Mg isotopic heterogeneity, Al-Mg isochrons, and canonical $^{26}\text{Al}/^{27}\text{Al}$ in the early solar system

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Abstract—There is variability in the Mg isotopic composition that is a reflection of the widespread heterogeneity in the isotopic composition of the elements in the solar system at approximately 100 ppm. Measurements on a single calcium-aluminum-rich inclusion (CAI) gave a good correlation of $^{26}\text{Mg}/^{24}\text{Mg}$ with $^{27}\text{Al}/^{24}\text{Mg}$, yielding an isochron corresponding to an initial $(^{26}\text{Al}/^{27}\text{Al})_0 = (5.27 \pm 0.18) \times 10^{-5}$ and an initial $(^{26}\text{Mg}/^{24}\text{Mg})_0 = -0.127 \pm 0.032\%$ relative to the standard. This isochron is parallel to that obtained by Jacobsen et al. (2008), but is distinctively offset. This demonstrates that there are different initial Mg isotopic compositions in different samples with the same $^{26}\text{Al}/^{27}\text{Al}$. No inference about uniformity/heterogeneity of $^{26}\text{Al}/^{27}\text{Al}$ on a macro scale can be based on the initial $(^{26}\text{Mg}/^{24}\text{Mg})_0$ values. Different values of $^{26}\text{Al}/^{27}\text{Al}$ for samples representing the same point in time would prove heterogeneity of $^{26}\text{Al}/^{27}\text{Al}$. The important issue is whether the bulk solar inventory of $^{26}\text{Al}/^{27}\text{Al}$ was approximately 5×10^{-5} at some point in the early solar system. We discuss ultra refractory phases of solar type oxygen isotope composition with $^{26}\text{Al}/^{27}\text{Al}$ from approximately 5×10^{-5} to below 0.2×10^{-5} . We argue that the real issues are: intrinsic heterogeneity in the parent cloud; mechanism and timing for the later production of ^{16}O -poor material; and the relationship to earlier formed ^{16}O -rich material in the disk. ^{26}Al -free refractories can be produced at a later time by late infall, if there is an adequate heat source, or from original heterogeneities in the placental molecular cloud from which the solar system formed.

INTRODUCTION

The purpose of this report is to demonstrate that there are intrinsic variations in the isotopic composition of Mg that make up the solar system as a result of incomplete isotopic homogenization. It is well known that almost every element that has been investigated in meteorites exhibits isotopic variations that are not only due to mass-dependent fractionation effects, but must also be due to some nuclear effects representing intrinsic heterogeneity within the solar nebula at rather low levels (cf. Wasserburg et al. 1979, 1980). This heterogeneity is a reflection of different stellar nucleosynthetic sites contributing to the source material. A host of more recent publications clearly demonstrate this isotopic heterogeneity at a typical level of approximately 100 ppm for almost every element investigated (e.g., Dauphas et al. 2002, 2008; Yin et al. 2002a; Andreasen and

Sharma 2006; Ranen and Jacobsen 2006; Carlson et al. 2007; Quitté et al. 2007, 2010; Trinquier et al. 2007, 2009; Yokoyama et al. 2007; Chen et al. 2009, 2010; Irisawa et al. 2009; Reisberg et al. 2009; Moynier et al. 2010; Burkhardt et al. 2011; Qin et al. 2011; Huang et al. 2012). Some of the isotopic variations in Mg are not directly related to the initial abundance of ^{26}Al (mean life $\tau = 1.06$ Ma). The discovery of depletions in $^{26}\text{Mg}/^{24}\text{Mg}$ of approximately -1.6 per mil (‰) by Lee and Papanastassiou (1974) in the highly fractionated calcium-aluminum-rich inclusion (CAI) “C-1” and -3.5% in EK1-4-1 (Wasserburg et al. 1977) made it clear that the problem of isotopic heterogeneity could not be ignored for Mg. Similar effects were reported in two hibonites from CM meteorites (e.g., Liu et al. 2012). We will show that measurements of individual samples only permit the “initial” Mg isotopic composition of that particular object to be determined. The different initial $^{26}\text{Mg}/^{24}\text{Mg}$

ratios in different samples are in no way directly connected to the timing of ^{26}Al injection or the degree of homogeneity of $^{26}\text{Al}/^{27}\text{Al}$ in the solar nebula, but simply reflect a low level of isotopic heterogeneity. It will be further shown that the isotopic fractionation effects present in an individual inclusion are somewhat variable. The question of the degree of homogenization of $^{26}\text{Al}/^{27}\text{Al}$ in the early solar nebula is discussed with regard to the absence/presence of this nuclide in many samples of refractory phases.

The above issues were addressed by an investigation of the Mg isotopic composition and the ^{26}Al - ^{26}Mg systematics of a type B CAI called “Egg-3” found in the carbonaceous chondrite Allende (CV3). The Egg-3 inclusion exhibits isotopic anomalies in Ti (Niederer et al. 1980, 1981, 1985) and shows large mass fractionation effects in Mg isotopes of approximately 7‰/amu (Esat et al. 1980). It has a well-defined ^{26}Al - ^{26}Mg isochron with $^{26}\text{Al}/^{27}\text{Al} = 4.9 \times 10^{-5}$ (Armstrong et al. 1984; Wasserburg 1987). Work by Esat et al. (1980) found indications of variability of $^{26}\text{Mg}/^{24}\text{Mg}$ in phases in a single CAI with low Al/Mg ratio and indicate an apparent deficit in $(^{26}\text{Mg}/^{24}\text{Mg})_0$ of approximately -1‰. These results caused considerable consternation to the authors and were extensively discussed (Esat et al. 1980; Wasserburg and Papanastassiou 1982). As these data were reported several decades ago on very small samples, we felt that it is important to test the validity of this claim.

As the type B CAIs are justifiably considered to result by crystallization from a silicate melt, it is most reasonable for an individual CAI to have initially been isotopically well mixed, but subject to different degrees of isotopic fractionation when each crystal in that inclusion formed, but prior to any significant decay of ^{26}Al .

Our first efforts to check this using ion probe techniques (Jacobsen et al. 2008a) did not provide any evidence for a deficiency in ^{26}Mg as large as reported by Esat et al. (1980) or of any Mg isotopic variability in the low Al/Mg phases. A hint of a lower intercept $(\delta^{26}\text{Mg})_0 = -0.089 \pm 0.058\text{‰}$ was reported relative to an assumed solar initial of -0.038‰ (Jacobsen et al. 2008a). Here $(\delta^{26}\text{Mg})_0$ is defined as per mil deviation (excess/deficiency) of the initial $^{26}\text{Mg}/^{24}\text{Mg}$ value relative to the terrestrial standard at $^{27}\text{Al}/^{24}\text{Mg} = 0$ in ^{26}Al - ^{26}Mg isochron diagram (Lee et al. 1977). However, the precision of the data with secondary ion mass spectrometry (SIMS) was clearly inadequate to resolve the matter. We present here new measurements on macroscopic samples of Egg-3 with the improved, high-precision multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) technique and a more extensive discussion of the issues involved. The initial report of this work was presented by Wasserburg et al.

(2011) at the *Workshop on Formation of the First Solids in the Solar System* in Kauai, Hawai'i.

