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Cadmium stable isotope cosmochemistry

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Abstract

Cadmium stable isotope compositions are reported for a comprehensive suite of carbonaceous, ordinary, enstatite, and Rumuruti chondrites as well as achondrites and lunar samples (soils, breccias, pristine anorthosite). The Cd isotope analyses were performed by multiple collector ICP-MS with an external reproducibility of $\pm 0.43\%$ (2 sd) for $\delta^{114/110}\text{Cd}$. None of the samples shows evidence of nucleosynthetic anomalies and cosmogenic isotope effects from neutron-capture by ^{113}Cd were only observed for two lunar samples.

The Cd stable isotope compositions of type 1, 2, and some type 3 carbonaceous chondrites, EH4 enstatite chondrites, eucrites, and the Earth are essentially identical at $\delta^{114/110}\text{Cd} \approx 0.0 \pm 0.4$. This suggests that the portion of the solar nebula from which the inner solar system bodies accreted was homogeneous with respect to its Cd isotope composition. It also indicates that the primary volatile element depletion of the inner solar system did not involve partial kinetic Rayleigh evaporation or condensation. Furthermore no resolvable Cd isotope effects were generated during the accretion and initial differentiation of the planetary bodies.

In contrast, the analyses reveal large Cd isotope effects for ordinary and some enstatite chondrites, which display $\delta^{114/110}\text{Cd}$ values between about -8 and $+16$. Smaller fractionations are observed for the Rumuruti and some type 3 to 5 carbonaceous chondrites. These Cd isotope variations are thought to reflect secondary depletion or redistribution of Cd, due to open system thermal metamorphism on the meteorite parent bodies.

One CAI and chondrule separates from the Allende meteorite have unexpectedly high Cd concentrations and fractionated light Cd isotope compositions with $\delta^{114/110}\text{Cd} \approx -1$ to -4 . These characteristics may have been established by the interaction of originally Cd-poor materials with a volatile-rich gas prior to the final accretion of the Allende parent body. The general Cd enrichment of the lunar soil and regolith mainly reflects early volcanic activity. However, decreasing Cd abundances in lunar soils correlate well with an enrichment of the heavy Cd isotopes. This relationship is best explained by suppressed Rayleigh fractionation in response to space weathering.

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1. INTRODUCTION

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The formation of the solar system and the accretion of planetesimals and planets involved various stages of thermal processing. This processing potentially generated stable

isotope fractionations if it was associated with either partial evaporation or condensation. Evaporation and/or condensation may have played an important role in the nebular processes that led to the depletion of the inner solar system in volatile elements and to the formation of refractory inclusions and chondrules (e.g. Larimer and Anders, 1967; Grossman, 1972; Anders et al., 1976; Wai and Wasson, 1977; Wolf et al., 1980; Davis et al., 1990; Humayun and Clayton, 1995a; Cassen, 1996; Ebel and Grossman, 2000; Yu et al., 2003; Alexander, 2005; Bland et al., 2005). Likewise, evaporation (and condensation) could have accompanied the impact-driven growth of planetary bodies (Poitrasson et al., 2004), and parent body processes such as shock heating (Friedrich et al., 2004), thermal metamorphism (Dodd, 1969), as well as (lunar) space weathering and volcanism (e.g. Ding et al., 1983; Humayun and Clayton, 1995b).

Stable isotope ratios of volatile elements can thus provide unique constraints on evaporation and condensation processes that occurred in the early solar system. Ideally, such studies should utilize elements that do not display significant geological/chemical isotope fractionations. One element that meets this requirement is K (Humayun and Clayton, 1995a). Potassium is moderately volatile and has a remarkably uniform isotope composition in meteorites, chondrules, terrestrial materials and lunar samples other than soils (Humayun and Clayton, 1995a,b; Alexander et al., 2000; Alexander and Grossman, 2005). The highly volatile element Cd also displays only minor stable isotope effects on Earth due to inorganic geochemical processes (Wombacher et al., 2003; Cloquet et al., 2005), but large Cd isotope effects were previously identified in ordinary and Rumuruti chondrites (Rosman and De Laeter, 1976; Rosman et al., 1980; Rosman and De Laeter, 1988; Wombacher et al., 2003). The difference in behavior between Cd and K isotopes may be due to the higher volatility of Cd (T_C (Cd) = 652 K; T_C (K) = 1006 K; Lodders, 2003). This warrants a more detailed study of Cd stable isotope compositions in meteorites and here we present a comprehensive dataset for carbonaceous, enstatite, ordinary and Rumuruti chondrites, various achondrites, four lunar samples and two Martian meteorites.

2. ANALYTICAL PROCEDURES

2.1. Cadmium isotope notation

To facilitate inter-laboratory comparisons, it has been proposed that Cd stable isotope data should be reported as variations of the $^{114}\text{Cd}/^{110}\text{Cd}$ isotope ratio, either as $\delta^{114/110}\text{Cd}$ (in ‰) or as $\epsilon^{114/110}\text{Cd}$ (in parts per 10,000) (Wombacher and Rehkämper, 2004). As the present data display Cd isotope variations of $\sim 25\%$, we have chosen to use the δ -notation, where

$$\delta^{114/110}\text{Cd}_{\text{sample}} = [(\frac{^{114}\text{Cd}}{^{110}\text{Cd}})_{\text{sample}} / (\frac{^{114}\text{Cd}}{^{110}\text{Cd}})_{\text{JMC std}} - 1] * 1000 \quad (1)$$

No universally accepted primary “zero delta” Cd isotope reference material is available at present. Here, all data are reported relative to our JMC Cd standard (Wombacher et al., 2003; Wombacher and Rehkämper, 2004).

In a previous study, we reported Cd isotope data using an $\epsilon\text{Cd}/\text{amu}$ notation (Wombacher et al., 2003) based on the measurement of $^{112}\text{Cd}/^{114}\text{Cd}$. These results can be converted into $\delta^{114/110}\text{Cd}$ values using:

$$\delta^{114/110}\text{Cd} = [(\epsilon\text{Cd}/\text{amu} * (m_{112} - m_{114}) / 10,000 + 1)^\beta - 1] * 1000 \quad (2)$$

where the exponent is defined as $\beta = \ln(m_{110}/m_{114}) / \ln(m_{114}/m_{112}) = -2.018$ (Young et al., 2002).

Also, the $\delta^{114/110}\text{Cd}$ values of Table 1 were calculated from the measured $^{112}\text{Cd}/^{114}\text{Cd}$ isotope data, because this ratio provided the best long-term reproducibility (Wombacher et al., 2003). The equation to calculate $\delta^{114/110}\text{Cd}$ from the measured $^{112}\text{Cd}/^{114}\text{Cd}$ ratio assumes a kinetic mass dependence between both Cd isotope ratios. The kinetic law of (Young et al., 2002) is simply inserted into Eq. (1) with the exponent β as defined above:

$$\delta^{114/110}\text{Cd}_{\text{sample}} = [((\frac{^{112}\text{Cd}}{^{114}\text{Cd}})_{\text{sample}} / (\frac{^{112}\text{Cd}}{^{114}\text{Cd}})_{\text{JMC std}})^\beta - 1] * 1000 \quad (3)$$

As neutron capture effects increase the ^{114}Cd abundance at the lunar surface, the nominal $\delta^{114/110}\text{Cd}$ values of lunar samples were derived from the measured $^{112}\text{Cd}/^{111}\text{Cd}$ ratios using an equation similar to Eq. (3) with $\beta = \ln(m_{110}/m_{114}) / \ln(m_{111}/m_{112})$.

2.2. Sample preparation

A comprehensive description of the laboratory methods is given in Wombacher et al. (2003). Here, we provide only a summary and details of any procedures that are specific to this study.

Between 3 and 1660 mg of the powdered samples were dissolved in HF–HNO₃ mixtures. The Cd separation was carried out by anion exchange chromatography followed by a clean-up step that utilized Eichrom® TRU Spec resin. Laboratory blanks were negligible at ≤ 20 pg Cd. All meteorite finds analyzed in this study are from North African deserts, except Leoville, Brownfield (1937), Dimmitt, Gladstone and Kenna, which are from the US. It is possible that terrestrial Cd contaminated the meteorite finds or that Cd loss occurred during weathering. As a precautionary measure, these specimens were thus mildly leached in very dilute HNO₃ and then rinsed with clean water before further processing. It is unlikely that terrestrial weathering of chondrite samples results in significant Cd isotope fractionations, since analyses of low temperature minerals yielded Cd isotope compositions that were not resolvable from other terrestrial samples with the current measurement precision (Wombacher et al., 2003).

Matrix, chondrules and other components (Table 1) were separated from Allende, Semarkona, Bishunpur and Sarir Qattusah 001. Allende and Semarkona were gently crushed in an agate mortar, and matrix-rich pieces, chondrules, chondrule fragments and one Ca–Al-rich refractory inclusion were handpicked under a binocular microscope. The Allende separates (Table 1) were prepared from three different slices of a single large piece. Two separates were

Table 1
Cadmium stable isotope compositions

Sample	S ^a	W ^b	int. ^c	$\delta^{114/110}\text{Cd}^{\text{d,e}}$
<i>Carbonaceous chondrites</i>				
Orgueil CI regolith breccia ^f		Fall	40	−0.1
Orgueil CI regolith breccia ^f		Fall	45	−0.3
Murchison CM2 breccia ^f	1–2	Fall	45	0.4
Acfer 209 CR2 breccia	2	2	45	0.3
Acfer 209 CR2 breccia	2	2	45	0.5
Acfer 094 C2 ungrouped breccia	1	2	40	−0.3
Acfer 094 C2 ungrouped breccia	1	2	45	−0.4
Allende CV3 oxidized (mean) ^f	1	Fall		−0.1
Allende evaporation residue (AA2P)			30	−0.9
Allende separates:				
Matrix (split 1) ^g			30	0.2
Matrix (split 2) ^g			40	−0.1
Matrix (split 2) ^g			15	−0.4
Matrix (CAI-rich)			30	−0.5
Ca-Al-rich refractory inclusion ^h			20	−2.2
Chondrules + fragments < 1 mm ^h			40	−3.9
Chondrules with coarse-grained rims			30	−1.7
Small chondrules & fragments			20	−0.5
Leville CV3 reduced	3		20	1.8
Colony CO3.0 (split 1)	1		45	1.1
Colony CO3.0 (split 2)	1		15	1.5
Dar al Gani 005 CO3	2	2	45	4.5
Watson 002 CK3-anomalous			45	0.4
Watson 002 CK3-anomalous			45	0.5
Dar al Gani 275 CK4/5	2	4	45	−1.0
Dar al Gani 412 CK5	2	3	40	−0.8
<i>Enstatite chondrites</i>				
Sahara 97166 EH3			45	3.4
Qingzhen EH3	3	Fall	45	16.0
Indarch EH 4	3	Fall	40	0.0
Indarch EH 4	3	Fall	45	−0.4
Abee EH4 impact melt breccia	2–4	Fall	40	−0.1
Abee EH4 impact melt breccia	2–4	Fall	45	−0.7
Abee EH4 impact melt breccia	2–4	Fall	45	−0.1
Hvittis EL6 breccia	2	Fall	20	7.6
Ilafegh 009 EL7 with impact melt	4	0/1	45	4.3
<i>Lunar samples</i>				
Dar al Gani 400 anorthositic breccia			20	1.1 ^e
Dar al Gani 262 polym. anorth. breccia			45	10.0 ^e
Pristine ferroan anorthosite (60025,771)		Apollo	16	7.8 ^e
Soil (14163,910)		Apollo	40	11.3 ^e
<i>Shergottites</i>				
Dar al Gani 476			20	0.9
Sayh al Uhaymir005	High		15	0.5
<i>Eucrites-monomict breccias</i>				
Hammadah al Hamra 059		3	30	−0.2
Millbillillie		Fall	20	0.0
<i>Ureilite</i>				
Kenna	Low		10	1.1
<i>Winonaite</i>				
Hammadah al Hamra 193	1	3	45	−0.8
Hammadah al Hamra 193	1	3	15	−0.3
<i>Ordinary chondrites</i>				
Acfer 171 H3.7	1	2	40	−6.1
Brownfield (1937) H3.7 ^f	b	B	60	11.2
Dimmitt H3.7 regolith breccia ^f	3	B	45	7.1

Table 1 (continued)

