POTASSIUM IN THE EARTH'S CORE

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Abstract

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Submitted to the Department of Earth and Planetary Sciences on January 15, 1975 in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

Progress in understanding the condensation of planetary constituents from the solar nebula necessitates a re-examination of models for the origin and composition of the Earth. All models which appear to be viable require the Earth to have an Fe-FeS core and the full, or nearly full, solar (i.e. chondritic) K/Si ratio. The crust and upper mantle do not contain the requisite potassium for the entire Earth to have the solar K/Si ratio. Therefore, these models require that much of the Earth's potassium must be in the deep interior -- in the lower mantle, or in the core.

The hypothesis that a significant fraction of the Earth's potassium is in the Fe-FeS core is based on the chalcophile behavior of potassium. Data including the stability of K_2S, the occurrence of potassium in sulfide phases in meteorites and in metallurgical systems, and most importantly, experiments on potassium partitioning between solid silicates and Fe-FeS melts support this hypothesis. Fe-FeS melts equilibrated with potassium feldspar contained 195 and 290 ppm K at 1030°C and 1070°C, respectively. Rough extrapolation of these data to potassium-bearing plagioclase feldspar at higher temperatures suggests that a significant fraction of the Earth's potassium may be partitioned into Fe-FeS melts, and thus extracted into the core. Present data are not sufficient to calculate directly the probable potassium content of the core.

However, the present data appear to require at least several percent, and possibly much more, of the Earth's potassium to be in the core. It is likely that ^{40}K is a significant heat source in the core. Decay of ^{40}K is a plausible energy source to drive core convection to maintain the geomagnetic field, and to drive mantle convection and sea-floor spreading.

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Part I

MODELS FOR THE ORIGIN AND COMPOSITION OF THE EARTH, AND THE HYPOTHESIS OF POTASSIUM IN THE EARTH'S CORE

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ABSTRACT

Progress in understanding the condensation of planetary constituents from the solar nebula necessitates a re-examination of models for the origin and composition of the Earth. All models which appear to be viable require the Earth to have an Fe-FeS core and the full, or nearly full, solar (i.e. chondritic) K/Si ratio. The crust and upper mantle do not contain the requisite potassium for the entire Earth to have the solar K/Si ratio. Therefore, these models require that much of the Earth's potassium must be in the deep interior -- in the lower mantle or in the core.

The hypothesis that a substantial fraction of the Earth's potassium is in the Fe-FeS core is based on the chalcophile behavior of potassium. Data including the stability of K_2S, the occurrence of potassium in sulfide phases in meteorites and in metallurgical systems, and most importantly, experiments on potassium partitioning between solid silicates and Fe-FeS melts support this hypothesis. Present data are not sufficient to calculate directly the probable potassium content of the core. However, the present data appear to require at least several percent, and possibly much more, of the Earth's potassium to be in the core. It is likely that ^{40}K is a significant heat source in the core. Decay of ^{40}K is a plausible energy source to drive core convection to maintain the geomagnetic field, and to drive mantle convection and sea-floor spreading.

1. INTRODUCTION

The similarity between estimates of the Earth's composition and the composition of chondritic meteorites led several early workers, including Goldschmidt (1922, 1933) and Washington (1925), to develop Earth models based on meteorites. As detailed information on the composition of terrestrial rocks and meteorites became available, extensive comparisons of terrestrial and chondritic elemental abundances were made (e.g. Taylor, 1964a,b). The overall agreement was strikingly good, but several elements, most notably sulfur and the heavy alkali metals (K, Rb, and Cs), appeared to be markedly depleted in the Earth relative to chondrites. K/U ratios of terrestrial rocks (Wasserburg et al., 1964) Rb-Sr isotope studies (Gast, 1960), and studies of the degassing of radiogenic ^{40}Ar (Hurley, 1968a,b) were generally interpreted as confirmation of the hypothesis that the Earth is depleted in potassium. This apparent depletion in potassium was one of the major features which Ringwood (1966) sought to explain with his carbonaceous chondrite model for the Earth. In Ringwood's model, potassium, sulfur, and many other moderately volatile elements were postulated to have been lost from the Earth during a high temperature in situ reduction of FeO to form the Earth's core and the subsequent escape of the massive primitive atmosphere generated by this core formation process.

However, recent progress (Lord, 1965; Larimer, 1967, 1973; Larimer and Anders, 1967, 1970; Grossman, 1972; Lewis, 1972a,b,

1973) in understanding the condensation of planetary constituents from the primitive solar nebula has necessitated a thorough re-examination of models for the origin and composition of the Earth. Lewis (1972a, 1973) has presented a detailed model for the formation of the terrestrial planets. This model, which assumes chemical equilibrium during condensation in the solar nebula, predicts that the Earth has an Fe-FeS core and the full solar K/Si ratio, and thus that the Earth is not depleted in either sulfur or potassium. Virtually all of the major competing models for the Earth, including inhomogeneous accretion models (Turekian and Clark, 1969; Clark et al., 1972) and the multi-component mixing model (Ganapathy and Anders, 1974), as well as simple chondritic models or models based based on mixtures of meteorite classes are also compatible with the Earth having the solar K/Si ratio.

If the Earth does have the solar K/Si ratio, a substantial fraction of the Earth's total potassium must be in the lower mantle or in the core, since the K/U, Rb-Sr, and ^{40}Ar data strongly suggest that the Earth's crust and upper mantle do not contain the requisite amount of potassium. Murthy and Hall (1970, 1972) have presented persuasive arguments that the Earth's core formed by gravitational segregation of Fe-FeS melts and that the core may contain about 15% sulfur by weight. A considerable body of evidence supports the hypothesis that substantial amounts of potassium may be partitioned into Fe-FeS melts and thus extracted into the core at the time of core

formation very early in Earth history. Goles (1969) noted that the existence of djerfisherite, a potassium-iron sulfide, in some enstatite chondrites and achondrites lends plausibility to the suggestion that potassium may have significantly chalcophilic properties in the reducing conditions of the Earth's primitive mantle. He concluded that potassium, rather than having been lost from the Earth by volatilization as suggested by Ringwood (1966), could be present in appreciable amounts in the lower mantle or in the core. Lewis (1971) discussed the stability of K_2S, data on potassium in sulfide phases in metallurgical systems, and data on potassium in sulfide phases in meteorites; he concluded that a substantial fraction of the Earth's potassium is likely to be in the Earth's Fe-FeS core. Hall and Murthy (1971) discussed the early chemical history of the Earth and also concluded that potassium would be extracted into the core. Experimental data documenting the partitioning of significant amounts of potassium into Fe-FeS melts equilibrated with potassium-bearing silicates (roedderite and potassium feldspar) were presented by Goettel (1972, 1975a,b). Oversby and Ringwood (1972, 1973) argued against the hypothesis of potassium in the core; however, Goettel and Lewis (1973) rebutted the conclusions drawn by Oversby and Ringwood.

The purpose of the present paper is to examine critically the current status of the evidence for potassium in the Earth's core. However, the question of potassium in the core cannot

be discussed in a logical manner without considering the overall chemical composition of the Earth; some of the competing models for the origin and composition of the Earth predict different total potassium contents and different core compositions. Therefore, the major models for the Earth are discussed in some detail and compared with existing observational data to test their overall consistency; data from all of the terrestrial planets are reviewed in order to test the competing models as rigorously as possible. Evidence bearing directly on the Earth's total potassium content and geochemical evidence bearing on potassium in the core are extensively considered. The major geochemical and geophysical implications of potassium in the Earth's core are summarized.

2. MODELS FOR THE ORIGIN AND COMPOSITION OF THE EARTH

(a) The Solar Abundance of Potassium

It is generally accepted that the materials constituting the Earth and the other planets condensed from a primitive solar nebula of solar composition. Therefore, the potassium content of solar material is of considerable interest when discussing the potassium content of the Earth. The solar abundance of potassium has been determined directly from photospheric Fraunhofer absorption lines (Goldberg et al., 1960; Lambert and Warner, 1968a); however, these direct measurements involve a number of assumptions (see Pagel, 1973), and are subject to relatively large errors which are difficult to estimate quantitatively. The error range for the photospheric potassium abundance (relative to silicon) is estimated, perhaps optimistically, to be approximately ±25% (Lambert and Warner, 1968a,b).

The most reliable estimates of elemental abundances in solar material, except for extremely volatile elements, have been derived primarily from meteoritic elemental abundances. Cameron's (1973) most recent solar system abundance table is based largely on Type 1 carbonaceous chondrites; eight well-determined elements were used to normalize meteoritic and solar values. Cameron's estimate of the potassium abundance in solar material was also influenced by nucleosynthesis theory in the mass region ^{28}Si to ^{40}Ca.

Recent values of the K/Si atomic ratio in the solar

photosphere, in various classes of meteorites, and Cameron's estimate for the solar system are compiled in Table I. The range in K/Si ratios is quite narrow -- from 3200 to 4200 K atoms per 10^6 Si atoms. If the Earth has the solar K/Si ratio, this range in K/Si ratios corresponds to bulk potassium contents for the Earth of about 650 to 900 parts per million.

Table I

Potassium Abundances in Solar Material and Meteorites

	K atoms per 10^6 Si atoms	Reference
solar photosphere	3200	(1)
carbonaceous chondrites (C1)	3800	(2)
carbonaceous chondrites (C1)	3000	(3)
ordinary chondrites (H,L)	3300	(3)
ordinary chondrites (L)	3200	(3)
solar system	4200	(4)

References

(1) Lambert and Warner, 1968a,b

(2) Nichiporuk and Moore, 1974

(3) Goles, 1971

(4) Cameron, 1973

(b) Condensation Models

Models for the origin and composition of the Earth generally fall into two categories: 1) condensation models, which are based on calculations, with varying assumptions, of the condensation of planetary constituents from the solar nebula, and 2) meteorite or mixing models, which are based on single classes of meteorites, mixtures of meteorite classes, or mixtures of assumed primary components in meteorites. There are two simple, end-member models for condensation in the solar nebula:

i) chemical equilibrium/homogeneous accretion,

ii) disequilibrium/inhomogeneous accretion.

i) The Chemical Equilibrium/Homogeneous Accretion Model

The chemical equilibrium/homogeneous accretion model (Lewis, 1972a, 1973) assumes that chemical equilibrium is maintained during the condensation process; gas/solid equilibrium is assumed as well as equilibrium in the gas phase. The rate of agglomeration of condensed solids is assumed to be slow relative to the condensation rate; the dimensions of condensed solids remain small enough to permit gas/solid reactions to maintain equilibrium. In this model, accretion of planetary size bodies occurs after ignition of the proto-sun has blown off the remaining uncondensed nebular material. Planets accrete with initially homogeneous compositions.

In the end-member chemical equilibrium/homogeneous accretion model, density and composition differences among

the terrestrial planets are primary features resulting directly from differing formation temperatures; complex fractionation processes are not required. The major and minor element composition, and the content of major volatiles for each of the terrestrial planets are determined by the formation temperature. Lewis discussed the major element compositions predicted for each of the terrestrial planets by this model: the predicted mean densities of Mercury, Venus, Earth, and Mars match the observed values. Although compositional data for planets other than Earth are rather sparse, the quantitative predictions of this model appear to be consistent with existing observational data.

In this model, the high density of Mercury results from a formation temperature too high for complete condensation of magnesium silicates. Refractories (including Al, Ca, Ti, Ba, Sr, U, and Th), and Fe-Ni are present in solar proportions, but Mg and Si are present in less than solar proportions. Lower temperature condensates such as the alkali metals, sulfur, FeO, and H_2O should be virtually absent. Mercury is thus predicted to have a very large Fe-Ni core surrounded by a small magnesium silicate mantle. Refractories should be enriched in the crust, if differentiation of the planet is fairly complete.

Venus has a lower formation temperature: refractories, Fe-Ni, Mg, and Si, plus Na and K should all be present in solar proportions. Venus is thus predicted to have a large Fe-Ni core

and a massive magnesium silicate mantle. Refractories and alkali metals should both be enriched in the crust if differentiation of the planet is fairly complete. If the high potassium content (4%) measured by the Venera 8 lander (Vinogradov et al., 1973) is representative of the entire Venus crust, then the Venus crust is much richer in potassium than the average Earth crust. Sulfur, H_2O, and FeO are predicted to be nearly absent from Venus because its postulated formation temperature is above the condensation temperatures of S (as FeS), H_2O (as hydrated silicates), and FeO (in solution in magnesium silicates). These predictions are consistent with the very low abundances of sulfur compounds (Owen, 1968; Cruikshank, 1967; Cruikshank and Kuiper, 1967), and H_2O (Belton, 1968; Jones et al., 1972; Fink et al., 1972) in the Venus atmosphere. Rather than being endogenous, the trace amounts of H_2O and S which are present on Venus may result from infall of carbonaceous chondrite or cometary material (Lewis, 1974a). The mass influx of such volatile-rich material which is required to provide the H_2O and S on Venus is, however, extremely small and has virtually no effect on Venus' major element composition, or even on the abundance of the major volatile species, CO_2.

The chemical equilibrium model predicts that the Earth, as well as Venus, should have the solar proportions of refractories, Fe-Ni, Mg, Si, Na, and K. In addition, because of its lower formation temperature, the Earth is predicted to

have also the solar proportion of S, about 10% FeO in the silicates, and a significant amount of H_2O. Retention of S (as FeS) increases the mean atomic weight of the Earth, and may, as suggested by Lewis (1972a) increase Earth's mean zero pressure density. Therefore, retention of S by the Earth is a possible explanation for Earth's zero pressure mean density being about 1% greater than Venus' zero pressure mean density. The amount of sulfur that this model predicts for the Earth's core, about 15%, is consistent with the geophysical constraints (Anderson et al., 1972) of outer core density and seismic velocity, which require 10-20% of a light element in the core.

In the chemical equilibrium model, the low mean density of Mars is a direct result of formation at a temperature low enough for complete, or nearly complete, oxidation of Fe to FeS and FeO. Mars is thus expected to have a predominately FeS core, and a dense, FeO-rich mantle. The high mean moment of inertia of Mars is consistent with this predicted density structure. This model predicts that H_2O should be more abundant on Mars than on Earth, since Mars' formation temperature is well within the stability range of many hydrous silicates. The H_2O on Mars is presumably retained as hydrous silicates or as subsurface ice beds.

ii) Inhomogeneous Accretion Models

The second end-member model for condensation in the solar nebula is the disequilibrium/inhomogeneous accretion model. This model assumes that equilibrium is obtained in the gas phase, but that condensed solids are isolated from further reactions with the remaining gas. The rate of agglomeration of condensed solids is assumed to be rapid relative to the condensation rate; the dimensions of the condensed solids are too large to permit gas/solid equilibrium. In this model, accretion of planets occurs during the condensation process. A planet's initial structure is layered: refractory condensates form a proto-core, followed by an Fe-Ni metal layer, a magnesium silicate layer, and finally by a veneer of low-temperature, volatile-rich condensates.

An inhomogeneous accretion model which is similar to the end-member disequilibrium/inhomogeneous accretion model, but somewhat more complex, has been advocated by Turekian and Clark (1969), Clark et al. (1972), Grossman (1972), and Grossman and Larimer (1974). These authors assumed that gas/solid equilibrium was obtained for high-temperature condensates, and that the inhomogeneous accretion process was incomplete. For example, some S could be retained by the Earth in these modified inhomogeneous accretion models because some Fe metal was assumed to remain in the nebula after most of the Fe had accreted to form the Earth's core and had been covered by a massive magnesium silicate mantle; the Fe remaining in the

nebula can then be accreted by the Earth as FeS in the late stages of accretion. Inhomogeneous accretion models predict that the Earth has the solar proportion of potassium (solar K/Si ratio), since a formation temperature low enough for condensation of the final veneer of volatile-rich material is well below the temperature at which potassium is fully condensed.

Neither the predictions of the end-member disequilibrium/ inhomogeneous accretion model nor the predictions of the modified inhomogeneous accretion models advocated by Turekian and co-workers have been worked out in full, quantitative detail. Nevertheless, it is possible to test these models by comparing their logical predictions with existing observational data.

Inhomogeneous accretion models produce the primary core/ mantle dichotomy of the Earth as a direct result of the accretion process. However, the geophysical data (Anderson et al., 1972) requiring 10-20% of a light element in the outer core are difficult to reconcile with inhomogeneous accretion models for the Earth. Ringwood (1966) has offered persuasive arguments that S and Si are the only two elements which have the correct properties, and are sufficiently abundant to possibly constitute 10-20% of the outer core. Inhomogeneous accretion of the Earth appears to preclude either S or Si as the major light element in the core. Sulfur in the core is not possible, because the Fe core is assumed to be covered

by a massive magnesium silicate mantle before temperatures are low enough to allow retention of S as FeS. Silicon in the core is not possible, because the Si content of Fe-Ni alloy condensed directly from the solar nebula is several orders of magnitude too low. Modified inhomogeneous accretion models allow some S to be retained by the Earth and possibly incorporated into the core; however, the geophysical constraints on the core require essentially the full solar proportion of S, if S is to be the light element in the core, and this much S in the Earth is incompatible with inhomogeneous accretion of the Earth.

Inhomogeneous accretion models have difficulty in explaining why Earth is about 1% denser than Venus; according to inhomogeneous accretion models, Earth should be slightly less dense than Venus, because its lower formation temperature will result in greater retention of light volatiles. This discrepancy can be removed by postulating that Earth simply received a greater proportion of Fe than did Venus, but this added postulate is somewhat arbitrary.

Another difficulty for inhomogeneous accretion models is the great difference in the H_2O content of Earth and Venus. The models predict that volatiles are retained as a late-stage, low-temperature veneer; the great difference in H_2O/CO_2 ratios for Earth and Venus would thus require the existence of two distinct types of volatile-rich material in the early solar system, differing in relative H and C content by several orders

of magnitude. However, there is no evidence that two such distinct types of low-temperature condensates can be produced; none of the types of carbonaceous chondrites exhibit evidence for such drastic variations in H/C ratios. The great difference in H_2O/CO_2 ratios on Venus and Earth thus appears to be a good argument against retention of volatiles as a thin veneer of low-temperature condensates, as required by inhomogeneous accretion models, unless great differences exist in photochemical and escape processes in the Venus and Earth atmospheres.

A simple inhomogeneous accretion model would predict that Mars should have a large Fe-Ni core. Since the low mean density of Mars is incompatible with a large Fe-Ni core, it becomes necessary to invoke a special mechanism for Mars. Turekian and Clark (1969) suggested that Mars began to accrete after most of the Fe-Ni had been captured by the other planets, but this special mechanism for Mars is somewhat ad hoc.

(c) Meteorite and Mixing Models

The second general type of model for the origin and composition of the Earth is based on a single meteorite class, mixtures of meteorite classes, or mixtures of assumed primary components in meteorites. The following models of this type are considered:

i) carbonaceous chondrite model,

ii) ordinary chondrite and mixtures of meteorites models,

iii) multi-component mixing model.

i) The Carbonaceous Chondrite Model

Ringwood's (1966) model is based on the assumption that all of the terrestrial planets had initial compositions similar to the Type 1 carbonaceous chondrites. Density and composition differences among the terrestrial planets are attributed to varying degrees of reduction and volatile element loss. A very high temperature evolution is postulated to reduce iron oxides and some silicon dioxide by carbon, and to volatilize elements such as sulfur and the alkali metals. This is the only major model which requires the Earth to be markedly depleted in potassium. However, examination of this model reveals several aspects which appear to be implausible or to contradict existing observational data.

Material similar to carbonaceous chondrites condenses from the solar nebula at temperatures below about 400 ^{o}K (Lewis, 1972a,b). In order for each of the terrestrial planets to have initial compositions similar to carbonaceous chondrites,

as required by Ringwood's model, the temperature gradient in the solar nebula would have to be nearly isothermal. However, realistic models for the nebula (Cameron and Pine, 1973; Lewis, 1974b) require an adiabatic temperature gradient. By choosing a suitable adiabat, the formation temperature of one of the terrestrial planets could be set to be compatible with carbonaceous chondrite composition, however, the requirement of an adiabatic temperature gradient in the solar nebula appears to rule out the possibility that all of the terrestrial planets had very similar initial compositions rich in carbonaceous material.

