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Alkali elements in the Earth's core: Evidence from enstatite meteorites

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Abstract–The abundances of alkali elements in the Earth's core are predicted by assuming that accretion of the Earth started from material similar in composition to enstatite chondrites and that enstatite achondrites (aubrites) provide a natural laboratory to study core-mantle differentiation under extremely reducing conditions. If core formation on the aubrite parent body is comparable with core formation on the early Earth, it is found that 2600 (±1000) ppm Na, 550 (±260) ppm K, 3.4 (±2.1) ppm Rb, and 0.31 (±0.24) ppm Cs can reside in the Earth's core. The alkali-element abundances are consistent with those predicted by independent estimates based on nebula condensation calculations and heat flow data.

INTRODUCTION

The observed depletion of K and other alkali elements in the Earth's mantle and crust is a classic problem in geochemistry (Urey, 1955; Hurley, 1957; Gast, 1960; Wasserburg *et al*., 1964). Figure 1 illustrates the range of alkali-element abundances in the Earth's upper mantle and crust taken from the recent compilation by Kargel and Lewis (1993), who critically evaluated a large number of geochemical analyses and terrestrial abundance estimates. The silicate Earth abundances of Li, Na, K, and Rb are all uncertain by about a factor of 1.3, while the Cs abundance is uncertain by a factor of 2. The Rb/Cs ratio (and in particular the Cs abundance) is a subject of contention (McDonough *et al.*, 1992, 1994; Jones and Drake, 1993, 1994) but even within the uncertainties of the data, the silicate Earth alkali abundances are much lower than those in chondrites. Because it is commonly believed that alkali elements only reside in silicates, consistent with their lithophile character under the current mantle oxidation state, it is also believed that the depletion of the alkali elements in the silicate portion reflects the depletion of alkali elements in the whole Earth. However, while the alkali-element abundances in chondrites reflect volatility-related fractionations (*e.g.*, Palme *et al.*, 1988), the even lower alkali-element abundances in the silicate portion of the Earth may not be due to volatility-related fractionations alone. Here we will discuss new evidence from enstatite meteorites that the Earth's core can host alkali elements, as also indicated by thermodynamic calculations and partitioning experiments (Lewis, 1971; Hall and Murthy, 1971; Jacobs, 1987 and references therein). If the core also contains alkali elements, the conclusion that the Earth's alkali element inventory is restricted to the silicate portion of the Earth and that the abundances in the silicate portion are representative for the whole Earth no longer holds.

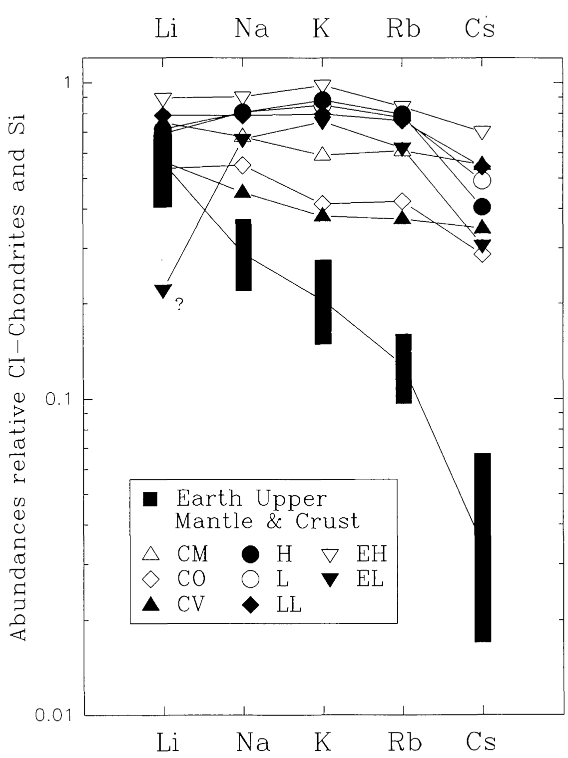

FIG. 1. Alkali-element abundances in chondrites and in the Earth's upper mantle and crust relative to CI-chondrites and Si. Alkali-element abundances in the Earth's upper mantle and crust are generally lower than in chondrites. Data sources—Earth: Compilation by Kargel and Lewis, 1993; CI-chondrites: Anders and Grevesse, 1989; EH-chondrites: see Appendix; other data: Wasson and Kallemeyn, 1988. The Li data for EL-chondrites appear to be low, but data are based on three measurements only (Nichiporuk and Moore, 1970).

ALKALI-ELEMENT FRACTIONATION DURING ACCRETION AND CORE FORMATION IN THE EARLY EARTH

We now explore the possibilities that could have led to the alkali-element depletions in the Earth's upper mantle and crust during accretion and differentiation processes in the early Earth. If we accept the concept of a chondritic Earth, there are several possibilities for the alkali-element depletions in the Earth's upper mantle and crust.

One possible mechanism of alkali-element depletion in the Earth's silicates relative to chondrites is that the Earth never accreted a full complement of moderately volatile (Na, K, Rb) or volatile elements (Cs) because condensation and accretion were proceeding simultaneously at high temperatures from the nebula gas. Thus, the inner solar nebula must have been depleted in volatile elements before temperatures dropped to allow volatile condensation to Earth. However, this is unlikely because chondrites also formed from condensates in the inner solar nebula before the Earth formed, and chondrites have *higher* alkali element/Si ratios than the Earth. Because the chondrite parent bodies are probably located in the asteroid belt, one may argue that chondrites formed in that region further away from the sun at lower temperatures allowing volatile condensation. Then chondrites may not be representative of the matter from which the Earth formed. However, formation of all chondritic matter, displaying wide ranges in oxidation states and oxygen-isotope compositions, within a narrow zone in the solar nebula is not easy to imagine.

