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NOTE

An effect of variations in relative sensitivity factors on Al-Mg systematics of Ca-Al-rich inclusions in meteorites with secondary ion mass spectrometry

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Instrumental mass fractionation of Mg-isotopes and the relative sensitivity factor (RSF) for ^{27}Al/^{24}Mg ratios for *in situ* analysis by secondary ion mass spectrometry were investigated for minerals in Ca-Al-rich inclusions (CAIs) of meteorites, to verify systematic errors in Al-Mg chronological systematics of CAIs. We synthesized seventeen glasses with different chemical compositions that imitate those for CAI minerals and measured their Al-Mg isotopic compositions. In particular, the variation range of RSFs for six melilite glasses almost covering chemical compositions of CAI melilite is 2.0 ± 0.3%, indicating that systematic error for ^{27}Al/^{24}Mg for melilite is less than 2.0 ± 0.3% and likely corresponds to that of an ^{26}Al-^{26}Mg relative age of ~0.01 Myr for melilite-rich CAIs. Our data strongly support the robustness of variations in initial ^{26}Al/^{27}Al ratios among CAIs, corresponding to a formation age spread of ~0.4 Myr at the very beginning of the Solar System formation.

Keywords: Ca-Al-rich inclusions, Al-Mg systematics, secondary ion mass spectrometry, instrumental mass fractionation, relative sensitivity factor

INTRODUCTION

Ca-Al-rich inclusions (CAIs) in meteorites are the oldest objects formed in the Solar System and contained live-^{26}Al, a short-lived radionuclide with a half-life of ~0.7 Myr, at the time of their formation (e.g., Krot, 2019 and references therein). High-precision Al-Mg mineral isochron studies using secondary ion mass spectrometry (SIMS) revealed detailed distributions of initial ^{26}Al/^{27}Al values, (^{26}Al/^{27}Al)$_0$, for individual CAIs in the CV chondrites (e.g., Krot, 2019; Kawasaki *et al.*, 2020 and references therein) ranging from ~5.2 to ~3.4 × 10^{-5}. Both condensate CAIs without signatures of later extensive melting and igneous CAIs which experienced melting of precursor solids and crystallization from the melt show significant variations in (^{26}Al/^{27}Al)$_0$, implying that thermal processes of condensation and melting for CAI formation occurred contemporaneously and continued for ~0.4 Myr at the very beginning of Solar System formation, under the assumption of homogeneous distributions of ^{26}Al in the forming region (Kawasaki *et al.*, 2020).

Among the data available, an example of the smallest analytical errors in (^{26}Al/^{27}Al)$_0$ for CAIs has been obtained from a fluffy Type A CAI from Vigarano, with (^{26}Al/^{27}Al)$_0$ = (4.703 ± 0.082) × 10^{-5} (Kawasaki *et al.*, 2019); the relative error is 1.7%. (^{26}Al/^{27}Al)$_0$ for CAIs is determined from the slope of the regression line for CAI mineral data on the Al-Mg evolution diagram (^{27}Al/^{24}Mg vs. radiogenic excess of ^{26}Mg, ^{26}Mg*) for each CAI. ^{26}Mg* values for CAI minerals are accurately determined with SIMS by correcting both natural mass-dependent fractionation and instrumental mass fractionation (IMF) of SIMS for Mg-isotopes (Itoh *et al.*, 2008; Kita *et al.*, 2012; Kawasaki *et al.*, 2017). On the other hand, relative

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*Corresponding author (e-mail: kawasaki@ep.sci.hokudai.ac.jp) sensitivity factors (RSFs) for ^{27}Al/^{24}Mg in SIMS measurements for CAI minerals are reported to exhibit variations depending on their chemical compositions (e.g., Kita *et al.*, 2012; Luu *et al.*, 2013). Since the smallest relative errors in (^{26}Al/^{27}Al)$_0$ for CAIs are less than 2%, the accuracy of the measured ^{27}Al/^{24}Mg ratios (i.e., estimations of the RSFs for ^{27}Al/^{24}Mg) for CAI minerals should also be better than 2%.

In addition, CAI minerals exhibit significant variations of mass-dependent fractionation of Mg-isotopes, which are critical to constrain their formation processes (e.g., Kawasaki *et al.*, 2017). In SIMS measurements, permil orders of matrix effects on the IMF of Mg-isotopes among CAI minerals have been reported (e.g., Itoh *et al.*, 2008; Kita *et al.*, 2012). In this study, we synthesized glasses with chemical compositions matched to major minerals of CAIs and measured their chemical and Al-Mg isotopic compositions with electron probe microanalyzer (EPMA), multi-collector inductively coupled plasma-mass spectrometry (MC-ICP-MS), and SIMS, in order to verify the Al-Mg data of CAIs measured with SIMS in similar analytical conditions in the same laboratory.

