CALIBRATING SIMS RELATIVE SENSITIVITY FACTOR FOR Al/Mg IN PRESOLAR SILICON CARBIDE.

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Introduction: As *bona fide* stardust, the inferred initial ^{26}Al/^{27}Al ratios of presolar grains provide us an invaluable tool to constrain the production of ^{26}Al in the various stellar sources that contributed materials to the Solar System. Among the various types of presolar phases that have been identified so far, silicon carbide (SiC) is one of the best candidates for investigating the Al-Mg isotope systematics, given its high Al (up to several wt.%) and low Mg contents, e.g., [1]. However, a precise determination of the initial ^{26}Al/^{27}Al ratios in presolar SiC grains is hampered by uncertainties in the SIMS Mg/Al relative sensitivity factor ($\Lambda_{\mathrm{Mg/Al}}$) that is commonly calibrated by measuring Burma spinel and NIST glass standards, e.g., [2]. These O-rich standards differ significantly from SiC in the sample matrix, which thus raises the question whether the adopted calibration procedure is appropriate. It is questionable because although the SIMS ionization efficiency for positive ions shows a strong correlation with the first ionization potential, variations are expected to depend on the sample matrix and the element itself. In particular, the presence of O enhances the positive ion yield for many elements. O_2 flooding can be used to boost yields in some instruments, but not the NanoSIMS.

The best standard for calibrating $\Lambda_{\mathrm{Mg/Al}}$ in presolar SiC grains is, in fact, presolar X SiC grains, which are inferred to have come from Type II core-collapse supernovae based on their unique isotopic signatures [3]. Hoppe et al. [4] recently showed that the intrinsic Mg signals of X grains are essentially pure ^{26}Mg from the decay of radiogenic isotope ^{26}Al ($t_{1/2}$ = 0.72 Ma). In addition, Liu et al. [5] found that the Mg (i.e., ^{26}Mg) and Al contents of X grains are sufficiently high so that they can be determined by state-of-the-art SEM-EDX analysis. Therefore, coordinated SEM and NanoSIMS analyses of presolar X grains provide us a unique opportunity to calibrate $\Lambda_{\mathrm{Mg/Al}}$ and thus determine the inferred initial ^{26}Al/^{27}Al ratios in presolar SiC grains more accurately. Also, compared to synthetic SiC standards, X grains have crystal structures and trace element abundances that are generally similar to the other groups of presolar SiC grains, which, in turn, minimizes uncertainties in the determined $\Lambda_{\mathrm{Mg/Al}}$ for presolar SiC.

Experimental Methods: The SiC grains in this study were extracted from Murchison (CM2) using the CsF dissolution technique [6]. SiC grains on the mount were first identified by automatic SEM-EDX particle analyses by adopting the procedure described in [5]. A total of 450 SiC grains were measured for their C, N, and Si isotopes, based on which 22 X grains were identified. The overabundance of X grains in our sample results from a sample selection bias because we prioritized the analyses of Mg-rich SiC grains – X grain candidates (see [5] for details). The X grains were further analyzed for their V-Ti and Al-Mg isotopes with the Carnegie NanoSIMS 50L ion microprobe following the procedures reported in [7]. Burma spinel and NIST NBS 610 glass were both measured as standards during the Al-Mg isotope analysis session. An O^- beam of 1–3 pA produced by the Hyperion radio-frequency plasma source was used for the analyses. All the isotope data were collected in imaging mode at a spatial resolution of ~100–200 nm. Vanadium-Ti isotope data were obtained for 10 of the 22 X grains and are reported separately in [8]. Aluminum-Mg isotope data were obtained for the 22 X grains, all of which have available high resolution SEM images and EDX spectral data that had been taken prior to the NanoSIMS analyses.

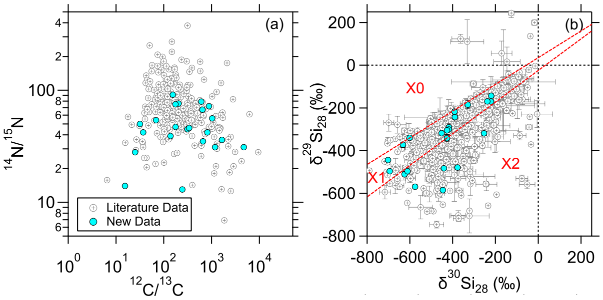

Figure 1. *Plots comparing our X grains with those from the literature in C, N, and Si isotopes. The subtype classification scheme in panel (b) was introduced in [9].*

Results and Discussion: Figure 1 shows that (*i*) our new C and Si isotope data are in good agreement with the literature data, and (*ii*) our new X grains have a more restricted range of ^{14}N/^{15}N ratios as compared to those from the literature, pointing to reduced terrestrial/asteroidal N contamination sampled in this study. According to the Si isotope ratios, seven of our X grains belong to the subtype X2. We, however, will not adopt the subtype classification for the following discussion since we did not find any systematic differences between X1 and X2 grains in their C, N, and inferred initial ^{26}Al/^{27}Al ratios.

Our NanoSIMS ion images show that the intrinsic Mg signals are monoisotopic, i.e., ^{26}Mg, consistent with the finding of [4]. The $\Lambda_{\text{Mg/Al}}$ values determined from Burma spinel and NBS 610 glass are 1.28±0.04 (1σ errors) and 1.28±0.18, respectively, which are in excellent agreement with each other. The larger uncertainties in the latter are mainly caused by uncertainties in its Mg and Al contents reported in the literature [10]. Figure 2 summarizes the inferred initial ^{26}Al/^{27}Al ratios of our X grains by adopting the $\Lambda_{\text{Mg/Al}}$ value of Burma spinel. The initial ^{26}Al/^{27}Al ratios were calculated using the equation $^{26}\text{Al}/^{27}\text{Al} = (^{26}\text{Mg}_{\text{meas}} - {}^{24}\text{Mg}_{\text{meas}} \times \text{std}) / (^{27}\text{Al}_{\text{meas}} \times \Lambda_{\text{Mg/Al}})$, where "std" is the terrestrial ^{26}Mg/^{24}Mg ratio.

