Shock Compression of KFeS$_2$ and the Question of Potassium in the Core

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The Hugoniot equation of state of KFeS$_2$ (initial density 2.663 g/cm^3) has been determined for pressures up to 110 GPa. The Hugoniot data demonstrate a transformation at 13 ± 1 GPa to a phase with an apparent zero-pressure density of 3.7 ± 0.2 g/cm^3. A comparison of the inferred isentrope of KFeS$_2$ (high-pressure phase) with those of Fe, Fe$_{0.9}$S, and FeS$_2$ indicates that the atomic volume of potassium in KFeS$_2$ is approximately twice that of iron at 75 GPa. In the temperature and pressure range of the experiments, potassium fails to meet the empirical Hume-Rothery and Raynor (HRR) criterion for solubility of an element in iron, namely, that the molar volume of the element should not exceed that of iron by a factor greater than ~1.4. However, both the applicability of the HRR solubility criterion and the inferred isentrope of KFeS$_2$ at high pressure are uncertain. Thermochemical calculations of the partitioning of K between a sulfide and silicate phase (e.g., KFeS$_2$ and KAlSiO$_4$ or KAlSi$_3$O$_8$ (hollandite)) indicate that pressure does not have a pronounced effect on the relative stability of solid KFeS$_2$ and potassium aluminosilicate high-pressure phases. The calculations suggest that the high-pressure phase of KFeS$_2$ would not be stable in relation to KAlSiO$_4$ (kalsilite) in the upper mantle, or in relation to KAlSi$_3$O$_8$ (hollandite) in the lower mantle. However, the calculations do not bear directly on the question of partitioning of K into an iron sulfide melt from lower mantle aluminosilicate phases. Although the present results cannot absolutely rule out the hypothesis that a large fraction of the terrestrial potassium budget has dissolved into a molten iron sulfide-bearing core, the present analysis of the pressure-volume relation for potassium, iron, iron sulfides, potassium aluminosilicate, and potassium iron sulfide yields no evidence in support of this hypothesis.

INTRODUCTION

From a comparison of K/U ratios of chondrites and accessible terrestrial rocks, *Wasserburg et al.* [1964] concluded that the earth is depleted in potassium by a large factor, ~8, in relation to chondrites. Recently, it has been argued that the earth does have a chondritic or cosmic proportion of potassium, the apparent deficit being due to strong fractionation of potassium into the core. *Lewis* [1971] and *Hall and Murthy* [1971] suggested that if the earth accreted homogeneously, most of its potassium inventory would dissolve in iron sulfide which became segregated in the core. With three quarters of a chondritic complement of potassium in the core, amounting to a mass fraction of ~0.15%, the rate of radiogenic heat production in the core would be ~10^{13} W, sufficient, according to *Gubbins et al.* [1979], to maintain the geomagnetic dynamo. Radiogenic heat production in the core would amount to a substantial fraction, approximately one third, of the present surface heat flow.

Oversby and Ringwood [1972] fused a synthetic basalt together with iron and potassium sulfides at 1450°C and 1.5 GPa and reported a minimum distribution coefficient of 25–50 favoring potassium in the aluminosilicate over the sulfide quench product: they concluded that not more than 1 or 2% of the earth's potassium could be in the core. *Goettel* [1976] conducted experiments in which iron sulfide melts were equilibrated with K feldspar at 1030° and 1070°C and found that the solubility of potassium in the melt increased rapidly with temperature. Extrapolating his ambient pressure results, Goettel calculated potassium contents of iron sulfide melts equilibrated with plagioclase of chondritic composition, Ab$_{82}$An$_{12}$Or$_6$, at 1500° and 2000°C; at these temperatures the melt was calculated to contain 10% and 62%, respectively, of

the total potassium. *Seitz and Kushiro* [1974] studied the melting relations of the Allende carbonaceous chondrite in a series of experiments at pressures up to 2.5 GPa. In these experiments, two immiscible liquid phases were obtained. Seitz and Kushiro reported that the iron-nickel sulfide melt contained no detectable potassium (limit of detection ~0.01%) and concluded that the core could contain very little of the earth's potassium. *Goettel* [1976], however, pointed out that the most appropriate experiment would be to examine the partitioning of K between sulfide melt and solid silicate at high pressure. (Recent experiments by *Wendlandt and Eggler* [1980] indicate that at upper mantle temperatures and pressures the appropriate silicate would be KAlSiO$_4$ (kalsilite).) *Ganguly and Kennedy* [1977] carried out a series of partitioning experiments to 3.0 GPa and 1150°C with an omphacitic pyroxene as the solid phase and with oxygen fugacity in the field of metallic iron. They found that the solid silicate phase directly in contact with the potassium-bearing sulfide melt became enriched in K by a factor of about 40, in relation to the sulfide. This result thus generally agreed with the results of *Oversby and Ringwood* [1972] and *Seitz and Kushiro* [1974].

Bukowinski [1976] suggested that 'disputes based on results of laboratory experiments carried out at low pressure are quite pointless, since the data themselves are of little relevance to the actual physics and chemistry in the lower mantle and core.' Bukowinski obtained augmented plane wave solutions to Schroedinger's equation for the electronic states of potassium in the static (0°K) *bcc* lattice and determined that 4s → 3d transitions occur at pressures of 24.5, 29, and approximately 50 GPa. The pressure required for the lowest of these transitions is close to the 20-GPa value suggested by *Drickamer and Frank* [1973] on the basis of low-temperature electrical conductivity measurements. Bukowinski concluded that at about 50 GPa the ionic radius of potassium becomes comparable to that of iron and its electronic structure becomes similar to that of a transition metal. These electronic transitions could, in principle, greatly increase the miscibility of metallic

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TABLE 1. X Ray Diffraction Results for KFeS$_2$

Intensity* (Observed)	Lattice Spacing d (Observed),* Å	Indexing (Calculated)†	
		d, Å	hkl
10	5.5	5.6405	110
		5.6400	020
8	3.24	3.2567	200
		3.2564	130
8	2.90	2.9014	$\bar{2}$21
2	2.45	2.4945	002
		2.4939	$\bar{2}$02
1	2.283	2.2813	022
		2.2809	$\bar{2}$22
1	2.135	2.1320	310
		2.1318	240
		2.1317	150
6	1.876	1.8802	330
		1.8800	060
		1.8772	151
1	1.733	1.7312	$\bar{1}$52
3	1.626	1.6283	400
		1.6282	260
		1.6262	$\bar{3}$51
1	1.563	1.5644	420
		1.5644	350
		1.5643	170

* CoK_α, NiO standard. Sample synthesis was by fusion of K$_2$CO$_3$, Na$_2$CO$_3$, Fe, and S. Archimedian densities of 15 pressed-powder samples were 2.655 ± 0.013 g/cm^3. S. Hill, California Institute of Technology, analyst.

