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The origin of volatile element depletion in early solar system material: Clues from Zn isotopes in chondrules



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ABSTRACT

Volatile lithophile elements are depleted in the different planetary materials to various degrees, but the origin of these depletions is still debated. Stable isotopes of moderately volatile elements such as Zn can be used to understand the origin of volatile element depletions. Samples with significant volatile element depletions, including the Moon and terrestrial tektites, display heavy Zn isotope compositions (i.e. enrichment of ⁶⁶Zn vs. ⁶⁴Zn), consistent with kinetic Zn isotope fractionation during evaporation. However, Luck et al. (2005) found a negative correlation between $\delta^{66}\text{Zn}$ and $1/[\text{Zn}]$ between CI, CM, CO, and CV chondrites, opposite to what would be expected if evaporation caused the Zn abundance variations among chondrite groups.

We have analyzed the Zn isotope composition of multiple samples of the major carbonaceous chondrite classes: CI (1), CM (4), CV (2), CO (4), CB (2), CH (2), CK (4), and CK/CR (1). The bulk chondrites define a negative correlation in a plot of $\delta^{66}\text{Zn}$ vs $1/[\text{Zn}]$, confirming earlier results that Zn abundance variations among carbonaceous chondrites cannot be explained by evaporation. Exceptions are CB and CH chondrites, which display Zn systematics consistent with a collisional formation mechanism that created enrichment in heavy Zn isotopes relative to the trend defined by CI–CK.

We further report Zn isotope analyses of chondrite components, including chondrules from Allende (CV3) and Mokoia (CV3), as well as an aliquot of Allende matrix. All chondrules are enriched in light Zn isotopes (~500 ppm on ⁶⁶Zn/⁶⁴Zn) relative to the bulk, contrary to what would be expected if Zn were depleted during evaporation, on the other hand the matrix has a complementary heavy isotope composition. We report sequential leaching experiments in un-equilibrated ordinary chondrites, which show sulfides are isotopically heavy compared to silicates and the bulk meteorite by ca. +0.65 per mil on ⁶⁶Zn/⁶⁴Zn. We suggest isotopically heavy sulfides were removed from either chondrules or their precursors, thereby producing the light Zn isotope enrichments in chondrules.

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1. Introduction

Carbonaceous chondrites (CC) are chemically primitive early Solar System materials that provide important clues toward understanding the origin and evolution of the terrestrial planets. Carbonaceous chondrites consist of assemblages of four components in different proportion: high-temperature condensates in

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the form of Calcium Aluminum-rich Inclusions (CAIs), roughly spherical small igneous objects known as chondrules, metallic FeNi and sulfides, and a fine-grained matrix (Krot et al., 2009; Scott and Krot, 2014). Carbonaceous chondrites are undifferentiated meteorites that are relatively volatile-rich and did not experience high-temperature processing sufficient to result in melting, but they do show evidence of variable degrees of aqueous alteration and thermal metamorphism (Scott and Krot, 2014). Although CC are in general considered as chemically primitive, individual carbonaceous chondrite classes exhibit distinct patterns in volatile element (here “volatile” refers to those elements with a

50% condensation temperature, T_c , between 250 K and 1250 K, Lodders, 2003) abundances relative to solar composition (Palme et al., 2014a). The CI-type CC are believed to be the closest in composition to the solar nebula due to elemental abundances that closely match the composition of the solar photosphere, with the exception of lithium, the highly volatile elements ($T_c < 250$ K: H, C, N, O), and the noble gases (Palme et al., 2014a). The other CC classes show volatile depletion increasing in the order CI-CM-(CO, CV)-CK (Palme et al., 2014a). The origin of this chemical trend is as yet unresolved. Hypotheses for the volatile element depletion in bulk chondrites include incomplete condensation from the solar nebula (Wasson and Chou, 1974), volatile loss by evaporation during accretion (Ringwood, 1966), or mixing of distinct primordial reservoirs consisting of a volatile-rich CI-like component and a volatile-poor refractory component (Larimer and Anders, 1967; Clayton and Mayeda, 1999; Luck et al., 2003). Chondrules are one proposed carrier of the volatile depletion for the latter case, such that volatile element depletions in bulk meteorites are a signature of distinct chondrule compositions and the different CC classes represent varying mixtures of a compositionally uniform CI-like matrix and compositionally variable chondrules (e.g. Alexander, 2005).

The mechanism of chondrule formation is still debated and it has numerous implications for the origin of volatile elements in the terrestrial planets and for dynamical processes in the early Solar System. Central questions concern the relationship between chondrules and matrix, namely, whether these two chondritic components formed together in the same region of the solar nebula or formed in separate reservoirs and were later combined (Zanda et al., 2006; Hezel and Palme, 2008, 2010; Palme et al., 2015 and references therein). The formation of the first solid materials is therefore directly linked to conditions in the solar environment during early planetary formation and can support or contradict models of Solar System formation. The difficulty lies in reconciling the contrasting formation conditions of CAIs (high temperatures, variable isotopic reservoirs, short formation timescale several Myr before incorporation into chondrites), chondrules (moderately high temperatures, episodic formation likely at higher total pressures), and matrix (lesser thermal processing, volatile-rich) with the incorporation of all three components into a coherent aggregate at a particular time and place in the protoplanetary disk (Krot et al., 2009).

Proposed chondrule formation models that attempt to account for these constraints include the flash heating of chondrule precursors by a shockwave (Connolly and Love, 1998; Ciesla and Hood, 2002; Desch and Connolly, 2002; Connolly and Desch, 2004) or formation in plumes generated by impacts (Asphaug et al., 2011). The flash heating model reproduces the chemical relationships between chondritic components, including the thermal history of chondrules, chondrule-matrix complementarity, and episodic chondrule formation (Asphaug et al., 2011). On the other hand, the impact origin would predict a high gas pressure and dust density that would explain the retention of volatile elements in chondrules. Alternatively, the x-wind model (Shu et al., 1996) is based on astronomical observations of extra-solar systems and theoretical modeling of stellar magnetic fields. It suggests that CAIs and chondrules formed close to the young sun and were later transported radially outward in the disk where they mixed with thermally unprocessed matrix material. This model accounts for the contrasting thermal history between chondrules/CAIs and matrix but fails to explain genetic relationships between chondrules and matrix.