Sample	S ^a	W ^b	int. ^c	$\delta^{114/110}\text{Cd}^{\text{d,e}}$
Gladstone H4	3		45	0.7
Forest Vale H4 ^f	2	Fall	45	2.9
Forest Vale H4 ^f	2	Fall	45	3.4
Ucera H5	c	Fall	30	-0.3
Dar al Gani 216 L3	3	2	15	5.7
Tanezrouft 039 L3	2	1	15	6.6
Dar al Gani 085 L3-4 breccia	2	2	45	0.2
Dar al Gani 085 L3-4 breccia	2	2	15	0.2
Dar al Gani 085 L3-4 breccia	2	2	45	0.7
Dar al Gani 085 L3-4 breccia/fusion crust	2	2	45	-0.8
Dar al Gani 085 L3-4 breccia/fusion crust	2	2	40	-0.4
Homestead L5 breccia	4	Fall	20	3.2
Adrar 003 L/LL3.2	2	2	60	6.3
Sarir Qattusah 001 L/LL3 ^f	2	3	45	14.3
Sarir Qattusah 001 L/LL3 ^f	2	3	45	14.3
Sarir Qattusah 001 L/LL3 ^f	2	3	45	15.0
Sarir Qattusah 001 L/LL3 ^f	2	3	45	15.0
Sarir Qattusah separate:				
Matrix-rich ^g			40	14.5
Semarkona LL3.0 ^f	2	1 – Fall	45	-7.8
Semarkona LL3.0 ^f	2	1 – Fall	45	-7.8
Semarkona separates:				
Matrix-rich			40	-7.4
Matrix-rich			45	-7.7
Matrix-rich with some fusion crust			40	-7.6
Fine fraction pipetted in ethanol			40	-6.7
Chips from large chondrule			15	-9.2
Chondrule minerals			15	-7.4
Bishunpur LL3.1 ^f (split 1)	2	1 – Fall	20	11.1
Bishunpur LL3.1 ^f (split 2)	2	1 – Fall	20	11.7
Bishunpur separates:				
Matrix-rich ^g			20	12.2
With fusion crust and large chondrule			20	11.2
Chondrule-rich ^g			20	11.0
Dar al Gani 022 LL3-6 breccia	2	3	45	0.7
<i>Rumuruti chondrites</i>				
Northwest Africa 755 R3.7 ^f	2	4	45	2.7
Northwest Africa 755 R3.7 ^f	2	4	45	3.1
Northwest Africa 753 R3.9	2	2	45	2.1
Northwest Africa 753 R3.9	2	2	45	2.7
Hammadah al Hamra 119 R4	3	4	45	1.0
Hammadah al Hamra 119 R4	3	4	30	1.1
Dar al Gani 013 R3.5–6 breccia	1	4	30	-1.6

^a Shock stage.^b Degree of weathering.^c Number of 5s integrations during analysis.^d $\delta^{114/110}\text{Cd}$ calculated from $^{112}\text{Cd}/^{114}\text{Cd}$; external reproducibility (2 sd) is $\pm 0.43\%$ (Wombacher et al., 2003).^e Lunar samples with neutron capture effects: $\delta^{114/110}\text{Cd}$ calculated from $^{112}\text{Cd}/^{111}\text{Cd}$; external reproducibility (2 sd) is $\pm 0.79\%$ for Dar al Gani 262 & 400 and $\pm 0.92\%$ for Apollo samples 60025 and 14163.^f From Wombacher et al. (2003).^g Micro-drill samples.^h Freeze-thaw.

prepared employing the freeze-thaw method (Table 1), whereby the solid sample was suspended in water and subjected to repeated cycles of heating and freezing by immersion in boiling water and liquid nitrogen. A single chondrule-rich and four matrix-rich separates were obtained from Allende, Bishunpur and Sarir Qattusah (Table 1) using a microdrill that was operated under a binocular microscope. The two Bishunpur separates were drilled with-

in drops of water to catch the fine dust produced during the operation. Drill blanks were determined by extensive wet drilling of a quartz crystal (40 pg Cd) and a Zhamanshinite impact melt (720 pg Cd) that was previously found to be almost free of Cd (<1 ng/g). If a Cd blank of 40 pg is assumed to have an unfractionated terrestrial isotope composition, this has a negligible effect for all drilled samples. Contamination by 720 pg of terrestrial Cd would have no significant

effect for the two drilled Allende matrix samples, but the Cd isotope compositions of the matrix-rich separates from Sarir Qattusah 001 (147) and Bishunpur, as well as the Bishunpur chondrule separate would change by -0.4 , -0.8 and -1.2 $\delta^{114/110}\text{Cd}$, respectively.

2.3. Mass spectrometry

All but two Cd isotope data were obtained with a Nu Plasma MC-ICP-MS (multiple collector inductively coupled plasma mass spectrometer) in combination with a Cetac MCN 6000 membrane desolvator at the ETH Zürich (Wombacher et al., 2003). An Ag solution was added to samples and standards prior to the analyses, and the raw Cd isotope ratios were normalized to $^{107}\text{Ag}/^{109}\text{Ag}$ to correct for the drift in the instrumental mass bias. Typically 40 to 45 integrations of 5 s duration were acquired during the sample measurements with ion beam intensities of about 0.5×10^{-11} A for ^{112}Cd . If only small amounts of Cd were available for measurement, as little as 10 integrations of 5 s duration were obtained (Table 1). The accuracy of the method was tested by comparison of the MC-ICP-MS results with published double-spike data acquired by thermal ionization mass spectrometry (see Wombacher et al., 2003). The long-term reproducibility of ± 0.43 for $\delta^{114/110}\text{Cd}$ (2 sd) was estimated from multiple analyses of separate dissolutions of Allende meteorite and other rock powders. The $\delta^{114/110}\text{Cd}$ values of the lunar samples, which were calculated from $^{112}\text{Cd}/^{111}\text{Cd}$, are estimated to have a long-term reproducibility of ± 0.79 .

Additional analyses of two Apollo samples were performed with an Axiom MC-ICP-MS equipped with a Cetac Aridus membrane desolvator at the IFM-GEOMAR in Kiel, using methods outlined in Wombacher and Rehkämper (2004). Mass bias drift was corrected by normalization to Ag isotopes. Measurements of standard solutions with 50 ppb Cd and 100 ppb Ag in 0.1 M HNO_3 , utilized 40 integrations of 5 s with ion beam intensities of $\sim 0.75 \times 10^{-11}$ A for ^{112}Cd and $\sim 2.8 \times 10^{-11}$ A for ^{109}Ag . For samples 60025 and 14163 (Table 1), the Cd ion beams were corrected for ^{114}Sn interferences of 50 ppm and 23 ppm, and for ^{113}In interferences of 35 and 1 ppm, respectively. The data are estimated to have a reproducibility of $\pm 0.92\%$ (2 sd) for $^{114}\text{Cd}/^{110}\text{Cd}$, based on 17 accompanying measurements of the JMC Cd standard. The accuracy of the results was tested by measurements of samples that were previously analyzed in Zürich. Two analyses of a shale (NZ 404c) yielded $\delta^{114/110}\text{Cd}$ values of $+0.2$ and -0.3 and two analyses of a gneiss bomb core yielded $+0.2$ and $+0.1$. These results are identical, within uncertainty, to the previously determined $\delta^{114/110}\text{Cd}$ values of -0.4 ± 0.4 for the NZ 404c shale and -0.1 ± 0.4 for the gneiss bomb.

2.4. Data assessment

The data presented in Table 1 were obtained with ion beams of $>0.15 \times 10^{-11}$ A for ^{112}Cd , except for Dar al Gani 216 and two chondrule-rich separates from Semarkona which yielded ^{112}Cd ion beams of $>0.10 \times 10^{-11}$ A. All measurements consumed ≥ 4 ng Cd, and typically 20

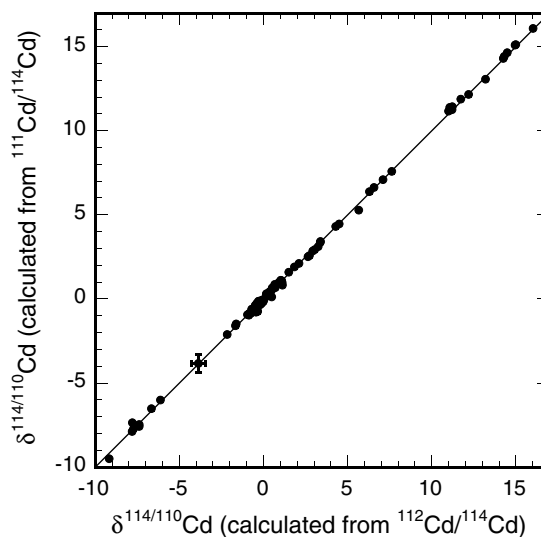


Fig. 1. Comparison of $\delta^{114/110}\text{Cd}$ values recalculated from measurements of $^{112}\text{Cd}/^{114}\text{Cd}$ and $^{111}\text{Cd}/^{114}\text{Cd}$, with analytical uncertainties of ± 0.43 and $\pm 0.52\%$ (2 sd), respectively. The two different $\delta^{114/110}\text{Cd}$ values agree to within $\pm 0.43\%$ for all samples. This indicates that spectral interferences and nucleosynthetic or other non-mass-dependent isotope anomalies are insignificant.

to 50 ng Cd. The ion beams of ^{112}Cd and ^{114}Cd were corrected for Sn interferences and this correction was accurate even for sample 111-Hvittis which displayed the highest observed Sn level (Wombacher et al., 2003). Some Ru elutes together with Cd during the chemical separation and the highest Ru/Cd ratio ($\text{Ru}/\text{Cd} = 2$) was observed for 163-Homestead. However, Wombacher et al. (2003) have shown that Ru/Cd ratios up to 3 can be tolerated and cause no significant oxide interferences or matrix effects. Possible matrix-induced mass bias effects were evaluated by comparing the results obtained from different mass bias correction procedures. If the results from standard-sample-bracketing and Ag-normalization did not agree to within ± 1.2 for $^{114}\text{Cd}/^{110}\text{Cd}$, the data were rejected (Wombacher et al., 2003). The $\delta^{114/110}\text{Cd}$ values that were calculated from $^{112}\text{Cd}/^{114}\text{Cd}$ and $^{111}\text{Cd}/^{114}\text{Cd}$ agree to within the external reproducibility of $\pm 0.43\%$ for all data presented in Fig. 1. Four additional results that did not meet this criterion were discarded, due to the likelihood of spectral interferences.

3. FUNDAMENTALS

3.1. Cosmochemical definitions of volatile elements

- The *moderately volatile elements* comprise elements with half-mass condensation temperatures T_C (at 10^{-4} bar) between about 1250 and 650 K (Palme et al., 1988), including P, Mn, Li, As, Au, Cu, K, Ag, Sb, Ga, Na, Cl, B, Ge, Rb, F, Zn, Te, Sn, Se and S.
- The *highly volatile elements* (e.g. Anders and Grevesse, 1989) include Br, Cd, In, Cs, Tl, Pb and Bi with T_C according to Lodders (2003) between 800 and 532 K.

- The following discussion also refers to the group of *very volatile elements*, which are defined as having $T_C \leq 800$ K. This includes the moderately volatile elements S, Zn, Se, Sn, Te and all highly volatile elements.

The half-mass condensation temperatures and therefore the above definitions apply to condensation at low pressure in a solar nebula environment. In other environments such as the lunar surface or within asteroidal bodies, the above definitions provide only an estimate of the relative volatility of the elements.

