Magnesium isotopic fractionation in chondrules from the Murchison and Murray CM2 carbonaceous chondrites

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Abstract–We present high-precision measurements of the Mg isotopic compositions of a suite of types I and II chondrules separated from the Murchison and Murray CM2 carbonaceous chondrites. These chondrules are olivine- and pyroxene-rich and have low $^{27}Al/^{24}Mg$ ratios (0.012–0.316). The Mg isotopic compositions of Murray chondrules are on average lighter ($\delta^{26}Mg$ ranging from $-0.95‰$ to $-0.15‰$ relative to the DSM-3 standard) than those of Murchison ($\delta^{26}Mg$ ranging from $-1.27‰$ to $+0.77‰$). Taken together, the CM2 chondrules exhibit a narrower range of Mg isotopic compositions than those from CV and CB chondrites studied previously. The least-altered CM2 chondrules are on average lighter (average $\delta^{26}Mg = -0.39 \pm 0.30‰$, 2SE) than the moderately to heavily altered CM2 chondrules (average $\delta^{26}Mg = -0.11 \pm 0.21‰$, 2SE). The compositions of CM2 chondrules are consistent with isotopic fractionation toward heavy Mg being associated with the formation of secondary silicate phases on the CM2 parent body, but were also probably affected by volatilization and recondensation processes involved in their original formation. The low-Al CM2 chondrules analyzed here do not exhibit any mass-independent variations in ^{26}Mg from the decay of ^{26}Al, with the exception of two chondrules that show only small variations just outside of the analytical error. In the case of the chondrule with the highest Al/Mg ratio (a type IAB chondrule from Murchison), the lack of resolvable ^{26}Mg excess suggests that it either formed >1 Ma after calcium-aluminum-rich inclusions, or that its Al-Mg isotope systematics were reset by secondary alteration processes on the CM2 chondrite parent body after the decay of ^{26}Al.

INTRODUCTION

Chondrules are millimeter-sized igneous spherules that formed shortly after the oldest known solids in the solar system (i.e., the Ca-, Al-rich refractory inclusions or CAIs), and witnessed the first stages of accretion and melting in the solar nebula (Wood 1963). They constitute approximately 10–80% by volume of ordinary, enstatite, and carbonaceous chondrites. Chondrules were formed by flash heating (perhaps associated with episodic shock processes in the solar nebula; Desch and Connolly 2002; Morris and Desch 2010) of solid precursors, followed by rapid cooling (1–1000 °C hr^{-1}) and crystallization

(Hewins et al. 1996, 2005; Wick and Jones 2012). It is generally inferred that they formed in a dusty nebular environment (Jones et al. 2005), but it has also been suggested that they may have an impact (Bunch et al. 1991; Krot et al. 2005a; Fedkin et al. 2012; Grossman et al. 2012) or a planetary origin (Libourel and Chaussidon 2011). The processes and time scales that led to the formation of chondrules and CAIs place important constraints on the lifetime of the solar protoplanetary disk and on their relationship to the accretion of larger bodies such as planetesimals and planets. Investigation of the magnesium isotopic compositions of chondrules can place stringent constraints on the timing and processes

(such as evaporation, condensation, or secondary alteration) involved in their formation and accretion into chondrite parent bodies.

Magnesium has three stable isotopes: ^{24}Mg, ^{25}Mg, and ^{26}Mg, which have been known to fractionate by up to a few per mil/amu during processes occurring in the natural environment. Additionally, ^{26}Mg excesses (^{26}Mg*) from the decay of live ^{26}Al (half-life approximately 0.73 Ma) may be detectable in samples that formed within approximately five half-lives of the synthesis of this short-lived radionuclide in the early solar system (Lee et al. 1976). As such, the ^{26}Al-^{26}Mg chronometer is capable of providing high time resolution for events, such as chondrule formation, that occurred within the first approximately 5–6 Ma of solar system history (e.g., Kita et al. 2000; Villeneuve et al. 2009). When combined with Pb-Pb chronometry, the relative ages from the ^{26}Al-^{26}Mg chronometer can be mapped to an absolute time scale using a chronological anchor such as CAIs or basaltic achondrites (e.g., Amelin et al. 2010; Bouvier and Wadhwa 2010; Bouvier et al. 2011).

Most previous measurements of the stable isotopic compositions of chondrules have been made on samples from the CV3 chondrites. Isotopic variations have been reported for moderately volatile elements such as Mg (Galy et al. 2000; Young et al. 2002a; Bizzarro et al. 2004), Si and Fe (Molini-Velsko et al. 1986; Georg et al. 2007; Hezel and Palme 2010), as well as for more refractory elements such as Sr (Patchett 1980; Moynier et al. 2010) and Eu (Moynier et al. 2006). The stable isotopic data for chondrules bring new insights into the compositions of their precursors in the solar nebula, and the fractionation processes that they underwent during their formation and subsequently on chondrite parent bodies. We present here the first report of Mg isotopic compositions of 23 chondrules from two CM2 chondrites, Murchison and Murray. The CM2 chondrites have experienced aqueous alteration at low temperature without being subjected to the thermal metamorphism and large planetary scale impact processes inferred for the CV and CB chondrite parent bodies, respectively (Krot et al. 1995, 2005a). The compositions of CM2 chondrules can thus yield new information about the process of isotopic fractionation during aqueous alteration.

ANALYTICAL METHODS

Sample Documentation and Preparation

Whole, round chondrules from the CM2 carbonaceous chondrites Murchison (MRC) and Murray (MRY) were hand picked from density separates of the products of freeze-thaw disaggregation of these two meteorites performed at the University of Chicago (UC). Samples were placed on carbon tape (without polishing or carbon-coating) and examined using the JEOL JEM-5800LV scanning electron microscope (SEM) at UC, which is equipped with an Oxford/Link ISIS-300 quantitative energy-dispersive X-ray analysis system (EDS). Preliminary classifications of chondrules were made based on estimated olivine/pyroxene ratios and Mg/Fe ratios determined by EDS. Those with magnesian olivine and/or low-Ca pyroxene compositions, i.e., with less than approximately 10 mole% fayalite (Fa) or ferrosilite (Fs), were designated as type I. Those with more iron-rich mafic phases were designated as type II. Additionally, olivine-rich chondrules are designated as "A," pyroxene-rich ones as "B," and those having both mafic phases in subequal modal abundances as "AB." For a brief review of chondrule classification schemes, see Brearley and Jones (1998). Based on the preliminary examination of the unpolished chondrules, a suite of samples, including at least one of each chondrule type we found, was selected for analysis. An additional criterion for selecting chondrules during this preliminary examination was the apparent lack of adhering matrix. We selected a total of 23 chondrules, 15 from Murchison and 8 from Murray. Of these, there are 19 type I and 4 type II chondrules, with diameters ranging from 380 to 600 μm for Murchison and from 200 to 390 μm for Murray. Each chondrule was removed from the carbon tape, inspected again under an optical microscope to verify lack of adhering matrix, and then crushed between sapphire disks in a clean lab. One or more fragments from each chondrule were mounted in epoxy for a polished section, and the remainder, weighing between 10 and 248 μg (and one sample that could not be weighed), was reserved for bulk chemical and isotopic analysis. Mineralogical and petrological characterization of the fragments in the polished sections was conducted using the SEM at UC. The fayalite and ferrosilite contents of olivine and pyroxene, respectively, were determined on 1–7 spots in each selected chondrule fragment and are given in Table 1. The degree of alteration is estimated based on the abundances of secondary silicates (e.g., phyllosilicate) determined by area analysis of backscattered electron images using ImageJ software.