† Calculated from lattice parameters determined by Weissenberg photography by Boon and MacGillavry [1942]: a = 7.05 Å, b = 11.28 Å, c = 5.40 Å, β = 112.5°, density is 2.663 g/cm^3.

potassium in iron or iron sulfide melts. However, Bukowinski did not address quantitatively the question of whether the electronic transitions in potassium would occur at comparable pressures when it is in the environment of an ionic or covalent phase.

Clarke et al. [1977] reported the discovery, in a kimberlite, of a potassium-bearing iron sulfide phase in a clinopyroxene-ilmenite intergrowth. The composition of the phase was found to be similar to that of djerfisherite, K$_6$Cu$_2$(Fe, Ni)$_{24}$S$_{28}$, a mineral identified in several meteorites. Later experiments suggested, however, that the kimberlite potassium iron sulfide phase could have a relatively low pressure hydrothermal paragenesis [Clarke, 1979].

In this paper we report a series of dynamic compression ex-

periments on potassium thioferrite, KFeS$_2$, in the pressure range up to 110 GPa. An estimate is obtained for the atomic volume of K, at high pressure, in the high-pressure phase of KFeS$_2$. Experimental data on the compression of potassium aluminosilicates are reviewed briefly, and an equation of state for KAlSi$_3$O$_8$ (hollandite) is obtained. Thermochemical calculations are carried out in an attempt to determine whether KFeS$_2$ would be stable in relation to potassium in aluminosilicate phases at high pressure and to examine the possibility of partition of potassium into the core.

EXPERIMENTS

Potassium thioferrite crystals of purity ≥99% were prepared by fusion of K$_2$CO$_3$, Na$_2$CO$_3$, Fe, and S under nitrogen at 900°C by Research Organic/Inorganic Chemical Corporation (Menlo Park, California). Potassium thioferrite crystallizes as purple fibers of metallic luster. Its structure, determined by Boon and MacGillavry [1942] using the Weissenberg method, is monoclinic, consisting of chains of (FeS$_2$)$_n$ with K in the interstices. The space group is C 2/c. Table 1 compares lattice spacings determined from a powder diffraction pattern by S. Hill (California Institute of Technology) with spacings calculated from the lattice constants of Boon and MacGillavry. With respect to the calculated lines, the present powder pattern is more accurate than the standard ASTM 3-0103.

The preparation of polycrystalline samples and the construction of targets for Hugoniot experiments were carried out under dry nitrogen or argon. Powdered KFeS$_2$, passed through a 100-μm mesh, was pressed for several hours at 200°C and 0.5 GPa in cylindrical 13-mm- and 16-mm-diameter dies. Fifteen discs prepared in this way had bulk densities of 2.593 ± 0.019 g/cm^3 and Archimedian densities of 2.655 ± 0.013 g/cm^3. Using the X ray density 2.663 g/cm^3, the average porosity is calculated to be 2.6%, while the average apparent porosity is 2.3%, indicating the presence of 0.3% unfilled pore space in the Archimedian density determinations.

Experimental methods and error analyses are the same as described by Jeanloz and Ahrens [1977] and Jackson and Ahrens [1979], respectively. Flash X ray photography of projectiles emerging from the muzzle of the 40-mm gun confirmed the accuracy of the laser-interrupt system used to measure projectile velocity.

The raw Hugoniot data, listed in Table 2 and illustrated in Figure 1, are interpreted in terms of three segments as in-

TABLE 2. Hugoniot Data for KFeS$_2$

Shot	Flyer/ Driver*	Impact Velocity, km/s	Initial Density, g/cm^3	Shock Velocity, km/s	Particle Velocity, km/s	Hugoniot Density, g/cm^3	Hugoniot Pressure, GPa
451	Lexan/Al	0.810 ± 0.005	2.552 ± 0.005	2.74 ± 0.04	0.223 ± 0.004	2.78 ± 0.04	1.56 ± 0.04
444	Al/Al	0.785 ± 0.005	2.575 ± 0.005	3.22 ± 0.04	0.515 ± 0.005	3.06 ± 0.04	4.27 ± 0.04
450	Lexan/Al	1.930 ± 0.010	2.583 ± 0.005	3.41 ± 0.05	0.630 ± 0.010	3.17 ± 0.05	5.55 ± 0.11
455	Al/Al	0.991 ± 0.002	2.598 ± 0.008	3.49 ± 0.03	0.635 ± 0.002	3.18 ± 0.03	5.76 ± 0.04
440	Al/Al	1.348 ± 0.002	2.611 ± 0.005	3.73 ± 0.03	0.851 ± 0.002	3.38 ± 0.03	8.29 ± 0.06
437	Al/Al	1.74 ± 0.02	2.60 ± 0.02	4.14 ± 0.10	1.06 ± 0.02	3.50 ± 0.07	11.4 ± 0.3
458	Al/Al	2.13 ± 0.01	2.563 ± 0.006	4.35 ± 0.05	1.31 ± 0.01	3.67 ± 0.04	14.6 ± 0.1
470	W/W	1.660 ± 0.006	2.607 ± 0.006	4.54 ± 0.05	1.45 ± 0.01	3.83 ± 0.05	17.15 ± 0.15
467	W/W	1.872 ± 0.005	2.586 ± 0.006	4.67 ± 0.03	1.630 ± 0.006	3.97 ± 0.03	19.7 ± 0.2
436	W/W	2.06 ± 0.04	2.600 ± 0.005	4.84 ± 0.03	1.79 ± 0.04	4.13 ± 0.08	22.5 ± 0.5
435	W/W	2.37 ± 0.05	2.605 ± 0.005	5.13 ± 0.03	2.05 ± 0.05	4.34 ± 0.09	27.4 ± 0.7
449	W/W	2.514 ± 0.005	2.635 ± 0.005	5.27 ± 0.03	2.160 ± 0.006	4.47 ± 0.04	30.0 ± 0.3
LGG56	Al/Al	4.80 ± 0.02	2.589 ± 0.010	6.24 ± 0.08	2.79 ± 0.02	4.68 ± 0.06	45.1 ± 0.6
LGG54	Ta/Ta	5.69 ± 0.02	2.590 ± 0.007	8.70 ± 0.10	4.45 ± 0.02	5.30 ± 0.07	100.3 ± 1.1
LGG69	Ta/Ta	6.05 ± 0.02	2.597 ± 0.018	9.08 ± 0.10	4.72 ± 0.02	5.40 ± 0.08	111.1 ± 1.3

