Isotopic evidence for primordial molecular cloud material in metal-rich carbonaceous chondrites

Elishevah M. M. E. Van Kooten[a], Daniel Wielandt[a], Martin Schiller[a], Kazuhide Nagashima[b], Aurélien Thomen[b], Kirsten K. Larsen[a], Mia B. Olsen[a], Åke Nordlund[a], Alexander N. Krot[a,b], and Martin Bizzarro[a,1]

[a]Centre for Star and Planet Formation and Natural History Museum of Denmark, University of Copenhagen, DK-1350 Copenhagen, Denmark; and [b]Hawai'i Institute of Geophysics and Planetology, University of Hawai'i at Mānoa, Honolulu, HI 96822

Edited by Mark H. Thiemens, University of California, San Diego, La Jolla, CA, and approved January 4, 2016 (received for review September 12, 2015)

The short-lived ^{26}Al radionuclide is thought to have been admixed into the initially ^{26}Al-poor protosolar molecular cloud before or contemporaneously with its collapse. Bulk inner Solar System reservoirs record positively correlated variability in mass-independent ^{54}Cr and ^{26}Mg*, the decay product of ^{26}Al. This correlation is interpreted as reflecting progressive thermal processing of in-falling ^{26}Al-rich molecular cloud material in the inner Solar System. The thermally unprocessed molecular cloud matter reflecting the nucleosynthetic makeup of the molecular cloud before the last addition of stellar-derived ^{26}Al has not been identified yet but may be preserved in planetesimals that accreted in the outer Solar System. We show that metal-rich carbonaceous chondrites and their components have a unique isotopic signature extending from an inner Solar System composition toward a ^{26}Mg*-depleted and ^{54}Cr-enriched component. This composition is consistent with that expected for thermally unprocessed primordial molecular cloud material before its pollution by stellar-derived ^{26}Al. The ^{26}Mg* and ^{54}Cr compositions of bulk metal-rich chondrites require significant amounts (25–50%) of primordial molecular cloud matter in their precursor material. Given that such high fractions of primordial molecular cloud material are expected to survive only in the outer Solar System, we infer that, similarly to cometary bodies, metal-rich carbonaceous chondrites are samples of planetesimals that accreted beyond the orbits of the gas giants. The lack of evidence for this material in other chondrite groups requires isolation from the outer Solar System, possibly by the opening of disk gaps from the early formation of gas giants.

molecular cloud | outer Solar System | metal-rich chondrites | isotopes | chondrite accretion regions

Low-mass stars like our Sun form by the gravitational collapse of the densest parts of molecular clouds comprising stellar-derived dust and gas. Collapsing clouds swiftly evolve into deeply embedded protostars that rapidly accrete material from their surrounding envelopes via a protoplanetary disk (1), in which planetesimals and planetary embryos form over timescales of several million years (2). Chondritic meteorites (chondrites) are fragments of early-formed planetesimals that avoided melting and differentiation and, therefore, provide a record of the earliest evolutionary stages of the Sun and its protoplanetary disk. Most chondrites contain calcium–aluminum-rich inclusions (CAIs) and chondrules, which formed by high-temperature processes that included evaporation, condensation, and melting during short-lived heating events (3). CAIs represent the oldest dated solids and, thus, define the age of the Solar System at 4,567.3 ± 0.16 Ma (4). It is inferred that CAIs formed near the proto-Sun during a brief time interval (<0.1 My) and record transient variability in the initial abundance of the stellar-derived short-lived ^{26}Al radionuclide (^{26}Al decays to ^{26}Mg with a half-life of 0.705 My) in the innermost protoplanetary disk (5–7). Following their formation, CAIs were transported to large radial distances (8). Chondrule formation started contemporaneously with CAIs and continued for several million years (4). Chondrules appear to have formed in different disk regions and sampled a wider range of radial distances from the Sun than CAIs (3). Collectively, chondritic components provide time-sequenced samples allowing us to probe the composition of the disk material that accreted to form planetesimals and planets.

Unraveling the accretion regions of planetesimals is critical for understanding the dynamical evolution of the protoplanetary disk, including radial mass transport processes. However, the location of the accretion region(s) of the most primitive planetesimals represented by the carbonaceous chondrites is poorly understood. According to a dynamical model (9), carbonaceous chondrite parent bodies (C-, P-, and D-type asteroids) accreted between and beyond the formation regions of the giant planets, and were implanted in the main asteroid belt during the outward migration of Jupiter. However, the inferred deuterium/hydrogen (D/H) ratios of water in extensively aqueously altered CI (Ivuna type) and CM (Mighei type) carbonaceous chondrites are distinct from those of Oort Cloud and Jupiter family comets as well as Saturn's moon Enceladus, implying that these bodies formed in different regions (10). Based on these observations, a competing model proposes that CI and CM chondrite parent bodies accreted in the inner Solar System, possibly close to the main asteroid belt (10, 11).

In this work, we aim to constrain the chondrite accretion regions by combining high-precision magnesium and chromium isotope measurements of bulk chondrites and their components. In the inner Solar System, bulk planetary materials with solar or near-solar ^{27}Al/^{24}Mg ratios record positively correlated variability in μ^{26}Mg* and μ^{54}Cr (Fig. 1). This correlation is interpreted as reflecting progressive thermal processing of in-falling ^{26}Al-rich molecular cloud material, which resulted in preferential loss by sublimation of thermally unstable and isotopically anomalous

EARTH, ATMOSPHERIC, AND PLANETARY SCIENCES

Significance

Comets are pristine, volatile-rich objects formed beyond the orbits of the gas giants and, thus, thought to preserve a record of the primordial molecular cloud material parental to our Solar System. We use magnesium and chromium isotopes to show that a class of pristine chondrites, the metal-rich carbonaceous chondrites, has a signature distinct from most inner Solar System planets and asteroids. This signature is consistent with that predicted for unprocessed primordial molecular cloud material, suggesting that—similar to comets—metal-rich carbonaceous chondrites are samples of asteroids that accreted in the outer Solar System. Therefore, these objects may provide a direct window into the formation history of the outer Solar System.

Author contributions: E.M.M.E.V.K. and M.B. designed research; E.M.M.E.V.K., D.W., M.S., K.N., A.T., K.K.L., M.B.O., A.N.K., and M.B. performed research; E.M.M.E.V.K., Å.N., A.N.K., and M.B. analyzed data; and E.M.M.E.V.K., A.N.K., and M.B. wrote the paper.

The authors declare no conflict of interest.