Another more likely and generally accepted possibility is that after condensation, planetesimals formed by sampling chondritic matter in a cold environment. These planetesimals then accreted further to form the Earth and other terrestrial planets (*e.g.*, Safronov, 1969; Wetherill, 1986). It should also be mentioned that loss of volatile elements during accretion of the terrestrial planets from chondritic matter may also be unlikely because no correlation of volatile element abundances with planetary size is observed (Taylor, 1988).

We now address the question of which type of planetesimals accreted to the Earth. The different chondrites and achondrites in our meteorite collections offer a wide range in possible oxidation states and metal-sulfide contents for the accreting planetesimals. Accretion of the Earth most probably started from very reduced material to obtain enough metal for a core comprising about one-third of the Earth's mass. Among chondrites, only the enstatite chondrites represent such reduced and metal-rich solar nebula material.

The proposal that accretion of the Earth started with highly reducing material was made in the two-component accretion models by Wänke and Ringwood (for summaries, see Wänke, 1981 and Ringwood, 1984). The reduced component in these models is postulated to be devoid in elements more volatile than Na, but a highly reduced *and volatile free* meteorite class has not yet been observed. Note also that the second CI-chondrite like component, which brings volatile elements in these models, would establish CI-chondritic ratios of volatile elements in the Earth and does not lead to the observed fractionated mantle abundances. In this paper, we will assume that chondrites are representative of the nebular material accreted by the Earth rather than using postulated (unobserved) components.

In order to study alkali-element fractionation in the early Earth, we assume that the Earth mainly accreted from EH-chondrites. A natural laboratory for studying how enstatite chondrites differentiated into a mantle and core is provided by the aubrites (enstatite achondrites). We regard the aubrites as a direct analog to the mantle after core formation in the early Earth, before more oxidized material accreted and oxidized the mantle to its current state. This approach is attractive for two reasons. First, the oxygen-isotopic signature of the Earth and Moon matches well with enstatite chondrites and aubrites but not with other meteorite groups (*e.g.*, Clayton, 1993 and references therein). Second, only reducing conditions can lead to a large metallic core and can also explain the depletion of V in the Earth's mantle. Volatilization of V is unlikely because V is refractory (*e.g.*, Kornacki and Fegley, 1986), and the observed V depletion is more plausibly explained by partitioning of V into the Earth's core during early planetary differentiation (*e.g.*, Ringwood 1990, Wänke *et al.*, 1984). Experimental metal-sulfide/silicate partitioning coefficients for V (Drake *et al.*, 1989) indicate that removal into a metal-sulfide core requires oxygen fugacities appropriate to the enstatite chondrites and aubrites, which are much more reduced than the current mantle and crust.

The approach here predicts S as the major light constituent in the Earth's core, as was suggested by Murthy and Hall (1970). Among other suggested light elements in the core are Si (Ringwood, 1966; Wänke, 1981) and C (Wood, 1993). The model here also results in some minor fraction of these elements in the core, but the amount of C as graphite or cohenite (Fe_3C) in E-chondrites (~0.5 wt% C total) or the amount of Si in metal of E-chondrites or aubrites (0.06–3.5 wt%; Wasson and Wai, 1970) is insufficient to account for about 12 wt% light element in the Earth's core.

Here we will not speculate about the nature of the oxidized material accreted later or about the amount of volatile elements which were added from the oxidized component, because alkali-element removal into the core would have occurred only under highly reducing conditions.

CORE FORMATION IN THE AUBRITE PARENT BODY

To investigate alkali-element fractionation under reducing conditions, we have to know the element distributions in the highly reduced aubrite parent body (APB), which most likely differentiated from EH-chondritic material (Lodders *et al.*, 1993). The silicate portion of the APB is represented by the brecciated, magmatic aubrites, which consist mainly of Fe-free pyroxene. Other abundant minerals are plagioclase, diopside, and forsterite (*e.g.*, Watters and Prinz, 1979). The low abundances of siderophile (Ni, Co, Ir, Au) and chalcophile (Cu, Cr, Mn, V) elements in aubrites indicate that a minimum of 31 wt% FeNi metal and sulfide segregated to form a core on the APB (Lodders *et al.*, 1993). Only material like the EH-chondrites can supply enough metallic FeNi and sulfide to account for such a large core size. The maximum core size for the APB of about 38 ± 2 wt% results from the amount of Fe, Ni, and S in EH-chondrites, for which compositional ranges were compiled from literature data (see Appendix) to allow error estimates in the following calculations. The silicate portion of the APB, which is represented by aubrites, makes up about 62 wt% of the aubrite parent body.

Core formation on the APB was not able to completely remove metal and sulfide phases from the residual mantle silicates, because minor amounts of metal and sulfide (up to 0.7 and 1.1 vol%, respectively; Watters and Prinz, 1979) are now observed in aubrites. These phases may reflect the composition of segregating metal-sulfide(s). Small amounts of djerfisherite [$K_3(Cu,Na)(Fe,Ni)_{12}(S,Cl)_{14}$] and caswellsilverite ($NaCrS_2$), which are sulfides with high alkali-element contents (Table 1) are found associated with kamacite, Ti-bearing troilite, daubreelite, and

TABLE 1. Composition of Alkali-Bearing Minerals in Enstatite Meteorites.