3.2. Kinetic isotope fractionation during evaporation and condensation

Isotope fractionation between a condensed phase and a gas phase can occur at kinetic and equilibrium conditions. In the case of partial kinetic evaporation, the isotope composition of the residual condensed Cd is given by the Rayleigh equation:

$$\frac{(^{114}\text{Cd}/^{110}\text{Cd})_{\text{residue}}}{(^{114}\text{Cd}/^{110}\text{Cd})_{\text{initial}}} = f^{(\alpha_{\text{kin}}-1)} \quad (4)$$

where f is the mass fraction of Cd remaining in the solid and α_{kin} the kinetic isotope fractionation factor. The kinetic isotope fractionation that occurs during evaporation and condensation results from the different velocities of isotopic species and this property is considered to be independent of temperature. The kinetic isotope fractionation factor α_{kin} is directly governed by the masses of the isotopes, and generally calculated using the square root of the mass (sqrm) dependence:

$$\begin{aligned} \alpha_{\text{kin-sqrm}} &= (^{114}\text{Cd}/^{110}\text{Cd})_{\text{flux}} / (^{114}\text{Cd}/^{110}\text{Cd})_{\text{residue}} \\ &= \sqrt{m_{110}/m_{114}} = 0.9823 \end{aligned} \quad (5)$$

where m_{114} and m_{110} are the atomic masses of ^{114}Cd and ^{110}Cd , respectively. However, Richter et al. (2002) observed smaller fractionations as calculated from $\sqrt{m_{24}/m_{25}}$ for the evaporation of Mg, even when isotope fractionation was not limited by diffusion and recondensation. Richter (2004) suggested that this may reflect slightly different sticking coefficients for the Mg isotopes and Simon and Young (2007) argued that the lower observed values for $\alpha_{\text{kin-obs}}$ may result from different bond vibration frequencies in the melt. If ideal kinetic isotope fractionation is assumed for the Cd evaporation experiment of Wombacher et al. (2004), the data yield an observed fractionation factor $\alpha_{\text{kin-obs}}$ of about 0.9890 to 0.9908. This corresponds to a $1 - \alpha_{\text{kin-obs}}$ value that is 40% to 50% lower than $1 - \alpha_{\text{kin-sqrm}}$ (Eq. 5). It is interesting that the fractionation factor observed by Richter et al. (2002) for kinetic evaporation of Mg also generates isotope effects that are only about half as large as those expected from $\alpha_{\text{kin-sqrm}} = \sqrt{m_{24}/m_{25}}$. It appears possible that isotope fractionation during the evaporation of a melt into vacuum may often be characterized by fractionation factors that are considerably smaller than values calculated from expressions similar to Eq. (5). However, kinetic evapora-

tion will still result in large isotope fractionations provided that: (i) the vapor is instantaneously removed from the surface of the evaporation residue to avoid recondensation (back reaction) and (ii) the isotope composition of the evaporation residue remains homogeneous during the evaporation process (e.g., Davis et al., 1990; Esat, 1996; Young et al., 1998; Wang et al., 1999a; Tsuchiyama et al., 1999; Nagahara and Ozawa, 2000; Ozawa and Nagahara, 2001; Davis and Richter, 2003; Richter, 2004). Recondensation is negligible if the partial pressure p of an element in the surrounding gas phase is much smaller than its saturation pressure p_{sat} . This applies to evaporation into vacuum (free evaporation). Recondensation becomes significant if p/p_{sat} approaches 1 in the vicinity of the condensed phase. Under these conditions, partial evaporation may occur without detectable kinetic isotope fractionation. If the diffusion in the evaporation residue is slow compared to the evaporation rate (as is the case for evaporating solids), then the residues are not expected to exhibit large isotopic fractionations. In summary, the isotope fractionation calculated for kinetic Rayleigh evaporation using α_{kin} (Eq. 5) represents an upper limit that may be approached if small liquid samples are evaporated into vacuum. The true value for $1 - \alpha_{\text{kin}}$ may typically be smaller than $1 - \alpha_{\text{kin-sqrm}}$.

The isotope composition of an instantaneously formed condensate established by kinetic Rayleigh condensation is:

$$\frac{(^{114}\text{Cd}/^{110}\text{Cd})_{\text{inst. condensates}}}{(^{114}\text{Cd}/^{110}\text{Cd})_{\text{initial}}} = \alpha_{\text{kin}}(1-f)^{(\alpha_{\text{kin}}-1)} \quad (6)$$

and the isotope composition of the accumulated condensate is given by:

$$\frac{(^{114}\text{Cd}/^{110}\text{Cd})_{\text{accu. condensates}}}{(^{114}\text{Cd}/^{110}\text{Cd})_{\text{initial}}} = \frac{1 - (1-f)^{\alpha_{\text{kin}}}}{f} \quad (7)$$

Kinetic Rayleigh condensation is expected to enrich the light isotopes in the condensates (e.g. Kehm et al., 2003; Davis and Richter, 2003). Kinetic Rayleigh condensation is an ideal case, which requires the absence of any back-reaction between condensate and gas phase. Back-reaction is likely to occur, however, during slow cooling at isothermal conditions (Humayun and Cassen, 2000). Kinetic Rayleigh condensation may be relevant if condensation takes place: (i) onto a cooler substrate (Esat and Taylor, 1999) or (ii) from a rapidly cooling vapor phase (Kehm et al., 2003; Richter, 2004; Luck et al., 2005), or (iii) if the ambient vapor is highly supersaturated (Davis and Richter, 2003).

3.3. Equilibrium isotope fractionation during evaporation and condensation

The evaporation and condensation of refractory and moderately volatile elements in the solar system generally occurs at temperatures that are inferred to be too high to generate measurable isotope fractionations between equilibrated vapor and condensates (e.g. Humayun and Clayton, 1995a; Davis and Richter, 2003). This conclusion may not apply to highly volatile elements, however, and Wombacher et al. (2004) argued that equilibrium isotope fractionation

may be relevant for the Cd isotope effects observed in chondritic meteorites.

If equilibrium can be maintained in a closed system throughout partial condensation or evaporation, the isotope composition of the actually condensed Cd is given by:

$$\frac{(^{114}\text{Cd}/^{110}\text{Cd})_{\text{condensate}}}{(^{114}\text{Cd}/^{110}\text{Cd})_{\text{bulk Cd in system}}} = \frac{1}{\alpha_{\text{eq}} * (1 - f) + f} \quad (8)$$

It is possible that loss of Cd vapor may occur during equilibrium evaporation. In this case, equilibrium evaporation is better described using an evaporation model, which assumes that multiple batches of equilibrated vapor are lost in a stepwise fashion (Wombacher et al., 2004), such that:

$$R_n = \frac{R_{n-1}}{(1 - F_s) + \alpha_{\text{eq}} * F_s} \quad (9)$$

Here R_{n-1} and R_n refer to the isotope composition of the evaporation residue before and after the extraction of vapor batch n ($n = 1, 2, 3, \dots$), and the step-size F_s denotes the mass fraction of Cd vapor that is removed in each cycle. Calculations for equilibrium evaporation with small step sizes ($F_s \leq 0.1$) approach the results that are obtained for Rayleigh fractionation (Eq. (4) with α_{eq}). This is important, because it indicates that partial evaporation of Cd under equilibrium conditions with contemporaneous loss of the gas phase can produce strongly fractionated residues, even for small equilibrium isotope fractionation factors, if the evaporation process runs to near completion.

Batch equilibrium evaporation may be a possible scenario for: (i) volatilization of Cd from chondrules, as has

been suggested for K and Fe isotopes (Alexander et al., 2000; Alexander and Wang, 2001; Yu et al., 2003) and (ii) volatile loss from parent bodies, where a significant Cd partial pressure can build up in pore spaces. Ngo and Lipschutz (1980) observed that Cd is lost from the Allende meteorite upon heating to 673 K which is similar to the condensation temperature for Cd (652 K; Lodders, 2003). This indicates that roughly similar equilibrium fractionation factors would apply for condensation processes in the solar nebula and evaporation within chondrite parent bodies.

Equilibrium condensation in multiple steps is also a possible scenario, for example if the first Cd that condenses is isolated from the gas phase by the accretion of the condensates. The isotope composition of the instantaneously formed condensate is given by:

$$R_n = \frac{R_{n-1}}{(1 - F_s) + \frac{\alpha_{\text{eq}}}{F_s}} \quad (10)$$

We note that the calculations for equilibrium evaporation and condensation in multiple steps (Fig. 2) ignore further complicating factors that may play an important role in nature, such as variations in F_s (i.e., the rate of gas removal or isolation of the condensate) during the process and changes of α_{eq} with temperature.

Wombacher et al. (2004) inferred an equilibrium fractionation factor of $\alpha_{\text{eq}} \approx 0.9930$ for Cd (at ~ 450 K), based on the observation that the mass-dependence of Cd isotope fractionation during the evaporation of liquid Cd into vacuum was intermediate to that expected for kinetic and equilibrium isotope fractionation (see Young et al., 2002). The

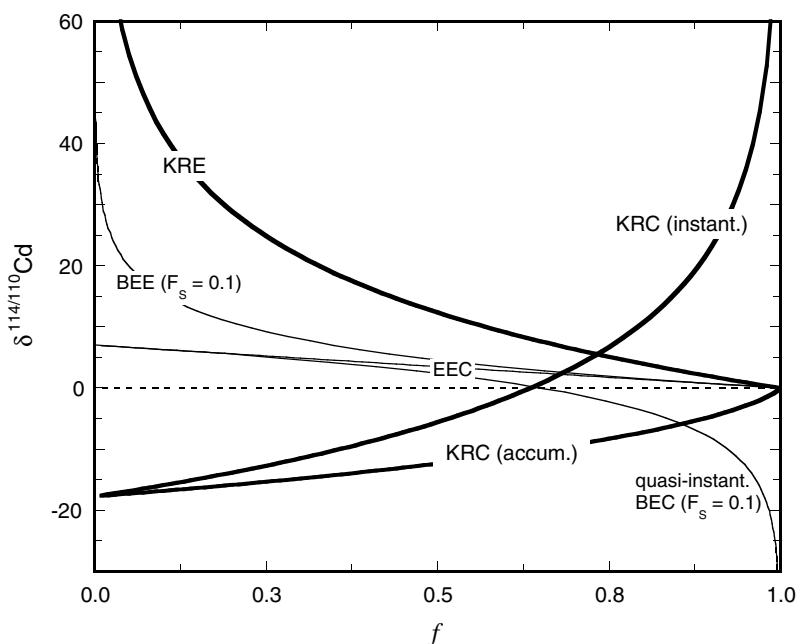


Fig. 2. Calculated Cd isotope compositions of the condensed phase for different modes of partial evaporation and condensation. The parameter f denotes the mass fraction of condensed Cd. For $f = 1$ the bulk condensate equals $\delta^{114/110}\text{Cd} = 0$ by definition. Kinetic Rayleigh evaporation (KRE) and condensation (KRC) was calculated with $\alpha_{\text{kin-sqr}} = 0.9823$ (Eq. (5)). The possible effects of equilibrium isotope fractionation during evaporation and condensation in a closed system (EEC) were evaluated using $\alpha_{\text{eq}} = 0.9930$ (Wombacher et al., 2004; see text for arguments that $1 - \alpha_{\text{eq}}$ is probably smaller in nature). Open system batch equilibrium evaporation (BEE) and condensation (BEC) were calculated with a step size $F_s = 0.1$. All fractionation factors are for $^{114}\text{Cd}/^{110}\text{Cd}$.

mass-dependence of an isotope fractionation process is defined by the slope β in a linearized three isotope plot (Young et al., 2002). For any three isotope system, the observed slope β can be compared by fitting the exponent q of the generalized power law (Maréchal et al., 1999; Wombacher et al., 2004) such that:

$$\beta_{\text{observed}} = (m_1^q - m_2^q)/(m_1^q - m_3^q) \quad (11)$$

Here, mass m_1 refers to the denominator isotope, and m_2 and m_3 are the masses of the numerator isotopes at the ordinate and abscissa, respectively. The observed mass-dependence for the evaporation of liquid Cd corresponds to $q = -0.34 \pm 0.05$, where $q = -1$ refers to β for equilibrium isotope fractionation and $q \rightarrow 0$ was expected for β in the case of kinetic isotope fractionation (see Wombacher et al., 2004 and references therein). Likewise Davis et al. (2005) observed a mass-dependence for Mg during evaporation that can be parameterized by a generalized power law exponent of $q = -0.30 \pm 0.02$, which is indistinguishable from the result for the evaporation of liquid Cd. This similarity suggests a common cause. It is therefore notable that the Mg data of Davis et al. (2005) were determined for evaporation at very high temperatures between 1600 and 1900 °C (Richter et al., 2005) where equilibrium isotope fractionation will be negligible. This indicates that Wombacher et al. (2004) are likely to have significantly overestimated the equilibrium isotope fractionation factor for Cd evaporation, because their evaluation assumed kinetic slopes defined by $q \rightarrow 0$ in linearized three isotope space. It follows that equilibrium isotope fractionation during evaporation/condensation of Cd will probably be insignificant at the temperatures that are relevant for volatile element processing in the early solar system. However, direct experimental evidence is lacking.