This article is a PNAS Direct Submission.

Freely available online through the PNAS open access option.

[1]To whom correspondence should be addressed. Email: bizzarro@snm.ku.dk.

This article contains supporting information online at www.pnas.org/lookup/suppl/doi:10.1073/pnas.1518183113/-/DCSupplemental.

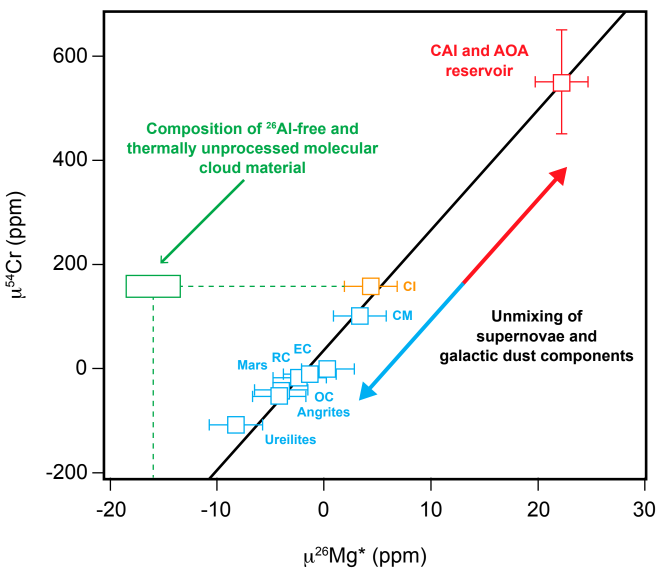

Fig. 1. Inner Solar System μ^{26}Mg*–μ^{54}Cr correlation. The μ-notation reflects the deviation in parts per millions (ppm) of the internally normalized ^{26}Mg/^{24}Mg and ^{54}Cr/^{52}Cr ratios from the terrestrial compositions. Uncertainties reflect the external reproducibility or internal errors, whichever is larger. The μ^{54}Cr uncertainties are typically smaller than symbols. AOA, amoeboid olivine aggregates; EC, enstatite chondrites; OC, ordinary chondrites; RC, Rumuruti chondrites. Data are from ref. 13 and this study. The μ^{54}Cr and μ^{26}Mg* compositions of the ^{26}Al-free and thermally unprocessed molecular cloud material, including their uncertainties, are defined by CI chondrites and the initial μ^{26}Mg* value of the Solar System (13). AOA and CAIs represented here are objects that formed with the canonical ^{26}Al/^{27}Al of ∼5 × 10^{-5}. Although CI chondrites are commonly viewed as reflecting the bulk Solar System composition for most elements, it is unclear whether this assumption is correct for the μ^{26}Mg* and μ^{54}Cr values. This can be tested through high-precision Mg and Cr isotope measurements of the Sun, which is currently not possible at a level of precision relevant to our discussion. See *SI Appendix*, Fig. S8, for additional information with respect to the end-member compositions considered in the model.

presolar carriers, producing residual isotopic heterogeneity (12–15). In this model, the correlated μ^{26}Mg*–μ^{54}Cr array represents the unmixing of distinct dust populations with contrasting thermal properties, namely unmixing of old, galactically inherited homogeneous dust from a young supernovae-derived dust component formed shortly before or during the evolution of the giant molecular cloud structure parental to the protosolar molecular cloud core.

Planetesimals formed in the outer Solar System could have accreted a significant fraction of primordial and, hence, thermally unprocessed molecular cloud matter. This material may reflect the nucleosynthetic makeup of the molecular cloud before the last addition of stellar-derived ^{26}Al. The least thermally processed meteorites, CI carbonaceous chondrites, contain high abundances of presolar grains and record the highest level of nucleosynthetic enrichment for nuclides such as μ^{54}Cr among bulk planetary materials (12, 16). Thus, CI chondrites provide a lower limit for the average μ^{54}Cr value of thermally unprocessed molecular cloud material. Primordial molecular cloud material unpolluted by ^{26}Al is expected to have a μ^{26}Mg* value consistent with the Solar System initial composition, which is inferred to be −20.4 ± 2.9 ppm relative to CI chondrites (13). Therefore, unlike inner Solar System objects, the isotopic signature of the thermally unprocessed and ^{26}Al-poor primordial molecular cloud matter is expected to show a decoupling between their μ^{26}Mg* and μ^{54}Cr values (Fig. 1).

Isotopic Evidence for Primordial Molecular Cloud Matter

To search for the signature of primordial molecular cloud material, we focused on the CH (high metal), CB (Bencubbin type), and CR (Renazzo type) metal-rich carbonaceous chondrites, which are among the most pristine (unmetamorphosed) meteorites in our collections. Several observations suggest that these meteorites may have accreted a significant fraction of pristine material of possible outer Solar System origin. CH chondrites contain the highest abundance of early-formed ^{26}Al-poor CAIs (17); these solids are inferred to have been transported to larger radial distances from the Sun compared with the later-formed ^{26}Al-rich CAIs. In addition, CH chondrites have incorporated chondrite lithic clasts characterized by ^{15}N-rich (up to 1,000‰) compositions (18, 19), which are thought to be indicative of low-temperature environments that existed in the outer Solar System (20–22). Enrichments in ^{15}N are also observed in bulk CH (up to 1,100‰), CB (up to 1,500‰), and CR (120–190‰) chondrites (23). Moreover, CR chondrites are characterized by the highest abundance of presolar grains among carbonaceous chondrites (24). Absolute ages of CH and CB chondrules constrain the accretion of their parent bodies to ∼5 My after CAIs (25), that is, later than other carbonaceous chondrite parent bodies [i.e., ∼2.5–3.5 My (26)]. In an accreting disk, later-formed planetesimals are expected to incorporate a high proportion of outer disk material. Collectively, these observations suggest that CR, CH, and CB chondrite components or their precursors may have incorporated a significant proportion of primordial, outer Solar System material compared with other meteorites.