Djerfisherite			Caswellsilverite			Roedderite	
$K_3(Cu,Na)(Fe,Ni)_{12}(S,Cl)_{14}$			$NaCrS_2$			$(Na,K)_2Mg_5Si_{12}O_{30}$	
	(1)	(2)		(1)	(2)		(1)
K	8.4±1	9.5±1	Na	15.7	15.7	Na	2.8±0.4
Na	0.9±0.4	0-0.3	Fe	0.78		K	3.1±0.6
Fe	52.3±1.9	51.3±1.3	Cr	37.3	37.4	Si	33
Ni	1.5±1	1.7±1	Mn	0.1	0.08	Al	0.22±0.02
Cu	3.3±1	0.8±0.6	Ti		0.18	Mg	11.7±0.2
S	31.3±1.5	34.6±0.8	S	46.8	46.3	Ca	0.09
Cl	1.4±0.2	1.4±0.3				Fe	1.6
Rb	0.07						

Weight percent, ± indicates 1σ range observed. Data sources: Fuchs, 1966a,b; El Goresy *et al.*, 1971, 1988; Okada and Keil, 1982; Woolum *et al.*, 1984; Rambaldi *et al.*, 1986; Lipschutz *et al.*, 1988; Lodders *et al.*, 1993. (1) EH-chondrites. (2) Aubrites.

ferromagnesian alabandite (*e.g.*, El Goresy *et al.*, 1971; Okada and Keil, 1982).

Sodium and K in aubrites are mainly present in albite-rich plagioclase. A wide range of plagioclase abundances is reported (1.3–16.2 vol%, Watters and Prinz, 1979), which is due to the heterogeneity of these brecciated rocks. In Fig. 2a, the whole-rock Na and K abundances are plotted *vs.* the bulk-Al abundances in aubrites. Measured bulk-abundances of Al, Na, and K range from 0.14 to 1.4 wt%, 250 to 9900 ppm, and 50 to 1500 ppm, respectively (see Fig. 2 for references), and therefore representative Na and K abundances for the silicate portion of the APB (*i.e.*, the aubrites) are difficult to obtain.

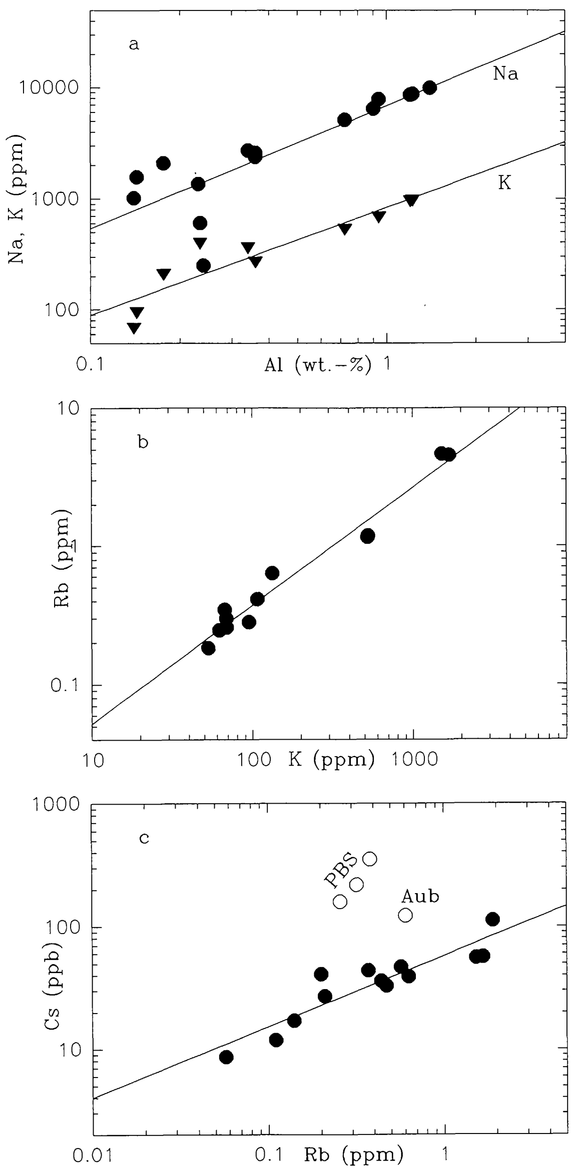

FIG. 2. Element correlations in aubrites from literature data are used to derive a representative bulk composition for the silicate portion in the APB (a) Na/Al, K/Al, (b) Rb/K, and (c) Cs/Rb. Only data pairs analyzed in the same sample are considered. Uncertainties in the alkali-element abundances obtained from these correlations are indicated in Table 2. Cesium abundances in the Pena Blanca Spring aubrite (PBS) and in one sample from Aubres (Aub) are higher than found otherwise in aubrites (indicating probable contamination) and were not considered. Data sources: (a) Easton, 1985; Schmitt *et al.*, 1972; (b) Bogard *et al.*, 1967; Minster and Allegre, 1976; Minster *et al.*, 1979; (c) Biswas *et al.*, 1980; Wolf *et al.*, 1983.

However, the APB is close in composition to EH-chondrites and has an EH-chondritic inventory of refractory elements such as Al. Aluminum is only contained in the silicate portion of the APB because it does not partition into the metal-sulfide core. We can calculate the Al abundance in the silicate portion from the mass balance equation:

$$C_{tot} = C_{aubrites} \, X_{silicate} \qquad \text{Equ. (1)}$$

where C_{tot} = 0.82% is the bulk abundance of Al in EH-chondrites, $C_{aubrites}$ is the abundance of Al in the silicate portion of the APB, which is represented by the aubrites, and $X_{silicate}$ = 0.618 is the silicate weight fraction of the aubrite parent body.