EXPERIMENTAL TECHNIQUES

We synthesized seventeen glasses with different chemical compositions covering almost the entire ranges of those for CAI minerals of anorthite, melilite, and Al-Ti diopside called "fassaite". Synthesized, two anorthite glasses, six melilite glasses, and nine fassaite glasses and Miyakejima anorthite were embedded in a single polished epoxy mount. Their chemical compositions were studied with EPMA (JEOL JXA-8530F). Mg-isotopic compositions of the glasses and reagent MgO powders were measured using MC-ICP-MS (Thermo Fisher Scientific Neptune) at Kochi Institute for Core Sample Research, JAMSTEC. Mg-isotopic compositions and ^{27}Al/^{24}Mg ratios of the glasses and Miyakejima anorthite were measured with the SIMS instrument (Cameca ims-1280HR) at Hokkaido University. The analytical conditions essentially followed those in Kawasaki *et al.* (2017, 2018, 2019, 2020) to verify their data. We used the peak-jumping mode and multicollection mode based on the secondary ion intensities for Mg-isotopes from the minerals. Details of the experimental techniques are described in Supplementary materials.

RESULTS AND DISCUSSION

Chemical and Mg-isotopic compositions of standard materials

Chemical compositions of the synthesized glasses and Miyakejima anorthite are listed in Supplementary Table S1. The glasses exhibit almost stoichiometric compositions corresponding to those of melilite, fassaite, and anorthite. The Mg-isotope ratios in DSM-3 scale (Galy *et al.*, 2003) for reagent MgO powders and the glasses are listed in Supplementary Tables S2 and S3. Six melilite glasses exhibit constant $\delta^{25}\mathrm{Mg}_{\mathrm{DSM3}}$ values of -1.76 ± 0.06‰ (2SD) with an external error of 0.13‰. The variations are consistent with the internal errors (2SE) of each analysis. Nine fassaite glasses and two anorthite glasses also exhibit constant $\delta^{25}\mathrm{Mg}_{\mathrm{DSM3}}$ values of -0.07 ± 0.10‰ (2SD). As confirmed by Mg-isotope analyses of two different MgO reagents, Kanto Kagaku MgO 4N ($\delta^{25}\mathrm{Mg}_{\mathrm{DSM3}} = -1.69 \pm 0.13$‰) used for the melilite glasses and Sigma Aldrich MgO 529699 ($\delta^{25}\mathrm{Mg}_{\mathrm{DSM3}} = 0.05 \pm 0.13$‰) used for the fassaite and anorthite glasses, the difference in Mg-isotope ratios between melilite glasses and fassaite or anorthite glasses is derived from the difference in reagents. These data show that no significant mass-dependent fractionations occurred during the glass synthesis.

The instrumental mass fractionation of Mg-isotope measurements for CAI minerals with SIMS

Data for Al-Mg isotope measurements with SIMS for the glasses and Miyakejima anorthite are summarized in Table S4. Relationships between the IMF of Mg-isotopes and chemical compositions are shown in Fig. 1. The IMF of Mg-isotopes is expressed as $\delta^{25}\mathrm{Mg}_{\mathrm{IMF}} = [(1 + \delta^{25}\mathrm{Mg}_{\mathrm{SIMS}}/1000)/(1 + \delta^{25}\mathrm{Mg}_{\mathrm{DSM3}}/1000) - 1] \times 1000$, where $\delta^{25}\mathrm{Mg}_{\mathrm{SIMS}} = [(^{25}\mathrm{Mg}^+/^{24}\mathrm{Mg}^+)_{\mathrm{SIMS}}/(^{25}\mathrm{Mg}/^{24}\mathrm{Mg})_{\mathrm{ref}} - 1] \times 1000$. $^{25}\mathrm{Mg}^+/^{24}\mathrm{Mg}^+_{\mathrm{SIMS}}$ indicates the ion intensity ratio for the SIMS measurement. The reference, absolute Mg-isotope ratio of ^{25}Mg/^{24}Mg = 0.12663 (Catanzaro *et al.*, 1966) is used for the calculation, although the δ^{25}Mg value for actual samples after the IMF correction is independent of the reference ratio. $\delta^{25}\mathrm{Mg}_{\mathrm{DSM3}}$ of Miyakejima anorthite is assumed to be zero.