We measured μ^{26}Mg* and μ^{54}Cr values of Isheyevo (CH/CB) components, including five hydrated lithic clasts, three porphyritic olivine–pyroxene chondrules, and six skeletal olivine chondrules, as well as three bulk CR chondrites and three porphyritic and skeletal CR chondrules (Table 1). We also determined the timing of aqueous alteration of the lithic clasts by ^{53}Mn–^{53}Cr systematics of their carbonates (see *SI Appendix*). The initial ^{53}Mn/^{55}Mn in these carbonates corresponds to an aqueous alteration age that is $1.54^{+0.92}_{-1.11}$ My younger than that inferred for the CM and CI parent asteroids (27), confirming the late accretion of the CH/CB parent body. The lithic clasts record identical μ^{26}Mg* values corresponding to an average of −6.3 ± 3.1 ppm, whereas Isheyevo and CR chondrules define μ^{26}Mg* values ranging from −5.7 ± 2.5 ppm to −18 ± 2.0 ppm. The bulk CR chondrites have μ^{26}Mg* compositions varying from −1.8 ± 2.2 ppm to −6.3 ± 2.5 ppm. In contrast to their μ^{26}Mg* values, all Isheyevo components, CR chondrules, and bulk CR chondrites show excesses in μ^{54}Cr relative to the terrestrial value. Lithic clasts define a homogeneous composition corresponding to μ^{54}Cr of 115 ± 24 ppm, which is identical to the mean value of 115 ± 16 ppm recorded by the three bulk CR chondrites. In contrast, the Isheyevo and CR chondrules show variable μ^{54}Cr values ranging from 86 ± 12 ppm to 177 ± 10 ppm. In μ^{26}Mg* versus μ^{54}Cr space, the Isheyevo components and the bulk CR chondrites and components fall off the Solar System μ^{26}Mg*–μ^{54}Cr line, defining a negatively correlated array extending to an end-member composition depleted in μ^{26}Mg* and enriched in μ^{54}Cr relative to CI chondrites (Fig. 2). We note that chondrules from the CB chondrites Hammadah al Hamra 237 and Gujba show the same decoupling in their μ^{26}Mg*–μ^{54}Cr systematics (28, 29). These observations indicate that metal-rich carbonaceous chondrites and their components formed from precursor material distinct from the bulk of the inner Solar System. Some of the Isheyevo and CR chondrules analyzed here define a μ^{26}Mg* deficit comparable to the inferred Solar System initial composition of −16.0 ± 2.5 ppm (13) and a μ^{54}Cr value similar to CI chondrites. This signature is consistent with the predicted composition of the least thermally processed, ^{26}Al-free, molecular cloud material. Therefore, we interpret the trend in Fig. 2 as a mixing array between two end members defined by the compositions of primordial molecular cloud matter and ^{26}Al-polluted, thermally processed inner Solar System material, akin to that of bulk CM chondrites. If correct, this interpretation requires the presence of at least 25% and up to

Table 1. Magnesium and chromium isotope compositions of bulk CM and CR chondrites as well as CR chondrules, Isheyevo chondrules, and lithic clasts

Sample[†]	Type	$^{27}Al/^{24}Mg$	$\mu^{26}Mg^*$	$\mu^{25}Mg$	*N*	$\mu^{54}Cr$	*N*
Bulk Chondrites							
Jbilet Winselwan (1)	CM	0.114	3.8 ± 1.2	35 ± 7	9	101 ± 12	11
Jbilet Winselwan (2)	CM	0.116	2.8 ± 1.2	23 ± 6	10		
NWA 6043	CR	0.096	−6.3 ± 2.1	13 ± 14	10	124 ± 10	10
EET 92161	CR	0.128	−5.0 ± 1.4	−88 ± 10	10	119 ± 12	10
NWA 7837	CR	0.137	−1.8 ± 2.2	−52 ± 6	10	106 ± 8	11
Isheyevo components							
A2-LC-1	Lithic clast	0.096	−7.8 ± 5.7	−110 ± 6	5	117 ± 18	7
A2-LC-2	Lithic clast	0.115	−8.9 ± 5.5	−2 ± 6	10		
A2-LC-3	Lithic clast	0.092	−7.9 ± 3.5	−56 ± 5	10	142 ± 28	5
B4-LC-1	Lithic clast	0.086	−8.1 ± 3.4	−186 ± 8	5		
B4-LC-BC	Lithic clast	0.093	−3.5 ± 2.6	−77 ± 6	10	102 ± 16	6
A2-Ch-1	Skel. Chon.	0.092	−11.3 ± 1.8	130 ± 19	10	142 ± 12	10
Cd-Ch-1	Skel. Chon.	0.087	−10.2 ± 1.8	75 ± 6	10	115 ± 16	10
Cd-Ch-3	Por. Chon.	0.092	−8.4 ± 1.3	206 ± 5	10	128 ± 16	12
Cd-Ch-4	Skel. Chon.	0.288	−8.6 ± 1.5	−61 ± 11	10	112 ± 9	16
Cd-Ch-5	Skel. Chon.	0.264	−13.1 ± 2.4	321 ± 5	10	124 ± 12	16
D-Ch-2	Skel. Chon.	0.120	−12.3 ± 2.4	4 ± 10	9	121 ± 18	16
D-Ch-3	Por. Chon.	0.098	−9.2 ± 1.7	205 ± 11	10	145 ± 15	16
D-Ch-4	Skel. Chon.	0.235	−18.1 ± 2.0	412 ± 19	9	176 ± 9	14
D-Ch-5	Por. Chon.	0.087	−13.2 ± 1.3	−41 ± 11	10	139 ± 14	16
CR chondrules							
CR10 (NWA 6043)	Por. Chon.	0.099	−14.9 ± 1.0	−90 ± 4	10	134 ± 20	10
MUS5 (NWA 801)	Skel. Chon.	0.112	−5.7 ± 2.5	8 ± 12	10	113 ± 20	10
LAP1 (LAP 02342)	Por. Chon.	0.038	−15.9 ± 1.9	−36 ± 21	10	130 ± 22	10

[†]Isotope compositions are expressed in the μ-notation, which reflect 10^6 deviations (ppm) from the terrestrial standard. *N*, number of individual analyses; Por. Chon., porphyritic chondrule; Skel. Chon., skeletal chondrule. All uncertainties are 2 SE. The $^{27}Al/^{24}Mg$ ratios are accurate to 2%.

50% of primordial molecular cloud material in bulk CR chondrites and Isheyevo lithic clasts, respectively.

Accretion Region of Metal-Rich Carbonaceous Chondrites

The $\mu^{26}Mg^*$–$\mu^{54}Cr$ systematics of metal-rich carbonaceous chondrites and their components suggest that their precursor material included significant amounts of thermally unprocessed, ^{26}Al-free primordial molecular cloud matter. Such high fractions of primordial molecular cloud material are expected to survive only in the outer part of the Solar System, where cometary bodies accreted (30). This could reflect inward drift of material from very large orbital distances (i.e., >100 astronomical units), including the accretion of pristine envelope material during the late evolutionary stage of the protoplanetary disk (31) to the formation region(s) of cometary bodies. Thus, we infer that, similar to comets, metal-rich carbonaceous chondrites are fragments of planetesimals that accreted in the outer Solar System.