Equation (1) gives a value of 1.33 wt% Al for the silicate portion of the APB. From the correlation of Na and K with Al in aubrites, Na and K abundances of 9800 ppm Na and 1030 ppm K are calculated for the silicate portion (Fig. 2a, Table 2). If no other K- and Na-bearing minerals were present the total APB (aubrites + core) would have bulk abundances of 6060 ppm Na and 640 ppm K. However, the APB should have an EH-chondritic inventory of 7050 ppm Na and 850 ppm K. About 1000 ppm Na and 200 ppm K are apparently missing in this mass balance for the entire APB (Table 2, last column). Similar calculations were made for Rb and Cs. Representative Rb and Cs abundances for the silicate portion of the APB were obtained from K/Rb and Rb/Cs analyses from aubrites (Fig. 2b,c). In all cases, only data pairs obtained from analyses of the same sample are plotted to avoid sampling errors. The resulting abundances are 2.9 ± 1.1 ppm (Rb) and 0.15 ± 0.10 ppm (Cs). The Cs abundance in aubrites can also be calculated from the Cs/U correlation given by Wolf *et al.* (1983). The abundance of refractory U in the silicate portion is calculated as 0.015 (±0.002) ppm using Equ. (1) and Cs is calculated from the Cs/U correlation as 0.14 ± 0.1 ppm, in agreement with the value obtained from the Rb/Cs correlation. However, more analyses of Rb, Cs, and U from aubrites are required to improve the correlations. The Rb and Cs abundances for the entire APB given in Table 2, column (3), were calculated assuming that Rb and Cs are only sited in the silicate portion (the aubrites). We find that the resulting values are lower than expected for an APB made out of EH-chondrites (Table 2, column (1)).

TABLE 2. Alkali Element, U, and Al Abundances (ppm) in EH-Chondrites, Aubrites, and the Aubrite Parent Body (APB).

	EH-Chondrites source material for APB[a]	Concentration in Aubrites [b]	Amount in entire APB supplied by silicates [c]	Amount in APB not accounted for [d]
	(1)	(2)	(3)	(4)
Al	8200±200	13300±500	8200±200	0
U	0.009±0.001	0.015±0.002	0.009±0.001	0
Na	7050±60	9800±500	6060±370	990±380
K	850±60	1030±120	640±80	210±100
Rb	3.1±0.4	2.9±1.1	1.8±0.7	1.3±0.8
Cs	0.21±0.06	0.15±0.10	0.09±0.06	0.12±0.09

For detailed explanation see text. (a) see appendix. (b) from element correlations. (c) calculated from column (2) x (0.618±0.02). (d) calculated from column (1)-(3).

There are three possibilities to explain the missing alkali-element inventory in the aubrite parent body. First, Na and K could have been lost by *volatilization* during accretion and differentiation of the APB. However, as discussed above, it is unlikely that volatile loss occurred from very reduced planetesimals. In addition, enstatite chondrites are enriched in volatile elements such as Na, K, Au. The CI normalized ratios of Na/Si = 0.90 and K/Si = 0.98 in EH chondrites indicate no significant alkali element fractionation by volatilization or incomplete condensation. The relative abundances of Na and K in aubrites (Na/Al = 0.74, K/Al = 0.077) are also higher than in CI-chondrites (Na/Al = 0.58, K/Al = 0.064).

The second possibility is that other Na and K host phases could be present in the *silicate* portion. This is unlikely because the good Na/Al and K/Al correlations in aubrites indicate that Na and K are dominantly sited in plagioclase. The only other possible silicate host mineral is roedderite [$(Na,K)_2Mg_5Si_{12}O_{30}$, Table 1). However, in order to account for the missing Na, about 3.3 wt% roedderite has to be present in aubrites and to explain the missing K about 0.8 wt% of roedderite is necessary. If both Na and K were in this mineral, the mass balance calculation should give the same amount of roedderite present, which is not the case. In addition, only trace amounts ($\leq$0.1%) of roedderite have been reported in EH-chondrites (Fuchs, 1966b), which are far below the amounts required to account for the missing Na and K.

Finally, the third possibility is that Na and K were lost as *sulfide minerals*, which were extracted to the core. This alternative is supported by the occurrence of two accessory sulfide minerals, djerfisherite and caswellsilverite (Table 1) and their unusually high concentrations of K and Na (about 10% and 16%, respectively). The removal of K into the core by djerfisherite was previously suggested by Lewis (1971) and the discovery of caswellsilverite by Okada and Keil (1982) gives us a sulfide phase that can transport Na into the APB core. Djerfisherite in aubrites contains ~1% more K than djerfisherite in EH-chondrites, which may suggest that djerfisherite gains K during magmatic processing. Note, that even if we assume some volatilization loss on the APB, the extraction of alkali elements into the core is a very likely competing reaction. This is comparable to the retention mechanism of S, which is cosmochemically more volatile than Na or K but is retained in FeS.

The concentration of alkali elements in the core (last column in Table 3) was calculated by dividing the amount of alkali elements missing in the entire APB (last column in Table 2) by the weight fraction of the APB core:

$$C_{core} = C_{missing} / 0.382 \qquad \text{Equ. (2)}$$

To calculate the amount of djerfisherite or caswellsilverite required on the entire APB to extract the missing amounts of alkali elements into the core, we use the general mass balance equation:

$$C_{tot} = C_{aubrites}\, X_{silicates} + C_{djer.\ or\ casw.}\, X_{djer.\ or\ casw.} \qquad \text{Equ. (3)}$$

where C_{tot} is the concentration in EH-chondrites (assumed to represent the composition of the APB), $C_{aubrites}$ is the concentration in the silicate portion of the APB (aubrites), $X_{silicate} = 0.618$ is the silicate weight fraction of the APB, $C_{djer.\ or\ casw.}$ is the concentration in djerfisherite or caswellsilverite, and $X_{djer.\ or\ casw.}$ is the unknown weight fraction of mineral phase in the APB. The results for these calculations are shown in Table 3.

The amount of missing K and Na correspond to the removal of 0.22 wt% djerfisherite and 0.63 wt% caswellsilverite, respectively.

TABLE 3. Calculation of the Weight Fractions of Djerfisherite and Caswellsilverite removed on the APB.

