Rubidium isotopes in primitive chondrites: Constraints on Earth's volatile element depletion and lead isotope evolution

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ABSTRACT

The bulk silicate Earth (BSE) shows substantial deficits in volatile elements compared to CI-chondrites and solar abundances. These deficits could be caused by pre-accretionary depletion in the solar nebula during condensation of solids, or by later heat-driven evaporation during collision of small bodies that later accreted to form the Earth. The latter is considered to result in isotope fractionation for elements with low condensation temperatures that correlates with the degree of depletion. Here, we report first high-precision isotope ratio measurements of the moderately volatile and lithophile trace element Rb. Data from seventeen chondrite meteorites show that their Rb isotope abundances are nearly indistinguishable from Earth, not deviating more than 1 per mil in their $^{87}Rb/^{85}Rb$. The almost uniform solar system Rb isotope pool suggests incomplete condensation or evaporation in a single stage is unlikely to be the cause of the volatile element deficit of the Earth. As Rb and Pb have similar condensation temperatures, we use their different degrees of depletion in the BSE to address the mechanisms and timing of terrestrial volatile depletion. The Rb isotope data are consistent with a scenario in which the volatile budget of the Earth was generated by a mixture of a highly volatile-element depleted early Proto-Earth with undepleted material in the course of terrestrial accretion. Observed Pb and Rb abundances and U–Pb and Rb–Sr isotope systematics suggest that volatile addition occurred at approximately the same time at which last core–mantle equilibration was achieved. In line with previous suggestions, this last equilibration involved a second stage of Pb (but not Rb) depletion from the BSE. The timing of this second Pb loss event can be constrained to ~110 Ma after the start of the solar system. This model supports a scenario with core storage of Pb in the aftermath of a putative Moon forming giant impact that also delivered the bulk of the volatile elements to the Earth.

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1. Introduction

The Earth has a substantial deficit in volatile elements relative to carbonaceous chondrites (e.g., Halliday, 2004; Albarède, 2009), its potential building blocks. The extent of this depletion and the processes that caused it remain elusive. Current suggestions include incomplete condensation or volatile loss from small planetesimals with negligible gravity fields during the early stages of solar system formation (e.g., Wänke and Dreibus, 1988; Wolf and Palme, 2001; Bland et al., 2005). It is also debated whether Earth is made of material with similar depletion patterns (Wood and Halliday, 2010) or if the observed element abundances are the consequence of mixing materials with different degrees of depletion (Wänke and Dreibus, 1988; O'Neill, 1991; Davis and Richter, 2003; O'Neill and Palme, 2008;

Albarède, 2009). Earth's so-called 'volatility trend' (e.g., McDonough, 2003), i.e., the semi-regular increase in BSE abundance deficit with decreasing condensation temperature (Fig. 1) is thought to reflect these primordial processes.

Deciphering the timing and nature of volatile element depletion is complicated by the combined depletion of volatile elements that also exhibit, to various extents, siderophile and/or chalcophile behaviour (e.g., Zn, Ag, Pb, Cd, In, K, Cs; Lodders, 1995; Gessmann and Wood, 2002; Murthy et al., 2003; Mills et al., 2007; Corgne et al., 2008), since only material from the silicate Earth is accessible for direct study. Part of the deficits shown in Fig. 1 could have been caused by incorporation of moderately volatile elements into the core (e.g., Lodders, 1995) or into a sulphide melt that segregated during or soon after the main stages of core segregation (Wood and Halliday, 2005). Most of the observed depletion patterns in siderophile and chalcophile elements can be reconciled with these models through high-pressure, high-temperature metal-silicate partitioning experiments (Gessmann and Wood, 2002; Murthy et al., 2003; Mills et al., 2007; Corgne et al.,
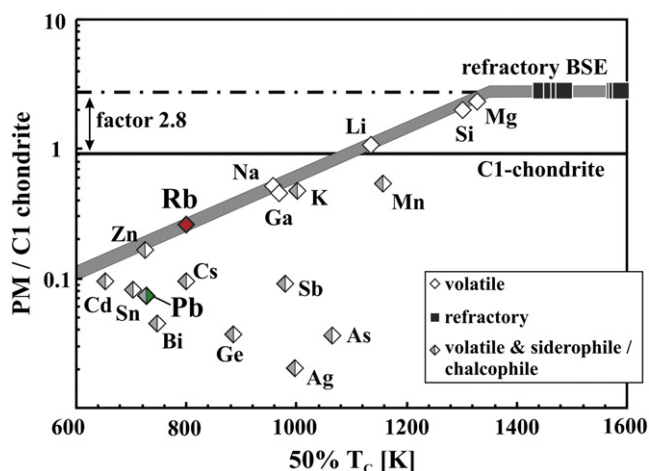
Fig. 1. Symbols show the ratio between elemental abundances in the Bulk Silicate Earth (McDonough and Sun, 1995) represented by a primitive mantle (PM) and in C1 carbonaceous chondrites (Anders and Grevesse, 1989) plotted as a function of 50% condensation temperature T_C (Lodders, 2003). The volatile elements shown are either lithophile or chalcophile/siderophile. The latter were additionally depleted by metal core formation that may have involved sulphide segregation as well. Rubidium falls on the terrestrial 'volatility trend' (grey shaded area), whereas Pb plots below it with ~75% additional depletion. The depletion in moderately volatile elements is considered to be the result of either incomplete condensation, volatile loss in the course of Earth's accretion or accretion of material that consists of a mixture of volatile-poor and C1-chondrite components.

2008), but the required conditions of metal-silicate equilibration vary significantly depending on the element(s) considered.