Dissolution and chemical separation of Mg from the samples was performed under clean laboratory conditions in the Isotope Cosmochemistry and Geochronology Laboratory (ICGL) in the Center for Meteorite Studies (CMS) at Arizona State University (ASU) using procedures similar to those described by Bouvier et al. (2011). Prior to dissolution, each of the chondrule fractions was cleaned by ultrasonicating in

Table 1. Textures, sizes, and isotopic compositions of chondrule fragments from the Murchison and Murray CM2 chondrites. Precision on Mg isotopic compositions (δ^{25}Mg, δ^{26}Mg, and δ^{26}Mg*) is reported as 2SD.

Sample ID#	Type[a]	Texture[a]	Alteration[a]	Vol%[b]	Ol. Fa %[b]	Px. Fs%[b]	Ø (mm)[c]	Weight (µg)[d]	^{27}Al/^{24}Mg	δ^{25}Mg (‰)	2SD	δ^{26}Mg (‰)	2SD	δ^{26}Mg* (‰)	2SD	n (runs)
Murchison																
MRC1-9	IIA	No section	—	—	—	—	320	57.1	0.068	0.13	0.06	0.29	0.10	0.03	0.08	4
MRC1-10	IAB	Porphyritic	Light	9	3.9	4.7	550	154.5	0.064	-0.08	0.03	-0.16	0.02	-0.01	0.06	3
MRC1-21	IAB	Porphyritic	Moderate	18	1.1	0.2	550	248.3	0.043	-0.10	0.03	-0.20	0.06	-0.02	0.01	4
MRC1-36	IB	Porphyritic	Clean	0	—	2.7	500	132.4	0.073	0.41	0.07	0.77	0.07	-0.04	0.10	8
MRC1-45	IAB	Porphyritic	Moderate	18	3.3	3.5	550	63.3	0.079	0.06	0.02	0.17	0.02	0.06	0.03	4
MRC2-4	IAB	Porphyritic	Heavy	21	1.0	1.1	530	94.7	0.054	-0.12	0.04	-0.20	0.02	0.02	0.07	3
MRC2-13	IIB	Fine-grained	Light	7	16.6	—	340	25.2	0.052	-0.28	0.03	-0.50	0.05	0.04	0.08	4
MRC2-18	IA	Porphyritic	Clean	0	6.2	7.1	390	9.8	0.175	-0.65	0.09	-1.27	0.02	0.00	0.18	4
MRC2-27	IB	Porphyritic (?)	Heavy	26	1.8	—	440	23.6	0.073	0.05	0.06	0.10	0.04	0.01	0.10	4
MRC2-39	IAB	Porphyritic	Clean	0	0.4	0.1	480	120.9	0.316	-0.15	0.06	-0.30	0.08	-0.01	0.08	7
MRC2-40	IB	Unknown—small chips	Moderate (?)	Insuff. material	0.5	1.5	600	40.0	0.044	-0.09	0.08	-0.19	0.01	-0.01	0.16	3
MRC2-45	IAB	Porphyritic	Light	4	0.8	1.0	580	124.3	0.160	-0.06	0.08	-0.17	0.12	-0.06	0.02	3
MRC3-41	IAB	Barred	Moderate	14	1.2	0.6	380	—	0.081	0.02	0.04	0.05	0.09	0.00	0.08	3
MRC3-49	IAB	Porphyritic	Moderate	15	1.8	1.3	410	17.3	0.102	-0.02	0.04	-0.03	0.06	0.01	0.08	4
MRC3-53	IAB	Porphyritic, fine	Moderate	13	0.7	—	410	77.0	0.095	0.14	0.01	0.28	0.03	-0.02	0.05	3
Murray																
MRY1-1	IAB	Porphyritic	Moderate	13	0.8	0.5	390	87.2	0.060	-0.06	0.01	-0.15	0.04	-0.04	0.05	4
MRY1-3	IAB	Porphyritic	Moderate	13	0.8	1.1	400	44.0	0.051	-0.48	0.05	-0.95	0.03	-0.01	0.10	4
MRY1-5	IAB	Porphyritic (?)	Light	5	0.6	1.0	600	194.7	0.016	-0.32	0.01	-0.61	0.04	0.00	0.01	4
MRY3-18	IA	Porphyritic (?)	Light	3	0.1	—	400	100.4	0.012	-0.24	0.04	-0.50	0.04	-0.03	0.04	4
MRY3-22	IIA	Porphyritic (?)	Unknown—single grain	—	18.3	—	300	94.5	0.004	-0.29	0.02	-0.58	0.04	-0.03	0.05	4
MRY3-26	IAB	Porphyritic	Light	5	8.7	7.4	300	51.1	0.017	-0.22	0.03	-0.42	0.13	0.00	0.05	4
MRY3-33	IAB	Unknown—no clear grain boundaries	Light (?)	3	0.2	—	200	13.3	0.050	-0.35	0.02	-0.69	0.05	-0.02	0.06	4
MRY4-16	IIA	Fine, porphyritic	Clean	0	37.1	—	330	14.2	0.040	-0.22	0.04	-0.45	0.08	-0.01	0.03	4

[a]Texture and the degree of alteration were inferred from fragments (mounted in polished sections) of the chondrules for which the magnesium isotope compositions were determined here (see Data S1 and Analytical Methods section of the text for details). Question marks indicate uncertainty for some chondrules for which only small fragments could be mounted in the polished sections, such that only a relatively small surface area was exposed. Also, only a single grain was exposed in polished sections prepared from fragments of some coarse-grained chondrules and, therefore, their texture and/or degree of alteration were (was) difficult to infer.
[b]Estimation based on abundance of Fe-rich phyllosilicate, as determined by area analysis of backscattered electron images of the chondrule fragments using ImageJ software. Categories of degrees of alteration are based on phyllosilicate abundance: clean—no phyllosilicate visible; light—1–10%; moderate—11–20%; heavy—>20%. Olivine fayalite and pyroxene ferrosilite contents are averages of 1–7 measurements by EDS.
[c]Diameter before splitting the chondrule.
[d]Fragment weight (in µg) dissolved for chemical and isotopic analyses.

acetone and subsequent rinsing with ultrapure water. Each chondrule sample was then digested in 100–200 μL concentrated HF-HNO$_3$ (5:1), evaporated to dryness, and then ultrasonicated and refluxed with 100 μL concentrated HNO$_3$ until completely dissolved. The sample solution was then evaporated to dryness and the residue was dissolved in 100 μL 1 M HNO$_3$; an approximately 2–10% aliquot was reserved for the determination of Al/Mg ratios, while Mg was separated from another fraction (20–90%) of the solution using cation chromatography. A sample amount equivalent to approximately 0.5 μg of Mg for the smallest sample, and up to a maximum of 10 μg, was loaded onto a pressurized 1 mL precleaned cation exchange column packed with AG50W-X8 (200–400 dry mesh size) resin, and elution of Mg was achieved in a 1 M HNO$_3$ medium. We calibrated our column chemistry protocol by loading 2–20 μg of Mg (using the DSM-3 pure Mg standard, and sample amounts equivalent to this range of Mg content of the Kilbourne Hole and San Carlos terrestrial olivines, as well as BCR-2 terrestrial basaltic and the Allende chondritic whole-rock samples) and determined an elution interval that ensured quantitative recovery for this range of Mg amounts. For mafic samples (typically with low Al/Mg ratios similar to those in the chondrule samples processed here), we found that two passes through this column with this elution interval was sufficient to separate the Mg (with >99% yield) from elements such as Al, Ca, Na, or Ti. We checked the chondrule sample solution concentrations and made sure to load a maximum of 10 μg of Mg for the largest chondrules. For the largest chondrule fragments having more than 10 μg total Mg, the remainder of the sample solution was reserved for future isotopic studies. For the smallest chondrule samples, we found that loading only 0.5 μg Mg did not shift the Mg peak outside of the eluted fraction that we collect to ensure quantitative recovery of the loaded Mg. The purified Mg sample solution was dried down and redissolved in 3% HNO$_3$ for mass spectrometric analyses. The total procedural blank was approximately 1–2 ng, which were negligible compared to the amount of Mg present even in the smallest samples (approximately 0.5 μg).