One major consequence of the formation of the Earth's core by reduction of iron oxides by carbon, as postulated by this model, is the generation of a massive primitive atmosphere composed principally of CO, but also including many elements volatilized during the high temperature reduction process. Ringwood estimated that this primitive atmosphere would amount to about one-half the present total mass of the Earth. Since neither the present atmosphere nor early Precambrian rocks show any evidence of this primitive atmosphere, complete escape of this massive atmosphere is a critical requirement of this model. However, it is difficult to envision a viable mechanism for completely removing such heavy gases as CO, S, the alkali metals, and very heavy metals such as Pb, Hg, and Bi; the molecular weights of these gases are far too high to be removed by thermal diffusion. The implausibility of complete

escape of this massive, high atomic weight, primitive atmosphere and the lack of a quantitative model to explain the escape, appear to be serious problems for this model of the Earth.

Even if the postulated carbonaceous chondrite initial compositions, and the escape of the primitive atmospheres are accepted, the carbonaceous chondrite model fails to explain adequately the observed mean densities of the terrestrial planets. Mercury's mean density of 5.42 g/cm^3 (Ash et al., 1971) is far to high to be explained solely by a reduction process. Ringwood found it necessary to postulate selective volatilization of magnesium silicates from Mercury during a Hayashi phase (Hayashi, 1961) of extreme solar super-luminosity during the sun's early evolution. However, the absence of observational confirmation that stars do evolve through a Hayashi phase, and current theories of stellar evolution which conclude that such a phase does not occur (Larson, 1974), appear to rule out this mechanism for volatilizing magnesium silicates from Mercury. Thus, Mercury's high mean density seems to be incompatible with an origin by reduction of carbonaceous material.

In Ringwood's model, Mars is composed of highly oxidized, primordial material; lack of reduction is attributed to the small content of carbonacaeous material in the primordial material from which Mars accreted. However, the carbonaceous chondrite model for the terrestrial planets requires that Mercury, Venus, and Earth form from carbonaceous-rich material.

Temperature in the solar nebula must decrease with increasing heliocentric distance; therefore, it is difficult to understand how primordial material at the distance of Mars could have less low-temperature, carbonaceous-rich material than Earth, Venus, or even Mercury. Recent observations (Johnson and Fanale, 1973; McCord and Gaffey, 1974) have shown that the asteroid belt is composed mainly of carbonacaeous chondrite material. Thus, Ringwood's model for Mars requires that the entire inner solar system from Mercury to the asteroid belt, with the sole exception of Mars, was rich in carbonaceous material. This postulate is rather implausible, and therefore, this model for Mars appears to be incompatible with current understanding of condensation in the solar nebula.

The carbonaceous chondrite model also fails to explain the present volatile content of the terrestrial planets. Ringwood attributes the Earth's retention of H_2O, N_2, CO_2, and the rare gases to the non-attainment of equilibrium. However, retention of these volatiles is difficult to reconcile with the very high temperature reduction process, the melting of the mantle, and the escape of the massive primitive atmosphere which are required by this model. It is difficult to see how H_2O could be retained while the alkali metals are volatilized, or how the massive primitive CO atmosphere could escape and leave behind the large amount of CO_2 presently in the Earth's crust, oceans, and atmosphere. Furthermore, the rare gas data presented by Boulos and Manuel (1971) require the retention of

radiogenic ^{129}Xe in the first few million years of the Earth's history. These data on the Earth's volatile content are difficult to reconcile with the very high temperature evolution required by the carbonaceous chondrite model.

Plots of the relative abundances of various volatiles in the Earth's crust and upper mantle, and in carbonaceous and ordinary chondrites show that sulfur is markedly more depleted in the Earth's crust and upper mantle than are H_2O, the halogens, and the rare gases (Murthy and Hall, 1970, 1972). This volatile element pattern may be readily understood in terms of a low temperature formation of the Earth, and retention of sulfur as FeS in the core. However, the extreme depletion of sulfur relative to other more volatile species in the upper portion of the Earth does not appear to be consistent with the high temperature evolution and escape of volatiles required in Ringwood's model for the Earth.

In the carbonaceous chondrite model, Venus is slightly more oxidized than Earth; therefore, Venus might be expected to contain slightly more water than Earth. However, the water content of Venus (Belton, 1968; Jones et al., 1972; Fink et al., 1972) is about 10^4 times less than the water content of Earth. To overcome this discrepancy, Ringwood postulated that the primordial material from which Venus accreted had a much higher C/H ratio than the material from which Earth accreted. However, his model requires a very large amount of carbonaceous material in order to reduce iron oxides to form the cores of Venus and

Earth. Only very carbon-rich material such as Type 1 or Type 2 carbonaceous chondrites can provide enough carbon. All of these carbonaceous chondrites contain large amounts of water (Kaplan, 1971); moreover, the C and H contents of these meteorites are well correlated. Thus, these data from carbonaceous chondrites offer no evidence for the orders-of-magnitude variation in C/H ratios required by Ringwood's model for Venus. The very low H_2O content of Venus relative to the Earth thus appears to be incompatible with the carbonaceous chondrite model for the terrestrial planets.

ii) The Ordinary Chondrite and Mixtures of Meteorites Models

For more than 50 years (e.g. Goldschmidt, 1922; Washington, 1925) many Earth models have been based on single classes of meteorites or on mixtures of meteorite classes. Mason (1966) proposed that the bulk composition of the Earth is similar to the bronzite chondrites. Murthy and Hall (1970, 1972) suggested that the composition of the Earth is similar to a mixture of iron meteorites, ordinary chondrites, and carbonanceous chondrites. Numerous similar models may be found in the literature.

As noted by Taylor (1964a,b) the bulk composition of the Earth appears to be very similar to the composition of ordinary chondrites. The major exceptions, sulfur and the heavy alkali metals (K, Rb, and Cs), are also similar in abundance in chondrites and in the Earth, if the Earth has an Fe-FeS core containing a significant fraction of the Earth's total heavy alkali metal inventory. Therefore, the simple ordinary chondrite model appears to be a reasonable approximation for the composition of the Earth. Likewise, models based on mixtures of meteorite classes generally are in good agreement with data for the Earth because the proportions of the various classes postulated by a given model are adjusted to fit whichever suite of terrestrial data is chosen for comparison.

The simple ordinary chondrite model for the Earth predicts, obviously, that the Earth has the chondritic (i.e. solar) K/Si ratio. Models based on mixtures of meteorite classes vary

somewhat in predicted K/Si ratios, depending on the proportions of the various meteorite classes in the model, but generally predict K/Si ratios equal or close to the chondritic value.

The primary objection to Earth models based on meteorites is philosophical. As noted by Ganapathy and Anders (1974), Earth models constructed from a single meteorite class, or a mixture of meteorite classes, with the proportions adjusted to match mean density and chemical characteristics, are "esthetically objectionable", because this approach is basically arbitrary and ad hoc. Furthermore, models based on meteorites are generally non-predictive: i.e., knowing that the Earth is made of a given mixture of meteorites does not enable one to make quantitative predictions about the other planets.

iii) The Multi-component Mixing Model

Ganapathy and Anders (1974) have proposed a detailed geochemical model for the Earth, based on the assumption that the planets formed by the same processes as chondritic meteorites. This model assumes that three basic condensates (refractories, nickel-iron, and magnesium silicates) were fractionated from each other during condensation in the solar nebula, and were transformed by condensation and remelting to a total of seven components: early condensate; remelted and unremelted Fe-Ni-Co alloy; remelted and unremelted (Fe-Mg)-silicates; FeS; and a carbonaceous, volatile-rich silicate. The proportions of these components in the Earth and in the Moon were estimated by assuming that the planets were differentiated, and applying assumed geochemical constraints such as K/U ratio, bulk U and Fe content, etc. This multi-component mixing model appears to be in fairly good agreement with what is known about the bulk composition of the Earth, because the proportions of the postulated seven components were adjusted to assure a good fit to the Earth.

This model implicitly postulates an Fe-FeS core for the Earth, since Si^{o} is absent and S is far too abundant to be entirely in the crust and mantle. The postulated amount of S is, however, about a factor of three too low to be consistent with the requirement of about 15% of a light element in the outer core. This discrepancy could be readily rectified by increasing the proportion of the FeS component in the Earth.

In their existing model, Ganapathy and Anders predict that K is depleted in the Earth by a factor of about four, relative to solar or chondritic abundances. However, this apparent depletion is an artifact of the overly-restrictive assumption that the K/U ratio in upper mantle rocks is indicative of the Earth's total K content. This assumption is not valid if part of the Earth's total K is in the Fe-FeS core or in the lower mantle. Ganapathy and Anders acknowledge the possiblity of extracting Rb and Cs into the core as sulfides, but, interestingly, they have overlooked this possiblity for K. The K/Si ratio predicted by this model could easily be raised to the solar value by increasing the proportions of the K-rich components in this model for the Earth.

Although the multi-component mixing model has not yet been extended to planets other than the Earth and the Moon, one difficulty is evident: the low H_2O content of Venus. Variations in the proportions of the seven components proposed by Ganapathy and Anders cannot produce the several orders of magnitude difference in H_2O/CO_2 ratio observed between Earth and Venus.

Ganapathy and Anders commented that models constructed from a single meteorite class or a mixture of meteorite classes are basically arbitrary and ad hoc. This same criticism may be applied to the multi-component mixing model proposed by Ganapathy and Anders. Their model is completely flexible; the relative proportions of their seven components can be

arbitrarily varied to match the mean density or observed chemical composition of a planet.

A fundamental assumption in the model proposed by Ganapathy and Anders is that fractionation of their seven postulated components occurred on a planetary scale. The observed variations in major and trace element composition in the various meteorite classes indicate clearly that fractionation processes have been important in meteorites. It appears that igneous differentiation, physical fractionations, and multi-component mixing have markedly affected the compositions of meteorites. However, meteorites have dimensions of a few millimeters to at most a few meters, and meteorite parent bodies are many orders of magnitude smaller than the Earth. For a planet as large as Earth, gravitational accretion must be the dominant mechanism for planetary accumulation, and gravitational accretion is completely composition-independent. It is difficult to see how components which were initially fractionated in meteorite parent bodies or in planetesimals could be so well physically separated that gravitational accretion of the Earth would not sample all components in proportion to their initial abundances, and thus, effectively re-homogenize the starting material. Therefore, it appears that temperature, pressure, and degree of equilibrium between condensed solids and nebula gases in the portion of the nebula sampled by a given planet, rather than physical fractionations between various components, may be the primary determinants of a planet's bulk composition.

(d) A Working Model for the Composition of the Earth

The preceding discussion suggests that several models including the chemical equilibrium/homogeneous accretion model (Lewis, 1972, 1973), the ordinary chondrite model (Mason, 1966), models based on mixtures of meteorite classes (Murthy and Hall, 1970, 1972), and the multi-component mixing model (Ganapathy and Anders, 1974) are generally viable models which are approximately consistent with what is known about the bulk composition of the Earth. Inhomogeneous accretion models (Turekian and Clark, 1969; Clark et al., 1972; Grossman, 1972; Grossman and Larimer, 1974) are consistent with some aspects of the composition of the Earth, but appear to be inconsistent with other data for the Earth and the other terrestrial planets. Thus, inhomogeneous accretion models appear to be considerably less viable. The carbonaceous chondrite model (Ringwood, 1966) appears to be inconsistent with current understanding of condensation in the solar nebula, and fails to explain numerous aspects of the compositions of the terrestrial planets. This model does not appear to be viable, and, therefore, will not be considered further.

The present author prefers the chemical equilibrium/homogeneous accretion model as a working model for the origin and composition of the Earth and the other terrestrial planets. The other, generally-viable models -- ordinary chondrite, mixtures of meteorites, and multi-component mixing -- predict compositions for the Earth which are quite similar to the composition predicted by the chemical equilibrium model.

However, these models are somewhat arbitrary in their postulates of compositions for the Earth corresponding to a single meteorite class, mixtures of meteorite classes, or mixtures of assumed primary components. Furthermore, these other models are non-predictive in the sense that matching the composition of the Earth with one of these models does not enable one to make testable predictions about any of the other terrestrial planets.

The chemical equilibrium model, however, is based on a quantitative physical model for the solar nebula (Cameron and Pine, 1973), and on quantitative calculations of the condensation of planetary constituents from the solar nebula. As shown by Lewis (1972, 1973), this model appears to be consistent with the mean densities and compositions of all of the terrestrial planets without requiring special postulates for each planet.

The chemical equilibrium model is an end-member model which assumes complete equilibrium between condensed solids and gases in the solar nebula, and completely homogeneous accretion of the Earth. As an end-member model, this model is almost certainly an over-simplification of the actual physical and chemical processes of planetary formation. However, the good agreement between the predictions of this model and current observational data suggests that this model is a reasonable approximation.

The major features of the chemical equilibrium model for the Earth are compiled in Table II. In the context of the present discussion of the abundance and distribution of potassium in the Earth, two postulates of this model are of

Table II

Chemical Equilibrium Model for the Earth

Core: primarily Fe-Ni-S, also siderophile and chalcophile trace elements

Mantle: primarily pyroxene and olivine ($\frac{Fe}{Fe+Mg} \approx .10$), plus some Ca, Al, Na, etc.

Crust: enriched in large-ion incompatible elements: U, Th, Sr, rare earths, etc.

Bulk Composition of the Earth:

1) solar proportions (relative to Si) of all major rock-forming elements, including Fe, Mg, Ni, S, Ca, Al, Na, etc.

2) solar K/Si, U/Si, Th/Si ratios

3) bulk K content of the Earth $\approx$ 750±150 ppm

particular interest:

1) the Earth has a core of Fe-FeS, and the solar S/Si ratio,

2) the Earth has the solar (or chondritic) K/Si ratio.

It is important to note, however, that these two important postulates -- that the Earth has an Fe-FeS core, and the solar K/Si ratio -- do not depend entirely on acceptance of the chemical equilibrium model for the Earth.

Independent evidence for sulfur in the Earth's core has been presented by Murthy and Hall (1970, 1972). These authors compared the abundances of a number of volatile elements in the Earth's crust and mantle to the abundances of these volatiles in carbonaceous chondrites, ordinary chondrites, and a mixture of meteorite classes. Regardless of which meteorite class was used to normalize the abundances, sulfur was found to be depleted in the Earth's crust and mantle by a larger factor than H_2O, the halogens, or the rare gases. This important observation strongly suggests that high-temperature volatilization (Ringwood, 1966) is not a viable mechanism for depleting the Earth in sulfur. However, incorporation of sulfur (as FeS) into the core is consistent with the observed volatile element abundance pattern.

Murthy and Hall noted that an Fe-FeS melt will be the first melt formed in the early Earth because the Fe-FeS eutectic temperature is only 988 ^{o}C, and increases only slowly with pressure (Brett and Bell, 1969; Usselman, 1975a, b). Therefore, core formation by gravitational segregation of Fe-FeS melts

may be expected to occur very early in Earth history at a relatively low temperature. This model of core formation does not require very rapid accretion (Hanks and Anderson, 1969), or another mechanism for strongly heating the Earth. Relatively low-temperature formation of an Fe-FeS core early in Earth history is consistent with the U/Pb data (Oversby and Ringwood, 1971) requiring core formation no later than 10^8 years after accretion, and is also consistent with the presence in mantle-derived gases of excess ^{129}Xe from extinct ^{129}I (Boulos and Manuel, 1971). These rare gas data require that the Earth's mantle was cool enough to retain radiogenic ^{129}Xe within the first few million years of Earth history.

The end-member chemical equilibrium model (Lewis, 1972, 1973) predicts that the Earth has the full solar S/Si ratio. Departures from equilibrium (i.e. incomplete reaction of H_2S with Fe to form FeS) would result in a somewhat lower sulfur abundance for the Earth. However, the arguments presented by Murthy and Hall suggest that the Earth is not drastically depleted in sulfur, and does, in fact, contain approximately the solar proportion. The other, generally-viable models for the Earth -- ordinary chondrite, mixtures of meteorites, and multi-component mixing -- also predict that the Earth has substantial amounts of sulfur, and thus an Fe-FeS core.

The conclusion that the Earth has the solar K/Si ratio is not dependent on the assumptions of the chemical equilibrium model; in fact, departures from the chemical equilibrium model

do not reduce the Earth's predicted potassium content. The potassium contents predicted for the Earth by each of the major models are summarized in Table III. In the end-member chemical equilibrium model, potassium condenses as feldspar near 1000 ^{o}K (Lewis, 1972, 1973). If complete gas/solid equilibrium is not obtained, potassium would partially condense as feldspar, and the remaining potassium would condense at a lower temperature as the oxide or sulfide. In the end-member disequilibrium/inhomogenous accretion model, potassium condenses as the oxide or sulfide, and the Earth is still predicted to have the solar K/Si ratio. The requirement that the Earth's formation temperature be low enough for volatile retention means that the temperature must be low enough for complete condensation of potassium.

The chondritic model for the Earth, and models based on mixtures of meteorites also predict that the Earth has the full chondritic (or solar) K/Si ratio, or very nearly this much potassium. The multi-component mixing model, with modification to allow for the possibility of potassium in the Earth's core, is compatible with a solar K/Si ratio for the Earth. The only major model which definitively predicts that the Earth has markedly less than the solar K/Si ratio is the carbonaceous chondrite model of Ringwood (1966). However, as discussed previously, the carbonaceous chondrite model does not appear to be a viable model for the origin and composition of the Earth. The conclusion that the Earth does have the solar K/Si ratio appears to be firm.

Table III

Predicted Potassium Content of the Earth

Model	Initial K-bearing Phase	Predicted K/Si Ratio
Condensation Models		
Chemical Equilibrium	feldspar	solar
Incomplete Equilibrium	feldspar + K_2O (or K_2S)	solar
Inhomogeneous Accretion	K_2O (or K_2S)	solar
Meteorite and Mixing Models		
Chondritic	feldspar	solar
Mixtures of Meteorites	feldspar	$\approx$ solar
Multi-component Mixing	feldspar	$\approx$ solar
Carbonaceous Chondrite	feldspar	$<<$ solar

3. BULK POTASSIUM CONTENT OF THE EARTH

(a) Terrestrial Heat Flow Data

Urey (1956), Hurley (1957), and Birch (1958) all noted that the present steady-state heat production of an Earth with the chondritic proportions of K, U, and Th closely matches the observed mean heat flow of the Earth. This "chondritic coincidence" is one of the classic arguments for a chondritic model of the Earth. For continuity in the present discussion, it should be noted that the chondritic proportions of K, U, and Th are essentially identical to the solar proportions discussed previously in this paper.

A more detailed consideration of the Earth's heat flow is consistent with the conclusions that:

1) the Earth has solar K/Si, U/Si, and Th/Si ratios,
2) a substantial fraction of the Earth's potassium must be in the lower mantle or in the core.

The concentrations of K, U, and Th in the crust and upper mantle in continental regions are sufficient to generate the observed continental heat flow. However, the concentrations of these radioactive nuclides in the oceanic crust and uppermost mantle are far too low to generate the observed heat flow in oceanic areas; a deep-seated oceanic heat source is required. Lewis (1971) suggested that heat from ^{40}K in the core could be released through the oceanic crust via mantle convection, and thus produce the observed heat flow pattern.

A recent upward revision (Williams and Von Herzen, 1974) of

the average heat flow in oceanic areas, which includes the important and previously ignored contribution from the cooling lithosphere, has increased the Earth's estimated mean heat flow by about 30%, and has greatly increased the proportion of the observed oceanic heat flow which is unsupported by near-surface radioactivity. This new estimate raises the Earth's mean heat flow above the steady-state chondritic value. However, this higher estimated heat flow is consistent with the Earth having solar K/Si, U/Si, and Th/Si ratios, if the short half life of ^{40}K, and the large time tag required to transport heat from potassium in the lower mantle or in the core to the surface are considered.

The observed mean heat flow of the Earth is a problem for models postulating that potassium is markedly depleted in the Earth relative to its solar or chondritic abundance. In an Earth with the solar proportions of K, U, and Th, decay of ^{40}K presently accounts for nearly 60% of the Earth's total radiogenic heat production (Wasserburg et al., 1964). Earlier in Earth history, the proportion of heat due to ^{40}K is even greater. One alternative explanation of the observed heat flow is that a substantial fraction of the present heat flow represents "initial heat" from a very high temperature period early in Earth history. However, the ^{129}Xe data (Boulos and Manuel, 1971) requiring a relatively low temperature early evolution of the Earth do not appear to be consistent with the "initial heat" hypothesis.

