^{26}Al – ^{26}Mg and ^{207}Pb – ^{206}Pb systematics of Allende CAIs: Canonical solar initial $^{26}\text{Al}/^{27}\text{Al}$ ratio reinstated

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ABSTRACT

The precise knowledge of the initial $^{26}\text{Al}/^{27}\text{Al}$ ratio [$(^{26}\text{Al}/^{27}\text{Al})_0$] is crucial if we are to use the very first solid objects formed in our Solar System, calcium–aluminum-rich inclusions (CAIs) as the “time zero” age-anchor and guide future work with other short-lived radio-chronometers in the early Solar System, as well as determining the inventory of heat budgets from radioactivities for early planetary differentiation. New high-precision multi-collector inductively-coupled plasma mass spectrometry (MC-ICP-MS) measurements of $^{27}\text{Al}/^{24}\text{Mg}$ ratios and Mg-isotopic compositions of nine whole-rock CAIs (six mineralogically characterized fragments and three micro-drilled inclusions) from the CV carbonaceous chondrite, Allende yield a well-defined ^{26}Al – ^{26}Mg fossil isochron with an $(^{26}\text{Al}/^{27}\text{Al})_0$ of $(5.23 \pm 0.13) \times 10^{-5}$. Internal mineral isochrons obtained for three of these CAIs (A44A, AJEF, and A43) are consistent with the whole-rock CAI isochron. The mineral isochron of AJEF with $(^{26}\text{Al}/^{27}\text{Al})_0 = (4.96 \pm 0.25) \times 10^{-5}$, anchored to our precisely determined absolute ^{207}Pb – ^{206}Pb age of 4567.60 ± 0.36 Ma for the same mineral separates, reinstate the “canonical” $(^{26}\text{Al}/^{27}\text{Al})_0$ of 5×10^{-5} for the early Solar System. The uncertainty in $(^{26}\text{Al}/^{27}\text{Al})_0$ corresponds to a maximum time span of ± 20 Ka (thousand years), suggesting that the Allende CAI formation events were culminated within this time span. Although all Allende CAIs studied experienced multistage formation history, including melting and evaporation in the solar nebula and post-crystallization alteration likely on the asteroidal parent body, the ^{26}Al – ^{26}Mg and U–Pb-isotopic systematics of the mineral separates and bulk CAIs behaved largely as closed-system since their formation. Our data do not support the “supra-canonical” $^{26}\text{Al}/^{27}\text{Al}$ ratio of individual minerals or their mixtures in CV CAIs, suggesting that the supra-canonical $^{26}\text{Al}/^{27}\text{Al}$ ratio in the CV CAIs may have resulted from post-crystallization inter-mineral redistribution of Mg isotopes within an individual inclusion. This redistribution must be volumetrically minor in order to satisfy the mass balance of the precisely defined bulk CAI and bulk mineral data obtained by MC-ICP-MS. The radiogenic $^{208}\text{Pb}^*/^{206}\text{Pb}^*$ ratio obtained as a by-product from the Pb–Pb age dating is used to estimate time-integrated $^{232}\text{Th}/^{238}\text{U}$ ratio (κ value) of CAIs. Limited κ variations among the minerals within a single CAI, contrasted by much larger variations among the bulk CAIs, suggest Th/U fractionation occurred prior to crystallization of igneous CAIs. If interpreted as primordial heterogeneity, the κ value can be used to calculate the mean age of the interstellar dust from which the CAIs condensed.

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1. Introduction

Ca- and Al-rich inclusions (CAIs) play a pivotal role in the early Solar System chronology, since they mark the beginning of the Solar

System evolution (Lee et al., 1977; Amelin et al., 2002). Over three decades of scrutiny with the ^{26}Al – ^{26}Mg chronometry ($t_{1/2} = 0.73$ Ma, million years) reveals that most CAIs define the initial $^{26}\text{Al}/^{27}\text{Al}$ ratio [$(^{26}\text{Al}/^{27}\text{Al})_0$] of $\sim 5 \times 10^{-5}$ referred to as the solar “canonical” value. Some CAIs subsequently experienced a complex thermal history in the solar nebula and on their host meteorite parent asteroids extending over 0.1–3 Ma (e.g. MacPherson et al., 1995; Hsu et al., 2000; Young et al., 2005; MacPherson, 2007). The “canonical” $(^{26}\text{Al}/^{27}\text{Al})_0$ value has recently been revised upwards to a “supra-canonical” value of ~ 5.85 – 7×10^{-5} using high-precision MC-ICP-MS and multi-collector secondary ion mass spectrometer (MC-SIMS) measurements of Mg-isotopic

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compositions in individual CAI minerals (Young et al., 2005; Taylor et al., 2005) and “whole-rock” CAIs (Galy et al., 2004; Bizzarro et al., 2004, 2005; Thrane et al., 2006). The tight spread of $(^{26}\text{Al}/^{27}\text{Al})_0 = (5.85 \pm 0.05) \times 10^{-5}$ obtained for bulk CAIs from four CV chondrites using high-precision MC-ICP-MS measurements was interpreted as an evidence for a very short (less than 20 thousand years, Ka) formation interval of CV CAIs or their precursors (Thrane et al., 2006). These results are in apparent conflict with each other, because the internal ^{26}Al – ^{26}Mg isochrons inferred from Mg-isotopic measurements of individual minerals in coarse-grained, igneous CV CAIs, which date their crystallization age, cannot be steeper, thus older than the whole-rock ^{26}Al – ^{26}Mg isochrons of CV CAIs, which date the formation of CAI precursors. An important question to resolve is what was the duration of CAI formation in the early solar nebula? The resolution to the current disparity in the ^{26}Al – ^{26}Mg data has profound implications in limiting the sources of ^{26}Al in the early Solar System, the astrophysical sites of CAI formation, and the inventory of radioactive heat source for early planetary differentiation.

To resolve this apparent conflict and gain further insight into the earliest history of the Solar System, we have investigated bulk Mg-isotopic compositions of six mineralogically well-characterized CAIs and three additional micro-drilled CAIs using analytical techniques similar to those used by Bizzarro et al. (2004, 2005) and Thrane et al. (2006).

2. Mineralogy and petrography of CAIs

Prior to high-precision Mg-isotope measurements of CAIs by MC-ICP-MS, it is essential to adequately document and describe the mineralogy, petrography, and chemistry of the samples being analyzed. The following information, together with extensive online supplementary materials, is provided for the purpose.

2.1. Analytical techniques

Fragments of six Allende CAIs A33, A39, A43, A44A, A60, and AJEF were polished and studied by X-ray elemental mapping (using Mg, Ca, Al, Ti, Na, and Cl K α), backscattered electron (BSE) imaging, and electron probe microanalysis. The BSE images were obtained with the JEOL JSM-5900LV scanning electron microscopy (SEM) equipped with Thermo Electron energy dispersive spectrometer (EDS) using a 15 kV accelerating voltage. X-ray elemental maps with a resolution of 2–4 $\mu\text{m}/\text{pixel}$ were acquired using five spectrometers of a Cameca SX-50 electron microprobe at 15 keV accelerating voltage, 100 nA beam current and ~2–3 μm beam size. The elemental maps in Mg, Ca, and Al K α were combined using an RGB-color scheme and ENVI (ENvironment for Visualizing Images) software package. Electron probe microanalyses were performed with a Cameca SX-50 electron microprobe using a 15 keV accelerating voltage, 20 nA beam current, beam size of ~1–2 μm and wavelength dispersive X-ray spectroscopy. For each element, counting times on both peak and background were 30 s (10 s for Na and K). Matrix effects were corrected using the PAP procedure. The detection limits were (in wt.%): MgO, 0.02; SiO₂, TiO₂, Al₂O₃, CaO, K₂O, 0.03; MnO, Na₂O, 0.05; Cr₂O₃, FeO, 0.06. Representative chemical compositions of primary and secondary minerals in the Allende CAIs studied are listed in Supplementary Table S1.

2.2. Brief description of individual CAIs

A33 is a fragment of a compact Type A or a Type B CAI composed of melilite (Åk_{9-21}) and fassaite (up to 16 wt.% TiO₂, up to 20 wt.% Al₂O₃, Table S1), both poikilitically enclosing abundant spinel grains (Fig. S1). Spinel is largely concentrated in fassaite. The CAI is surrounded by the Wark-Lovering rim sequence composed of spinel with inclusions of perovskite, anorthite, and Al-diopside. Melilite along grain boundaries and along veins is replaced by grossular and monticellite. Secondary

nepheline and sodalite replacing melilite and anorthite are minor and observed only near the Wark-Lovering rim.

