

**HIGH PRECISION MAGNESIUM ISOTOPIC MEASUREMENT OF CAI MINERALS WITH LOW AL/MG RATIO FROM ALLENDE UTILIZING A NANOSIMS 50L ION MICROPROBE.** Motoo Ito and Scott Messenger. Robert M. Walker Laboratory for Space Science, ARES, NASA JSC, 2101 NASA Parkway, Houston TX 77058, USA. (motoo.ito-1@nasa.gov, scott.r.messenger@nasa.gov).

**Introduction:** The  $^{26}\text{Al}$ - $^{26}\text{Mg}$  decay system ( $t_{1/2}(^{26}\text{Al}) = 0.72 \text{ Ma}$ ) has been of great interest for determining the fine scale (<1 Ma) chronology of early solar system events [1]. The  $^{26}\text{Al}$ - $^{26}\text{Mg}$  system has been used to establish the relative ages of the CAIs and chondrules [e.g., 2,3]. This chronometer is also useful for resolving the time elapsed between multiple metamorphic/heating processes in CAI constituent minerals with a time resolution of 0.02 to 0.4Ma [e.g., 4-7]. The higher resolution is necessary to unravel the complex formation histories of CAIs.

Most measurements of initial  $^{26}\text{Al}/^{27}\text{Al}$  ratios in CAIs have been obtained from minerals with high Al/Mg ratios, i.e., plagioclase, because of experimental limitations [reviewed in 2]. Recent advances in instrumentation, multi-collector (MC) ICPMS [e.g., 4-6] and MC-ion microprobes [e.g., 8-11], have enabled higher precision Mg isotopic measurements that yield chronological data for low Al/Mg minerals such as melilite, spinel, and Al-Ti-pyroxene (fassaite). Some of these studies have suggested that the initial solar system  $^{26}\text{Al}/^{27}\text{Al}$  ratio may have been higher  $(6-7) \times 10^{-5}$  than the “canonical” value of  $5 \times 10^{-5}$  [4,5]. However, it is unclear whether model isochrons obtained from bulk samples and mineral separates (ICPMS) can be directly compared with internal isochrons determined by measurements of individual mineral phases in a single CAI (ion probe).

Parent body thermal alteration introduces additional complications in the interpretation of Al-Mg systematics because of the potential for redistributing Mg by diffusion during thermal metamorphism [12,13]. Anorthite is especially susceptible to thermal resetting owing to its high Mg diffusivity [12]. This process may also affect other minerals, such as melilite and spinel [14]. The extent of Mg redistribution in CAI minerals may vary considerably with the grain size, geometry and composition of its mineral assemblages and the conditions of thermal metamorphism [14].

Here we report results from a study of the high precision Mg isotopic measurement in spinel, fassaite and melilite having low Al/Mg ratio (<15) in Type A CAIs, 7R19-1d and 7R19-1e, utilizing the JSC NanoSIMS 50L ion microprobe. The purposes of this study are (1) to establish procedures for high precision Mg measurements with the NanoSIMS, and (2) to resolve the chronology of complex formation events of CAIs in the early solar system using  $^{26}\text{Al}$ - $^{26}\text{Mg}$  internal isochron.

**Experimental:** 7R19-1 is a fassaite-rich, compact Type-A CAI. It consists mainly of coarse-grained melilites ( $\sim \text{Åk}_{20}$ ), large blocky fassaite and small spinel grains. Hibonites, perovskites, and anorthites occur in the CAI as minor minerals. The detailed petrographic texture, chemical compositions, and isotopic distributions of O, Mg and K in 7R19-1 were published in [7,15,16]. The epoxy-mounted samples of 7R19-1d and 7R19-1e were studied by optical microscopy, and SEM, BSE imaging and X-ray elemental mapping by JEOL JSM-5910LV at JSC both before and after ion probe measurements. The samples were coated with a thin carbon film prior to SEM and ion probe analyses.