The oxygen isotopic composition of meteorites and their components is commonly used to infer genetic relationships between early-formed solids, asteroids, and planetary bodies and, as such, provide constraints on the nature of the precursors to the terrestrial planets (32). However, in contrast to the $\mu^{26}Mg^*$–$\mu^{54}Cr$ systematics, the oxygen isotopic compositions of metal-rich carbonaceous chondrites and their chondrules are not anomalous. In a three-isotope oxygen diagram, these objects define compositions that approach the terrestrial fractionation line (33–35). In addition, the bulk oxygen isotopic composition of the primordial thermally unprocessed molecular cloud material is currently debated. Indeed, values that are similar to the inferred composition of the Sun [$\Delta^{17}O = -28 \pm 2‰$ (36)] or, alternatively, comparable to the terrestrial value have been proposed (37, 38).

The lack of evidence for the signature of primordial molecular cloud matter in the bulk isotopic compositions of most chondritic and differentiated planetesimals as well as terrestrial planets indicates limited influx of this material in their accretion regions. This could reflect temporal or spatial variations in the distribution of components with a primordial molecular cloud signature in the protoplanetary disk. However, CR, CI, and CM chondrites record comparable aqueous alteration ages (39). This observation suggests that the accretion region of CR chondrites was spatially isolated from that of CI and CM chondrites. A possible mechanism to limit the inward migration of outer Solar System material is the formation of gas giants opening gaps in the protoplanetary disk (40), providing that the gas giants are able to accrete most of the solids attempting to cross the gap. Recent numerical simulations show that rapid formation of gas and ice giants can occur by accretion of centimeter-to-meter-sized particles by the mechanism of pebble accretion (41). In these models, pebbles are concentrated by aerodynamic drag and gravitationally collapse to form objects of up to 1,000 km in diameter; these planetary embryos can then efficiently accrete leftover pebbles and directly form the cores of giant planets. Therefore, the growth of giant cores by pebble accretion provides an efficient means of limiting the influx of material through disk gaps. Our data are thus consistent with the idea that the source regions of most chondrites were sunward of the gas giants (10).

^{26}Al-Poor Composition of Outer Solar System Material

Recent high-resolution comparison of the U-corrected Pb–Pb and ^{26}Al–^{26}Mg ages of pristine rapidly cooled igneous meteorites derived from the angrite parent body indicate that these objects formed with a reduced initial abundance of ^{26}Al relative to the value of canonical $^{26}Al/^{27}Al$ of $\sim 5 \times 10^{-5}$ defined by CV (Vigarano type) CAIs (42). This provides evidence that the $\mu^{26}Mg^*$ variability observed for inner Solar System reservoirs with solar or near-solar $^{27}Al/^{24}Mg$ ratio (13) predominantly reflect ^{26}Al heterogeneity. As such, we

EARTH, ATMOSPHERIC, AND PLANETARY SCIENCES

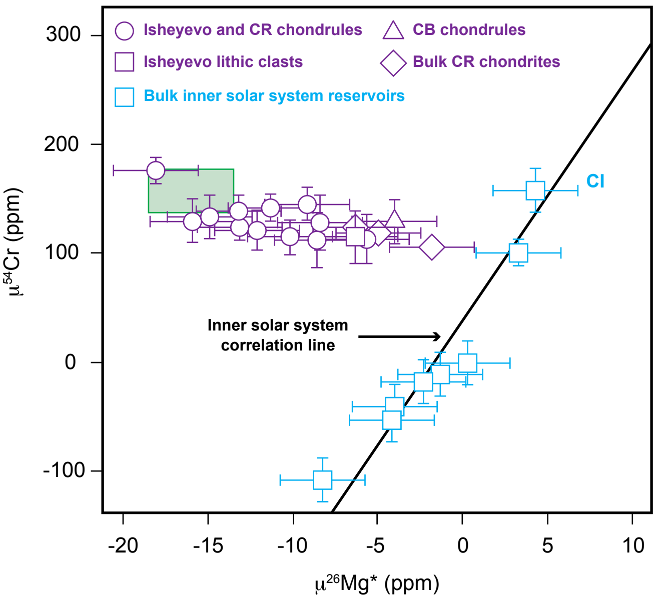

Fig. 2. The μ^{26}Mg* and μ^{54}Cr compositions of metal-rich chondrites and their components. Uncertainties reflect the external reproducibility or internal errors, whichever is larger. Some of the μ^{54}Cr uncertainties are smaller than symbols. The green box represents the predicted μ^{54}Cr and μ^{26}Mg* compositions of the ^{26}Al-free and thermally unprocessed molecular cloud material, including their uncertainties. The plotted compositions of Isheyevo lithic clasts and CB chondrules represent averages of individual samples. The metal-rich chondrites and their components define a negative correlated array with a slope of 0.039 ± 0.018 that intercepts the Solar System correlation line at a μ^{54}Cr value of 89 ± 20 ppm. Note that admixing of CAIs to a CI-like composition cannot account for the trend defined by metal-rich chondrites, as this would result in a mixing hyperbola that falls below the inner Solar System correlation line.

interpret the μ^{26}Mg* deficits observed in metal-rich carbonaceous chondrites and their components as reflecting depletions in the initial ^{26}Al/^{27}Al value of their precursors relative to the value defined by CI chondrites, requiring a contribution from a ^{26}Al-poor reservoir different from most inner Solar System bodies. We calculate an average model initial ^{26}Al/^{27}Al ratio of (1.05 ± 0.34) × 10^{-5} for the accretion region of metal-rich carbonaceous chondrites, restricting our analysis to a bulk CR aliquot, one CR chondrule as well as three chondrules and three lithic clasts from Isheyevo, all having an ^{27}Al/^{24}Mg ratio within 10% of the solar value of 0.09781 ± 0.00029 defined by CI chondrites (43). Some of the CR and Isheyevo chondrules, however, record μ^{26}Mg* compositions requiring their formation from essentially ^{26}Al-free precursor material.