Two moderately volatile elements that are of particular interest with respect to the timing and degree of volatile loss are Rb and Pb, because they belong to long-lived radioactive decay systems (Rb–Sr and U–Pb) that provide key constraints on the evolution of geochemical reservoirs in the Earth and other planets (e.g., Galer and Goldstein, 1996; Allègre et al., 2001; Halliday, 2008). Compared to the abundances of highly refractory elements in primitive carbonaceous (CI) chondrites, the bulk silicate Earth (BSE) is 'missing' ~90% of Rb and ~98% of Pb (e.g., Palme and O'Neill, 2003). The Pb deficit in the BSE is of particular importance for the understanding of early Earth evolution, because measured Pb isotope compositions in terrestrial rocks through time require a massive fractionation of U from Pb and subsequent Pb removal from the BSE ~60–120 Ma after the start of the solar system (SS$_{start}$) (Allègre et al., 1995, 2001; Galer and Goldstein, 1996; Wood and Halliday, 2005; Yin and Jacobsen, 2006; Halliday, 2008). This timing coincides with the currently favoured time of a putative Moon-forming giant impact (Carlson and Lugmair, 1988; Halliday, 2008; Touboul et al., 2009) and with the I–Xe model age of the Earth (Pepin, 1997; Ozima and Podosek, 1999).

The relative importance of the processes that can be responsible for the depletion of Pb in the BSE, i.e., incomplete condensation, high-energy volatile evaporation and segregation of Pb into the Earth's core, is a matter of intense debate (Lagos et al., 2008; Wood et al., 2008; Albarède, 2009; Baker et al., 2010; Wood and Halliday, 2010). The resolution of this issue hinges on the condensation behaviour of Pb during the formation of solids in the early solar system, its ability to escape the gravitational field of early formed planetesimals during high-energy collisions and during the early stages of Earth formation, and its geochemical affinity during core–mantle segregation, which may be chalcophile (Wood and Halliday, 2005) or siderophile (Allègre et al., 1995; Wood and Halliday, 2010).

The range of acceptable models resulting from uncertainty about the timing and degree of Pb depletion by possible core segregation (e.g., Allègre et al., 1995; Albarède, 2009; Wood and Halliday, 2010) can be narrowed by the investigation of a purely lithophile element

with a similar volatility (based on 50% condensation temperatures, T_{HC}) during condensation in the early solar nebula and evaporation by impacts of small planetesimals. Rubidium is an element that due to its apparent depletion in the BSE compared to chondrites (Fig. 1), its moderately volatile nature and its importance for the Rb–Sr isotope system, is ideally suited to investigate the fate of volatile elements in the BSE. Rubidium, in contrast to Pb, is lithophile under essentially all geological conditions such that significant core storage cannot be invoked to explain the observed Rb deficit. Experiments have shown that the lighter alkali metal K may exhibit slightly chalcophile behaviour at high pressures and temperatures (Gessmann and Wood, 2002; Murthy et al., 2003). In contrast, the heavier alkali metal Cs shows much smaller affinity for metal sulphide (Mills et al., 2007). In both cases, chalcophile behaviour is not significant enough to be considered a major cause for the alkali element depletion of the Earth and the Moon (Mills et al., 2007). Alkali metal storage under highly reducing conditions in sulphide minerals such as djerfisherite or oldhamite has been reported in enstatite chondrites (e.g., Torigoye and Shima, 1993), but their modal abundance is too small to significantly affect the planetary Rb budget. As there is no evidence that Rb could be significantly siderophile or chalcophile under the pressure, temperature and oxygen fugacity conditions prevailing in Earth, it is highly suited for mass balance estimations with respect to Pb. In addition, because Rb and Pb have similar T_{HC} i.e., 800 K (Rb in feldspar) and 727 K (Pb in Fe-rich metal) (Lodders, 2003) their CI normalized abundances in the bulk Earth are expected to be very similar, making Rb a valuable tracer for Pb depletion by processes other than core formation and sulphide melt segregation.

A diagnostic test for partial evaporative volatile loss is the study of stable isotope abundances (Alexander and Wang, 2001; Davis and Richter, 2003; Alexander and Grossmann, 2005). Incomplete condensation and partial evaporation of volatile and semi-volatile elements result in isotope fractionation between isotopically light vapour and isotopically heavy residue by kinetic fractionation along with Rayleigh-type distillation (e.g., Humayun and Clayton, 1995a,b). Lead stable isotope fractionation is masked by radiogenic ingrowth from coupled U–Th decay for three out of four stable Pb isotopes, precluding studies of evaporation effects with Pb isotopes. In contrast, isotope abundances of Rb are not affected by radiogenic ingrowth and their variation thus record only fractionation effects.

Here, we apply recent analytical improvements (Nebel et al., 2005) to report the first stable Rb isotope analyses of extraterrestrial material and asses the Rb isotope compositions of a series of primitive chondritic meteorites with respect to volatile depletion. The investigated different meteorite classes show a wide range of volatile element deficits relative to CI chondrite compositions (e.g., Scott and Krot, 2003), making them particularly suitable objects for the search for isotope effects.

2. Analytical methods

Meteorite samples investigated in this study were previously analysed for their Cd isotope composition, and sample preparation procedures are reported in detail in these previous studies (Wombacher et al., 2003, 2008). High-precision Rb isotope analytical techniques were based on previously published methods (Waight et al., 2002; Nebel et al., 2005), with modifications detailed below to further increase the precision of the measurements.

Dissolved sample material was first loaded onto columns filled with strong base anion exchange resin (BioRad AG1-X8, 100–200 mesh) for the chemical separation of Cd (Wombacher et al., 2003). Under these conditions, Rb is not absorbed and is quantitatively eluted together with most of the whole rock matrix. After drying the sample, Rb was separated from the whole rock matrix using conventional cation columns (DOWEX AG 50 W–X8, 100–200 mesh) and further purified using Eichrom Sr-Spec (Nebel et al.,

2005). This ion chromatographic separation resulted in Rb samples that had insignificant amounts of Sr ($^{88}Sr/^{85}Rb = 1–4 \times 10^{-4}$, Nebel et al., 2005). To test for possible contamination during the purification procedures, pure reagents were passed through both Cd and Rb separation procedures. In all instances, the amounts of Cd and Rb were below the detection limits, i.e., <1 mV signal intensity. To exclude isotope fractionation induced by incomplete sample recovery during the chemical purification, NBS-984 Rb reference material standard solution was treated with both Cd and Rb chemical purification procedures. The eluted solution was isotopically indistinguishable from the pristine standard solution.