METHODS—SAMPLE PREPARATION AND ANALYSES

We analyzed three fractions of the original Egg-3 sample that were originally separated based on density and grain size. These fractions are: < 60 μm (sinks in 3.3 g cc $^{-1}$ heavy liquid mostly spinel and pyroxene); < 100 μm (no heavy liquid); and 60–200 μm (floats in 3.3 g cc $^{-1}$ heavy liquid, melilite, some plagioclase, and a substantial fraction of inter-grown spinel/pyroxene). We also analyzed a bulk fragment recently taken from Egg-3, and a bulk fragment of the Allende CAI “WA,” in which the original discovery of the canonical $^{26}\text{Al}/^{27}\text{Al}$ approximately 5×10^{-5} was reported by Lee et al. (1977). Sample dissolutions and chemical purification of Mg for all four fractions of Egg-3 were repeated three times separately (Dissolutions 1, 2, 3 as indicated in Table 1). Duplicate samples, each weighing approximately 0.5 mg, were first dissolved by using the standard HF:HNO $_3$ dissolution technique in Savillex 3 mL high pressure vials (hexagonal cap, square body type) (Jacobsen et al. 2008b). After dissolution, approximately 1% aliquot of the solution was saved for $^{27}\text{Al}/^{24}\text{Mg}$ analyses. The remainder was centrifuged and then processed through a cation exchange resin. This ensures separation of Mg from potential interferences to accurately measure the Mg isotope ratios. Another set of dissolutions (Dissolution 3) and analyses were carried out on these samples using Parr bombs that ensured the complete dissolution of spinel. That this procedure dissolves spinel was confirmed by dissolution and analysis of terrestrial spinel samples. Both Mg isotope compositions and $^{27}\text{Al}/^{24}\text{Mg}$ ratios were measured on a Thermo Neptune Plus HR-MC-ICP-MS in the Geology Department at the University of California at Davis.

$^{27}\text{Al}/^{24}\text{Mg}$ ratios of CAI samples were obtained directly by measuring ^{27}Al and ^{24}Mg ion beams and calibrating against five reference materials with a range of well-known $^{27}\text{Al}/^{24}\text{Mg}$ ratios (BCR-2 [3.77], BHVO-2 [1.87], AGV-2 [9.45], Peace River Chondrite [0.093], San Carlos Olivine [0.01]). Magnesium isotope ratios were bracketed against the DSM-3 standard solution with each sample solution measured a minimum of 3–11 times (as indicated by “n” column in Table 1).

Data Analysis

The procedure provides a direct measure of shifts in the isotopic ratios of a sample relative to a standard during each run. The variable instrumental fractionation during the run is thus eliminated as it is assumed that the

Table 1. Mg isotopic composition of the Egg-3 CAI.

SAMPLE	$^{27}\text{Al}/^{24}\text{Mg}$	$\delta^{26}\text{Mg}$	2σ	$\delta^{25}\text{Mg}$	2σ	$\delta^{26}\text{Mg}^*$	2σ	n
BCR-2	3.77	-0.155	0.019	-0.080	0.010	0.001	0.006	12
BHVO-2	1.87	-0.200	0.024	-0.100	0.011	-0.004	0.011	10
Allende WA	4.22	12.285	0.035	5.485	0.026	1.506	0.020	9
<i>Dissolution 1</i>								
Egg-3 Frag	2.14	12.548	0.011	6.050	0.004	0.667	0.007	11
Egg-3 < 60 μm	2.17	12.296	0.006	5.912	0.006	0.685	0.008	9
Egg-3 < 100 μm	2.63	12.126	0.039	5.742	0.026	0.849	0.018	8
Egg-3 60–200 μm	2.50	11.996	0.046	5.705	0.029	0.792	0.021	8
<i>Dissolution 2</i>								
Egg-3 Frag	2.25	12.621	0.013	6.059	0.006	0.722	0.004	8
Egg-3 < 60 μm	1.97	11.982	0.020	5.792	0.014	0.610	0.010	9
Egg-3 < 100 μm	2.67	12.401	0.034	5.864	0.018	0.883	0.006	8
Egg-3 60–200 μm	2.71	12.220	0.020	5.767	0.014	0.893	0.015	8
<i>Dissolution 3</i>								
Egg-3 Frag	2.30	12.764	0.029	6.136	0.015	0.712	0.010	3
Egg-3 < 60 μm	2.19	12.322	0.083	5.921	0.043	0.694	0.006	3
Egg-3 < 100 μm	2.65	12.303	0.045	5.825	0.022	0.862	0.003	3
Egg-3 60–200 μm	2.97	13.016	0.059	6.129	0.035	0.975	0.010	3
<i>A43 CAI</i>								
A43-81	2.64	6.830	0.020	2.985	0.006	0.974	0.019	4
A43-82	2.95	6.837	0.013	2.952	0.008	1.046	0.010	4
A43-83	2.18	6.509	0.020	2.914	0.014	0.794	0.021	4
A43-85	3.22	6.934	0.048	2.956	0.018	1.135	0.014	4

All uncertainties on isotope ratios are 2 SE. n = number of repeat analyses for each individual sample. Uncertainties on $^{27}\text{Al}/^{24}\text{Mg}$ are approximately 1%. Each sample was dissolved, purified, and analyzed in three separate analytical sessions (Dissolution 1, 2, and 3).[†]

fractionation factors for each isotope ratio are the same for both sample and the bracketing standards. The actual instrumental fractionation is large and thought to be caused by space charge effects in the source interface of the mass spectrometer (Wieser and Schwieters 2005). If the instrumental fractionation factor $\alpha_{ij}(t)$ (for masses i and j) is closely monitored for each standard (STD) and sample (S) and fixed at the time of measuring one set of ratios, then:

$$\frac{(I_i^{\text{STD}}/I_j^{\text{STD}})}{(N_i^{\text{STD}}/N_j^{\text{STD}})} = [1 + \alpha_{ij}(t)] = \frac{(I_i^{\text{S}}/I_j^{\text{S}})}{(N_i^{\text{S}}/N_j^{\text{S}})} \quad (1)$$

where I_i are the measured ion beam intensities, and N_i the number of atoms of isotopes i (and j) in the standard and sample solutions. This gives the measured quantity for isotopes i and j relative to a standard whose absolute isotopic ratios are not precisely known.

$$\frac{(N_i^{\text{S}}/N_j^{\text{S}})}{(N_i^{\text{STD}}/N_j^{\text{STD}})} = \frac{(I_i^{\text{S}}/I_j^{\text{S}})}{(I_i^{\text{STD}}/I_j^{\text{STD}})} = 1 + 10^{-3}\delta_{ij}^{\text{S}} \quad (2)$$

where δ_{ij}^{S} represents fractional shifts in isotopic ratio (i over j) of the CAI sample relative to our standard expressed in the conventional delta notation (i.e., in parts per thousand deviation from the standards isotopic ratio of i over j). Notice that the instrumental fractionation factor $\alpha_{ij}(t)$ in

Equation 1 is not present in Equation 2 as a result of the standard-sample-standard bracketing technique. Therefore δ_{ij}^{S} reflects only the degree of isotopic shift in the sample relative to the standard. This is the usual approach used in MC-ICP-MS analyses. Any isotopic fractionation associated with chemical processing of the sample would be effectively removed by ensuring approximately 100% recovery of Mg. Typical reproducibility of Mg isotope ratios relative to the STD is better than 0.015‰ (2 SE). Assessment of the reproducibility was determined by repeat measurements of BCR-2, giving a $\delta^{26}\text{Mg}$ value of 0.001 ± 0.006 ($n = 12$).[†] Considerable care is required in the data treatment because the measurements now possible are of increasingly higher precision and effects are very small.

RESULTS

Data

All data obtained here on Egg-3 are shown in Table 1. The first column lists the $^{27}\text{Al}/^{24}\text{Mg}$ as directly measured in

[†]This article was corrected after original online publication on November 30, 2012. The values in Table 1 were corrected, and figures 2 and 5 were replaced.

each sample using the procedure described in the Methods section. The columns labeled $\delta^{26}\text{Mg}$ and $\delta^{25}\text{Mg}$ are the differences in ‰ of the measured values relative to the standard with the associated errors without any corrections.

It can be seen that all of the Egg-3 samples are significantly fractionated and lie within a restricted band near $\delta^{25}\text{Mg}$ approximately 5.9 (Table 1). This is in accord with the earlier results of Esat et al. (1980), but with much greater precision. A histogram of the Egg-3 results for $\delta^{25}\text{Mg}$ is shown in Fig. 1. The range in values for repeat analyses of the same specific sample is shown, with a typical $\delta^{25}\text{Mg}$ range of 0.1‰. Analyses of different sub-samples of the same material generally have similar $\delta^{25}\text{Mg}$ values. However, there is a distinct difference in the $\delta^{25}\text{Mg}$ for the different fractions of Egg-3, which cover a range of 0.4‰. We infer that the degrees of fractionation undergone by different parts of Egg-3 were different and are taken to reflect the fact that the fractionation process was ongoing during the growth of various crystals and mineral phases.