The observed positive correlation between μ^{26}Mg* and μ^{54}Cr among inner Solar System materials (Fig. 1) is interpreted as reflecting progressive destruction of their carriers by thermal processing (12–15). In this model, ^{26}Al- and ^{54}Cr-rich presolar silicate carriers are thermally processed during infall of envelope material to the inner protoplanetary disk. As the freshly synthesized supernova-derived carriers are expected to be more thermally labile compared with older, galactically inherited interstellar dust, the carriers of ^{26}Al and ^{54}Cr are preferentially incorporated into a gas phase. This results in an enrichment in the abundance of ^{26}Al and ^{54}Cr in the gas phase relative to residual midplane dust, which translates into a positively correlated relationship between μ^{26}Mg* and μ^{54}Cr. The apparent linearity of the array suggests that the individual carrier phases of ^{26}Al and ^{54}Cr have comparable thermal properties. However, as evidenced from the decoupled μ^{26}Mg* and μ^{54}Cr systematics for metal-rich carbonaceous chondrites and their components, this process cannot explain the inferred low initial ^{26}Al/^{27}Al ratio of some material present in the outer Solar System. Instead, it must represent a primary ^{26}Al disk heterogeneity inherited from the giant molecular cloud parental to our Solar System.

The existence of a primary ^{26}Al disk heterogeneity does not necessarily imply that all short-lived radioisotopes present at the birth of the Solar System were heterogeneously distributed in the early evolutionary stages of the protoplanetary disk. Assessing the level of short-lived radioisotopes heterogeneity requires a better understanding of their stellar sources and carriers. For example, the contrasting initial abundances of ^{26}Al and ^{182}Hf in early-formed Solar System condensates imply distinct stellar sources for these nuclides (7, 44). In contrast to ^{26}Al, which reflects late-stage contamination of the protosolar molecular cloud by a massive star(s), the Solar System inventory of ^{182}Hf is thought to have been inherited from steady-state galactic stellar nucleosynthesis (45), which, in turn, is consistent with the inferred homogeneous distribution of ^{182}Hf at the time of formation of the Solar System's first solids. The age we report for the timing of aqueous alteration of the lithic clasts is based on the ^{53}Mn−^{53}Cr decay system, which could potentially yield inaccurate age information if ^{53}Mn was heterogeneously distributed in the protoplanetary disk. However, the good agreement between the absolute U-corrected Pb−Pb and relative ^{53}Mn−^{53}Cr ages of chondrules from the Gujba CB chondrite (25) supports a homogeneous distribution of ^{53}Mn and, hence, the validity of the reported age.

The μ^{26}Mg*−μ^{54}Cr array defined by metal-rich carbonaceous chondrites and their components reflects the binary mixing of two distinct reservoirs, namely an ^{26}Al-free primordial molecular cloud component and thermally processed inner Solar System matter akin to CM chondrites (Fig. 2). This observation indicates large-scale outward transport of thermally processed inner disk solids to the outer Solar System, which is consistent with the presence of refractory inclusions (CAIs) formed in the innermost disk in the accretion region of cometary objects (46). The paucity of CAIs in the accretion regions of terrestrial planets and most differentiated asteroids as well as ordinary and enstatite chondrites (12) implies that outward transport of inner disk solids did not occur via diffusion along the disk midplane (8) but rather through protostellar outflows or disk winds (47), resulting in the transport of material in ballistic trajectories above the disk (Fig. 3). As protostellar outflows are more intense in the deeply embedded stage of stellar evolution [i.e., class 0 protostars (50)], this model predicts that efficient outward transport of material to the outer Solar System may be limited to the early evolutionary stage of the proto-Sun. Thus, the bulk of the material located in the accretion region of cometary objects may reflect variable proportions of thermally processed (^{26}Al-poor and ^{26}Al-rich) inner disk solids and primordial ^{26}Al-poor molecular cloud matter (Fig. 3).

Origin of High-Temperature Cometary Components

One of the key discoveries of the Stardust sample-return mission to the Jupiter family comet Wild2 is the common presence of chondrules and chondrule fragments in its nucleus (51, 52). Some of these chondrules, characterized by low initial ^{26}Al/^{27}Al ratios $<5 \times 10^{-6}$ (53, 54), are interpreted as reflecting the products of late-stage transient heating events in the inner protoplanetary disk followed by large-scale radial transport to the cometary accretion region. Based on these observations, it is inferred that, similar to chondrites, comets accreted considerable amounts of high-temperature inner Solar System components, limiting their significance for understanding the chemistry of the protosolar molecular cloud. However, the existence of chondrules in CR, CH, and CB chondrites with an isotopic signature requiring the incorporation of a ^{26}Al-poor primordial molecular cloud component suggests that chondrule formation was not limited to