Mass Spectrometry

The Mg isotopic compositions and Al/Mg ratios were measured using a Thermo-Finnigan Neptune multicollector inductively coupled plasma mass spectrometer (MC-ICPMS) in the ICGL using methods similar to those described in Spivak-Birndorf et al. (2009) and Bouvier et al. (2011). For the Mg isotopic analyses of the purified Mg sample solutions, the ^{24}Mg, ^{25}Mg, ^{26}Mg, and ^{27}Al ion beams were measured simultaneously on Faraday cups at medium resolution. The ^{27}Al signal, which was negligible for all purified Mg samples analyzed here, was monitored during Mg isotopic analyses to verify the purity of the Mg extracted from the sample matrix. Sample solutions (typically approximately 300 ppb, but diluted to approximately 125 ppb for the smallest samples that contained only 0.5 μg total Mg) in 3% HNO$_3$ produced a ^{24}Mg signal of approximately 6×10^{-11} A using an ESI Apex desolvating nebulizer with a flow rate of 100 μL min^{-1}. To correct for instrumental mass bias, each sample analysis was bracketed by measurements of the DSM-3 Mg isotope standard (concentration matched to the sample to within approximately 10%). Each sample (bracketed by DSM-3) was analyzed 3 to 4 times during an analytical session; for samples that had sufficient Mg, measurements were repeated another 3–4 times on another day for comparison. The ^{25}Mg/^{24}Mg and ^{26}Mg/^{24}Mg ratios in the chondrule samples are reported as the average and corresponding 95% confidence interval (2 standard deviations, 2SD) of these repeated measurements relative to the DSM-3 standard in per mil (‰) (i.e., δ^{25}Mg and δ^{26}Mg, respectively). Regarding the errors reported on δ^{25}Mg and δ^{26}Mg (Tables 1 and 2), in the case of measurement runs where the instrumental mass bias varied significantly, the error on the measured ratios is dominated by this mass bias shift and is typically twice as large for ^{26}Mg/^{24}Mg as for ^{25}Mg/^{24}Mg. However, if the instrumental mass bias was relatively stable during the isotopic measurements, then other sources of error (e.g., instrumental noise, signal stability) apply more or less equally to both isotope ratios, and it is possible to have similar or even slightly higher errors on ^{25}Mg/^{24}Mg than on ^{26}Mg/^{24}Mg.

To determine mass-independent anomalies in the ^{26}Mg/^{24}Mg ratio due to the decay of ^{26}Al (i.e., δ^{26}Mg*), the measured ^{26}Mg/^{24}Mg ratio was normalized to ^{25}Mg/^{24}Mg = 0.12663 (Catanzaro et al. 1966) using the exponential law, with the fractionation factor β = 0.512. To assess the accuracy and precision of our Mg isotope measurements and to allow inter-laboratory comparisons, during each analytical session, we measured the isotopic compositions of one or more of the terrestrial and meteoritic rock and mineral standards that were processed along with the chondrule samples through the same chemical procedures. Terrestrial rock and mineral standards that were analyzed included aliquots of a homogenized powder of San Carlos olivine prepared at Harvard University (SCOL Harvard), a sample of the Kilbourne Hole olivine, a USGS basaltic rock standard (BCR-2), a terrestrial shale composite (D-119; Teng et al. 2007),

Table 2. Magnesium isotope compositions of terrestrial mineral and rock standards, and chondrite whole-rock samples relative to the DSM-3 Mg standard. See text (Sample Documentation and Preparation section) for more details on these samples.

Sample	$^{27}Al/^{24}Mg$ (±2SD)	$\delta^{25}Mg$ (‰)	2SD	$\delta^{26}Mg$ (‰)	2SD	$\delta^{26}Mg^*$ (‰)	2SD	n
Terrestrial mineral and rock samples								
San Carlos olivine (Harvard)	0.0031 (±0.0004)	−0.16	0.07	−0.31	0.09	0.00	0.05	36
Kilbourne Hole olivine	–	−0.13	0.05	−0.25	0.05	0.01	0.02	12
BCR-2 basalt (USGS)	3.76 (±0.04)	−0.16	0.07	−0.32	0.15	0.00	0.02	12
D119 shale composite	–	−0.01	0.05	−0.03	0.07	−0.01	0.02	4
GBW 07102 basalt	–	−0.08	0.04	−0.15	0.07	0.00	0.10	4
GBW 07123 diabase	–	−0.10	0.06	−0.22	0.04	−0.01	0.11	4
Bulk chondrite samples								
Allende WR CV3 chondrite (SI)	0.1294 (±0.0007)	−0.16	0.03	−0.29	0.05	0.03	0.05	7
Murray CM2 chondrite (CMS)	–	−0.11	0.02	−0.16	0.06	0.04	0.03	2

n = number of total repeated measurements. USGS = United States Geological Survey, SI = Smithsonian Institution, and CMS = Center for Meteorite Studies.

and two terrestrial igneous rocks (an ultramafic basalt GBW07102 and a diabase GBW07123, provided by F.-Z. Teng) (Table 2). We also analyzed a homogenized whole-rock (WR) powder of the Allende CV3 chondrite from the Smithsonian Institution, as well as a bulk sample of the Murray CM2 chondrite from the CMS collection (Table 2). Fractions of dissolved solutions of these terrestrial and meteoritic mineral and rock standards equivalent to 2–10 μg of Mg were processed through the same column chemistry procedures as the chondrule samples, and then one or more of these samples were measured 2–4 times before measuring the unknown chondrule samples. The 2SD errors on the average Mg isotope ratios of the mineral and rock standards (Table 2) as well as of the unknown chondrule samples (Table 1) were calculated from all the repeats measured on different days. We consider that the 2SD errors on the repeat measurements of the mineral and rock standards with the most number of repeat runs ($n \geq 12$ in Table 2) are representative of the external long-term reproducibility of our Mg isotopic measurements (i.e., ±0.07‰/amu for the mass-dependent Mg isotope composition and ±0.05‰ for the $\delta^{26}Mg^*$).

Prior to making Mg isotopic analyses of natural samples in our laboratory, we had performed tests to assess potential matrix effects and isobaric interferences by measuring the Mg isotopic compositions of the DSM-3 Mg standard doped with different proportions of a given element (i.e., Al, Ca, Na, Ti, and Fe). No resolvable deviations were found for the measured mass-dependent ($\delta^{25}Mg$ and $\delta^{26}Mg$) and mass-independent ($\delta^{26}Mg^*$) Mg isotopic compositions of these doped solutions for element/Mg ratios <0.1 (substantially higher than those found in our purified Mg sample solutions, for which typical element/Mg ratios were <0.005 for each of the elements noted

above). We additionally verified that our Mg separation procedures do not produce any analytical artifacts by processing both pure DSM-3 and DSM-3 doped with the matrix (excluding the Mg cut) of an Allende WR solution through our cation exchange column procedures. We did not detect any deviations in the mass-dependent and mass-independent Mg isotopic compositions of these DSM-3 solutions after our Mg purification procedure. All the analytical details and results related to these tests are given in table 3 of Bouvier et al. (2011).

The $^{27}Al/^{24}Mg$ ratios of the chemically unprocessed aliquots of the sample solutions were determined against a calibration curve generated using gravimetrically prepared pure SPEX Claritas™ ICPMS standard solutions with a range of Al/Mg ratios. The accuracy and reproducibility of the $^{27}Al/^{24}Mg$ ratio measurements during each analytical session were assessed by the analysis of rock and mineral standard solutions such as San Carlos olivine and BCR-2 basalt (Table 2). Based on the reproducibility of repeated measurements of these rock standards, the error on our $^{27}Al/^{24}Mg$ analyses is estimated to be better than ±2% (2SD).