Isotope measurements of Rb were carried out on a Micromass Isoprobe multi-collector inductively coupled plasma mass spectrometer (MC-ICP-MS) in Münster. Rubidium isotope compositions are reported as $\delta^{87}Rb$, which is defined as the deviation from the terrestrial NBS-984 Rb standard:

$$\delta^{87}Rb = \left[\frac{^{87}Rb/^{85}Rb_{sample}}{^{87}Rb/^{85}Rb_{NBS-984}} - 1 \right] \times 10^3 \qquad (1)$$

Operating conditions of the MC-ICPMS for Rb isotope analyses were previously outlined in Nebel et al. (2005).

Isotope ratio determinations using a MC-ICP-MS are subject to large, instrumentally induced mass discrimination effects. These have to be corrected for to determine natural mass dependent fractionation. To overcome this problem, previous studies used an external normalisation procedure where the drift in mass bias is monitored using an isotope pair from a different element in a similar mass range (Longerich et al., 1987; Maréchal et al., 1999). This normalisation does not remove natural mass-dependent stable isotope fractionation effects and is therefore suitable for the investigation of stable isotope variations (e.g., Hirata, 1997; Maréchal et al., 1999; Albarède and Beard, 2004; Rehkämper et al., 2004). For Rb isotope analyses, Zr isotopes can be used to correct for instrumental Rb isotope mass bias (Waight et al., 2002). The resulting reproducibility for Zr-normalised $^{87}Rb/^{85}Rb$ on the instrument is $\pm 0.5\permil$ (2 s.d.), i.e., $\pm 0.5\ \delta^{87}Rb$ (Nebel et al., 2005). This reproducibility was determined from repeated Rb standard analyses. These repeat analyses also showed instrument-dependent drift during individual analytical sessions of ~$\pm 0.2\permil$ for the measured Rb isotope composition of the standard (see Fig. 5 in Nebel et al., 2005).

To correct for this drift, we applied additional standard-sample bracketing and combined each analysis with external Zr mass bias normalisation to fully correct for instrumental fractionation. A tracer artificially enriched in ^{87}Rb was used to determine the external reproducibility of the combined external mass bias control and standard-sample bracketing method. This tracer was mixed from pure Oak Ridge Rb spike with $\delta^{87}Rb = +126,438$ and NBS-984 with $\delta^{87}Rb = 0$. The mix-solution was designed to have $\delta^{87}Rb = +14$ (± 0.5, estimated uncertainty).

The Rb concentrations in most stony meteorites are low (~1 ppm), resulting in low signal intensities. In addition, the instrumental background on the Isoprobe instrument needs to be reduced by operating the instrument in soft extraction mode, i.e., an opposite cone charge compared to sample ions in the plasma, which results in further loss of sensitivity. The loss of intensity in soft-extraction mode provides substantial benefits by reducing the Rb and Sr backgrounds of the instrument. We performed analyses on two standard solutions with low intensities, i.e., 50 and 25 ppb, to simulate variable analytical conditions (Table 1). Repeat analyses of the isotopically enriched standard solution, analysed as unknowns between NBS-984 standards, yield a mean $\delta^{87}Rb = +14.2 \pm 0.2$ (2.s.d., Table 1). Fig. 2 shows repeat analyses of the standard from different analytical sessions. The resulting uncertainty of $\pm 0.2\ \delta^{87}Rb$ refers to the non-weighted two

Table 1

Analyses of the 87* Rb in-house standard solution, which is artificially enriched in ^{87}Rb.

mV ^{85}Rb	ppb Rb	δ87Rb	±2 s.e.
74	25	14.33	0.19
72	25	14.09	0.21
76	25	14.38	0.23
149	50	14.12	0.07
149	50	14.15	0.09
147	50	14.12	0.06
152	50	14.13	0.08
149	50	14.17	0.10
152	50	14.16	0.08
149	50	14.17	0.08
151	50	14.11	0.11
150	50	14.15	0.11
150	50	14.28	0.08
151	50	14.26	0.09
150	50	14.01	0.08
149	50	14.19	0.08
average with 2 s.d.		14.19	0.19

standard deviation, constituting a factor of 2.5 increase in precision compared to previous studies (Waight et al., 2002; Nebel et al., 2005).

Rubidium isotope ratio determinations by plasma source mass spectrometry are susceptible to isobaric, doubly charged and molecular interferences, not only on Rb but also on the Zr isotope masses used for mass bias correction (see Table 1 in Nebel et al., 2005). Care was taken to ensure that cations responsible for isobaric, doubly charged and molecular interferences on Rb and Zr were either quantitatively removed during chemical purification, or accurately corrected for Sr and Mo (Nebel et al., 2005). All Rb isotope ratios were corrected relative to both $^{92}Zr/^{90}Zr$ and $^{94}Zr/^{90}Zr$. As shown in Fig. 3, no differences outside analytical uncertainties were observed for the two correction modes, demonstrating that no residual interferences were present on Zr masses.

Matrix-related interferences and related memory effects previously reported for other isotope systems (e.g., Carlson et al., 2001; Galy et al., 2001) are more difficult to quantify. Because Rb was quantitatively and qualitatively purified from the rock matrix, no such effects should be observed. To test if pure Rb was analysed during sample measurements, raw isotope ratios from terrestrial rock samples were analysed with bracketing NBS-984 standard solutions. No convergence in the $^{87}Rb/^{85}Rb$ ratio of the standard and sample was observed, arguing against matrix effects causing potential isotope anomalies when analysing meteorites.