The study of zinc (Zn) isotopes in chondrites and their components has the potential to investigate the numerous questions outlined above. Zinc is a moderately volatile element ($T_c = 726$ K) with a condensation temperature significantly below that of many other moderately volatile elements, including K ($T_c = 1006$ K), Na

($T_c = 958$ K), and Rb ($T_c = 800$ K) (Lodders, 2003). Further, Zn exhibits both chalcophile and lithophile behavior and, hence, provides information about the history of silicate as well as sulphide phases. Zinc displays significant heavy isotope enrichments coupled with volatile depletion, as observed in lunar basalts and unbrecciated eucrites (Paniello et al., 2012a, 2012b; Kato et al., 2015; Moynier et al., 2017). Impact events have been shown to volatilize Zn and drive the composition of the residue toward isotopically heavier compositions (Moynier et al., 2009a), making Zn a powerful probe of volatility-dependent processes during chondrite and chondrule formation. The pioneer study of Luck et al. (2005) reported a negative correlation between $\delta^{66}\text{Zn}$ and $1/[\text{Zn}]$ in bulk CC, such that they are progressively enriched in the light isotopes of Zn in the order CI-CM-(CO, CV). This observation is opposite to the effect expected during Zn isotope fractionation due to evaporation and suggests that the abundance of volatile elements in CC is inherited from pre-accretionary processes, reflecting mixing between at least two isotopically distinct reservoirs. The Zn isotope composition of several CC groups (CK, CB, CH), as well as individual components such as chondrules and matrix, which are the major reservoirs of Zn, have not yet been analyzed. However, these samples may provide critical clues toward further understanding the origin of the volatile element variations among CC.

Here we present Zn isotope data for a comprehensive set of CC, including samples from the CI, CM, CO, CV, CK, CB, and CH classes, to further assess the origin and evolution of volatile elements in the inner Solar System. We also present Zn isotope measurements of individual chondrules from Allende (CV3) and Mokoia (CV3) as well as an aliquot of Allende matrix to investigate the formation of solid materials in the early Solar System and the compositions of the primitive materials that represent the building blocks of the terrestrial planets.

2. Samples and methods

2.1. Samples

The 20 bulk chondrites studied include one CI (Y-980115), four CM (Murchison, Murray, Cold Bokkeveld, LON 94101), two CV (Allende, GRA 06101), four CO (Felix, Ornans, Lancé, Isna), two CB (Gujba, MIL 05082), two CH (PCA 91467, A-881020), four CK (ALH 85002, Karoonda, EET 92002, Maralinga), and one CK/CR (A-881595). Y-980115 is CI-like but has mineralogical characteristics that suggest it experienced thermal metamorphism (King et al., 2015). In addition its high Zn content (337 ppm, see below) is similar to other CI chondrites and support its classification as a CI chondrite. A-881595 is classified as a CR2, but more likely is a CK based on O isotopes (Schrader et al., 2011). The bulk compositions of the selected meteorites represent a range in Zn concentration of more than two orders of magnitude, from ~ 3 ppm to ~ 300 ppm. Since Zn is highly mobile in aqueous fluids, meteorite falls were selected over finds when possible. In addition, three unequilibrated ordinary chondrites (UOC), including Clovis (H3.6), GRA 95208 (H3.7), and ALH 90411 (L3.7), were subjected to a sequential dissolution procedure to isolate and analyze the Zn isotope composition of various Zn carrier phases. Finally, nine individual chondrules (including eight from Allende and one from Mokoia) as well as one matrix-rich aliquot from Allende were extracted and their Zn isotope compositions were analyzed.

2.2. Methods

For bulk chondrites, >500 mg of sample was crushed into a homogeneous powder. Approximately 20–50 mg of each sample powder was dissolved using a mixture of concentrated HF/HNO₃ and heated at 130 °C in PTFE beakers. After evaporation of the

HF/HNO₃, 6N HCl was added to the residue and again heated to dissolve remaining fluoride complexes. Samples were then evaporated to dryness. Whole individual chondrules were separated by hand, crushed, and dissolved using the same procedure as for the bulk chondrites except that the volume of acids was reduced to limit the procedural blank.

The three UOC were further subjected to physical phase separation (to separate magnetic and non-magnetic phases) and sequential acid dissolution on the non-magnetic phase to isolate specific carriers of Zn following the procedure described by Moynier et al. (2011). After crushing, the magnetic and non-magnetic fractions were separated with a hand magnet. The magnetic phase was dissolved in aqua-regia. The non-magnetic fraction was first dissolved in cold 3N HCl for 6 h; this dissolution contained the sulfide fraction (see Luck et al., 2005). The remaining residue was then dissolved in HF/HNO₃ to completely dissolve the silicate fraction.

Chemical purification of Zn was achieved following the procedure described by Moynier and Le Borgne (2015). Samples were loaded in 1.5N HBr on AG-1 X8 (200–400 mesh) anion-exchange resin in PTFE columns. Matrix elements were removed by an additional wash of 1.5N HBr and Zn was eluted using 0.5N HNO₃. The collected sample solutions were then evaporated to dryness. This procedure was performed for a total of three column passes to ensure clean separation of Zn: samples were passed once through columns containing 0.5 mL resin and then twice through columns containing 0.1 mL resin. Procedural blank is <7 ng and insignificant relative to the amount of Zn in the sample mass analyzed for bulk chondrites (>1 μg Zn). For chondrules, we have slightly modified the method where we only passed the samples twice through the 0.1 mL columns. This limits the amount of acids used and reduced the blank to <1 ng which represents up to 3% of the total signal.

Zinc isotope compositions of bulk carbonaceous chondrites were measured using a Thermo Scientific Neptune Plus Multi-Collector Inductively-Coupled-Plasma Mass-Spectrometer (MC-ICP-MS) at either Washington University in Saint Louis (WUSTL) or the Institut de Physique du Globe in Paris (IPGP) following protocol recently described elsewhere (Chen et al., 2013; Moynier and Le Borgne, 2015). Carbonaceous chondrite components were measured at IPGP, while UOC leachates were measured at WUSTL. External reproducibility was assessed through full procedural replicate analyses of the same sample to be 40 ppm for ⁶⁶Zn/⁶⁴Zn and 50 ppm for ⁶⁸Zn/⁶⁴Zn (Chen et al., 2013). The Zn isotope composition of the USGS basalt standard BHVO-2 was measured throughout the study; the data are in agreement with currently accepted literature values (see Table 1; Moynier et al., 2017). Additionally, one sample (Murray) was independently processed through the entire procedure (dissolution, chemical purification, mass spectrometry) at both Washington University in Saint Louis and at the Institut de Physique du Globe in Paris; these replicates yield identical results within analytical error, signifying that the method is reproducible.

The Zn concentrations were obtained by comparison of the intensity of the standard and of the samples on the MC-ICP-MS for which we estimate the error to be ~10%. This method gives a Zn concentration of 103 ppm in BHVO, which compares well with the USGS certification (103 ± 6 ppm).