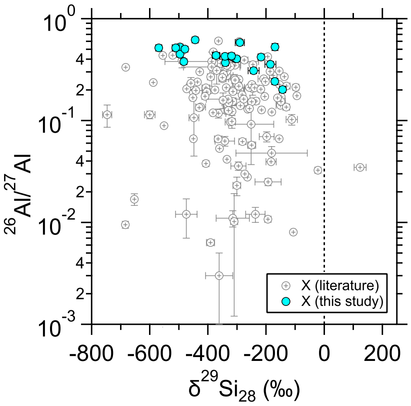

Figure 2*. Plot of inferred initial ^{26}Al/^{27}Al versus δ^{29}Si$_{28}$ comparing X grains from this study with those from the literature. The initial ^{26}Al/^{27}Al ratios were all calculated based on $\Lambda_{\text{Mg/Al}}$ values determined from Burma spinel.*

Figure 3 compares the Mg/Si and Al/Si ratios determined by SEM-EDX and NanoSIMS analyses. We excluded several X grains that had adjacent Mg-rich and/or Al-rich grains in their NanoSIMS ion images, which must have been sampled during the EDX analyses given their worse spatial resolution (~1 μm). The data comparisons in Fig. 3 suggest that the Al/Si and Mg/Si ratios in SiC grains determined based on NanoSIMS measurements of Burma spinel are overestimated, i.e., the $\Lambda_{\text{Mg/Si}}$ and $\Lambda_{\text{Al/Si}}$ values are underestimated by factors of 1.27 and 1.96, respectively. The linear trends in Fig. 3 are in line with the previous observation of [1] for mainstream SiC grains, but the X grain NanoSIMS and EDX data from this study are better correlated because of (*i*) the improved spatial resolution of the NanoSIMS Mg-Al isotope analyses, and (*ii*) the higher ^{26}Mg contents of X grains mainly because of their higher initial ^{26}Al/^{27}Al ratios. In turn, it means that the $\Lambda_{\text{Mg/Al}}$ value is overestimated by a factor of 1.55 (i.e., true $\Lambda_{\text{Mg/Al}}$) so that the inferred initial ^{26}Al/^{27}Al ratios reported in Fig. 2 should be increased by a factor of 1.55. The fact that a number of X grains lie to the right side of the linear fit in Fig. 3b, could point to Al contamination sampled from the grains that lie along the fit line by EDX analyses, which would mean that the true linear fit has a shallower slope and that the true $\Lambda_{\text{Mg/Al}}$ value is even lower than 0.82 (i.e., even higher initial ^{26}Al/^{27}Al).

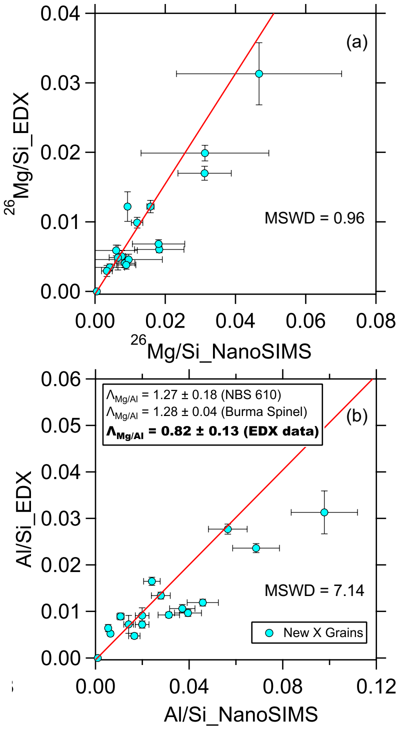

Figure 3*. (a) Plot of ^{26}Mg/Si determined by EDX versus those by NanoSIMS for X grains from this study. (b) Same as panel (a) but for Al/Si ratios.*

Conclusions: Our data confirms that the $\Lambda_{\text{Mg/Al}}$ value for SIMS analyses depends on the sample matrix and that the Burma spinel standard adopted in previous NanoSIMS Mg-Al isotope analyses of presolar SiC grains leads to an underestimate of the inferred initial ^{26}Al/^{27}Al ratios by at least a factor of 1.55. The result from this study enables a more accurate determination of the inferred initial ^{26}Al/^{27}Al ratio for presolar SiC grains, which can thus be used to provide more stringent constraints on the productions of ^{26}Al in their parent stars.

References: [1] Liu N. (2020) *ApJL* **920**, L26. [2] Groopman E. et al. (2015) *ApJ* **809***,* 31. [3] Nittler L. R. et al. (1996) *ApJ* **462**, L31. [4] Hoppe P. et al. (2022) *85th metsoc*, 6036. [5] Liu N. et al. (2017) *MAPS* **52**, 2550–2569. [6] Nittler L. R. & Alexander C. M. O'D. (2003) *GCA* **67**, 4961–4980. [7] Liu N. et al. (2018) *Sci. Adv.* **4**, aao1054. [8] Liu N. et al. (2023) *54th LPSC*, this volume. [9] Lin Y. et al. (2010) *ApJ* **709**, 1157–1173. [10] Pearce N. J.G. et al. (1997) *Geostand. Geoanal. Res.* **21**, 115–144.

Acknowledgement: This work was funded by NASA Emerging Worlds program through grant 80NSSC20K0387 to N.L.