4. RESULTS

4.1. Cosmogenic isotope effects

Due to the large neutron capture cross-section of ^{113}Cd ($\sim 20,000$ barn for thermal neutrons), neutron irradiation can alter Cd isotope compositions according to the reaction $^{113}\text{Cd} (n, \gamma) ^{114}\text{Cd}$. Hence, any irradiation-induced decrease in the abundance of ^{113}Cd will be accompanied by a concomitant increase in the ^{114}Cd abundance. In this study, large neutron-capture effects of $\delta_{\text{n.c.}} ^{113}\text{Cd}/^{114}\text{Cd} \approx -3.5$ were observed for two lunar samples, the polymict anorthositic breccia Dar al Gani 262 and the Apollo soil 14163. Here, $\delta_{\text{n.c.}} ^{113}\text{Cd}/^{114}\text{Cd}$ denotes the deviation of the *mass-fractionation corrected* $^{113}\text{Cd}/^{114}\text{Cd}$ ratio of a sample from the JMC Cd standard in permil (see caption of Fig. 3). Sands et al. (2001a,b) and Schediwy et al. (2006) previously analyzed a subsample of Apollo soil 14163. They observed no mass-dependent fractionation and no neutron capture effects for Cd, although neutron capture effects were detected for Sm and Gd. These authors, however, reported Cd concentrations that were much higher than published values. They therefore suspected that their subsample (14163,848) was strongly contaminated by terrestrial Cd that masks the cosmogenic effects and Cd isotope fraction-

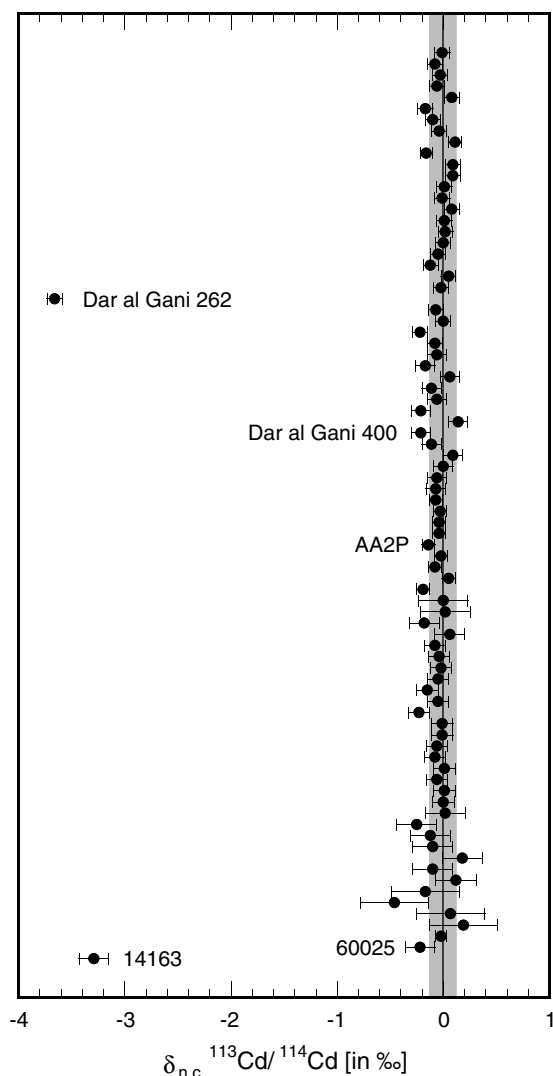


Fig. 3. Neutron capture effects reported as $\delta_{\text{n.c.}} ^{113}\text{Cd}/^{114}\text{Cd}$, which denotes the deviation of $^{113}\text{Cd}/^{114}\text{Cd}$ for samples from the JMC Cd standard in ‰, after normalization of $^{113}\text{Cd}/^{114}\text{Cd}$ to $^{111}\text{Cd}/^{112}\text{Cd}$ with the exponential law in order to remove the effects of instrumental mass discrimination and natural stable isotope fractionation. The $\delta_{\text{n.c.}} ^{113}\text{Cd}/^{114}\text{Cd}$ values of the samples are arranged in the sequence of the measurements. The gray bar denotes the analytical uncertainty for $\delta_{\text{n.c.}} ^{113}\text{Cd}/^{114}\text{Cd}$ ($\pm 0.13\text{‰}$; 2 sd) as estimated from eight repeated measurements of the Allende meteorite. The individual error bars represent the analytical uncertainty (2 sd) for the JMC Cd standard measurements that accompanied the respective measurement session. Larger analytical uncertainties mainly result from further dilution in order to match the Cd signal intensities of samples with lower Cd concentrations. All data are corrected for Sn (Section 2.3) and In interferences. Indium interferences were usually < 10 ppm and never more than 85 ppm. Two lunar samples, the anorthositic breccia Dar al Gani 262 and the Apollo soil sample 14163 display large $\delta_{\text{n.c.}} ^{113}\text{Cd}/^{114}\text{Cd}$ anomalies of $-3.66 \pm 0.14\text{‰}$ and $-3.29 \pm 0.07\text{‰}$ due to neutron capture. All other data display no resolvable anomalies. The evaporation residue from Allende (AA2P) had been irradiated for instrumental neutron activation analysis (Wulf, 1990), but neutron capture effects were not detected.

ation. This conclusion is in accord with the results of the present study for a different subsample.

The two other lunar samples that were analyzed in this study display no irradiation effects that exceed the analytical uncertainty. Aside from the lunar samples, one Semarkona separate (chips from large chondrule) displays a low $\delta_{n.c.}^{113}\text{Cd}/^{114}\text{Cd}$ value of -0.46 . If this result indeed reflects neutron irradiation, this would only be associated with an increase of $\delta^{114/110}\text{Cd}$ by $+0.14$, which is a third of the analytical uncertainty. For all other samples, the measured $\delta_{n.c.}^{113}\text{Cd}/^{114}\text{Cd}$ values correspond to insignificant changes in $\delta^{114/110}\text{Cd}$ of less than ± 0.07 .

4.2. Cadmium stable isotope data for lunar samples and achondritic meteorites

Among the lunar samples, the anorthositic breccia Dar al Gani 400 displays only a slight enrichment of the heavy Cd isotopes ($+1.1\%$), but the remaining three samples exhibit heavy isotope compositions with $\delta^{114/110}\text{Cd}$ of $+7.8$ to $+11.3$ (Fig. 4, Table 1).

The achondrites have $\delta^{114/110}\text{Cd}$ values ranging from -0.8 to $+1.1$ (Fig. 4, Table 1). Both Martian meteorites (shergottites) display slight enrichments of the heavy Cd isotopes ($+0.9\%$ and $+0.5\%$) and two monomict eucrite breccias have $\delta^{114/110}\text{Cd}$ values (-0.2 and 0.0) that are indistinguishable from the JMC Cd laboratory standard. The ureilite Kenna has a heavy Cd isotope composition, with $\delta^{114/110}\text{Cd} = +1.1$. The data for Kenna, however, were obtained from only about 5 ng of Cd and the sample solution was repeatedly treated with aqua regia and H_2O_2 to oxidize large amounts of residual carbon, which were finally removed by centrifugation. Due to the unusual sample treatment, the data quality for Kenna is difficult to assess and the result should be interpreted with caution. Two analyses of a winonaite sample (HH 193) yielded light isotope compositions (-0.3% and -0.8%).

4.3. Carbonaceous chondrites, Allende separates and enstatite chondrites

Carbonaceous chondrites of petrological type 1 (Orgueil) and 2 have Cd isotope compositions that are indistinguishable from the terrestrial standard. This is also true for the Allende CV3 chondrite and the CK3 chondrite Watson 002 (Fig. 4 and Table 1). In contrast, the other type 3 chondrites, Leoville CV3, Colony CO3.0 and Dar al Gani 005 CO3, show heavy Cd isotope compositions with $\delta^{114/110}\text{Cd}$ between $+1.1$ and $+4.5$. The two metamorphosed CK meteorites of type 4/5 and 5 (Dar al Gani 275 and 412) have similar $\delta^{114/110}\text{Cd}$ (which may reflect a possible pairing relationship) of about -1 .

All matrix separates from Allende have isotope compositions that are identical to the bulk meteorite, but three out of four refractory separates clearly display light isotope compositions (Fig. 4 and Table 1). An eleven mg separate of a Ca–Al-rich refractory inclusion of unknown type is characterized by $\delta^{114/110}\text{Cd} = -2.2$ and a high Cd concentration of ~ 1200 ppb. The separate with the most fractionated Cd isotope composition is from the same piece of

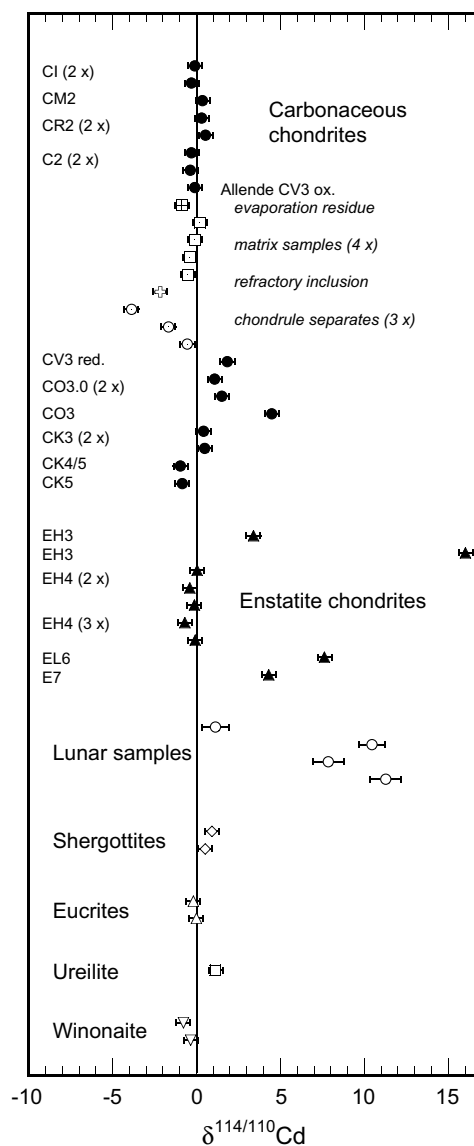


Fig. 4. Cadmium stable isotope data for bulk carbonaceous chondrites (solid circles), matrix and refractory separates from the Allende meteorite (open symbols immediately below bulk Allende), enstatite chondrites (filled triangles), lunar samples (open circles) and various achondrites (other open symbols). The error bars denote the long-term reproducibility of $\pm 0.43\%$ for $\delta^{114/110}\text{Cd}$ (2 sd). The uncertainties for the lunar samples are discussed in the text and the caption of Table 1.

Allende and it consists of ca. 180 chondrules and chondrule fragments with diameters < 1 mm (-3.9% ; ca. 300 ppb Cd). A second set of about 100 small chondrules and chondrule fragments was separated from a different piece of Allende and its Cd isotope composition is nearly identical to the terrestrial standard (-0.5% ; ca. 100 ppb Cd). In contrast, a second separate from the latter piece, which consists largely of chondrules with coarse-grained rims (or fragments thereof), displays $\delta^{114/110}\text{Cd} = -1.7$ and a Cd content of about 300 ppb. An evaporation residue from the Allende meteorite (AA2P) is also isotopically light (-0.9%). This sample was heated to 1100 °C for four days in a semi-open

system with the oxygen fugacity buffered at Ni–NiO ($\log f_{O_2} \sim -8.8$) (Wulf, 1990; Wulf et al., 1995). The light isotope composition of the Allende evaporation residue AA2P may be inherited from refractory host minerals.

Two metamorphosed EL-type enstatite chondrites have heavy $\delta^{114/110}\text{Cd}$ values of +4.3 and +7.6. The two unequilibrated EH3 samples also display heavy isotope compositions and Qingzhen has the highest $\delta^{114/110}\text{Cd}$ value of +16.0 observed so far. The EH4 chondrites Abee and Indarch, however, display no Cd isotope effects relative to the terrestrial standard.

4.4. Ordinary and Rumuruti chondrites

The total variation of Cd isotope compositions observed for eleven unequilibrated ordinary chondrites is about 23‰, with $\delta^{114/110}\text{Cd}$ ranging from -7.8 to $+15.0$. In contrast, four equilibrated ordinary chondrites vary by only 3.5‰, with results from -0.3 ‰ to $+3.2$ ‰ (Fig. 5, Table 1).

For Bishunpur and the Dar al Gani 085 breccia, we analyzed one piece each with abundant fusion crust. For Bishunpur, the sample with fusion crust has the same Cd isotope

composition (within uncertainty) as the bulk meteorite. For Dar al Gani 085, the piece with fusion crust is about 0.9‰ lighter compared to the bulk sample. Partial evaporation of Cd from a fusion crust cannot generate isotopically light evaporation residues. This indicates (i) that the different results for the Dar al Gani 085 breccia are due to sample heterogeneity and (ii) that the fusion of meteorite surfaces during passage through the Earth's atmosphere does not significantly affect the Cd isotope compositions of the samples.