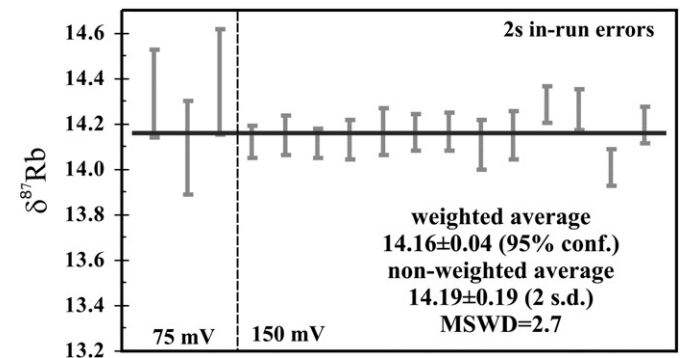**Fig. 2.** Reproducibility of an in-house standard, artificially enriched in ^{87}Rb with calculated $\delta^{87}Rb$ of $+14.0 \pm 0.5$ from a 1:50,000 dilution from the pure spike solution. The standard was analysed by standard-sample-standard bracketing to a NBS-984 solution ($\delta^{87}Rb = 0$). The weighted average yields a reproducibility of $\pm 0.2\ \delta^{87}Rb$, which is referred to as the external reproducibility in this study.
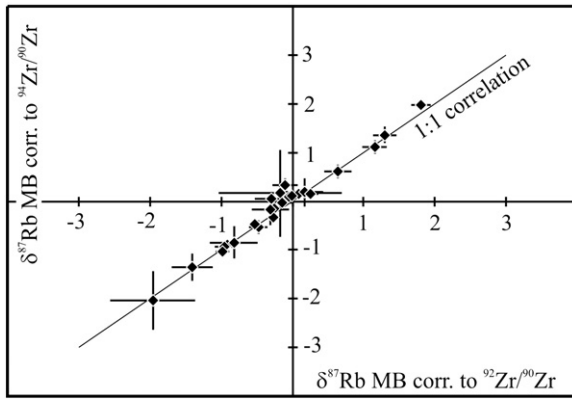
Fig. 3. Comparison between δ^{87}Rb of the analysed samples mass bias corrected to ^{94}Zr/^{90}Zr and ^{92}Zr/^{90}Zr, showing no offset between both mass bias correction methods, attesting to the robustness of the analytical method used.

3. Results

The Rb isotopes in seventeen chondritic meteorites comprising four classes of stony, primitive meteorite, i.e., carbonaceous chondrites (CC), ordinary chondrites (OC), enstatite chondrites (EC), and rumuruti chondrite (RC) were measured (Table 2, Fig. 4). The Rb isotope compositions (expressed in the delta notation (δ^{87}Rb, Eq. (1))) of the five EC and the RC are indistinguishable from the terrestrial value (δ^{87}Rb = 0) with the exception of one EC (Ilafegh 009, EL6/7), which has a δ^{87}Rb of + 1.8. The four CC show different Rb isotope compositions slightly outside the analytical precision of ± 0.2 δ^{87}Rb. Individual splits of the Allende CV3 carbonaceous chondrite show Rb isotope compositions from δ^{87}Rb = $- 0.5 \pm 0.2$ (weighted average of replicate analyses) to δ^{87}Rb = $+ 0.6 \pm 0.2$, which argues for minor heterogeneity in Rb isotopes in this meteorite. The Rb isotope compositions of metamorphosed CK4/5 chondrites (DAG 275 and DAG 412) are similar to Earth. Only DAG 005 (CO3), a chondrite with elevated chondrule content (Brearley and Jones, 1998), has a slightly heavier Rb isotope composition than the Earth.

Five out of seven OC show a slightly lighter Rb isotope composition with an average of δ^{87}Rb = $- 0.8$ compared to the bulk silicate Earth. The remaining two are indistinguishable from the terrestrial value.

Table 2
Rubidium isotope composition of chondrites.

Meteorite	Group	Class	Comment	δ^{87}Rb $\pm$ 2 s.e.
NWA-753	Rumuruti	R3.9	WR	− 0.21 ± 0.07
Abee	Enstatite	EH4		+ 0.26 ± 0.10
Ilafegh 009	Enstatite	EL 6/7	WR incl. impact melt	+ 1.80 ± 0.14
Acfer 287	Enstatite	E4	WR	− 0.27 ± 0.07
Sahara 97166	Enstatite	EH3	WR	− 0.26 ± 0.11
Replicate				− 0.14 ± 0.13
Hvittis	Enstatite	EL6	Breccia	− 0.01 ± 0.08
Homestead	Ordinary	H3	WR	− 0.99 ± 0.10
Ucera	Ordinary	H5	WR	− 0.10 ± 0.18
Dimmit	Ordinary	H3.7	Regolith breccia	− 0.05 ± 0.09
Acfer 171	Ordinary	H3.7	WR	− 0.53 ± 0.08
Gladstone	Ordinary	H6	WR	− 0.91 ± 0.10
Sarir Qattusah 001	Ordinary	H6	Matrix enriched	− 0.48 ± 0.13
Bishunpur	Ordinary	LL3	WR	− 0.96 ± 0.13
Allende	Carbonaceous	CV3	WR	− 0.30 ± 0.22
Allende	Carbonaceous	CV3	Matrix enriched	− 0.31 ± 0.26
Replicate				− 0.82 ± 0.34
Allende	Carbonaceous	CV3	Matrix enriched	+ 0.64 ± 0.19
DAG 005	Carbonaceous	CO3	~13% CAI	+ 1.36 ± 0.16
Replicate				+ 1.16 ± 0.17
DAG 275	Carbonaceous	CK4/5	WR	+ 0.17 ± 0.26
DAG 412	Carbonaceous	CK5	WR	+ 0.09 ± 0.10