FRACTIONATION CORRECTIONS

To establish the $^{26}\text{Mg}/^{24}\text{Mg}$ ratios relating to the decay of ^{26}Al , it is necessary to correct for fractionation effects in the samples as are clearly exhibited in the $^{25}\text{Mg}/^{24}\text{Mg}$ data. This is a difficult problem for samples with low $^{27}\text{Al}/^{24}\text{Mg}$ and therefore very small enrichments of ^{26}Mg due to ^{26}Al decay. As is well recognized, there is no known a priori law that can be used to convert the fractionation effects observed in $^{25}\text{Mg}/^{24}\text{Mg}$ to correct the measured $^{26}\text{Mg}/^{24}\text{Mg}$ in a sample. In its more general form of exponential “law”

$$\ln \left[\frac{(N_i^S/N_j^S)}{(N_i^{S,0}/N_j^{S,0})} \right] = \beta \ln \left[\frac{(N_k^S/N_j^S)}{(N_k^{S,0}/N_j^{S,0})} \right] \quad (3)$$

the correction requires determination of the parameter $\beta = \ln f(m_i, m_j) / \ln f(m_k, m_j)$, where the exact functions $f(m_i, m_j)$ and $f(m_k, m_j)$ with various masses are unknown for materials processed in the early solar nebula when the CAIs formed.

It is usual to simply treat β as $\ln(m_i/m_j)/\ln(m_k/m_j) = 0.511$ for atomic masses of Mg isotopes (e.g., Jacobsen et al. 2008b). This was shown to yield the most robust results for Ca isotopes (Russell et al. 1978). We have used the approach of Jacobsen et al. (2008b) to identify the choice of β to be used in reducing the data. They showed that for a given β value, the dispersion of a best fit isochron is much greater for β values significantly above that of 0.511 (i.e., 0.514 to 0.521). The results obtained here using $\beta = 0.511$ are shown in Fig. 2 yielding an intercept of $(\delta^{26}\text{Mg})_0 = -0.127 \pm 0.032\text{‰}$. This would correspond to a difference of $-0.089 \pm 0.032\text{‰}$ below the assumed

Fig. 1. Histogram showing the $\delta^{25}\text{Mg}$ composition of Egg-3 samples. Each sample was dissolved, purified, and analyzed in three separate analytical sessions (Dissolution 1, 2, and 3). The number of analyses (n) for each individual sample is bracketed.

initial solar value of -0.038‰ calculated with a canonical $^{26}\text{Al}/^{27}\text{Al} = 5.23 \times 10^{-5}$ and $(^{27}\text{Al}/^{24}\text{Mg})_{\text{solar}} = 0.101$.

We have pursued the matter of choices of β further and will use the criterion that the minimum mean square of weighted deviation (MSWD) value (near unity), which gives the best fit isochron is the applicable parameter to determine β . Figure 3 shows the results for MSWD versus β for the data obtained here as well as those data reported by Jacobsen et al. (2008b) and Larsen et al. (2011). Figure 3A shows MSWD for isochrons of the Egg-3 data as a function of β . It can be seen that the minimum lies near 0.511. Values of β displaced from approximately 0.511 give increasingly larger values of MSWD. A similar graph for data reported by Jacobsen et al. (2008b) is shown in Fig. 3B (for CAI “A44A” internal mineral isochron) and Fig. 3C for their bulk CAI isochron, with the minimum occurring at $\beta = 0.508$, and 0.510 respectively (with MSWD closer to unity when $\beta = 0.511$ for the bulk CAI isochron). Note in the original treatment, Jacobsen et al. (2008b) did not consider any cases for $\beta < 0.511$. In Fig. 3D, we also show this calculation for the CAI data of Larsen et al. (2011). The minimum for their data set is near 0.511 with an MSWD = 5.6. As a consequence of the very high precision they report, the MSWD scale is much greater. Data points for amoeboid olivine aggregates (AOAs) and forsterite-rich accretionary rims (Fo-rich AR) on the Larsen et al. (2011) isochron are excluded from the regression, as they clearly plot above their bulk CAI-only isochron (Fig. 2B) and typically postdate CAI formation (Wasserburg et al. 2011).

Figure 4 further illustrates how the MSWD, isochron slope, and intercept change as a function of β , using Egg-3 CAI data (this study) and the bulk CAI data from Jacobsen et al. (2008b) as two examples. While the

Fig. 2. A) Allende “Egg-3” CAI internal ^{26}Al - ^{24}Mg isochron (grey diamonds) from this study. Whole rock CAI isochrons of Larsen et al. (2011) (black solid circles) and Jacobsen et al. (2008b) regression lines, respectively, for comparison. Solid red squares are A43 samples of Jacobsen et al. (2008b) repeated in this study, red open squares (A43) and black open squares (bulk CAIs) are Jacobsen et al. (2008b) data. B) Regressing bulk CAI, AOA, and Fo-rich accretionary rim data from Larsen et al. (2011) (dotted black line) gives a different initial $\delta^{26}\text{Mg}$ value of -0.0159‰ , with an offset from their bulk CAI intercept (solid black line) by 0.0141‰ .[†]

MSWD deviates substantially from unity when β is moving away from 0.511 ± 0.02 (panels A and B), the corresponding isochron slopes are not greatly affected outside the error bars (panel C and D). However, it is evident that the intercept is strongly dependent on the value of β chosen. It can be shown that the intercept ranges from $-0.365 \pm 0.032\text{‰}$ for $\beta = 0.501$ to $+0.097 \pm 0.031\text{‰}$ for $\beta = 0.521$. Using the criterion that the choice of β should be based on obtaining an isochron with low MSWD (approximately 1), we conclude that β in the range between 0.509 and 0.513 is the preferred value to be used in reducing the data to correct for isotopic fractionation effects. In all subsequent treatment of the data in this report, we will use 0.511 although the basic issues relating to the fractionation “law” remain. For Egg-3, the intercepts are $-0.174 \pm 0.032\text{‰}$ and $-0.086 \pm 0.032\text{‰}$ for $\beta = 0.509$ and 0.513, respectively, compared to the intercept of $-0.127 \pm 0.032\text{‰}$ for $\beta = 0.511$ (see Fig. 5 for details). In no case does the MSWD criterion justify significantly high values of β . In the extreme example, as shown in Fig. 3D for the Larsen et al. (2011) data, if $\beta = 0.514$, the MSWD goes to 404, with the isochron slope being $(5 \pm 7) \times 10^{-5}$, and intercept $(\delta^{26}\text{Mg}^*)_0 = 0.5 \pm 1\text{‰}$. For $\beta > 0.514$, it is no longer possible to regress an isochron with Larsen et al. (2011) data.

DISCUSSION

Offset Isochrons

Figure 2 shows the internal isochron using $\beta = 0.511$ for our data on Egg-3. It can be seen that the results lie on a well-defined line with an intercept of $(\delta^{26}\text{Mg})_0 = -0.127 \pm 0.032\text{‰}$. This is in agreement with the results we reported earlier (Wasserburg et al. 2011). For comparison, we show the line representing the previous results by Jacobsen et al. (2008b) and Larsen et al. (2011), again using $\beta = 0.511$.