3. Results

Zinc isotope compositions are reported in Table 1, Table 2, and Table 3 and Fig. 1, Fig. 2, Fig. 3, Fig. 4, and Fig. 5 as permil deviations from the JMC-Lyon (Moynier et al., 2017) Zn isotope standard,

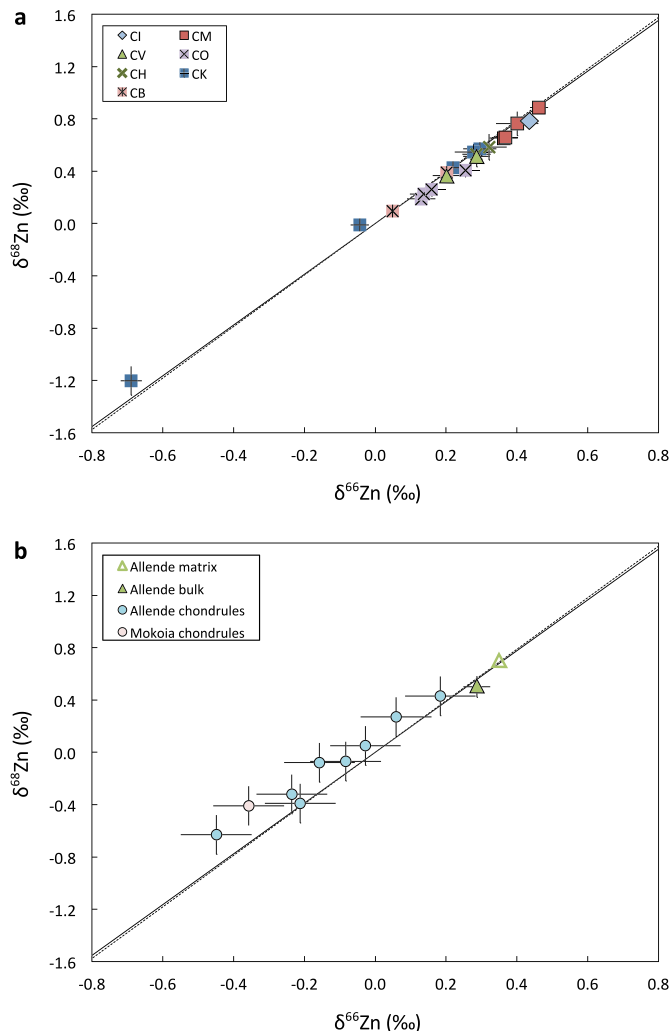


Fig. 1. Three isotope plot of $\delta^{68}\text{Zn}$ versus $\delta^{66}\text{Zn}$ for bulk chondrites. Samples plot along the calculated equilibrium (solid; slope 1.94) and kinetic (dashed; slope 1.97) mass-dependent fractionation lines (± 2 se).

$$\delta^x\text{Zn} = \left[\frac{(\text{}^x\text{Zn}/\text{}^{64}\text{Zn})_{\text{sample}}}{(\text{}^x\text{Zn}/\text{}^{64}\text{Zn})_{\text{JMC-Lyon}}} - 1 \right] \times 1000 \quad (1)$$

where $x = 66$ or 68 . Errors are given as the 2 standard deviation (2sd) of replicate measurements. Where only one measurement was possible we use the error obtained on multiple analyses of full procedural replicates (see Section 2.2) for the bulk chondrites or the error obtained for the single chondrule with multiple analyses (see Table 2). All the data fall on a mass-dependent fractionation line in a plot of $\delta^{68}\text{Zn}$ versus $\delta^{66}\text{Zn}$ (Fig. 1) consistent with Moynier et al. (2009b), with the exception of three chondrules slightly off the line, which is likely due to an error underestimation due to the low Zn content of these samples and the fact that replicate analyses could not be performed.

Bulk CC (Table 1 and Fig. 2) span a range of $\delta^{66}\text{Zn}$ from +0.43‰ (Y-980115, CI) to -0.69‰ (A-881595, CK/CR). The values for the single CI ($\delta^{66}\text{Zn} = 0.43\text{‰} \pm 0.01$) and the class averages for the CM ($\delta^{66}\text{Zn} = 0.38\text{‰} \pm 0.04$), CV ($\delta^{66}\text{Zn} = 0.24\text{‰} \pm 0.12$), and CO ($\delta^{66}\text{Zn} = 0.17\text{‰} \pm 0.11$) are similar to previously reported data (Luck et al., 2005; Barrat et al., 2012, see Fig. 2). Notably, each CC class has a characteristic Zn isotope composition. As previously observed, $\delta^{66}\text{Zn}$ values correlate with Zn concentration, [Zn] (Fig. 3); samples with the lowest [Zn] are the most enriched in light Zn isotopes (Luck et al., 2005). The CK (on average, $\delta^{66}\text{Zn} = 0.19\text{‰} \pm 0.31$) are more variable in both Zn isotope

Table 1
Zinc isotopic compositions and concentration data for bulk carbonaceous chondrites.

Sample	Class	Fall/find	$\delta^{66}\text{Zn}$	2sd ^a	$\delta^{68}\text{Zn}$	2sd ^a	n ^b	[Zn] (ppm)
BHVO-2			0.30	0.03	0.59	0.06	11	103
Y-980115 ^c	CI1	find	0.43	0.01	0.79	0.03	5	337
Murchison ^c	CM2	fall	0.40	0.06	0.76	0.09	6	186
Murray (1) ^c	CM2	fall	0.38	0.02	0.68	0.05	5	187
Murray (2) ^d	CM2	fall	0.36	–	0.65	–	1	
<i>Average-Murray</i>			0.37	0.02	0.67	0.04	2	187
Cold Bokkeveld ^c	CM2	fall	0.46	0.03	0.89	0.04	4	145
LON 94101 ^c	CM2	find	0.37	0.04	0.66	0.02	5	184
<i>Average-CM</i>			0.38	0.04	0.70	0.12	3	172
Allende (1) ^c	CV3	fall	0.27	0.04	0.48	0.08	2	112
Allende (2) ^c	CV3	fall	0.30	0.02	0.54	0.02	5	108
<i>Average-Allende</i>			0.29	0.04	0.51	0.08	2	110
GRA 06101 ^d	CV3	find	0.20	–	0.37	–	1	120
<i>Average-CV</i>			0.24	0.12	0.44	0.21	2	110
Felix ^d	CO3.3	fall	0.14	–	0.22	–	1	99
Ornans ^d	CO3.4	fall	0.13	–	0.19	–	1	105
Lancé ^d	CO3.5	fall	0.16	–	0.26	–	1	103
Isna ^d	CO3.8	find	0.25	–	0.41	–	1	100
<i>Average-CO</i>			0.17	0.11	0.27	0.19	4	102
Gujba ^d	CB	fall	0.20	–	0.39	–	1	3
MIL 05082 ^d	CB	find	0.05	–	0.10	–	1	6
<i>Average-CB</i>			0.13	0.22	0.24	0.41	2	5
PCA 91467 ^c	CH3	find	0.32	0.05	0.58	0.10	2	39
A-881020 ^c	CH3	find	0.29	0.04	0.53	0.07	2	31
<i>Average-CH</i>			0.30	0.05	0.56	0.08	2	35
ALH 85002 ^c	CK4	find	0.22	0.01	0.43	0.02	4	78
Karoonda ^c	CK4	fall	0.30	0.05	0.57	0.05	4	83
EET 92002 ^c	CK5	find	0.28	0.05	0.54	0.06	4	90
Maralinga ^c	CK4	find	–0.04	0.03	–0.01	0.02	3	57
<i>Average-CK</i>			0.19	0.31	0.38	0.54	4	77
A-881595 ^c	CK/CR2	find	–0.69	0.03	–1.20	0.11	2	22