Different analyses for Allende are individual sample dissolutions; analyses termed 'replicate' denote re-analyses of the same solution during a different analytical session.
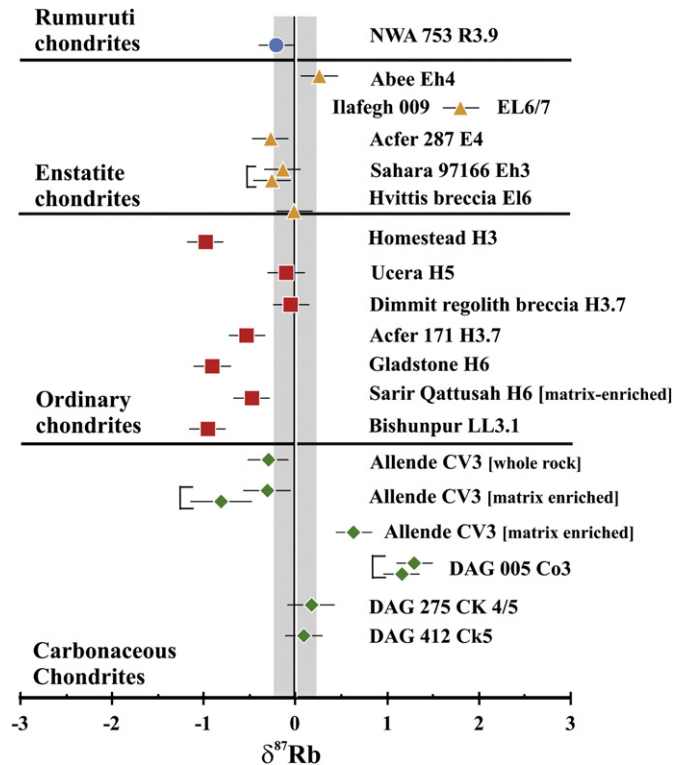

Fig. 4. Rubidium isotope compositions of primitive solar system materials, expressed in the delta notation δ^{87}Rb, which is defined as the deviation of the ^{87}Rb/^{85}Rb of a sample normalised to the terrestrial standard NBS-984 times 10,000 (Eq. 1).

There is no systematic variation of Rb isotopes with petrologic type for OC.

4. Discussion

4.1. Origin of ^{87}Rb/^{85}Rb variations in chondrites

The small variations in meteoritic Rb isotopes can potentially result from nucleosynthetic processes, resulting in mass-independent isotope variations, or isotope fractionation during volatilisation, which is a mass dependent process. Because Rb has only two isotopes, mass dependent fractionation cannot be resolved from mass-independent fractionation through measurements of Rb isotopes alone. If the isotope variations are caused by volatile loss fractionation (see also Schönbächler et al., 2010), Rb isotope variations should show a correlation with isotopic variations in other volatile elements such as Ag or Cd. All three elements are moderately volatile and thus temperature-related isotope fractionation processes would result in coupled isotope variations. Five meteorites that were analysed for their Ag isotope compositions (Ucera, Dimmit, Gladstone, Homestead, and Abee, Schönbächler et al., 2008) were also analysed for Rb isotopes here. There is no correlation of the two isotope systems in these five meteorites, suggesting there was no common depletion history. Schönbächler et al. (2008) suggested open system metamorphism as the reason for Ag isotope variations in OC. The lack of co-variation of both isotope systems for OC is consistent with a metamorphic effect on Ag isotopes, but Rb isotopes remained unaffected by such a process.

The meteorites analysed for Ag and Rb isotopes were also analysed for their Cd isotope compositions. Cadmium shows large isotopic variations in some meteorites (Wombacher et al., 2008). Some of these variations are interpreted to be related to the high volatility of Cd, whereas others seem to originate from high-temperature fractionation during metamorphism on the parent bodies. There is

no systematic correlation among the variations of Ag, Rb and Cd isotopes (Schönbächler et al., 2008). In addition to the observed differences between OC and CC in Ag isotopes (Schönbächler et al., 2008), other isotope systems including Li (Seitz et al., 2007), and Cu and Zn (Luck et al., 2005) also indicate a systematically lighter isotope composition of moderately volatile elements in OC, which is in agreement with the data for some meteorites analysed in the present study. The overall lack of systematic variation between isotope systems precludes identification of any particular processes as the single cause for the observed isotope variations.

To explain the observed variations in Rb isotopes and the absence of correlated variations with other isotope systems, we suggest that different components in meteorites such as chondrules and matrix minerals were subject to variable degrees of isotope fractionations. The mixture of these small-scale isotope variations results in different isotope compositions of elements on a whole-rock scale, depending on the proportion of variable components taken for analyses and the element distribution in these components. Recent studies of Na distribution in chondrules argue for re-precipitation of Na due to ambient gas pressure after partial volatilisation (Alexander et al., 2008). This process could explain the small variations in Rb isotope composition of on the order of 1 δ^{87}Rb unit in some ordinary chondrites relative to the terrestrial average. Moynier et al. (2010) reported small non-systematic variations in stable Sr isotopes in different meteorites. These authors attribute these isotope effects to secondary processes, not related to volatile loss, which may be the case for Rb as well. In order to understand the systematics behind these small variations, coupled future analyses of Rb and other isotope systems, such as Sr, Zn or K in single chondrules are needed to identify and possibly quantify potential volatile loss during chondrule formation.

The occurrence of pre-solar grains in some meteoritic components (i.e., CAIs or chondrules) with highly variable isotope compositions compared to those of the solar nebula (e.g., Palme, 2001) indicates the possibility of these causing the observed variations in ^{87}Rb/^{85}Rb. Pre-solar grains constitute precursor material to the birth of the solar system. In detail, formation of neutron-rich elements such as Rb are initiated in the thermal pulsing, asymptotic giant branch phase prior to the T-tauri stage of a star (García-Hernández et al., 2006). An elevated production rate of ^{87}Rb (relative to ^{85}Rb) from s-process formation (slow neutron capture) from branching ^{85}Kr may significantly be enhanced in such a proto solar disc (Beer and Macklin, 1989), strongly depending on the proto star mass. With increasing mass this results in highly variable and presumably elevated ^{87}Rb abundances (Beer and Macklin, 1989; Tomkin and Lambert, 1999; Abia et al., 2001); i.e., positive δ^{87}Rb. García-Hernández et al. (2006) suggested that prior to the T-tauri stage of the Sun, possible admixture of extra-solar material may be incorporated into CAIs, which are found in most stony meteorites. Consequently, if pre-solar grains contain variable Rb isotope abundances, bulk meteorites may be affected by mixtures of these components depending on the proportion of CAIs in bulk chondrites, and isotope variability in CAIs. There is further evidence from O, Mg, and Cr isotopes for such contributions from nearby massive stars in proximity of our proto-stellar disk (e.g., Palme, 2001; Zinner et al., 2005). García-Hernández et al. (2006) remark that 'huge' amounts of extra-solar Rb might have been transferred into our forming solar system, which would have resulted in highly spatial variations in Rb/Sr, and equivalently variable ^{87}Rb/^{85}Rb.