	C_{APB} [a]	$C_{sil.}$ [b]	$C_{djer.\ or\ casw.}$ [c]	$X_{djer.\ or\ casw.}$ [d]	C_{core}
Na(casw.)	7050±60	9800±500	15.7±1.0	0.0063±0.0025	2590±1000
K (djer.)	850±60	1030±120	9.5±1.0	0.0022±0.0011	550±260
Rb (djer.)	3.1±0.4	2.9±1.1	660	0.0020	3.4±2.1
Cs	0.21±0.06	0.15±0.10	?	?	0.31±0.24

(a) APB = EH-chondritic. (b) Concentration (ppm) in silicate fraction of APB as dervied from aubrite composition. (c) Concentration (Na, K wt.-%, Rb ppm) in djerfisherite or caswellsilverite. (d) Weight fraction (X_i) of djerfisherite or caswellsilverite in the whole APB: $X_i=(C_{APB} - C_{sil.}\cdot 0.618)/ C_{djer.\ or\ casw.}$ (e) Concentration (ppm) in core of APB: $C_{core}= (C_{APB} - C_{sil.}\cdot 0.618)/0.382$.

Because traces of these minerals are found in aubrites as solidified products of relict sulfide melt and the fraction of each mineral required to remove the missing alkali elements into the core is fairly low, it is plausible to assume that the core of the APB is the host for the missing Na and K. The core of the APB then contains about 2600 ppm Na, 550 ppm K, and 4 ppm Rb (corresponding to ~1% each of djerfisherite and caswellsilverite in the core). No analytical data are available for Cs abundances in the sulfide minerals. However, it seems likely that Cs is sited together with Rb and also migrated into the core.

ALKALI-ELEMENT TRANSPORT INTO THE CORE OF THE EARLY REDUCED EARTH

As discussed earlier, the Earth may have started accreting from planetesimals similar in composition to EH chondrites. Therefore, fractionation processes comparable to those on the aubrite parent body may have occurred on the early, reduced Earth. We assume that alkali-element partitioning during core formation on the APB is analogous to that on the early Earth. As a consequence, the Earth's core could contain similar amounts of alkali elements as calculated for the core in the APB.

One could argue that a comparison between the presumably small APB and the growing Earth does not hold once the Earth got larger than asteroid-sized bodies because then increasing temperature and pressure conditions on the Earth could have altered element distributions. However, as discussed below, there are no very compelling arguments that alkali-element (or other element) partitioning took place under substantially different circumstances on the APB than on the early reduced Earth.

Stevenson (1981) pointed out that element distributions between silicates and metal-sulfide were most likely established by chemical equilibrium under low pressures. In the top layer of any differentiating planetary body, the dispersed metal/sulfide from an incoming undifferentiated planetesimal would have equilibrated with the surrounding silicate melt, until the metal-sulfide melt accumulated to blobs massive enough to sink to the core. Because the pressure regime in the top layers is independent of total planetary size, metal-sulfide/silicate equilibrium in the top portions of the Earth would result in element distributions indistinguishable from those in smaller differentiated meteorite parent bodies established under the same redox conditions and temperatures.

Differences in the element distributions between metal-sulfides and silicates in the small APB and the growing Earth may have occurred if metal-sulfide/silicate equilibrium proceeded into lower portions of the Earth where higher pressures and temperatures may affect the partitioning. This process depends on the size of the metal-sulfide blobs formed in the top layers and their sedimentation velocity to the core. However, large changes in elemental distributions are unlikely because large scale metal-sulfide/silicate equilibration competed with rapid sinking of the metal-sulfide blobs towards the core (Stevenson, 1981). In addition, gravitational and impact heating of the growing Earth would have generated much higher temperatures in the Earth's interior than in a small meteorite parent body, so that the Earth's mantle silicate melt was less viscous, thereby facilitating the sinking of metal-sulfide melts to the core. Therefore, we suggest that the distribution of the alkali elements between metal-sulfide and silicates was predominately established at low pressures and was not significantly altered during metal-sulfide migration to the core.

However, none of the current accretion models can definitively exclude that some metal-sulfide/silicate equilibration occurred under elevated pressure and temperature conditions. In that case, we have to ask if alkali partitioning between sulfide phases and silicate was altered. Imagine the fate of a metal-sulfide phase that had already gained alkali elements by equilibration with silicates in the top layers of the planetary body. During migration toward the core, the metal-sulfide phase progressively experienced higher temperature and pressure conditions and alkali elements in the metal-sulfide either (a) stayed, (b) partitioned out of the metal-sulfide into the surrounding silicate, or (c), more alkali elements from the silicate partitioned into the metal sulfide. Cases (a) and (c) are most probable because the terrestrial djerfisherite occurrences in diamond (Bulanova *et al.*, 1980) indicate that a higher pressure regime allows alkali partitioning into sulfides. In addition, the high-pressure partitioning data for K obtained at 4–6 GPa and T = 1525–2585 °C by Ohtani *et al.* (1992) show that partition coefficients for K between Fe-sulfide and silicate liquid are higher than those obtained at lower pressures. Thus, there is no evidence that equilibration of metal-sulfides and silicates under high pressures in the Earth would significantly decrease the K partitioning into the core (see more discussion below).

Two component models (Ringwood, 1984; Wänke, 1981) postulated that after about two-thirds of the present Earth's mass accreted, more oxidized matter was supplied to the Earth and oxidized the mantle to its current state. In principle, progressive extraction of alkali elements from a further accreting, more oxidized mantle could have increased the abundances of alkali elements in the Earth's core as long as the overall oxidation state allowed metal-sulfide and djerfisherite to form and segregate. In fact, the stability of djerfisherite under slightly more oxidizing conditions is indicated by its terrestrial occurrence in ores, alkalic and kimberlitic rocks, and in diamond (*e.g.*, Gorbachev and Nekrasov, 1980; Bulanova *et al.*, 1980) and its occurrence in the Toluca iron meteorite (El Goresy *et al.*, 1971). Bunch *et al.* (1970) note that the minor-element distributions in silicate inclusions from the Toluca (and other IAB iron meteorites) are similar to those reported for ultramafic inclusions in basaltic rocks and kimberlites, and thus it is plausible to assume that the terrestrial and iron meteoritic djerfisherite formed under similar conditions. The FeO content (expressed as FeO/(MgO+FeO)) of ferromagnesian silicates in the silicate inclusions is 3–7 mol% (Bunch *et al.*, 1970), indicating that the oxidation state, which allows djerfisherite to form in these environments, is between that of enstatite chondrites (~0.05 mol%) and ordinary (H)-chondrites (~17 mol%).