* Lexan is polycarbonate plastic; Al is 2024 aluminum alloy.

dicated. Inclined mirrors employed to record the free surface velocity in the nine lowest-pressure experiments showed no evidence of two-wave structures. In Figure 2 the data are transposed to the pressure-density plane using the Rankine-Hugoniot relations for single-shock propagation. The curve drawn through the data at lower pressures corresponds to a linear shock velocity (U_s) versus particle velocity (U_p) relation

$$U_s = C_0 + S\ U_p \tag{1}$$

with $C_0 = 2.4$ km/s and $S = 1.6$, and illustrates that the data cannot be fit with a single compression curve. The onset of phase transformation occurs at a Hugoniot pressure of 13 ± 1 GPa, bracketed by 40-mm gun experiments 437 and 458.

EQUATIONS OF STATE OF KFES$_2$

Estimates of STP-centered isentropes for the nonporous low-pressure phase and for the high-pressure phase were obtained from the Hugoniot data using the relation

$$P_H = \frac{P_s - (\gamma/V)(E_s + E_{TR})}{1 - (\gamma/2)[(V_{00}/V) - 1]} \tag{2}$$

where P_s is the isentropic pressure of the phase at specific volume V, P_H is the pressure of the Hugoniot centered at STP on the porous low-pressure phase of specific volume V_{00}, and E_s is the isentropic compression energy of the phase. Equation (2) describes the Hugoniot data, in relation to isentropes only in the high-pressure and low-pressure regimes and not in the mixed phase regime (Figures 1 and 2). In the high-pressure region an additional energy E_{TR}, the STP energy of transition from low- to high-pressure phases, is included. The Grüneisen function $\gamma(V)$ of both the low- and high-pressure phases was assumed to be
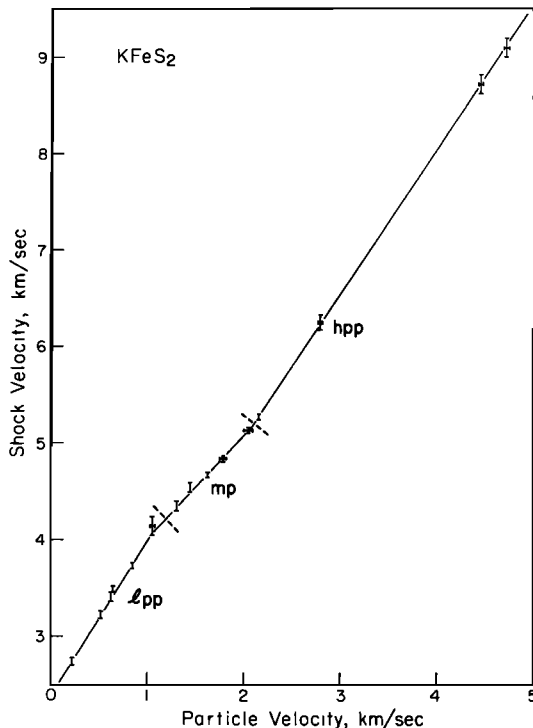
$$\gamma = 1.5(V/V_0)^{1.5} \tag{3}$$

Fig. 1. Shock velocity versus particle velocity Hugoniot data, KFeS$_2$. The range of data for the low-pressure phase (lpp), mixed phase (mp), and high-pressure phase (hpp) regime is indicated.
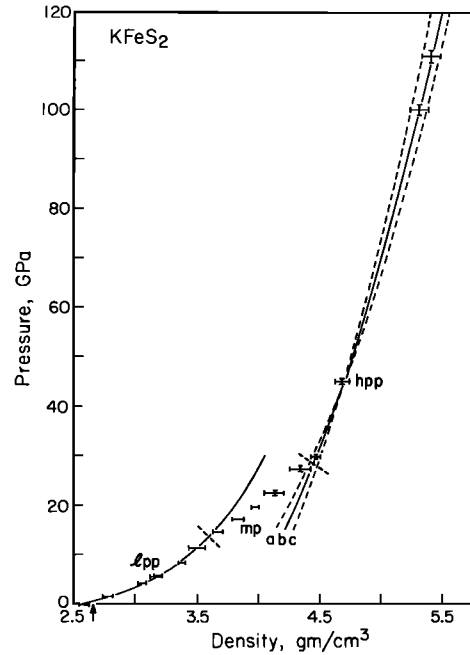

Fig. 2. Shock pressure versus density Hugoniot data, KFeS$_2$. Equation of state parameters corresponding to theoretical curves drawn through low-pressure regime (lpp) and high-pressure regime (hpp) data are given in Table 3.

where V_0 is the specific volume of either the high- or low-pressure phase at STP. The assumed γ_0 is similar to the value 1.45 for pyrite (Table 4). The third-order equation of state of Ullmann and Pan'kov [1976; also Walzer et al., 1979] was employed to represent the isentropes. The isentrope pressure and compression energy are given by

$$P_s = \frac{-K_{s0}}{u}(x^{2u-1} - x^{u-1}) \tag{4}$$

$$E_s = \frac{K_{s0}V_0}{2u^2}(x^u - 1)^2 \tag{5}$$

where

$$x = V/V_0 \qquad u = \tfrac{3}{2}(2 - K_{s0}')$$

and K_{s0} and K_{s0}' are the STP isentropic bulk modulus and pressure derivative. A transition energy E_{TR} of 0.8 kJ/g was calculated in the manner of McQueen et al. [1967], assuming a Clapeyron slope of 3 MPa/K (for zero Clapeyron slope, E_{TR} would be 0.84 kJ/g).