We have included a new set of analyses in our study of dissolutions of some mineral separates of CAI A43 studied by Jacobsen et al. (2008b). These data were carried out in conjunction with the Egg-3 analyses. The results reported here (Table 1) are in good agreement and confirm those of Jacobsen et al. (2008b). Inspection of Fig. 2 shows that there is a clear displacement of all the Egg-3 data from those of Jacobsen et al. (2008b) and Larsen et al. (2011) with distinct differences in intercept $(\delta^{26}\text{Mg})_0$, whereas the isochron lines are parallel with indistinguishable $^{26}\text{Al}/^{27}\text{Al}$ values. The difference in initial values for these sets of samples is quantitatively preserved if the same data are processed with $\beta = 0.509$ or $\beta = 0.513$ (Figs. 4–6). Figure 6 in particular shows the difference of intercepts between Egg-3 and Jacobsen et al. (2008) isochrons, shown as $\Delta(\text{intercept})$ as a function of β . As can be seen clearly, $\Delta(\text{intercept})$ remains negative, and is clearly resolved from zero. The

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Fig. 3. A–D) Plots showing the fit of regression lines (MSWD) versus the fractionation factor β for A) mineral separates from Egg-3 CAI, excluding the anomalous fragment data (EggFrag) from dissolution 3, B) mineral separates from the A44A CAI from Jacobsen et al. (2008b), C) whole rock CAIs from Jacobsen et al. (2008b), and D) whole rock CAIs from Larsen et al. (2011).

exceptions are when those β deviate significantly away from the minimum MSWD valley as shown in Figs. 3 and 4, the quality of regression is such that large uncertainties of intercepts do not permit the resolution of $\Delta(\text{intercept})$ from zero. We therefore conclude that the initial $^{26}\text{Mg}/^{24}\text{Mg}$ in Egg-3 and in the samples reported by Jacobsen et al. (2008) are distinctly different, whereas all the CAIs sampled in both studies have the same inferred value of $^{26}\text{Al}/^{27}\text{Al}$. The results presented here require that the $^{26}\text{Mg}/^{24}\text{Mg}$ ratios in the early solar system must have been somewhat variable prior to any significant decay of ^{26}Al .

However, if the samples had an anomalous initial $^{25}\text{Mg}/^{24}\text{Mg}$ (as opposed to $^{26}\text{Mg}/^{24}\text{Mg}$) relative to the standard due to intrinsic isotopic heterogeneity, then we would have introduced an apparent offset in the value of intercept ($\delta^{26}\text{Mg}$)_o by forcing $^{25}\text{Mg}/^{24}\text{Mg}$ to be equal to the standard value during the fractionation correction process. To obtain an offset of ($\delta^{26}\text{Mg}$)_o = −0.127‰, a +0.065‰ shift in $^{25}\text{Mg}/^{24}\text{Mg}$ is required. It is not possible to determine which isotopic ratio is shifted, but

we will assume it to be in the ratio $^{26}\text{Mg}/^{24}\text{Mg}$. This problem has been long known to be associated with three isotope systems (cf. Wasserburg and Papanastassiou 1982).

The point of view taken here is that a suite of samples which share the appropriate co-evolution from ^{26}Al decay and are fractionated by some common assumed law should yield $^{26}\text{Al}/^{27}\text{Al}$ that is self-consistent and adequately describes the initial value if they were produced at exactly the same time. Different individual samples may not have the same initial $^{26}\text{Mg}/^{24}\text{Mg}$. Thus efforts to precisely determine an initial value should be restricted to a single object that may justifiably be considered to have a single, homogeneous state prior to the decay of ^{26}Al . The observed differences in measured $^{25}\text{Mg}/^{24}\text{Mg}$ found here (Fig. 1) in different subsamples of Egg-3 are taken to reflect the differences in fractionation undergone by individual crystals that were forming during the crystallization of Egg-3 during an ongoing fractionation process as argued earlier.

Fig. 4. Plots showing how the MSWD, slope, and intercept of regressed $\delta^{26}\text{Mg}^*$ and $^{27}\text{Al}/^{24}\text{Mg}$ data are dependent on the fractionation factor (β). Mineral separate data from Egg-3 CAI are presented in A), C), and E) and whole rock data from Jacobsen et al. (2008) are presented in B), D), and F). All regressions were produced using Isoplot v3 (Ludwig 2003), and errors associated with the slope and intercept are 2σ . The β value which produces the minimum MSWD is marked with a grey vertical band in each panel. The point at which β is cut by the data array marks the minimum MSWD, slope, and intercept of the regression line (solid line). Note that at the slopes within errors are insensitive to the choice of β . The corresponding intercepts values at the minimum MSWD are clearly distinct between Egg-3 (E) and the bulk CAI isochron of Jacobsen et al. (2008b).

Larsen et al. (2011) Mg Isotope Data

In preparing this report, we note a recent paper by Larsen et al. (2011) who presented Mg isotope data with

extraordinary levels of precision that we are not able to achieve. Larsen et al. (2011) analyzed a suite of different CAIs, Fo-rich AR, and some AOAs. They demonstrated that the data again yield a good linear array with a slope

Fig. 5. Comparison of isochron regressions (slopes, intercepts, and MSWDs) for $\beta = 0.511 \pm 0.02$ for Egg-3 samples. Samples from dissolution 1, 2, and 3 are represented by open squares, grey circles, and black diamonds, respectively. The lower panels include all data, whereas the top panels exclude the anomalous “EggFrag” from dissolution 3. This appears to be an outlier as the EggFrag samples from dissolution 1 and 2 plot on the isochrons.[†]

Fig. 6. A plot showing the difference in intercept values (Δ intercept) between regressed Al-Mg data from Egg-3 and bulk CAIs from Jacobsen et al. (2008), plotted as a function of β between 0.501–0.521. Using a beta of 0.511 (shaded), we obtain a Δ intercept value of 0.089‰ , a value clearly resolvable from zero.

corresponding to the “canonical” value for $^{26}\text{Al}/^{27}\text{Al} = (5.252 \pm 0.019) \times 10^{-5}$, however with a higher intercept value, i.e., a smaller deficiency relative to their terrestrial standard of $(\delta^{26}\text{Mg})_0$ of $-0.0159 \pm 0.0014\text{‰}$. We note that this result for the initial $^{26}\text{Mg}/^{24}\text{Mg}$ is in

contradiction to the $(\delta^{26}\text{Mg})_0$ of $-0.0317 \pm 0.0038\text{‰}$ reported by the same group (Thrane et al. 2006). Larsen et al. (2011) interpreted their results as demonstrating wide variability of $^{26}\text{Al}/^{27}\text{Al}$ in the solar nebula, building on an implicit assumption that initial $^{26}\text{Mg}/^{24}\text{Mg}$ was homogeneous to within $\pm 1.4\text{ ppm}$ ($[\delta^{26}\text{Mg}]_0 = -0.0159 \pm 0.0014\text{‰}$) for all the materials in the inner solar system.

Insofar as there is intrinsic Mg isotopic heterogeneity as demonstrated here (Fig. 2), we cannot, a priori, lump different objects together to determine precise “initial $^{26}\text{Mg}/^{24}\text{Mg}$ ” values for the aggregate system. Larsen et al. (2011) presented data on four different CAIs (31E, 22E, E104, and E48) ($^{27}\text{Al}/^{24}\text{Mg} < \sim 3.3$) and include forsterite-rich accretion rims on E-48 (AR-E48) and on E104 (AR-E104). They also present results from bulk amoeboid olivine aggregates (E1s, E2s, E3s, and E4s), which are distinct objects, not part of the CAIs. As they noted, these olivine-rich samples are important as they have very low Al/Mg and permit a determination of their initial values without any

[†]This article was corrected after original online publication on November 30, 2012. The values in Table 1 were corrected, and figures 2 and 5 were replaced.

Fig 7. A) $\delta^{25}\text{Mg}$ versus $\delta^{26}\text{Mg}$ for mineral separate data from the Egg-3 CAI and bulk CAI, AOA, and Fo-rich AR data from Larsen et al. (2011). B) Expanded region showing the spread of the Mg isotope data for the Egg-3 CAI in more detail. The dotted line represents a fractionation line constructed from $\ln(1 + 10^{-3} \times \delta^{26}\text{Mg}) = 1/\beta \times \ln(1 + 10^{-3} \times \delta^{25}\text{Mg})$, where $\beta = 0.511$, $\delta^{25}\text{Mg}$, and $\delta^{26}\text{Mg}$ are per mil deviation of the $^{25}\text{Mg}/^{24}\text{Mg}$ and $^{26}\text{Mg}/^{24}\text{Mg}$ relative to a terrestrial standard.

significant extrapolation just using the appropriate fractionation corrections.