A39 is a fragment of a Type B CAI composed of melilite (Åk_{33-72}), fassaite (4–7 wt.% TiO₂, 19–20 wt.% Al₂O₃, Table S1), spinel and anorthite (Fig. S2). Melilite is replaced by various secondary minerals. In the anorthite-free regions, melilite along veins and grain boundaries is replaced by grossular + Ti-free, Al-rich (8–13 wt.% Al₂O₃, Table S1) diopside. The replaced regions are enriched in Na and depleted in Ca. In the anorthite-rich regions, melilite is extensively replaced by coarse-grained grossular, monticellite and Cl-bearing aluminosilicate–wadalite (Ishii et al., 2008). Spinel grains in altered regions are slightly enriched in FeO (Table S1). Secondary nepheline and sodalite are minor in the fragment studied.

A43 is a fragment of a Type B CAI composed of melilite (Åk_{15-38}) and fassaite (5–9 wt.% TiO₂, 20–21 wt.% Al₂O₃, Table S1), both poikilitically enclosing abundant spinel grains (Fig. S3). Melilite grains are crosscut by rare fine-grained veins of secondary grossular, monticellite, and forsterite. Secondary nepheline and sodalite are virtually absent.

A44A is a fragment of a Type B CAI (original weight was 500 mg, with fragments A and E, each weighting ~250 mg, Floss et al., 1992). A44A was studied for isotopic anomalies of Mo (Yin et al., 2002a) and

Table 1

MC-ICP-MS Al–Mg-isotope data for whole-rock fragments, micro-drilled CAIs, and mineral separates

Sample	CAI Type	Weight (mg)	$\frac{^{27}\text{Al}}{^{24}\text{Mg}}$	2% error	n	$\delta^{26}\text{Mg}^*$ (‰)	$2\sigma_{\text{mean}}$
A33	A						
Whole-rock fragment		24.05	4.07	0.08	6	1.468	0.019
A39	B						
Whole-rock fragment		11.82	2.22	0.04	6	0.789	0.018
A43	B						
Whole-rock fragment		18.80	2.54	0.05	4	0.924	0.018
Bulk fraction		~5	2.59	0.05	3	0.918	0.024
Fine fraction		~2	2.55	0.05	4	0.908	0.022
Pyroxene		2.28	2.19	0.04	6	0.793	0.011
Melilite–pyroxene		2.15	2.64	0.05	4	0.956	0.008
Melilite		2.56	2.93	0.06	3	1.045	0.026
Plagioclase		2.09	3.21	0.06	3	1.106	0.013
A44A	B						
Whole-rock fragment		21.11	2.24	0.04	6	0.817	0.017
Fine fraction		~2	3.32	0.07	4	1.227	0.020
Pyroxene		0.33	2.91	0.06	4	1.084	0.010
Melilite–pyroxene		1.04	3.55	0.07	6	1.274	0.008
Melilite–spinel		0.18	3.03	0.06	4	1.128	0.015
Melilite $\gg$ pyroxene		4.27	4.17	0.08	5	1.509	0.008
Melilite		0.45	5.65	0.11	5	2.025	0.015
Melilite		0.12	6.43	0.13	6	2.357	0.018
Plagioclase		3.06	6.70	0.13	5	2.462	0.015
A60	A						
Whole-rock fragment		14.12	2.98	0.06	7	0.945	0.009
AJEF	B						
Whole-rock fragment		17.42	3.07	0.06	6	1.086	0.013
Pyroxene		1.17	2.23	0.04	3	0.762	0.028
Melilite–pyroxene		1.36	2.67	0.05	3	0.929	0.032
Melilite		1.51	3.50	0.07	6	1.235	0.016
Melilite		0.58	4.55	0.09	3	1.598	0.016
Plagioclase		1.32	4.28	0.09	4	1.489	0.017
AM10-21 CAI-1	A						
Micro-drilled CAI		~2	8.64	0.17	5	3.224	0.021
AM10-21 CAI-2	A						
Micro-drilled CAI		~2	4.13	0.08	4	1.275	0.019
AM5-63 RI	RI (px-ol)						
Micro-drilled		~5	0.114	0.002	5	0.052	0.012

n: Number of repeat measurements.

$\delta^{26}\text{Mg}^*$ is radiogenic ^{26}Mg excess expressed as parts per 1000 deviation from the terrestrial standard DSM-3. Mass bias of samples was corrected for using an exponential law and assuming a mass fractionation factor (β) for the CAIs is 0.511.

AM5-63 RI irregular shaped refractory inclusions consisting of coarse-grained pyroxene (px) and fine-grained olivine (ol) matrix (see sample description in Section 2.3).

was used to establish solar initial $^{182}\text{Hf}/^{180}\text{Hf}$ of $(1.00 \pm 0.08) \times 10^{-4}$ (Yin et al., 2002b). It is composed of melilite (Åk_{21-55}), spinel, fassaite (2–8 wt.% TiO_2 , 18–20 wt.% Al_2O_3 , Table S1), minor anorthite and metal-sulfide nodules (Fig. S4). Melilite grains show complex chemical zoning, which probably reflects chemical evolution of the CAI melt during its crystallization. Melilite around anorthite grains is almost completely replaced by secondary grossular, monticellite, and forsterite. Outside anorthite-bearing regions, melilite grains are crosscut by fine-grained veins of these secondary minerals. Secondary nepheline and sodalite are minor.

A60 is a fragment of a very extensively altered CAI, tentatively classified as a fluffy Type A inclusion (Fig. S5). The only primary minerals identified include melilite (Åk_{2-14}), spinel and hibonite (Table S1). Spinel, however, is enriched in FeO (6–10 wt.%). Melilite is nearly completely pseudomorphed by the secondary Na- and Fe-bearing aluminosilicate, suggesting open-system alteration in the presence of aqueous solutions (Table S1).

AJEF is a Type B CAI composed of melilite, fassaite, spinel, and minor anorthite (Fig. S6). Both melilite (Åk_{19-64}) and fassaite (2–11 wt.% TiO_2 , 14–18 wt.% Al_2O_3 , Table S1) are chemically zoned. The åkermanite-rich melilite is enriched in Na relative to the gehlenitic melilite, the former around anorthite grains is extensively replaced by secondary grossular, monticellite, wollastonite, and wadalite (Ishii et al., 2008). Secondary nepheline and sodalite are minor.

2.3. Additional CAIs from two Allende slabs

In addition to the CAI fragments described above, two Allende slabs (AM10-21 and AM5-63) were examined before micro-drilling for the ^{26}Al – ^{26}Mg study for their mineralogy using SEM at the Lawrence Livermore National Laboratory.

AM10-21 is a $\sim 15 \times 25 \text{ mm}^2$ piece (Fig. S7-a) with a polished sample surface. It consists mainly of fine-grained matrix and chondrule inclusions. It also includes four individual millimeter-sized CAIs of which two were drilled out using a micromill for the study. AM10-21-CAI-1 is a $\sim 1.5 \times 3 \text{ mm}^2$ and $\sim 1 \text{ mm}$ deep Type A CAI composed of nepheline ± melilite and spinel (Fig. S7-b). This sample has the highest $^{27}\text{Al}/^{24}\text{Mg}$ ratio and most radiogenic $\delta^{26}\text{Mg}^*$ (Table 1 and Fig. 4). AM10-21-CAI-2 is a $\sim 1.5 \times 2 \text{ mm}^2$ sized and $\sim 1 \text{ mm}$ deep Type A inclusion (Fig. S7-c). The mineralogy of AM10-21-CAI-2, characterized using only optical microscopy, revealed no primary minerals such as melilite, anorthite or pyroxene, suggesting high degree of secondary alteration.

AM5-63 (Fig. S8-a) is a $\sim 15 \times 20 \text{ mm}^2$ piece similar in petrology to slab AM10-21. The slab surface of AM5-63 contains two individual millimeter-sized CAIs and an irregularly shaped, $\sim 5 \times 5 \text{ mm}^2$ in size, 1–2 mm deep, CAI-like object AM5-63-RI (Fig. S8-b). AM5-63-RI consists of medium-grained pyroxene and fine-grained interstitial olivine and may represent an amoeboid olivine aggregates. This sample has the lowest $^{27}\text{Al}/^{24}\text{Mg}$ ratio (0.110 ± 0.002) and the least radiogenic $\delta^{26}\text{Mg}^*$ (Table 1 and Fig. 4), similar to the very low $^{27}\text{Al}/^{24}\text{Mg}$ ratio (0.093 to 0.148) observed in micro-drilled sample of Bizzarro et al. (2004) and Thrane et al. (2006). Since the validity of using such a sample to constrain the negative solar initial $\delta^{26}\text{Mg}^*$ is questionable, we did not include AM5-63-RI in the isochron regression (Fig. 4).