A second alternative is that the Earth is depleted in K, but enriched in U and Th, relative to the solar proportions of these elements (Wasserburg et al., 1964). However, enrichment of U and Th above the solar proportions requires elemental fractionations on a planetary scale, which, as discussed in section 2(c)(iii) does not appear to be a particularly viable assumption. Another objection to this alternative is the requirement that a large fraction of the Earth's U and Th would probably have to be in the lower mantle or in the core to explain the observed heat flow pattern. Several authors, including Birch (1958) and Gast (1960), have shown that the Earth's crust contains nearly the full amount of U (and presumably Th as well) expected in an entire chondritic Earth. The present author is not aware of any evidence supporting the hypothesis that a significant fraction of the Earth's U and Th are retained in the lower mantle or in the core.

The Earth's mean heat flow thus appears to be consistent with the Earth having solar K/Si, U/Si, and Th/Si ratios, as predicted by the chemical equilibrium model for the Earth. Retention of a substantial fraction of the Earth's potassium in the lower mantle or in the core, which is a necessary consequence of the Earth's having the solar K/Si ratio, also appears necessary to explain the observed heat flow pattern.

(b) The Earth's K/U Ratio

Wasserburg et al. (1964), Gast (1972), and others have noted that the Earth's K/U ratio appears to be distinctly lower than the chondritic K/U ratio. K/U weight ratios for a wide variety of terrestrial igneous rocks cluster near a value of 1×10^4, while chondritic K/U ratios cluster near 8×10^4. This difference between the terrestrial and chondritic K/U ratios has been interpreted as confirmation that the Earth is markedly depleted in potassium. Since the Earth's inventory of U appears to be almost entirely concentrated in the crust and uppermost mantle, the K/U data demonstrate convincingly that the full solar proportion of K is not in the crust and upper mantle. However, unless K and U are assumed to be geochemically coherent during the entire differentiation history of the Earth, the observed K/U ratio cannot be applied to the entire Earth. In particular, if a significant fraction of the Earth's K is partitioned into the Fe-FeS core at the time of core formation, as suggested by Lewis (1971), the Earth can still have the full solar proportion of K. Thus, the hypothesis that the Earth has the solar K/Si ratio is not invalidated by the K/U ratios observed in crustal and upper mantle rocks.

(c) Sr Isotope Evidence

From the $^{87}Sr/^{86}Sr$ ratio in oceanic volcanic rocks, and the estimated initial ratio for the whole Earth, Gast (1972) estimated that the mean Rb/Sr ratio of the upper mantle is

about 10 times less than the average chondritic or solar value. From this Rb/Sr ratio and the K/Rb ratio in a wide range of igneous rocks, Gast concluded that K is markedly depleted in the Earth. This argument based primarily on the isotopic composition of Sr has been one of the strongest arguments against a chondritic Earth, or in the context of the present discussion, an argument against the Earth having the solar proportions of K and Rb.

However, Gast (1960), in a more complete discussion of the Sr isotope evidence, acknowledged another possible explanation of these data: an Earth differentiation in which a substantial fraction of the Earth's total K and Rb are separated from Sr very early in Earth history, and retained deep in the Earth's interior. If a substantial fraction of the Earth's K and Rb were partitioned into the Fe-FeS core at the time of core formation, then the Rb/Sr and K/Rb data discussed by Gast are compatible with the Earth having the solar proportions of K and Rb. Thus, the Sr isotope evidence does not necessarily invalidate the hypothesis of a solar K/Si ratio for the Earth.

(d) K-Rb-Ar Systematics

Hurley (1968a, b) and Gast (1968) have concluded that the bulk potassium content of the Earth is only about one-seventh of the potassium content of chondrites. This conclusion is based on the assumption that radiogenic ^{40}Ar (from ^{40}K) is differentiated into the atmosphere at least as efficiently as

Rb is differentiated into the crust, on assumed geochemical constraints on K/Rb ratios, and on limits on Rb from Sr isotope data. However, these assumptions are not entirely valid if K and Rb are partitioned into the core. In this case, a substantial fraction of the Earth's K, Rb, and radiogenic Ar could be effectively decoupled from the crust and upper mantle. Therefore, the K-Rb-Ar data discussed by Hurley and Gast do not necessarily invalidate the present model for the Earth in which the Earth has the solar K/Si ratio.

(e) Discussion

Evidence such as the Earth's K/U ratio, Sr isotope evidence, and K-Rb-Ar data which bears directly on the Earth's potassium content must be interpreted in the context of a model for the origin, composition and evolution of the Earth. The conclusion that the Earth has the full solar K/Si ratio appears to be very firm. In the context of this model for the Earth, the K/U, Sr isotope, and K-Rb-Ar evidence may logically be interpreted as indications that much of the Earth's K and Rb must be deep in the Earth, either in the lower mantle or in the core. The presence of an Fe-FeS core raises the possiblity that a substantial fraction of the Earth's K and Rb could be partitioned into the core at the time of core formation. The consensus that these data indicate that the Earth is depleted in K and Rb relative to chondritic or solar abundances may thus be an artifact of overly-restrictive assumptions about the geochemical behavior of these elements.

4. EVIDENCE FOR POTASSIUM IN THE CORE

(a) Stability of K_2S

Lewis (1971) noted that several elements, most notably potassium, which are generally regarded as lithophilic, have appreciable chalcophilic tendencies. He considered a number of reactions of the form

$$K_2O + H_2S = K_2S + H_2O \qquad (1)$$

for the sole purpose of portraying the relative stabilities of pure sulfides and oxides. Although this reaction is not directly applicable to the partitioning of potassium into the core, some important inferences may be drawn from data of this type. At 1000 ^oK, the equilibrium constant for reaction (1) is $10^{14.8}$; this strikingly high value demonstrates the stability of K_2S and suggests that potassium may indeed have appreciable chalcophilic tendencies under the appropriate chemical conditions. If sodium is substituted for potassium in reaction (1), the equilibrium constant at 1000 ^oK, is $10^{9.57}$; thus Na appears to be significantly less chalcophilic than is K. One possible explanation for the observation that K is markedly depleted in the Earth's crust and mantle relative to chondrites, but Na apparently is not as depleted, is that substantial amounts of K, but only minor amounts of Na, may be partitioned into Fe-FeS melts at the time of core formation in the Earth.

Hall and Murthy (1971) considered a variety of chemical reactions representative of both the present oxidized crust and the more reducing conditions existing during core formation.

Thermodynamic data for reactions of the form

$$MeO + FeS = MeS + FeO \qquad (2)$$

where Me indicates any cation, demonstrate the extreme stability of K_2S, and also that K may be expected to be more chalcophile than Na. Data for reactions of the form

$$MeSO_4 + FeS = MeS + FeSO_4 \qquad (3)$$

$$MeCO_3 + FeS = MeS + FeCO_3 \qquad (4)$$

which reflect the highly oxidized present crust, suggest that all of the alkali metals will be lithophile under crustal conditions. However, data for reactions of the form

$$MeSiO_3 + FeS = MeS + FeSiO_3 \qquad (5)$$

$$\tfrac{1}{2}Me_2SiO_4 + FeS = MeS + \tfrac{1}{2}Fe_2SiO_4 \qquad (6)$$

which reflect the more reducing conditions existing in the mantle during core formation, suggest that Li and Na remain lithophile, but that K, Rb, and Cs are chalcophile. These data presented by Hall and Murthy suggest that the heavy alkali metals (K, Rb, and Cs) may be appreciably chalcophile under the conditions relevant to core formation, and thus may be partitioned into the core. However, uncertainty about the effect of Al on alkali metal partitioning, uncertainty about the effect of high pressure, and the lack of the requisite thermodynamic data make a direct calculation of the extent of K, Rb, or Cs partitioning into the core impossible.

(b) Metallurgical Evidence

Chalcophilic behavior of potassium has also been documented in metallurgical systems. Cissarz and Moritz (1933) have

reported detailed chemical analyses of co-existing metal, sulfide, and silicate phases from the smelting of the Mansfeld copper ores. The sulfide matte contains 0.8% K_2S; extremely low Si (0.05%) and Al (0.01%) abundances in the sulfide matte eliminate the possibility that the high K_2S value was due to contamination by K-bearing silicates. The co-existing silicates contain 17% Al_2O_3, which demonstrates that the presence of alumino-silicates does not preclude the formation of K_2S. The silicates also contain 4% FeO. The oxygen fugacity is probably somewhat below the iron-wüstite buffer, and thus is compatible with the oxygen fugacity expected in the primitive, differentiating Earth.

A more recent microprobe study of blast furnace byproducts (vom Ende et al., 1966) provided additional data on the entry of potassium into sulfide phases. A K-Fe-S compound and an alkali-Mn-S compount were identified as constituents of the lowest temperature melt. The textural evidence indicated that the K-bearing sulfide and the Mn-sulfide crystallized from a common FeS-rich melt. These data confirm the plausibility of partitioning potassium into an Fe-FeS melt.

In addition to documenting the chalcophilic behavior of potassium, data from the metallurgical systems discussed also provide evidence that partitioning K into sulfide melts may be a viable means of fractionating K and Na in the Earth. In both metallurgical systems discussed, K is several times more abundant in the sulfide mattes than Na.

(c) Meteoritic Evidence

Fuchs (1966) reported the discovery of djerfisherite, a potassium-iron sulfide, in two enstatite chondrites and one enstatite achondrite. El Goresy et al. (1971) reported the occurrence of djerfisherite in several more enstatite meteorites and also one occurrence in a sulfide nodule within an iron meteorite. In enstatite chondrites, djerfisherite occurs in the silicate matrix and is always associated with troilite; many grains of djerfisherite are associated with both troilite and kamacite. Troilite inclusions were observed in some grains. These observations suggest that djerfisherite may crystallize from an FeS-rich melt. In the Bishopville achondrite, a djerfisherite-troilite-kamacite inclusion was found in sodic plagioclase; this striking observation demonstrates the chalcophile behavior of potassium even in the presence of feldspar. Although oxygen fugacities in enstatite meteorites are somewhat lower than expected for a differentiating, approximately chondritic Earth, the occurrence of the potassium sulfide djerfisherite is significant because it documents the chalcophile behavior of potassium in meteoritic systems which have overall chemical compositions similar to the composition of the Earth.

Djerfisherite contains some sodium substituting for potassium; however, the maximum Na content measured by El Goresy et al. was less than 10% of the K content, and the Na content of many grains was below detection limits. Thus, these

meteoritic data, as well as the thermodynamic and metallurgical data discussed previously, demonstrate that K appears to be significantly more chalcophile than Na.

Shima and Hondo (1967) measured the K contents of component minerals of the Abee enstatite chondrite. They found 3.7% of the total K in oldhamite (CaS), and 3.1% in troilite (FeS). Oversby and Ringwood (1972) have argued that the amount of K observed in the Abee troilite places an upper limit of about 2.5% of the Earth's K in the core, since Abee has more FeS than the Earth's core, and the Earth is more oxidized than Abee. However, as discussed by Goettel and Lewis (1973), this argument is not valid because the Abee data represent low-temperature partitioning of potassium between solid silicates and solid FeS. The relevant partitioning for the Earth involves an Fe-FeS melt and solid silicates at temperatures several hundred degrees above the Abee equilibration temperature (Murthy and Hall, 1970; Lewis, 1971). Thus, the low-temperature partitioning of potassium between solid phases in Abee cannot be used to set an upper limit on the amount of potassium in the Earth's core.

(d) Experimental Results

Goettel (1972) investigated the partitioning of potassium between solid roedderite ($K_2Mg_5Si_{12}O_{30}$) and an Fe-FeS melt. Roedderite and merrihueite (the Fe analogue) are the only two silicates containing essential potassium which have been identified in chondrites; therefore, roedderite appears to be

a reasonable choice for one of the potassium-bearing phases in the early Earth. At 1030 ^{o}C, a K_2S/FeS weight ratio of (3.340±0.150) x 10^{-3} was measured. If the Earth has solar K/Si and S/Si ratios, then a K_2S/FeS weight ratio of about 9 x 10^{-3} would suffice to extract all of the Earth's potassium into the core. The potassium content of the Fe-FeS melt was found to increase significantly with increasing temperature. The oxygen fugacity is these experiments was somewhat below the iron-wüstite buffer, and thus compatible with the oxygen fugacity expected in the early, differentiating Earth. These data suggest the plausibility of partitioning a significant fraction of the Earth's potassium into Fe-FeS melts at the time of core formation. However, uncertainty about the identity of the K-bearing phases in the early Earth, and uncertainty about the effect of high pressures on potassium partitioning into Fe-FeS melts preclude direct application of these experimental results to estimate quantitatively the potassium content of the core.

Goettel (1975a, b) investigated the partitioning of potassium between solid potassium feldspar ($KAlSi_3O_8$) and Fe-FeS melts. Feldspar is the major potassium-bearing phase in chondrites (Shima and Honda, 1967), and feldspar is also the predicted potassium-bearing condensate in the chemical equilibrium model for the Earth. Therefore, feldspar is likely to be an important K-bearing phase in the early Earth.

Fe-FeS melts equilibrated with potassium feldspar contained 195 and 290 ppm K at 1030 and 1070 ^{o}C, respectively. This

sharp increase in K content of the Fe-FeS melt with increasing temperature is expected on thermodynamic grounds. ΔS for the reaction partitioning K from feldspar (where K is a major constituent) to an Fe-FeS melt (where K is in dilute solution) will be large, and therefore, K in the dilute solution (Fe-FeS melt) will be strongly favored with increasing temperature. Using the ideal dilute solution approximation, the experimental data may be extrapolated to higher temperatures. At 1500 ^{o}C, the calculated K content of an Fe-FeS melt equilibrated with potassium feldspar is 1900 or 2100 ppm, depending on whether the 1030 or 1070 ^{o}C data are extrapolated. Thus, if this rough extrapolation were valid, and if pure potassium feldspar were the major K-bearing phase in the early, differentiating Earth, virtually all of the Earth's potassium would be partitioned into Fe-FeS melts at temperatures above about 1500 ^{o}C, and thus extracted into the core.

However, pure potassium feldspar is probably not a realistic K-bearing phase for the early Earth. A more likely K-bearing phase is plagioclase feldspar with potassium feldspar in solid solution. If the composition of chondritic feldspar, $Ab_{82}An_{12}Or_{6}$ (Van Schmus and Ribbe, 1968), is adopted as a reasonable estimate of the feldspar composition in the early Earth, and if the assumption of ideal solution in the feldspar solution at the relevant temperatures above 1000 ^{o}C is made, then the activity of potassium feldspar in the early Earth will be equal to the mole fraction of about 0.06. With these

assumptions and the additional assumption of ideal dilute solution of K in Fe-FeS melts, the potassium content of an Fe-FeS melt equilibrated with plagioclase feldspar (activity of potassium feldspar equal to 0.06) may be calculated as a function of temperature from the experimental results on pure potassium feldspar. The calculated potassium contents of Fe-FeS melts equilibrated with plagioclase of this composition are 255 and 1580 ppm at 1500 and 2000 ^{o}C, respectively. If this extent of potassium partitioning into Fe-FeS melts were directly applicable to the core, these potassium contents would correspond to about 10 and 62%, respectively, of the Earth's total potassium content.

However, at the high pressures relevant to much of the mantle, plagioclase feldspar is not stable. The most likely high-pressure, potassium-bearing phases are a jadeite solid solution, or $KAlSi_3O_8$ in the hollandite structure (Ringwood et al., 1967). In either case, because of the limited solubility of K in jadeite, and the high K content of hollandite-structure $KAlSi_3O_8$, the activity of potassium is likely to be quite high. The potassium content of Fe-FeS melts equilibrated with one of these possible high-pressure K-bearing phases may thus be roughly equal to, or perhaps higher than, the rough estimates for K-bearing plagioclase solid solutions.

The absence of high-temperature, high-pressure partition coefficients for potassium partitioning between Fe-FeS melts and the likely high-pressure K-bearing silicate phases presently

precludes direct calculation of the potassium content of the Earth's core. However, these experimental data on the partitioning of potassium between Fe-FeS melts and solid feldspar suggest that a significant fraction, and possibly most, of the Earth's total potassium is likely to be partitioned into Fe-FeS melts and thus extracted into the core.

(e) Evidence Against Potassium in the Core

Oversby and Ringwood (1972, 1973) presented data on the partitioning of potassium between basaltic liquids and Fe-FeS melts, and argued against the hypothesis of potassium in the Earth's core. A detailed rebuttal to their arguments was presented by Goettel and Lewis (1973); however, for the present paper it suffices to outline two major points. First, the chemical and physical conditions which are relevant to the partitioning of potassium into the core are the conditions existing during the primary differentiation of the Earth into metal/sulfide core and silicate mantle, and not the conditions presently existing in the crust or upper mantle. Therefore, experiments involving differentiated, basaltic material may not be relevant to the partitioning of potassium at the time of core formation. The basaltic composition used by Oversby and Ringwood contained 13% Al_2O_3. This proportion of Al_2O_3 greatly exceeds the amount of Al_2O_3 expected in an Earth with the solar or chondritic Al/Si ratio ($< 2\%$ Al_2O_3), and may bias the experiment in favor of alkali alumino-silicate formation.

Second, Oversby and Ringwood examined the partitioning of potassium between an Fe-FeS melt and a silicate liquid. As emphasized by Murthy and Hall (1970, 1972), the Fe-FeS eutectic is likely to be the first melt formed in the early Earth, and the eutectic temperature increases only slowly with pressure (Brett and Bell, 1969; Usselman, 1975a,b). At a pressure of even a few tens of kilobars, an Fe-FeS melt will form at temperatures several hundred degrees below the silicate solidus. Therefore, experiments relevant to the partitioning of potassium into the core are likely to involve solid silicates rather than silicate liquids. Hall and Murthy (1971) noted that K, Rb, and Cs are selectively enriched in the liquid phase during partial melting of silicates because their large ionic size makes them incompatible in many mineral structures. These authors suggested that this ionic size incompatibility may be a major factor in the partitioning of these elements into Fe-FeS melts at the time of core formation.

Seitz and Kushiro (1974) conducted high-pressure partial melting experiments on samples of the Allende Type 3 carbonaceous chondrite which were partially reduced before the experiments. The compositions of the co-existing sulfide and silicate melts formed at 1350 ^{o}C and 20 kilobars were analyzed: the silicate melt contained 0.1% K_2O, while K in the sulfide melt was below the detection limit of 0.01%. However, as discussed in the preceeding paragraph, experiments relevant to potassium in the Earth's core are likely to involve partitioning

of potassium between Fe-FeS melts and solid silicates. In a subsolidus silicate assemblage, potassium will be concentrated in K-rich phases (e.g. feldspar) in which the mole fraction of K_2O is likely to be one or perhaps even two orders of magnitude greater than in the bulk liquid above the liquidus temperature. For this reason, Fe-FeS melts equilibrated with a subsolidus silicate assemblage containing a K-rich phase may be expected to have much higher K contents than Fe-FeS melts equilibrated with silicate assemblages above the liquidus temperature. Thus, it appears that these experimental data above the liquidus temperature may only be of marginal significance with respect to potassium partitioning between core-forming Fe-FeS melts and solid mantle silicates.

5. IMPLICATIONS

(a) Geochemical Implications

Two distinct periods in the geochemical differentiation of the Earth must be considered: (1) the primary differentiation into metal/sulfide core and silicate mantle, and (2) the subsequent differentiation of the silicate mantle. The geochemical behavior of many elements, most notably potassium, may be markedly different in these two differentiation processes. Geochemical data such K/U ratios, Sr isotope data, and K-Rb-Ar data must be interpreted in the context of the two-stage differentiation history of the Earth. Inferences drawn from the geochemistry of the crust and upper mantle must be extrapolated very cautiously if they are to be extended to the entire mantle or to the entire Earth.