^a 2sd = 2 × standard deviation.

^b n = number of measurements.

^c Measured at IPGP.

^d Measured at WUSTL.

Table 2
Zinc isotopic compositions and concentration data for individual chondrules from Allende and Mokoia and an Allende matrix-rich aliquot.

Sample	$\delta^{66}\text{Zn}$	2sd ^a	$\delta^{68}\text{Zn}$	2sd ^a	n ^b	Mass (mg)	[Zn] ppm
<i>Allende</i>							
CH4	–0.21	0.10	–0.39	0.15	2	1.7	60
CH5	–0.03	–	0.05	–	1	3.3	32
CH6	0.18	–	0.43	–	1	1.9	31
CH8	–0.45	–	–0.63	–	1	0.7	42
CH10	0.06	–	0.27	–	1	0.7	71
A64	–0.08	–	–0.07	–	1	1.6	94
A70	–0.24	–	–0.32	–	1	2	52
A78	–0.16	–	–0.08	–	1	2.2	47
Matrix-rich	0.35						150
<i>Mokoia</i>							
M53	–0.36	–	–0.41	–	1	9	59

^a 2sd = 2 × standard deviation.

^b n = number of measurements.

composition and [Zn], but range from values similar to those for CV-CO towards lighter Zn isotope compositions, further extending the trend relating $\delta^{66}\text{Zn}$ and Zn depletion defined in Luck et al. (2005). The chondrite with the lowest bulk $\delta^{66}\text{Zn}$, A-881595 (CK/CR; $\delta^{66}\text{Zn} = -0.69 \pm 0.03\%$) is >10x more depleted in Zn and offset by > 1‰ on the $^{66}\text{Zn}/^{64}\text{Zn}$ ratio compared to CI. Chondrites

from the CB and CH classes (on average, $\delta^{66}\text{Zn} = 0.13 \pm 0.22\%$ and $\delta^{68}\text{Zn} = 0.30 \pm 0.05\%$, respectively) have low Zn concentrations (3–39 ppm) but fall off the trend defined by the CI-CK classes, with higher $\delta^{66}\text{Zn}$ values for a given [Zn]. In addition, there is a clear trend between $\delta^{66}\text{Zn}$ and $\varepsilon^{54}\text{Cr}$ for CI-CK chondrites, while the CB fall off the trend defined by CI-CK (Fig. 6).

Table 3
Zinc isotope compositions of equilibrated ordinary chondrite leachates.

Sample	Component	$\delta^{66}\text{Zn}$	$\delta^{68}\text{Zn}$	Mass fraction	[Zn] ppm	$\Delta^{66}\text{Zn}_{\text{sulfide-silicate}}^a$
Clovis (H3.6)	Magnetic	−1.64	−2.92	0.12	28	0.64
	Silicate	−2.57	−4.98	0.43	68	
	Sulfide	−1.93	−3.73	0.44	62	
	Whole rock	−2.42	−4.65			
GRA 95208 (H3.7)	Magnetic	−0.42	−0.79	0.14	41	0.79
	Silicate	0.37	0.75	0.46	58	
	Sulfide	0.37	0.75	0.40	44	
	Whole rock	−0.04	0.07			
ALH 90411 (L3.7)	Magnetic	−1.07	−1.94	0.08	20	0.50
	Silicate	−0.91	−1.74	0.47	72	
	Sulfide	−0.41	−0.75	0.45	33	
	Whole rock	−0.75	−1.41			

$$^a \Delta^{66}\text{Zn}_{\text{sulfide-silicate}} = \delta^{66}\text{Zn}(\text{sulfide}) - \delta^{66}\text{Zn}(\text{silicate}).$$

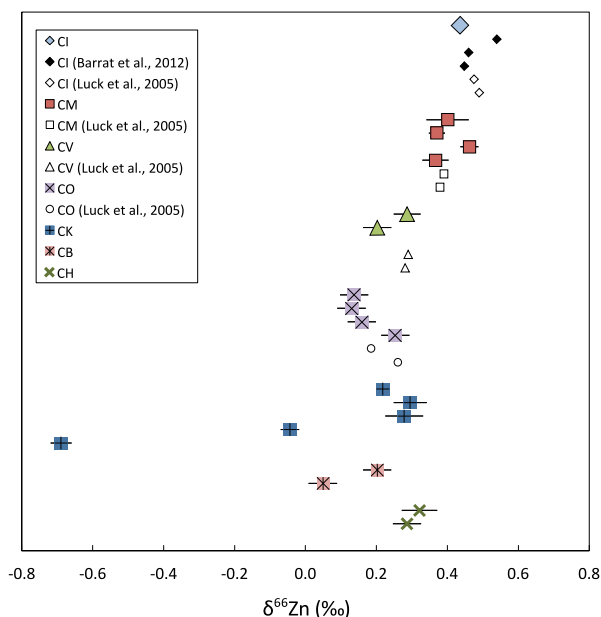


Fig. 2. Zinc isotope data for bulk CC from this study as well as literature data for CI, CM, CV, and CO (Luck et al., 2005; Barrat et al., 2012). The $\delta^{66}\text{Zn}$ values from this study are in good agreement with literature data. Error bars are 2sd.