Melilite glasses show the IMF variations slightly correlated with ^{27}Al/^{24}Mg ratios; the $\delta^{25}\mathrm{Mg}_{\mathrm{IMF}}$ values decrease with increasing ^{27}Al/^{24}Mg ratios (Figs. 1a and 1b). The $\delta^{25}\mathrm{Mg}_{\mathrm{IMF}}$ values for the Åk20 glass obtained from the two analytical protocols, the multicollection mode (Fig. 1a) and the peak-jumping mode (Fig. 1b), are distinct from each other, which could be due to the difference in analytical conditions (e.g., primary ion beam current). The IMF variations for melilite glasses are 1.4 ± 0.7‰, based on a difference between their maximum and minimum $\delta^{25}\mathrm{Mg}_{\mathrm{IMF}}$ values. This indicates that the systematic error for δ^{25}Mg for CAI melilite is less than 1.4 ± 0.7‰, even if a single melilite glass standard is used for the IMF correction of the CAI melilite. These results show that variations in mass-dependent Mg-isotope fractionation, up to 7‰ in δ^{25}Mg, found in individual melilite crystals with åkermanite contents of ~2–27 (^{27}Al/^{24}Mg ~ 10–150) in a fluffy Type A CAI from Vigarano (Kawasaki *et al.*, 2017) cannot be attributed to the IMF