Many elements with significantly chalcophilic or siderophilic properties will be preferentially partitioned into the Fe-FeS core at the time of core formation very early in Earth history. The elements partitioned into the core may include K, Rb, and Cs, as well as many other elements such as Ni, Co, Pt-group metals, Au, Ag, Pb, Cu, Cd, Bi, etc. A major consequence of the partitioning of these elements into the core is that the composition of the Earth may be very similar to the composition of ordinary chondrites; or in the context of the chemical equilibrium model, that the Earth may have the solar proportions of nearly all of the rock forming elements including refractories (Al, Ca, Ti, Ba, Sr, U, Th, rare earths,

etc.), Fe, Ni, Mg, Si, S, Na, and K.

In the absence of high-temperature, high-pressure data on the partitioning of potassium between Fe-FeS melts and the relevant high-pressure, potassium-bearing silicate phases, it is not possible to calculate directly the potassium content of the Earth's core. Geochemical data such as K/U ratios, Rb-Sr isotope data, K/Rb ratios, and K-Rb-Ar data suggest that the crust and upper mantle contain no more than about 10 to 20% of the total potassium in an Earth with the solar or chondritic K/Si ratio. Therefore, the conclusion that the Earth does have the solar K/Si ratio requires that about 80 to 90% of the Earth's total potassium content must be in the lower mantle or in the core.

Thermodynamic data on the stability of K_2S, and data on the occurrence of potassium in sulfide phases in meteorites and in metallurgical systems, suggest the plausibility of partitioning potassium into Fe-FeS melts under the moderately reducing conditions existing at the time of core formation in the Earth. The experimental data, particularly on potassium partitioning between feldspar and Fe-FeS melts, are somewhat more directly applicable to the Earth. These data suggest that a significant fraction, and perhaps most, of the 80 to 90% of the Earth's potassium which the present model requires to be deep in the Earth, may be in the core. The thermodynamically rigorous statement that high temperature will favor potassium in dilute solution in Fe-FeS melts as opposed to K-rich silicates, seems

to require that at least a few percent, if not more, of the Earth's total potassium content will be in the core. Even a few percent of the Earth's potassium in the core would have important geophysical implications.

(b) Geophysical Implications

The presence of sulfur and potassium in the Earth's core may eliminate the need for the very rapid accretion and the very high-temperature evolution of the Earth which were previously thought necessary to melt Fe-Ni alloy to form the core, and to volatilize elements such as sulfur and potassium. The Fe-FeS eutectic temperature is so low (988 ^{o}C) and increases so slowly with pressure that core formation could occur very early in Earth history, even if the Earth retained very little of its accretional gravitational potential energy. At high pressures, the solidus temperature for mantle silicates is so much higher than the Fe-FeS eutectic temperature that core core formation may not necessitate large-scale mantle melting.

The relatively slow, low-temperature accretion and low-temperature core formation postulated by this model necessitate a substantial revision of existing thermal history models for the Earth. Also, most previous thermal history calculations have assumed that K, U, and Th are geochemically coherent during the Earth's differentiation; partitioning of K into the core results in a major redistribution of the radiogenic heat sources in the Earth. One consequence of the postulated solar K/Si ratio for the Earth, and the short half life of ^{40}K is that

a large fraction of the total radiogenic heat production of the Earth is released early in Earth history.

Decay of ^{40}K in the core may provide a major internal heat source which could drive core convection. For a K content of 0.1%, the rate of heat production is about 10^{13} joules/sec (Verhoogen, 1973); this K content is about 40% of the total K in an Earth with the solar K/Si ratio. Verhoogen noted that the rate of heat production by ^{40}K is likely to be several orders of magnitude greater than the rate of dissipation of magnetic energy in the core. Even if the efficiency of conversion of thermal to magnetic energy is very low, it appears that there may be sufficient energy from ^{40}K to maintain the geomagnetic field. Heat from ^{40}K in the core will produce a large heat flux through the mantle; this heat is a possible energy source for mantle convection and sea-floor spreading.

Despite the high heat flux through the lower mantle which is likely from ^{40}K in the core, Verhoogen suggested that the lowest 100 or 150 kilometers of the mantle (layer D") may be stabilized by a steep density gradient and may not convect. The recent data of Mao and Bell (1972) and Mao (1973, 1974) indicate that the thermal conductivity of silicates may increase by as much as several orders of magnitude at high pressures. These data suggest an interesting, but rather speculative, hypothesis: despite the probably large heat flux from the core, the entire lower mantle may not convect. From simple geometric considerations, the heat flux per unit surface area in the

mantle will decrease as the square of the distance from the core/mantle interface. The data of Mao and Bell suggest that the thermal conductivity of the mantle may decrease more rapidly with distance from the core/mantle boundary than the heat flux. The transition between the lower, possibly non-convecting mantle, and the upper, convecting mantle could be at the depth where the thermal conductivity has become low enough for the adiabatic gradient to be exceeded. Because of the short half life of ^{40}K, the heat flux through the lower mantle from the core may be expected to decrease with time. Therefore, the depth in the upper mantle to which convection extends may be decreasing with time. If this speculative hypothesis is valid, it may have important implications for the differentiation and evolution of the mantle, and for paleo-sea-floor spreading, since the depth and rate of upper mantle convection will be strongly time-dependent. Interestingly, Sun and Hanson (1975) have recently proposed on purely geochemical grounds (trace element, and Sr and Pb isotope data on alkali basalts and Precambrian tholeiites), that the depth to which upper mantle convection extended was greater in the Precambrian than at present.

6. SUMMARY

All apparently viable models for the origin and composition of the Earth -- including the chemical equilibrium model, the chondritic model, mixtures of meteorites models, and the multi-component mixing model -- require the Earth to have an Fe-FeS core and the full, or nearly full, solar (or chondritic) K/Si ratio. K/U ratios in terrestrial rocks, Rb-Sr isotope data, and K-Rb-Ar data demonstrate convincingly that the Earth's crust and upper mantle contain only about 10 to 20% of the total potassium in an Earth with the solar K/Si ratio. Therefore, the present model requires that about 80 to 90% of the Earth's total potassium must be in the deep interior -- either in the lower mantle or in the core.

Data on the stability of K_2S, and the occurrence of potassium in sulfide phases in meteorites and in metallurgical systems suggest the plausibility of partitioning potassium into Fe-FeS melts. Experimental data on the partitioning of potassium between solid silicates and Fe-FeS melts are more directly applicable to the Earth, and suggest the possibility of extracting a significant fraction of the Earth's total potassium into the core. The absence of high-temperature, high-pressure data on the partitioning of potassium between Fe-FeS melts and the relevant high-pressure potassium-bearing silicates precludes direct calculation of the probable potassium content of the core. However, the present data, and the thermodynamically rigorous statement that high temperature will favor potassium in dilute

solution in Fe-FeS melts at the expense of potassium in K-rich silicate phases seem to require at least a few percent of the Earth's potassium to be in the core, and quite possibly, much more than a few percent.

Decay of ^{40}K in the core is likely to be a significant heat source. This energy is a plausible means of driving core convection to maintain the geomagnetic field. The heat flux from the core may exceed the flux which can be conducted through the mantle, and thus, ^{40}K in the core is a possible energy source for mantle convection and sea-floor spreading.

Two important areas for future research are evident:

1) experimental investigation at high temperatures and high pressures of potassium partitioning between Fe-FeS melts and the likely high-pressure K-bearing phases, hollandite-structure $KAlSi_3O_8$ or jadeite solid solutions, and

2) revision of thermal history models for the Earth to account for the relatively slow, low-temperature accretion, low-temperature core formation, and incorporation of ^{40}K into the core which are postulated by the present model.

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Part II

PARTITIONING OF POTASSIUM BETWEEN SOLID SILICATES AND FE-FeS MELTS

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Abstract

Partitioning experiments were conducted in which Fe-FeS melts were equilibrated with solid, potassium-bearing silicates, including roedderite, potassium feldspar, and bulk samples of the Forest City chondrite. Fe-FeS melts equilibrated with roedderite at 1030 ^{o}C contained 1170 ppm K. Fe-FeS melts equilibrated with potassium feldspar at 1030 and 1070 ^{o}C contained 195 and 290 ppm K, respectively. Fe-FeS melts equilibrated with Forest City at 1030 and 1070 ^{o}C contained about 10 ppm K, but these Forest City results are of marginal statistical significance. Rough extrapolation of the potassium feldspar data to potassium-bearing plagioclase feldspar at higher temperatures suggests that a significant fraction of the Earth's total potassium may be partitioned into Fe-FeS melts at temperatures above about 1500 ^{o}C, if plagioclase feldspar were a major potassium-bearing phase in the early Earth. The absence of high-pressure, high-temperature potassium partitioning data precludes direct calculation of the probable potassium content of the Earth's core. However, the present data, and the fact that high temperature will favor potassium in dilute solution in Fe-FeS melts at the expense of potassium in potassium-rich silicates, suggest that at least a few percent, and perhaps much more, of the Earth's total potassium content is likely to be in the core.

Introduction

The geochemical arguments for potassium in the Earth's core are based on the chalcophile behavior of potassium during the process of core formation (Lewis, 1971; Hall and Murthy, 1971; Goettel, 1972; Goettel and Lewis, 1973). Potassium, as well as many other chalcophile and siderophile elements, has been postulated to be partitioned into Fe-FeS melts, and thus extracted into the core at the time of core formation very early in Earth history. Therefore, experiments relevant to the distribution of potassium between the Earth's core and mantle involve the partitioning of potassium between silicates and Fe-FeS melts. The melting temperatures of silicates increase sharply with increasing pressure; however, the eutectic temperature in the Fe-S system increases only slowly with pressure (Brett and Bell, 1969; Usselman, 1975a, b). Therefore, for nearly the entire range of pressures existing in the mantle, the relevant potassium partitioning is likely to be between solid silicates and Fe-FeS melts. A review of the abundance of potassium in the Earth, and the evidence for potassium in the Earth's core has recently been presented by Goettel (1975).

Three series of partitioning experiments in which an Fe-FeS melt was equilibrated with a solid, potassium-bearing silicate were conducted. The silicates chosen for investigation were roedderite, potassium feldspar, and bulk samples of the Forest City chondrite. The bulk composition of the Earth appears to be quite similar to the composition of ordinary chondrites

(Taylor,1964a, b; Lewis, 1972, 1973); therefore, the potassium-bearing phases in ordinary chondrites may be plausible choices for the potassium-bearing phases in the early, differentiating Earth. Roedderite ($K_2Mg_5Si_{12}O_{30}$) was chosen as a potassium-bearing phase because roedderite and merrihueite (the Fe analogue) are the only silicate minerals containing essential potassium which have been identified in chondrites. Potassium feldspar was chosen as a potassium-bearing phase because the feldspar phases in ordinary chondrites appear to contain most of the alkali metals present (Shima and Honda, 1967). Direct calculations on the equilibrium condensation sequence in the solar nebula (Lewis, 1972, 1973) provide further justification for the choice of potassium feldspar: feldspar is the major potassium-bearing condensate. Partitioning experiments involving bulk samples of the Forest City chondrite were undertaken as a first-order approximation to the actual phase assemblage present in the early, differentiating Earth. The potassium content of Forest City is about 800 ppm (Goles, 1971); most of this potassium is probably in the plagioclase feldspar.

Most of the partitioning of potassium between Fe-FeS melts and silicate phases during core formation probably occurred at high pressures. However, the author chose to establish firmly the low pressure partitioning behavior before attempting to investigate the effect of pressure. Therefore, all of the experiments conducted in this study were done in evacuated, fused quartz capsules, rather than at high pressures.

Experimental Methods

Experimental runs containing Fe, FeS, and roedderite, potassium feldspar, or Forest City material were made at 1030 and 1070 ^{o}C. Roedderite runs were made in evacuated, fused quartz capsules; potassium feldspar and Forest City runs were made in Fe foil capsules sealed in evacuated, fused quartz. Excess potassium (as $KFeS_2$) was added to the initial sulfide phase of some of the runs to check the attainment of equilibrium. All runs were terminated by rapid quenching in cold water; quench times were approximately five seconds.

Roedderite, Fe, and FeS for these experiments were prepared as described by Goettel (1972). Potassium feldspar was prepared by heating cleaned, hand-picked, transparent cleavage fragments of Amelia (Virginia) albite for 21 days at 1050 ^{o}C, and then twice ion-exchanging the resulting high albite in KCl for 15 hours at 900 ^{o}C. The resulting potassium feldspar was analyzed using the x-ray diffraction techniques and data of Orville (1967) and Wright (1968); the potassium feldspar was determined to be high sanidine of composition Or_{99} to Or_{100}. A fresh 25 gram piece of the Forest City chondrite was prepared by removing the fusion crust with a steel abrasion bit, crushing in a steel percussion mortar, and pulverizing in a hardened steel ball-mill pulverizer; possible adsorbed water was removed by heating at 110 ^{o}C in nitrogen. $KFeS_2$ was prepared using the method of Deutsch and Jonassen (1960).

Run products were analyzed by electron microprobe. In

preparation for analyses, run products were mounted in epoxy. Coarse grinding was done dry; samples were rinsed in reagent grade xylene between successive grit sizes. Final polishing was done with alumina grit using xylene as a polishing fluid. Xylene was chosen as a polishing fluid because preliminary experiments indicated that the use of water resulted in considerable leaching of alkalis from the quenched Fe-FeS melts.

Run products were analyzed using an automated Materials Analysis Company electron microprobe (take-off angle = 38.5^{o}) operated at an accelerating potential of 15 kilovolts. For most analyses, a counting time of 100 seconds, a beam current of .1000 microamps, and a beam diameter of 25 microns were utilized. The long counting time and high beam current were chosen to maximize the count rate and thus improve the precision of analyses of elements present in low concentrations. The 25 micron beam diameter was chosen to average over small-scale sample inhomogeneities, and also to reduce the beam intensity per unit surface area and thus reduce possible volatility problems for Na and K analyses. Volatility of Na and K was checked by repeated analyses of the same spot; no decrease in Na or K count rate in either alkali feldspar or quenched Fe-FeS melts was observed even when 15 successive 100 second counts were taken at the same spot. During regular analyses of the run products, Na and K background and peak counts were completed in the first 200 seconds of an analysis; therefore, volatility of Na and K was found to be negligible.

The quenched Fe-FeS melts from all of the experimental runs were analyzed for Fe, S, Si, and K; in addition, some of the Forest City runs were also analyzed for Na and Ni. Troilite or quenched Fe-FeS melts prepared from high purity reagents were used as standards for the Fe and S analyses. A Ni-bearing pyrrhotite was used as the Ni standard. Background offsets and background factors for Fe, S, and Ni were determined from multiple step scans around the peak positions.

An initial attempt to use a prepared Fe-FeS melt with K added as $KFeS_2$ for a K standard was abandoned because of inhomogeneity in the K distribution. Thereafter, an orthoclase glass was used as the K and Na standard. SiO_2 was used as the Si standard. In analyses of elements present in low concentrations, the peak to background ratios are low, and therefore, errors in choosing background factors can produce appreciable errors in the analyses. Optimum offsets for measuring the backgrounds for K, Na, and Si were chosen from multiple, detailed step scans around the peak positions in an Fe-FeS matrix. The Si background was found to be very smooth; the background factor was determined by curve fitting of step scans around the Si peak position in an Fe-FeS matrix. K and Na background factors were determined by direct measurement of the count rates at the background offset and peak positions in a K- and Na-free Fe-FeS matrix prepared from high purity reagents. This is the most accurate method: the background count rates directly at the peak positions were measured in a

K- and Na-free matrix with composition identical to the matrix in the experimental runs. If any K or Na were present in the prepared pure Fe-FeS, then the error introduced into the analyses would result in an underestimate of the actual K or Na content of the unknowns.

A modified version of the computer program developed by Boyd et al. (1968) was used to correct the microprobe data for differences in composition between the standards and unknowns. Despite the rather large composition differences between some of the standards and unknowns, the computed corrections were quite small; e.g. about 16% for Si, and about 7% for K. As a check on the accuracy of the correction program, standards of known composition were analyzed using other standards of greatly different composition as standards. Fe in cossyrite was analyzed using FeS as the standard, and Si in orthoclase was analyzed using SiO_2 as the standard. In both cases, the correction program corrected the measured concentrations to within 1% of the actual values. Therefore, it is concluded that the differences in composition between some of the standards and unknowns probably do not introduce significant errors into the analytic results.

Results

Results of the roedderite, potassium feldspar, and Forest City experiments are reported in Tables 1-5. The principle uncertainty in the analytic results is probably due to sample inhomogeneity, rather than to the errors associated with individual analyses. At a concentration of 200 ppm, for example, the counting statistics errors associated with an individual analysis are only 17% for K, and 12% for Si. At higher concentrations, or for multiple analyses, the counting statistics errors are substantially smaller.

Results of the roedderite-Fe-FeS experiments (Table 1) indicate a mean Si content of 320 ppm and a mean K content of 1170 ppm in the quenched Fe-FeS melt phase. For comparison, the Fe-FeS microprobe standard which was prepared from high purity reagents in an evacuated fused quartz capsule contained 420 ppm Si. In the roedderite experiments, the mean K/Si weight ratio in the quenched Fe-FeS melt was 3.66, but K/Si ratios as high as 11 were observed. The K/Si ratio of roedderite is only 0.232. Therefore, these data clearly confirm the presence of K in the Fe-FeS melts; the K values in the Fe-FeS melts cannot be attributed to roedderite contamination of the sulfide phase.

Considerable inhomogeneity in the K distribution within the quenched Fe-FeS melt was noted; K concentrations as high as 3640 ppm were observed. The high concentrations of K appear to be located primarily at grain boundaries. Two possible explanations of the inhomogeneous K distribution are:

Table 1

Roedderite-Fe-FeS Experiments (1030 °C, 133 hours)

Run #	Run Composition (grams)			Analysis of Fe-FeS Melts*			
	Roedderite	Fe	FeS	Fe	S	Si	K
43	.0518	.0528	.1011	69.42	29.18	350	1110
44	.0493	.0502	.0963	68.13	29.82	290	1230

*Fe, S in percent

Si, K in ppm

Table 2

Potassium Feldspar-Fe-FeS Experiments (1030 °C, 133 hours)

	Run Composition (grams)				Analysis of Fe-FeS Melts*			
Run #	K-feldspar	Fe	FeS	$KFeS_2$	Fe	S	Si	K
35	.0499	.0751	.1003	none	69.70	28.86	450	190
36	.0504	.0759	.1013	none	70.91	29.36	500	200
39	.0496	.0773	.0990	.0014	see note below table			
40	.0492	.0767	.0982	.0014	68.47	29.26	510	610

*Fe, S in percent

Si, K in ppm

Run 39: no analyses reported because of poorly exposed surfaces in the mounted run products

Table 3

Potassium Feldspar-Fe-FeS Experiments (1070 °C, 133 hours)

	Run Composition (grams)				Analysis of Fe-FeS Melts*			
Run #	K-feldspar	Fe	FeS	$KFeS_2$	Fe	S	Si	K
37	.0508	.0765	.1021	none	69.60	28.66	580	260
38	.0456	.0687	.0917	none	70.16	28.36	600	320
41	.0490	.0764	.0979	.0014	68.32	29.65	410	430
42	.0500	.0779	.0998	.0014	69.92	29.72	370	430

*Fe, S in percent

Si, K in ppm

Table 4

Forest City-Fe-FeS Experiments (1030 °C, 136 hours)

Run #	Run Composition (grams) Forest City	Fe	FeS	$KFeS_2$
27	.2132	.0833	.1086	none
28	.2041	.0797	.1040	none
31	.2182	.0820	.1089	.0020
32	.2150	.0808	.1073	.0020

Average Composition of Quenched Fe-FeS Melts

Fe = 69.80%

S = 30.15%

Ni = 380 ppm

Si = 370 ppm

Na = 20 $\pm$18 ppm

K = 10 $\pm$9 ppm

Table 5

Forest City-Fe-FeS Experiments (1070 °C, 136 hours)

	Run Composition (grams)			
Run #	Forest City	Fe	FeS	$KFeS_2$
29	.2239	.0874	.1140	none
30	.2351	.0918	.1198	none
33	.2208	.0829	.1102	.0021
34	.2223	.0835	.1109	.0021

Average Composition of Quenched Fe-FeS Melts

Fe = 70.33

S = 29.57

Si = 490 ppm

K = 10 $\pm$9 ppm

Na = 0 ppm

1) presence of a separate K-rich sulfide melt coexisting at 1030 ^{o}C with an Fe-FeS melt containing less K, or 2) quench effects -- exclusion of K from nucleating FeS grains and thus concentration of K at grain boundaries, or exsolution of a K-rich phase during quench. The first explanation seems unlikely, since the total amount of K present in the sulfide melt is small; however, no solubility data exist for the FeS-K_2S system. The second explanation, quench effects, seems more plausible. Goettel (1972) conducted similar roedderite-Fe-FeS experiments at 1030 ^{o}C; he found that appreciable diffusion of K from Fe-FeS melts into coexisting silicates could occur if the quench was not rapid enough.