The $\delta^{66}\text{Zn}$ values for individual chondrules are highly variable and range from +0.18‰ to −0.45‰ (Table 2 and Fig. 4), with a mean $\delta^{66}\text{Zn}$ of $-0.12 \pm 0.39\%$ (2sd). In addition the Zn content of the chondrules is also variable as previously observed by Rubin and Wasson (1987) and Palme et al. (2014b). All Allende chondrules are enriched in light Zn isotopes relative to the composition of the bulk (Allende bulk $\delta^{66}\text{Zn} = 0.29 \pm 0.04\%$). For the individual chondrules the full procedural blank can represent a maximum of 3% of the total beam intensity during MC-ICP-MS analysis. If a terrestrial isotopic composition of $\delta^{66}\text{Zn} = 0.28$ (Chen et al., 2013; note that it is not possible to analyze the isotopic composition of the blank due to the extremely low total content of Zn) is assumed for the blank, then this could shift the measured isotopic composition of a chondrule towards heavier $\delta^{66}\text{Zn}$ values by a maximum of only 0.03‰. The matrix-rich aliquot of Allende has a slightly heavier Zn isotope composition ($\delta^{66}\text{Zn} = 0.35\%$) relative to the bulk. The Zn concentration is about three times higher in Allende matrix (~150 ppm) compared to Allende chondrules (~50 ppm). The Zn isotope composition of the single Mokoia chondrule ($\delta^{66}\text{Zn} = -0.36\%$) falls within the range of the Allende chondrules.

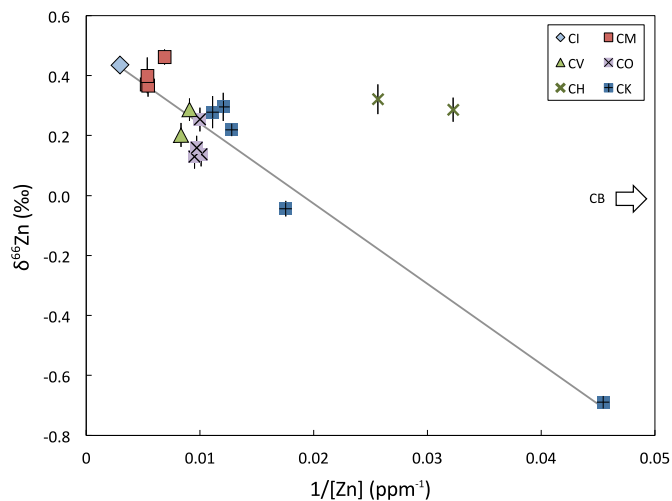


Fig. 3. $\delta^{66}\text{Zn}$ versus Zn depletion (represented by $1/[\text{Zn}]$ in ppm) for bulk chondrites. Most CC classes define a trend of light Zn isotope enrichment with increasing degree of Zn depletion, as indicated by the grey best-fit line. The exceptions are the CH and CB chondrites, which plot above and to the right of this trend; their Zn isotope compositions may have been modified by evaporation during parent-body formation.

The $\delta^{66}\text{Zn}$ values for the bulk UOC span a wide range, from −2.42‰ to −0.04‰ (Table 3 and Fig. 5). Although the bulk UOC have varying Zn isotope compositions, the leachates display consistently systematic behavior. Notably, the sulfide and the silicate phases make a similar contribution to the Zn budget of the whole rock: each contain between 40–50% of the bulk Zn. The sulfide phase is consistently enriched in the heavy isotopes of Zn compared to the bulk, while the silicate phase is enriched in the lighter isotopes of Zn. This confirms the results found by Luck et al. (2005) for the UOC Krymka (LL3.1). The difference between $\delta^{66}\text{Zn}$ in the sulfides and in the silicates (denoted $\Delta^{66}\text{Zn}_{\text{sulfide-silicate}}$) ranges from 0.5‰ to 0.79‰.

4. Discussion

4.1. Zinc isotope variations in bulk carbonaceous chondrites

Evaporative loss would create elemental abundance variations as a function of elemental volatility and would be expected to produce isotopic fractionation if evaporation occurred in an open system. However, as previously noticed by Luck et al. (2005) and confirmed by our new data there is a strong negative correlation between $\delta^{66}\text{Zn}$ and $1/[\text{Zn}]$. Carbonaceous chondrites are progressively enriched in the light isotopes of Zn in the order CI-CM-(CV,

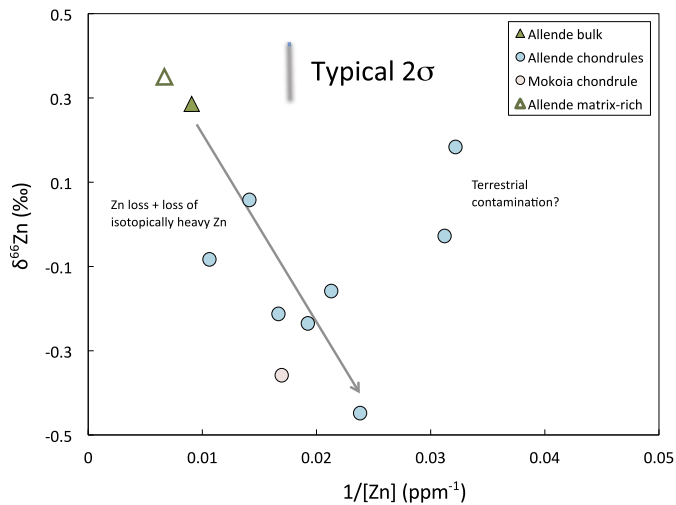


Fig. 4. $\delta^{66}\text{Zn}$ versus Zn depletion (represented by $1/[\text{Zn}]$ in ppm) for CV chondrite components, including individual chondrules from Allende and Mokoia and a matrix-rich aliquot of Allende. All analyzed Allende chondrules have $\delta^{66}\text{Zn}$ values lower than that of bulk Allende, while Allende matrix has a slightly higher $\delta^{66}\text{Zn}$ value. Chondrules show a trend of light Zn isotope enrichment coupled with increasing Zn loss, opposite to the effect expected during evaporation of Zn.

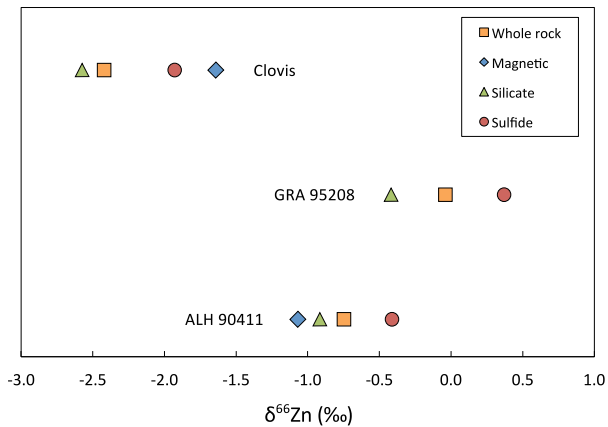


Fig. 5. Zinc isotope data for bulk UOC and UOC leachates. Zinc-bearing phases of the UOC Clovis (H3.6), GRA 95208 (H3.7), and ALH 90411 (L3.7) were separated using a sequential acid dissolution. Plotted are the $\delta^{66}\text{Zn}$ values of the bulk rock, silicate, sulfide, and metal phases. In all cases the sulfides are enriched in the heavy isotopes of Zn compared to the silicates (by $\sim 0.65\text{‰}$ for $\delta^{66}\text{Zn}$, also see Table 3).