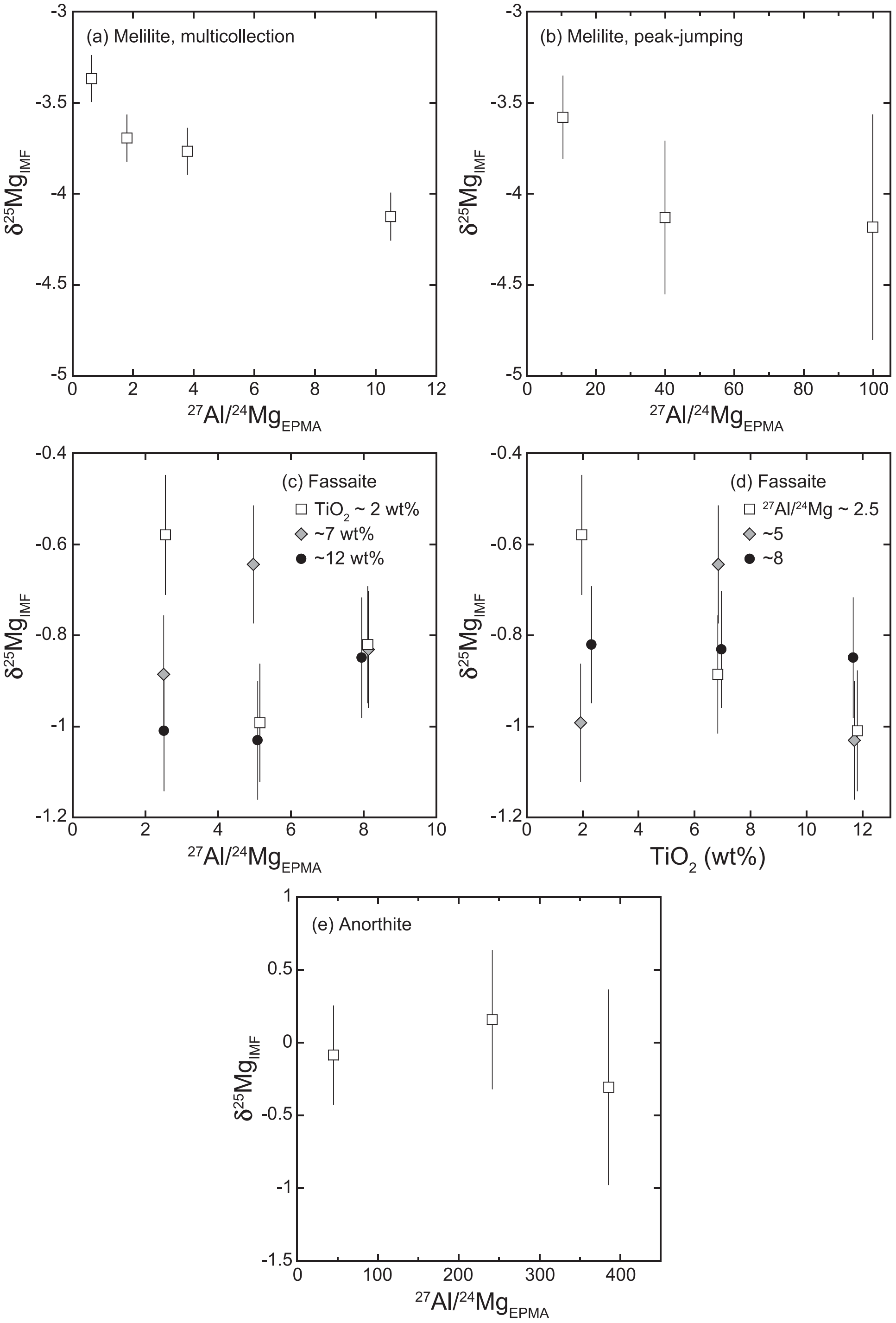

Fig. 1. Relationships between the instrumental mass fractionation of Mg-isotopes, indicated as $\delta^{25}Mg_{IMF}$, of SIMS and chemical compositions of synthetic glasses and Miyakejima anorthite.

variations.

The IMF variations for nine fassaite glasses complexly correlate with both ^{27}Al/^{24}Mg ratios and TiO_2 contents (Figs. 1c and 1d). Since the chemical composition range of the fassaite glasses almost covers chemical compositions of CAI fassaite, the data indicate that a systematic error for δ^{25}Mg for CAI fassaite is less than 0.45 ± 0.18‰. The $\delta^{25}Mg_{IMF}$ values for two anorthite glasses and Miyakejima anorthite are constant within analytical errors of ~0.7‰, irrespective of ^{27}Al/^{24}Mg (Fig. 1e).