Semarkona is the only known type 3.0 ordinary chondrite. It displays the highest Cd concentration (1248 ppb Cd; Rosman and De Laeter, 1988) reported for a meteorite in this study and is characterized by the lowest $\delta^{114/110}\text{Cd} = -7.8$. Various separates from the Semarkona chondrite all have light, but variably fractionated Cd isotope compositions. The “fine fraction” was rinsed off the crushed material with ethanol (Table 1). This material represents the most matrix-rich sample and its Cd isotope composition is 1.1‰ heavier than the bulk sample. The “matrix-rich” and “matrix-rich with some fusion crust” fractions are residues from the separation of chondrules. They contain about 40% and 50% of matrix material, respectively, and their isotope compositions are identical to the bulk sample, within uncertainty. The two chondrule separates of Semarkona consists of (i) transparent, colorless or greenish fragments of minerals or glass that are probably derived from chondrule interiors and (ii) four chips from a large chondrule. The Cd isotope compositions of these samples are identical to and about 1.4‰ lighter than bulk Semarkona. Both the chondrule-rich (+11.0‰), and the matrix-rich (+12.2‰) fraction of Bishunpur are isotopically indistinguishable from the bulk sample, which displays $\delta^{114/110}\text{Cd} = +11.4$, but the matrix-rich separate is about 1.2‰ heavier than the chondrule-rich separate. It is possible, however, that this difference reflects variable drill blanks. For Bishunpur, the chondrule-rich separate contained about 94 ppb Cd, compared to ~ 263 ppb for the bulk sample. This appears to be inconsistent with the very high Cd abundances reported in Sears et al. (1995) for seven Bishunpur chondrules (480 to 11,000 ppb). The chondrule separates from Semarkona were estimated to contain 180 and 370 ppb Cd, which compares with 120 to 5400 ppb reported by Sears et al. (1995). The observation that the matrix-rich separates have higher Cd contents than the bulk samples also applies to Sarir Qattusah 001. Sarir Qattusah 001, however, is a find and it is therefore possible that its Cd distribution was altered on Earth. The matrix-rich separate of this sample exhibits the same heavy Cd isotope composition as the bulk meteorite. The Cd isotope compositions of the four Rumuruti chondrites ranges from $\delta^{114/110}\text{Cd} = -1.6$ to $+2.9$.

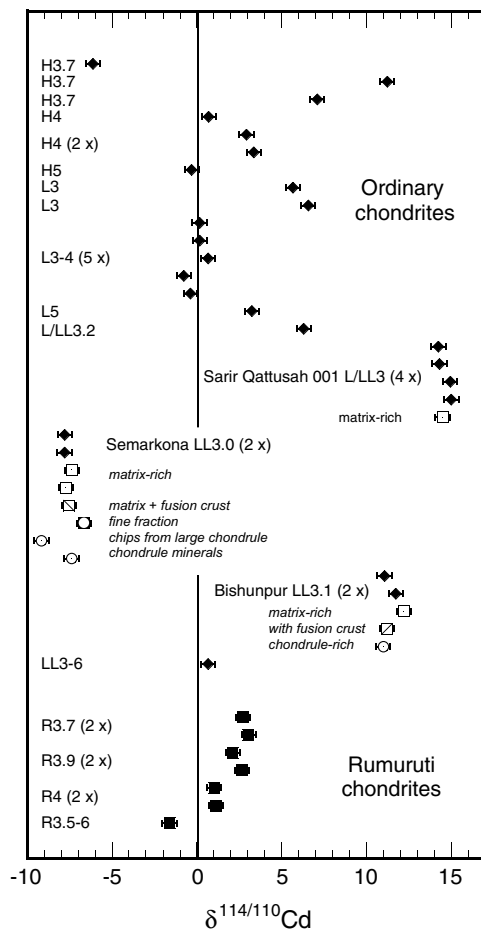


Fig. 5. Cadmium stable isotope data for bulk ordinary chondrites (solid diamonds), various separates from ordinary chondrites (open symbols) and Rumuruti chondrites (solid squares). The error bars denote the long-term reproducibility of ± 0.43 ‰ for $\delta^{114/110}\text{Cd}$ (2 sd).

5. DISCUSSION

5.1. Cadmium and Zn abundances in chondritic meteorites

The following brief review of the abundances of Cd and Zn in bulk chondrite samples provides the necessary framework for the interpretation of the Cd isotope data. Cadmium and Zn have similar geochemical properties, but

Cd is a highly volatile element (with a 50% condensation temperature of $T_C = 652$ K, Lodders, 2003), while Zn is a moderately volatile element (with $T_C = 726$ K, Lodders, 2003). A compilation of literature data for Cd and Zn concentrations in chondritic meteorites is presented in Fig. 6. Very volatile elements are typically depleted to a similar extent in most carbonaceous chondrites (Larimer and Anders,

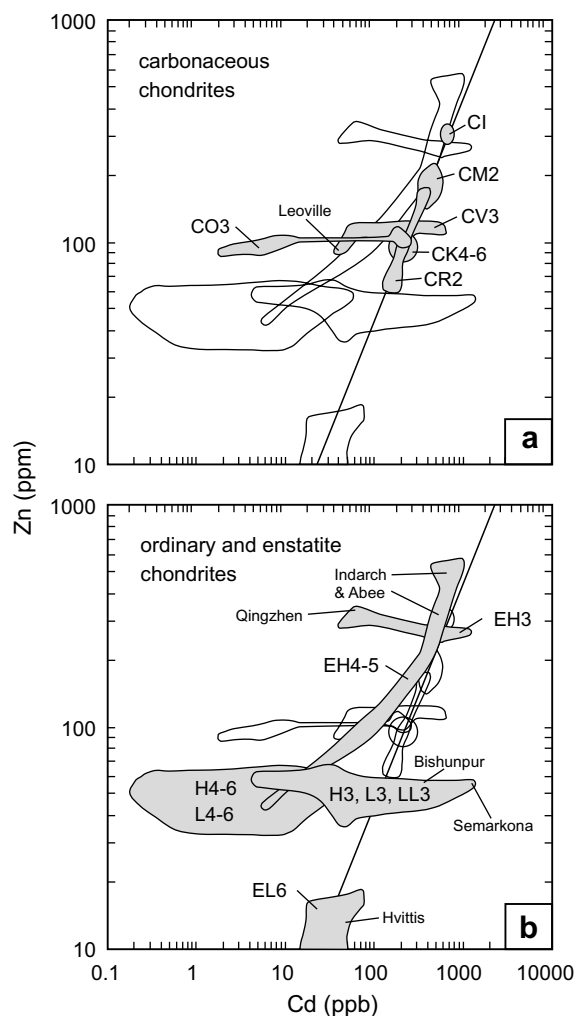


Fig. 6. Published Cd and Zn concentration data for (a) carbonaceous and (b) ordinary and enstatite chondrites. The primitive Cd/Zn reference line with $Cd \times 1000 / Zn = 2.29$ is defined by the CI data. Cadmium and Zn depletion along the primitive Cd/Zn reference line is interpreted to reflect primary volatile element depletion. Preferential Cd depletion or heterogeneous distribution is evident for CV3, CO3, EH3 and ordinary chondrites. Data from: Keays et al., 1971; Laul et al., 1973; Krähenbühl et al., 1973b; Binz et al., 1974; Rosman and De Laeter, 1974; Binz et al., 1976; Takahashi et al., 1978; Wolf et al., 1980; Bhandari et al., 1980; Rosman et al., 1980; Kallemeyn and Wasson, 1981; Ebihara et al., 1982; Kallemeyn and Wasson, 1982; Walsh and Lipschutz, 1982; Hertogen et al., 1983; Huston and Lipschutz, 1984; Morgan et al., 1985; Dennison and Lipschutz, 1987; Linger et al., 1987; Kaczaral et al., 1988; Rosman and De Laeter, 1988; Kaczaral et al., 1989; Xiao and Lipschutz, 1992; Wolf and Lipschutz, 1995a; Wolf and Lipschutz, 1995b; Zolensky et al., 1997; Wang and Lipschutz, 1998; Wang et al., 1999b.

1967; Wolf et al., 1980). Indeed, most carbonaceous chondrites are depleted to the same extent in both Cd and Zn and hence they plot along a reference line defined by a primitive (i.e., CI-like) Cd/Zn ratio ($1000 \times Cd/Zn = 2.29$) (Fig. 6a). However, the CV3 and CO3 chondrites define horizontal trends. These trends reflect a process that preferentially affected the highly volatile element Cd, but not the moderately volatile Zn. For the CO3 chondrites, the trend may be better described as a bimodal distribution in Cd abundances with Cd-rich and Cd-depleted samples. Likewise, the low-Cd end of the CV3 trend appears to be defined by members of the reduced subgroup (Leoville, Vigarano), while all oxidized samples plot closer to the Cd/Zn reference line.

Zinc depletion in ordinary chondrites (Fig. 6b) is fairly uniform, with a typical Zn concentration of about 50 ppm. In contrast, Cd concentrations scatter over four orders of magnitude. There also appears to be a tendency that very volatile elements with $T_C \leq 800$ K (e.g., Zn, Te, Sn) are depleted to approximately the same extent in ordinary chondrites (Palme et al., 1988; Alexander, 2005). Because of the well defined main trend shown in Fig. 6, it appears possible that Cd and Zn in ordinary chondrite matter were originally depleted to the same extent. In this case, the Zn depletion to 50 ppm corresponds to a Cd concentration of ~ 115 ppb, based on $Cd \times 1000 / Zn = 2.29$ as defined by CI chondrites. In fact, the metamorphosed ordinary chondrites of type 4 to 6 all have Cd contents significantly lower than 115 ppb. In contrast, the unequilibrated (type 3) ordinary chondrites display both Cd depletions and enrichments relative to the 115 ppb reference value. The enstatite chondrite trends are less well defined, but this may reflect the much smaller dataset. The EH3 group appears to define a horizontal trend with preferential Cd depletion. One EH5 (Saint-Sauveur) and most EH4 chondrites display no or only minor depletions in Cd and Zn compared to CI-abundances (the higher than CI abundances in some EH chondrites may primarily reflect the presence of water in CI chondrites). However, Adhi Kot (EH4), St. Mark's (EH5) and EL6 enstatite chondrites are depleted in both Cd and Zn.

We suggest that the depletion trend that is defined by carbonaceous chondrites with CI-like Cd/Zn ratios results from primary volatile element depletion. The preferential depletion of Cd in ordinary chondrites, some CV3, CO3 and enstatite chondrites, and the enrichment in some unequilibrated ordinary chondrites, however, probably results from secondary processes.

5.2. The homogeneity of Cd isotopes in the solar nebula

The chondrite samples (and separates) analyzed in this study do not exhibit nucleosynthetic Cd isotope anomalies for the s- and r-process nuclides ^{111}Cd , ^{112}Cd , ^{113}Cd and ^{114}Cd (Figs. 1 and 3), nor for ^{110}Cd , which is produced solely by the s-process (data not shown). This conclusion is in accord with the results of previous isotope studies of other volatile elements, such as Zn and Te (Luck et al., 2005; Fehr et al., 2005, 2006), that also do not show any nucleosynthetic anomalies in chondrites (and iron meteorites). This

indicates that anomalies in r- and s-process isotopes that are due to the heterogeneous distribution of presolar host grains among *bulk* chondrite samples may be restricted to refractory elements such as Mo, Ba and Os, (Dauphas et al., 2002; Yin et al., 2002; Hidaka et al., 2003; Brandon et al., 2005; Carlson et al., 2007; Andreasen and Sharma, 2007). In this regard, however, it should be noted that other studies were unable to identify r- and s- process isotope anomalies for Sm, Nd, Mo, Zr and Os in bulk chondrite samples (Becker and Walker, 2003; Schönbachler et al., 2003; Andreasen and Sharma, 2006; Yokoyama et al., 2007).

It has also been suggested that mass-independent nuclear field-shift-induced isotope fractionations accompany evaporation/condensation related mass-dependent isotope fractionations for low- or mid-mass elements like Ca, Ti, Cr, Sr and Ba (Fujii et al., 2006). However, such effects were neither observed in the present study nor in the highly fractionated evaporation residues (up to about +50‰ for $^{114}\text{Cd}/^{110}\text{Cd}$) of Wombacher et al. (2004).

The data obtained for type 1, 2 and two type 3 carbonaceous chondrites, the EH4 chondrites and the eucrites display no mass-dependent Cd isotope fractionations relative to the JMC Cd standard, which is taken to be representative for the (silicate) Earth (Wombacher et al., 2003). The Cd isotope fractionations in two Martian meteorites (+0.5‰ and +0.9‰) are furthermore only barely resolvable, and these small effects may be due to planetary surface processes, such as admixing of a fractionated soil component. Similarly, two lunar samples (Dar al Gani 400 with $+1.1 \pm 0.8\%$ and high-Ti basalt 10017 from Schediwy et al. (2006), with $+1.2 \pm 3.6\%$), the winonaite and the ureilite also have Cd isotope compositions that are nearly identical to the terrestrial standard. This similarity amongst very different planetary materials indicates that the inner solar system featured an initially homogeneous Cd stable isotope composition.