RESULTS

Petrographic Description of Chondrules

Our sample suite is comprised of 15 chondrules from Murchison and 8 from Murray, and includes at least one of each of the four main types of chondrules described in the Sample Documentation and Preparation section. Backscattered electron images of representative samples are shown in Figs. 1 and 2. They range from essentially unaltered (Fig. 1) to heavily altered (Fig. 2B), with abundant Fe-rich phyllosilicates. By type, the most abundant chondrules are type IAB
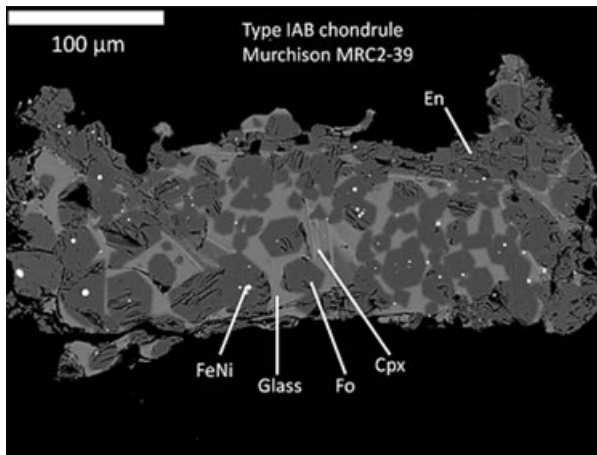
Fig. 1. Backscattered electron image of a fragment of a Murchison type IAB chondrule (MRC2–39), showing phenocrysts of enstatite (En), euhedral forsterite (Fo) with metal inclusions (FeNi), and late clinopyroxene (Cpx) enclosed in an FeO-free feldspathic glass; no secondary alteration products are present. This chondrule has a $^{27}Al/^{24}Mg$ ratio of 0.316, but shows no resolvable excess in $^{26}Mg^*$ (see text for details).

(14 samples; one is shown in Fig. 1). We also analyzed two type IA (Fig. 2A), three type IB (Fig. 2B), one type IIA (Fig. 2C), and three type IIB (Fig. 2D) chondrules. Most have porphyritic textures, several are cryptocrystalline, and one is a barred chondrule. The chondrule shown in Fig. 2D is unusual. It consists predominantly of low-Ca (approximately 1 wt% CaO) pyroxene. In the interior of the object, there is void space between the pyroxene grains, but in the outer approximately 50 μm the interstices are occupied by secondary, hydrated Fe-rich phyllosilicate. Petrographic features of each of the analyzed chondrules based on SEM examination of the polished sections are summarized in Table 1 and presented in Data S1.

Mg Isotopic Compositions

The Mg isotopic compositions of terrestrial rocks and minerals, as well as two bulk chondrite samples that were analyzed in this study are reported in Table 2 and shown in Fig. 3. For the terrestrial samples, the
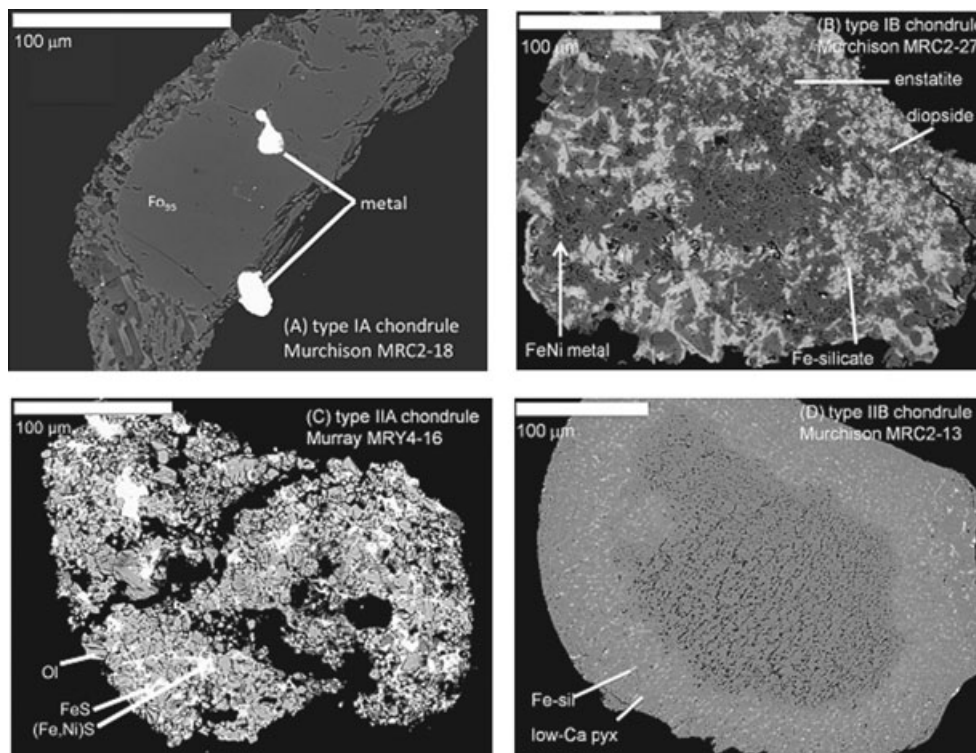

Fig. 2. Backscattered electron images of chondrules from Murchison and Murray. (A) MRC2–18 (Murchison type IA), represented here by a single large grain of olivine (Fo) having approximately 5 wt% FeO, and some smaller grains of low-Ca pyroxene and SiO_2-rich, Na-bearing mesostasis. Two large metal inclusions (FeNi) are present, along with a few smaller blebs. (B) MRC2–27 (Murchison type IB), containing enstatite (dark) and diopside (medium), abundant Fe-phyllosilicate (Fe-silicate; light), and trace FeNi metal. (C) MRY4–16 (Murray type IIA), a fine-grained chondrule mostly composed of olivine (Ol) with minor clinopyroxene, interstitial troilite (FeS), and pentlandite ((Fe,Ni)$_9$S$_8$). (D) MRC2–13 (Murchison type IIB), containing mostly low-Ca pyroxene (low-Ca pyx) of uniform composition (approximately 1 wt% CaO, 30% MgO, and 11% FeO), as indicated by the uniform gray color. The interior of this unusual chondrule is porous, but there is interstitial, secondary Fe-phyllosilicate in the outer (approximately 50 μm wide) region.
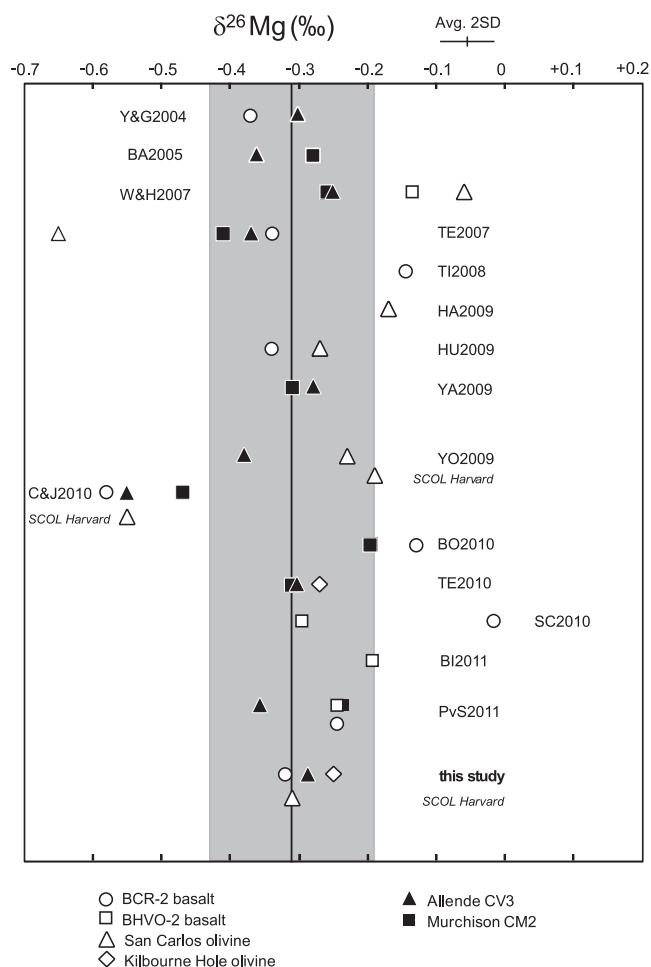
Fig. 3. Comparison of Mg isotopic compositions (relative to the DSM-3 terrestrial standard) measured in this study with those reported previously for terrestrial samples BCR-2 basalt, BHVO-2, the San Carlos (including the homogenized powder prepared at Harvard University, labeled as "SCOL Harvard") and Kilbourne Hole olivines, and the whole-rock samples of the carbonaceous chondrites Allende and Murchison. The vertical black line and gray band represent the average $\delta^{26}Mg$ and corresponding 2SD, respectively (-0.31 ± 0.11 ‰; $n = 16$) for all reported Allende and Murchison whole-rock compositions, based on this and previously published studies (included within the references below, and see text for further details). Literature data shown here are from Young and Galy (2004) (Y&G2004), Baker et al. (2005) (BA2005), Wiechert and Halliday (2007) (W&H2007), Teng et al. (2007) (TE2007), Tipper et al. (2008) (TI2008), Handler et al. (2009) (HA2009), Huang et al. (2009) (HU2009), Yang et al. (2009) (YA2009), Young et al. (2009) (YO2009), Chakrabarti and Jacobsen (2010) (C&J2010), Bourdon et al. (2010) (BO2010), Teng et al. (2010a) (TE2010), Schiller et al. (2010) (SC2010), Bizzarro et al. (2011) (BI2011), and Pogge von Strandmann et al. (2011) (PvS2011). The average of the 2SD uncertainties (0.08‰) on the measured $\delta^{26}Mg$ values from all these studies is shown on the upper right (Avg. 2SD).