CO)-CK; this is in fact opposite to the effect expected due to Zn isotope fractionation during evaporation. Therefore, as suggested by Luck et al. (2005), Zn isotope fractionation during free evaporation on CC parent bodies or their precursors does not explain the Zn isotope variability in CC.

Aqueous alteration on the chondrite parent bodies could modified the Zn isotope composition of CC, as observed in laboratory experiments (see Moynier et al., 2017 and references therein). Aqueous alteration was prevalent for CC and likely occurred under a variety of conditions, including variable pressures, temperatures, water/rock ratios, and oxygen fugacities (Brearley, 2003). The high solubility of Zn could result in open-system loss of Zn if the water-rock interaction on the surface of the chondrite parent body was coupled with subsequent fluid loss. This is unlikely, as Zn abundances are in fact highest in CC that are the richest in $-\text{OH}/\text{H}_2\text{O}$ (i.e. CI, CM). Since aqueous alteration was a parent-body specific process that occurred under a range of conditions, genetically unrelated samples should not show systematic relationships of $\delta^{66}\text{Zn}$. The linear correlation of Zn concentration and isotopic composition

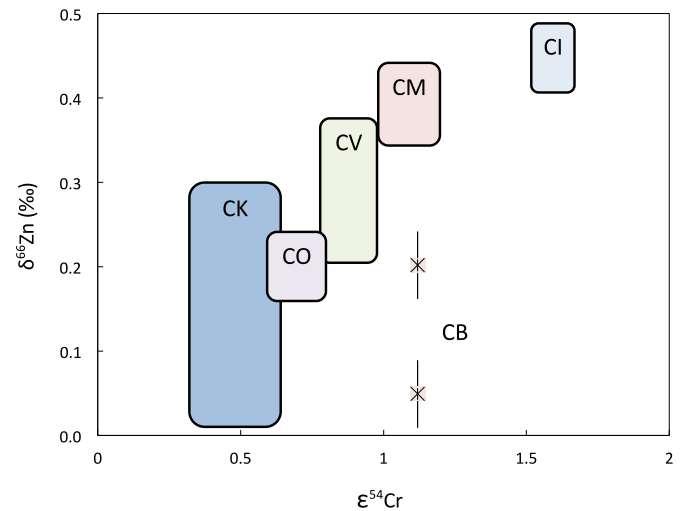


Fig. 6. $\delta^{66}\text{Zn}$ versus $\epsilon^{54}\text{Cr}$ (in parts per ten thousand) for bulk carbonaceous chondrites. Shown are group averages for carbonaceous chondrites with bulk analyses for CI, CM, CV, CO, and CK. Since CB $\delta^{66}\text{Zn}$ and $\epsilon^{54}\text{Cr}$ bulk rock analyses are limited and no CB has been analyzed for both $\delta^{66}\text{Zn}$ and $\epsilon^{54}\text{Cr}$, the $\delta^{66}\text{Zn}$ data from this work are plotted against $\epsilon^{54}\text{Cr}$ data for the CB Bencubbin (Trinquier et al., 2007). There is a clear relationship between $\delta^{66}\text{Zn}$ and $\epsilon^{54}\text{Cr}$ for CI-CK chondrites. The CB fall below the trend defined by CI-CK ($\epsilon^{54}\text{Cr}$ data from Trinquier et al., 2007; Qin et al., 2010. $\delta^{66}\text{Zn}$ data from Luck et al., 2005; Barrat et al., 2012; this work).

observed through the range of most CC classes would not be expected if aqueous alteration was responsible for generating the Zn isotope variations in bulk CC.

Finally, the variable degrees of volatile element depletion among the different CC classes may reflect the mixing of chemically and isotopically distinct reservoirs during CC accretion (Clayton and Mayeda, 1999; Luck et al., 2003, 2005). Evidence for this may be observed in the relationships between $\delta^{66}\text{Zn}$ and measures of stable isotope anomalies, such as $\epsilon^{54}\text{Cr}$ (see Fig. 6). Varying mixtures of volatile-rich material relatively enriched in heavy Zn isotopes and volatile-poor material relatively enriched in light Zn isotopes could explain the volatile contents and Zn isotope compositions of the chondrite classes on the CI-CK trend. Chondrules have been proposed as a carrier of the volatile depletion in CC and a possible explanation for Zn isotope variations observed previously in CC (Luck et al., 2005). In this case, a CI-like matrix combined with varying amounts of chondrules (with a Zn-depleted, isotopically light Zn signature) could be responsible for the CI-CK variations. However, such a model is not compatible with what is currently known from chondrule-matrix complementarity which argue that the matrix of each chondrites group has a different composition which is complementary to the chondrule composition (Hezel et al., 2010; Palme et al., 2015).

4.2. The unique impact-plume formation of CH and CB chondrites

Two CC classes in the current dataset do not lie on the trend defined by CI-CK; specifically, the CH and CB chondrites have higher $\delta^{66}\text{Zn}$ values than expected based on their low Zn concentrations (on average, 35 ppm and 5 ppm, respectively). This is an indicator that CB and CH chondrites experienced a different formation history compared to the other CC. CB chondrites have high metal content, are highly depleted in volatile elements, and the metal compositions suggest direct condensation from a gas (Weisberg et al., 2001). The CB chondrites have chemical and isotopic characteristics that are similar to CH, and both seem to be related to CR (Weisberg et al., 2001). Chondrules in CB are highly depleted in moderately volatile elements. It is believed that they

condensed from a gas–melt plume produced during a high-energy impact event in the early Solar System (Krot et al., 2005). Additionally, Pb–Pb dating of individual chondrules from the CB Gajba indicates that the chondrules have uniform ages and formed during a single event – in contrast to the range of individual chondrule ages (spanning ~ 2 Myr) determined for chondrites from other CC classes (Bollard et al., 2015).