While the AOAs are clearly separate objects to the CAIs, the relationship between the accretionary rims to the two CAIs studied by these workers requires serious attention. In Fig. 7, we show data from Egg-3 and Larsen et al. (2011) on a $\delta^{26}\text{Mg}$ versus $\delta^{25}\text{Mg}$ diagram. It can be seen that all of the Larsen et al. (2011) data show rather large fractionation effects ranging from -2.4 to $+12\text{‰}$, whereas all of the Fo-rich AR and AOA samples have strong negative values of $\delta^{26}\text{Mg}$ and $\delta^{25}\text{Mg}$. Note in particular that while the bulk CAI E48 has highly positive $\delta^{25}\text{Mg}$ ($10\text{--}12\text{‰}$), the accretionary rims of E48 (Fo-rich AR-E48) have negative $\delta^{25}\text{Mg} = -1.1\text{‰}$. It is plausible that isotopically heavy (positive) values would result in evaporative residues, while the isotopically light (negative) values indicate condensation effects from a gaseous phase.

The AOAs and ARs require reconsideration of the pertinent fractionation “law” and the question of the source of the particular condensate that is a later addition to the CAI. Petrographic and isotopic evidence clearly shows that many CAIs are multigenerational systems (cf. Wark and Lovering 1977; El Goresy et al. 1985; Hsu et al. 2000). The accretion rims have been extensively studied in terms of petrochemistry, textures, and the oxygen isotopic systematics (e.g., Krot et al. 2001, 2002, 2008; Cosarinsky et al. 2008; Simon et al. 2011). These workers conclude that the rims are later formed condensates from a gas phase that had to be enriched in ^{16}O (assumed to be the solar nebula) and

were later altered along with the host CAI in a planetary ^{16}O -poor environment during metamorphism. This has also been inferred for “normal” chondrules by Chaussidon et al. (2008). Their inference that the rims are a vapor deposit is strongly supported here by the enrichment of the lighter Mg isotopes which is expected for this model.

If we consider the simplest case where the vapor (V) and CAI residue (RES) are closed systems, then the equation governing the delta values between the gas phase and the remaining residue is:

$$\delta_{ij}^{\text{RES}}(N_j^{\text{RES}}/N_j^0) = -\delta_{ij}^{\text{V}}(1 - N_j^{\text{RES}}/N_j^0) \quad (4)$$

where (N_j^{RES}/N_j^0) is the fraction of j remaining after evaporation. Applying this to the data on E48 and AR-E48, for masses 25 and 24 (or 26 and 24), we find that $(N_{24}^{\text{RES}}/N_{24}^0) = 0.1$. That is, approximately 90% of the ^{24}Mg in the original sample would have to be evaporated to produce a gas phase with the observed delta in the rim. From all of the above considerations, we conclude that the specific source of the Mg in the accretion rims and the fractionation processes associated with the formation of the rims by some condensation process indicate that they cannot simply be lumped together with their host CAI.

We here regress only the bulk CAI data from Larsen et al. (2011) and obtain a different $(\delta^{26}\text{Mg})_0$ value from the one found by regressing their data together with AR and AOA data (Fig. 2B). The bulk CAI-only regression gives a $(\delta^{26}\text{Mg})_0$ value of $-0.030 \pm 0.040\text{‰}$, similar to

initial values of $-0.036 \pm 0.026\%$ (Jacobsen et al. 2008b) and $-0.0317 \pm 0.0038\%$ (Thrane et al. 2006), as opposed to $-0.0159 \pm 0.0014\%$ (Larsen et al. 2011) when CAIs were regressed together with AR and AOA. If we regress only the AOA and accretionary rims, separate from their bulk CAIs, we get an intercept $(\delta^{26}\text{Mg})_0$ value of $-0.014 \pm 0.002\%$ with $^{26}\text{Al}/^{27}\text{Al} = (5.08 \pm 0.15) \times 10^{-5}$ (Wasserburg et al. 2011). Clearly, the intercept reported by Larsen et al. (2011) was governed by AOA and accretionary rims, not by CAIs. Radiogenic ingrowths in $\delta^{26}\text{Mg}$ from an initial value of -0.038% to obtain -0.014% (AOA initial) would take only 24 Kyr in a reservoir with $(^{27}\text{Al}/^{24}\text{Mg})_{\text{reservoir}} = 2.8$ and canonical $^{26}\text{Al}/^{27}\text{Al}$. The free decay from the canonical $^{26}\text{Al}/^{27}\text{Al} = 5.23 \times 10^{-5}$ to 5.08×10^{-5} takes approximately 30 Kyr. Itoh et al. (2002) showed an example where AOA could postdate CAI by 0.5 Myr. Recent work by Olsen et al. (2011) highlights the disturbed nature of AOA in Allende. We thus further caution the use of AOA to define the “solar initial” $^{26}\text{Mg}/^{24}\text{Mg}$ ratio.

Mg Fractionation Law

We are still left with the “ β problem” and do not have a sound independent basis for estimating the fractionation “law.” It has been shown by Davis et al. (2005) and Richter et al. (2007) that evaporation of silicates in a vacuum indicates a $\beta = 0.51400 \pm 0.00024$. This value will not yield good isochrons with the data using the MSWD criterion discussed here. As it is generally considered that the observed effects in CAI samples are due to evaporative losses, then there is a conflict between these two results. Most nebular condensation calculations assume a pressure regime of approximately 10^{-3} to 10^{-5} bars both for solar compositions and for material highly enriched in dust relative to gas ($\times 10^3$) (Ebel and Grossman 2000; Petaev and Wood 2005; Grossman et al. 2008). These pressures are much greater than those obtained in the evaporation experiments (Richter et al. 2007; Knight et al. 2009). Evaporation experiments by Nagahara’s group in the presence of H_2 to maintain a slightly higher steady-state pressure shows that β for Mg isotopes is shifted to lower value of 0.5108 ± 0.0030 (see Young et al. [2002] for details). It is possible that this difference in pressure regime is the cause of the difference in values of β , although the precision obtained by these workers was still not adequate to answer this question. This remains a fundamental issue that needs addressing by further laboratory studies.

Heterogeneity of $^{26}\text{Al}/^{27}\text{Al}$ in the Solar System

As there was intrinsic isotopic heterogeneity in the solar system, it is not possible to determine the precise

bulk solar values for isotopic ratios from analysis of individual meteoritic and planetary samples. Thus, inferences about the uniformity of the ratio $^{26}\text{Al}/^{27}\text{Al}$ in early solar system cannot be drawn from small effects in $^{26}\text{Mg}/^{24}\text{Mg}$ nor can this be proven by reasonable evolution models of bulk solar evolution (e.g., Villeneuve et al. 2009). A small deficit of an initial $^{26}\text{Mg}/^{24}\text{Mg}$ (50–100 ppm) from what one considers to be the bulk solar value cannot be used to demonstrate that there was an absence of ^{26}Al in parts of the early solar system when there is intrinsic isotopic heterogeneity at that level. It cannot be used to infer either the source of ^{26}Al , the timing of ^{26}Al injection, or the degree of uniformity of the $^{26}\text{Al}/^{27}\text{Al}$ in the early solar system. The argument that a deficiency in an isotope is related to gross heterogeneity in a radioactive progenitor nuclide was used previously by Bizzarro et al. (2007) on the source of ^{60}Fe and the timing of its injection into the solar system. This was based on $^{60}\text{Ni}/^{58}\text{Ni}$ ratios in iron meteorites that are approximately 25 parts per million lower than samples from Earth, Mars, and chondrite parent bodies. They inferred that this was due to the presence of differentiated planetesimals *prior* to the formation of CAIs and that ^{60}Fe was later injected into the protoplanetary disk approximately 1 Myr after solar system formation. This argument was made in the known presence of general isotopic heterogeneities and also in the particular samples they measured. It has since been shown that their Ni measurements were in error (Dauphas et al. 2008; Regelous et al. 2008; Chen et al. 2009).