The inhomogeneous K distribution within quenched Fe-FeS melts from these roedderite experiments makes it difficult to obtain an accurate analysis of the bulk K content. The microprobe data reported in Table 1 are about a factor of two less than the K values reported previously by Goettel for similar roedderite-Fe-FeS experiments. In the previous experiments, atomic absorption spectrometry was used to determine the bulk K content of the quenched Fe-FeS melts. In the microprobe analyses, large areas of Fe-FeS melt were deliberately chosen for analysis to minimize problems such as accidentally analyzing part of a silicate grain. Therefore, areas near silicate/Fe-FeS boundaries (with possibly higher than average K contents) were preferentially excluded from the microprobe analyses. A reasonable interpretation of the factor

of two difference between the atomic absorption and microprobe data is that the microprobe data are too low because they did not adequately sample the inhomogeneous K distribution in the quenched Fe-FeS melts.

Results from the potassium feldspar-Fe-FeS experiments are reported in Tables 2 and 3. Experiments were run with and without the addition of excess K (as $KFeS_2$) to the initial charge. Experiments without excess K added show a mean K concentration in the quenched Fe-FeS melt of 195 ppm at 1030 ^{o}C (Runs 35 and 36), and 290 ppm at 1070 ^{o}C (Runs 37 and 38). The K distribution in the quenched Fe-FeS melt appeared to be rather homogeneous; no marked enrichment in K at grain boundaries was noted. At this level of K content of the Fe-FeS melts, exsolution during quench may not be significant.

Results of the experiments in which excess K was added show higher K concentrations in the Fe-FeS melts than the experiments without excess K added. This effect is seen both at 1030 ^{o}C (Run 40), and at 1070 ^{o}C (Runs 41 and 42). One interpretation of the higher K values obtained in the experiments in which K was added is that equilibrium was not attained. Departures from equilibrium would mean that the K values in the quenched Fe-FeS melts would be too low for those experiments without excess K added, and too high for those experiments with excess K added. However, a second interpretation of these data is possible. Potassium feldspar is the only silicate phase present in these experiments; it may be very difficult for

excess K in the Fe-FeS melt to partition into the feldspar, since there is no room in the crystal structure for extra potassium ions. Partitioning of infinitesmal amounts of excess K into the potassium feldspar could raise the activity of K sufficiently that the high K values in experiments with excess K could in fact be equilibrium values for experiments with excess K added. In this case, the K values from the experiments without excess K added could still be low if complete equilibrium were not attained, but the departure from equilibrium, if any, need not be large.

Results of the Forest City chondrite experiments are reported in Tables 4 and 5. The Na and K concentrations in the quenched Fe-FeS melts are reported as averages for the 1030 and 1070 ^{o}C experimental runs, because the concentrations are too low for individual run analyses to be statistically significant. Runs in which excess K was added to the charge do not appear to have higher K values in the Fe-FeS melts. Therefore, it appears that equilibrium was attained in these experiments. The average K content of the Fe-FeS melts is 10 ppm for both the 1030 and 1070 ^{o}C experiments. However, the counting statistics error (one standard deviation) for this low concentration is about 9 ppm; therefore, these Forest City results are only of marginal significance. At the 90% confidence limit, these results are not statistically significant.

The composition of the Forest City feldspar is approximately $Ab_{82}An_{12}Or_{6}$ (Van Schmus and Ribbe, 1968). At

temperatures above about 800 ^{o}C, alkali feldspar solid solutions appear to approach ideality (Waldbaum and Thompson, 1969). If the assumption of ideal solution in the plagioclase feldspar is made for temperatures above 1000 ^{o}C, then the activity of potassium feldspar in the Forest City feldspar may be estimated as being equal to the mole fraction of about 0.06. Therefore, the potassium content of Fe-FeS melts equilibrated with Forest City feldspar should be about 16 times less than Fe-FeS melts equilibrated with pure potassium feldspar. Using the experimental data on pure potassium feldspar, the calculated K content of Fe-FeS melts equilibrated with Forest City feldspar is about 12 ppm at 1030 ^{o}C, and about 18 ppm at 1070 ^{o}C. The experimental results for Forest City are roughly concordant with these calculated values, but as noted above, the Forest City experimentally determined K values are too low to be statistically significant.

Effect of Oxygen Fugacity on Potassium Partitioning between Silicates and Fe-FeS Melts

Potassium partitioning between silicates and Fe-FeS melts is somewhat dependent on oxygen fugacity. The most straightforward way to examine the effect of f_{O_2} is to consider the reaction:

$$K_2S + \tfrac{1}{2}O_2 = K_2O + \tfrac{1}{2}S_2 \qquad (1)$$

For this reaction,

$$\frac{a_{K_2O}}{a_{K_2S}} = K_1\frac{f_{O_2}^{\frac{1}{2}}}{f_{S_2}^{\frac{1}{2}}}, \qquad (2)$$

where K_1 is the equilibrium constant for reaction (1). The sulfur fugacity, f_{S_2}, is very nearly buffered by the reaction:

$$Fe + \tfrac{1}{2}S_2 = FeS, \qquad (3)$$

since $a_{Fe} = 1$ (pure Fe present), and a_{FeS} (in Fe-FeS melt) is large and nearly constant. Actually, a_{FeS} will decrease slightly with increasing f_{O_2}, since a_{FeO} in the Fe-FeS melt will increase with f_{O_2}. However, for low f_{O_2}, the changes in a_{FeS} are very small, and f_{S_2} is effectively buffered by reaction (3). Therefore,

$$\frac{a_{K_2O}}{a_{K_2S}} \propto f_{O_2}^{\frac{1}{2}}, \qquad (4)$$

at a given temperature. Thus, <u>if</u> a_{K_2O} were constant, a_{K_2S} would be proportional to $f_{O_2}^{\frac{1}{2}}$. However, more realistically, a_{K_2O} will simultaneously increase with increasing f_{O_2}. If it is assumed that a_{K_2O} increases at the same rate that a_{K_2S} is decreasing, then a_{K_2S} will be proportional to $f_{O_2}^{\frac{1}{4}}$.

Thus, a 4 orders of magnitude increase in f_{O_2} would only decrease a_{K_2S} by 1 order of magnitude. Over moderate concentration ranges, the activity coefficients for K_2O and K_2S are likely to be relatively constant. Thus, the potassium content of an Fe-FeS melt will be a function of f_{O_2}, with nearly the same f_{O_2} dependance as estimated for a_{K_2S}.

In the experimental potassium feldspar-Fe-FeS runs, pure Fe was always present, so the oxygen fugacity will be governed by the activity of FeO in the system. If the assumption is made that negligible amounts of FeO will enter the feldspar, then FeO will be primarily in solution in the Fe-FeS melt. From the reaction:

$$FeS + K_2O = FeO + K_2S, \qquad (5)$$

it is evident that one mole of FeO will be produced for each mole of K_2S. At 1030 ^{o}C, the potassium content of the Fe-FeS melt, 195 ppm, implies a mole fraction of FeO of 2×10^{-4} in the Fe-FeS melt. If the assumption of ideal solution is made, a_{FeO} may be estimated as 2×10^{-4}. Therefore, the data of Robie and Waldbaum (1968) for the reaction:

$$Fe + \tfrac{1}{2}O_2 = FeO, \qquad (6)$$

may be used to estimate the f_{O_2} in the experimental runs. At 1030 ^{o}C (1300 ^{o}K), the calculated f_{O_2} is 3×10^{-23}.

In the early Earth at the time of core formation, f_{O_2} will be governed by a metal/silicate assemblage in which metallic iron ($a_{Fe} \sim 1$) coexists with FeO-bearing silicates. If olivine of composition $Fo_{90}Fa_{10}$ is chosen as an approximation

for the major FeO-bearing silicate in the early Earth, then the data of Larimer (1968) on f_{O_2} for coexisting metal/olivine assemblages may be used to estimate the f_{O_2} relevant to the Earth at the time of core formation. At 1030 ^{o}C, for comparison to the experimental runs, the calculated f_{O_2} for a Fe metal/olivine ($Fo_{90}Fa_{10}$) assemblage is 10^{-23}.

Therefore, the estimated f_{O_2} for the experimental potassium feldspar-Fe-FeS runs is in very good agreement with the f_{O_2} expected in the early Earth, for the same temperature. Actually, the estimated experimental f_{O_2} is likely to be lower than the actual experimental f_{O_2}; because the experimental f_{O_2} is so small, any additional FeO in the charge from water absorption or oxidation of Fe will substantially raise the f_{O_2}. Thus, it appears that application of the experimental data on potassium partitioning between potassium feldspar and Fe-FeS melts to the early Earth will not be significantly in error, at least with respect to the effect of oxygen fugacity. In fact, the extent of potassium partitioning into Fe-FeS melts in the early Earth may be underestimated, if the experimental f_{O_2} actually was higher than estimated.

Implications

The roedderite-Fe-FeS experiments presented in this study are consistent with the previous conclusions of Goettel (1972). Substantial amounts of K were contained in the Fe-FeS melt equilibrated with solid roedderite. To the extent that roedderite may be a significant potassium-bearing phase in the early Earth, these results suggest that a substantial fraction of the Earth's potassium is likely to be partitioned into Fe-FeS melts, and thus extracted into the core.

However, the potassium feldspar results are potentially more significant that the roedderite results because feldspar is the major potassium-bearing phase in chondrites (Shima and Honda, 1967), and feldspar is the major potassium-bearing condensate in the chemical equilibrium model for condensation of planetary constituents from the solar nebula (Lewis, 1972, 1973). Therefore, feldspar is likely to be an important potassium-bearing silicate in the early, differentiating Earth.

The potassium content of Fe-FeS melts equilibrated with potassium feldspar increased from 195 ppm at 1030 ^{o}C to 290 ppm at 1070 ^{o}C. This sharp increase in the K content of Fe-FeS melts with increasing temperature is expected on thermodynamic grounds. ΔS for the reaction partitioning potassium from feldspar (where K is a major constituent) to an Fe-FeS melt (where K is in dilute solution) will be large, and therefore, potassium in the dilute solution (Fe-FeS melt) will be strongly favored with increasing temperature. The temperature dependance

determined experimentally is in good agreement with the temperature dependance expected for ideal solubility of a fixed composition solute. If ideal solubility (Castellan, 1971) is assumed, potassium in an Fe-FeS melt equilibrated with potassium feldspar increases with temperature as

$$\ln X_{T_2} = \frac{T_1}{T_2} \ln X_{T_1},$$

where X_{T_1} and X_{T_2} are the mole fractions of K in Fe-FeS at temperatures T_1 and T_2, respectively. This ideal solubility approximation was used to extrapolate the experimental data to higher temperatures.

At 1500 ^{o}C, the calculated K content of an Fe-FeS melt equilibrated with potassium feldspar is 1900 or 2100 ppm, depending on whether the 1030 or 1070 ^{o}C data are extrapolated. The bulk potassium content of the Earth is about 800 ppm in either the chondritic (Taylor, 1964a,b) or chemical equilibrium (Lewis, 1972, 1973) models for the Earth. Thus, if this rough extrapolation were valid, and if pure potassium feldspar were the major potassium-bearing phase in the early Earth, then virtually all of the Earth's potassium would be partitioned into Fe-FeS melts at temperatures above about 1500 ^{o}C, and thus extracted into the core.

However, pure potassium feldspar is probably not a realistic K-bearing phase for the early Earth. A more likely K-bearing phase is plagioclase feldspar with potassium feldspar in solid solution. If the composition of chondritic feldspar, $Ab_{82}An_{12}Or_{6}$ (Van Schmus and Ribbe, 1968), is adopted as a

Table 6

Estimated Potassium Contents of Fe-FeS Melts Equilibrated with Plagioclase Feldspar with the Activity of Potassium Feldspar Equal to 0.06

T (^{o}C)	K in Fe-FeS Melt (ppm)	Percent of Earth's Total[1] K in Fe-FeS Melt
1500	255	10
1600	400	15
1700	590	23
2000	1580	61

[1]Earth with the solar or chondritic K/Si ratio.

reasonable estimate of the feldspar composition in the early Earth, and if the assumption of ideal solution in the feldspar at the relevant temperatures above 1000 ^{o}C is made, then the activity of potassium feldspar in the early Earth will be equal to the mole fraction of about 0.06. With the additional assumption of ideal solubility of K in Fe-Fes melts, the potassium content of an Fe-FeS melt equilibrated with plagioclase feldspar (activity of potassium feldspar equal to 0.06) may be calculated as a function of temperature from the experimental results on pure potassium feldspar. Results of this calculation are shown in Table 6. This extrapolation suggests that even if the activity of potassium feldspar in the early Earth is as low as 0.06, Fe-FeS melts at temperatures above about 1500 ^{o}C will contain a significant fraction of the Earth's total potassium content.

However, at the high pressures relevant to much of the mantle, plagioclase feldspar is not stable. The most likely high-pressure, potassium-bearing phases are a jadeite solid solution, or $KAlSi_3O_8$ in the hollandite structure (Ringwood et al., 1967). In either case, because of the limited solubility of potassium in jadeite, and the high potassium content of hollandite-structure $KAlSi_3O_8$, the activity of potassium is likely to be quite high. The potassium content of Fe-FeS melts equilibrated with one of these possible high-pressure potassium-bearing phases may thus be roughly equal to, or perhaps higher than, the rough estimates for potassium-bearing plagioclase

solid solutions.

The absence of high-temperature, high-pressure data on potassium partitioning between Fe-FeS melts and the likely high-pressure, potassium-bearing silicate phases presently precludes direct calculation of the probable potassium content of the Earth's core. However, the present data, and the fact that high temperature will favor potassium in dilute solution in Fe-FeS melts at the expense of potassium in potassium-rich silicates suggest that at least a few percent, and perhaps much more, of the Earth's total potassium is likely to be partitioned into Fe-FeS melts, and thus extracted into the core.

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Part III

Related Papers by Kenneth A. Goettel

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PARTITIONING OF POTASSIUM BETWEEN SILICATES AND SULPHIDE MELTS: EXPERIMENTS RELEVANT TO THE EARTH'S CORE

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The partitioning of potassium between roedderite, $K_2Mg_5Si_{12}O_{30}$ and an Fe–FeS melt was investigated at temperatures about 40 °C above the Fe–FeS eutectic. Roedderite was considered a prime candidate for one of the potassium-bearing phases in the primitive Earth because roedderite and merrihueite are the only two silicates containing essential potassium which have been identified in stony meteorites. A mean K_2S/FeS weight ratio of $(3.340 \pm 0.015) \times 10^{-3}$ was determined in these experiments; a K_2S/FeS weight ratio of about 1.0×10^{-2} would be sufficient to extract all potassium in a chondritic Earth into the core. Application of these results to a primitive chondritic Earth is discussed and it is concluded that extraction of most of the Earth's potassium into the Fe–FeS core would occur under the conditions in the early Earth.

1. Introduction

The low abundance of sulphur and potassium in the crust and mantle has been a serious difficulty for Earth models based on chondritic or solar abundances of rock forming elements. However, an Earth model with an Fe–FeS core containing most of the Earth's potassium resolves these difficulties and has widespread geophysical and geochemical implications. ^{40}K in the core would be a major heat source which could provide energy for convection in the core to maintain the geomagnetic field and convection in the mantle to drive continental drift.

MURTHY and HALL (1970) have presented convincing arguments that sulphur is the light element which brings the density of the outer core into agreement with seismological estimates. Sulphur would be incorporated into the core during the accretion process as part of the lowest melting components in the Fe–S–O system. This model of an Fe–FeS core leads to early differentiation of the Earth and early core formation without necessitating high accretion temperatures or very rapid accretion rates. The anomalous depletion of sulphur in the crust and mantle relative to other volatile elements reinforces this argument. LEWIS (1971) has extended this model of an Fe–FeS core and suggested that potassium and the other heavy alkali metals may have appreciable chalcophilic tendencies and may be enriched in the Earth's core. Lewis based his argument on:

(1) the extreme stability of these sulphides relative to the oxides,

(2) the occurrence of a potassium sulphide mineral in enstatite chondrites and achondrites,

(3) data from blast furnace and smelting processes which show significant amounts of potassium in the sulphide phase (CISSARZ and MORITZ, 1933; VOM ENDE *et al.*, 1966).

Differentiation of the primitive Earth involving Fe–FeS melts may explain the depletion of potassium and the other heavy alkalis in the crust and mantle.

Experiments relevant to the question of potassium in the core involve the partitioning of potassium between silicates and an Fe–FeS melt since potassium occurs predominately in silicates in chondrites and also presumably in the early Earth. The identity of the potassium-bearing phases and the chemical and physical conditions in the early Earth are all important factors. The only minerals containing essential potassium which have been identified in stony meteorites (MASON, 1969) are djerfisherite ($K_3CuFe_{12}S_{14}$), merrihueite ($(K, Na)_2Fe_5Si_{12}O_{30}$) and roedderite ($(K, Na)_2Mg_5Si_{12}O_{30}$). The observation that these minerals are not the ordinary potassium minerals found in the Earth's crust emphasizes the fact that the mineralogy and chemical and physical conditions which are relevant to the question of potassium in the core are the conditions which existed in the early, differentiating Earth and not the conditions in the present crust or

mantle. To begin the experimental work, I have investigated the partitioning of potassium between roedderite and an Fe–FeS melt.

2. Experimental methods

Roedderite ($K_2Mg_5Si_{12}O_{30}$) was synthesized hydrothermally from SiO_2 glass, $K_2Si_2O_5$ glass and MgO; runs were 24 h at 1 kbar and 800 °C. No phases other than roedderite were detected in the X-ray diffraction pattern. Trace amounts of quartz and MgO (less than 0.5%) were the only other phases detected optically. Unit cell dimensions were calculated and refined by the least squares method:

$$a_0 = 10.213 \pm 0.001 \text{ Å},$$
$$c_0 = 14.141 \pm 0.002 \text{ Å}.$$

These values are slightly smaller than cell dimensions found by SEIFERT and SCHREYER (1969). Most grains had diameters of 4 to 12 μm; grain sizes ranges from sub-micron to about 75 μm.

Iron for troilite synthesis and experimental runs was prepared by heating iron powder in hydrogen to reduce any oxides present. Troilite (FeS) was synthesized from sulphur and previously reduced iron in evacuated fused quartz capsules. The troilite used in these experiments was stoichiometric FeS; troilite/pyrrhotite compositions were determined using the X-ray diffraction data and methods of BARTON and TOULMIN (1964). Troilite and reduced iron were stored in evaculated vycor capsules and exposed to the atmosphere only during weighing procedures. (See table 1.)

TABLE 1
Reagent list for mineral synthesis

SiO_2	Corning lump cullet glass (lot no. 062221)
MgO	Fisher Certified Reagent (lot no. 787699)
$K_2Si_2O_5$	glass, prepared by D. R. Wones from SiO_2 glass and $KHCO_3$ using the method of SCHAIRER and BOWEN (1955)
Fe	Johnson–Matthey Specpure (lot no. S50612A)
S	Alfa Ventron Ultrapure (lot no. 012571)

Experimental runs containing FeS, iron and roedderite were made for 50, 100 and 200 h in evacuated fused quartz capsules. Temperatures for most runs were 1030 °C, about 40 °C above the Fe–FeS eutectic. At 1030 °C, the system consisted of solid roedderite, solid iron and an Fe–FeS melt containing potassium sulphide phases. Runs were terminated by quenching in cold water. The Fe, FeS and K_2S phases were dissolved in HCl; careful blank and solubility experiments (see table 5) demonstrated that negligible amounts of potassium entered the solutions from the roedderite. The solutions were analyzed for potassium by atomic absorption. General atomic absorption techniques were adopted from REYNOLDS and ALDOUS (1970). (See table 2.)