The unique impact-plume formation process proposed for CH and CB chondrites may explain their enrichment in heavy Zn isotopes relative to the CI–CK trend (i.e. they have higher $\delta^{66}\text{Zn}$ values for a given [Zn] and thus fall above the trend line defined by CI–CK in Fig. 3). In this model, the Zn reservoir of the CB and CH precursors may have initially been on the CI–CK trend, but subsequently Zn isotope compositions were modified by isotope fractionation associated with Zn loss by evaporation. Loss of isotopically light Zn to the vapor phase, which was not fully incorporated during the condensation of CB and CH parent body-forming materials, led to heavy Zn isotope enrichment coupled with Zn depletion on the CB and CH parent bodies. Therefore, the new Zn isotope data for CB and CH further support the origin of the CH and CB parent body as a consequence of collisional accretion.

4.3. Mechanisms capable of generating Zn isotope fractionation in chondrules

Based on the igneous texture of chondrules, their formation occurred during a high-temperature process under conditions of rapid heating and cooling to retain volatile elements and to preserve relict grains from previous chondrule generations (e.g. Jones, 2012). High-temperature heating at low pressure in the solar nebula should be recorded in the evaporative loss of volatile elements from chondrules. However, the absence of volatile loss of Na or large isotope fractionations indicates chondrule formation at a solid/gas ratio several orders of magnitude higher than solar (e.g. Alexander et al., 2000; 2008; Hezel et al., 2010).

It has been shown that CC matrix has a different composition across the different classes, with varying degrees of volatile element depletion relative to CI (Rubin and Wasson, 1987; Bland et al., 2005). Furthermore, the degree of depletion is not strictly related to elemental volatility (i.e. elements with similar volatilities may show very different depletions relative to CI; Bland et al., 2005). Particularly, moderately volatile lithophile elements show relatively small depletions, whereas moderately volatile chalcophile and siderophile elements are generally depleted to a greater degree relative to CI (Bland et al., 2005).

In all cases, Allende chondrules are depleted in Zn and their Zn isotope compositions are light relative to bulk Allende (see Fig. 4). The Mokoia chondrule has a Zn isotope composition and concentration within the range of the Allende chondrules, showing that the light Zn isotope signature in chondrules is not limited to Allende but may be widespread. There are two general cases that could result in light Zn isotope enrichments in chondrules: either this is an effect of parent body alteration or it is a signature of the chondrule formation process, namely condensation, evaporation, or some other process.

Chemical exchange between chondrule and matrix during alteration on the parent body could lead to Zn isotope fractionation if Zn was sufficiently (and directionally) redistributed among chondrite components. Since this study analyzed bulk chondrules only, Zn isotope redistribution between phases within an individual chondrule would not cause any observable effect. Aqueous alteration in CV chondrites is variable, with Mokoia exhibiting indicators of a higher degree of aqueous alteration compared to Allende (Brearley, 2003). While we have data for only one chondrule from Mokoia, it has a similar Zn abundance and isotopic compositions than most Allende chondrules; this is unlikely to be the case

if alteration was the cause of the light Zn isotope enrichment in most chondrules considering the differing aqueous alteration history of Allende and Mokoia. It should be noted that in contrast to the oxidized CV3 analyzed here, reduced-type CV3 show minimal evidence for aqueous alteration (Brearley, 2003); future study of the Zn isotope composition of chondrules from reduced CV3 will be important to confirm these results. Finally, the low permeability observed in Allende would not allow for fluid movement over large scales; this would restrict aqueous alteration to local domains only (Hezel et al., 2013). For these reasons, it appears that aqueous alteration is unlikely to be the cause of the light Zn isotope enrichment in chondrules; instead this isotopically light signature is derived from the chondrule forming process. However, it is still possible that aqueous alteration may affect the most Zn-poor chondrules and be the origin of the deviation from the general trend of the two chondrules that fall out of it (Fig. 4). These two chondrules have the lowest concentrations of Zn (~ 30 ppm, see Table 2, Fig. 4); Therefore they would be the most susceptible to aqueous alteration that would pull the composition up toward the bulk value.

Condensation can result in isotopically light solids under specific conditions (Richter, 2004). This raises the question of whether the Zn isotope composition of chondrules merely records the Zn isotope composition inherited during the condensation of the chondrule precursors. One possibility is that chondrule-forming material condensed from a gas enriched in light Zn isotopes compared to CI, which resulted from the partial evaporation of Zn-bearing solids. This early partial evaporation would require that the light Zn isotope-enriched gas was separated from the remaining solids and that such a separation (e.g. by an inefficient dynamic coupling of the gas and solids) happened before isotope equilibration could occur. Evidence for a nebular gas enriched in light Zn isotopes compared to CI may exist in CAI rims. Although CAIs are not a major carrier of Zn, Allende CAIs exhibit Zn elemental enrichments at the surface (Chou et al., 1976). Limited data indicate that Allende CAIs may record very light Zn isotope compositions ($\delta^{66}\text{Zn} = -2.65\%$) relative to bulk Allende, suggesting that CAIs interacted with a gas enriched in light Zn isotopes (Luck et al., 2005); a CAI from Murchison shows similar light isotope enrichment ($\delta^{66}\text{Zn} = -1.28\%$; Moynier et al., 2007). However, an isotopically light nebular gas also implies a complementary volatile-depleted reservoir enriched in the heavy Zn isotopes, but such a reservoir has not been identified. Furthermore, the timing, duration, and prevalence constraints surrounding chondrule formation (e.g. Jones, 2012) suggests that Zn isotope fractionation as a result of chondrule condensation is unlikely to be a significant process, and that another mechanism is required to explain the light Zn isotope enrichments in chondrules.

If chondrules experienced open system evaporation (under Rayleigh conditions) then the residue should be enriched in heavy isotopes for volatile elements. The absence of heavy isotope enrichment for moderately volatile elements (e.g. K, Humayun and Clayton, 1995; Zn, this study) in chondrules leads to one of following conclusions regarding chondrule evaporation:

(1) The isotope signature of chondrule evaporation was erased by subsequent parent body processes, e.g. aqueous alteration. As previously discussed, this is unlikely for the chondrules in the present study.

(2) Open-system chondrule evaporation occurred, but the isotope signature was erased during subsequent gas–melt interaction (Friend et al., 2016) before the chondrules were accreted to a parent body. Back-reaction of chondrules and nebular gas has been previously suggested to explain the lack of K isotope fractionation (Alexander et al., 2000) and the constant Na contents in chondrules (Alexander et al., 2008). Chondrule formation could have involved evaporative volatile loss without isotope fractionation under

specific conditions, if such a reaction between evaporated gases and the residue suppressed isotope fractionation. This is consistent with the absence of heavy Zn isotope enrichments in chondrules but does not explain their light Zn isotope enrichments.