The variability in isotopic ratios of non-radiogenic isotopes now extends to approximately 25% for oxygen (Clayton et al. 1973; Kobayashi et al. 2003; Sakamoto et al. 2007) and typically much less than 0.01% for most other elements (Wasserburg et al. 1979, 1980; Dauphas et al. 2002, 2008; Yin et al. 2002a; Andreasen and Sharma 2006; Ranen and Jacobsen 2006; Carlson et al. 2007; Quitté et al. 2007, 2010; Trinquier et al. 2007, 2009; Yokoyama et al. 2007; Chen et al. 2009, 2010; Irisawa et al. 2009; Reisberg et al. 2009; Moynier et al. 2010; Burkhardt et al. 2011; Qin et al. 2011; Huang et al. 2012). Thus, reasonably good (but not perfect) mixing of the isotopes appears to be dominant in bulk meteorite samples and in most macroscopic inclusions (e.g., see fig. 2 of Moynier et al. 2011). However, the discovery of CAI (EK-1-4-1) with a deficiency in ^{26}Mg ($\delta^{26}\text{Mg} = -3.7$), and large isotopic anomalies in many refractory elements showed that incomplete mixing of the heterogeneous source materials was preserved in meteorite samples (cf. Wasserburg et al. 1979). We consider samples with isotopic compositions of all refractory elements very close (sub per mil effects) to bulk meteorite values to represent material “processed”

within the solar system so that gross isotopic effects inherited from individual stellar components have been mostly erased. Insofar as one may consider $^{26}\text{Al}/^{27}\text{Al}$ to be similar to the isotopic ratios of stable and long-lived nuclei, then one might argue that this ratio should not show large variations at a given time.

The ^{26}Al Problem

It is evident that ^{26}Al was present in the early solar system at a rather elevated level. The simplest assumption is that it was, at some point in time, distributed with a constant bulk value of $^{26}\text{Al}/^{27}\text{Al}$ in the solar nebula. However, the possibility that $^{26}\text{Al}/^{27}\text{Al}$ may have been highly variable within the solar nebula cannot be rejected. To demonstrate heterogeneity of $^{26}\text{Al}/^{27}\text{Al}$ simply requires determining this ratio in two objects formed at the same time. Differences found for samples formed at different times can simply result from radioactive decay. It is readily possible to produce refractories today without any ^{26}Al as it is no longer present. Thus, the demonstration of heterogeneity in $^{26}\text{Al}/^{27}\text{Al}$ is dependent on finding objects with different $^{26}\text{Al}/^{27}\text{Al}$ ratios and establishing simultaneity of formation of the objects to a very precise degree. This may possibly be done using multiple short-lived chronometers, as well as the long-lived U-Pb chronometer with adequate precision.

The very plausible proposal that ^{26}Al was produced by nuclear reactions induced by T-Tauri activity in the early Sun had the difficulty, in that a wide range of ^{26}Al abundances are expected, including very high values, and ^{26}Al should be found correlated with other predictable nuclear effects (Shu et al. 1997, 2001; Lee et al. 1998; Feigelson et al. 2002). This model has, so far, not achieved wide acceptance. Stellar nuclear sources are possible as demonstrated by the excesses of ^{26}Mg in Al-rich presolar dust grains from which $^{26}\text{Al}/^{27}\text{Al}$ up to 4×10^{-1} is inferred (Zinner 2007). Extensive theoretical studies show that this level can be reached during normal stellar evolution with deep mixing during the AGB phase for low mass stars (Wasserburg et al. 1995; Nollett et al. 2003).

No samples have been found of processed solar system material with values in significant excess of $^{26}\text{Al}/^{27}\text{Al}$ approximately 5×10^{-5} (cf. Jacobsen et al. 2008b). Thus, there do not appear to be any identifiable “hot spots.” All of the data on processed solar system material show that there are abundant samples (including ultra-refractory phases) with values of approximately 5×10^{-5} down to zero (i.e., no ^{26}Al). The existence of ultra-refractories that do not contain significant ^{26}Al has been known since the discovery of HAL (Lee et al. 1979, 1980; Allen et al. 1980) and isotopic studies of microscopic grains of hibonite and

corundum by Ireland (1990) and Sahijpal et al. (2000). In particular, the extensive study by Ireland (1990) showed both positive and negative Mg isotopic fractionation in ultra-refractory grains and one grain (#13-13) with high Al/Mg and had no evidence of ^{26}Al , but with very large isotopic anomalies in ^{48}Ca (10%) and ^{50}Ti (27%). A recent extensive study by Makide et al. (2011) and Krot et al. (2009) showed that the $^{26}\text{Al}/^{27}\text{Al}$ in a large suite of micron size corundum grains, which formed in an ^{16}O -enriched reservoir had abundant samples with inferred $^{26}\text{Al}/^{27}\text{Al} \sim 5 \times 10^{-5}$ (within errors); a number of samples (approximately 52%) with intermediate values; and a substantial number of samples with $^{26}\text{Al}/^{27}\text{Al} < 2 \times 10^{-6}$. An extensive study by Liu et al. (2012) of CM hibonite grains also found the same wide spread in inferred $^{26}\text{Al}/^{27}\text{Al}$ with a high frequency of grains showing negative mass fractionation. There is a hint in two samples of a deficiency in ^{26}Mg , but the uncertainties are largely due to the very low Mg contents. Most workers associate the CAIs and ultra-refractory oxides with enriched ^{16}O to formation in the solar nebula. Sahijpal and Goswami (1998) proposed that such grains with no ^{26}Al were formed in the solar nebula prior to the injection of ^{26}Al . Simon et al. (2002) also state that hibonites they found in Murchison with no ^{26}Al were first-generation condensates from the solar nebula prior to the injection of ^{26}Al . All of these arguments are based on the fact that these grains are shown to represent ^{16}O -enhanced material and are thus attributed to a nebular source. One possibility is that many ultra-refractories and some CAIs were produced by earlier formed matter from ^{16}O -rich material containing ^{26}Al that formed planetesimals. If these bodies were later disrupted by impacts, they could provide low $^{26}\text{Al}/^{27}\text{Al}$ ultra-refractories. Another possibility is that earlier formed matter fell in close passage to the Sun, got heated with the loss of Mg, and then ejected back into the disk. Yet another and more straightforward possibility is that some micro samples were processed in the solar system, but represent restricted samples of the precursor material that was extensively heterogeneous in the parent dense molecular cloud. In that case, the $^{26}\text{Al}/^{27}\text{Al}$ ratio cannot serve as a chronometer.

In more recent years, it has been possible to obtain reasonable ^{26}Al - ^{26}Mg isochrons on “normal” chondrules. The demonstration that elevated amounts of ^{26}Al existed in chondrules with $^{26}\text{Al}/^{27}\text{Al} \sim 9 \times 10^{-6}$ to 3×10^{-6} (e.g., Russell et al. 1996; Kurahashi et al. 2008; Villeneuve et al. 2009) makes it clear that ^{26}Al was present in the events that produced “normal” chondrules. Some of these cannot have been produced under “nebular” conditions because of the very high Na content in glasses (Russell et al. 1996; MacPherson and

Huss 2005; Alexander et al. 2008). As many of these chondrules are of ^{16}O -depleted material (Krot et al. 2009), it follows that ^{26}Al was incorporated into that class of early solar system debris. Now, there is abundant evidence that normal chondrules often do not have just ^{16}O -deficient oxygen, but have ranges in $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ from (0, 0) down to (−20 and −20). This is often dependent on the position within individual crystals (see extensive oxygen isotope studies by Ushikubo et al. [2012] and the extensive Al-Mg studies of such chondrules by Kurahashi et al. 2008; Ushikubo et al. 2010; Tenner et al. 2012). Thus normal chondrules have distinctive ^{16}O -rich parts, which may correlate with the Mg content and have excesses of ^{26}Mg correlated with Al/Mg and give $^{26}\text{Al}/^{27}\text{Al}$ approximately $0.3\text{--}0.5 \times 10^{-5}$. These chondrules had been formed in an ^{16}O -rich environment and subsequently exchanged some O and Fe in a ^{16}O -poor environment. It is further of note that CAIs with large $^{26}\text{Mg}^*$ excesses are found in plagioclase and melilite which give $^{26}\text{Al}/^{27}\text{Al} \sim 5 \times 10^{-5}$ but have oxygen closer to the “planetary” value, while pyroxenes and spinels in the same CAI have very strong excesses of ^{16}O (Lee and Papanastassiou 1974; Clayton and Mayeda 1977; Clayton 2003; Krot et al. 2009). This clearly must result from later exchange of oxygen in some of these phases during a process where CAIs with enriched ^{16}O reacted with matter depleted in ^{16}O during metamorphic processes (without seriously disturbing Al-Mg). The alteration of O in the rims of melilite crystals has recently been observed on a micro scale in CAIs (Simon et al. 2011). This oxygen exchange process with selective replacement of certain phases is believed to have occurred widely, but direct evidence pointing to a mechanism is still lacking.