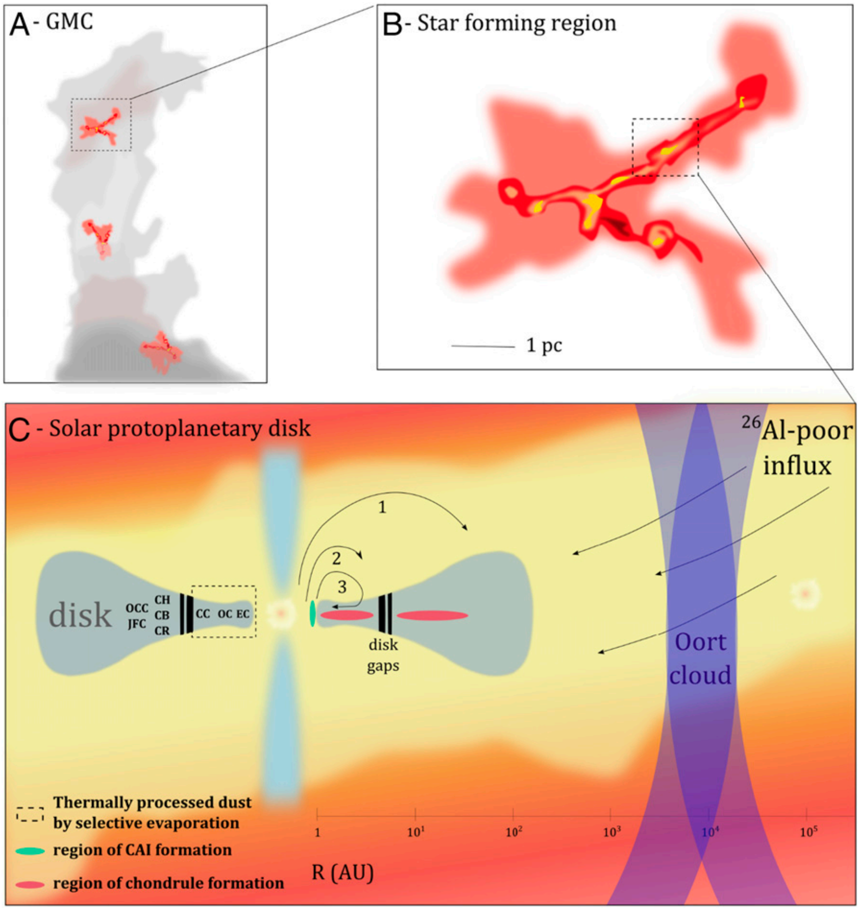

Fig. 3. (*A*) Cartoon depicting a giant molecular cloud with multiple star forming regions. (*B*) Zoom-in on a star-forming region where dense cores form, which eventually collapse to form protostars that accrete material from their surrounding envelopes of molecular cloud material. Note that protostellar environments in star-forming regions are not isolated but connected through large-scale dense filaments of molecular cloud material (48). (*C*) Schematic overview of the proto-Sun and its surrounding protoplanetary disk. Filamentary accretion of envelope material to the proto-Sun occurs via the protoplanetary disk. Formation of refractory inclusions (CAIs) is restricted to the innermost disk during the class 0 stage of the protostar, whereas chondrules formation takes place both in the inner and outer Solar System for the entire disk lifetime (8). Outward transport of solids occurs via stellar outflows and is most efficient in the early evolutionary stages, when material is transported to large orbital distances, namely the accretion regions of metal-rich carbonaceous chondrites and cometary bodies (arrow 1). In later stages, outward transport may be restricted to recycling of material within the inner Solar System (arrows 2 and 3). Opening of disk gaps from the early formation of gas and ice giants limits the influx of our Solar System material to the accretion region of most inner Solar System bodies. Variations in the initial $^{26}Al/^{27}Al$ of inner Solar System material result from selective thermal processing of young supernova-derived ^{26}Al-rich dust (13). Objects accreted in the outer Solar System, namely CR, CH, and CB chondrites, as well as Oort cloud and Jupiter family comets (OCC and JFC, respectively), reflect a mixture of thermally processed, inner Solar System material radially transported to large distances together with accreting primordial ^{26}Al-free molecular cloud material. This may include contributions from material originally located in the outermost part of neighboring systems (49), which could have had contrasting initial $^{26}Al/^{27}Al$ inventories.

the inner Solar System. We suggest that at least a fraction of the chondrules present in the Wild2 comet formed from outer Solar System material characterized by a low initial $^{26}Al/^{27}Al$ ratio. This implies that multiple chondrule formation mechanisms were operating in distinct regions of the protoplanetary disk. The high surface densities and high-energy environments typical of the inner protoplanetary disk may provide a regime for chondrule formation through shock-related transient heating events (55), whereas chondrule formation in the outer Solar System may occur via impacts and bow shocks (56–58). Therefore, comets are still the best candidates to provide insights into the composition of the primordial interstellar matter parental to our Solar System.

Materials and Methods

We have selected a number of pristine carbonaceous chondrites and chondritic components to identify the isotope signature of primordial molecular cloud material in their precursors. In detail, we sampled bulk CR (NWA 6043, EET 92161, and NWA 7837) and CM (Jbilet Winselwan) chondrites along with individual hydrated lithic clasts and chondrules from the Isheyevo CH/CB carbonaceous chondrite and individual chondrules from the NWA 6043, NWA 801, and LAP 02342 CR chondrites. Before isotope investigation, careful characterization of all chondritic components selected for analysis was conducted using compositional images and electron microprobe analyses of individual minerals with the University of Hawaii (UH) field-emission electron JEOL JXA-8500F operated at 15-kV accelerating voltage, 15-nA beam current, and fully focused beam using five wavelength spectrometers. Based on their petrography and mineralogy, the hydrated lithic clasts are classified as group I (59). The CR and Isheyevo chondrules include both porphyritic and skeletal types. We determined the timing of aqueous alteration on the parent body of the hydrated lithic class by $^{53}Mn–^{53}Cr$ dating of dolomitic carbonates present in the clast matrices, which were mapped using high-resolution backscattered electron images. The $^{55}Mn/^{52}Cr$ and $^{53}Cr/^{52}Cr$ ratios of individual carbonates were measured in situ by secondary ionization mass spectrometry using the UH Cameca ims-1280 ion microprobe. For the bulk Mg and Cr isotope measurements of chondrites, fresh fragments were extracted from the interior parts of the NWA7837 (~250 mg), EET92161 (~280 mg), and NWA 6043 (~3 g) CR chondrites, as well as the Jbilet Winselwan CM chondrite (two aliquots of ~100 mg and ~200 mg) and the Ivuna CI chondrite (five aliquots of ~200 mg) and crushed to a fine powder with an agate pestle and mortar. Five hydrated lithic clasts and nine chondrules from Isheyevo as well as three chondrules from CR chondrites (LAP 02342, NWA 801, and NWA 6043) were sampled using a computer-assisted microdrilling device. All samples were digested with mixtures of $HF–HNO_3$ acids for 2 d using Parr bombs at 210 °C, after which they were redissolved in aqua regia overnight. After complete digestion, a 5% aliquot by volume of each of the samples was taken for $^{27}Al/^{24}Mg$ ratio determination with an accuracy of 2% using the ThermoFisher X-series inductively coupled plasma source mass spectrometer (ICPMS) at the Centre for Star and Planet Formation, University of Copenhagen. Magnesium and chromium were purified from sample matrices by ion exchange chromatography based on protocols developed in Bizzarro et al. (60) and Schiller et al. (61) and adapted for the typically smaller sample sizes processed in this study. In detail, Mg was separated using a six-step purification scheme that combines cation, anion, di-éthylhexyldiglycolamide (TODGA), and Ni-spec resins (60). The Cr-rich separate was retrieved from the second step of the Mg chemical purification (60) and further processed through a two-step scheme using TODGA resin (61). An additional step using cation resin (AG50 × 8 200–400 mesh, 100-μL resin volume) was added to the Cr separation method to remove sodium, organics (0.5 M HNO_3), and potential remaining high field-strength elements (1 M HF). Afterward, the Cr separates were dissolved in concentrated aqua regia for 1 wk and concentrated HNO_3 for 3 d at 130 °C to remove any remaining organics. Chemistry yields for Mg and Cr are >99% and >95% respectively. Total Mg and Cr procedural blanks were less than 5 ng and 0.5 ng, respectively and, thus, negligible for all samples analyzed in this study. The isotopic composition of the purified Mg was determined using the ThermoFisher Neptune Plus multiple collector inductively coupled plasma source mass spectrometer (MC-ICPMS) at the Centre for Star and Planet Formation, University of Copenhagen based on analytical procedures reported in Bizzarro et al. (60). The isotopic composition of the purified Cr was determined using the Triton thermal ionization mass spectrometer at the Natural History Museum of Denmark using a filament exhaustion sample standard bracketing approach. The accuracy and external reproducibility of our measurements was determined by repeated analyses of column-processed Ivuna CI chondrite and terrestrial rock standards (DTS-2b and BHVO-2). A full description of the samples reported in this study and procedures used for data acquisition are presented in *SI Appendix*.