3. Sampling

3.1. Strategy of multi-scale sampling

To fully characterize and understand the ^{26}Al – ^{26}Mg systematics of CAIs, we adopted a multi-scale sampling strategy for the isotopic analyses. In addition to bulk fragments analyses, we have also obtained mineral separates for MC-ICP-MS analyses. It is desirable to work on whole-rock CAI samples because their Mg-isotopic compositions are not affected by secondary inter-mineral Mg-isotope exchange reactions that

are known to have been important in the Allende CAIs (LaTourrette and Wasserburg, 1998; Bizzarro et al., 2004). However, the potential of the ^{26}Al – ^{26}Mg chronometry for understanding the history of CAI formation is enhanced if multi-scale sampling is used. ^{26}Al – ^{26}Mg isochrons obtained at different sampling levels could have potentially recorded timing of different events. An isochron defined by several whole-rock CAIs, each of which remained closed to exchange with the outside medium since their formation, probably dates Al/Mg fractionation during evaporation–condensation processes in the solar nebula and can potentially provides the age of CAI precursors. An isochron based on various mineral species separated by physical properties (e.g., density, magnetic susceptibility etc.), or based on various proportions of CAI minerals sampled by micro-drilling (Bizzarro et al., 2004, 2005; Thrane et al., 2006) or by laser ablation (Young et al., 2005) can potentially provide crystallization age of the CAIs (if ^{26}Al – ^{26}Mg systematics of individual minerals has not been disturbed since formation). These different ways of sampling, however, are likely to respond differently to secondary processes experienced by CAIs (e.g., thermal metamorphism or post-crystallization alteration): sampling with better spatial resolution are more sensitive to volume diffusion caused by heating, whereas mineral fractions separated by physical properties (which, in turn, reflect the differences in composition), would be more sensitive to secondary alteration.

3.2. Mineral separation

3.2.1. Crushing

CAI fragments A43 and AJEF, that did not contain any visible matrix material attached to them, were gently crushed in an agate mortar. In order to avoid losses, no sieving of the crushed material was performed. The crushed material was rinsed with ethanol several times, to remove very fine-grained fractions and preserved separately.

The CAI A44A contained rather abundant matrix overgrowths. Most of it was removed with a needle, but complete cleaning was difficult because of the complex surface and matrix “bays” within the CAI. After mechanical cleaning, the chip was cleaned in an ultrasonic bath in ethanol, and crushed together with remaining matrix.

3.2.2. Mineral separation

Mineral separation was done by magnetic susceptibility on a Frantz barrier separator. About 5–8 fractions were collected from each CAI, from most magnetic to the least magnetic. Allende matrix is far more magnetic than any CAI minerals, with exception of metal. In the separation of A44A, almost all fragments with matrix overgrowths are in the most magnetic fractions. Most of material has medium magnetic susceptibility. These fractions are mixtures of melilite and pyroxene, and intergrown melilite and pyroxene. Some pyroxene and melilite grains contained variable amount of small spinel inclusions. Frantz magnetic separator does not efficiently separate melilite from pyroxene. Less magnetic fractions are increasingly rich in anorthite. The least magnetic fractions consist mostly of anorthite, with occasional pyroxene and melilite grains.

Melilite and pyroxene are easy to recognize by appearance under binocular: melilite is white or light grey (if contains spinel inclusions), pyroxene is grey to dark grey and has a bit of a metal luster. Anorthite is white, and is hard to recognize from melilite. There were a number of melilite and pyroxene fragments sufficiently large to be analyzed for ^{26}Al – ^{26}Mg systematics individually. Fine material was analyzed without additional separation.

3.2.3. Mineral compositions

The compositions of representative grains from bulk (medium magnetic) fractions and from least magnetic samples from each CAI were roughly estimated using EDS on rough surfaces, so the estimates are no better than semi-quantitative. The compositions of anorthite, spinel and pyroxene are fairly constant in all CAIs studied, whereas melilite grains are compositionally variable both among and within

CAIs. Al/Mg ratios in CAI minerals increase in the order of pyroxene, spinel, melilite, and anorthite. The spread of Al/Mg ratios among the fractions is controlled by mixing between pyroxene, melilite and anorthite, and by compositional variations of melilite. It might be possible to construct a precise Al–Mg isochron based on melilite fragments only. The details of mineral fractions are shown in Table S2.

3.3. Micro-drilling of CAIs from Allende slabs: motivation and method

In the study of Bizzarro et al. (2004, 2005) and Thrane et al. (2006), CAIs were sampled exclusively by a micro-drilling technique. However, it is not clear to us why such a sampling technique would ensure a more representative bulk CAI composition as argued by Young and Shahr (2007), than whole-rock CAI fragments. A meteorite slab used for micro-drilling with a flat polished surface will expose portions of CAIs randomly. Therefore it could not be more representative of a whole CAI than any fragments used in this study, in which large bulk CAI samples were used (see Table 1 for sample weights).

Nonetheless, to carefully address the issue of sampling heterogeneity, we micro-drilled three CAIs from polished sections of Allende slabs AM10-21 and AM5-63, thus using a similar sampling technique as Bizzarro et al. (2004) and Thrane et al. (2006). Inclusions AM10-21-CAI-1, AM10-21-CAI-2, and AM5-63-RI were sampled by micro-drilling and ~2–5 mg samples were obtained for isotopic analyses. To avoid sampling the rims and the matrix in the irregularly shaped CAIs of Allende, drillings were only taken in the center of the inclusions. Drilled powder from the samples was transferred into pre-cleaned Savillex Teflon beakers. Prior to drilling and between each sample, the drill bit was rinsed and cleaned in an ultrasonic bath ~10 min in MQ-water. After the ultrasonic bath the drill bit was carefully inspected under a microscope to make sure all material from the previous sample had been removed from the drill bit. Subsequently, samples were dissolved and processed as described in Section 4.

4. Analytical details

4.1. Procedures for Mg-isotope analyses

The six whole-rock CAI fragments, weighing between 11 and 24 mg, three micro-drilled samples from the Allende meteorite slabs weighing between ~2 and 5 mg, and the mineral separates weighing between 0.2 and 3 mg from A44A, AJEF, and A43 were dissolved in concentrated HF and HNO₃ acid (mixed 3:1) at 150 °C.

To eliminate fluoride complexes and ensure complete dissolution samples were subsequently attacked in *aqua regia* (3:1 concentrated HCl:HNO₃ mixture). In order to separate and purify Mg from sample matrix, aliquots of each sample corresponding to between ~5 and 10 µg Mg were passed through cation-exchange resin (Bio-Rad AG®50W-12X, 200–400 mesh). Prior to collecting Mg in 2 N HNO₃, elements such as Cr, Al, Fe, Na, and K were eluted with 1 N HCl, 1 N HNO₃ + 0.5 N HF, and 2 N HNO₃, respectively. To ensure the purity of Mg fraction, the chemistry was repeated three times for each sample. Quantitative recovery of Mg (~100% yield) was achieved throughout this study.

Mg isotopes were measured on the UC Davis Nu Plasma high-resolution MC-ICP-MS. Samples were introduced to the plasma torch via a DSN-100 desolvating nebulizer. Analyses were made in static mode simultaneously measuring ²⁶Mg, ²⁵Mg, and ²⁴Mg isotopes. To avoid isobaric interference on ²⁶Mg from species such as ¹²C¹⁴N (Fig. 1), measurements were performed in pseudo-high-resolution mode with a mass-resolving power at around 2500. The contribution from ¹²C¹⁴N is small but it is critical to resolve it from true ²⁶Mg peak. This is especially important in high-precision Mg-isotope analyses in low Al/Mg ratio samples (applies to MC-ICP-MS data), as “shifts in the initial ²⁶Mg/²⁴Mg of 0.02% would cause 10–20% shifts in the estimated ²⁶Al/²⁷Al.” (Wasserburg et al., 2006).

Instrumental drift was corrected for using the standard-sample-standard bracketing and time extrapolation method. Multiple replicate measurements were obtained for all samples. An exponential law, with a fractionation factor $\beta = \ln(m_1/m_2)/\ln(m_1/m_3) = 0.511$, where m_1 , m_2 , and m_3 are masses of isotopes ²⁴Mg, ²⁵Mg and ²⁶Mg, respectively (Russell et al., 1978; Young et al., 2002), was used to correct for mass fractionation. The $\delta^{26}\text{Mg}^*$ is reported relative to the international DSM-3 Mg standard (Galy et al., 2003) as in Bizzarro et al. (2004), where * denotes the radiogenic ²⁶Mg component.

In addition to two pure chemical standards DSM-3 and Aristar, and two terrestrial basalt standards BIR-1 and BCR-2, four synthetic and terrestrial standards, gravimetrically spiked with different levels of excess ²⁶Mg*, J11 olivine (+15 ppm ²⁶Mg*), Aristar (+20 ppm ²⁶Mg*), Aristar (+30 ppm ²⁶Mg*), BCR-2 (+30 ppm ²⁶Mg*) (provided by the courtesy of Joel Baker) were measured (Table S3 and Fig. 2).