From the observations given above, it is evident that ^{26}Al containing material was present in many samples of ^{16}O -rich matter and also in matter that is dominated by ^{16}O -poor material. The ^{26}Al in the ^{16}O -poor material may be the result of incorporation of some ^{16}O -rich matter in the dominant ^{16}O -poor terrestrial planetary material or it could have also been present in the ^{16}O -poor matter.

A fundamental problem, first addressed by Urey, was the necessity of a heat source to cause the melting and differentiation of planetesimals (Urey 1955). He proposed ^{26}Al as a most plausible source. It should be noted that if the material accreting to make planets had $^{26}\text{Al}/^{27}\text{Al} < 8 \times 10^{-6}$, then there would not be an adequate heat source for planetary melting and differentiation. In the case that there was one homogeneous reservoir with $^{26}\text{Al}/^{27}\text{Al}$ initially at the canonical 5×10^{-5} level, then there would be a heat source readily capable of melting even very small protoplanets, resulting in intense magmatic activity and

producing molten interiors. As melting of even small protoplanets would occur in less than 2×10^5 yr from the canonical $^{26}\text{Al}/^{27}\text{Al}$, this would be the dominant heat source and permit the formation of Fe-Ni cores on a rapid time scale. This is in accord with the observations of the ^{182}Hf - ^{182}W chronometer by analyses of both CAIs and some iron meteorites (Harper and Jacobsen 1996; Jacobsen and Yin 1998; Yin et al. 2002b; Burkhardt et al. 2008; Kleine et al. 2009). These results that indicate times of approximately 1 Myr to differentiate further show that planets with molten interiors were present very early in the history of the solar system. Subsequent collisions of such planets could provide refractory material with values of $^{26}\text{Al}/^{27}\text{Al}$ that were low to extremely low depending on the time the interiors remained hot/molten.

The simple scenario of a single oxygen and ^{26}Al source is not applicable because of the well-known existence of two distinctive oxygen isotopic reservoirs. Two ^{26}Al sources do not in any way explain the oxygen conundrum. As shown by Clayton et al. (1973), the CAIs are derived from a reservoir enriched in ^{16}O with $^{17}\text{O}/^{18}\text{O}$ approximately at the terrestrial value. The second reservoir is associated with the terrestrial planets and bulk meteorites and has a lower abundance of ^{16}O with the same $^{17}\text{O}/^{18}\text{O}$. The reservoir with enriched ^{16}O is associated with the bulk solar value as indicated from the difficult and elegant experimental analyses of the solar wind (McKeegan et al. 2011). This is then the O value to be associated with the bulk solar nebula. Neither the solar or planetary types of oxygen can be due to distinct nucleosynthetic sources as there are no correlated large nuclear anomalies. As the discovery of “mass independent” isotopic shifts in experiments in the laboratory and in the upper atmosphere (Thiemens and Heidenreich 1983; Mauersberger 1987), a sound theoretical model for such a process for producing the ozone isotopic effects was found by Gao and Marcus (2001). Thus, an alternative to stellar nucleosynthesis effects is known to exist. It has been generally concluded that some chemical-physical fractionation process (possibly self-shielding) is responsible for the isotopic shifts in O found in meteorites as no large nuclear effects are present in all other elements in the samples with very different O isotopic ratios (cf. Navon and Wasserburg 1985; Clayton 2002; Yurimoto and Kuromoto 2004; Lyons and Young 2005). This then leads to the problem of how/when these distinctive reservoirs are formed, physically separated, and how they interact. Certainly, some of the ^{16}O -rich material was incorporated in the terrestrial type material. If the $^{26}\text{Al}/^{27}\text{Al}$ ratios were, at some point in time, the same in both reservoirs, then there is no problem with a heat source. If the ^{26}Al is only in the ^{16}O -rich matter, then an adequate heat source would

require more than approximately 16% of ^{16}O -enhanced material with ^{26}Al in the bulk terrestrial planet inventory. If the conversion of material to ^{16}O -deficient matter took place at a later time (approximately 2×10^6 yr) after the ^{16}O -enhanced gas had disappeared, then there would be no problem with the low $^{26}\text{Al}/^{27}\text{Al}$ observations on ultra-refractories. This would yield problems with regard to a heat source for planetary melting and differentiation. From the $^{26}\text{Al}/^{27}\text{Al}$ observations on “normal” chondrules given earlier (cf. Kurahashi et al. 2008; Ushikubo et al. 2010; Tenner et al. 2012), it follows that ^{26}Al was, at some reduced level, present in the ^{16}O -depleted material. From the meteorite samples studied, one can see that aggregations of silicate material were formed and some of that matter must have accumulated into protoplanetary bodies from the ^{16}O -rich reservoir, and some of this aggregation occurred from a separate ^{16}O -poor region. In this case, there would be two populations of protoplanets and an incomplete mixing in the two materials in some regions. The samples of ultra-refractories with low or no ^{26}Al could then also have their origin in the disruption of such ^{16}O -rich protoplanets due to ongoing decay. This would not require that grains with no ^{26}Al were formed in the solar nebula, as suggested by Sahijpal and Goswami (1998), Krot et al. (2010), and Makide et al. (2011). All of the refractory grains observed are inclusions in meteoritic material and have chemically interacted with that host material which has no ^{16}O enrichment. From all the observations, there clearly was some mixing between the two reservoirs in some regions that are preserved in the agglomerated material we call chondrites.

Infall

As the inventory of ^{26}Al is plausibly from previous stellar sources, then the condition that a uniform ratio of $^{26}\text{Al}/^{27}\text{Al}$ existed in the solar nebula at an instant of time requires some discussion. This would require (1) that the source region in the placental molecular cloud was homogeneous or that it was homogenized during the infall process; and (2) that the time scale over which the infall took place in forming the solar system occurred on a time significantly less than approximately 2×10^6 yr. The time scale for free-fall collapse is $T_{\text{FF}} = (3\pi/32G\rho)^{1/2}$, where ρ is the mass density in the dense molecular cloud and G is the universal constant of gravitation. This gives $T_{\text{FF}}^2 \sim 3 \times 10^3/N$ where the free-fall time is in units of 10^6 yr and N is the number of hydrogen nuclei per cubic centimeter. If the source region were heterogeneous in $^{26}\text{Al}/^{27}\text{Al}$, then a particular mass of the infalling material could have any arbitrary value of $^{26}\text{Al}/^{27}\text{Al}$. All other elements (except oxygen) in these different regions would then be required to have isotopic ratios that were the typical meteoritic and

terrestrial values to within approximately 0.01%. The $^{26}\text{Al}/^{27}\text{Al}$ ratios would then not have any direct and precise time meaning, but no “spike” would be needed to explain the different $^{26}\text{Al}/^{27}\text{Al}$ ratios. Whatever the stellar source of the ^{26}Al was, the final Al must have been in the dust inventory and mixing would be more difficult than with species in the gas phase.

Using the free-fall time as a guide, this implies a number density of approximately 10^5 H cm^{-3} for T_{FF} approximately 0.1 Myr. In contrast, for a free-fall time scale of 1 Myr, the number density would be 3×10^3 . Both values are in general accord with observations on dense molecular clouds, but the lower value is not to be associated with dense star-forming regions. It appears plausible that the infall rates which led to the solar system formation could be sufficiently rapid to provide a single $^{26}\text{Al}/^{27}\text{Al}$ value in a short time (cf. Gritschneder et al. 2012). In contrast, the result for the lower number density with an infall rate comparable to the mean life of ^{26}Al ($\bar{\tau}_{^{26}\text{Al}} = 1.06 \times 10^6$ yr) will give values of $^{26}\text{Al}/^{27}\text{Al}$, which change over the time when accretion takes place. Lower values of $^{26}\text{Al}/^{27}\text{Al}$ correspond to later infall. In that case, the later infall would range from the earliest value to ratios decreased by a factor approximately $\exp(-t/\bar{\tau}_{^{26}\text{Al}})$, where t is the time when objects formed and were stored as cool/cold matter in the disk of the accreting Sun. The “time” t depends on the detailed knowledge of condensed matter formation during the highly variable and complex accretion process. For time scales in significant excess of 10^5 yr, this would require a higher value of ^{26}Al in the source region, but would give a range in $^{26}\text{Al}/^{27}\text{Al}$ in the more recently added material. The differences in observed $^{26}\text{Al}/^{27}\text{Al}$ would then correspond to the times of infall and storage and not directly to ages in the solar system. It is thus possible to explain the lower $^{26}\text{Al}/^{27}\text{Al}$ in this manner, although the very low densities are not usually associated with star formation.