The high precision Mg isotope measurement of CAI minerals were performed with the JSC Cameca NanoSIMS 50L, using four Faraday cups in multidection. We evaluate the measurement conditions, the instrumental mass fractionation, relative sensitivity factor, and the precision and accuracy for Mg measurement through analyses of terrestrial augite, spinel, synthetic åkermanite,  $\text{Åk}_{70}\text{Ge}_{30}$  and  $\text{Åk}_{50}\text{Ge}_{50}$  standards. Measurements of samples and standards were performed by rastering a 5-35 nA, 8keV negative oxygen primary ion beam over  $\sim 5 \times 5 \mu\text{m}$  regions (64x64 pixels). Due to the strong primary ion beam current, crater sizes increased to about 15-25  $\mu\text{m}$ . Positive secondary ions of  $^{24}\text{Mg}$ ,  $^{25}\text{Mg}$ ,  $^{26}\text{Mg}$ , and  $^{27}\text{Al}$  were measured by four Faraday cup (FC) detectors in multidetection at a high mass resolution of  $M/\Delta M = \sim 4000$  that is sufficient to resolve all molecular ion interferences (e.g.,  $^{24}\text{MgH}^+$  on  $^{25}\text{Mg}^+$ ). We used beam blanking to minimize crater edge effects. In this mode, secondary ions from the edge (accounting for  $\sim 10\%$  of the scanned area) are excluded from the dataset. Before and after each measurement, we monitored the baseline and noise for each FC detector. Each measurement consisted of 50 cycles of with 10-18 sec/cycle (3000-5000  $\mu\text{s}/\text{pixel}$ ) counting time depending on Al/Mg ratio, lasting 12-20 minutes. We monitored the  $^{27}\text{Al}/^{24}\text{Mg}$  ratio during the measurement to check instability of secondary ion intensities due to phases other than the target minerals. Each run was started after stabilization of the secondary ion beam following pre-sputtering procedure of  $\sim 3-4 \text{ min}$ . During the isotopic analysis, the mass peaks were centered automatically after every 10 cycles.

Terrestrial spinel, augite, and synthetic melilite ( $\text{Åk}_{100}$ ,  $\text{Åk}_{70}\text{Ge}_{30}$  crystals, and  $\text{Åk}_{50}\text{Ge}_{50}$  glass) standards were used to correct instrumental mass fractiona-

tion for Mg isotopes and relative sensitivity factor for  $^{27}\text{Al}/^{24}\text{Mg}$  ratio for mineral phases. Excess  $^{26}\text{Mg}$  ( $\Delta^{26}\text{Mg}^*$ ) was calculated using an exponential mass fractionation law with a fractionation factor of 0.514 derived from evaporated CAI-like materials [17]. Typical precision and accuracy was  $\sim 0.3\text{-}0.8\%$  ( $2\sigma$ ) for  $\Delta^{26}\text{Mg}^*$  in the spinel, pyroxene and melilite.

**Results and Discussions:** Figure 1 is a BSE image of a melilite-fassaite area in 7R19-1d. We carefully checked ion probe spots on the sample surface after the measurements. Some measured points were rejected because of relatively large primary beam overlap with another phase or crack.