Isentrope equation of state parameters corresponding to the theoretical Hugoniots shown in Figure 2 are given in Table 3. Also indicated in Table 3 is the slight effect on equation of state parameters when the Birch-Murnaghan (third-order Eulerian finite strain) equation is employed instead of the Ullmann-Pan'kov equation. The range of solutions for the high-pressure phase (hpp) indicated in Figure 2 and Table 3 incorporates the uncertainty in the Hugoniot data but not the uncertainty in the Grüneisen function: with the latter included, the range of equation of state parameters might be doubled. The best fitting solution, $\rho_0 = 3.7$ g/cm^3 and $K_{s0} = 85$ GPa, for the hpp equation of state corresponds approximately with the C_0-ρ_0 systematics for sulfides [Ahrens, 1979]. For $\rho_0 = 3.7$ g/cm^3 these systematics would predict $K_{s0} = 75$ GPa.

Hugoniot temperatures calculated with γ given by (3) are

TABLE 3. Isentropic Equation of State Parameters, $KFeS_2$

Equation of State	Density, g/cm³	Bulk Modulus (K_{s0}), GPa	$(\partial K_{s0}/\partial P)_s$
Equation (2), lpp	2.663	20	4.4
Equation (2), hpp	3.5	60	4.8
	3.7	85	4.4
	3.9	120	4.0
Birch-Murnaghan	3.7	83	4.6

Fit to data of Table 2 using (2), assuming average bulk density of 2.593 g/cm³, E_{TR} = 0.8 kJ/g, and γ = 1.5$(V/V_0)^{1.5}$.

approximately 600°K, 1300°K, and 7000°K at pressures of 13, 30, and 110 GPa. These states are the lower and upper limits of the Hugoniot mixed-phase region and the maximum Hugoniot compression attained, respectively. The onset of melting, not considered in the foregoing calculations, probably occurs near the onset of the high-pressure phase regime. In the pressure range 30–50 GPa the Hugoniot temperatures are comparable with terrestrial temperatures in the same pressure range: above 50 GPa the Hugoniot probably lies above the ancient and present terrestrial geotherm. It is possible that at high pressure the calculated isentrope is metastable, i.e., further phase transformation(s) may intervene between the higher temperature states and the much cooler calculated isentrope.

COMPARISON OF FE, FES, FES₂, K, AND KFES₂ COMPRESSION CURVES

First-order estimates of the atomic volume of K in the high-pressure phase of $KFeS_2$ can be obtained from the isentropes centered at STP (compression curves) of Fe, FeS, FeS_2, and $KFeS_2$ by applying the additive-volume approximation. There is an uncertainty of order 1–10% in the volumes of these phases along cool principal isentropes upon reducing the Hugoniot data, for pressures up to about 100 GPa. There is a comparable probable error in the additive-volume approximation.

STP-centered equation of state parameters for FeS_2 (pyrite) and the high-pressure phases of Fe, FeS, and $KFeS_2$ are listed in Table 4. Ullmann-Pan'kov isentropes of these phases are compared in Figure 3 in terms of atomic volume or mean atomic volume. Small pressure differences (<1%) between isentropes and isotherms are neglected. The compression curves are shown as dotted lines where metastable and as dashed lines where extrapolated. Also shown are the volume differences $V(KFeS_2)$ − $V(FeS_2)$ and $V(KFeS_2)$ − $2V(FeS)$, which yield estimates of $V(K)$ in $KFeS_2$ according to the additive volume approximation. At 75 GPa the estimated atomic volume of K in $KFeS_2$ (12.5 cm³/mol) is approximately twice that of metallic iron (5.5 cm³/mol).

According to empirical relations developed by *Hume-Rothery and Raynor* [1962] a condition for the solubility of an element in iron is that its molar volume should not exceed that of iron by a factor greater than ~1.4. The compression curves of Figure 3 suggest that metallic potassium fails, by a wide margin, to meet this condition. However, the stability of the calculated cool compression curves with respect to variation of the many unknown parameters in reducing Hugoniot data for Fe, $Fe_{0.9}S$, FeS_2, and $KFeS_2$ and the applicability of the solubility condition at high pressure have not been demonstrated.

It is of interest to compare the foregoing estimates of the volume of K in $KFeS_2$ with the compression curve of metallic potassium. The Hugoniot data of *Bakanova et al.* [1965] extend to a pressure of 86 GPa and a compression of 3.43. At this compression the elastic radiation accounts for more than half of the STP-centered Hugoniot pressure. The uncertainty in the Grüneisen parameter at high compression leads to a very large uncertainty in the reduced cool compression curve, as pointed out by *Bukowinski* [1976]. Rather than assuming a Grüneisen function $\gamma(V)$ to reduce the Hugoniot to an adiabat or isotherm in the usual manner, it seems preferable to determine a cool-compression equation of state whose parameters match those of the Hugoniot in the zero-pressure limit. The third-order Ullmann-Pan'kov equation is an appropriate form because of its compatibility with the linear shock wave equation of state (equation (1)). With full adiabatic variables the third-order Ullmann-Pan'kov equation assumes for the second derivative of the bulk modulus

$$-K_0K_0'' = (K_0' + 1)(2K_0' - 1)/9 \quad (6)$$

while for the linear shock wave equation of state,

$$-K_0K_0'' = S(4 - 2S + 2\gamma_0) = (K_0' + 1)(7 - K_0' + 4\gamma_0) \quad (7)$$