5.3. Lunar surface processes

Volatile elements are strongly enriched in lunar soils and polymict breccias relative to pristine or monomict highland rocks and mare basalts (Keays et al., 1970; Haskin and Warren, 1991). A widely held view is that this enrichment results largely from the addition of meteorites to the lunar surface (Haskin and Warren, 1991). This conclusion is supported by the elevated abundance of the highly siderophile element Ir at the lunar surface, which clearly reflects a meteorite contribution (Haskin and Warren, 1991). An alternative explanation, however, suggests that the high volatile concentrations of the soils are derived from lunar magmatic activity (Chou et al., 1973; Krähenbühl et al., 1973a; Boynton et al., 1976). A compilation of data from 140 lunar soils (Haskin and Warren, 1991; Fig. 8.26a) demonstrates that Cd and Ir have similar CI-normalized abundances, which is consistent with the model of a CI-like meteorite contribution. However, the compilation also shows that several moderately volatile elements (S, Se, Sb and Te) have CI-normalized abundances that are one order of magnitude lower than those of Cd and Ir. The high Cd

contents in soils would thus require a meteorite flux that features strong enrichments of Cd relative to the moderately volatile elements. Only very few Cd-enriched unequilibrated ordinary chondrites satisfy this criterion and this strongly suggests that the bulk of the Cd present in lunar soils is not derived from meteorites, but from lunar volcanic activity.

Cadmium isotope data are available for five soil samples from the present and a previous study (Schediwy et al., 2006) and all show heavy Cd isotope compositions with $\delta^{114/110}\text{Cd}$ values between +11 and +20 (Fig. 7). Importantly, the soil data and the Apollo regolith breccia 15059 (Schediwy et al., 2006) define an excellent “Moon-wide” correlation of increasing Cd isotope fractionation with decreasing Cd abundance. This trend is qualitatively consistent with vaporization of Cd from lunar soils, but contrasts with S isotopes, that display increasing ^{34}S with increasing S abundance (Kerridge et al., 1975). On the basis of O, Mg, Si, S, K, and Ca isotopes, Russel et al. (1977) and Humayun and Clayton (1995b) suggested that the isotope fractionation patterns of lunar soil samples are governed by volatility. This conclusion is corroborated by the observation that Cu, Zn and Cd display much larger variations of stable isotope compositions in lunar soils than the more refractory element Fe (Wiesli et al., 2003; Schediwy et al., 2006; Moynier et al., 2006). It has been suggested that vaporization (and isotope fractionation) of volatile elements may occur in response to micrometeorite impacts and this process may be aided by gravitational isotope separation in the lunar exosphere (Clayton et al., 1974; Housley, 1979; Humayun and Clayton, 1995b). In addition, it is also possible that ion sputtering by the solar wind may cause volatilization and generate heavy isotope enrichments in lunar soils (Switkowski et al., 1977).

The trend of the lunar soil data in Fig. 7 is not compatible with partial Rayleigh evaporation, if an (unsuppressed) fractionation factor of $\alpha_{\text{kin-sqrm}} = 0.9823$ is assumed. This conclusion stands, regardless of the exact Cd isotope composition and concentration of the starting material. An almost perfect fit to the data can be obtained, however, by suppressed partial Rayleigh evaporation. For an effective isotope fractionation factor $\alpha_{\text{eff}} = 0.9938$ (where $1 - \alpha_{\text{eff}}$ is about 35% of $1 - \alpha_{\text{kin-sqrm}}$) an excellent fit is obtained if a starting material with $\delta^{114/110}\text{Cd} = 0$ and a Cd content of ~ 800 ppb is chosen. In general, reasonable fits to the data can be obtained if $1 - \alpha_{\text{eff}}$ varies between about 20% and 50% of $1 - \alpha_{\text{kin-sqrm}}$, but this requires endmembers with different $\delta^{114/110}\text{Cd}$ values and Cd concentrations. Suppressed Rayleigh distillation may be caused by micrometeorite bombardment and perhaps ion sputtering. In this case, the excellent correlation shown in Fig. 7 requires that the lunar starting material had a homogeneous Cd isotope composition and concentration. Such a large-scale homogeneity may have been produced by impact-induced redistribution of Cd that resides in fine dust and/or a vapor phase. In this case, however, Cd will show a different exposure history to thermal neutrons than the refractory elements Sm and Gd, for the same samples. The mobility of Cd thus complicates the interpretation of thermal neu-

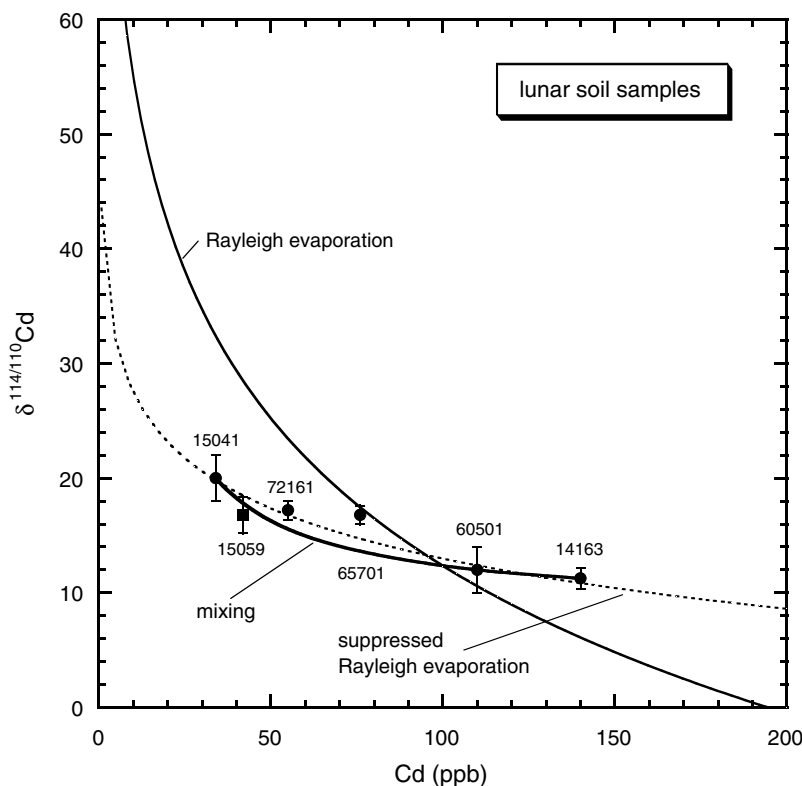


Fig. 7. Relationship between Cd isotope fractionation and Cd concentration for lunar soils (circles) and a single breccia (square). The data can be described by suppressed Rayleigh distillation from unfractionated starting materials or by two-component mixing between endmembers with heavy Cd isotope composition. Five data are from Schediwy et al. (2006); note that the somewhat heavier Cd isotope compositions reported by Sands et al. (2001b) were ignored here, since Schediwy et al. (2006) reanalyzed the same samples with the more robust double spike technique. The $\delta^{114/110}\text{Cd}$ values in ‰ were recalculated from the %/mass unit-notation used by Schediwy et al. (2006) simply by multiplication with 40. The Cd concentration for sample 14163 is from Morgan et al. (1972). Unsuppressed kinetic Rayleigh evaporation: $\alpha_{\text{kin-sqrm}} = 0.9823$; starting composition: 200 ppb Cd with $\delta^{114/110}\text{Cd} = 0$. Suppressed Rayleigh evaporation: $\alpha_{\text{eff}} = 0.9938$; starting composition: 800 ppb Cd with $\delta^{114/110}\text{Cd} = 0$. The mixing curve was calculated using samples 15041 and 14163 as endmembers.

tron energy spectra obtained from combined studies of Sm, Gd and Cd neutron capture effects (Sands et al., 2001a).

An alternative explanation for the data of Fig. 7 is given by the mixing of soil components. Two-component mixing can only account for the results, however, if both endmembers have heavy Cd isotope compositions with $\delta^{114/110}\text{Cd} \geq 8\text{‰}$ because the mixing curves would otherwise plot below the observed trend. A serious drawback of this model is the lack of suitable endmembers (Sands et al., 2001b). It is conceivable that agglutinates, which form by melting associated with micrometeorite impacts (McKay et al., 1991), have low Cd contents and particularly heavy Cd isotope compositions, due to Cd loss by volatilization. The data for the agglutinate-rich soil 14163 (which contains ~70% agglutinates; McKay et al., 1991), however, argues against an agglutinate endmember, because soil 14163 has the lowest $\delta^{114/110}\text{Cd}$ value of all soil samples (Fig. 7). On the other hand, the rough correlation between $\delta^{114/110}\text{Cd}$ and isotope anomalies from neutron-capture in Fig. 8 appears to be in accord with two-component mixing between soil components of different provenance, one of which features heavy $\delta^{114/110}\text{Cd}$, large neutron capture effects and comparatively low Cd abundances.

The pristine cataclastic ferroan anorthosite 60025 (Warren and Wasson, 1977) displays an almost soil-like heavy Cd isotope composition (+7.8‰), but a neutron capture effect is barely resolvable (Figs. 3 and 8). This appears to rule out a significant contamination with modern lunar soil Cd. It follows that the Cd present in 60025 was hidden from thermal neutrons for most of its history, and this may suggest that a significant part of the observed Cd isotope fractionation in lunar surface samples predates the neutron capture effects. Such an early Cd reservoir with heavy Cd isotope compositions could have been produced by Cd volatilization and preferential escape of the lighter Cd isotopes from the lunar surface, maybe due to an early phase of intense meteorite bombardment. Alternatively, the heavy Cd isotope composition of anorthosite 60025 may reflect local isotope fractionation during loss of Cd from this sample by partial evaporation.

5.4. Absence of Cd isotope fractionation during primary volatile depletion and planetary accretion

The ultimate cause of primary volatile element depletion is still under debate, but it is generally thought to be due to either incomplete condensation from a hot solar nebula

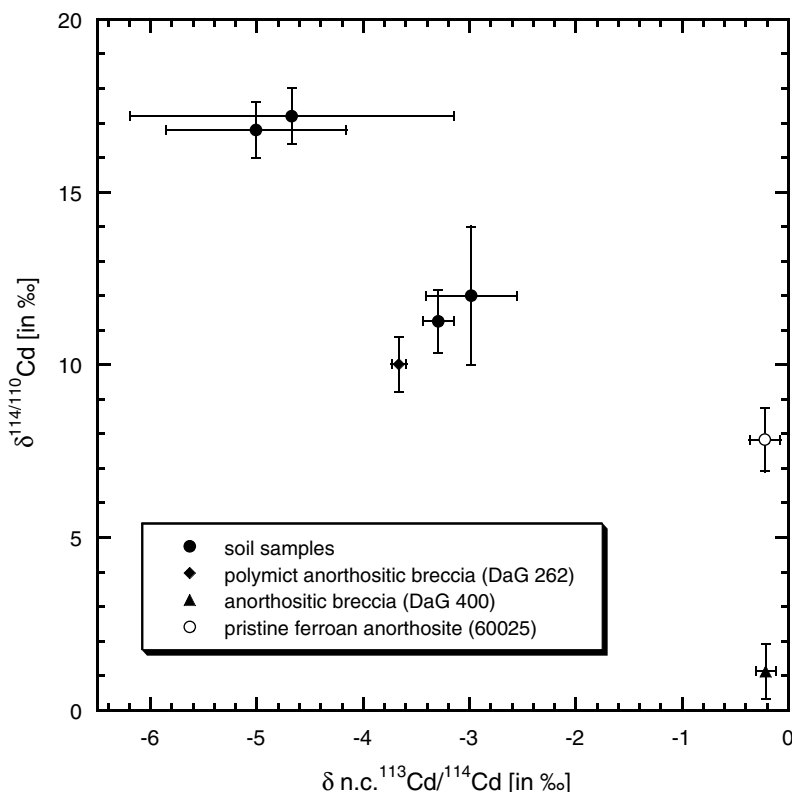


Fig. 8. Cadmium isotope fractionation versus cosmogenic Cd isotope effects for lunar soils, anorthositic breccias and a single anorthosite. Additional data: three soil $\delta^{114/110}\text{Cd}$ values are from Schediwy et al. (2006); $\delta_{\text{n.c.}}^{113}\text{Cd}/^{114}\text{Cd}$ was recalculated from the mass-bias and Sn-interference corrected data reported by Sands et al. (2001a). Note that the $\delta^{114/110}\text{Cd}$ results for the lunar samples were recalculated from $^{112}\text{Cd}/^{111}\text{Cd}$ such that changes in the abundance of ^{114}Cd due to neutron capture are not relevant.