However, we argue here that a pre-solar grain component as a cause for the variations seen in Fig. 4 is unlikely. First, the percentage of pre-solar Rb being admixed to bulk meteorites is small and due to its volatility the abundance of Rb is low in refractory grains. Estimates of the total proportion of pre-solar grains in bulk meteorites suggest a maximum contribution of only a few ppm. The resulting effect on the Rb isotope composition of bulk meteorites is <<1 δ^{87}Rb unit if the Rb

content of presolar grains is similar to that of other meteoritic materials. However, the absolute abundance of Rb in such grains is still unknown (Witt, 2001) and pre-solar material cannot be totally excluded on the basis of this argument. However, the isotopically heavy Rb isotope composition predicted for extra-solar grains is inconsistent with the fact that the isotope composition in most meteorites analysed here is lighter than the terrestrial value. Overall this suggests negligible effects of pre-solar matter contribution.

Fig. 5 shows that the overall small Rb isotope variations in materials from the inner solar system contrast with expected isotope effects during evaporation processes. The calculated difference in the Rb isotope ratio between residue and evaporated component due to kinetic/equilibrium fractionation is up to ~12‰ (αkin = $\sqrt{m1/m2}$ = 1.01169, Nebel et al., 2005) by secondary evaporation/condensation processes (Cassen, 1996) for 90% evaporation, which would correspond to the amount of Rb observed in the Earth relative to a CI starting composition. During open-system Rayleigh-type distillation with constant removal of the evaporated gaseous phase in the course of collisional impacts, the isotope effect in the residue exceeds 30 δ^{87}Rb units after evaporation of ~90% of Rb (Fig. 5). The observed variations of the Rb isotope composition (Fig. 4) between meteorites and silicate Earth are thus at least more than one order of magnitude smaller than expected for fractionation during evaporation/condensation processes.

The BSE-like Rb isotope composition of chondrites is in general agreement with previously reported measurements from other isotope systems such as Ag (Schönbächler et al., 2008, 2010) that can be used to constrain timescales of the terrestrial volatile history. Likewise, isotopic compositions of K, which shows similar geochemical behaviour as Rb, do not show any significant variations in chondrites, the Earth and the Moon (Humayun and Clayton, 1995a). A key difference is that Rb has a T_{HC} that is ~200 K lower than that of K (Fig. 1; Lodders, 2003). Although the absolute mass difference between stable K isotopes makes this system more sensitive to fractionation from condensation and evaporation effects than Rb, the lower condensation temperature for Rb (Lodders, 2003) mostly compensates for this effect.

4.2. Linking Rb and Pb depletion in the early Earth

The very similar Rb isotope compositions of Earth and meteorites coupled with the observed Rb deficit of ~90% in the BSE relative to C1
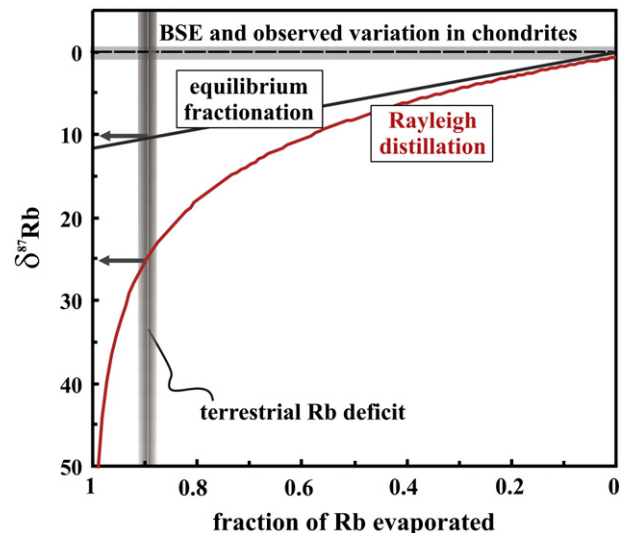

Fig. 5. Theoretical fractionation of a vapour reservoir with Rayleigh-type distillation fractionation. Equilibrium isotope fractionation is shown for comparison. The removal of Rb by Rayleigh-type distillation would result in Rb isotope compositions far exceeding measured values indicated by the grey band centred.

chondrite provide important and independent constraints on the nature of the volatile-loss process, and, because of the similar condensation/evaporation behaviour of Rb and Pb (Lodders, 2003), on the terrestrial Pb budget. The lack of pronounced Rb isotope differences between Earth and the different meteorite groups shows that a single stage incomplete condensation or volatile loss event cannot account for the volatile element deficit in the BSE as it would result in a pronounced enrichment of ^{87}Rb relative to ^{85}Rb (Fig. 5). Accretion of moderately depleted primordial material with fractionated Rb isotope compositions can therefore be excluded. In the absence of single-stage processes that involve either incomplete condensation or volatile loss as the causes for the terrestrial volatile element deficit, more complex scenarios are required to explain the Rb and Pb budgets and the Rb-isotope composition of the Earth.

One model that can account for the observed elemental and isotopic signature of Rb in the Earth is binary mixing of two dramatically different components, i.e. a strongly depleted and an undepleted component. In this model, the strongly depleted component is very poor in volatile elements including Rb. The depletion of this component may be due to incomplete condensation or early volatile depletion, and as a consequence this component would show strong enrichment of ^{87}Rb relative to ^{85}Rb (Fig. 5). A mixture of a even large amount of this strongly depleted material of extremely heavy Rb isotope composition with only a small amount of undepleted material will result in a mixture that shows elemental depletion associated with the Rb isotope composition of the undepleted end member. This model of extreme end member binary mixing is considered here as a likely scenario, because it is consistent with the observed lack of isotope fractionation coupled with strong elemental depletion. In this scenario, siderophile and chalcophile element abundances must have been affected by core formation processes in order to account for the observed BSE abundances of e.g., Au, Bi or Ag (Wood et al., 2010).