4.2. Preparation of gravimetric Al/Mg standard

A gravimetric Al/Mg standard was prepared by dissolving (6 N HCl) 0.13083 g and 0.10203 g of pure Al (99.9995%) and Mg (99.98%) metal purchased from Alfa Aesar. After ~4 h on the hotplate (~120 °C) both

Fig. 1. Pseudo-high-resolution scan of masses 26 (black), 25 (blue), 24 (greenish yellow) showing background ²⁶Mg (low mass side, left) overlain by ¹²C¹⁴N peak on the high mass side (to the right) obtained in 0.1 N HCl acid solution deliberately “contaminated” with minute amount of Mg in order to show the ¹²C¹⁴N peak in relation to Mg isotopes. With a mass-resolving power of about 2500 it is possible to resolve such peaks (in pseudo-high-resolution mode on the Nu Plasma MC-ICP-MS). HCl acid instead of HNO₃ is used throughout the work to reduce the contribution of ¹²C¹⁴N. We note all prior published works with MC-ICP-MS on Mg isotopes in CAIs were measured in low-resolution mode. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fig. 2. $\delta^{26}\text{Mg}^*$ deviation from various spiked and unspiked terrestrial standards, which gives an estimate of the external reproducibility. The overall deviation from the gravimetric or terrestrial “normal” is $\pm 0.005\text{‰}$ (2σ).

the Al and Mg metal were completely dissolved and were subsequently diluted to the desired concentration in 0.1 N HCl. Based on the gravimetry, the $^{27}\text{Al}/^{24}\text{Mg}$ for our standard solution (UCD Al/Mg 1) is calculated to be 1.462 (Table S4).

4.3. Note on $^{27}\text{Al}/^{24}\text{Mg}$ determination

$^{27}\text{Al}/^{24}\text{Mg}$ ratios were measured directly from the standard and sample solutions without any pretreatment in “wet plasma” mode on the UC Davis Nu Plasma high-resolution MC-ICP-MS. “Wet plasma” (i.e., without using desolvating nebulizer), compared to “dry plasma” (using a desolvating nebulizer), reduces bias on the measured $^{27}\text{Al}/^{24}\text{Mg}$ that appears to be related with sample matrix. We note that this is especially important for CAIs that are rich in Al, Ca, Ti, etc. in addition to Mg. The effects on the Al/Mg sensitivity from sample matrix were tested by spiking aliquots of the “UCD Al/Mg 1” with different levels of “CAI-like” matrix solution (standard:matrix = 1:10, 1:20, 1:50) with the elemental proportions 80 wt.% Ca, 15 wt.% Fe, 4 wt.% Ti, and 1 wt.% Na. The results are shown in Table S4 and Fig. 3a. Even with high levels of matrix added to the Al–Mg standard, our procedure can measure $^{27}\text{Al}/^{24}\text{Mg}$ to within a level of $<0.2\%$. Furthermore, $^{27}\text{Al}/^{24}\text{Mg}$ ratios measured on three basaltic USGS standards and one pyroxene glass are shown to be within 0.8% from their nominal value (Table S4; Fig. 3b).

In deriving the solar initial $^{26}\text{Al}/^{27}\text{Al}$ ratio, it is critical to determine the $^{27}\text{Al}/^{24}\text{Mg}$ atomic ratio accurately (Figs. 3a,b and 5a,b, Jacobsen et al., 2007a,b). We used MC-ICP-MS to measure atomic $^{27}\text{Al}/^{25}\text{Mg}$ ratios directly from an aliquot of very dilute sample solution without chemistry; ^{26}Mg is avoided because of radiogenic effects, while ^{24}Mg is too distant from ^{27}Al for the Nu Plasma collector array. The measured ratio is normalized to a gravimetrically prepared standard Al–Mg mixture using the relation Eq. (1):

$$\left(\frac{^{27}\text{Al}}{^{25}\text{Mg}}\right)_{\text{sample}}^{\text{corr}} = \left(\frac{^{27}\text{Al}}{^{25}\text{Mg}}\right)_{\text{sample}}^{\text{measured}} \times \frac{\left(\frac{\text{Al}}{\text{Mg}}\right)_{\text{std}}^{\text{gravimetric}} \times \frac{1}{X_{\text{Ab}^{25}\text{Mg}}} \times \frac{A_{\text{Al}}}{A_{\text{Mg}}}}{\left(\frac{^{57}\text{Al}}{^{25}\text{Mg}}\right)_{\text{std}}^{\text{measured}}} \quad (1)$$

where Ab^{25}Mg refers to isotopic abundance of ^{25}Mg , and A_{Al} and A_{Mg} refer to atomic weight of Al and Mg, respectively. Standard-sample-standard bracketing and time extrapolation methods were used throughout the analysis. The corrected $^{27}\text{Al}/^{25}\text{Mg}$ ratio was then converted to the $^{27}\text{Al}/^{24}\text{Mg}$ ratio using the nominal $^{25}\text{Mg}/^{24}\text{Mg}$ ratio. Measurements based on ^{26}Mg instead of ^{25}Mg as the denominator in Eq. (1) show very little difference ($<0.3\%$, partly due to the radiogenic effect on ^{26}Mg for CAI samples). Fig. 3b demon-

strates that our technique reproduces the $^{27}\text{Al}/^{24}\text{Mg}$ ratio of USGS standard values to within 0.8%, comparable to or slightly better than $\pm 2\%$ reported by (Bizzarro et al., 2004) using similar technique. All CAI analyses were repeated multiple times and in multiple sessions to ensure there is no systematic error associated with our technique beyond $\pm 0.8\%$.

Both Al and Mn are mono-isotope elements. We have also measured $^{55}\text{Mn}/^{52}\text{Cr}$ with similar method (Moynier et al., 2007), and compared our determinations to the measurements by ICP-OES (optical emission spectrometry, an analytical method different from mass spectrometry) performed by Shukolyukov and Lugmair (2006) on various carbonaceous chondrites. The consistency between two independent methods adds weights and assurance to our methodology.

4.4. Procedures for Pb isotope analyses

For mineral separates of CAI A_{JEF} and A₄₃, we have also performed U–Pb-isotopic analyses (Tables 2, S2 and S5). All fractions

Fig. 3. (a) To determine the reproducibility of the $^{27}\text{Al}/^{24}\text{Mg}$ ratio and the effects of sample matrix on the measured $^{27}\text{Al}/^{24}\text{Mg}$ ratios, the gravimetric Al/Mg metal standard was mixed with different proportions of “CAI-like” matrix. Even with high concentrations of CAI-like matrix, the gravimetric $^{27}\text{Al}/^{24}\text{Mg}$ ratios are reproduced to within $\sim 0.2\%$. (b) The $^{27}\text{Al}/^{24}\text{Mg}$ ratio of USGS standard and other matrix-based standards are reproduced throughout this work to within 0.8%. The figure shows our measured atomic $^{27}\text{Al}/^{24}\text{Mg}$ ratio relative to nominal $^{27}\text{Al}/^{24}\text{Mg}$ ratios of the matrix-based standards.

Table 2
U–Pb data for Allende CAIs *AJEF* and *A43*

CAI	Fraction	U	Pb	$^{206}\text{Pb}/^{206}\text{Pb}$	$^{206}\text{Pb}/^{204}\text{Pb}$	$^{204}\text{Pb}/^{206}\text{Pb}$	$^{204}\text{Pb}/^{206}\text{Pb}$	$^{207}\text{Pb}/^{206}\text{Pb}$	$^{207}\text{Pb}/^{206}\text{Pb}$	Error corr.	$^{207}\text{Pb}^*/^{206}\text{Pb}^*$	$^{207}\text{Pb}^*/^{206}\text{Pb}^*$	$^{238}\text{U}/^{206}\text{Pb}^*$	%	$^{232}\text{Th}/^{238}\text{U}$
		(ppm)	(ppm)	(raw)	(tot.)	(tot.)	%err	(tot.)	%err	4/6–7/6	Date (Ma)	Date err.	Date (Ma)	Discord.	(from Pb)
AJEF	Pyroxene	nd	0.161	1385	2096	4.8E-04	30.5	0.62696	0.092	0.963	4566.8	0.4	nd	nd	5.71
AJEF	Melilite coarse	nd	0.062	602	946	1.1E-03	34.2	0.62946	0.221	0.991	4566.6	0.7	nd	nd	5.72
AJEF	1.8 A m+nm medium-coarse	0.020	0.056	1823	13,490	7.4E-05	402	0.62553	0.184	0.990	4567.7	0.6	4761	–6.0	5.22
AJEF	Pyroxene first wash	0.060	0.161	157	163	6.1E-03	2.78	0.65339	0.091	0.877	4569.6	0.9	4301	8.1	5.41
AJEF	Pyroxene second wash	0.065	0.162	603	798	1.3E-03	23.1	0.63006	0.172	0.950	4565.9	1.0	4340	6.8	5.38
A43	Pyroxene from 0.4–1.1 A	0.058	0.196	2034	2386	4.19E-04	10.1	0.62667	0.038	0.673	4566.7	0.4	4827	–8.1	7.65
A43	0.4–1.1 A mag med-coarse	0.041	0.136	1822	4142	2.41E-04	79.7	0.62648	0.292	0.401	4568.2	3.9	4741	–5.3	7.63
A43	0.4–1.1 A mag med-fine	0.042	0.139	604	845	1.18E-03	28.8	0.62960	0.224	0.695	4565.6	2.7	4663	–3.0	7.78
A43	0.4–1.1 A mag	0.071	0.252	1297	1743	5.74E-04	30.9	0.62700	0.081	0.645	4565.9	1.4	4858	–9.1	8.11

were washed and analyzed, and the quality of the data was evaluated, as described by Amelin (2008). The washing procedure was identical to the second washing scheme of Amelin (2008). The fractions were washed 4–5 times in 0.5 M HNO₃ with ultrasonic agitation during each leaching step. Ultrasonic washes were combined as Wash-1. This was followed by hot acid washing – 6 M HCl and twice in hot 7 M HNO₃, with heating for approximately 1 h on a 120 °C hot plate. Hot washes were combined as Wash-2. A detailed record of raw and processed data is presented in the Electronic Supplemental Table S5.

