite and a few spinel grains (10-20µm). They are surrounded by Fe-rich silicates, in which numerous irregularly-shaped micronmeter-sized perovskite grains are uniformly distributed. Perovskite probably is the exsolution product from the rapidly cooling melt. Backscattered electron images of the two inclusions are shown in Fig. 2.

We found 5 ultra refractory metal grains in these inclusions. The sizes of the observed grains ranged 1-3µm.

### Result 1 (SEM-EDS):

We investigated elemental compositions of 5 ultra refractory metal grains using SEM-EDS. The results show Fe:15-60%, Ni:0.1-17%, Pt:4-23%, Rh:1-5%, Mo:1-31% and Ru:7-37%. Note that some of the data have large uncertainties due to severe

overlapping of the X-ray peaks. The observed compositions normalized to solar and Pt are shown in Fig. 3. The abundances of highly refractory metals, more refractory than Rh, are consistent with the solar abundances [5], but Fe and Ni show significant depletions by factors of  $10^{-4}$  to  $10^{-7}$ , suggesting Fe and Ni were preferentially evaporated due to its higher volatility.

### Result 2 (Simulation):

Evaporation simulations for a metallic grain, initially 100µm in diameter with a solar metal composition, were carried out at temperatures of 1500-2500K to constrain the evaporation temperature of MC037 and MC040. We assume a Rayleigh fractionation process, in which the metal grain is a molten droplet of homogeneous composition throughout the evaporation process. The evaporation flux of each metallic element is estimated using the Hertz-Knudsen equation [6,7]:

$$J_i = \frac{\gamma_i P_{i,\text{sat}}}{\sqrt{2\pi m_i RT}}$$

where  $J_i$  is the net flux of  $i$  (element) in moles per unit areas per unit time,  $P_{i,\text{sat}}$  is the saturation pressure of  $i$ ,  $\gamma_i$  is the evaporation coefficient of  $i$  (assuming unity in this calculation),  $m_i$  is the molecular weight of  $i$ ,  $R$  is the gas constant and  $T$  is the absolute temperature. Based on this equation, we calculated the composition and the size of the metal droplet at each time step until the depletion factor of Fe becomes less than  $\sim 10^{-6}$ . An example is shown in Fig. 4.

The results clearly demonstrate that highly refractory elements (Rh to Re) show essentially no depletion, while Fe and Ni become increasingly depleted with time, which is consistent with the observation. This is also true for any temperatures investigated (1500 to 2500 K). On the other hand, fractionation between Fe and Ni is rather large and not consistent with the observation: for example, the calculated depletion factor of Ni is only  $10^{-2}$  to  $10^{-3}$  when that of Fe is  $\sim 10^{-6}$ . This may be explained by addition of small amount(s) of Fe (and Ni) into the ultra-refractory metal grains at a later stage.

### Discussion:

It is not possible to constrain from the present simulations the temperature of the evaporation event. However, other pieces of information may be used to constrain the temperature. First, in order to produce large fractionation between highly refractory

elements (Rh to Re) and less refractory ones (Fe and Ni), the metal grain must be molten during the evaporation event (i.e., diffusion rate  $\gg$  evaporation rate). Hence, the temperature must be higher than the melting point of the metal grain ( $>$  the melting point of Fe, 1536 C).

Second, spinel in the two inclusions also shows highly fractionated Mg isotopes. This suggests that fractionation of Mg was established prior to crystallization of spinel. This gives an estimate of the temperature of the evaporation event to be  $\sim 1600\text{C}$  assuming a CAI-like initial composition for the precursor of the inclusions [8]. This is consistent with the former estimation.

### References:

[1] Ireland T.R., (1988) *Geochim. Cosmochim. Acta*, 52:2827-2839. [2] Liu M.-C et al. (2009) *Geochim. Cosmochim. Acta*, 73:5051-5079. [3] Sasaki et al. (2011) *NIPR Antarctic Meteorite XXXV*. [4] Ushikubo T. et al. (2007) *EPSL*, 254:115-126. [5] Lodders K. (2003) *ApJ*, 591:1220-1247. [6] Davis A.M and Richter F.M. (2005) *In Treatise on Geochemistry*, Pergamon, Oxford, 1-31. [7] Richter F. M et al. (2007) *Geochim. Cosmochim. Acta*, 71:5544-5564. [8] Stolper (1982) *Geochim. Cosmochim. Acta*, 46:2159-2180. [9] Davis et al. (2005) *Lunar Planet. Sci. XXXVI*, Abstr. #2334.