ACKNOWLEDGMENTS. This work was funded by grants from the Danish National Research Foundation (DNRF97) and from the European Research Council (ERC Consolidator Grant Agreement 616027-STARDUST2ASTEROIDS) to M.B.

1. Williams JP, Cieza LA (2011) Protoplanetary disks and their evolution. *Annu Rev Astron Astrophys* 49:67–117.
2. Kleine T, et al. (2009) Hf–W chronology of the accretion and early evolution of asteroids and terrestrial planets. *Geochim Cosmochim Acta* 73(17):5150–5188.
3. Krot AN, et al. (2009) Origin and chronology of chondritic components: A review. *Geochim Cosmochim Acta* 73(17):4963–4997.
4. Connelly JN, et al. (2012) The absolute chronology and thermal processing of solids in the solar protoplanetary disk. *Science* 338(6107):651–655.
5. Sahijpal S, Goswami JN (1998) Refractory phases in primitive meteorites devoid of ^{26}Al and ^{41}Ca: Representative samples of first solar system solids? *Astrophys J* 509(2):L137–L140.
6. Makide K, et al. (2011) Heterogeneous distribution of ^{26}Al at the birth of the solar system. *Astrophys J* 733:L31.
7. Holst JC, et al. (2013) ^{182}Hf-^{182}W age dating of a ^{26}Al-poor inclusion and implications for the origin of short-lived radioisotopes in the early Solar System. *Proc Natl Acad Sci USA* 110(22):8819–8823.
8. Ciesla FJ (2007) Outward transport of high-temperature materials around the midplane of the solar nebula. *Science* 318(5850):613–615.
9. Walsh KJ, Morbidelli A, Raymond SN, O'Brien DP, Mandell AM (2011) A low mass for Mars from Jupiter's early gas-driven migration. *Nature* 475(7355):206–209.
10. Alexander CMOD, et al. (2012) The provenances of asteroids, and their contributions to the volatile inventories of the terrestrial planets. *Science* 337(6095):721–723.
11. Doyle PM, et al. (2015) Early aqueous activity on the ordinary and carbonaceous chondrite parent bodies recorded by fayalite. *Nat Commun* 6:7444.
12. Trinquier A, et al. (2009) Origin of nucleosynthetic isotope heterogeneity in the solar protoplanetary disk. *Science* 324(5925):374–376.
13. Larsen KK, et al. (2011) Evidence for magnesium isotope heterogeneity in the solar protoplanetary disk. *Astrophys J* 735(2):L37.
14. Paton C, Schiller M, Bizzarro M (2013) Identification of an ^{84}Sr-depleted carrier in primitive meteorites and implications for thermal processing in the solar protoplanetary disk. *Astrophys J* 763(2):L40.
15. Schiller M, Paton C, Bizzarro M (2015) Evidence for nucleosynthetic enrichment of the protosolar molecular cloud core by multiple supernova events. *Geochim Cosmochim Acta* 149:88–102.
16. Scott ERD (2007) Chondrites and the protoplanetary disk. *Annu Rev Earth Planet Sci* 35:577–620.
17. Krot AN, et al. (2008) Multiple generations of refractory inclusions in the metal-rich carbonaceous chondrites Acfer 182/214 and Isheyevo. *Astrophys J* 672(1):713–721.
18. Briani G, et al. (2009) Pristine extraterrestrial material with unprecedented nitrogen isotopic variation. *Proc Natl Acad Sci USA* 106(26):10522–10527.
19. Bonal L, et al. (2010) Highly ^{15}N-enriched chondritic clasts in the CB/CH-like meteorite Isheyevo. *Geochim Cosmochim Acta* 74(22):6590–6609.
20. Rodgers SD, Charnley SB (2008) Nitrogen superfractionation in dense cloud cores. *Mon Not R Astron Soc* 385(1):L48–L52.
21. Wampfler SF, Jørgensen JK, Bizzarro M, Bisschop SE (2014) Observations of nitrogen isotope fractionation in deeply embedded protostars. *Astron Astrophys* 572:A24.
22. Busemann H, et al. (2009) Ultra-primitive interplanetary dust particles from the comet 26P/Grigg-Skjellerup dust stream collection. *Earth Planet Sci Lett* 288(1-2):44–57.
23. Krot AN, Meibom A, Weinberg MK, Keil K (2002) The CR chondrite clan: Implications for early solar system processes. *Meteorit Planet Sci* 37(11):1451–1490.
24. Leitner J, Vollmer C, Hoppe P, Zipfel J (2012) Characterization of presolar material in the CR chondrite Northwest Africa 852. *Astrophys J* 745(1):38.
25. Bollard J, Connelly JN, Bizzarro M (2015) Pb-Pb dating of individual chondrules from the CB_a chondrite Gujba: Assessment of the impact plume formation model. *Meteorit Planet Sci* 50(7):1197–1216.
26. Fujiya W, Sugiura N, Hotta H, Ichimura K, Sano Y (2012) Evidence for the late formation of hydrous asteroids from young meteoritic carbonates. *Nat Commun* 3:627.
27. Fujiya W, Sugiura N, Sano Y, Hiyagon H (2013) Mn–Cr ages of dolomites in CI chondrites and the Tagish Lake ungrouped Carbonaceous chondrite. *Earth Planet Sci Lett* 362:130–142.
28. Olsen MB, et al. (2013) Magnesium isotope evidence for single stage formation of CB chondrules by colliding planetesimals. *Astrophys J* 776:L1.
29. Yamashita K, Maruyama S, Yamakawa A, Nakamura E (2010) ^{53}Mn-^{53}Cr Chronometry of CB Chondrite: Evidence for Uniform Distribution of ^{53}Mn in the Early Solar System. *Astrophys J* 723(1):L1.
30. Irvine WM, et al. (1996) Spectroscopic evidence for interstellar ices in comet Hyakutake. *Nature* 383(6599):418–420.
31. Padoan P, Kritsuk A, Norman ML, Nordlund Å (2005) A solution to the pre-main-sequence accretion problem. *Astrophys J* 622(1):L61–L64.