5. Results

5.1. Mg isotopes

Al–Mg data for CAIs analyzed are reported in Table 1. $^{27}\text{Al}/^{24}\text{Mg}$ ratios and $\delta^{26}\text{Mg}^*$ compositions in the measured CAIs are in the range of 0.11–8.53, and 0.052–3.224, respectively. The whole-rock and micro-drilled samples of Type B and Type A CAIs yield a well-defined $^{26}\text{Al}/^{27}\text{Al}$ slope of $(5.23 \pm 0.13) \times 10^{-5}$ with an intercept of $\delta^{26}\text{Mg}^*_i = -0.040 \pm 0.029$ (Fig. 4a). Including the respective mineral separates data of selected CAIs (A44A, AJEF, and A43) gives a single slope with $(^{26}\text{Al}/^{27}\text{Al})_0 = (5.11 \pm 0.14) \times 10^{-5}$ and intercept $\delta^{26}\text{Mg}^* = -0.020 \pm 0.034$ (Fig. 4b). Our results are consistent with the “canonical” $(^{26}\text{Al}/^{27}\text{Al})_0$ of $\sim 5 \times 10^{-5}$ for the Solar System (Lee et al., 1977; MacPherson et al., 1995; MacPherson, 2007) and do not support the supra-canonical $^{26}\text{Al}/^{27}\text{Al}$ ratio (Galy et al., 2004; Bizzarro et al., 2004, 2005; Taylor et al., 2005; Young et al., 2005; Thrane et al., 2006). Moreover, the initial $\delta^{26}\text{Mg}^*$ of the CAI isochron is consistent within error with Mg-isotopic homogeneity in the Solar System expected from our measured $(^{26}\text{Al}/^{27}\text{Al})_0$ ratio for the CAIs and bulk solar $^{27}\text{Al}/^{24}\text{Mg}$ ratio. Two CAIs, A60 (extensively altered, fluffy Type A, see Fig. S5) and AM10-21-CAI-2 (no primary CAI minerals), are displaced by $\sim 3\sigma$ below the isochron. The two outliers both show evidence of extensive secondary alteration compared to the other more pristine CAIs that fall on the main slope and are therefore not included in the final regression.

Our new results for CAI whole-rock fragments, mineral separates, and micro-drilled CAIs are in excellent agreement with the data originally reported by Bizzarro et al. (2004; Fig. 5a), but disagree with both the revised data presented in a corrigendum by Bizzarro et al. (2005) as well as recent new data in Thrane et al. (2006) (Fig. 5b). A combined slope of ^{26}Al – ^{26}Mg isochron in Allende CAIs from Bizzarro et al. (2004) and this study yields a $^{26}\text{Al}/^{27}\text{Al}$ ratio of $(5.12 \pm 0.15) \times 10^{-5}$ and intercept $\delta^{26}\text{Mg}^* = -0.018 \pm 0.020$ (Fig. 5a). The revised slope of Bizzarro et al. (2005) and the new data of Thrane et al. (2006) is a factor of 1.11 higher than in Bizzarro et al. (2004), and a factor of 1.12 ± 0.03

higher than the slope reported here (Fig. 4a). The significance of this factor will be discussed further in Section 6.2.

Three internal ^{26}Al – ^{26}Mg mineral isochrons measured on mineral separates from CAIs A44A, AJEF, and A43 are shown in Figs. 6a–c. All three mineral isochrons are internally consistent and yield well-defined slopes suggesting closure of the ^{26}Al – ^{26}Mg system in the minerals at the same point in time within the margin of error. Both A44A and AJEF yield mineral isochrons $[(5.03 \pm 0.18) \times 10^{-5}]$, and $(4.96 \pm 0.25) \times 10^{-5}$, respectively, Fig. 6a,b) that are within error consistent with the canonical $^{26}\text{Al}/^{27}\text{Al}$ ratio determined for the whole-rock CAIs (Fig. 4a). The mineral isochron for A43 (Fig. 6c) has a slightly shallower slope of $(4.47 \pm 0.42) \times 10^{-5}$ that is outside error of our whole-rock isochron slope. Whether this reflects a younger crystallization age or secondary thermal resetting of the ^{26}Al – ^{26}Mg system in the minerals of A43 is not clear. It is apparent that the mineral isochron for A43 suffers from the lower spread in $^{27}\text{Al}/^{24}\text{Mg}$ ratios (2.19–3.21) and $\delta^{26}\text{Mg}^*$ (0.793–1.106‰), compared to the mineral isochrons of A44A (2.24–6.70 and 0.817–2.462‰) and AJEF (2.23–4.55 and 0.762–1.598‰).

Our data for the micro-drilled sample of AM10-21-CAI-1 are consistent with the ^{26}Al – ^{26}Mg systematics of the whole-rock fragments and mineral separates with a canonical $(^{26}\text{Al}/^{27}\text{Al})_0$ (Fig. 4). We have thus demonstrated that sampling scale of CAIs (fragments vs. micro-drilling) cannot explain the discrepancy between the canonical and supra-canonical $^{26}\text{Al}/^{27}\text{Al}$ ratios (Fig. 5a, b). Both sampling techniques reported here give a slope indistinguishable from each other. Therefore, it would be incorrect to argue that the current disparity between the slopes of ^{26}Al – ^{26}Mg fossil isochrons is due to the sampling bias (Young and Shahar, 2007).

5.2. Pb isotopes

Measured U and Pb concentrations and isotopic ratios are reported in Table 2. A detailed record of raw and processed data is presented in the Electronic Supplemental Table S5.

The concentration of U in acid-washed fractions, reported relative to the total weights of fractions before leaching, between 20 and 71 ppb, and Pb concentrations between 56 and 252 ppb, are similar to the values reported previously for Allende and Efremovka CAIs (Chen and Tilton 1976; Tatsumoto et al., 1976; Chen and Wasserburg, 1981; Amelin et al., 2002; Connelly et al., 2008). Pb-isotopic compositions in the residues are rather radiogenic, with measured $^{206}\text{Pb}/^{204}\text{Pb}$ of 602–2034 and blank-corrected $^{206}\text{Pb}/^{204}\text{Pb}$ of 845–13,490.

Pb-isotopic data are plotted in a $^{207}\text{Pb}/^{206}\text{Pb}$ vs. $^{204}\text{Pb}/^{206}\text{Pb}$ isochron diagram in Fig. 7a. Acid-washed fractions from both CAIs and the pyroxene second wash from AJEF plot on a single isochron, corresponding to the age of 4567.44 ± 0.34 Ma. Separate isochron regressions for AJEF and A43 yield the dates of 4567.60 ± 0.36 Ma, MSWD (mean square

of weighted deviates)=1.6, and 4567.5 ± 1.4 Ma, MSWD=0.60, respectively, identical to the age given by the combined isochron. These dates also agree, within error, with the ages of the recently dated CAIs from Efremovka and Allende (Amelin et al., 2002, 2006; Connelly et al., 2008).