[*Ruoff*, 1967], contingent only upon the assumption of the Mie-Grüneisen form for the equation of state [*Mao*, 1971]. Substituting $\gamma_0 = K_0' - 5/6$, according to *Vaschenko and Zubarev* [1963], we obtain

$$-K_0K_0'' = (K_0' + 1)(K_0' + 11/3)/8 \quad (8)$$

TABLE 4. Equations of State for Estimating the Volume of K in $KFeS_2$

	ρ_0, g/cm³	K_{s0}, GPa	K_{s0}'	$-K_{s0}K_{s0}''$ (Ullmann-Pan'kov)[a]	C_0, km/s	S	γ_0	$-K_{s0}K_{s0}''$ (Linear Shock Wave Equation of State)[b]
	8.335[c]	178[c]	5.0[c]	6.00				
FeS III	5.6[d]	150[e]	4.0[e]	3.89				
FeS_2	5.013	146	4.8	5.54	5.4[f]	1.45[f]	1.45[g]	5.80
$KFeS_2$ (hpp)	3.7	85	4.4	4.68				
K	0.86[h]	3.58	3.68	3.31	2.04[h]	1.17[h]	1.3[h]	3.64

[a] $-K_{s0}K_{s0}'' = 1/9(K_{s0}' + 1)(2K_{s0}' - 1)$.
[b] $-K_{s0}K_{s0}'' = S(4 - 2S + 2\gamma_0)$.
[c] *Andrews* [1973].
[d] *Pichulo et al.* [1976].
[e] Estimates based on Hugoniot data for pyrrhotite [*Ahrens*, 1979].
[f] Unpublished Hugoniot data (C. Creaven et al., 1980).
[g] Thermal expansivity from *Skinner* [1962].
[h] *Bakanova et al.* [1965].

which is very close to the Ullmann-Pan'kov expression, for K_0' up to about 8.

Hugoniot and isentropic equation of state parameters for potassium are given in Table 4. Note that the two estimates of K_0'' differ by only 10%. The isentrope of metallic potassium is shown in Figure 3: the pressure difference between calculated isentrope and isotherm is again neglected. At pressures exceeding 45 GPa the isentrope is extrapolated beyond the experimental range of compression. At these pressures, and perhaps at considerably lower pressure, the calculated isentrope may be metastable, i.e., phase transformation(s) (specifically, electronic transitions calculated by *Bukowinski* [1976]) may intervene between the Hugoniot and the calculated isentrope. According to the isentropes shown in Figure 3 the volume of K in $KFeS_2$ at 45 GPa is similar to the volume of metallic potassium. If the potassium isentrope represents the compression of untransformed potassium, then it would appear that potassium also remained untransformed in the $KFeS_2$ Hugoniot experiments. Alternatively, as pointed out by *Bukowinski* [1976], electronic transitions may be smeared out at high temperatures and not be recognized in the potassium Hugoniot data. The same could apply in the case of $KFeS_2$ but evidently not in the case of $KAlSi_3O_8$, discussed below.

COMPRESSION OF POTASSIUM ALUMINOSILICATES

Substantial evidence has accumulated concerning high-pressure alkali aluminosilicate and alkali aluminogerminate phases [*Ringwood et al.*, 1967; *Liu*, 1978]. *Ringwood et al.* [1967] synthesized a hollandite-structure phase from sanidine at 12 GPa and 900°C. The STP density of the hollandite phase, 3.84 g/cm³, is 50% greater than that of sanidine and 3.5% greater than the mixed-oxide density 3.71 g/cm³ (SiO_2 as stishovite). The large density increase is attributable to octahedral coordination of all silicon and aluminum atoms in hollandite [*Ringwood et al.*, 1967] rather than to shortening of K-O bonds. In $KAlSi_3O_8$ (hollandite) the K-O bond length is 2.78 Å at STP [*Ringwood et al.*, 1967]. This is not significantly different from K-O bond lengths in K_2O (antifluorite, 2.787 Å) and $KAlSiO_4$ (kalsilite, 2.8 Å) or the shortest bond lengths, 2.7 Å in $KAlSi_2O_6$ (leucite) and $KAlSi_3O_8$ (sanidine) [*Deer et al.*,
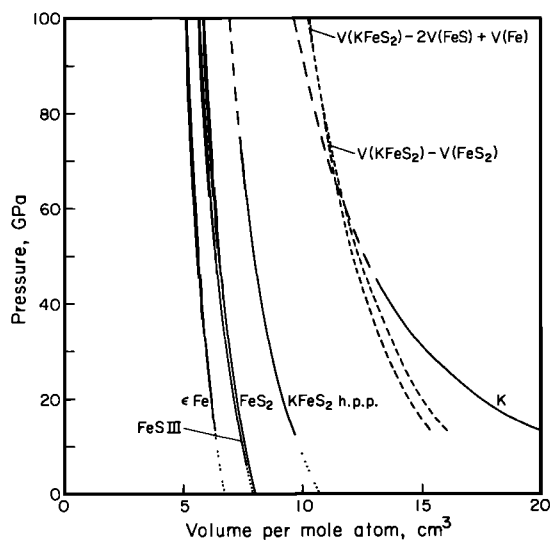
Fig. 3. Volume per mole atom versus pressure for K in $KFeS_2$ and metallic K along isentrope in comparison to FeS III, ε iron, and FeS_2 (hpp).
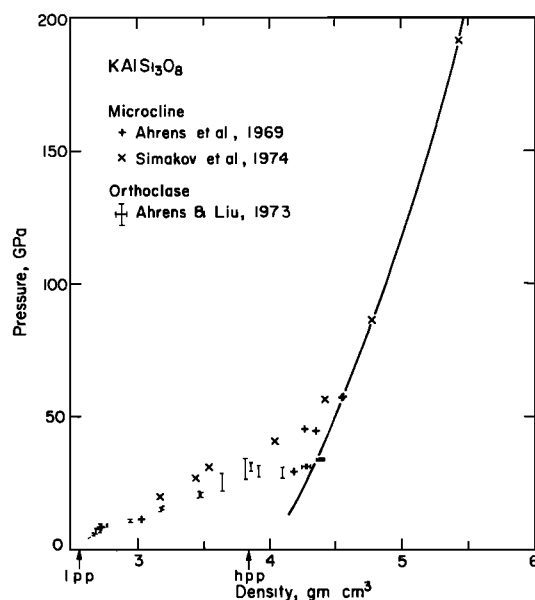
Fig. 4. Pressure versus density Hugoniot data for potassium feldspars. Arrows indicate zero-pressure density of orthoclase and hollandite-structured $KAlSi_3O_8$ [*Ringwood et al.*, 1967].