$\delta^{26}Mg$ values range from -0.32 ± 0.15‰ (for BCR-2) to -0.03 ± 0.07‰ (for D-119) relative to the DSM-3

Mg standard. The Mg isotopic compositions of the two carbonaceous chondrite (CV3 Allende and CM2 Murray) bulk samples are similar, within the uncertainties, to each other and to those of the BCR-2 basalt, GBW basalt and diabase, the homogenized San Carlos olivine powder, and the Kilbourne Hole olivine.

Relative to DSM-3, the $\delta^{26}Mg$ values of Murchison chondrules range from -1.27 to $+0.77$‰ and the range is from -0.95‰ to -0.15‰ for Murray chondrules (Table 1; Fig. 4). There appears to be no correlation between the Mg isotopic composition and the petrologic type of the chondrules (Fig. 5). A type IA chondrule (MRC2-18) has the lowest $\delta^{26}Mg$ value (-1.27‰) and a type IB chondrule (MRC1-36) has the highest $\delta^{26}Mg$ value ($+0.77$‰); both of these chondrules are from Murchison. When comparing the Mg isotopic variations with the degree of alteration of chondrules, there is not a clear relationship although there may be a systematic effect. Specifically, the 11 least-affected chondrules (classified as clean or lightly altered in Table 1) have an average $\delta^{26}Mg$ of -0.39 ± 0.30‰ (2SE). The 10 chondrules classified as having moderate or heavy alteration have a systematically heavier average $\delta^{26}Mg$ of -0.11 ± 0.21‰ (2SE).

The $^{27}Al/^{24}Mg$ ratios of the Murchison and Murray chondrules range from 0.004 to 0.316, with most values being sub-chondritic to near-chondritic ($^{27}Al/^{24}Mg$ ratio approximately 0.1 for bulk chondrites; e.g., Thrane et al. 2006). No variations in $\delta^{26}Mg^*$ from the terrestrial standard value are detectable in most of the chondrules measured here. Only two chondrules from Murchison show deviations in $\delta^{26}Mg^*$ that are slightly outside of our reported uncertainties. MRC1-45, with a sub-chondritic Al/Mg ratio, has a slight excess while MRC2-45, with a super-chondritic Al/Mg, has a slight deficit in $\delta^{26}Mg^*$ (Table 1) relative to bulk chondritic composition ($\delta^{26}Mg^* = -0.0010 \pm 0.0023$ at $^{27}Al/^{24}Mg \approx 0.1$; Thrane et al. 2006). The chondrule MRC2-39 (Fig. 1) has the highest $^{27}Al/^{24}Mg$ ratio of 0.316 but shows no resolvable ^{26}Mg excess from the decay of ^{26}Al ($\delta^{26}Mg^* = -0.01 \pm 0.08$‰) (Table 1).

DISCUSSION

Interlaboratory Comparison

There have been several recently published studies of the Mg isotopic compositions of terrestrial minerals and rocks as well as various types of meteorites and their components. These studies have focused on aspects such as assessing the degree of homogeneity of Mg isotopes in the solar nebula, defining the Mg isotope composition of the bulk silicate Earth (BSE), and characterizing the mass-dependent fractionation of Mg
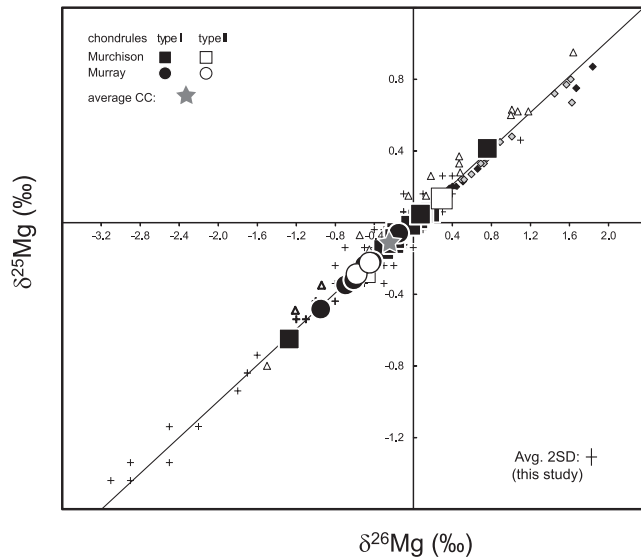
Fig. 4. Mg isotope compositions of the Murchison and Murray chondrules reported here. For comparison, the compositions of Allende chondrules by solution MC-ICPMS (gray filled diamonds, Galy et al. 2000; black filled diamonds, Bizzarro et al. 2004) and LA-MC-ICPMS (black crosses, Young et al. 2002a), and CB chondrules by LA-MC-ICPMS (open triangles, Gounelle et al. 2007) are also shown. For the sake of clarity, the 2SD errors are not shown, but are typically ±0.05 to 0.07‰/amu for solution MC-ICPMS data (this study; Galy et al. 2000; Bizzarro et al. 2004) and ±0.15 to 0.20‰/amu for the LA-MC-ICPMS data (Young et al. 2002a; Gounelle et al. 2007). The average Mg isotope composition of the Allende and Murchison carbonaceous chondrites (illustrated as the black line in Fig. 3) is shown as the star symbol; see text for details. Solid line is the best-fit line to the Murchison and Murray chondrule data (this study) and has a weighted-regression slope of 0.502 ± 0.020 (2σ).
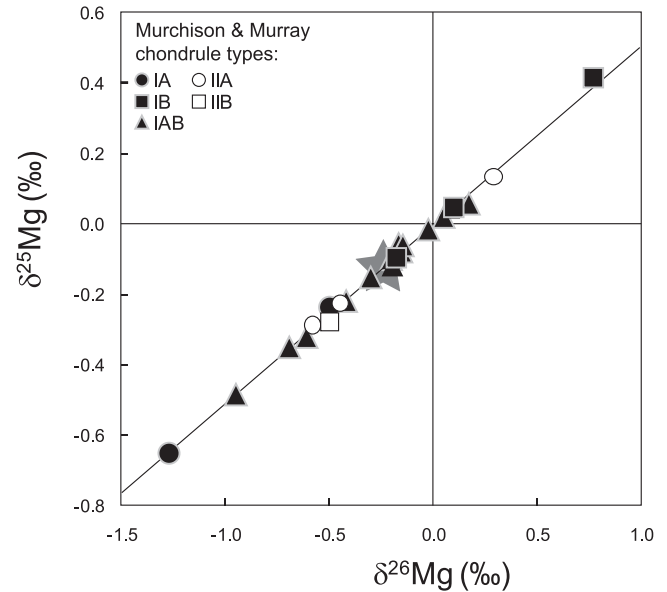