In this simple two-component mixing model, assuming a C1-chondrite concentration for the undepleted component for Rb ([Rb] ~2.32 ppm; Anders and Grevesse, 1989), the similar Rb-isotope composition of the BSE and its low Rb content (BSE$_{today}$ [Rb] ~0.6 ppm; McDonough and Sun, 1995) can be achieved with a mixture of 90% proto-Earth that was essentially fully Rb depleted ([Rb]~0) and 10% C1 meteorite material. A scenario that is consistent with this binary mixing model is the giant impact model (Hartmann and Davis, 1975; Cameron and Ward, 1976) that has been proposed for the final accretion of the Earth, final core–mantle equilibration and Moon formation (Wänke and Dreibus, 1988; Holland et al., 2009; Schönbächler et al., 2010). This model also satisfies Pd-Ag and Kr isotope systematics, which argue for a late delivery of volatiles after ^{107}Pd was essential extinct (e.g., 35 Ma after SS$_{start}$ or later (Holland et al., 2009; Schönbächler et al., 2010)) and can be consistent with the Pb systematics of the silicate Earth (Albarède, 2009).

The above simple calculations can also be used to model the Pb-content of the Earth because of the similar calculated half condensation temperatures of Rb and Pb, i.e., 727 K (Pb in Fe-rich metal) and 800 K (Rb in feldspar) (Fig. 1, Lodders, 2003). These model calculations imply that the degree of initial Pb depletion in the BSE is similar to that of Rb and thus can also be constrained to ~90% relative to CI chondrites. However, compared to the depletion expected from Rb, Pb is further depleted in the BSE by a factor of approximately four (Anders and Grevesse, 1989; McDonough and Sun, 1995), even considering uncertainties in the absolute Rb and Pb abundances in the BSE. This discrepancy requires additional Pb loss from the BSE after, or concomitant with, final accretion of the Earth. Similar discrepancy exist for numerous volatile elements with chalcophile/siderophile behaviour, including Tl, Bi, and Ag (e.g., Wood et al., 2010). This additional loss of Pb increases the U/Pb in the BSE that, on the basis of the constraints provided by the Rb abundances and isotope compositions, cannot be related to the volatility of Pb, and requires an additional process that needs to satisfy core segregation models as well as terrestrial U–Pb systematics.

4.3. Concordance of Rb–Pb systematics with the terrestrial Pb isotope evolution

The elevated and super-chondritic U/Pb observed in terrestrial rocks has traditionally been explained by Pb loss during core formation (Allègre et al., 1995; Galer and Goldstein, 1996) either by segregation of a metallic (Allègre et al., 1995; Wood and Halliday, 2010) or a sulphide melt (Wood and Halliday, 2005). Our Rb isotope data suggest that the elevated U–Pb ratio is best explained by a combination of two Pb depletion events, consistent with previous models for the Pb isotope evolution of the Earth (Galer and Goldstein, 1996). Based on Rb–Pb systematics, the timing of this second Pb-depletion event that was associated with an additional ~50–75% Pb loss can be constrained with Pb isotopes due to the coupled ^{238}U–^{235}U decay.

It has been recognised for some time that the evolution of Pb isotopes in terrestrial rocks sampled throughout Earth's history is inconsistent with the time of Earth accretion (Allègre et al., 1995; Galer and Goldstein, 1996) and subsequent rapid core–mantle equilibrium at ~30 Ma after start of the solar system (SS$_{start}$), the earliest possible time of core formation as constrained by W isotopes (Kleine et al., 2002; Schönberg et al., 2002; Yin et al., 2002). Current best estimates for the μ value (μ = ^{238}U/^{204}Pb) for the BSE range from 8 to 10 (Stacey and Kramers, 1975). To satisfy the age misfit and to model the terrestrial common Pb isotope evolution, a present day value of μ = 9.735 was suggested in a two stage model from initially μ = 7.192 until ~3.7 Ga (Stacey and Kramers, 1975).

Using the constraints derived from Rb concentrations and the Rb isotope compositions of meteorites and the BSE (this study), a model for the Pb evolution in the BSE can be derived: A mixture of 90% of strongly depleted material with a very high μ and thus negligible amounts of Pb combined with 10% of chondritic material (SS$_{start}$ μ = 0.15; Allègre et al., 1995) yields a μ = 1.6 for the initial BSE. This value must have been increased to μ~8–10 sometime later to satisfy the present-day U/Pb and Pb isotope composition of the crust and ocean floor basalts (Hofmann, 2003). This second change in U/Pb did not affect the Rb abundance of BSE, and is here referred to as the second Pb loss event (Galer and Goldstein, 1996).

The relative difference in depletion of Rb and Pb in the present-day BSE thus independently supports substantial secondary Pb loss. Using best estimates for the abundances of Rb and Pb in the BSE and the constraints on depletion obtained from Rb isotope systematics, a model for the Pb isotope evolution of the Earth can be constructed. For a μ = 8–9, a 98.00–98.25% Pb depletion of the present day BSE relative to the C1 is required, which would constrain the present-day [Pb]$_{BSE}$ to 0.200–0.175 ppm. This value is in agreement with current estimates of [Pb]$_{BSE}$ = 0.180–185 ppm (McDonough and Sun, 1995; Palme and O'Neill, 2003), fully supporting the mass balance constraints. Using these values results in a present-day Pb isotope composition of the BSE that is in full agreement with measured present-day terrestrial Pb isotope compositions (Fig. 6).