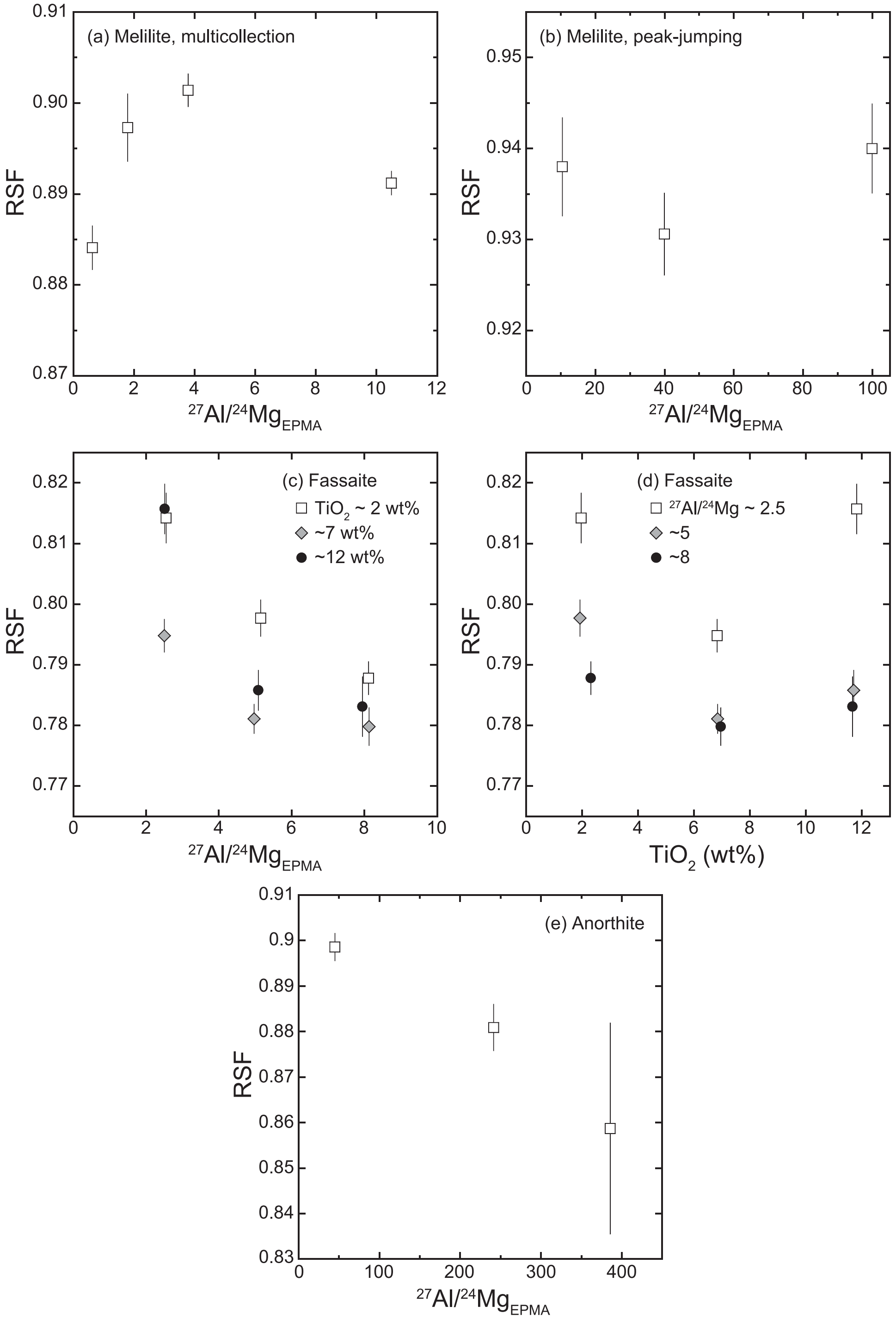

Fig. 2. Relationships between the relative sensitivity factors (RSFs) for ^{27}Al/^{24}Mg by SIMS and chemical compositions of synthetic glasses and Miyakejima anorthite.

Relative sensitivity factors for ^{27}Al/^{24}Mg for CAI minerals

Relationships between the RSFs for ^{27}Al/^{24}Mg and chemical compositions are shown in Fig. 2. The RSF is defined as $(^{27}\mathrm{Al}^{+}/^{24}\mathrm{Mg}^{+})_{\mathrm{SIMS}}/(^{27}\mathrm{Al}/^{24}\mathrm{Mg})_{\mathrm{EPMA}}$. All the SIMS and EPMA analyses were conducted on the same surface of the single polished mount.

Melilite glasses show variations in RSFs without simple correlations with ^{27}Al/^{24}Mg ratios (Figs. 2a and 2b). The RSFs for the Åk20 glass obtained from the two analytical protocols are distinct from each other, which could be due to the difference in analytical conditions. The RSF variations for melilite glasses are 2.0 ± 0.3%, based on a difference between their maximum and minimum RSFs. This indicates that the systematic error for ^{27}Al/^{24}Mg for melilite is less than 2.0 ± 0.3%, even if a single melilite glass standard is used for the RSF corrections of the CAI melilite.

The RSFs for nine fassaite glasses complexly correlate with both ^{27}Al/^{24}Mg ratios and TiO_2 contents (Figs. 2c and 2d). The range of variation for the RSFs for fassaite glasses is 4.6 ± 0.6%. The use of fassaite standard glasses with similar chemical compositions to CAI fassaite would be efficient for high-precision studies, although analytical errors of ^{26}Mg* are more critical than those for ^{27}Al/^{24}Mg for CAI fassaite. The RSFs for two anorthite glasses and Miyakejima anorthite are also variable with a similar variation range of 4.6 ± 2.7%.

Kawasaki *et al.* (2019, 2020) discussed variations in (^{26}Al/^{27}Al)$_0$ among CAIs inferred from Al-Mg mineral isochrons mainly consisting of melilite and spinel. They used a Russian spinel, nearly pure $MgAl_2O_4$, and the melilite glasses for the standards. One of the smallest analytical errors in (^{26}Al/^{27}Al)$_0$ for CAIs studied is (^{26}Al/^{27}Al)$_0$ = (4.703 ± 0.082) × 10^{-5} for a fluffy Type A CAI from Vigarano (Kawasaki *et al.*, 2019). Its relative error of ±1.7% is about two times larger than the maximum systematic error of ±1.0% caused by the ^{27}Al/^{24}Mg variation of the CAI melilite. This systematic error corresponds to a relative age of ~0.01 Myr. The errors in (^{26}Al/^{27}Al)$_0$ for CAIs are dominated by statistical errors of isochrons. Therefore, the inferred range of variation in (^{26}Al/^{27}Al)$_0$ among CAIs, from (5.19 ± 0.17) to (3.35 ± 0.21) × 10^{-5} (Kawasaki *et al.*, 2020), cannot be attributed to the systematic error in the RSFs.

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SUPPLEMENTARY MATERIALS

URL (http://www.terrapub.co.jp/journals/GJ/archives/data/55/MS634.pdf)