Fig. 5. Mg isotopic compositions of Murchison and Murray chondrules reported here, represented according to their petrologic type (see text for details); the 2SD errors are typically ±0.07‰/amu (smaller than the symbols). As also shown in Fig. 4, the average Mg isotope composition of carbonaceous chondrites is illustrated as the star symbol. The best-fit line to the Murchison and Murray chondrule Mg data has a weighted-regression slope of 0.502 ± 0.020 (2σ).

isotopes at high temperature to constrain the effects of planetary differentiation processes. Some studies concluded that there is little variation of Mg isotopes during magmatic differentiation between phases, such as pyroxene and olivine, within the same basalt (Handler et al. 2009; Yang et al. 2009) or during granite differentiation (Liu et al. 2010). However, Mg isotopic fractionation of as much as 3.6×10^{-2}‰/amu/°C was found experimentally in silicate melt by chemical and thermal diffusion (Richter et al. 2008). Detectable Mg, as well as Fe, isotopic variations were indeed found between spinel and olivine in mantle xenoliths (Young et al. 2009) and also within zoned olivine crystals from Hawaiian basalts (Teng et al. 2011). These differences in the Mg isotope composition between cogenetic minerals were interpreted as the consequence of the temperature dependence of isotopic exchange and thermal diffusion during magmatic differentiation. It was suggested that the Mg isotopic composition of the BSE is well

represented by the average composition of all the chondrite groups (Bourdon et al. 2010; Chakrabarti and Jacobsen 2010; Teng et al. 2010a). Furthermore, these studies indicate homogeneity of Mg isotopes in the protoplanetary disk.

Nevertheless, some of these studies have shown that there are variations in the compositions of the same samples analyzed in different laboratories using different analytical protocols and mass spectrometers. Figure 3 shows a comparison of the Mg isotopic compositions of several rocks and minerals (all relative to the DSM-3 terrestrial Mg standard) measured in this study with those analyzed in several different laboratories. Specifically, the compositions reported here for San Carlos (homogenized powder prepared at Harvard University or SCOL Harvard) and Kilbourne Hole olivines, the BCR-2 basalt, and the Allende CV3 whole-rock sample are in agreement (within the typical 2SD errors) with those reported for the same samples in other previous studies, with the exception of two recent investigations (Chakrabarti and Jacobsen 2010; Schiller et al. 2010). While the study by Chakrabarti and Jacobsen (2010) reports systematically lighter Mg isotope compositions for all the terrestrial and bulk chondrite samples, with BSE at −0.54 ± 0.04‰ (2SE)

similar to their average chondrite composition, the study by Schiller et al. (2010) finds a significantly heavier composition only for the BCR-2 terrestrial basalt at $\delta^{26}Mg = -0.03 \pm 0.19‰$ (2SE, $n = 18$). Furthermore, although not plotted in Fig. 3, our measured Mg isotope composition for the D119 shale composite also agrees with that reported previously for this same sample by Teng et al. (2007). The reason for the apparent discrepancy between the data for silica-rich terrestrial samples reported by Chakrabarti and Jacobsen (2010) and the BCR-2 data reported by Schiller et al. (2010) on the one hand, and those from other recent studies (including ours) on the other hand, is unclear at present.

Our Mg isotopic data for the Allende and Murray whole-rock samples agree with those for other carbonaceous chondrite bulk samples reported in nine other investigations (Young and Galy 2004; Baker et al. 2005; Teng et al. 2007, 2010a; Wiechert and Halliday 2007; Yang et al. 2009; Young et al. 2009; Bourdon et al. 2010; Pogge von Strandmann et al. 2011). The average composition of Allende and Murchison carbonaceous chondrites (i.e., $\delta^{26}Mg = -0.31 \pm 0.12‰$; 2SD, $n = 16$) based on measurements of whole-rock samples that were analyzed in 10 different laboratories, including ours but excluding those reported by Chakrabarti and Jacobsen (2010), is shown as the black line (with the 2SD errors shown as the gray band) in Fig. 3, and is hereafter referred to as the composition of bulk carbonaceous chondrites. In the following section, we discuss the fractionation of Mg isotopes in Murchison and Murray chondrules relative to the average Mg isotopic composition of bulk carbonaceous chondrites, as this is likely to be representative of the bulk Mg isotope composition of the solar nebular reservoir from which the chondrules originated.

Fractionation of Mg Isotopes in Chondrules from CM2 Chondrites: Implications for Processes and Formation Environments

Previous studies have shown that isotopic fractionation of moderately volatile elements such as K, Fe, Mg, or Si in CV and LL chondrules is relatively limited (Cuzzi and Alexander 2006). We find a total variation of approximately 1‰/amu in the Mg isotopic compositions of the 23 chondrules we measured in two CM2 (i.e., aqueously altered) chondrites. Specifically, the range of Mg isotopic compositions of chondrules from Murchison ($\delta^{26}Mg$ from $-1.27‰$ to $+0.77‰$) extends to compositions that are heavier and lighter than bulk carbonaceous chondrites ($\delta^{26}Mg = -0.31 \pm 0.11‰$; 2SD, $n = 16$), while the range of $\delta^{26}Mg$ in chondrules

from Murray (from $-0.95‰$ to $-0.15‰$) is smaller and systematically lighter than bulk chondrites (Figs. 4 and 5). For comparison, the only other carbonaceous chondrite chondrules for which high-precision Mg isotope compositions have been previously reported are from the CV3 chondrite Allende (Galy et al. 2000; Young et al. 2002a; Bizzarro et al. 2004) and the CB chondrites HaH 237 and QUE 94411 (Gounelle et al. 2007). The ranges of Mg isotope compositions reported in this study for the Murchison and Murray CM2 chondrules are significantly narrower than that measured in chondrules from the Allende CV3 chondrite ($\delta^{26}Mg$ from $-3.10‰$ to $+1.84‰$) (Galy et al. 2000; Young et al. 2002a; Bizzarro et al. 2004) (Fig. 4). However, some of these analyses of Allende chondrules were conducted in situ by laser ablation MC-ICPMS (Young et al. 2002a), and the wider range of Mg isotope compositions could be, at least in part, a sampling artifact. If only the high-precision Mg isotope data from solution analyses of Allende chondrules are considered (Galy et al. 2000; Bizzarro et al. 2004), the total range of their Mg isotope compositions is still broader than those of Murchison and Murray chondrules reported here (Fig. 4). Even if the laser ablation data are excluded from consideration, the high-precision Mg isotope database for Allende chondrules is much larger than that for the CM2 chondrules, and we cannot rule out the possibility that with additional analyses the range of CM2 chondrule compositions would approach that of Allende chondrules.

The range of compositions of 15 chondrules from CB chondrites ($\delta^{26}Mg$ from $-1.50‰$ to $+1.64‰$; Gounelle et al. 2007) is also broader than that of Murchison and Murray chondrules. However, these analyses too were conducted by laser ablation MC-ICPMS and so may not be directly comparable to the results of the solution analyses reported here. Furthermore, these CB chondrules formed significantly later than chondrules of other carbonaceous chondrites, and their compositions have been interpreted as reflecting isotopic fractionation during their formation in an impact-related vapor plume (Krot et al. 2005a).