However, modeling how the alkali-element inventory in the silicate portion in the Earth was established during the continuing accretion of more oxidized matter is more difficult. After core formation, the mantle of the reduced early Earth would have an aubritic alkali-element inventory. From Table 2 (column 2) and Table 4, we can see that terrestrial mantle abundances are much lower than aubritic abundances. Because continuing accretion of a more oxidized component is likely to add even more alkali elements to the Earth's mantle, severe loss of alkali elements from the silicate portion of the Earth must have occurred to establish the currently observed abundances. As mentioned above, some removal of alkali elements by sulfide segregation under more oxidizing conditions may have occurred but this cannot account for a massive depletion. The loss most likely occurred during the (hypothesized) giant impact which vaporized some of the Earth's silicates and led to the formation of the Moon by recondensation of evaporated terrestrial silicates and impactor material. Lunar Na/Si and K/Si ratios are about 4x lower than those in the present terrestrial mantle and crust, indicating that moderately volatile elements must have been lost from the Earth-Moon system. The silicates recondensing to the Earth probably were also depleted in alkali elements. Relative to the amount of alkali-elements removed into the core prior to the impact, the vaporization process removed a substantially larger fraction of alkali elements from the terrestrial silicates and, as a consequence, the present abundance pattern in the Earth's mantle and crust is dominated by this process. This could explain the trend of observed alkali-element depletion as a function of volatility (*i.e.*, highly volatile Cs is more depleted than less volatile Na). More detailed modeling of how the chemistry of the Earth's silicates was altered by the impact process is required. However, we argue here that this impact process does not rule out that some fraction of the alkali elements can reside in the Earth's core.

Because the Moon lacks a large core, core formation in the Earth was basically complete, and the alkali-element abundances in the Earth's core were established prior to the impact. Although the high temperatures generated from the impact (*e.g.*, Benz and Cameron, 1990) could have led to large scale re-equilibration of the core with the mantle, the siderophile-element abundances in the

TABLE 4. Alkali Element Abundances in the Earth's Mantle, Core and Whole Earth and Comparison with Chondrite Data.

	Na	K	Rb	Cs	Ref.
	ppm				
Earth Mantle	2932	232	0.6	0.013	[1]
range[a]	2330-3640	175-300	0.48-0.73	0.007-0.025	[1]
Earth Core	2590±1000	550±260	3.4±2.1	0.31±0.24	[2]
Earth Core	1400 ?	210 ?	1.1 ?	0.14 ?	[1]
Bulk Earth	2820	340	1.5	0.11	[2]
Bulk Earth	2450	225	0.76	0.055	[1]
CI-Chondrites	5000	558	2.3	0.187	[3]
Ordinary Chondrites	6400-7000	780-825	2.9 - 3.1	0.12 - 0.18	[4]
EH-Chondrites	7050±610	850±60	3.1±0.4	0.21±0.6	[5]

a: Range from uncertainty factor given by [1].
[1] Kargel and Lewis, 1993; [2] This work; [3] Anders and Grevesse, 1989; [4] Wasson & Kallemeyn, 1988; [5] see appendix.

mantle argue against this process. Newsom (1990) reviewed low-pressure partition coefficients between metal-sulfide and silicate and concluded that they cannot be used to successfully model the siderophile-element abundances in the Earth's mantle by core mantle equilibrium (*e.g.*, the chondritic Co/Ni ratio in the mantle is not explained). With respect to core–mantle equilibrium, high-pressure partition coefficients are more applicable. However, even the metal/silicate partition coefficients obtained under the highest pressure conditions investigated so far (25–27 GPa, 2000 K, Ohtani *et al.*, 1992) rule out core–mantle equilibrium. Other studies at 10 GPa pressures (Walker *et al.*, 1993; Hillgren *et al.*, 1994) also reach that conclusion. However, the inconsistent partition coefficients from these experiments (*e.g.*, Au, which is highly siderophile, displays lower metal/silicate partitioning coefficients than Ni, which is moderately siderophile) strongly suggest that the experimental charges are non-equilibrium assemblages. Here we conclude that once the alkali elements were extracted into the core, no re-partitioning into the mantle occurred (see also discussion below).

ALKALI-ELEMENT DISTRIBUTION IN THE EARTH AND COMPARISON WITH OTHER DATA

Combining our alkali-element abundances derived for the Earth's core with alkali-element abundances for the Earth's upper mantle and crust, which are assumed to be representative for the entire silicate portion of the Earth (Kargel and Lewis, 1993 and references therein), allows us to calculate the alkali-element abundances in the whole Earth using a mass balance equation similar to Equ. (3). The abundances for the mantle, core, and bulk Earth are shown in Table 4 and are compared to chondrite meteorite abundances. About 30% (Na), 52% (K), 74% (Rb) and 92% (Cs) of the Earth's alkali elements are located in the core. The derived Na and K data for the bulk Earth are 40–60% lower than those expected from other chondritic Earth models (*e.g.*, Hall and Murthy, 1971; Lewis, 1971), which imply that about 1800 ppm K are in the core (75% of the K in ordinary chondrites), and the model here results in about 550 ppm.