TABLE 2
Reagent list for atomic absorption solutions

La	La_2O_3, City Chemical Corporation 99.997% (lot no. XA 876)
Fe	Fe, Johnson–Matthey Specpure (lot no. S50612A)
Mg	MgO, Spex Industries 99.999% (lot no. 03691)
K	K_2CO_3, Alfa Ventron Ultrapure (lot no. 10299)

3. Data

The experimental data are presented in tables 3, 4 and 5. Partitioning experiment runs (tables 3 and 4) consisted of roedderite, troilite and iron. Runs were heated for 50 to 200 h, quenched and the contents analyzed for potassium in the Fe–FeS melt. Blanks (table 5) were empty capsules prepared, handled and analyzed in exactly the same manner as capsules containing partitioning experiments. These blanks were run to check for handling or reagent contamination. Solubility experiments (table 5) consisted of capsules containing roedderite which were prepared, handled and analyzed in exactly the same manner as the partitioning experiments. These solubility experiments were run to determine if the solubility of roedderite in HCl was low enough to justify the use of differential solubility to separate silicate and sulphide phases.

TABLE 5
Blank and solubility experiments: Runs at 1030 °C

Run no.	Contents (mg)	Run (h)	K[a] (μg/ml)	Mg[a] (μg/ml)
Blanks				
15	none	none	0.035 ± 0.010	0.067 ± 0.012
25	none	none	0.033 ± 0.008	0.093 ± 0.015
38	none	none	0.040 ± 0.006	0.157 ± 0.006
			Mean 0.036 ± 0.004	0.106 ± 0.046
Roedderite solubility				
16	49.8	50	0.082 ± 0.015	1.097 ± 0.006
49	50.5	100	0.053 ± 0.013	1.217 ± 0.018
18	49.5	200	0.047 ± 0.010	0.937 ± 0.006
			Mean 0.061 ± 0.019	1.084 ± 0.140

[a]) See table 3, footnote a.

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TABLE 3

Partitioning experiments: Runs at 1030 °C

Run no.	Roedderite (mg)	Fe (mg)	FeS (mg)	Run (h)	Mg[a] (μg/ml)	K[a] (μg/ml)	Corrected K[b] (μg/ml)	K_2S/FeS ($\times 10^{-3}$) Weight fraction	K_2S/FeS ($\times 10^{-3}$) Mole fraction
19	51.8	49.4	99.5	50[c]	2.183 ± 0.006	4.135 ± 0.101	4.074 ± 0.013	2.887	2.301
40	50.8	51.3	102.2	50[c]	5.470 ± 0.035	4.410 ± 0.066	4.349 ± 0.069	3.000	2.392
43	52.3	51.0	101.8	50[c]	5.213 ± 0.012	4.406 ± 0.114	4.345 ± 0.116	3.009	2.399
							Mean	2.965	2.364
								±0.068	±0.055
20	48.9	51.2	102.2	100[c]	4.697 ± 0.025	4.657 ± 0.125	4.596 ± 0.126	3.170	2.528
41	50.8	51.4	99.6	100[c]	4.207 ± 0.015	4.175 ± 0.081	4.114 ± 0.083	2.912	2.322
44	50.1	54.3	104.5	100[c]	4.280 ± 0.017	4.807 ± 0.088	4.746 ± 0.090	3.202	2.553
47	51.8	51.9	101.9	100[c]	3.573 ± 0.006	4.498 ± 0.114	4.437 ± 0.116	3.070	2.447
							Mean	3.089	2.463
								±0.130	±0.104
50	51.5	51.1	98.8	200[d]	4.528 ± 0.034	4.733 ± 0.041	4.672 ± 0.045	3.334	2.658
53	52.6	50.6	99.6	200[d]	4.580 ± 0.020	4.757 ± 0.031	4.696 ± 0.036	3.324	2.650
56	51.3	51.1	99.7	200[d]	4.058 ± 0.043	4.810 ± 0.047	4.749 ± 0.047	3.358	2.677
59	51.6	51.8	97.3	200[d]	4.498 ± 0.032	4.678 ± 0.040	4.617 ± 0.044	3.345	2.667
							Mean	3.340	2.663
								±0.015	±0.012

[a]) Standard deviations on concentrations in tables 3, 4 and 5 reflect only the precision of atomic absorption determinations.
[b]) Standard deviations on concentrations corrected by subtraction of solubility results in tables 3 and 4 reflect only the precision of atomic absorption determinations and the precision of solubility measurements.
[c]) Runs were quenched in cold water but the precise quench procedure was not standardized; there may be some variation in quench time (quench time $\leq$ 10 s).
[d]) Runs were quenched as rapidly as possible (quench time $\leq$ 3 s).

TABLE 4

Partitioning experiments (quench time effects): Runs at 998 °C

Run no.	Roedderite (mg)	Fe (mg)	FeS (mg)	Run (h)	Mg[a] (μg/ml)	K[a] (μg/ml)	corrected K[b] (μg/ml)	K_2S/FeS ($\times 10^{-3}$) Weight fraction	K_2S/FeS ($\times 10^{-3}$) Mole fraction
51	52.1	50.0	99.4	50[c]	6.870 ± 0.069	3.702 ± 0.026	3.641 ± 0.032	2.582	2.059
54	49.6	51.9	103.0	50[c]	6.403 ± 0.022	3.717 ± 0.042	3.656 ± 0.046	2.502	1.995
							Mean	2.542	2.027
								±0.057	±0.045
55	49.5	50.8	100.9	50[d]	6.532 ± 0.019	2.898 ± 0.046	2.837 ± 0.050	1.982	1.580
57	51.0	51.2	97.4	50[d]	6.525 ± 0.042	3.048 ± 0.074	2.987 ± 0.076	2.162	1.723
							Mean	2.072	1.651
								± 0.127	± 0.101
52	50.7	50.4	100.5	50[e]	6.058 ± 0.033	1.488 ± 0.062	1.427 ± 0.065	1.001	0.798
58	52.2	50.6	99.9	50[e]	6.707 ± 0.039	1.093 ± 0.026	1.032 ± 0.032	0.728	0.581
							Mean	0.865	0.698
								±0.193	±0.153

[a]) See table 3, footnote a.
[b]) See table 3, footnote b.
[c]) Runs were quenched as rapidly as possible (quench time $\leq$ 3 s).
[d]) Runs were cooled 15 s in air and then quenched as in [c]) above.
[e]) Runs were cooled to 250 °C in the furnace and then quenched as in [c]) above.

4. Discussion of results

Potassium in the sulphide melt has been calculated as K_2S; identification of the potassium bearing phase in the sulphide melt as something other than K_2S would not materially change the conclusions drawn from these experiments. The 200 h, 1030 °C roedderite–troilite–iron experiments have a mean K_2S/FeS weight ratio of $(3.340 \pm 0.015) \times 10^{-3}$. This best estimate of the K_2S/FeS ratio is, however, a *minimum* value. Data from 50, 100 and 200 hour runs (table 3) suggest that equilibrium is approached in 200 h, but that longer runs may be needed to achieve the higher equilibrium K_2S/FeS ratio. K_2S/FeS values from the 50 and 100 h runs may be slightly low because these runs were not quenched quite as rapidly as the 200 h runs. Data on quench time effects (table 4) show the marked effect of quench procedures. Potassium in the sulphide melt rapidly reenters a silicate or glass phase as the temperature is lowered below the Fe–FeS eutectic. Even the runs which were quenched most rapidly may have lower values than the actual K_2S/FeS ratio at 1030 °C. This quench time effect cannot be attributed to potassium in the vapor phase – vapor pressures of species involved are more than 5 orders of magnitude too low.

A silicate residue is left after the iron and sulphide phases are dissolved in HCl for atomic absorption analysis. This silicate residue from the roedderite–troilite–iron partitioning experiments was examined by X-ray diffraction; no phases other than roedderite were detected. Optical examination indicated that 1 or 2% quartz, 1 or 2% silica-rich glass and about 2% enstatite were present. Indices of the enstatite were indistinguishable from indices expected for the magnesium end-member (DEER *et al.*, 1966).

Formation of K_2S involves reactions such as

$$K_2Mg_5Si_{12}O_{30} + FeS \leftrightarrows K_2S + FeO + 7\,MgSiO_3 + 5\,SiO_2.$$

The cell dimensions of the remaining roedderite after the roedderite–troilite–iron runs were found to be

$$a_0 = 10.213 \pm 0.001\ \text{Å},$$
$$c_0 = 14.149 \pm 0.002\ \text{Å}.$$

The increase in c_0 from the initial value of 14.141 ± 0.002 Å may indicate entry of FeO into the roedderite.

The results indicating substantial amounts of potassium in the sulphide phase (table 3) cannot be attributed to the solubility of a potassium–silica glass formed during the runs. The very low potassium values from the solubility experiments (table 5) show that a soluble potassium bearing glass is not formed by thermal decomposition of roedderite. A potassium-bearing glass could be formed in the roedderite–troilite–iron experiments *if* magnesium were preferentially extracted into the sulphide melt, but this is thermodynamically unlikely and the potassium results do not show an effect of solution time as do the magnesium results.

One 50 h roedderite–troilite–iron run (no. 46) had a potassium value more than 3 standard deviations above the mean for the other 50 h runs. This high value was attributed to contamination and results from this run were discarded.

It is not possible to determine MgS/FeS ratios from the roedderite–troilite–iron experiments. The solubility experiments (table 5) show a mean magnesium value of 1.084 μg/ml; this high magnesium value is a result of a trace amount of MgO in the starting roedderite. The magnesium values from the roedderite–troilite–iron experiments vary by up to a factor of 3 between runs, and 50 h runs quenched from 998 °C have higher magnesium values than 50 h runs quenched from 1030 °C. Optical examination of the roedderite residue after iron and sulphide phases had been dissolved indicated that 1 or 2% glass was present; potassium extraction from roedderite into the sulphide melt may leave a magnesium–silica glass. The fluctuating magnesium values may be attributed to kinetic effects in the dissolving of a magnesium–silica glass; samples left in the HCl solutions for longer times show higher magnesium values due to leaching of magnesium from the glass.

If FeO were present at unit activity, then f_{O_2} would be on the Fe–FeO buffer, since free iron is present in all runs. For the reaction $Fe + \frac{1}{2}O_2 \leftrightarrows FeO$, $K = a_{FeO}/a_{Fe}(f_{O_2})^{\frac{1}{2}}$. If FeO were present at unit activity, then at 1300 K ($\approx$1030 °C), $\log K = 7.56$ (ROBIE and WALDBAUM, 1968), and f_{O_2} would be equal to 10^{-15}. However, in these experiments, a_{FeO} is less than unity since FeO enters the roedderite and enstatite present. If we assume ideal solution laws for FeO in roedderite (no free energy of formation data exist), then $a_{FeO} = N_{FeO} \approx 0.01$ and $f_{O_2} \approx 10^{-19}$. Absorption of water by the powders or oxidation of the iron during weighing would increase a_{FeO} in these runs; the oxygen fugacity

for these roedderite–troilite–iron experiments may be between 10^{-19} and 10^{-15}.

Atomic absorption analysis is a potential source of significant errors due to chemical interferences, ionization interferences, molecular absorption or matrix effects (REYNOLDS and ALDOUS, 1970). Use of an air–acetylene flame, addition of lanthanum as a suppressant and matching the bulk components (HCl, La, Fe, FeS) of sample and standard solutions has eliminated or greatly reduced the major errors possible with atomic absorption. Remaining errors have been minimized by aspirating standard solutions before and after the sample solutions to check for drift and by averaging a number of readings to reduce the effect of noise fluctuations.

5. Conclusion

A mean K_2S/FeS weight ratio of $(3.340 \pm 0.015) \times 10^{-3}$ was determined by 200 h, 1030 °C, roedderite–troilite–iron runs. Data from 50 h runs indicate that increasing the temperature from 998 to 1030 °C increases the K_2S/FeS ratio by at least 16% (see tables 3 and 4). A K_2S/FeS weight ratio of about 1.0×10^{-2} in the Earth would be sufficient to extract *all* potassium in a chondritic Earth into the core. Thus, the degree of potassium extraction into an Fe–FeS melt demonstrated in these experiments would be sufficient to extract most of the Earth's potassium into the core at temperatures only 100 or 200 °C above the Fe–FeS eutectic.

Partitioning of potassium between silicates and an Fe–FeS melt in the Earth must depend on the identity of the potassium bearing minerals, temperature, pressure and oxygen fugacity during the primary differentiation of the Earth into a metallic core and silicate mantle. Although none of these important parameters are known with certainty, reasonable estimates can be made which are consistent with present observations and the geologic record. It must be stressed that the chemical and physical conditions in the Earth which are relevant to the distribution of potassium between the Fe–FeS core and the silicate mantle are the conditions which existed in the primitive, differentiating Earth and not the conditions in the present crust or mantle.

The mineralogy of the primitive Earth is poorly known. However, minerals such as roedderite and merrihueite, the only silicate minerals containing essential potassium which have been identified in stony meteorites, must be considered prime candidates for potassium bearing phases in a primitive chondritic Earth. Temperatures in a differentiating Earth, with the possible exception of the outermost mantle, must have exceeded the Fe–FeS eutectic at the time of the primary differentiation of the Earth. The effect of pressure on the partitioning of potassium between silicates and an Fe–FeS melt is important; no experimental data exist. If the compressibility of Fe–FeS liquids is low, then pressure may not have a major effect on K_2S/FeS ratios; however, verification of this awaits future investigations. The degree of chemical reduction in the primitive Earth is also uncertain. Oxygen fugacities were certainly much higher than in enstatite chondrites and certainly much lower than in the present crust or mantle.

Several iron meteorites are interesting examples of possible extraction of potassium into Fe–FeS melts. A number of iron meteorites with silicate inclusions are markedly enriched in potassium and rubidium (BOGARD *et al.*, 1967; BUNCH and OLSEN, 1968; WASSERBURG *et al.*, 1968). Analysis of silicate inclusions in the Kodaikanal iron meteorite shows 2.57% K_2O, a Na/K ratio of 1.01 and a K/Rb ratio of only 49 (BUNCH and OLSEN, 1968). Enrichment of potassium and rubidium in an iron meteorite is difficult to explain but may involve extraction of these alkalis by an Fe–FeS melt. This meteorite may represent a partial separation of the Fe–FeS melt from the surrounding silicate phases. Potassium and rubidium in the sulphide melt could have re-equilibrated into the intermixed silicate phases when the meteorite cooled. The striking enrichment of rubidium relative to potassium may reflect the importance of ionic radii in the extraction of alkalis into sulphide melts. Potassium is known to remain in residual liquids during magmatic crystallization because its large ionic size inhibits its entry into many crystal lattice sites. This ionic radius argument may be extended to suggest that potassium and rubidium may prefer a Fe–FeS melt for the same reason. It is common in metallurgical processes for the alkalis to be concentrated in melt phases as a consequence of their large ionic sizes.

A critical distinction must be made between partitioning of potassium between an Fe–FeS melt and silicate minerals during the primary differentiation of the Earth into a metallic core and silicate mantle and

the partitioning of potassium between silicate minerals or between solid and liquid phases in the present crust or mantle. During the primary differentiation of the Earth, potassium enters Fe–FeS melts; gravitational segregation of the core physically separates the potassium in the sulphide phase from further interactions with the silicate mantle. This partitioning process is thus irreversible. In the iron meteorites with silicate inclusions, the Fe–FeS melt was not physically separated from the silicates, so that it was possible for the potassium to re-enter the silicate phase as the meteorite cooled. Partitioning of potassium between silicates or between solid and liquid phases during crystallization of silicate magmas in the present oxidized crust or mantle is merely a secondary differentiation of the small fraction of potassium not extracted into the core. This secondary differentiation has no bearing on the bulk distribution of potassium in the Earth except perhaps to emphasize the role ionic size plays in concentrating potassium in melt phases.

The stability of potassium sulphide relative to the oxide, the occurrence of a potassium sulphide mineral in enstatite chondrites, the data on potassium in sulphide phases of metallurgical systems and the experimental results presented in this paper are evidence that most of the potassium in a chondritic Earth may enter Fe–FeS melts during primary differentiation of the Earth and thus be incorporated into the core. LEWIS (1971) has summarized many of the important consequences of most of the Earth's potassium being in an Fe–FeS core. Among the important geochemical and geophysical implications of this model are:

(1). Abundances of major elements in the Earth, including sulphur and the alkalis, are consistent with a chondritic Earth. Depletion of these elements in the present crust is readily understandable.

(2). A major heat source, ^{40}K, exists in the Earth's core. This thermal source may provide energy for convection in the core to maintain the Earth's magnetic field and convection in the mantle to drive continental drift. Large scale heat flow patterns are consistent with U and Th in the continental crust producing the observed continental heat flow values. Upwelling under the oceans may produce the observed oceanic heat flow values and continental areas may be arranged over downwelling areas of the mantle.

(3). It is no longer necessary to postulate extreme chemical reduction in the Earth to form an Fe–Si core with massive degassing of CO and it is no longer necessary to postulate high temperature, rapid accretion to volatilize sulphur and the alkali metals. The major geochemical and geophysical features of the Earth can be readily explained without resorting to such extreme processes.

The importance of the conclusions drawn from this Earth model of potassium in an Fe–FeS core suggest further investigations in several areas of research. Future experiments in more realistic, complex systems will be required.

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COMMENTS ON A PAPER BY V.M. OVERSBY AND A.E. RINGWOOD (Earth Planet. Sci. Letters 14 (1972) 345–347)

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Oversby and Ringwood [1] have recently argued that no more than 1 or 2% of the earth's potassium can be in an Fe-FeS core. We wish to call attention to several points not discussed by these authors which cast considerable doubt upon their conclusions.

(1) Oversby and Ringwood [1] claim incorrectly that Lewis [2] and Hall and Murthy [3] based their arguments for potassium in the earth's core on metal oxide-metal sulfide thermodynamic data. Lewis [2] included metal oxide-metal sulfide data for the sole purpose of showing the extremely high stabilities of pure sulfides relative to oxides. He extensively discussed the occurrence of potassium in sulfide phases in both meteoritic and metallurgic systems. A sulfide mineral containing essential potassium has been found in enstatite chondrites [4]. Significant amounts of potassium have been found in the sulfide matte produced during the smelting of the Mansfeld copper ores [5]. Extremely low abundances of silicon and aluminum in the sulfides rule out the possibility that the potassium in the sulfide matte was due to silicate contamination. Microprobe studies of blast furnace byproducts [6] have identified a K-Fe-S compound and an alkali-Mn-S compound. The textural evidence suggested that the K-bearing sulfide crystallized from a common Fe-S-rich melt. Hall and Murthy [3] showed that K_2S is stable relative to potassium silicates. Therefore, the suggestion that potassium may be enriched in the earth's Fe-FeS core is based on a considerable body of meteoritic, metallurgic and thermodynamic data [2–6].

(2) Oversby and Ringwood [1] contend that formation of alkali alumino-silicates prevents appreciable K_2S formation in the earth. However, data from the smelting of the Mansfeld copper ores [5] where metallic iron and an Fe-Cu sulfide matte containing 0.8% K_2S coexist with silicates containing 17% Al_2O_3, demonstrates that the presence of alumino-silicates does not preclude K_2S formation. The Mansfeld silicates contain 4% FeO; the oxygen fugacity is probably somewhat below the Fe-FeO buffer and thus compatible with a differentiating, chondritic earth.

The possible stabilization of some of the earth's potassium by formation of alkali alumino-silicates does not rule out large amounts of K_2S in the Fe-FeS core. The fact that most of the earth's aluminum is likely to be in aluminous pyroxenes which cannot accept large alkali ions may further reduce the effect aluminum could have on the partitioning of potassium between silicates and a sulfide melt. Comparison of the abundances of sodium and potassium in the earth's supports the hypothesis that a mechanism other than alumino-silicate formation is involved in the distribution of potassium in the earth. Potassium is markedly depleted in the earth relative to the chondritic or solar abundances of rock forming elements; sodium is not

depleted. The fact that some of the earth's potassium is in alumino-silicates does not alleviate the need for another mechanism to fractionate sodium and potassium.