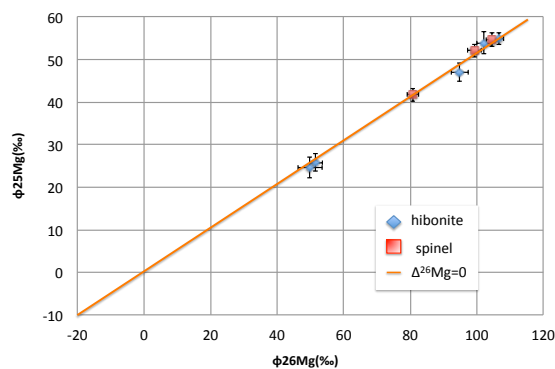


Fig.1. The  $\phi^{26}\text{Mg}-\phi^{25}\text{Mg}$  plot ( $\phi$  notation is similar to the conventional  $\delta$  notation [9]) for MC037 and MC040. Hibernite and spinel in these inclusions show extremely large mass fractionation of up to  $\sim 50\text{‰/amu}$ .

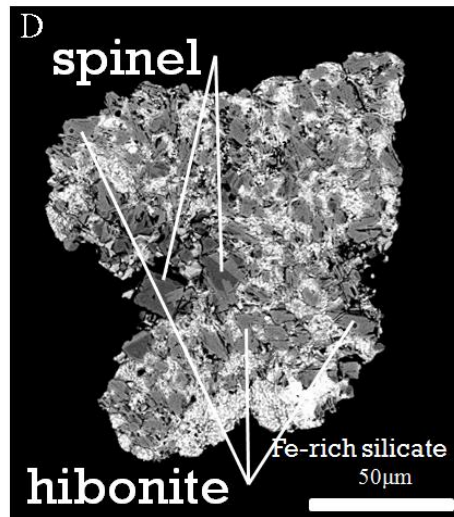
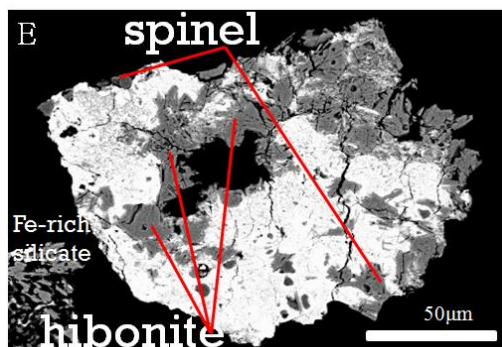


Fig. 2. Backscattered electron images of MC040 (D) and MC037 (E).

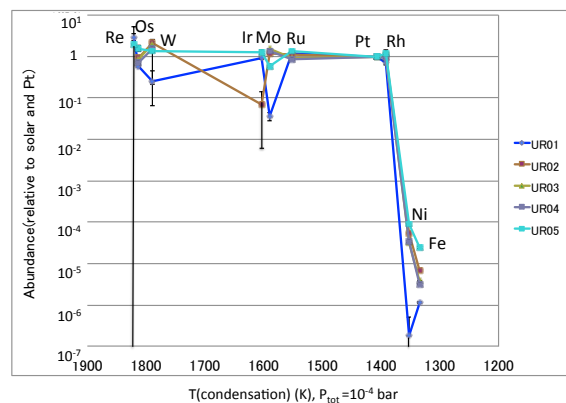


Fig.3. Compositions of ultra refractory metal grains relative to the solar abundance. These grains show a progressive depletion of Fe and Ni.

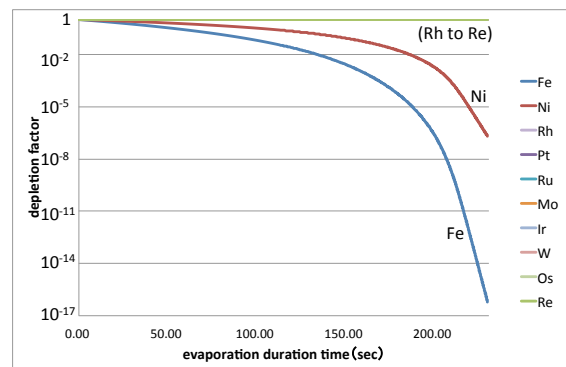


Fig.4. An example of evaporation simulations ( $T=1800\text{K}$ ). Depletion factors for various metallic elements are plotted against heating time. Relatively volatile Fe and Ni become significantly depleted, but more refractory elements (Rh up to Re) show almost no depletions.