The range of Mg isotopic compositions in chondrules from the CM2 chondrites reported here may be due to isotopic heterogeneity in the compositions of chondrule precursors, or isotopic fractionation during evaporation and recondensation, or aqueous alteration during secondary processing on the CM2 chondrite parent body. This range is about a factor of five wider than that for bulk chondrites (approximately 0.2‰/amu; Bourdon et al. 2010; Teng et al. 2010a). The average chondrite composition is also similar to that of the BSE and other planetesimals and planets in the inner solar system, such as the Moon and Mars, and

has been interpreted as evidence that Mg isotopes were homogeneously distributed in the solar nebula (Yang et al. 2009; Bourdon et al. 2010; Chakrabarti and Jacobsen 2010; Teng et al. 2010a).

The complementarity of major element compositions between chondrules and matrix has been previously established (Brearley 1996; Hezel and Palme 2010). The range of Mg isotopic compositions in chondrules and the relatively uniform compositions of bulk chondrites imply that such complementarity also exists for Mg isotopic compositions. This observed chemical and presumed isotopic complementarity of chondrules and associated matrix has implications for whether chondrules and matrix formed from the same reservoirs in the protoplanetary disk before accreting into their respective parent bodies (Hezel and Palme 2010), or if chondrules were formed closer to the Sun and were later transported and mixed with the matrix in colder accreting regions (e.g., Zanda 2004). Nevertheless, given the Mg isotopic homogeneity inferred for the solar nebula, we favor the idea that Mg isotopic variations in chondrules are likely due to fractionation processes either during their formation or during secondary processing on the chondrite parent body, and are not due to heterogeneity in their precursors. Chondrule precursors probably originated from the same reservoirs as the planetesimals and planets in the inner solar system.

On average, the Mg isotopic compositions of chondrules from Murray ($\delta^{26}Mg$ from $-0.95\permil$ to $-0.15\permil$) are lighter compared to those from Murchison ($\delta^{26}Mg$ from $-1.27\permil$ to $+0.77\permil$) (Fig. 4). As we only analyzed 8 Murray chondrules and 15 Murchison chondrules, this could be a sampling bias. We do not observe any clear correlation in individual CM2 chondrules between Mg isotopic composition and chondrule size, petrologic type, or the degree of alteration (Table 1). These two CM2 chondrites have similar low weathering grades, and have experienced similar degrees of aqueous alteration on their parent bodies, based on their bulk oxygen isotopic compositions (Clayton and Mayeda 1999) and petrologic properties (Rubin et al. 2007). We note, however, that if secondary processes, such as aqueous or thermal alteration, did indeed play a role in the fractionation of Mg isotopes in chondrules from CM2 and CV3 chondrites (which underwent different types of alteration), then this fractionation must have occurred in a closed system at the whole-rock scale since these chondrites have identical bulk Mg isotopic compositions (e.g., this study; Bourdon et al. 2010; Teng et al. 2010a).

It was previously suggested for Allende chondrules that deviations toward lighter Mg isotopic compositions from the bulk chondritic value could be associated with parent body alteration by aqueous fluids, whereas deviations toward heavier compositions may be associated with the presence of relict refractory olivines (Young et al. 2002b). While thermal metamorphism may have affected the isotopic compositions of Allende chondrules, that is not the case for the chondrules analyzed here. Among the Murchison samples, the chondrule with the lightest Mg isotopic composition (MRC2-18, $\delta^{26}Mg = -1.27\permil$) is an alteration-free type IA (olivine-rich). On the other hand, we find that the chondrule with the heaviest composition (MRC1-36, $\delta^{26}Mg = +0.77\permil$) is a type IB (pyroxene-rich) chondrule which is also alteration free and without any apparent relict olivines. It is possible, however, that although secondary phases are not present in the polished section, they may have been present in the split used for isotopic analysis.

We can compare the effects of aqueous alteration (i.e., CM2 chondrites) vs. thermal metamorphism (i.e., CV3 chondrites) on the Mg isotopic composition of chondrules by evaluating the compositions reported here of Murchison and Murray chondrules classified by degree of alteration (clean, light, moderate, and heavy, Table 1) with those previously reported for Allende chondrules. Because the Mg isotopic data obtained by laser ablation (Young et al. 2002a) are not representative of the bulk chondrule compositions, we compare our data only with isotopic data obtained by solution analysis on Allende chondrules (Galy et al. 2000; Bizzarro et al. 2004). For individual Murchison chondrules, there is no correlation between the Mg isotopic composition and the modal abundance of alteration products, which would otherwise reflect isotopic exchange during secondary alteration. We can instead consider the average Mg isotope compositions of groups of chondrules classified by degree of alteration. The Mg isotopic compositions vary from an average $\delta^{26}Mg = -0.39 \pm 0.30\permil$ (2SE) for the least altered chondrule group (classified as clean or with light alteration, Table 1) toward heavier compositions with an average $\delta^{26}Mg = -0.11 \pm 0.21\permil$ (2SE) for the group of chondrules classified as moderately to heavily altered. The average composition of the least-altered CM2 chondrules is slightly lighter than the bulk carbonaceous chondrites ($\delta^{26}Mg = -0.31 \pm 0.03\permil$, 2SE). The average Mg isotope compositions of both groups of CM2 chondrules are lighter than the average composition of bulk chondrules from Allende (average $\delta^{26}Mg = +0.40 \pm 0.24\permil$, 2SE) (Galy et al. 2000; Bizzarro et al. 2004), and may reflect the distinct secondary alteration histories experienced by chondrules from the CM2 and CV3 chondrules. Alternatively, this systematic difference could also reflect different isotopic compositions of chondrule precursors for the CM2 and

CV3 chondrules, although we do not favor this interpretation for the reasons noted earlier in this section.

There is growing evidence from studies of terrestrial materials that the Mg isotopic compositions of silicate secondary phases precipitated from aqueous solution are enriched in heavy isotopes (Tipper et al. 2006, 2010; Teng et al. 2010b; Wimpenny et al. 2010). In contrast, it has been found that carbonates have lighter Mg isotopic compositions than their source fluids (Galy et al. 2002). Experimental studies on calcite precipitation from solutions with a range of compositions and conditions (pH and $T°C$) have additionally confirmed fractionation of Mg isotopes toward lighter compositions (Saulnier et al. 2012). Moreover, the lighter Mg and Fe isotopic compositions of some CV3 chondrules have been suggested to be due to alteration processes (Young et al. 2002b; Hezel et al. 2010), possibly involving the introduction of isotopically light Mg and Fe from the matrix into the chondrules. However, alteration products within chondrules are dominated by phyllosilicates and not carbonates (that occur mostly in the matrix of CM2 chondrites; e.g., De Leuw et al. 2009). Therefore, the difference in the average Mg isotopic compositions of the CM2 chondrule groups with different degrees of alteration is more likely the consequence of late isotopic fractionation toward heavier compositions in the secondary silicate phases formed within chondrules during aqueous alteration on the CM2 parent body. In the present study, even if secondary silicate alteration products were not sampled in the limited area represented by the polished sections of a given chondrule, they might still have been present in the material analyzed by MC-ICPMS.

The systematic but not unambiguous nature of the relationship between degree of alteration (as represented by the phyllosilicate abundance) and the Mg isotope composition may be due to the fact that the effects of secondary alteration are superimposed upon Mg isotope compositions resulting from the primary processes involved in chondrule formation. More specifically, it is possible that the Mg isotopic compositions of CM2 chondrules record some degree of fractionation by volatilization and recondensation processes followed by the effects of secondary aqueous alteration. Chondrule precursor materials were partially melted during flash heating events, during which peak heating temperatures of up to approximately 2000 K were reached (Hewins et al. 1996). Evaporation from partial melts at high temperature is recognized as the process that resulted in fractionation of Mg and Si isotopes in CAIs toward heavier compositions (Grossman et al. 2000; Richter

et al. 2009). Therefore, evaporative processes could explain the heavier compositions (relative to bulk chondrites) found in some of the chondrules analyzed here. Conversely, partial recondensation may produce some of the chondrule compositions with lighter Mg isotopic compositions than bulk chondrites. It has been proposed that impact-related vapor plumes may be involved in the formation of all the chondrules (e.g., Fedkin et al. 2012; Grossman et al. 2012), and the volatilization and recondensation processes leading to isotopic fractionation of Mg isotopes may have occurred in this context. As it has been suggested previously for chondrules from other chondrite types, to account for the limited degree of Mg isotope fractionation in CM2 chondrules would require high gas pressures (Galy et al. 2000; Young et al. 2002a; Hezel et al. 2010), and/or enhanced dust/gas ratios (Cuzzi and Alexander 2006; Alexander et al. 2008) in their formation environment.