(3) Oversby and Ringwood [1] discussed the analyses reported by Shima and Honda [7] which show nearly 7% of the total potassium in the enstatite chondrite Abee in sulfide phases. We reject their idea that the low temperature partitioning of potassium between solid sulfides and solid silicates in meteorites sets an upper limit on the amount of potassium in the earth's Fe-FeS core. Lewis [2] and Hall and Murthy [3] have never claimed that large amounts of potassium would enter solid sulfide phases at low temperatures. These authors have suggested that significant amounts of potassium may be partitioned into sulfide melts at temperatures above the Fe-FeS eutectic. Since conditions relevant to the earth's core involve the high temperature partitioning of potassium between solid silicates and a Fe-FeS melt, the low temperature partitioning of potassium between two solid phases in meteorites cannot be used to set an upper limit on the amount of potassium in the earth's core.

(4) Goettel [8] has recently reported experimental results which show large amounts of potassium in the sulfide phase at temperatures above the Fe-FeS eutectic. He investigated the partitioning of potassium between solid roedderite ($K_2Mg_5Si_{12}O_{30}$) and an Fe-FeS melt. Roedderite and merrihueite are the only two silicates containing essential potassium which have been indentified in stony meteorites. Roedderite is thus a reasonable choice for one of the potassium bearing phases in a primitive, differentiating, chondritic earth. At 1030°C, a mean K_2S/FeS weight ratio of $(3.340 \pm 0.015) \times 10^{-3}$ was found; a K_2S/FeS weight ratio of about 1.0×10^{-2} would suffice to extract all the potassium in a chondritic earth into the Fe-FeS core. The oxygen fugacity in these experiments was somewhat below the Fe-FeO buffer and thus compatible with a differentiating, chondritic earth. Goettel's data [8] show that the potassium content in the sulfide phase drops rapidly when the temperature falls below the Fe-FeS eutectic and that the potassium content in the sulfide phase increases as the temperature increases above the Fe-FeS eutectic.

(5) Oversby and Ringwood [1] have criticized the chondritic earth models of Lewis [2] and Hall and Murthy [3] without acknowledging that these are chondritic models. The chemical and physical conditions which are relevant to the partitioning of potassium between the Fe-FeS core and the silicate mantle and crust are the conditions which existed during the primary differentiation of the chondritic earth into core and mantle and not the conditions in the present crust or mantle. Therefore, partitioning experiments using highly differentiated, basaltic material, as Oversby and Ringwood [1] have done, are not particularly relevant to the distribution of potassium in a primitive, differentiating, chondritic earth.

(6) Oversby and Ringwood [1] have strongly biased their experimental system (basalt with 13% Al_2O_3) in favor of alumino-silicate formation by greatly exceeding the chondritic proportion of aluminum. The majority of ordinary chondrites contain only about 2% Al_2O_3. The use of alundum capsules is unreasonable since a chondritic earth clearly does not have excess alumina. The fact that 73% of the potassium in the first run and 52% in the second run were lost to the alundum capsules emphasizes the irrelevance of experiments in alundum capsules to a chondritic earth.

(7) Oversby and Ringwood [1] have also ignored the important point stressed by Murthy and Hall [9] that an Fe-FeS melt is the first melt to form in a chondritic earth. Because the melting temperatures of silicates increase rapidly with pressure while the Fe-FeS eutectic temperature is virtually independent of pressure, it appears very likely that for nearly the entire differentiating earth potassium would be partitioned between solid silicates and an Fe-FeS melt. Thus, experiments relevant to the distribution of potassium in the earth involve the partitioning of potassium between solid silicates and an Fe-FeS melt, not between two melts as Oversby and Ringwood [1] have assumed.

(8) Oversby and Ringwood [1] quenched their two experiments by turning off the power supply. However, Goettel [3] has shown that potassium in an Fe-FeS melt very rapidly reenters silicate phases when the temperature drops below the Fe-FeS eutectic. *Very* rapid quenching is essential to determine properly the potassium content in a high temperature sulfide melt.

The chondritic model advocated by Lewis [2] and Hall and Murthy [3] in which a large fraction of the earth's potassium is in the Fe-FeS core is supported

by a diverse body of meteoritic, metallurgic and thermodynamic data [2–6] and by experimental results [8]. This chondritic model is considerably more direct than alternate models which invoke selective high temperature volatilization of some volatile elements. The entry of potassium into the Fe-FeS core can occur under far less extreme conditions than are required for a massive, disequilibrium reduction of silicon to enter the earth's core. Finally, we are not convinced that the full logical consequences of Oversby and Ringwood's experiments were realized by them. They seem to claim that their experiments constitute a sufficiently accurate simulation of the conditions of formation of the core so that they can use their results to argue against the presence of a particular element in the core. We must point out that the absence of silicon in the metal phase produced in their work would, by the same logic, demand the absence of silicon in the core, quite contrary to the claims of Ringwood [10].

Note added: In their reply to this comments, Oversby and Ringwood have incorrectly interpreted Goettel's data [8] by calculating a distribution coefficient for potassium between the phases roedderite and Fe-FeS melt and then applying this distribution coefficient to the multi-phase core and mantle system. Although we contend that substantial fractions of the earth's potassium are likely to be in the core, we note that Oversby and Ringwood, even by their own interpretation of their own data, allow up to 1.5% of the earth's potassium in the core. This amount of potassium would supply well over 10^{18} erg/sec of decay energy in the core, and would suffice to produce the geophysical effects we have described.

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NOTES AND CORRESPONDENCE

Ammonia in the Atmosphere of Venus[1]

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ABSTRACT

Several aspects of the chemistry of NH_3 in the Venus atmosphere are examined. Production of NH_3 and precipitation of NH_3 compounds are considered quantitatively. It is concluded that the high NH_3 mixing ratios reported by the Soviet Venera 8 landing probe appear to be inconsistent with the observed abundances of other gases in the Venus atmosphere.

The Soviet Venera 8 Venus landing probe has reported the presence of ammonia with a mixing ratio of 10^{-4} to 10^{-3} at 46 and 33 km above the surface (Surkov *et al.*, 1973). Bromophenol blue, a non-specific pH indicator, was used for the ammonia determination.

Previous discussions of the atmosphere of Venus have given little consideration to NH_3; the present note examines several aspects of the chemistry of NH_3 on Venus, including production of NH_3 and precipitation of NH_3 compounds at various levels in the atmosphere. We shall consider the important questions of whether the Venera NH_3 data are consistent with the spectroscopically observed abundances of other gases, and why the NH_3 mixing ratio in the upper atmosphere of Venus is below the current detection limit of earth-based spectroscopy.

Data on the composition of the Venus atmosphere are given in Table 1; calculations in the present paper were made assuming constant mixing ratios for these gases. In lieu of spectroscopic data for HBr and HI, equal mixing ratios for HCl, HBr and HI were assumed. In terms of solar or chondritic abundances, Cl > Br > I; however, because of ionic radius effects, a considerable fraction of the Cl on Venus, less Br, and even less I are likely to be bound in surface rocks. Therefore, the assumption of equal mixing ratios appears to be a reasonable approximation. HF is ignored because of the great instability of NH_4F.

The temperature-pressure profile used in the present paper is given in Table 2. This profile is very similar to the profile (Model VII) given in NASA (1972). None of the calculations in the present note would be appreciably affected by using a somewhat different temperature-pressure profile.

TABLE 1. Atmospheric composition.

Species	Mixing ratio adopted in present paper	Observational data
CO_2	0.97	0.93 to 0.97 (Avduevsky *et al.*, 1970)
N_2	1×10^{-2}	$<2\times10^{-2}$ (Surkov *et al.*, 1973)
CO	1×10^{-4}	$(1\text{–}3)\times10^{-4}$ (Belton, 1968)
		5×10^{-5} (Young, 1972)
H_2O	2×10^{-4} (upper limit)	$<2\times10^{-3}$ (Jones *et al.*, 1972)
		$(1\text{–}7)\times10^{-3}$ (Vinogradov *et al.*, 1968)
	1×10^{-4}	1×10^{-4} (Belton, 1968)
	1×10^{-6} (lower limit)	1×10^{-6} (Fink *et al.*, 1972)
HCl	1×10^{-6}	1×10^{-6} (Belton, 1968)
		6×10^{-7} (Young, 1972)
HBr	1×10^{-6}	not detected
HI	1×10^{-6}	not detected
NH_3		$\leq5\times10^{-8}$ (Benedict, 1968)

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Production of NH_3 is governed by the reaction

$$2NH_3+3CO_2 \rightleftharpoons N_2+3CO+3H_2O. \quad (1)$$

Uncertainties in the mixing ratios are negligible for CO_2 and probably about a factor of 2 or 3 for CO. However, the H_2O mixing ratio is subject to considerable uncertainty and disagreement. For this reason, equilibrium NH_3 mixing ratios have been calculated for three H_2O mixing ratios. The N_2 mixing ratio was assumed to be 1.0×10^{-2}; this is probably an upper limit. The calculated equilibrium NH_3 mixing ratios are shown in Fig. 1; thermochemical data were taken from Robie and Waldbaum (1968). At low temperatures, the equilibrium NH_3-producing reaction is kinetically limited. The temperature at which kinetics limits NH_3 production in the Venus atmosphere is unknown. Furthermore, at temperatures of 310–340K the NH_3 mixing ratio is subjected to a second absolute limit imposed by the total amount of H_2O or CO available in the atmosphere. For this reason, even if there were no kinetic inhibition, X_{NH_3} would reach a maximum near 325(±15)K. Above this altitude, H_2O or CO would be severely depleted by reaction (1).

Precipitation of the following NH_3 compounds is considered: NH_4Cl, NH_4Br, NH_4I, NH_4HCO_3 and $NH_4NH_2CO_2$; vapor pressure data were obtained from Kelly and Anderson (1935) and the *Handbook of Chemistry and Physics* (1962). NH_3 mixing ratios in equilibrium with the above five NH_3 compounds are shown in Fig. 1. For gases other than NH_3, the mixing ratios shown in Table 1 were used for the vapor pressure calculations.

The data plotted in Fig. 1 indicate that $NH_4NH_2CO_2$ and NH_4HCO_3 will not precipitate at any level in the atmosphere; these compounds require too high NH_3 mixing ratios. At temperatures dependent on the NH_3 mixing ratio, the NH_3 halides will precipitate. For X_{NH_3} corresponding to $X_{H_2O}=1\times10^{-4}$, the halides will precipitate at about the 400 to 350K level. If the production of NH_3 is kinetically limited at temperatures above 400K, X_{NH_3} will be lower and the halides will precipitate higher in the atmosphere at lower temperatures.

Ammonium chloride precipitation has been suggested by Lewis (1968a) and by Kuiper (1969), but the presence of HCl and absence of NH_3 above the cloud tops strongly suggests $X_{NH_3}<X_{HCl}$ at all levels in the atmosphere. X_{HCl} is observed to be 10^{-6} near the cloud tops, which is in accord with the idea that H_2O and HCl are in chemical equilibrium with the 750K surface (Lewis, 1968b, 1970) if $X_{H_2O}\approx3\times10^{-4}$ in the lower atmosphere. Ten times more water require three times more HCl, which is comparable to the observational uncertainty in the HCl abundance. However, the maximum value of X_{NH_3} for such a wet model is 2×10^{-3}, some 700 times the expected HCl abundance for that model. NH_4Cl precipitation would leave an enormous excess of NH_3, dense NH_4HCO_3 clouds, no observable HCl, and $X_{NH_3}=2\times10^{-6}$ at the 240K level.

If, following Kuiper, we consider the driest possible model ($X_{H_2O}=10^{-6}$), then we would expect $X_{HCl}=5\times10^{-8}$, and X_{NH_3} could be only as high as 7×10^{-7} at best. Thus, small amounts of NH_3 would still suffice to remove all HCl from the regions of the cloud tops. Certainly so dry a model cannot produce appreciable masses of ammonium-salt clouds.

TABLE 2. Temperature-pressure profile.

Temperature (°K)	Pressure (atm)
700	63
600	28
500	10.5
400	3.5
375	2.4
350	1.5
325	1.0
300	0.70
275	0.45
240	0.15

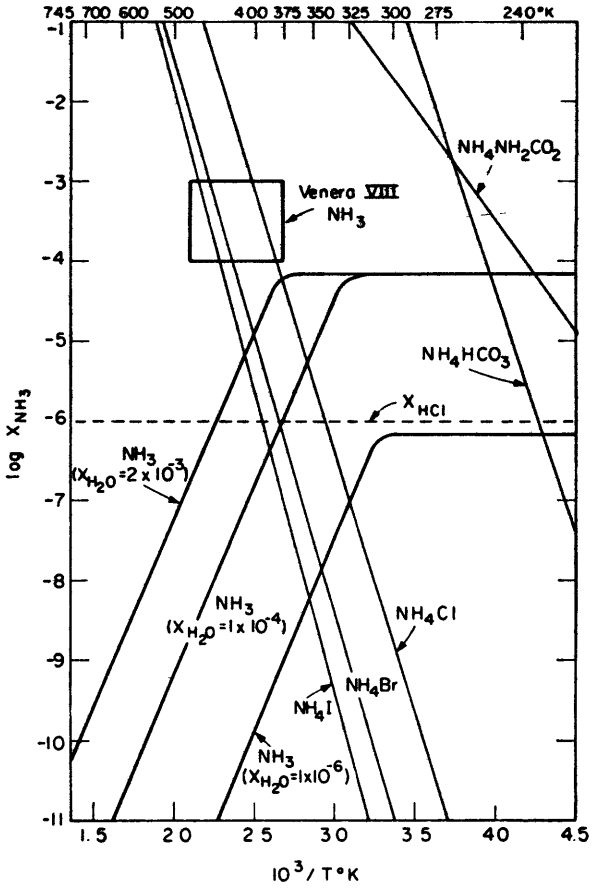


FIG. 1. Chemical equilibrium NH_3 mixing ratios [reaction (1)] for $X_{H_2O}=10^{-6}$, 10^{-4} and 2×10^{-3}; in each case, X_{NH_3} becomes constant when the total amount of H_2O or CO is exhausted. NH_3 mixing ratios in equilibrium with NH_4Cl, NH_4Br, NH_4I, NH_4HCO_3 and $NH_4NH_2CO_2$ and the Venera 8 NH_3 results are also shown.

We conclude that the Venera 8 NH_3 mixing ratio of 10^{-4} to 10^{-3} at 46 and 33 km above the surface (about the 375–475K level) appears to be inconsistent with the abundances of other gases in the Venus atmosphere. If X_{H_2O} were as high as 10^{-2}, then X_{NH_3} could exceed 10^{-4} near the 400K level. However, recent radar data (Jones *et al.*, 1972) have provided a secure upper limit of $X_{H_2O}=2\times10^{-3}$. With more reasonable H_2O mixing ratios of 10^{-4} to 10^{-6}, the NH_3 mixing ratios near the 375–475K level should be several orders of magnitude lower than reported by Venera 8, even if the possible kinetic inhibition of NH_3 formation is ignored.

Although there must be serious doubts about the validity of the Venera 8 NH_3 results, full understanding awaits publication of details of the analytic techniques used. A more sophisticated landing probe equipped to determine accurately a temperature-pressure-composition profile in the Venus atmosphere would permit an unambiguous resolution of the problems.

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Potassium in the Earth's Core: Evidence and Implications

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ABSTRACT

A critical review of the major competing chemical models for the Earth indicates that the chemical equilibrium model is the most realistic model. This model predicts that the Earth has an Fe-FeS core and the full solar or chondritic K/Si ratio. The crust and upper mantle do not contain sufficient potassium for the entire Earth to have the full solar K/Si ratio; therefore, a substantial fraction of the Earth's potassium must be in the lower mantle or in the core. The hypothesis that the Earth has the solar K/Si ratio and that a substantial fraction of the Earth's potassium must be in the deep interior is supported by terrestrial heat flow data, and is consistent with K/U ratios in terrestrial rocks, Rb-Sr isotope evidence, and ^{40}Ar degassing studies. Data documenting the chalcophile behavior of potassium, including thermodynamic data on the stability of K_2S, data on potassium in sulfide phases in metallurgic and meteoritic systems, and experimental results on potassium partitioning between silicates and Fe-FeS melts, strongly support the hypothesis of potassium in the Earth's core. Arguments against potassium in the core are rebutted. Trace elements which are siderophile or chalcophile, including potassium, will be partitioned into the Fe-FeS core at the time of core formation very early in the Earth's history. Decay of ^{40}K in the core is a major heat source which may provide energy to maintain the geomagnetic field, and drive mantle convection and continental drift.

1. INTRODUCTION

Many previous authors, including Ringwood (1966), Gast (1960, 1972), Wasserburg et al. (1964), and Hurley (1968), have concluded that the Earth is markedly depleted in potassium relative to ordinary chondrites. However, the recent progress (Larimer, 1967; Larimer and Anders, 1967; Lewis, 1972, 1973; Grossman, 1972) in understanding the condensation of planetary constituents from the primitive solar nebula has necessitated a re-examination of models for the chemical composition of the Earth. Lewis (1972, 1973) presented data in support of a model based on chemical equilibrium during the condensation process; this model predicts that the Earth has an Fe-FeS core and the full solar or chondritic K/Si ratio.

The purpose of the present paper is to review critically evidence bearing on the Earth's total potassium content and evidence bearing directly on the question of potassium in the Earth's core.

2. CHEMICAL MODELS FOR THE EARTH

The chemical equilibrium model (Lewis, 1972, 1973) appears to be the most realistic model for the formation of the terrestrial planets. The quantitative predictions of this model are consistent with the observed mean densities of Mercury, Venus, Earth, and Mars, and with existing data on the chemical composition of the terrestrial planets. In this model, differences in the major and trace element content, and in the

content of volatiles among the terrestrial planets are primary features resulting directly from differences in condensation temperature. This model predicts that the Earth has the solar proportions of nearly all of the rock-forming elements, including refractories (Ca, Al, Ti, U, Th, etc.), Fe, Ni, Si, Mg, S, Na, and K. The Earth is thus predicted to have an Fe-FeS core and the full solar K/Si ratio. There is not sufficient potassium in the crust and upper mantle for the entire Earth to have the solar K/Si ratio; therefore, the chemical equilibrium model implies that a substantial fraction of the Earth's potassium must be in the lower mantle or in the core. The presence of sulfur in the Earth's core is particularly significant, since the arguments for potassium in the core are based on the chalcophile behavior of potassium.

Strong, independent evidence for sulfur in the Earth's core was presented by Murthy and Hall (1970, 1972). These authors noted than an Fe-FeS melt will be the first melt formed in the early Earth; because the Fe-FeS eutectic temperature is so low (988 ^{o}C) and is virtually independent of pressure (Brett and Bell, 1969), core formation can occur very early in the Earth's history without necessitating a very hot thermal history for the Earth. Murthy and Hall compared the abundances of a number of volatile elements in the Earth's crust and upper mantle to the abundances of these volatiles in several meteorite classes. Sulfur was found to be depleted in the Earth's crust and mantle by a larger

factor than H_2O, the halogens, or the rare gases. Segregation of sulfur into the core, as predicted by the chemical equilibrium model for the Earth, readily explains this anomolous apparent depletion of sulfur relative to other, more volatile elements.

Inhomogeneous accretion models (Turekian and Clark, 1969; Clark et al., 1972) assume that planets accrete during the condensation process in the solar nebula. Planets accrete with initially layered structures: refractory condensates form a proto-core, followed by an Fe-Ni layer, a magnesium silicate layer, and finally by a veneer of low temperature, volatile-rich condensates. However, this type of model cannot match the observed mean densities of all of the terrestrial planets without resorting to secondary processes such as ad hoc major element fractionations among the planets. The four orders of magnitude difference in the H_2O/CO_2 ratio of Earth and Venus is not compatible with the retention of volatiles as a late-stage veneer as postulated by the inhomogeneous accretion models; none of the carbonaceous chondrites exhibit such a drastic variation in H/C ratio. This type of model also fails to produce the required light element in the Earth's core, since neither S nor Si are predicted to be in the core, and these are the only two elements which have the right properties and are sufficiently abundant (Ringwood, 1966). Several other important aspects of the Earth's composition, including the mantle's FeO content

and the patterns in the relative abundances of volatiles discussed by Murthy and Hall are difficult to reconcile with the predictions of inhomogeneous accretion models. The present author concludes that these models are not a realistic representation of the formation of the terrestrial planets.