Measured points from spinel, melilite, and fassaite show excess  $^{26}\text{Mg}^*$  with  $^{27}\text{Al}/^{24}\text{Mg}$  ratio of  $< 20$ , which might be the phases least susceptible to isotopic disturbance by thermal alteration (Fig. 2). The best fit to the data for 7R19-1d yields an initial  $^{26}\text{Al}/^{27}\text{Al}$  value of  $4.67 (\pm 0.22, 2\sigma) \times 10^{-5}$  and  $\delta^{26}\text{Mg}$  intercept of  $0.18 (\pm 0.05, 2\sigma) \%$  (Fig. 2). This initial value is in good agreement with an  $^{26}\text{Al}/^{27}\text{Al}$  canonical value  $\sim 5 \times 10^{-5}$  [2]. However, this is much smaller than that of previous measurement ( $6.6 \pm 1.3 \times 10^{-5}$ ,  $2\sigma$ ) for this CAI [7]. Data previously obtained from low Al/Mg phases are scattered on the Al-Mg diagram [Fig. 4 in 7], indicating that the higher initial  $^{26}\text{Al}/^{27}\text{Al}$  could be due to artifacts caused by the choice of isotopic mass fractionation correction law and limited precision from measurements for low Al/Mg phase using electron multipliers. Proper choice of isotopic mass fractionation correction is essential because it significantly affects the initial  $^{26}\text{Al}/^{27}\text{Al}$  ratios for CAIs with  $^{26}\text{Mg}$  isotope enrichments and low Al/Mg ratios [17].

The single isochron we obtained for this CAI gives the time interval ( $\Delta t$ ) from the initial canonical value ( $5 \times 10^{-5}$ ) to the lower limit  $^{26}\text{Al}/^{27}\text{Al}$  value ( $4.43 \times 10^{-5}$ ), is 0.12 Ma, assuming homogeneously  $^{26}\text{Al}$  distribution in the early solar nebula. This is consistent with  $\Delta t$  from previous studies of Allende CAIs [e.g., 5,11].

Spinel is more susceptible to disturbance of Al/Mg systematics in CAIs than melilite due to its higher Mg diffusivity and smaller grain size [14]. However spinels in this and other CAIs do show excess  $^{26}\text{Mg}$  (Fig. 2; 10,11). We calculated an initial cooling rate (CR) for the CAI at  $1450^\circ\text{C}$  using the grain size (20-100  $\mu\text{m}$ ) of spinel and Mg diffusion kinetics in spinel [18]. An initial CR of at least 0.5 to  $11^\circ\text{C}/\text{h}$  at  $1450^\circ\text{C}$  is required to preserve the original  $^{26}\text{Mg}^*$  in spinel through the formation process. This CR is consistent with that of melilite [14]. However, parent body metamorphism at  $650^\circ\text{C}$  may disturb the Al-Mg systematics in spinel without affecting melilite [Fig 2a in 14]. Further high precision Mg isotopic measurements at  $\mu\text{m}$  spatial scales will establish the extent of any disturbance

among low Al/Mg phases including spinel. Such studies are required to fully resolve the formation and alteration histories of CAIs.

**References:** [1] Lee T. et al. (1976) *GRL* 3:41-44. [2] MacPherson G.J. et al. 1995. *Meteoritics* 30:365-377. [3] Kita N. et al. (2000) *GCA* 64:3913-3922. [4] Bizzarro M. et al. (2004) *Nature* 431:275-278. [5] Young E.D. et al. (2005) *Science* 308:223-227. [6] Thrane K. et al. (2006) *ApJ* 646:L159-L162. [7] Ito M. et al. (2006) *MaPS* 41:1871-1881. [8] McKeegan K.D. et al. (2004) *MaPS* 37:A66. [9] Kita N. et al. (2008) *GCA* 72:A477. [10] Itoh S. and Yurimoto H. (2007) *Workshop on Chronology of Meteorites*, 4057. [11] Makide K. et al. (2009) *GCA in press*. [12] LaTourrette T. and Wasserburg G.J. (1998) *EPSL* 158:91-108. [13] Ito M. and Ganguly J. (2004) *MaPS* 39:1911-1919. [14] Ito M. and Ganguly J. (2009) *LPSC*, this volume. [15] Yurimoto H. et al. (1998) *Science* 282:1874-1877. [16] Ito M. et al. (2004) *GCA* 68:2905-2923. [17] Davis A. et al. (2005) *LPSC XXXVI*, 2334. [18] Liermann H-P. and Ganguly J. (2002) *GCA* 66:2903-2913.