1963]. The sanidine-hollandite transition presumably does not involve an electronic transition in potassium.

Hugoniot experiments by *Ahrens et al.* [1969] and *Ahrens and Liu* [1973] demonstrated the onset of phase transformations in microcline and orthoclase at 12 and 11.5 GPa: these data, together with the microcline data of *Simakov et al.* [1974] extending up to 200 GPa, are shown in Figure 4. The Ullmann-Pan'kov adiabat corresponding to the theoretical Hugoniot shown for hollandite has the parameters $K_{s0} = 170$ GPa, $K_{s0}' = 4.1$, $E_{TR} = 1.2$ kJ/g, and γ given by (3). In the hollandite field the Hugoniot data up to 200 GPa show no evidence of anomalous compression that could be attributed to further transformation of hollandite or electronic transitions in potassium. The inferred bulk modulus of hollandite, 170 GPa, is similar to what would be estimated on the basis of velocity-density systematics. The relation of *Shankland and Chung* [1974], with parameter $c = 0.16$, i.e.,

$$\left(\frac{K_{s0}}{\rho_0}\right)^{1/2} = 1.42\rho_0^{1.25}\left(\frac{20.2}{\bar{M}}\right)^{1.55} \tag{9}$$

yields an estimate of 187 GPa for the bulk modulus of hollandite ($\bar{M} = 21.41$).

Ringwood et al. [1967] reported that $KAlSi_2O_6$ (leucite) undergoes a disproportion reaction at 1000°C and 12 GPa, forming hollandite and potassium aluminate:

$$3KAlSi_2O_6 \rightleftarrows 2KAlSi_3O_8 + KAlO_2 \tag{10}$$
leucite   hollandite
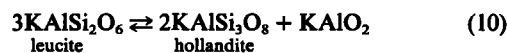
Experiments at pressures up to 20 GPa did not produce transformation in $KAlSiO_4$ (kalsilite), but *Ringwood* [1970] predicted that at sufficient pressure, kalsilite would undergo a disproportionation analogous to that observed in $KAlGeO_4$ at 9 GPa:

$$3KAlGeO_4 \rightleftarrows KAlGe_3O_8 + 2KAlO_2 \tag{11}$$
kalsilite   hollandite
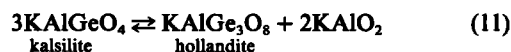
Ringwood [1970] concluded that $KAlSi_3O_8$ (hollandite) would be stable in the deep mantle.

TABLE 5. Thermochemical and Equation of State Data

Phase	Density ρ_0, g/cm³	Bulk Modulus K_{s0}, GPa	$\left(\dfrac{dK_{s0}}{dP}\right)_s$	Approximate Transformation Pressure P_T(298 K), GPa	Entropy $S_{298}{}^0$, J/mol K	Gibbs Free Energy $\Delta G_{f,298}{}^0$, J/mol
KAlSiO₄						
Kalsilite	2.641	42	4.4		133.26[a]	−2,015,642[a]
KAlSi₃O₈						
Microcline	2.560	54	4.4		213.93[a]	−3,746,245[a]
Hollandite	3.840	170	4.1	20[b]		
FeS						
Troilite	4.830	55	5.0		60.33[a]	−100,767[a]
FeS III	5.600	150	4.0	6		
KFeS₂						
lpp	2.663	20	4.4		124.0[c]	−340,900[d]
hpp	3.7	85	4.4	12		
Fe						
α	7.875	166	5.3		27.28[e]	0
ε	8.335	178	5.0	13		
Mg₂SiO₄						
Forsterite	3.222	128	5.0		95.19[a]	−2,056,704[a]
γ spinel	3.560	200	4.4	11		
MgSiO₃						
Enstatite	3.208	125	5.0		67.78[a]	−1,459,923[a]
Garnet	3.522	175	4.7	5		
Ilmenite	3.826	210	4.1	21		
Perovskite	4.098	260	4.1	20		
MgO						
Periclase	3.583	163	4.4	20	26.94[a]	−569,384[a]
Mg₂FeAl₂Si₃O₁₂						
Garnet	3.816	175	4.7		254.80[e,f]	−5,576,190[e,f]
Ilmenite	4.087	210	4.1	21		
Perovskite	4.377	260	4.1	25		

[a] *Helgeson et al.* [1978] free energy with respect to elements at STP.
[b] Reaction (equation (13)).
[c] Estimate from Latimer's rules.
[d] Assuming ideal solution of K₂S, FeS, and FeS₂.
[e] *Robie et al.* [1978].
[f] *Ahrens* [1973].

Experiments reported by *Wendlandt and Eggler* [1980] indicate that kalsilite, rather than sanidine, would be the stable potassium aluminosilicate phase under anhydrous upper mantle conditions. The reaction

$$KAlSiO_4 + 4MgSiO_3 \rightleftarrows KAlSi_3O_8 + 2Mg_2SiO_4 \qquad (12)$$
kalsilite   enstatite   sanidine   forsterite

was observed at 900°C at 1.75 GPa and at 1300°C at 3.0 GPa. The Fe-FeS eutectic temperature is 988°C at atmospheric pressure [*Brett and Bell*, 1969] and 998°C and 1190°C at 5.5 and 10.0 GPa, respectively [*Usselman*, 1975]. Therefore at the first appearance of an iron sulfide melt, kalsilite would be the stable potassium aluminosilicate phase at pressures in excess of about 2 GPa.