U–Pb data are plotted in a concordia diagram in Fig. 7b. All data show moderate discordance of less than 10%. The residues are reversely discordant (i.e., their $^{206}\text{Pb}^*/^{238}\text{U}$ dates are older than $^{207}\text{Pb}^*/^{235}\text{U}$ and $^{207}\text{Pb}^*/^{206}\text{Pb}^*$ dates), whereas the washes are normally discordant. Including or excluding the data point of the first wash has only a small effect on the regression. The upper intercept dates are identical, within

Fig. 4. a) ^{26}Al – ^{26}Mg isochron diagram for bulk CAIs fragments (red squares) from the Allende CV3 meteorite and micro-drilled CAIs samples (blue squares) from two Allende slabs. The best-fit line yields a $^{26}\text{Al}/^{27}\text{Al}$ slope of $(5.23 \pm 0.13) \times 10^{-5}$ with an intercept $\delta^{26}\text{Mg}^*_I = -0.040 \pm 0.029$ (all regression we report in this paper is based on York's original algorithm, i.e. Model 1 fit of Ludwig 2003). A60 "fluffy" Type A CAI and AM10-21 CAI-2 are both extensively altered samples (see text in Section 2 and supplementary Fig S5), clearly plotting off the isochron. Hence, these two data were excluded from the regression. Also shown is AM5-63 RI-1, an olivine- and pyroxene-rich inclusion. Due to the uncertainty of the nature of AM5-63 RI-1 (extremely low $^{27}\text{Al}/^{24}\text{Mg}$ precludes it being a typical CAI), it was not included in the regression. b) ^{26}Al – ^{26}Mg isochron diagram for bulk CAIs fragment (red squares), micro-drilled CAIs samples (blue squares) and mineral separates (yellow squares). The best-fit line yields a $^{26}\text{Al}/^{27}\text{Al}$ slope of $(5.11 \pm 0.14) \times 10^{-5}$ with an intercept $\delta^{26}\text{Mg}^*_I = -0.020 \pm 0.034$ (Mean Square of Weighted Deviates, MSWD=3.2). Excluding A43 mineral separates data (see Fig. 6c and text for details) from the composite isochron makes no significant difference in the slope, intercept and MSWD [$(^{26}\text{Al}/^{27}\text{Al})_0 = (5.13 \pm 0.12) \times 10^{-5}$, with an intercept $\delta^{26}\text{Mg}^*_I = -0.024 \pm 0.040$, and MSWD=3.3]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fig. 5. ^{26}Al – ^{26}Mg systematics in CAIs from the Allende CV3 carbonaceous chondrite. a) Summary of data from Bizzarro et al. (2004) and the current study. The red squares are from this study, which includes CAI whole-rock fragments, mineral separates, and micro-drilled inclusions. The blue diamonds are from Bizzarro et al. (2004). The precision for both $^{27}\text{Al}/^{24}\text{Mg}$ and $\delta^{26}\text{Mg}^*$ (* denotes the radiogenic ^{26}Mg component, as deviations in parts per 1000 from a terrestrial standard) is comparable in both studies. The plot shows excellent agreement between the current study and the original data of Bizzarro et al. (2004). b) Summary of data from Bizzarro et al. (2005), as reported in the corrigendum, Thrane et al. (2006), and the current study. In contrast to Fig. 5a, the systematic difference in the slope is apparent. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

error, to the Pb–Pb isochron dates. The lower intercept dates are zero, suggesting that the fractionation between U and radiogenic Pb occurred recently, possibly during washing.

6. Discussions

6.1. Note on the choice of exponent β for fractionation correction

As the choice of the exponent β used for fractionation correction in the mass spectrometry measurement affects the calculated slope of $^{26}\text{Al}/^{27}\text{Al}$ from the ^{26}Al – ^{26}Mg isochron diagram, it is essential to use the same and appropriate β when comparing with the literature data, in order to be consistent and to avoid confusion between different works using different β .

Fig. 6. Internal isochrons of mineral separates and whole-rock fragments from Allende CAI A44A, AJEF, and A43.

In order to obtain a precise measurement of radiogenic excess of $^{26}\text{Mg}^*$, mass dependent isotopic fractionation of Mg must be corrected, or prevented. Isotopic fractionation of Mg could occur in three different settings. (a) Chemical separation of Mg on ion exchange column can cause fractionation (e.g. Chang et al., 2003). This is avoided by ensuring a full 100% recovery of Mg, which was achieved throughout this work; (b) An isotopic fractionation is also caused by instrumental mass discrimination on the MC-ICP-MS. This fractionation is monitored and effectively corrected for by using the standard-sample-standard bracketing technique where the sample and standard are analyzed in identical conditions, and the fractionation determined from the standard analyses is applied to the samples, with appropriate interpolation. (c) Finally and most importantly, the fractionation could occur in nature during the CAI formation through evaporation and condensation processes in the early solar nebula.

We obtained the best fit to the ^{26}Al – ^{26}Mg data (Fig. 8) if we use the kinetic exponential fractionation law, where the fractionation factor $\beta = \ln(m_1/m_2)/\ln(m_1/m_3) = 0.511$ (Russell et al., 1978; Young et al., 2002), to correct for this fractionation. We have used different exponents, e.g., using $\beta = (1/m_1 - 1/m_2)/(1/m_1 - 1/m_3) = 0.521$ (the equilibrium fractionation factor), $\beta = (m_1^{-0.5} - m_2^{-0.5})/(m_1^{-0.5} - m_3^{-0.5}) = 0.516$ (Rayleigh distillation), $\beta = 0.517$ (determined on ^{26}Al -free, Mg-rich chondrules; UC Davis unpublished), or $\beta = 0.514$ (experimentally determined by vacuum evaporation of CAI-like material; Davis et al., 2005). Correcting for fractionation in our data, or in the data published by Bizzarro et al. (2004, 2005) and Thrane et al. (2006) using the β value other than 0.511 causes substantial deterioration in quality of the $\delta^{26}\text{Mg}^*$ vs. $^{27}\text{Al}/^{24}\text{Mg}$ linear fits (Fig. 8). Online supplementary Figs. S9–12 illustrate the sensitivity to the choice of beta factors for the whole-rock CAIs (Fig. S9), the A44A mineral isochron (Fig. S10), the AJEF mineral isochron (Fig. S11), and the A43 mineral isochron (Fig. S12), respectively.

Fig. 7. (a) $^{207}\text{Pb}/^{206}\text{Pb}$ vs. $^{204}\text{Pb}/^{206}\text{Pb}$ isochron diagram for acid-washed pyroxene, melilite and bulk rock fractions and a second (hot acid) wash of the pyroxene fraction from the CAIs AJEF (red) and A43 (blue). Data-point error ellipses are 2σ . (b) U–Pb concordia diagram for acid-washed pyroxene, melilite and bulk rock fractions and washes of the pyroxene fraction from the CAIs AJEF and A43. Data-point error ellipses are 2σ . The data points of the residues plot above concordia; data points of the washes are below concordia. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fig. 8. The effects on the calculated $^{26}\text{Al}/^{27}\text{Al}$ (the slope and its uncertainty in these diagrams) as well as the intercept using different mass fractionation factors ($\beta=0.511, 0.514, 0.521$). Panels on left and right columns are for all the data from this study, and those of Thrane et al. (2006), respectively.

The reason for this degradation is simply because the rotation (change of β) on the three-isotope plot of Mg, resulting from different fractionation “laws” (affecting the calculated $\delta^{26}\text{Mg}^*$ value), is independent of $^{27}\text{Al}/^{24}\text{Mg}$ ratio in the fossil isochron diagram. Note that the slope in the three Mg-isotope plot, in logarithmic form $\delta^{25}\text{Mg}'$ vs. $\delta^{26}\text{Mg}'$, defines β for $\alpha_{25/24} = \alpha_{26/24}^\beta$ where $\delta^x\text{Mg}' = \ln[(^x\text{Mg}/^{24}\text{Mg})_{\text{sample}} / (^x\text{Mg}/^{24}\text{Mg})_{\text{DSM-3}}] \times 1000$, $\alpha_{x/24} = (^x\text{Mg}/^{24}\text{Mg})_{\text{sample}} / (^x\text{Mg}/^{24}\text{Mg})_{\text{DSM-3}}$ and x refers to ^{25}Mg or ^{26}Mg (Young and Galy, 2004). In agreement with Bizzarro et al. (2004), we conclude that $\beta=0.511$ is the best value to describe the CAI data. The fact that the exponential law gives the best fit to the CAI data implies that kinetic fractionation is probably responsible for Mg-isotope fractionation for the majority of CAIs investigated by Bizzarro et al. (2004), Thrane et al. (2006) and this study. Contrary to Davis et al. (2005), Mg evaporation experiments performed by Nagahara's group at the University of Tokyo (c.f. Young et al., 2002) gave $\beta=0.510$, which is very close to $\beta=0.511$ used here. Davis et al. (2005) obtained $\beta=0.5139 \pm 0.0005$ from their vacuum furnace evaporation experiments of CAI-like composition, while the $^{26}\text{Mg}^*$ -free FUN inclusion (one of the kind CAI with

Fractionation and Unidentified Nuclear anomalies) give $\beta=0.513 \pm 0.009$. It is not clear to what extent the laboratory experiment applies to CAI evaporations in the early solar nebula. The heavily fractionated FUN inclusion with no radiogenic $^{26}\text{Mg}^*$ may be more suitable to derive a β -factor for the CAIs in general, but requires a more precise measurement than $\beta=0.513 \pm 0.009$, as the uncertainty covers the full range depicted in Fig. 8. Instead we argue that the solution can be found with the experiment nature did for us (i.e. Fig. 8). The best-fit regression using a $\beta=0.511$ thus strongly argues for a dominantly kinetic Mg-isotope mass fractionation during CAI formation. Nevertheless, it is important that the same β -factor is used in the discussion of canonical vs. supra-canonical $^{26}\text{Al}/^{27}\text{Al}$ ratio. The point is highlighted in Fig. 8. The problem becomes acute when comparing two sets of high-precision Mg-isotope data with low Al/Mg ratio between MC-SIMS and MC-ICP-MS data, as the SIMS community generally uses $\beta=0.514$ (e.g. Davis et al., 2005; Taylor et al., 2005) while the MC-ICP-MS community prefers $\beta=0.511$ (Bizzarro et al., 2004, 2005; Thrane et al., 2006; Baker, 2007; and this work).