(Wai and Wasson, 1977; Humayun and Clayton, 1995a; Cassen, 1996; Bland et al., 2005) or evaporative loss of volatile elements, for example during chondrule formation (Larimer and Anders, 1967; Anders et al., 1976; Anders et al., 1976; Alexander, 2005). Many carbonaceous chondrites, the Earth and various achondrites show no or only small Cd isotope fractionations, despite their variable Cd depletions relative to CI chondrites (Fig. 9a). This suggests that the primary depletion of very volatile elements is not the result of partial kinetic evaporation or condensation. Thus, the primary depletion is best explained by (i) partial evaporation/condensation at equilibrium or near-equilibrium conditions without significant isotope fractionation or (ii) a mixing model, which involves a refractory component (that may consist primarily of chondrules) that is nearly devoid of very volatile elements and a matrix-related component with approximately CI-chondritic relative volatile element abundances (Larimer and Anders, 1967; Wolf et al., 1980). Such a two-component mixing model is also consistent with the uniform depletion of very volatile elements, such as the CI-like Cd/Zn ratios of carbonaceous chondrites.

The CI-like Cd isotope compositions of many chondrites, achondrites, as well as the Earth, Mars, and Moon (Fig. 9a) show that no or only small Cd isotope fractionations were produced during the formation of planetesimals and planets by collisional growth. For the Earth–Moon sys-

tem, this includes the proposed Moon-forming giant impact (Cameron and Benz, 1991), which appears to have operated either without Cd loss or it did not involve partial kinetic evaporation/condensation of Cd (Wombacher et al., 2003). Furthermore, the initial differentiation of planetesimals is also constrained to have generated no significant Cd isotope effects.

5.5. Allende refractory inclusions and chondrules

Three of the four separates of refractory materials from the Allende chondrite display light Cd isotope compositions with $\delta^{114/110}\text{Cd}$ between -1.7 and -3.6 (Fig. 4). These data were obtained from two chondrule-rich fractions and a separate that consists mainly of fragments from one or more CAIs. In contrast, the bulk Allende sample and the matrix separates display no resolvable Cd isotope fractionations relative to the terrestrial standard. The data therefore indicate that chondrules and CAIs with light Cd isotope compositions of about -2% contribute less than 10% to the total Cd inventory of the Allende chondrite.

It is noteworthy that the CAI-rich fraction is isotopically light (with $\delta^{114/110}\text{Cd} = -2.2$) and surprisingly rich in Cd, with a concentration of ~ 1200 ppb. This is in accord with the results of Friedrich et al. (2005), who reported strong enrichments of siderophile and chalcophile elements, including In, Bi, Tl and Cd for CAIs. These workers noted

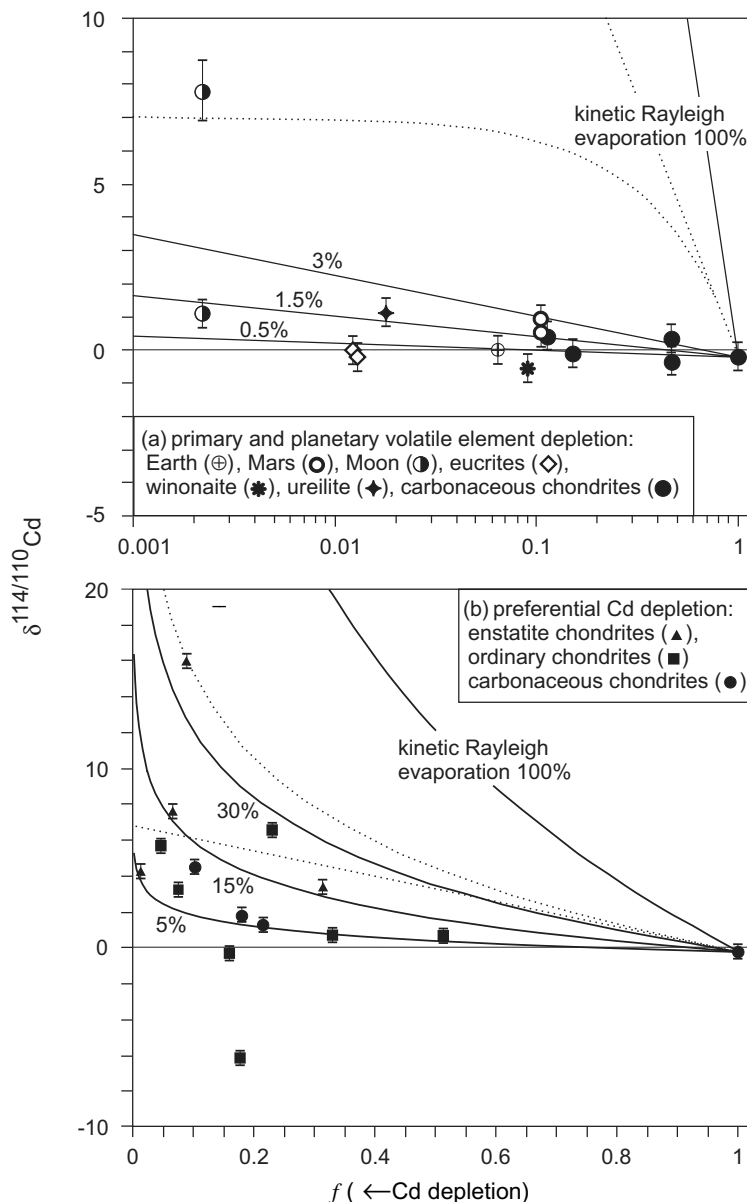


Fig. 9. Relationships between Cd depletion (as mass fraction f) and Cd isotope fractionation for (a) primary and planetary volatile element depletion (note logarithmic scale) and (b) preferential Cd depletion in chondrites. Thick solid lines: kinetic Rayleigh evaporation with variable suppression in % (i.e., 3% refers to $\alpha_{\text{eff}} = 0.03 * (\alpha_{\text{kin-sqrm}} - 1) + 1$). Stippled thin lines: qualitative pattern for equilibrium evaporation. Condensation curves were omitted for clarity, see Fig. 2 for comparison. (a) The two lunar $\delta^{114/110}\text{Cd}$ data refer to the ferroan anorthosite 60025, which may contain soil-derived Cd with a heavy isotope composition and to Dar al Gani 400. The result for Dar al Gani 400 is consistent with $\delta^{114/110}\text{Cd} = +1.2 \pm 3.6$ for the high-Ti basalt 10017 (Schediwiy et al., 2006). The bulk Cd contents of planetary bodies are difficult to estimate (due to the unknown core and mantle budgets), but rough estimates of the Cd depletions are sufficient for the present discussion. For the Earth, the Cd depletion was calculated from $(\text{Cd}/\text{Ti})_{\text{Earth}}/(\text{Cd}/\text{Ti})_{\text{CI}}$ using the data of McDonough and Sun (1995), McDonough (1999) and Lodders (2003). The Cd depletions of Mars and Moon are calculated conservatively from the Zn/Ti ratio of their silicate portions using data of O'Neil (1991) and Wänke and Dreibus (1988). The Cd depletions of the eucrites (both ~ 9 ppb Cd), the winonaite (~ 64 ppb Cd) and the ureilite Kenna (13 ppb Cd; Janssens et al., 1987) were estimated by dividing the Cd concentrations by that of dry CI-chondrites (710 ppb Cd; Rosman and De Laeter, 1974). The Cd concentrations for the two eucrites, the winonaite and two carbonaceous chondrites were estimated from the Cd contents of the sample solutions (see Wombacher et al., 2003). The Cd depletion for Allende and Murchison was calculated from the Cd and Ti data of Rosman and De Laeter (1974) and Shima and Hintenberger (1976). Panel b: The Cd depletion of the carbonaceous and ordinary chondrites was calculated relative to the assumed Cd abundances after primary volatile element depletion (ordinary chondrites: 115 ppb Cd; CV: 221 ppb; CO: 200 ppb). Panel (b) Only shows the depleted ordinary chondrites with < 115 ppb Cd. CI-like initial Cd abundances were assumed for the enstatite chondrites. Where available, Cd (Rosman and De Laeter, 1974; Hertogen et al., 1983; Kaczaral et al., 1988; Rosman and De Laeter, 1988) and Ti concentrations (Shima and Hintenberger, 1976; Newsom, 1995) from the literature were used, otherwise our own estimates from Cd contents of the sample solutions were applied.

that the volatile abundances clearly exceed the concentrations that would be expected for a nebular condensate and this indicates that the enrichments are due to secondary processes that occurred after CAI formation. Friedrich et al. (2005) suggested that the elemental enrichments reflect aqueous alteration processes. Aqueous alteration, however, is not expected to generate resolvable Cd isotope fractionations and is therefore inconsistent with the observation that chondrules and CAIs are isotopically light in Cd relative to the matrix and bulk carbonaceous chondrites. Important in this context is the recent finding of Luck et al. (2005), who observed that an Allende CAI also displayed a significantly lighter Zn isotope composition (about -2.7% for $\delta^{66/64}\text{Zn}$) compared to bulk carbonaceous chondrites (with $\delta^{66/64}\text{Zn} \approx +0.5$ to $+0.2$). Given that Cd and Zn have about similar chemical affinities and volatility, it is likely that the light isotope compositions of these elements have a common origin. The volatile element enrichments and fractionated Cd and Zn isotope compositions of CAIs and chondrules are not due to volatile redistribution in the Allende chondrite, because this would tend to erase the observed isotopic contrast between matrix and chondrules/CAIs. This suggests that the volatile element enrichment process predates the *final* assemblage of the Allende parent body, but postdates the initial formation of the refractory CAIs. A reasonable explanation is provided by the interaction of refractory materials with a vapor phase that features relatively high volatile contents and which is characterized by light isotope enrichments (Luck et al., 2005) due to earlier fractionation processes that involved partial evaporation. Alternatively, the isotope fractionation may have occurred during partial kinetic condensation, which can generate light isotope enrichments (Fig. 2). Possibly, interaction of refractory materials with a volatile element rich vapor could be related to the sulfidization of opaque assemblages in chondrules and CAIs that are largely restricted to the oxidized CV3 chondrites (Blum et al., 1989; Palme et al., 1994; Krot et al., 1995).

5.6. Cadmium isotope fractionation and redistribution during parent body metamorphism

Large Cd isotope fractionations were observed for chondrites that show evidence of preferential redistribution and/or depletion of Cd, whilst Zn abundances are largely unaffected. Such samples can be recognized in Fig. 6, as they plot off the trend defined by meteorites with CI-like Cd/Zn ratios. This group of samples includes primarily ordinary chondrites but also some enstatite and a few type 3 carbonaceous chondrites. The distinct behavior of Cd appears to be related to its comparatively high volatility because these meteorites feature (i) large redistributions only for the highly but not the moderately volatile elements and (ii) large isotope fractionations for Cd but no or comparatively small isotope effects for the moderately volatile elements S, K, Zn and Ag (Gao and Thiemens, 1993; Humayun and Clayton, 1995a; Luck et al., 2005; Woodland et al., 2005; Tachibana and Huss, 2005; Schönbächler et al., 2006). Luck et al. (2005), for example, observed that ordinary chondrites display Zn isotope variations of about 2‰

for $\delta^{66/64}\text{Zn}$ but the Cd isotope variability is more than one order of magnitude larger at about 23‰ for $\delta^{114/110}\text{Cd}$. Note, that roughly similar kinetic isotope fractionations can be expected for both elements because $^{114}\text{Cd}/^{110}\text{Cd}$ and $^{66}\text{Zn}/^{64}\text{Zn}$ display about the same relative mass difference.

There are several scenarios involving volatilization, which can potentially account for the fractionated Cd isotope compositions of most ordinary, and some carbonaceous and enstatite chondrites. Many scenarios, however, can be ruled out, based on constraints that are provided by the present and previously published data. Chondrule formation is unlikely to have generated the observed Cd isotope fractionations because the Cd isotope fractionation in the ordinary chondrites is clearly related to the Cd redistribution with depletions and enrichments (Fig. 6) and chondrule formation should not result in the enrichment of Cd in bulk samples. Furthermore, most chondrule and matrix separates of Bishunpur, Sarir Qattusah 001 and Semarkona have Cd isotope compositions that are nearly identical to one another and the bulk meteorites (Table 1 and Fig. 5). Chondrules are therefore not systematically heavier in Cd than the matrix and bulk samples, as would be expected for kinetic evaporation of Cd from chondrules.