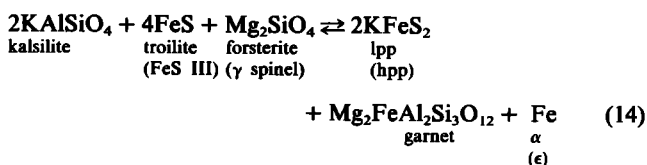The kalsilite-hollandite phase boundary in the mantle may be determined by the reaction

$$KAlSiO_4 + 2MgSiO_3 \rightleftarrows KAlSi_3O_8 + 2MgO \qquad (13)$$
kalsilite   perovskite   hollandite   periclase

From the thermochemical data given in Table 5 the reaction pressure at 298°K was calculated to be 20.0 GPa.
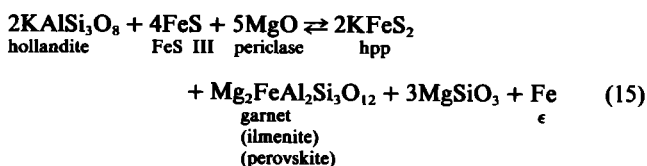
STABILITY OF KFES₂ IN THE MANTLE

The hypothesis advanced by *Lewis* [1971] and *Hall and Murthy* [1971] requires partitioning of potassium into a liquid iron sulfide phase at the expense of a more refractory aluminosilicate host for potassium. Lack of data, particularly

concerning the energetics of potassium iron sulfide melts at high pressure, precludes an adequate test of the hypothesis. However, the hypothesis would receive some measure of support if it were shown that KFeS₂ would be stable in relation to potassium aluminosilicates at high pressure: on the other hand, a negative outcome does not necessarily dismiss the hypothesis of solubility of K in an iron core. In order to investigate this question, calculations were made to evaluate the effect of pressure on the Gibbs energies of hypothetical reactions producing KFeS₂. The reactions that have been considered are

$$2KAlSiO_4 + 4FeS + Mg_2SiO_4 \rightleftarrows 2KFeS_2$$
kalsilite   troilite   forsterite   lpp
            (FeS III)   (γ spinel)   (hpp)

$$+ Mg_2FeAl_2Si_3O_{12} + Fe \qquad (14)$$
garnet   α
(ε)

for pressures up to 20 GPa and

$$2KAlSi_3O_8 + 4FeS + 5MgO \rightleftarrows 2KFeS_2$$
hollandite   FeS III   periclase   hpp

$$+ Mg_2FeAl_2Si_3O_{12} + 3MgSiO_3 + Fe \qquad (15)$$
garnet   ε
(ilmenite)
(perovskite)

at higher pressures. Choice of the reactant phase assemblages is partially justified by the foregoing discussion. Choice of the

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TABLE 6. Hypothetical Reactions Producing KFeS₂

| Reaction | | | | | | Pressure, GPa | Volume of Reaction, cm³ | Free Energy of Reaction, J/mol |
2KAlSiO₄	+4FeS	+Mg₂SiO₄	⇌2KFeS₂	+Mg₂FeAl₂Si₃O₁₂	+Fe			
kalsilite	troilite	forsterite	lpp	garnet	α	0		+437,736*
kalsilite	troilite	forsterite	lpp	garnet	α	0	0.61	+233,066
kalsilite	troilite	forsterite	lpp	garnet	α	6	−3.33	+220,076
kalsilite	FeS III	forsterite	lpp	garnet	α	6	3.19	+220,076
kalsilite	FeS III	forsterite	lpp	garnet	α	11	1.69	+231,561
kalsilite	FeS III	γ spinel	lpp	garnet	α	11	4.69	+231,561
kalsilite	FeS III	γ spinel	lpp	garnet	α	12	4.46	+236,135
kalsilite	FeS III	γ spinel	hpp	garnet	α	12	−3.92	+236,135
kalsilite	FeS III	γ spinel	hpp	garnet	α	13	−3.42	+232,461
kalsilite	FeS III	γ spinel	hpp	garnet	ε	13	−3.77	+232,461
kalsilite	FeS III	γ spinel	hpp	garnet	ε	20	−1.25	+216,076
kalsilite	FeS III	perovskite + periclase	hpp	garnet	ε	20	2.08	+216,076

| Reaction | | | | | | Pressure, GPa | Volume of Reaction, cm³ | Free Energy of Reaction, J/mol |
2KAlSi₃O₈	+4FeS	+MgO	⇌2KFeS₂	+Mg₂FeAl₂Si₃O₁₂ +3MgSiO₃	+Fe			
hollandite	FeS III	periclase	hpp	garnet	ε	20	18.64	+145,359
hollandite	FeS III	periclase	hpp	garnet	ε	21	18.50	+163,929
hollandite	FeS III	periclase	hpp	ilmenite	ε	21	8.02	+163,929
hollandite	FeS III	periclase	hpp	ilmenite	ε	25	7.95	+195,870
hollandite	FeS III	periclase	hpp	perovskite	ε	25	0.77	+195,870
hollandite	FeS III	periclase	hpp	perovskite	ε	75	1.89	+231,778

* At $T = 1000°C$. All subsequent figures are for $T = 298°C$.

product phases, apart from the silicates, is difficult to justify, except that KFeS₂ is the only potassium iron sulfide phase whose compression curve has been determined to high pressure!

Thermochemical and equation of state data for evaluating the Gibbs energies of these reactions are listed in Table 5, and the results are given in Table 6. Volumes of the phases were calculated from Ullmann-Pan'kov principal isentropes centered at room temperature: pressure differences between adiabats and isotherms were again neglected. Estimates of the pressures, at room temperature, at which new phases on either side of the reactions first appear as a result of phase changes are indicated in Table 5. Room temperature phase relations of the system $MgO-Al_2O_3-SiO_2$ are based on the results of Akaogi and Akimoto [1977] and Liu [1977]. A bulk modulus of 42 GPa for kalsilite was estimated from the Shankland and Chung [1974] velocity-density relation (equation (9)).