6.2. Discrepancy between “canonical” and “supra-canonical” ($^{26}\text{Al}/^{27}\text{Al}$)₀ ratio

If our data, and the data of Bizzarro et al. (2005) and Thrane et al. (2006) (Fig. 5b) are both correct, then the difference between the isochron slopes points to two major thermal events in the solar nebula separated by 142 ± 31 Ka. However, this interpretation appears improbable, considering that all our CAI samples in this study and those in (Bizzarro et al., 2004, 2005) are from the same meteorite, Allende (CV3), and it is highly unlikely to posit two distinct populations of CAIs characterized by different $^{26}\text{Al}/^{27}\text{Al}$ ratios, one population analyzed by Bizzarro and co-workers and the other by us, with no intermingling. For the same reason, the possibility that the discrepancy highlighted in Fig. 5b is due to ^{26}Al heterogeneity in the solar nebula can be ruled out. The CAIs studied by Bizzarro et al. (2004, 2005) and by us must belong to the same population of refractory inclusions. We therefore conclude that the observed discrepancy is more likely due to analytical artifacts, rather than natural causes.

The first possibility of analytical artifact is a distortion of the Al/Mg ratios due to matrix effects. The Al/Mg ratios measured in both Bizzarro et al. (2004, 2005) and Thrane et al. (2006) were determined with a desolvating nebulizer with no critical evaluation of the matrix effects (i.e., the presence of Ca and Ti) on measured Al/Mg (J. Baker, pers. comm.). Tests done by Baker (2007) and Schiller et al. (2007) show that these effects can be severe and result in lowering Al/Mg ratios in standards doped with Ca (i.e., to make CAI-like material). However, if this were the source of discrepancy between our results and those of Bizzarro et al. (2005) and Thrane et al. (2006), we would expect more scatter in their data, variable with the amount of Ca, rather than a well-defined isochron slope, precisely higher by a factor of 1.12 ± 0.03 than ours. We thus consider this explanation for the “steeper” isochron in those previous studies unlikely.

The second possibility, that the difference in slope is an artifact arising from procedures in data reduction algorithm, must be critically evaluated. In a corrigendum, Bizzarro et al. (2005) point out that the $^{27}\text{Al}/^{24}\text{Mg}$ ratios in their original paper (Bizzarro et al., 2004) have omitted a constant factor of 1.11, resulting in the systematic downward revision of $^{27}\text{Al}/^{24}\text{Mg}$ by the constant factor of 1/1.11, which happens to be $A_{\text{Mg}}/A_{\text{Al}}$ shown in the Eq. (1). Without this correction, the difference in slope in Fig. 5b would disappear within error (1.11 vs. 1.12 ± 0.03) (Fig. 5a). With the corrigendum (Bizzarro et al., 2005), the difference in slope in Fig. 5b becomes apparent. This apparent error (Bizzarro et al., 2005) leads to an 11% increase in the inferred initial abundance of ^{26}Al . Our new data from this study, however, fail to reproduce the revised, supra-canonical $^{26}\text{Al}/^{27}\text{Al}$ initial value (Fig. 5b).

To resolve the discrepancy through bilateral sample exchange and careful calibration against standards, six digested aliquots of our bulk Allende CAIs (A33, A39, A43, A44A, A60, AJEF) were provided to Martin Bizzarro. Al/Mg ratios were measured on these aliquots by ICP-MS at Victoria University of Wellington (New Zealand). After chemical processing to purify Mg, Mg-isotope ratios were measured in the same laboratory on a *NU Plasma HR* MC-ICP-MS, an instrument identical to the one used in this study. Data for the five unaltered CAIs (A33, A39, A43, A44A, AJEF) define an isochron with an initial ($^{26}\text{Al}/^{27}\text{Al}$)₀ = $(4.73 \pm 0.28) \times 10^{-5}$ and $\delta^{26}\text{Mg}^*$ intercept = $+0.029 \pm 0.057$ (J. Baker, pers. comm., and Town et al., 2007 and the presentation at the Kauai meeting). These data are completely consistent with a regression through our data for these same CAIs, which define an initial ($^{26}\text{Al}/^{27}\text{Al}$)₀ = $(4.98 \pm 0.27) \times 10^{-5}$ and $\delta^{26}\text{Mg}^*$ intercept = $+0.007 \pm 0.053\%$ (Jacobsen et al., 2007a). Because the aliquots of CAIs used in Bizzarro et al. (2004) and Thrane et al. (2006) were no longer available (M. Bizzarro, pers. comm.), we have not been able to do the vice versa experiments on their “supra-canonical” samples.

We thus face an odd situation where every single CAIs examined by Bizzarro et al. (2004, 2005) and Thrane et al. (2006) from all four CV chondrites (Allende, Vigarano, NWA 779, and SAH 98044) plot precisely on the slope of $^{26}\text{Al}/^{27}\text{Al} = (5.85 \pm 0.05) \times 10^{-5}$, without a single deviation outside the very small error of 0.85% of the slope in Thrane et al. (2006). Whereas no such data have been reproduced. The majority of the new

CAI samples examined by us and by several other laboratories (Jacobsen et al., 2007a,b; Jacobsen et al., 2008b; Teng et al., 2007; Town et al., 2007; Yin et al., 2008; Kita et al., 2007; Makide et al., 2007) yield slopes consistent with initial $^{26}\text{Al}/^{27}\text{Al}$ value of $\sim 5 \times 10^{-5}$.

6.3. Significance of “whole-rock” and “mineral” isochrons from this study

For any given pristine igneous rock, such as most common type CAIs, all mineral isotopic clocks would give the same age, and a whole-rock isochron (controlled by variations in the abundance of primary minerals) would give that same age. If we consider a CAI analogous to an “igneous complex”, then sampling fragments or drill cores would be equivalent to “whole-rock” sampling in traditional terrestrial geochronology. If CAIs formed by melting aggregates of early nebula condensates, instead of splashes of melt from some very early asteroid, then a “multi-whole-rock CAI” isochron would date Al/Mg fractionation in the solar nebula. In mineralogical terms, this would mean condensation of Al-rich phases, and their partial separation from the gas made of more volatile elements. The “CAI-isochron”, defined by whole-rock fragments of individual CAIs, suggests that all CAIs we have studied are co-genetic igneous objects derived from a “magmatic” system in the early solar nebula, within an uncertainty of ± 20 Ka.

Another possibility is that fractionation of Al and Mg in bulk CAIs is a result of partial evaporation of Mg during melting event(s). If this were the case, then a “multi-CAI” isochron would give the timing of that heating event(s). It may be unrelated to the timing of condensation. It is important to stress, however, that a process responsible for Al–Mg fractionation, whether it is condensation or evaporation, pre-dates the crystallization of the CAI melt. This means that a “multi-CAI” isochron always gives an older age than a mineral isochron, even for a pristine CAI, where a mineral isochron at any sampling level dates the crystallization of the melt. If a “multi-CAI” isochron for a collection of pristine CAIs, and mineral isochrons for the same CAIs, give the same age within error, then we have a proof that the timing between elemental fractionation and final melting and recrystallization of CAI materials was short, less than our isochron age errors. Such a situation is clearly established from our study (Figs. 4 and 6).

If the rock was heated at a later stage, and radiogenic isotope diffused out of primary minerals rich in parent isotope, then we can expect to see various patterns depending on the nature of the secondary events:

- 1) If the heating episode was fast (instantaneous at the scale of radioactive decay) but intensive (the temperature was high enough to re-equilibrate the distribution of radiogenic isotope, e.g. $^{26}\text{Mg}^*$, between adjacent mineral grains), then the mineral isochrons obtained by analyzing mineral separates, individual grains, grain fragments or ion microprobe spots would all give the age of this secondary event, whereas a “whole-rock” (in our case a “CAI fragment” isochron) would still give the primary age, if the “whole-rock” specimens include many mineral grains, which is the case given our sample size for the fragments range from 11–25 mg.
- 2) If a similar heating episode occurred after complete decay of the parent isotope, then mineral isochrons (for an extinct nuclide chronometer) at all scales of sampling would be horizontal – that is, the Mg-isotopic composition would be uniform among minerals. Isotopic heterogeneity may still be preserved at the scale of CAI fragments if these fragments are much larger than the mineral grains. This scenario is not observed, and is supported neither by our data, nor by the data of Bizzarro et al. (2004, 2005).
- 3) If the isotopic re-equilibration driven by diffusion was incomplete, then we can expect to see gradients of apparent ages across the minerals with high Al/Mg ratios (e.g., hibonite, anorthite, melilite), as predicted by the diffusion formalism and actually observed, for example, for ^{40}Ar in mica (c.f. Smith et al., 2005 and references therein). In this case, ion microprobe spot analyses may allow us to get the secondary age and possibly to reconstruct diffusion

parameters; whole-rock fragments will give the primary age, and mineral separates will give an apparent age intermediate between the timing of crystallization and secondary event. The issue is discussed in B. Jacobsen et al. (2008a) with high spatial resolution MC-SIMS data obtained for the same suite of samples.