^{26}Al-^{26}Mg Systematics and Time scales of Chondrule Formation

Constraining the high-resolution chronology of chondrules is important for assessing the lifetime of the nebular disk and the potential problem of chondrule storage in the solar nebula over an extended period. At present, besides the Pb-Pb absolute chronometer, the only other chronometers that offer the time resolution for addressing such issues are those based on the extinct radionuclides, such as the ^{26}Al-^{26}Mg system.

Most chondrules studied here have subchondritic to near-chondritic $^{27}Al/^{24}Mg$ ratios (i.e., approximately 0.1; Thrane et al. 2006) and, therefore, it was not possible to resolve significant variations of $\delta^{26}Mg^*$ values from the terrestrial standard outside our external long-term reproducibility (as represented by our 2SD uncertainty of $\pm 0.05‰$ based on repeat measurements of the San Carlos olivine; Table 2). Results are illustrated in Fig. 6. Only two chondrules from Murchison, MRC1-45 ($\delta^{26}Mg^* = 0.06 \pm 0.03‰$, with a slightly sub-chondritic $^{27}Al/^{24}Mg \sim 0.08$) and MRC2-45 ($\delta^{26}Mg^* = -0.06 \pm 0.02‰$, with a slightly super-chondritic $^{27}Al/^{24}Mg \sim 0.16$), have variations in $\delta^{26}Mg^*$ that are outside of the reported 2SD errors for these samples. Nevertheless, these variations only slightly exceed our 2SD external reproducibility ($\pm0.05‰$). The conservative interpretation would be that there is no statistical significance to these small apparent variations in $\delta^{26}Mg^*$ for these two chondrules and, therefore, no inferences regarding their time of formation may be obtained. Alternatively, if these small variations in these
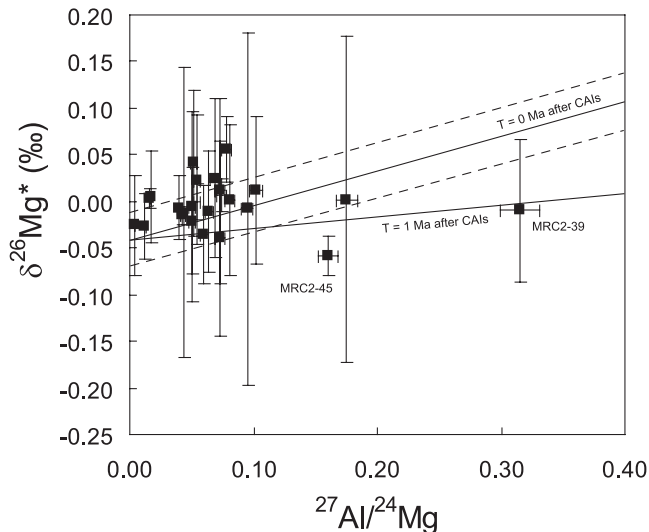
Fig. 6. Al-Mg systematics of CM2 chondrules from Murchison and Murray (black squares). For reference, the solid and dashed lines labeled as "$T = 0$ Ma after CAIs" represent a canonical isotopic evolution and associated error envelope, respectively, for CAIs (^{26}Al/^{27}Al$_0$ = 5.23 × 10^{-5} and δ^{26}Mg*$_0$ = −0.040 ± 0.029 ‰; Jacobsen et al. 2008). An Al-Mg isochron for 1 Ma after CAI formation labeled "$T = 1$ Ma after CAIs") is also shown.

two samples are taken at face value, they may hint toward the presence of a small degree of isotopic heterogeneity in the initial abundance of ^{26}Al or Mg isotope compositions in these chondrules as suggested recently by Larsen et al. (2011).

The absence of a resolvable ^{26}Mg* excess in the chondrule (MRC2-39) with the highest ^{27}Al/^{24}Mg ratio of 0.316 may be interpreted either as indicative of formation >1 Ma after CAIs or of resetting of the Al-Mg isotope systematics by secondary alteration processes on the CM2 parent body. This particular chondrule does not show petrographic evidence for secondary alteration (Fig. 1).

Recent in situ, high-precision Al-Mg analyses of chondrules from primitive ordinary and carbonaceous chondrites indicate that chondrule precursors formed as early as 0.9 ± 0.2 Ma after CAI formation, while chondrule crystallization from molten droplets lasted from 1.2 to 4.0 Ma, with formation peaks between 1.5 and 3.0 Ma, after CAI formation (Villeneuve et al. 2009). Such late episodes of formation could not be resolved in the low Al/Mg chondrules analyzed here (Fig. 6). Nevertheless, we may deduce from the lack of clearly resolved variations in ^{26}Mg* in the low-Al chondrules analyzed in this study that these chondrules were originally formed or were equilibrated >1 Ma after CAI formation.

CONCLUSIONS

We have measured the Al-Mg isotope systematics of 23 individual chondrules from the CM2 chondrites Murchison and Murray. We find that the Mg isotopic compositions of these CM2 chondrules are fractionated relative to the bulk isotopic compositions of chondrites, which have uniform compositions (Bourdon et al. 2010; Teng et al. 2010a). Specifically, Murchison chondrules have Mg isotopic compositions (δ^{26}Mg from −1.27‰ to +0.77‰) that extend to compositions that are lighter and heavier than bulk Allende and Murchison chondrites (δ^{26}Mg = −0.31 ± 0.11‰; 2SD, n = 16), whereas the compositions of Murray chondrules (δ^{26}Mg from −0.95‰ to −0.15‰) are systematically lighter. Chondrules from these CM2 chondrites have a smaller degree of Mg isotopic fractionation than the chondrules from CV3 and CB chondrites. Chondrules from CV3 chondrites probably experienced high-temperature thermal metamorphism (Krot et al. 1995) while those from the CB chondrites are hypothesized to have formed during large-scale impact processes in the early solar system (Krot et al. 2005b). The average Mg isotopic compositions for the groups of CM2 chondrules classified with different degrees of alteration suggest that aqueous alteration resulting in phyllosilicate formation may produce chondrules with heavier Mg isotopic compositions. Isotopic fractionation relative to bulk chondritic composition could also be related to evaporation and recondensation processes during chondrule formation but is found to be extremely limited for moderately volatile elements such as Mg. Given that there is no correlation of the Mg isotopic compositions of the CM2 chondrules with their size and petrology, it is likely that their compositions represent a complex combination of one or more of the above processes. The olivine- and pyroxene-rich chondrules studied here have mostly sub-chondritic to near-chondritic ^{27}Al/^{24}Mg ratios. As such, it was not possible to resolve variations in the δ^{26}Mg* values from the terrestrial standard. The absence of detectable ^{26}Mg* variations in the CM2 chondrules, even for one with the highest ^{27}Al/^{24}Mg ratio (0.316), indicates either formation >1 Ma after CAIs or possibly, resetting of the Al-Mg isotope systematics by secondary alteration processes on the CM2 parent body after the decay of ^{26}Al.

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SUPPORTING INFORMATION

Additional supporting information may be found in the online version of this article:

Data S1. Backscattered electron images of fragments of the individual chondrules from the Murchison and Murray CM2 chondrites that were analyzed for their Mg isotopic composition.