The timing and circumstances in which the dust would be stored and processed in the disk and when solids would accumulate are not clear. When in the accumulation of the total mass of the sun that this process occurs and the duration of significant gas in the disk are difficult to establish. In any case, the total mass of condensed matter in all of the terrestrial planets represents only 10^{-3} of bulk solar matter with approximately 70% of the oxygen tied up in the gas phase for a nebular gas. The mass of the terrestrial planets is approximately 10^{28} gram and would correspond to a dust disk of approximately $5 \times 10^{-6} M_{\odot}$ (in units of solar mass). This is approximately 0.1 of the mass found for dust discs around T-Tauri stars, but is more or less commensurate. The issue is then: when did this ^{16}O -poor disk form during the accretion process of the Sun? The complementary question is, when are dust and debris

from ^{16}O -rich matter processed and saved in the disk so that we have some today? How much of early infalling dust re-entered the disk considering the strong bipolar outflow processes is not clear. When the process took place that produced ^{16}O -poor material from solar matter is not understood. It could have been concurrent with the production and storage of ^{16}O -rich material, or it could have occurred much later with a much limited mass of ^{16}O -rich (e.g., solar) gas. We have no knowledge to the answers of these questions, but consider that the bulk of the dust and matter that is preserved in the terrestrial planets was probably stored during the later stages of the Sun's accretion.

In all considerations, it must be recognized that there was gross isotopic and chemical heterogeneity in the placental cloud from which the Sun formed. This is true on microscopic and macroscopic scales. The presence in meteorites of (1) circumstellar condensates from different stellar sources with gross isotopic shifts and (2) the substantial isotopic variations (several to tens of percent) found in refractory elements in some samples are clear testimony to the micro-scale heterogeneity in the source region. As some of these samples have no evidence of ^{26}Al , then the heterogeneity of ^{26}Al on some scale must have occurred in the placental cloud. These materials are not representative of the "bulk" solar system. This heterogeneity in the source could extend to a somewhat larger scale within the cloud as thorough mixing of dust grains over a large scale is not possible. Thorough mixing would require high densities and high temperatures to produce chemical reactions, which would erase the isotopic differences. This must happen during the infall phase during formation of the Sun and is obviously not complete.

Models of infall by Boss (2011) focus on very rapid infall rates (approximately $5 \times 10^{-3} M_{\odot} \text{ yr}^{-1}$). These models have virtually instant infall and would best preserve any inventory of short-lived nuclei in the parental cloud. In contrast, other models (e.g., Yang and Ciesla 2012) use a much slower mass accretion rate from the cloud core to the star-disk system of $3 \times 10^{-6} M_{\odot} \text{ yr}^{-1}$ with infall ending at approximately 0.3 Myr. Studies of discs in young clusters (e.g., Haisch et al. 2001) show that one half of stars lose their disks in approximately 3 Myr, with an overall disk lifetime of 6 Myr. This is the timescale for essentially all the stars to lose their disks. Studies of hot accretion discs associated with FU Orionis regimes (Fischer et al. 2012) have calculated accretion rates of approximately $2 \times 10^{-6} M_{\odot} \text{ yr}^{-1}$ to $10^{-5} M_{\odot} \text{ yr}^{-1}$ during the FU outburst when the forming star has mostly accreted. These results, like most available data, are based on IR measurements that are very sensitive to dust, but there are no definitive measurements of the corresponding gas content. The millimeter-wavelength continuum

observations provide a complementary picture of disk evolution by probing colder disk material that is not detectable in the infrared and has been applied to cold discs (Carpenter et al. 2005). An excellent review of the physics of inner regions of protoplanetary discs including radiative heating of an annulus is given by Dullemond and Monnier (2010) without attempting to explain the meteoritic data. An extensive analysis of grain formation in a disk is given by Cuzzi and Weidenschilling (2006).

The problem that is most demanding when considering the meteoritic data and the solar oxygen composition is that some mechanism of isotopic fractionation must be established to produce ^{16}O -deficient material and store it in the disk and preserve such material while being in a solar environment that is ^{16}O -rich. If this process occurs somewhat later (< 2 Myr) than that which formed the high $^{26}\text{Al}/^{27}\text{Al}$ CAIs, with $^{26}\text{Al}/^{27}\text{Al}$ approximately 5×10^{-5} , then a simple explanation may be possible. Producing low $^{26}\text{Al}/^{27}\text{Al}$ material with ^{16}O -rich oxygen only demands a late heating of such ^{16}O -rich matter. There must have existed an extensive reservoir of solid material that was ^{16}O -rich and contained ^{26}Al and a reservoir of ^{16}O -poor material that may or may not have contained ^{26}Al . These two interacted and the bulk of terrestrial planetary material is now dominated by ^{16}O -poor matter. The mystery of the mechanism for producing ^{16}O -poor material, the timing and role in the evolution of the accretion disk, has not yet been solved. It is this matter that requires attention before placing complex constraints on the ^{26}Al inventory and special stellar sources.

CONCLUSIONS

From our results, we conclude, once again, that there is strong evidence of widespread isotopic heterogeneity in many elements at a low level (including Mg) that produce isotopic differences from terrestrial "normal" samples. It is shown that inferences about the uniformity/heterogeneity of $^{26}\text{Al}/^{27}\text{Al}$ in the solar nebula cannot be made from these differences nor can requirements of late or special injection be properly inferred from that observation. Samples with the same $^{26}\text{Al}/^{27}\text{Al}$ and different initial $^{26}\text{Mg}/^{24}\text{Mg}$ values have been demonstrated. The existence of substantial isotopic variations (several to tens of percent) in the refractory elements in some CAIs proves that variability existed in the placental cloud from which the solar system formed. As some of these samples show no evidence of ^{26}Al , this also implies variability in $^{26}\text{Al}/^{27}\text{Al}$ on some scale within the cloud. The important problem is the bulk solar value of $^{26}\text{Al}/^{27}\text{Al}$. From the considerations presented, this is plausibly determined by samples with isotopic abundances of refractory elements very close to what we take to be bulk solar values (from meteorites).

There are several possible explanations of the observation of low $^{26}\text{Al}/^{27}\text{Al}$ in ultra-refractory grains with solar $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$. These include late infall with solar oxygen, some heterogeneity in the placental molecular cloud, or a late formation of ultra-refractories from a solar oxygen source. None of these requires a special or late injection of ^{26}Al . The use of the $^{26}\text{Al}/^{27}\text{Al}$ ratio as a chronologic guide continues to be plausible if applied to samples with only very small isotopic heterogeneities, but it need not be exact. The timing of the as-yet-unknown processes, which produced the high $^{17}\text{O}/^{16}\text{O}$ and $^{18}\text{O}/^{16}\text{O}$ in the material making up the terrestrial planets, is the more fundamental mystery.

We conclude that data from the distinct materials (AOAs and the later formed accretion rims) cannot, in general, be justifiably used to construct a self-consistent isochron and determine precise initial value of $(^{26}\text{Mg}/^{24}\text{Mg})_0$ for a CAI or a set of CAIs. Most data reported in the literature use samples of different CAIs to determine an isochron and an initial value. We consider that the only reliable means of obtaining a precise initial $^{26}\text{Mg}/^{24}\text{Mg}$ (at the level of 0.01 permil) is by investigation of a single CAI in which the phases can justifiably be argued to come from a single source.

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