6.4. Anchoring $^{26}\text{Al}/^{27}\text{Al}$ onto an absolute timescale

Combining our Mg and Pb isotope results from the same suite of CAI samples allows us to anchor the precisely determined $(^{26}\text{Al}/^{27}\text{Al})_0 = (5.11 \pm 0.14) \times 10^{-5}$ to an absolute ^{207}Pb – ^{206}Pb age of 4567.4 ± 0.34 Ma at the very beginning of the Solar System (or to be more technically accurate, $^{26}\text{Al}/^{27}\text{Al}$ ratio of $(4.96 \pm 0.25) \times 10^{-5}$ anchored on Pb–Pb age of 4567.60 ± 0.36 My, as both sets of the data are obtained on the same CAI – A/JEF mineral separates). It is a step forward over the earlier less precise results of $(^{26}\text{Al}/^{27}\text{Al})_0 = (4.63 \pm 0.44) \times 10^{-5}$ and 4567.2 ± 0.6 Ma obtained for Efremovka CAIs (Amelin et al., 2002). Compared to the angrite age-anchor, D'Orbigny (Amelin, 2008), the ^{207}Pb – ^{206}Pb age difference is 3.18 ± 0.38 Ma, while the ^{26}Al – ^{26}Mg age difference is 4.85 ± 0.07 Ma, if we use $^{26}\text{Al}/^{27}\text{Al}$ ratio for D'Orbigny obtained by Spivak-Birndorf et al. (2005). If we use Nyquist et al. (2003) value of $^{26}\text{Al}/^{27}\text{Al}$ ratio obtained for D'Orbigny and Sahara angrites, the ^{26}Al – ^{26}Mg age difference gets even bigger (5.69 ± 0.45 Ma). There is a discrepancy of 1.57–2.51 Ma between the two clocks, an area that requires resolution with future work.

6.5. Implications for the extinct radioactivities in the early Solar System

Accurate knowledge of the Solar System initial $^{26}\text{Al}/^{27}\text{Al}$ ratio is crucial if we are to use CAIs as the “time zero” age-anchor to guide future work with other short-lived radio-chronometers, such as the ^{41}Ca – ^{41}K system ($t_{1/2} = 0.1$ Ma). Well-established abundances of ^{26}Al and ^{41}Ca will significantly limit the possible sources of ^{41}Ca , ^{26}Al and other short-lived radionuclides in the early Solar System (energetic particle irradiation near the proto-Sun (e.g., Shu et al., 1996; Gounelle et al., 2006) vs. injection from nearby stars (e.g., Sahijpal et al., 1998; Wasserburg et al., 2006). Differences between the canonical and supra-canonical $^{26}\text{Al}/^{27}\text{Al}$ ratios have led some authors to increase the solar initial $^{41}\text{Ca}/^{40}\text{Ca}$ ratio by a factor of 26 to accommodate the ^{41}Ca overproduction problem encountered in the X-wind model (Gounelle et al., 2006). However, the tightly constrained initial $^{26}\text{Al}/^{27}\text{Al}$ ratio reported here, with an age uncertainty of only 20 Ka (Fig. 5), provides little support for this suggestion.

The tight spread in $^{26}\text{Al}/^{27}\text{Al}$ ratio in both whole-rock and mineral separate of Allende CAIs from our work limits the X-wind model (Shu et al., 2001) as the origin of ^{26}Al due to early solar irradiation, unless the impulsive solar flare events were operational only for < 20 Ka. It is implicit in the X-wind model that ^{26}Al distribution in the early Solar System would be heterogeneous and highly variable.

6.6. Variable κ value and the mean age of CAI precursor materials.

Model $^{232}\text{Th}/^{238}\text{U}$ ratios (κ values, Table 2) are calculated from radiogenic $^{208}\text{Pb}^*/^{206}\text{Pb}^*$ ratios and $^{207}\text{Pb}^*/^{206}\text{Pb}^*$ dates. The κ values are between 5.2 and 5.7 for the CAI A/JEF, and between 7.6 and 8.1 for A43, compared to average solar value of 3.77 (Lodders, 2003). Variations in the κ values among the minerals, or between residues and washes, in a single CAI, are much smaller than the variations between the CAIs. This suggests that the most significant U/Th fractionation occurred prior to formation of the CAIs. Considering high condensation temperatures of U and Th (Lodders, 2003), this interpretation suggests the presence of heterogeneous chemical reservoirs, not related with high temperature evaporation, in the early solar nebula. These distinct chemical reservoirs are possibly related to the isotopically distinct reservoirs in the early Solar System, argued for by Loss et al. (1994). Association of chemical heterogeneities in the inner solar nebula with ISM dust composition was argued by Yin (2005).

How the redox state changes within the early solar nebula could affect U/Th distribution needs to be critically evaluated. If the U/Th variation in the CAIs indeed reflects primordial chemical heterogeneity before CAI formation, we can calculate the mean age of the interstellar dust reservoirs from which CAI A/JEF and A43 condensed from, using the following equation (Cayrel et al., 2001; Frebel et al., 2007):

$$T_{\text{ISM}} = 21.8 * [\log (U/Th)_0 - \log (U/Th)_{\text{obs}}] \quad (2)$$

where T_{ISM} is expressed in Ga (billion years), and $(U/Th)_0$ is the production ratio (Cowan, 1999), and $(U/Th)_{\text{obs}}$ is $1/\kappa$ from this study. Our calculated T_{ISM} range from 10.0–10.9 Ga and 13.6–14.2 Ga, corresponding the two populations of the observed κ values, respectively. This is entirely consistent with the astronomical observation of U/Th ratio in extremely old metal poor stars and the derived age of the Galaxy of 10.3 and 14.0 Ga (Cayrel et al., 2001; Frebel et al., 2007). The meteoritic κ values can be determined much more precisely typically by orders of magnitude than astronomical observation of $(U/Th)_{\text{obs}}$, with a typical error margin of ~ 3 Ga for the calculated T_{galaxy} (Cayrel et al., 2001). Such an exercise, however, is subject to uncertainty in the theoretical production ratio of $(U/Th)_0$ in the supernova models (Cowan, 1999).

7. Conclusions

^{26}Al – ^{26}Mg -isotope systematics can be used to constrain the timing of evaporation and condensation events, recorded in bulk CAI data, and the timing of melting and crystallization events, recorded in data for primary igneous minerals (i.e., whole-rock vs. internal mineral isochrons). We have obtained ^{26}Al – ^{26}Mg -isotopic data in multiple bulk CAIs from Allende, and mineral separates from three of these CAIs (coarse-grained Type B CAI A44A, A/JEF and A43). The internal mineral isochrons yield initial $^{26}\text{Al}/^{27}\text{Al}$ ratios indistinguishable within analytical uncertainty from the value inferred from our bulk Allende CAI measurements, with a marginal exception for A43. Based on these observations, we infer that the formation of Allende CAIs, including processes of evaporation, condensation, melting and crystallization, occurred over a very short time interval. This period probably did not exceed ± 20 Ka, and could be as short as ± 8 Ka years (Thrane et al., 2006; Kita et al., 2007). Our new data underscore the need to understand more quantitatively the extent to which the deviations from an isochron often found with *in-situ* measurement techniques (laser ablation MC-ICP-MS and ion microprobe) reflect spatially localized diffusion and transport of Mg isotopes. Comparing internal isochrons obtained by *in-situ* methods are complicated for Allende CAIs because secondary alteration can disturb the ^{26}Al – ^{26}Mg system on a micron scale. However, local micron scale alteration does not affect bulk mineral separates in this study as the sampling scale differs by six-orders of magnitude by mass. Kita et al. (2007) obtained a well-defined Al–Mg isochron, using *in-situ* MC-SIMS method in a pristine CAI from Leoville, which is consistent with the data obtained in this study.

We also conclude that an analytical artifact or an error in the algorithm of the data reduction procedure as shown in Eq. (1) and Bizzarro et al. (2005 corrigendum) is the most likely explanation for the current disparity between canonical and supra-canonical initial $(^{26}\text{Al}/^{27}\text{Al})_0$ ratio in the Solar System between our data and that of Bizzarro et al. (2005) and Thrane et al. (2006).

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.epsl.2008.05.003.

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