The calculated amount of K in the core (52% of total) is much higher than the 1–2% of total K in the Earth calculated from partitioning experiments. Jacobs (1987) reviewed several Fe-sulfide/silicate partition studies which addressed the possibility of K partitioning into the core. In all experiments, the major fraction of K remained in the silicate phase, and the consensus of all partitioning studies is that only 1–2 % of the Earth's total K can reside in the Earth's core. However, the experimental results are not directly applicable to core formation because the experimental conditions (oxidation state, sulfide and silicate composition) might not be relevant to core formation. All the experiments show that a pure Fe-sulfide melt is incapable of extracting alkali elements efficiently. However, it is known from industrial smelting processes that Cu- and Cl-bearing melts lead to the formation of djerfisherite (*e.g.*, Riley, 1978). The partitioning of alkali elements between a silicate and a Cu- and Cl-bearing Fe-sulfide melt under conditions relevant for core formation has not yet been investigated experimentally. It is very important to consider the presence of Cu and Cl for K sulfide/silicate partitioning experiments. At oxygen fugacities below or around the Fe-wüstite buffer, the chalcophilic and siderophilic Cu will be efficiently removed into Fe metal and sulfide. The Cu/K and Cl/K weight ratios in djerfisherite from enstatite meteorites are about 0.005 to 0.13 and 0.1 to 0.2, respectively, and chondritic Cu/K and Cl/K ratios range from 0.1 to 0.23 and 0.09 to 1.26. This shows that in principle sufficient amounts of Cu and Cl are present to remove K as djerfisherite and that sulfide/silicate partition studies should include Cu and Cl. From other partitioning studies, it is known that trace amounts (>0.5% or more) of P, C, or S can alter the partitioning of siderophile and chalcophile elements between metal-sulfide and silicate under otherwise constant conditions (*e.g.*, Willis and Goldstein, 1982; Jones and Malvin, 1990). However, the amounts of Cu, Cl, and Cr, which could enter a Fe-S melt during enstatite chondrite differentiation, are relatively low (< 0.1%) and may not alter the partitioning of K between Fe-S and silicates in a strong fashion. On the other hand, it may not be the case that K_2S or Na_2S are dissolving in an Fe-S melt but that djerfisherite and caswellsilverite form independently from an Fe-S melt and then dissolve in Fe-S at higher temperatures. The fact that both minerals are always associated with FeS in E-chondrites and aubrites indicates that mineral solid solution may take place. Fuchs (1966a) suggested that the troilite inclusions in djerfisherite may indicate solid solubility of FeS at higher temperatures. In addition, caswellsilverite often occurs as exsolution lamellae in troilite, also indicating a high-temperature solid solution of these two minerals.

It has been argued that partitioning data obtained at low (*i.e.*, 1 bar) total pressure may be irrelevant to the question of K (and by analogy for the other alkali elements too), in the core (*e.g.*, Bukowinski, 1976; Liu, 1986). Theoretical studies (*e.g.*, Bukowinski, 1976; Liu, 1986) and recent liquid metal/microcline melt partition experiments at 2600 °C and 26 GPa by Ito *et al.* (1993) show that K becomes siderophile at high pressures and that small amounts (5 ppm) of K could be present in the core, but these experiments do not include a S-bearing phase. The high-pressure partitioning of K into Fe sulfide was investigated by Somerville and Ahrens (1980), who concluded that a large fraction of K in the core cannot be ruled out absolutely. As mentioned above, Ohtani *et al.* (1992) performed partition experiments between metal-sulfide and silicate at 4–6 GPa up to 2585 °C for several elements and found partition coefficients for K about a magnitude higher under these conditions than those obtained at lower pressures. One could expect that sulfide/silicate partition coefficients for K even increase if more reducing conditions and Cu and Cl are present.

However, it is necessary to emphasize that removal of K into the core does not require high-pressure conditions because it has apparently occurred on the low-pressure APB. As discussed above, we expect chemical equilibrium between silicates and metal-sulfide at low pressures in the upper regions of the planet and fast subsequent metal-sulfide segregation to be primarily responsible for removal of the alkali elements into the core.

Therefore, the argument by Liu (1986) that the depletion of K in the terrestrial planets should be a function of planetary size is flawed. He argues that Mars, which shows similar K depletions (relative to U) as the Earth and Venus, does not have a high enough internal pressure to allow K to become siderophile and be partitioned into the Martian core. Liu (1986) thus concludes that removal of K into the core cannot be the reason for the low K/U ratios exhibited by Venus, Earth, and Mars. Pressure effects are only relevant if we consider present-day partitioning into the core, but even in this case the experimental data of Ohtani *et al.* (1992) indicate that additional extraction of K from the lower mantle into the core may take place. Although K becomes siderophile under high pressures, we argued above that the extraction of chalcophile K under reducing conditions is more effective and independent of the (final) planetary size.

No comparison of calculated values with partition coefficients can be made for the other alkali elements, because no data are available for Rb or Cs. The limited data on Na sulfide/silicate partitioning result in values similar to those obtained for K (Lodders and Palme, 1991) and indicate no significant Na partitioning into "pure" Fe-sulfide melts. However, the relict caswellsilverite in aubrites shows that Cr sulfides are important for Na extraction. Thus, it is necessary to perform more Na partitioning experiments in the Na-Cr-Fe-S-silicate system in order to model Na loss during core formation.

Our predictions are consistent with alkali-element abundances derived by Kargel and Lewis (1993), who used a completely different approach to calculate the bulk composition of the Earth. They derived the bulk-elemental abundances from condensation calculations establishing a volatility trend for the Earth and then compared the predicted bulk-elemental abundances with observed abundances in the silicate portion of the Earth. The difference between abundances in the whole Earth and the silicate portion was assigned to the core. For comparison, their data are also shown in Table 4. The values obtained in this study are about 1.5–3x higher than the nominal core values from Kargel and Lewis; however, within the given uncertainties both studies are consistent.