(3) The loss of volatiles from chondrules by evaporation was insignificant and chondrule isotopic compositions record an alternate process. The loss of volatile elements from chondrules during evaporation could be minimized by rapid heating and cooling of and/or by high dust/gas ratios in the chondrule-forming environment (as proposed to explain Na abundances in chondrules; Alexander et al., 2008). There is some evidence that the elemental abundance of Zn in Allende chondrules is not strictly due to its lithophile or its chalcophile behavior; chondrule Zn could be hosted in silicates or in opaque phases. In Allende bulk chondrules, Zn abundances do not correlate with other elements, in contrast to intercorrelations among other elements such as the alkali elements (Grossman and Wasson, 1985; Rubín and Wasson, 1987). The absence of such correlations for Zn suggests that Zn is indeed hosted in both silicate and sulfide minerals (Grossman and Wasson, 1985). In addition, Zn is over-depleted relative to both the moderately volatile lithophiles and the moderately volatile chalcophiles (Rubín and Wasson, 1987). This suggests that Zn abundance in chondrules may be due to two separate contributions: a partial volatile loss via evaporation from chondrule silicates in which isotope fractionation was suppressed by gas–melt reaction and an additional Zn depletion related to the chalcophile behavior of Zn.

For these reasons, the Zn isotope data indicate that chondrules may have experienced evaporation under open system conditions as long as the isotope signature of evaporation was erased by back-reaction with the evaporated gas, or that evaporation may have occurred under non-Rayleigh conditions. However, neither process explains the light Zn isotope enrichment in chondrules, so an alternative explanation is required.

4.4. The origin of the isotopically light Zn in chondrules via sulfide removal

Looking at sulfides from UOC might help to understand how opaque phases produced isotopically light CC chondrules. Sulfides from UOC are strongly enriched in the heavy isotopes of Zn compared to both silicates and the bulk chondrite (by $\sim 0.65\%$ for $\delta^{66}\text{Zn}$, see Table 3 and Fig. 5; Luck et al., 2005 and this study). The segregation of an isotopically heavy sulfide phase from either chondrules or their precursors would therefore have two effects: it would deplete the chondrules in Zn and remove a reservoir of isotopically heavy Zn, which would leave the chondrules enriched in light Zn isotopes relative to the bulk chondrite. Such an effect would create the general negative correlation observed between $\delta^{66}\text{Zn}$ and $1/[\text{Zn}]$ (Fig. 4). A silicate-metal/sulfide phase separation has similarly been used to explain complementary W and Mo nucleosynthetic anomalies between Allende chondrules and matrix (Becker et al., 2015; Budde et al., 2016a, 2016b), and opaque phases are most probably also responsible for the variable Fe isotope compositions of Allende, Mokoia, and other CV chondrite chondrules (Hezel et al., 2010). The two chondrules that fall out of this correlation are the chondrules with the lowest concentrations of Zn (~ 30 ppm, see Table 2, Fig. 4); they would be the most susceptible to aqueous alteration that could partially overprint their inherent Zn isotope composition and concentration (see discussion of the aqueous alteration above).

The segregation of sulfides from chondrules or their precursors could occur through several different mechanisms, including immiscible liquid separation coupled with chondrule fission or quantitative evaporation of sulfides from chondrules (or their precursors). The ejection of metal and sulfide from the interior of chondrules has been modeled by Uesugi et al. (2008) and by

Wasson and Rubin (2010) to explain the siderophile element depletions in chondrules. These models involve the separation of metal/sulfide and silicate as immiscible liquids during the (brief) time that the chondrules were molten (Grossman and Wasson, 1985). Centrifugal forces within a rotating chondrule would further contribute to drive the denser metal/sulfide phase towards the surface of the melted chondrule. Finally, the metal/sulfide phase may be ejected from the chondrule due to the fact that silicate melt has a lower surface energy than Fe and FeS melt (Uesugi et al., 2008; Wasson and Rubin, 2010). In terms of Zn, the ejection of sulfide via chondrule fission could explain the Zn depletion and light Zn isotope enrichment observed in chondrules if there is an isotopic fractionation between Zn dissolved in the silicate melt and the Zn-bearing sulfides, as observed in UOC. However, there are a number of issues with the model. Only a small fraction of chondrules show textural evidence for loss of immiscible liquids by fission (Grossman and Wasson, 1985). Palme et al. (2014b) demonstrated that chondritic Ni/Co ratios of bulk Allende chondrules argue against significant loss of opaques. Additionally, the fate of the ejected metal/sulfide is unclear; a limit on the ubiquity of chondrule fission may be placed by the lack of corresponding metal or sulfide spheroidal droplets in the matrix.

Separation of sulfide and silicate may also have occurred during quantitative evaporation of sulfide from chondrules or their precursors. One advantage of this mechanism is that sulfide evaporation could occur below the silicate liquidus, so it would not necessarily need to occur during the short time that chondrules were molten. Evaporation of sulfides would need to be significant or occur in a high dust/gas environment (i.e. under a high partial pressure of Zn) to avoid kinetic Zn isotope fractionation during evaporation. If sulfide loss occurred during chondrule formation, then evaporation of Zn may have provided sufficient vapor pressure of Zn to limit kinetic isotope fractionation during any subsequent evaporative loss of Zn from chondrules (e.g. from chondrule silicates during flash heating), if it did occur. Finally, if the gas resulting from sulfide evaporation was heterogeneously lost from the CC-forming reservoir prior to the final assemblage of CC components, this scenario could also explain the Zn isotope systematics observed in bulk CC. Loss of the gas phase produced by sulfide evaporation would deplete the CC reservoir in Zn and heavy Zn isotopes, driving the entire reservoir to lighter Zn isotope composition and lower Zn concentrations. This would produce the CI-CK trend while allowing all components to originate from a single reservoir.

5. Conclusions

There is an inverse correlation between $\delta^{66}\text{Zn}$ and $1/[\text{Zn}]$ between bulk CC for the CI, CM, CO, CO, and CK classes, which cannot be explained by volatile loss during evaporation on the CC parent body. CB and CH fall off the trend defined by CI-CK, consistent with evaporative loss of Zn in line with the impact-plume formation hypothesis.

Individual chondrules from the CV chondrites Allende and Mokoia exhibit Zn depletions but enrichments in light Zn isotopes. The most likely explanation for the light Zn isotope enrichment in chondrules is the segregation of an isotopically light sulfide phase during chondrule formation. This most probably occurred during quantitative evaporation of sulfides from chondrules or their precursors, or sulfides were preferentially incorporated into matrix rather than into chondrule precursors. Loss of the gas phase that was produced during sulfide evaporation from chondrules from the CC-forming reservoir would create depletions in Zn and enrichments in light Zn isotopes. If this gas was heterogeneously lost from the CC-forming reservoir prior to the final assemblage of CC components, this scenario could also explain the Zn isotope systematics observed in bulk CC.

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