Previous studies suggested that shock heating can mobilize highly volatile elements in chondrites (e.g. Lipschutz and Woolum, 1988; Friedrich et al., 2004) and such mobilization may induce Cd isotope fractionation. Most of the ordinary chondrites analyzed in this study, however, are only very weakly shocked and classified as S2 (Table 1). Up to shock stage S2, melt formation and loss of noble gases is not observed (Stöffler et al., 1991). It is therefore implausible that shock metamorphism is primarily responsible for the widespread Cd isotope fractionations that were observed in the present study. This view is further supported by the absence of Cd isotope effects for two enstatite chondrites (Indarch and the impact melt breccia Abee) that record higher shock stages of S3 and S2–4, respectively.

The observed Cd isotope fractionations are most likely tied to the processes that determined the distribution of Cd and other highly volatile elements in ordinary chondrites (Fig. 6). Two different explanations have previously been proposed for this pattern: (i) the abundances of the highly volatile elements were established by redistribution during thermal metamorphism (Dodd, 1969; McSween and Labotka, 1993; Wombacher et al., 2003); (ii) the distribution reflects heterogeneous accretion in a cooling solar nebula that underwent equilibrium condensation. The inner parts of the parent bodies accreted first whilst the nebula was still hot enough to prevent significant condensation of highly volatile elements. The interiors therefore have lower volatile element contents than the outer layers, which consist of materials for which condensation proceeded to lower ambient temperatures (Larimer and Anders, 1967; Keays et al., 1971; Larimer, 1973; Laul et al., 1973; Takahashi et al., 1978; Morgan et al., 1985). However, equilibrium condensation would not be able to generate the large observed heavy and light Cd isotope compositions. Similarly, kinetically controlled Rayleigh condensation should produce light isotope enrichments for the most

Cd-poor samples (the equilibrated ordinary chondrites) but the data presented here do not display such a distribution. This indicates that primary condensation models are inconsistent with the Cd stable isotope data.

Taken together, the available evidence thus suggests that open system thermal metamorphism is the most plausible mechanism to explain the Cd distribution and isotope fractionation observed in ordinary chondrites (Wombacher et al., 2003). This model assumes that the parent bodies initially featured approximately uniform abundances of highly volatile elements (~ 115 ppb Cd, Fig. 6b). Following accretion, the interior parts of the parent bodies heated up until Cd and other highly volatile elements were volatilized. The gaseous Cd then migrated along thermal and pressure gradients, which probably involved numerous steps of partial condensation and volatilization that were associated with concurrent isotope fractionation. Eventually, some Cd will have recondensed in the cooler unequilibrated outer parts of the parent bodies. Importantly, such processes can generate enrichments and depletions of Cd, as well as light and heavy Cd isotope compositions, without producing a stringent relationship between Cd concentration and the sign and extent of isotope fractionation.

This redistribution model for the highly volatile elements may be best envisioned with an onion shell structure, whereby the strongly metamorphosed inner parts are more depleted in highly volatile constituents, than the cooler outer sections (e.g., Trierloff et al., 2003). On the other hand, the redistribution may have been enhanced by the disintegration and reassembly of parent bodies into rubble pile structures. In this regard, (early) impacts were potentially important for the generation of pathways for the highly volatile elements and shock heating perhaps assisted in the vaporization of these elements, as was suggested for the L chondrite parent body by Friedrich et al. (2004) among others.

Wang and Lipschutz (2007) observed that high Cd contents in unequilibrated ordinary chondrites generally coincide with the presence of carbide–magnetite-assemblages, which may have formed during hydrothermal alteration (Krot et al., 1997). They suggested that Cd in ordinary chondrites is first transported by fluids generated deeper in the parent bodies and then deposited during the formation of carbide–magnetite-assemblages. Cadmium would subsequently be re-mobilized following metamorphic destruction of the carbide–magnetite-assemblages, “possibly by the process suggested by Wombacher et al. (2003)”, i.e., volatilization. Wang and Lipschutz (2007) argued that (i) Cd is the only element affected by this process, (ii) Cs and Rb are the only other elements redistributed by fluids and (iii) all other volatile element abundances in unequilibrated ordinary chondrites reflect primary nebular condensation and accretion. We concede that fluids and carbide–magnetite-assemblages may be involved in the redistribution of Rb, Cs and Cd. However, it is much more likely that volatilization was the dominant process responsible for the redistribution of all highly volatile elements and, to a smaller extent, some moderately volatile elements. This is because: (i) the highly volatile elements Cs, In, Bi, Tl and Cd display much larger abundance variations in ordin-

ary chondrites (e.g., Fig. 6; Fig. 2 in Wang and Lipschutz, 2007) than geochemically similar but less volatile elements, such as Zn, Rb and K; (ii) isotope fractionation that is indicative for partial kinetic evaporation/condensation is also observed for the moderately volatile elements Zn and Ag (Luck et al., 2005; Schönbächler et al., 2006), albeit to a much smaller extent. Clearly, comprehensive data sets for the Tl, In and perhaps Hg stable isotope compositions of (ordinary) chondrites would help to clarify this issue, but Tl and Hg are currently available only for carbonaceous chondrites (Lauretta et al., 2001; Baker et al., 2007).

The Cd isotope fractionations observed in enstatite, carbonaceous and Rumuruti chondrites may also result from elemental redistribution on meteorite parent bodies. The CO3, CV3_{red.} and EH3 chondrites display heavy Cd isotope compositions and they are commonly depleted in Cd, relative to the Zn/Cd reference line of Fig. 6. Thus the data are best explained by Cd loss through kinetic evaporation. However, it is not yet clear whether the mild thermal metamorphism that affected EH3, CO3, CV3_{red.} (McSween et al., 1988; Keil, 2000) and Rumuruti chondrites was sufficient to generate Cd volatilization. Interestingly, the unequilibrated EH3 and the strongly metamorphosed EL6 and EL7 samples display heavy Cd isotope compositions with Cd depletion, but such effects are not observed for the EH4 chondrites of intermediate type. Rubin et al. (1997) argued that the petrologic type of some EH chondrites relates to impact melting rather than thermal metamorphism and this could perhaps explain the observed discrepancy. It is possible, for example, that the EH4 meteorites experienced shock heating and fast cooling without elemental redistribution or impact melting may have sealed the pathways required for Cd loss.

The EL6 sample Hvittis and the EL7 chondrite Ilafegh 009 display heavy Cd isotope compositions and both are strongly depleted in Cd and Zn (Fig. 6b). This suggests that Zn was affected by the same process that otherwise only depletes Cd. This conclusion is supported by two previous studies. Wang and Lipschutz (2005) suggested that the loss of volatile elements, including Cd and Zn, from E5 and E6 chondrites is due to open-system thermal metamorphism and Mullane et al. (2005) reported strongly fractionated heavy Zn isotope compositions for EL6 samples, which were also thought to reflect thermal metamorphism.

The chondrite data do not show a clear correlation between Cd depletion and isotope fractionation (Fig. 9b), and this may be due to a complex interplay of evaporation, vapor transport and recondensation. Nevertheless, large heavy isotope enrichments are often coupled to strong Cd depletions, characterized by $f < 0.15$ (Fig. 9b). Such systematics are indicative of Rayleigh evaporation but the observed extent of isotope fractionation is typically only $\leq 15\%$ of that expected by calculations using $\alpha_{\text{kin-sqrm}}$ (Eq. 5). In principle, the data shown in Fig. 9b are also consistent with equilibrium isotope fractionation, but for reasons presented earlier (Section 3.3), we consider this scenario much less likely than suppressed kinetic isotope fractionation. The lack of significant equilibrium isotope fractionation is also supported by the data of Fig. 9a, if it is accepted that the Cd depletion in these samples were

generated at equilibrium conditions either by condensation or evaporation (e.g., Wai and Wasson, 1977; Humayun and Clayton, 1995a; Alexander et al., 2000; Davis and Richter, 2003). The suppression of kinetic isotope fractionation may reflect back reaction, diffusion-limited isotope fractionation, or variable depletions whereby some carrier phases lost most of their Cd, while others (e.g., large grains and refractory phases) remained essentially undisturbed. Such effects are likely to have occurred in an asteroidal body. It is noteworthy, that metamorphosed (type 4 and 5) ordinary chondrites typically display smaller Cd isotope variations than the unequilibrated type 3 ordinary chondrites (Fig. 5 and Table 1). This may reflect higher degrees of back-reaction within the less porous and hotter interior domains of the respective parent bodies.

6. SUMMARY AND CONCLUSIONS

Cadmium isotope data were acquired for a comprehensive suite of extraterrestrial materials, including chondritic meteorites, achondrites and lunar samples. A number of observations and implications follow from the results:

- None of the samples displays evidence for non-mass-dependent isotope anomalies from nucleosynthesis or nuclear-field shift effects. Isotope effects from neutron capture are common in lunar regolith samples, but absent in other extraterrestrial materials.
- The enrichment of Cd in lunar soils is thought to result from lunar volcanic activity. The heavy Cd isotope compositions of lunar soils and the trend of increasing $\delta^{114/110}\text{Cd}$ with decreasing Cd abundance can be modeled by suppressed Rayleigh evaporation due to ongoing space weathering. However, this correlation could also reflect the mixing of soil components of different provenance. We anticipate, that future systematic studies of lunar soils and pristine lunar rocks will help to better constrain lunar surface processes and the fate of volatile elements on the Moon.
- Carbonaceous chondrites of type 1 and 2, EH4 enstatite chondrites, and eucrites were found to have Cd isotope compositions identical to that of the Earth. This indicates that the portion of the solar nebula from which inner solar system bodies accreted, was initially homogeneous with respect to its Cd stable isotope composition. The CI-like Cd isotope compositions of these samples (or reservoirs), furthermore indicates that the depletion of Cd (and presumably other highly volatile elements) in the inner solar system is not due to partial kinetic evaporation or condensation. Instead, the observed depletion is most reasonably explained by either: (i) partial equilibrium evaporation or condensation or (ii) two-component mixing between an isotopically unfractionated Cd-bearing component and a refractory endmember, which is essentially devoid of Cd.
- The similar Cd isotope compositions of most carbonaceous and some enstatite chondrites, achondrites, and the Earth also suggests that partial kinetic evaporation

or condensation of highly volatile elements were not significant during collisions and the accretion and early differentiation of planetary bodies.

- Chondrule and CAI separates from the Allende chondrite have high Cd concentrations and light Cd isotope compositions. This pattern may result from the interaction of volatile element depleted refractory materials with a volatile-rich gas phase prior to the *final* assembly of the Allende parent body. The light isotope composition is either due to partial kinetic condensation or inherited from a gas phase that was generated by partial evaporation.
- For bulk chondrites, Cd isotope fractionations are essentially restricted to meteorites with non-CI like Cd/Zn ratios. This includes primarily ordinary chondrites, but also Rumuruti chondrites, some type 3 carbonaceous and most enstatite chondrites. For the ordinary chondrites and probably also for the other chondrite samples with fractionated Cd isotope compositions, the data are best explained by volatilization and redistribution of Cd and other highly volatile elements during open system thermal metamorphism on the meteorite parent bodies.

The analyses of a wide range of extraterrestrial materials show that Cd stable isotope effects due to kinetic evaporation/condensation processes are widespread. Cadmium isotope compositions can thus be applied to detect and identify kinetic evaporation/condensation processes that affected the volatile element abundances of various solar system bodies. However, the complexity of these processes render quantitative statements about volatile loss difficult.

The generally larger Cd isotope fractionations in chondrites and lunar soils compared to moderately volatile elements such as K and Zn (Humayun and Clayton, 1995a,b; Luck et al., 2005; Moynier et al., 2006) is related to the higher volatility of Cd. It is to be expected that (highly) volatile elements other than Cd will display similar stable isotope fractionations. Such fractionations could severely complicate the application of the short-lived ^{205}Pb – ^{205}Tl and ^{107}Pd – ^{107}Ag decay systems for early solar system chronometry. These difficulties arise because both daughter elements are volatile and have only two isotopes, such that stable and radiogenic isotope effects cannot be readily distinguished. Cadmium isotope data, however, may be useful to predict the occurrence of stable Tl and Ag isotope effects in particular sample types. Further improvements in analytical precision (Schmitt et al., 2006; Ripperger and Rehkämper, 2007) will also make it possible to assess with confidence, whether volatile depleted carbonaceous chondrites display slight Cd isotope fractionations as was shown for Cu and Zn (Luck et al., 2003; Luck et al., 2005), and whether small differences occur in the Cd isotope compositions of various differentiated planetary bodies.

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