32. Warren PH (2011) Stable-isotopic anomalies and the accretionary assemblage of the Earth and Mars: A subordinate role for carbonaceous chondrites. *Earth Planet Sci Lett* 311(1-2):93–100.
33. Krot AN, Keil K, Goodrich C, Weisberg MK, Scott ERD (2013) Classification of meteorites and their genetic relationships. *Meteorites and Cosmochemical Processes*, ed Davis AM, Treatise on Geochemistry, eds Holland HD, Turekian KK (Elsevier, Oxford), Vol 1, pp. 1–63.
34. Krot AN, Nagashima K, Yoshitake M, Yurimoto H (2010) Oxygen isotope compositions of chondrules from the metal-rich chondrites Isheyevo (CH/CBb), MAC 02675 (CBb) and QUE 94627 (CBb). *Geochim Cosmochim Acta* 74:2190–2211.
35. Tenner TJ, Nakashima D, Ushikubo T, Kita NT, Weisberg MK (2015) Oxygen isotope ratios of FeO-poor chondrules in CR3 chondrites: Influence of dust enrichment and H_2O during chondrule formation. *Geochim Cosmochim Acta* 148:228–250.
36. McKeegan KD, et al. (2011) The oxygen isotopic composition of the Sun inferred from captured solar wind. *Science* 332(6037):1528–1532.
37. Lugaro M, Liffman K, Ireland TR, Maddison ST (2012) Can Galactic chemical evolution explain the oxygen isotopic variations in the Solar System? *Astrophys J* 759:51.
38. Krot AN, et al. (2010) Oxygen isotopic composition of the Sun and mean oxygen isotopic composition of the protosolar silicate dust: Evidence from refractory inclusions. *Astrophys J* 713(2):1159–1166.
39. Sugiura N, Fujiya W (2014) Correlated accretion ages and ε^{54}Cr of meteorite parent bodies and the evolution of the solar nebula. *Meteorit Planet Sci* 49(5):772–787.
40. Müller TWA, Kley W (2013) Modelling accretion in transitional disks. *Astron Astrophys* 560:A40.
41. Lambrechts M, Johansen A (2012) Rapid growth of gas-giant cores by pebble accretion. *Astron Astrophys* 544:A32.
42. Schiller M, et al. (2015) Early accretion of protoplanets inferred from a reduced inner solar system ^{26}Al inventory. *Earth Planet Sci Lett* 420:45–54.
43. Paton C, Schiller M, Ulfbeck D, Bizzarro M (2012) High-precision ^{27}Al/^{24}Mg ratio determination using a modified isotope-dilution approach. *J Anal At Spectrom* 27(4):644–652.
44. Thrane K, Nagashima K, Krot AN, Bizzarro M (2008) Discovery of a new FUN CAI from a CV carbonaceous chondrite: Evidence for multistage thermal processing in the protoplanetary disk. *Astrophys J* 680(2):L141–L144.
45. Lugaro M, et al. (2014) Early solar system. Stellar origin of the ^{182}Hf cosmochronometer and the presolar history of solar system matter. *Science* 345(6197):650–653.
46. Brownlee D, et al. (2006) Comet 81P/Wild 2 under a microscope. *Science* 314(5806):1711–1716.
47. Shu FH, Shan H, Lee T (1996) Towards an astrophysical theory of chondrites. *Science* 271:1545–1552.
48. André P, et al. (2014) From filamentary networks to dense cores in molecular clouds: toward a new paradigm for star formation. *Protostars and Planets VI*, ed Beuther H, Klessen RS, Dullemond CP, Henning T (Univ Arizona Press, Tucson, AZ), pp 27–52.
49. Levison HF, Duncan MJ, Brasser R, Kaufmann DE (2010) Capture of the Sun's Oort cloud from stars in its birth cluster. *Science* 329(5988):187–190.
50. Bontemps S, André P, Terebey S, Cabrit S (1996) Evolution of outflow activity around low-mass embedded young stellar objects. *Astron Astrophys* 311:858–872.
51. Nakamura T, et al. (2008) Chondrulelike objects in short-period comet 81P/Wild 2. *Science* 321(5896):1664–1667.
52. Nakashima D, et al. (2012) Oxygen isotopes in crystalline silicates of comet Wild 2: A comparison of oxygen isotope systematics betweenWild 2 particles and chondritic materials. *Earth Planet Sci Lett* 357-358:355–365.
53. Ogliore R, et al. (2012) Incorporation of a late-forming chondrule into Comet Wild 2. *Astrophys J* 745(2):L19.
54. Nakashima D, et al. (2015) Late formation of a comet Wild 2 crystalline silicate particle, Pyxie, inferred from Al–Mg chronology of plagioclase. *Earth Planet Sci Lett* 410:54–61.
55. Connolly HC, Desch SJ, Ash RD, Jones RH (2006) Transient heating events in the protoplanetary nebulae. *Meteorites and the Early Solar System II*, eds Lauretta DS, McSween HY (Univ Arizona Press, Tucson, AZ), pp 383–397.
56. Krot AN, Amelin Y, Cassen P, Meibom A (2005) Young chondrules in CB chondrites from a giant impact in the early Solar System. *Nature* 436(7053):989–992.
57. Johnson BC, Minton DA, Melosh HJ, Zuber MT (2015) Impact jetting as the origin of chondrules. *Nature* 517(7534):339–341.
58. Morris MA, Boley AC, Desch SJ, Athanassiadou T (2012) Chondrule formation in bow shocks around eccentric planetary embryos. *Astrophys J* 752(1):27.
59. Bonal L, et al. (2010) Chondritic lithic clasts in the CB/CH-like meteorite Isheyevo: Fragments of previously unsampled parent bodies. *Geochim Cosmochim Acta* 74(8):2500–2522.
60. Bizzarro M, et al. (2011) High-precision Mg-isotope measurements of terrestrial and extraterrestrial material by HR-MC-ICPMS implications for the relative and absolute Mg-isotope composition of the bulk silicate earth. *J Anal At Spectrom* 26(3):565–577.
61. Schiller M, Van Kooten E, Holst JC, Olsen MB, Bizzarro M (2014) Precise measurement of chromium isotopes by MC-ICPMS. *J Anal At Spectrom* 29(8):1406–1416.