Ganapathy and Anders (1974) have developed a chemical model for the Earth, based on the assumption that the Earth formed by the same processes as chondrites. Condensation and remelting in the solar nebular results in seven condensates: early condensate; remelted and unremelted Fe-Ni-Co alloy and (Fe,Mg)-silicates; FeS; and a carbonaceous, volatile-rich silicate. The proportions of these components in the Earth were estimated by applying assumed geochemical constraints such as K/U ratio, bulk U and Fe content, etc. Several other planetary models have been constructed from a mixture of meteorite types with the proportions adjusted to match the mean density and chemical composition of a planet. However, Ganapathy and Anders commented that the arbitrary, ad hoc nature of this approach is esthetically objectionable. This same criticism may be applied to the model proposed by Ganapathy and Anders. Their model is completely flexible: the relative proportions of their seven components can be arbitrarily varied to match the observed chemical composition of a planet. Another problem for this model is the great difference in H_2O/CO_2 ratio observed for Earth and Venus. In this model, volatiles are contained in a low temperature, carbonaceous silicate component;

however, none of the carbonaceous chondrites display such a large variation in H/C ratio. By a suitable choice of the proportions of the seven components, the model of Ganapathy and Anders could be adjusted to predict a composition for the Earth which is very similar to the composition predicted by the chemical equilibrium model. Other models such as the simple chondritic model, or models based on mixtures of meteorites also predict quite similar compositions. However, because the chemical equilibrium model predicts the correct densities and composition for each of the terrestrial planets without any ad hoc assumptions, the present author prefers the chemical equilibrium model.

The carbonaceous chondrite model proposed by Ringwood (1966) is the only model which unambiguously predicts that the Earth is markedly depleted in potassium relative to the potassium content of chondrites. In this model, each of the terrestrial planets has an initial composition similar to the composition of Type 1 carbonaceous chondrites. Density and composition differences among the terrestrial planets are attributed to varying degrees of reduction and volatile element loss. However, this model is incompatible with many observational data. The postulate that each of the terrestrial planets had initial compositions similar to carbonaceous chondrites is not compatible with current theories requiring an adiabatic temperature gradient in the primitive solar nebula (Cameron and Pine, 1973; Lewis, 1974); the steep temperature

gradient in the nebula must produce distinct composition differences among the terrestrial planets. In Ringwood's model, in situ reduction of iron oxides to form planetary cores results in the generation of a massive, primitive atmosphere. The escape of these primitive atmospheres, a basic requirement of the carbonaceous chondrite model, is a very implausible event for which no quantitative theory has ever been produced. This model even fails to explain the observed densities of the terrestrial planets. The model attempts to explain the high density of Mercury by invoking a Hayashi phase of extreme solar super-luminosity to evaporate silicates from Mercury; however , current theories of stellar evolution (Larson, 1974) conclude that the Hayashi phase does not occur. The low density of Mars is explained by assuming that the primordial material for Mars contained little carbonaceous material. However, in order for this assumption to be valid, the entire solar system, from Mercury to the asteroid belt, except for Mars, would have to be rich in carbonaceous material; the implausibility of this postulate seems evident. The volatile content of the Earth, including the abundance of H_2O, the presence of radiogenic ^{129}Xe (Boulos and Manuel, 1971) and the patterns in volatile abundances discussed by Murthy and Hall (1970, 1972) are all very difficult to reconcile with the high temperature in situ reduction and degassing required by the carbonaceous chondrite model for the Earth. The basic postulates of this model appear to be highly implausible, and

the model cannot explain the observed mean densities and volatile contents of the terrestrial planets. The present author concludes that this is not a viable model for the Earth; this model will not be considered further.

Notwithstanding the strong evidence favoring the chemical equilibrium model for the Earth, the conclusion that the Earth has a solar K/Si ratio is not entirely dependent on the assumptions of the chemical equilibrium model; in fact, departures from the chemical equilibrium model do not reduce the Earth's predicted potassium content. In the chemical equilibrium model, potassium condenses as alkali feldspar near 1000 ^{o}K. In the inhomogeneous accretion model, potassium condenses at a lower temperature as the oxide or perhaps as the sulfide because of the stability of K_2S. However, the requirement that the formation temperature of the Earth be low enough for retention of volatiles means that the temperature must be low enough for complete condensation of potassium. Therefore, even if the assumption of chemical equilibrium during the condensation process is not entirely valid, the Earth is still predicted to have the full solar K/Si ratio. Other models, including the model of Ganapathy and Anders, the simple chondritic model, or models based on mixtures of meteorites, are also compatible with the Earth having the solar K/Si ratio. However, the chemical equilibrium model predicts nearly the same composition for the Earth without any ad hoc assumptions, and is thus the preferred model. The conclusion

that the Earth has the solar K/Si ratio thus appears to be a very firm conclusion.

An extensive discussion of the evidence supporting the chemical equilibrium model for the Earth, and the evidence against inhomogeneous accretion models, the model of Ganapathy and Anders, and the carbonaceous chondrite model has been presented elsewhere (Goettel, 1975).

3. POTASSIUM CONTENT OF THE EARTH

One of the classic arguments supporting the chondritic model for the Earth is the "chondritic coincidence": the present heat production in an Earth with the chondritic or solar proportions of K, U, and Th closely matches the observed mean heat flow of the Earth (Urey, 1956; Hurley, 1957; Birch, 1958). The concentrations of K, U, and Th in the crust and upper mantle in continental regions are sufficient to produce the observed heat flow; however, in oceanic regions the concentrations of these elements are far too low to explain the observed heat flow. The recent revision of the mean heat flow in oceanic areas by Williams and Von Herzen (1974) has included the important contribution from the cooling lithosphere, and thereby greatly increased the estimated heat flow in oceanic areas, and the total heat flow of the Earth. This higher heat flow estimate compounds the difficulty which models predicting less than the solar proportion of potassium in the Earth have in explaining terrestrial heat flow data. Terrestrial heat flow data support the predictions of the chemical equilibrium model:

(1) the Earth has the solar K/Si ratio, and (2) a substantial fraction of the Earth's potassium must be in the deep interior.

The K/U ratio in terrestrial rocks (Wasserburg et al., 1964), Sr isotope evidence (Gast, 1960), and Ar degassing studies (Hurley, 1968) have all been interpreted as confirmation that the Earth, relative to chondrites, is strongly depleted in K and Rb. These data demonstrate convincingly that sufficient K and Rb are not contained in the crust and upper mantle for the entire Earth to have solar K/Si and Rb/Si ratios. However, the interpretation that these data may be applied to the entire Earth is based on overly restrictive assumptions about the geochemical behavior of K and Rb. If a substantial fraction of the Earth's total K and Rb are partitioned into the core at the time of core formation very early in the Earth's history, as suggested by Lewis (1971) and Hall and Murthy (1971), then the Earth may still have the full solar proportions of K and Rb. In this case, a substantial fraction of the Earth's K, Rb, and radiogenic Ar would be effectively decoupled from the crust and mantle. Therefore, the K/U data, Sr isotope evidence, and Ar degassing studies do not contradict the basic prediction of the chemical equilibrium model: the Earth has the full solar K/Si ratio.

4. EVIDENCE FOR POTASSIUM IN THE CORE

(a) Stability of K_2S

Lewis (1971) emphasized that several elements, including

potassium, which are normally considered lithophile have appreciable chalcophilic properties. Reactions of the form

$$K_2O + H_2S = K_2S + H_2O \qquad (1)$$

were considered for the purpose of portraying the relative stabilities of pure sulfides and oxides. At 1000 ^oK, the equilibrium constant for reaction (1) is $10^{14.8}$, this high value demonstrates the stability of K_2S and confirms that potassium may indeed have appreciable chalcophilic properties. If sodium is substituted for potassium in reaction (1), the equilibrium constant at 1000 ^oK is $10^{9.57}$; thus Na appears to be significantly less chalcophile than K. K is depleted in the Earth's crust and upper mantle relative to chondrites, but Na is not depleted; the explanation of this difference in the geochemical behavior of K and Na may be that K, but not Na, is partitioned into Fe-FeS melts at the time of core formation.

Hall and Murthy (1971) considered a variety of chemical reactions representative of both the present oxidized crust and the more reducing conditions existing during core formation. Data for reactions of the form

$$MeSO_4 + FeS = MeS + FeSO_4 \qquad (2)$$

$$MeCO_3 + FeS = MeS + FeCO_3 \qquad (3)$$

which reflect the highly oxidized present crust, suggest that all of the alkali metals will be lithophile under crustal conditions. However, data for reactions of the form

$$MeSiO_3 + FeS = MeS + FeSiO_3 \qquad (4)$$

$$\tfrac{1}{2}Me_2SiO_4 + FeS = MeS + \tfrac{1}{2}Fe_2SiO_4 \qquad (5)$$

which reflect the more reducing conditions existing during core formation, suggest that Li and Na remain lithophile, but that K, Rb, and Cs may be chalcophile and thus partitioned into the core. Uncertainty about the effects of Al and high pressure, and the paucity of relevant thermodynamic data preclude direct calculation of the amount of K expected in the core.

(b) Metallurgic Evidence

Chalcophile behavior of potassium has been documented in metallurgic systems. Cissarz and Moritz (1933) analysed co-existing metal, sulfide, and silicate phases from the smelting of the Mansfeld copper ores. The sulfide matte contains 0.8% K_2S; extremely low abundances of Si (0.05%) and Al (0.01%) in the sulfide matte indicate that the high K_2S value cannot be due to contamination by K-bearing silicates. The co-existing silicates contain 17% Al_2O_3 which demonstrates that the presence of alumino-silicates does not preclude the formation of K_2S. The silicates also contain 4% FeO; the oxygen fugacity is probably somewhat below the Fe-FeO buffer and is thus compatible with the oxygen fugacity expected in a differentiating, approximately chondritic Earth.

A recent microprobe study of blast furnace byproducts (vom Ende et al., 1966) provided additional data on potassium in sulfide phases. A K-Fe-S compound and an alkali-Mn-S compound were identified as constituents of the lowest temperature melt. Textural evidence indicated that the

K-bearing sulfide and the Mn sulfide crystallized from a common FeS-rich melt. These data verify the plausibility of partitioning potassium into an Fe-FeS melt. In both metallurgic systems discussed, K is several times more abundant than Na in the sulfide phases.

(c) Meteoritic Evidence

Djerfisherite, a potassium-iron-sulfide, has been discovered in several enstatite chondrites and achondrites, and in a sulfide nodule within an iron meteorite (Fuchs, 1966; El Goresy et al., 1971). In enstatite chondrites, djerfisherite occurs in the silicate matrix and is always associated with troilite, and usually with both troilite and kamacite; troilite inclusions were observed in some grains. These observations suggest that djerfisherite may crystallize from an FeS-rich melt. In the Bishopville achondrite, a djerfisherite-troilite-kamacite inclusion was found in sodic plagioclase; this striking observation demonstrates the chalcophile behavior of potassium even in the presence of feldspar. Although oxygen fugacities in enstatite meteorites are somewhat lower than expected for a differentiating, approximately chondritic Earth, the occurrence of the potassium sulfide djerfisherite is significant because it documents the chalcophile behavior of potassium in meteoritic systems which have overall chemical compositions similar to the composition of the Earth. Djerfisherite contains some sodium substituting for potassium;

however, the maximum Na content measured by El Goresy et al. was less than 10% of the K content, and the Na content of many grains was below detection limits.

Shima and Honda (1967) measured the potassium content of component minerals of the Abee enstatite chondrite. They found 3.7% of the total K in oldhamite (CaS) and 3.1% in troilite. Oversby and Ringwood (1972) argued that the amount of K observed in FeS in Abee places an upper limit of about 2.5% of the Earth's K in the core, since Abee has a greater proportion of FeS than the Earth and the Earth is more oxidized than Abee. However, this argument is not valid because the Abee data represent low temperature partitioning of potassium between solid silicates and solid FeS. The relevant partitioning for the Earth involves an Fe-FeS melt and solid silicates at temperatures hundreds of degrees above the Abee equilibration temperature (Murthy and Hall, 1970, 1972; Lewis, 1971). Thus, the Abee data do not place an upper limit on the amount of potassium in the Earth's core.

(d) Experimental Results

Goettel (1972) investigated the partitioning of potassium between solid roedderite ($K_2Mg_5Si_{12}O_{30}$) and an Fe-FeS melt. Roedderite and merrihueite (the Fe analogue) are the only two silicates containing essential potassium which have been identified in chondrites; therefore, roedderite is a reasonable choice for one of the potassium bearing phases in the early Earth. At 1030°C, a K_2S/FeS weight ratio of (3.340 ± 0.015)

x 10^{-3} was measured; if the Earth has a solar K/Si ratio, a K_2S/FeS weight ratio of about 9 x 10^{-3} would suffice to extract all of the Earth's potassium into the core. The potassium content of the quenched Fe-FeS melt was found to increase significantly with increasing temperature. The oxygen fugacity in these experiments was somewhat below the Fe-FeO buffer and thus compatible with a differentiating, approximately chondritic Earth. Uncertainty about the identity of the K-bearing phases in the early Earth, and uncertainty about the effect of pressure on potassium partitioning prevent calculation of the K content of the Earth's core from these data. However, these data certainly demonstrate the plausibility of partitioning significant amounts of K into Fe-FeS melts at the time of core formation.

Partial melting experiments are presently being conducted on samples of the Forest City H5 chondrite to examine the partitioning of potassium between the Forest City silicates and Fe-FeS melts. The composition predicted for the Earth by the chemical equilibrium model is similar to the composition of ordinary chondrites. Therefore, these Forest City experiments were undertaken as a first-order approximation to the primary differentiation of the Earth into an Fe-FeS core and a silicate mantle. Preliminary results have confirmed the presence of potassium in the quenched Fe-FeS melts, but reliable, quantitative results are not yet available. The full results of these experiments and results of an investigation of potassium partitioning between alkali feldspar and

Fe-FeS melts will be presented elsewhere (Goettel, 1975a,b, in preparation).

(e) Evidence Against Potassium in the Earth's Core

Oversby and Ringwood (1972, 1973) presented data on the partitioning of potassium between basaltic liquids and Fe-FeS melts, and argued against potassium in the Earth's core. However, experiments involving differentiated, basaltic material are not particularly relevant to the partitioning of potassium at the time of core formation. The basaltic composition used by Oversby and Ringwood contained 13% Al_2O_3; this proportion of Al_2O_3 greatly exceeds the proportion of Al_2O_3 in an Earth with a solar or chondritic Al/Si ratio, and strongly biases the experiment in favor of alkali alumino-silicate formation. The chemical and physical conditions which are relevant to the partitioning of potassium into the Fe-FeS core are the conditions which existed during the primary differentiation of the Earth into metal-sulfide core and silicate mantle, and not the conditions presently existing in the crust or upper mantle.

Oversby and Ringwood examined the partitioning of potassium between an Fe-FeS melt and a silicate liquid. However, at a pressure of even a few tens of kilobars, an Fe-FeS melt will form at temperatures several hundred degrees below the solidus temperature for mantle silicates. Therefore, experiments relevant to the partitioning of potassium into the core almost certainly involve solid silicates rather than

silicate liquids. Hall and Murthy (1971) noted that K, Rb, and Cs are selectively enriched in the liquid phase during partial melting of silicates because their large ionic size makes them incompatible in many mineral structures; this ionic size incompatibility may be a major factor in the partitioning of these elements into Fe-FeS melts at the time of core formation.

Seitz and Kushiro (1974) conducted melting experiments on partially reduced samples of the Allende Type 3 carbonaceous chondrite. At 1350°C and 20 kilobars, the silicate melt contained 0.1% K_2O, while K in the sulfide melt was below the detection limit of 0.01%. At 20 kilobars, the silicate solidus of the partially reduced Allende material is more than 300°C above the Fe-FeS eutectic temperature at this pressure. As discussed in the preceeding paragraph, experiments relevant to potassium in the Earth's core almost certainly involve partitioning of potassium between an Fe-FeS and solid silicates. Therefore, these experimental data may only be of marginal significance with respect to the potassium content of the Earth's core.

5. IMPLICATIONS OF POTASSIUM IN THE CORE

Two distinct periods in the geochemical differentiation of the Earth must be considered: (1) the primary differentiation into metal-sulfide core and silicate mantle, and (2) the subsequent differentiation of the silicate mantle. The geochemical behavior of many elements, most notably potassium, may

be markedly different in these two differentiation processes. Elements with significantly chalcophilic or siderophilic properties will be preferentially partitioned into the Fe-FeS core at the time of core formation very early in the Earth's history. The elements partitioned into the core may include K, Rb, and Cs, as well as many other elements such as Ni, Co, Pt-group metals, Pb, Cu, Ag, Au, Cd, Bi, etc. which are normally considered siderophile or chalcophile.

A major consequence of the partitioning of these elements into the core is that the composition of the Earth may be very similar to the composition of ordinary chondrites; or in the context of the chemical equilibrium model, that the Earth has the solar proportions of nearly all of the rock forming elements including refractories (Al, Ca, Ti, Ba, Sr, U, Th, rare earths, etc.), Fe, Ni, Mg, Si, S, Na, and K. Geochemical data such as K/U ratios, Sr isotope evidence, K-Rb-Ar data, and U/Pb isotope evidence must be interpreted in the context of the two-stage differentiation history of the Earth. Inferences drawn from the chemistry of the crust and upper mantle must be extrapolated very cautiously if they are to be extended to the entire mantle or the entire Earth.

The Fe-FeS eutectic temperature is so low (988^{o}C) and increases so slowly with pressure that core formation would occur very early in the Earth's history even if the Earth retained virtually none of its accretional gravitational potential energy; adiabatic compression alone is probably sufficient to

initiate core formation. At high pressures, the solidus temperature for mantle silicates is so much higher than the Fe-FeS eutectic temperature that core formation may not necessitate large scale mantle melting.

Most previous thermal history calculations have assumed that K, U, and Th are geochemically coherent during the Earth's differentiation; partitioning of K into the core results in a major redistribution of the radiogenic heat sources in the Earth. One consequence of the postulated solar K/Si ratio for the Earth and the short half life of ^{40}K is that a large fraction of the total radiogenic heat production of the Earth is released early in the Earth's history. Low-temperature core formation and the possibility of potassium in the core necessitate a complete revision of existing thermal history models for the Earth.

Decay of ^{40}K in the core will provide a major internal heat source to drive core convection. For a K content of 0.1%, the rate of heat production is about 2×10^{12} cal/sec (Verhoogen, 1973); this K content is about 40% of the total K in an Earth with the solar K/Si ratio. The rate of heat production by ^{40}K is likely to be several orders of magnitude greater than the rate of dissipation of magnetic energy in the core; even if the efficiency of conversion of thermal to magnetic energy is very low, it appears that there will be sufficient energy from ^{40}K to maintain the geomagnetic field. Heat from ^{40}K in the core will produce a large heat flux through the mantle;

this heat is an energy source to drive mantle convection and continental drift.

Despite the high heat flux through the lower mantle from ^{40}K in the core, the lower mantle may not convect. The recent data of Mao (1973) and Mao and Bell (1972) indicate that the thermal conductivity of silicates may increase by several orders of magnitude at high pressures. From simple geometric considerations, the heat flux per unit surface area in the mantle will decrease as the square of the distance from the core/mantle interface. The data of Mao and Bell suggest that the thermal conductivity of the mantle may decrease more rapidly than the heat flux. The transition between the lower, possibly nonconvecting mantle, and the upper, convecting mantle may be at the depth where the thermal conductivity has become low enough for the adiabatic gradient to be exceeded. Because of the short half life of ^{40}K, the heat flux through the lower mantle decreases with time. Therefore, the depth in the upper mantle to which convection extends may be decreasing with time. If this speculative hypothesis is valid, it may have important implications for paleo-continental drift, since the depth and rate of upper mantle convection will be strongly time dependent.

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