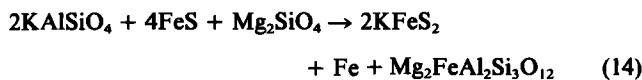The calculations yield the result that KFeS₂ would not be stable in relation to kalsilite or hollandite. However, this result should be taken with caution regarding the stability of a sulfide versus silicate host for potassium. First, it is possible that other potassium iron sulfide phase(s) are more stable than KFeS₂. Second, while pressure may not have a pronounced effect on the relative stability of solid potassium aluminosilicate and potassium iron sulfide phases, it may have a marked effect on the energetics of a potassium iron sulfide melt as well as the activities of the phases being considered. The present calculations were all carried out assuming activity coefficients of unity. As emphasized by Ganguly and Kennedy [1977], the marked miscibility gaps in the Fe-Mn-S and Fe-O-S systems [Hillart and Steffanson, 1976; Wendlandt and Heubner, 1979] indicate that factors other than ionic size and electronic configuration make miscibility in sulfide systems difficult to predict even qualitatively.
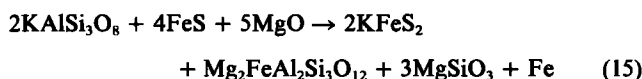
CONCLUSIONS

Hugoniot equation of state data for KFeS₂ (2.7 g/cm³, bulk modulus 20 GPa) demonstrate an apparent shock-induced phase change above 13 ± 1 GPa. High-pressure data extending to 110 GPa are consistent with complete shock-induced transformation to a high-pressure phase behavior between 30 and 110 GPa. The onset of shock-induced melting is calculated to occur at ~30 GPa. The high-pressure Hugoniot data are consistent with the high-pressure phase having a zero-pressure density of 3.7 ± 0.2 g/cm³ and a zero-pressure bulk modulus (K_{so}) of 85 GPa. These compare to a value of K_{so} of 75 GPa inferred from the density-sound speed relation of Ahrens [1979] for sulfides. In order to test the Lewis [1971] and Hall and Murthy [1971] hypothesis that most of the earth's (chondritic) inventory of potassium is stored in an iron-sulfide-bearing liquid core, we have applied the data for KFeS₂ to calculating the volume per mole of K atoms in this compound and comparing these with similar molar volumes calculated from shock wave data for metallic potassium, iron, and iron sulfides. We have also applied the present equation of state data for KFeS₂ and the data for other candidate mantle phases to carry thermochemical calculations of effect of pressure on partitioning of K between aluminosilicate and sulfide phases. Although a series of previous relatively low pressure (3 GPa) silicate sulfide partitioning experiments have all demonstrated a marked preference of K for the available aluminosilicate phase, Goettel [1976] has pointed out that a K content of only a few hundred parts per million would give rise to a significant core heat source. The possibly enhanced solubility of K in sulfide melts was proposed by Bukowinski [1976] on the basis of different arguments. He proposed using calculational results obtained via augmented plane wave solutions of Schroedinger's equation, that the 4s to 3d electronic

transition may occur in K and that this metal may have transition-element (siderophile) chemical affinities and hence be soluble in a liquid iron or iron sulfide core.

Although the possibly large errors in the corrections of shock wave data for thermal effects must be kept in mind, our present results, when taken with previous Hugoniot data for Fe, $Fe_{0.9}S$, and FeS_2, indicate that along the isentrope centered at STP the volume per mole of atoms of K in $KFeS_2$ at 75 GPa is ~12 cm³, in close agreement with that of metallic K. Neither *Bakanova et al.*'s [1965] data for K, the potassium feldspar shock data, nor the present $KFeS_2$ data indicate a marked phase transition, or even an anomalous region of compression which might be due to a gradual $4s \rightarrow 3d$ type electronic transition in K at high temperatures. On the basis of only relative atomic volume (at 75 GPa) of K (12 cm³/mol) versus that of iron (~5.5 cm³/mol) and *Hume-Rothery and Raynor*'s [1962] empirical relation that atomic volume of elements soluble in iron do not exceed the Fe atomic volume by a factor of 1.4, partitioning of even trace amount of K in the core appears extremely difficult. Utilizing the results of *Wendlandt and Eggler* [1980] and thermochemical calculations, we calculate that at pressures above ~2 GPa, kalsilite ($KAlSiO_4$) rather than sanidine ($KAlSi_3O_8$) is the stable potassium aluminosilicate and that above ~20 GPa the hollandite phase of $KAlSi_3O_8$ [*Ringwood et al.*, 1967] probably retains the mantle's complement of K. The calculated free energies of hypothetical exchange reactions up to 20 GPa such as

$$2KAlSiO_4 + 4FeS + Mg_2SiO_4 \rightarrow 2KFeS_2$$
$$+ Fe + Mg_2FeAl_2Si_3O_{12} \quad (14)$$

and, at higher pressures,

$$2KAlSi_3O_8 + 4FeS + 5MgO \rightarrow 2KFeS_2$$
$$+ Mg_2FeAl_2Si_3O_{12} + 3MgSiO_3 + Fe \quad (15)$$

are strongly positive (by ~10⁵ J/mol), indicating that the high-pressure phase of $KFeS_2$ is unstable throughout the (assumed low oxygen fugacity) mantle. Moreover, the calculated large positive free energies for the above reactions suggest that if the core differentiated from a nearly homogeneous primitive earth, it is unlikely that a core-forming liquid iron alloy carried even a trace of K into the earth's core. Subsequent addition of K to the core at the base of the mantle via exchange reactions, such as (14) and (15), as well as the above mentioned mutual solubility arguments, appear to be energetically highly unfavorable, and probably preclude, the addition of K in the core during the subsequent history of the earth.

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