The second depletion process that is required to account for the low Pb content of BSE and the terrestrial Pb isotope composition must have occurred in the final stages of Earth accretion. Our Rb isotope data show that secondary Pb depletion cannot have occurred through volatile loss, as a volatile depletion event of the BSE would have been accompanied by significant Rb isotope fractionation. In the absence of evidence for Pb being atmophile, Pb incorporation into a hidden terrestrial reservoir is the only viable alternative. From experimental considerations this reservoir could be the iron-rich core (Wood and Halliday, 2005; Wood et al., 2008) or a segregated sulphide melt (Wood and Halliday, 2005), the latter may be supported by a lunar model for Pb storage in a sulfide reservoir (Nemchin et al., in press). Using a range of μ-values and timescales of secondary Pb depletion, a best-fit scenario is proposed here with a μ = 9, a [Pb]$_{BSE}$ = 0.175 ppm and a depletion age of ~110 Ma after SS$_{start}$ (Fig. 6). This secondary Pb

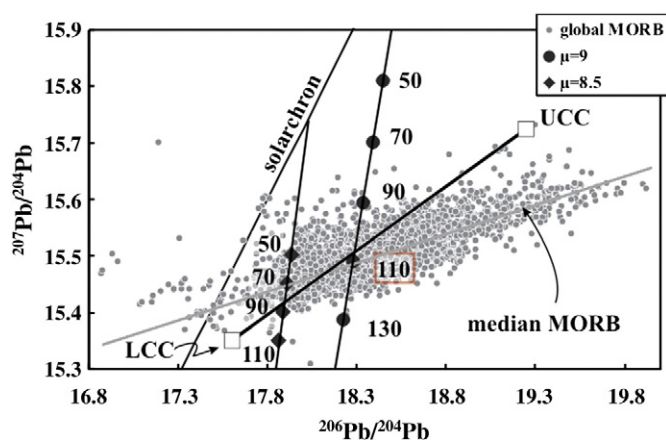**Fig. 6.** Lead isotope composition of mid ocean ridge basalts (MORB, PBDat database; http://www.petdb.org/), and upper- (UCC) and lower (LCC) continental crust (Hofmann, 2003). The line marked solarchron shows the isotope evolution of chondrites. Geochrons for a BSE with $\mu = 8.5$ (black diamonds) and $\mu = 9$ (black circles) assume a terrestrial initial of $\mu = 1.6$ (being shifted from a solar initial $\mu = 0.15$ to 1.6 by 10% addition of a C1 component to a 90% volatile-free Proto-Earth; see text for explanation) and markers indicate the time of secondary Pb loss in million years after solar system start. The timing of 10% volatile addition within ~30 million years after the start of the solar system is negligible with respect to the Pb evolution of the BSE. A present day $\mu = 9$ that was achieved at ~110 Ma after the start of the solar system shows an intercept between present-day crustal and MORB medians.

depletion event at ~4.46 Ga could be explained by removal of a sulphide melt or final core–mantle-equilibration related to a putative Moon forming giant impact (Wood and Halliday, 2005). Alternatively, it dates subsequent sulphide addition to the core with prolonged core–mantle equilibration for Pb that postdates the Moon-forming event (Wood and Halliday, 2005). Because the Pb–Pb age of the Earth broadly coincides with the terrestrial I–Xe age (Pepin, 1997; Ozima and Podosek, 1999), we favour the former model.

If the proto-Earth was extremely depleted in Pb and had a very high μ-value as suggested by the constraints from Rb concentrations and isotopes, the Earth's early evolution prior to ~4.46 Ga will not be recorded in present-day Pb isotope ratios of the BSE due to the dominance of the Pb derived from the late and undepleted component that delivered most of the volatile elements to Earth (e.g., Albarède, 2009; Holland et al., 2009).

Late delivery of volatiles to the Earth is also supported by the primitive Sr isotope composition of the Moon, which shows lower values than early solar system objects such as achondrites (Parai and Jacobsen, 2009). Because the full isotope equilibration between Earth and Moon at the time of lunar formation (Pahlevan and Stevenson, 2007) that is required to satisfy isotopic and elemental identities between Earth and Moon, it can be inferred that the early Earth had a similarly low Sr isotope composition, and with this a low Rb/Sr. Given the fact that a putative impactor constitutes only 10% of Earth's mass and that Sr is a refractory element, the Sr isotope budget of the Earth–Moon system is dominated by the proto-Earth's Sr isotope composition. Although constraints on the initial lunar Sr isotope signal are not firm enough to define the arrival of Rb to better than 50 to 110 Ma after SS_{start} (Halliday, 2008), very early delivery of Rb prior to 50 Ma after SS_{start} is unlikely, whereas volatile addition at about 110 Ma after SS_{start} is in agreement with the Rb–Pb systematics outlined above, with the terrestrial Pb isotope constraints, and with Pd–Ag isotope systematics that require volatile addition after ~35 Ma after SS_{start} (Schönbächler et al., 2010).

5. Conclusions

First high-precision Rb isotope analyses of chondritic meteorites show a uniform Rb isotope composition in most chondrites that is

similar to that of the terrestrial standard. Only few meteorites show subtle variations on the order of $\pm 1 \delta^{87}Rb$ that are interpreted here to reflect solar nebular processes. The overall absence of significant Rb isotope variations between Earth and chondrites suggests that the majority of Rb and by analogy other volatile elements that are 'missing' from the BSE were not lost during evaporation/condensation processes from the Earth but are inherited from the Earth's precursor materials.

The combination of Pb and Rb isotope compositions and concentrations in the BSE and different meteorites provides constraints on the composition of the Earth's individual building blocks and the timing of volatile accretion. The model implies accretion of compositionally very different material to form the Earth and implies strongly compositional heterogeneity in the early solar system (e.g. Wänke and Dreibus, 1988; Rubie et al., 2011). The presence of strongly volatile-depleted material as the major component of the Earth requires this material to originate from the earliest solid matter in the solar system, which formed at a time when volatile elements were not able to accrete. The Rb isotope systematics presented here are consistent with late accretion of a volatile-rich component, which either formed later in the history of the solar system or in a cooler and more volatile-rich environment.

The latter component delivered the volatile elements to the Earth and possibly also most of the hydrophile and atmophile elements (Albarède, 2009; Holland et al., 2009; Schönbächler et al., 2010) that allowed the Earth to develop into a habitable planet. This component was delivered to the Earth possibly during the Moon-forming event, which could also have triggered secondary Pb loss to the Earth's core. This scenario satisfies the similar Rb isotope signals between Earth and chondrites and is consistent with the Pb isotope evolution of the Earth.

Acknowledgements

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