Because djerfisherite also contains significant amounts of Cl, we can calculate that the core could contain about 80 ppm Cl, which is about 4% of the bulk EH-chondritic Cl inventory. Woolum *et al.* (1984) report 170 ppm Br in djerfisherite; therefore extraction of 0.22 wt% djerfisherite into the core would have led to about 1 ppm Br in the core (13% of bulk EH- chondritic abundance). Nominal Cl and Br abundances in the Earth's core were also calculated by Kargel and Lewis (1993). While their Cl abundance of 737 ppm is about a factor of 10 higher than the value derived here, their Br abundance of 0.35 ppm is relatively close to the 1 ppm determined here. However, given the uncertainties in the halogen abundance data for the Earth's mantle and crust (uncertainties of factors of 2.4 and 2, respectively, for Cl and Br; Kargel and Lewis, 1993) and the uncertainties in the condensation temperatures of halogens, little emphasis should be given to the estimated abundances of halogens in the core and more work needs to be done to resolve this issue.

Our calculated K abundance in the core can also be compared to the abundance obtained from heat flow data. Recently, Breuer and Spohn (1993, and references therein) calculated that the present day heat flow of $4.3 \cdot 10^{13}$ W can be matched if 20 ppb U are in the mantle and crust and about 400–800 ppm K are located in the core. If no K is assumed to be in the core, about 26 ppb U would be necessary, which is the upper limit for currently accepted abundances in the mantle and crust. Breuer and Spohn also discuss that other heat sources do not contribute significantly to the present-day heat flow. The 400–800 ppm K in the core required for the explanation of the heat flow agree well with the 550 ± 250 ppm K for the core determined here.

CONCLUSIONS AND OUTLOOK

We derived the abundances of alkali elements in the Earth's core by using the core–mantle differentiation process in enstatite meteorites as an analog to core formation for the reduced early Earth. The core abundances of 2590 ppm (Na), 550 ppm (K), 3.4 ppm (Rb) and 0.31 ppm (Cs) compare well to abundances derived by other independent methods.

More trace-element data on aubritic minerals could refine the calculations and help to understand fractionation processes of other elements (*e.g.*, Rb, Cs, halogens). Better designed partitioning experiments under conditions more relevant to core formation on the early Earth would be helpful to test the hypothesis made here. In particular, it is important to study Na, Rb and Cs sulfide/silicate partitioning under conditions as reducing as those observed in the enstatite meteorites and as those postulated for the early Earth.

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APPENDIX

Table A1. Selected Elemental Abundances in EH-Chondrites[a].

Meteorite	Type	Li ppm	#[b]	Na ppm	#	K ppm	#	Rb ppm	#	Cs ppb	#	U ppb	#
Parsa	EH3	-		6660±420	5	850±170	4	-		-		-	
Qingzhen	EH3	-		6260±810	7	620±250	6	-		-		-	
Abee	EH4	2.0±0.8	4	7890±980	4	870±110	5	3.32±0.8	7	250±20	6	9.1±0.3	3
Adhi Kot	EH4	-		7300	1	910±140	2	2.74±1.0	4	130±30	2	10	1
Indarch	EH4	1.8	1	7490±590	7	880±45	9	3.48±0.5	7	240	1	9.9±1.4	3
St. Mark's	EH5	0.81	1	6400±550	4	730±50	8	0.88±0.2	7	35	1	8.0±0.8	5
St. Sauveur	EH5	-		7350±640	2	885±15	3	2.74±0.8	3	230±20	2	7.8±0.3	2
TOTAL[c]		1.9±0.1[e]	2	7050±610	7	850±60	6[d]	3.07±0.40	4[e]	210±60	4[e]	9.0±1.0	5
Meteorite	**Type**	**Al wt.-%**	**#**	**Si wt.-%**	**#**	**Mg wt.-%**	**#**	**Fe wt.-%**	**#**	**Ni wt.-%**	**#**	**S wt.-%**	**#**
Parsa	EH3	0.83±0.07	5	-		10.68±0.71	5	28.42±1.17	5	1.81±0.09	5	-	
Qingzhen	EH3	0.83±0.07	6	17.0	1	11.28±0.64	6	30.56±1.85	7	1.89±1.79	7	-	
Abee	EH4	0.80±0.03	4	16.96±0.93	2	10.98±0.57	3	32.04±3	5	1.79±0.18	2	6.12	1
Adhi Kot	EH4	0.85	1	16.75	1	10.05	1	32.26±1.49	2	1.89±0.07	3	5.65	1
Indarch	EH4	0.78±0.03	7	16.54±0.16	2	10.63±0.24	5	29.48±2.07	7	1.72±0.15	5	5.78	1
St. Mark's	EH5	0.82±0.04	5	17.05±0.06	2	11.17±0.31	3	30.27±1.71	5	1.82±0.06	4	5.5	1
St. Sauveur	EH5	0.82±0.08	2	15.56	1	10.49±0.55	3	31.31±3.57	3	1.70±0.08	4	5.82	1
TOTAL[c]		0.82±0.02	7	16.64±0.56	6	10.75±0.26	7	30.62±1.38	7	1.80±0.07	7	5.77±0.23	5

(a) Observed falls only. Data sources: Baedecker and Wasson, 1975; Bhandari *et al.*, 1980; Gopalan and Wetherill, 1970; Grossman *et al.*, 1985; Hertogen *et al.*, 1983; Kallemeyn and Wasson, 1986; Krankowsky and Müller, 1964; Laul *et al.*, 1973; Manhes and Allegre, 1978; Mason, 1966; Minster *et al.*, 1979; Morgan and Lovering, 1968; Nichiporuk and Moore, 1970; Schmitt *et al.*, 1972; Sears *et al.*, 1982; Shima and Honda, 1967; von Michaelis *et al.*, 1969; Wang and Xie, 1982; Weeks and Sears, 1985. (b) Number of bulk analysis considered. (c) Unweighted mean. (d) Excluding Qingzhen. (e) Excluding St. Mark's.