Heideite, $(Fe,Cr)_{1+x}$ $(Ti,Fe)_2S_4$, A New Mineral in the Bustee Enstatite Achondrite

KLAUS KEIL

Department of Geology and Institute of Meteoritics, University of New Mexico, Albuquerque, New Mexico 87131

ROBIN BRETT

NASA, Johnson Space Center, Houston, Texas 77058

Abstract

Heideite, $(Fe, Cr)_{1+x}(Ti, Fe)_2S_4$ occurs as rare anhedral grains up to 100 μm in diameter in the Bustee enstatite achondrite. Other sulfides in Bustee are titanian troilite, ferroan alabandite, and daubreelite. Heideite (named after Professor Fritz Heide) has a distorted NiAs structure. It is probably monoclinic $(I2/m)$. Indexed X-ray powder data are given (14 lines). The strongest lines are: 2.06 **100** $\bar{1}14$, 2.64 **75** *202*, 1.72 **75** *310*, 2.97 **50** *110*. It is cream white in color in reflected light and exhibits moderately strong reflection birefringence. Electron microprobe analyses and crystallographic data indicate that heideite has the structural formula $(Fe^{2+}_{0.99}Cr^{2+}_{0.16})(Ti^{3+}_{1.70}Fe^{2+}_{0.30})S_4$. One grain of a chromian variety of heideite was found to contain 7.9 wt percent Cr substituting for Fe. The phase was synthesized at 650°C. Troilite in Bustee ranges in Ti content from 0.2 to 16.3 wt percent, suggesting that the sulfide assemblage formed and cooled under disequilibrium conditions.

Introduction

Grains of a phase that is cream-colored in reflected light caught our attention in the Bustee enstatite achondrite. Electron microprobe analyses indicate a formula of the type $(Ti, Fe, Cr)_{3+x}S_4$ in which Ti is more abundant than Fe, thus establishing it as a new mineral. Titanium-rich troilite had previously been reported in Bustee and other enstatite achondrites by Keil (1969) who recorded 16.3 wt percent Ti in one troilite grain from Bustee. He pointed out the strongly chalcophile behavior of Ti in enstatite chondrites and achondrites and also mentioned the discovery of a Ti, Fe sulfide in which Ti > Fe. This latter phase is the subject of the present paper. The mineral is named in honor of the late Professor Fritz Heide of Jena, Germany, in recognition of his many contributions to the field of meteoritics at a time when very little work was being done in this important field. The name and the mineral have been approved by the Commission on New Minerals and Mineral Names of the International Mineralogical Association.

Occurrence and Co-existing Sulfide Minerals

The Bustee enstatite achondrite consists predominantly of enstatite and diopside with minor amounts of other silicate minerals. Small quantities of metallic nickel-iron and osbornite (TiN) are also present. Ninety sulfide grains in one thin section of Bustee were analyzed; grains in order of abundance are: titanian troilite (78 percent), ferroan alabandite (11 percent), daubreelite (10 percent), chromian heideite (1 percent).

Compositional ranges of the above minerals are listed in Table 1; Ca was not determined except for alabandite. Selected analyses of troilite, alabandite, and daubreelite are listed in Table 2. Figure 1 shows the extent of Ti solid solution in titanian troilite in Bustee. It is noteworthy that a large proportion of compositions lie off the FeS-TiS join and that some compositions lie closer to the FeS-Ti₃S₄ join than to the FeS-TiS join. Most grains in Bustee are homogeneous; however, widespread heterogeneity from grain to grain indicates that chemical equilibrium was not achieved between distant grains.

Heideite occurs as rare, discrete, anhedral grains at the grain boundaries of silicate minerals in all three polished thin sections of Bustee that we examined. Grains range in diameter up to 100 μm, but most are of the order of 40 μm in diameter. One to four grains of heideite were found in each section (approximately 1 cm²) that we examined. Heideite

TABLE 1. Compositional Ranges (wt percent) of Troilite, Alabandite, and Daubreelite in Bustee as Measured by Electron Microprobe Techniques

Mineral	Ti	Fe	Cr	Mn	Mg	Ca	S
Troilite	16.3 – 0.2	61.8 – 44.7	1.4 – 0.2	0.5 – 0.01	0.5 – 0.05	*	40.4 – 36.0
Alabandite	0.09 – 0.01	16.2 – 11.3	0.18 – 0.11	44.9 – 31.3	7.3 – 1.6	0.72 – 0.20	40.7 – 37.6
Daubreelite	1.4 – 0.06	16.8 – 7.3	35.4 – 34.1	1.7 – 0.8	0.45 – 0.26	*	45.0 – 43.3

* = not determined.

is nowhere in contact with any other opaque mineral in the sections examined. The mineral has a creamy-white color in reflected light and has moderately strong reflection birefringence ranging from purple gray to cream gray. Based on the appearance of scratches and the relative polishing hardness of troilite and heideite in the same polished section, the hardness of heideite is similar to that of troilite. Surprisingly, the Bustee mineral has no discernible cleavage. The small grain size and rarity of the phase precluded a determination of cleavage, magnetic properties, specific gravity, and hardness.

Composition

Heideite was analyzed with an ARL-EMX-SM electron microprobe X-ray analyzer at an excitation potential of 15 kV. Minerals and synthetic compounds were used as standards, and corrections for instrumental and matrix effects were made following procedures described by Keil (1967). An analysis of heideite is listed in Table 3, with a calculated formula and charge balance. Heideite varies little in composition. In the six grains analyzed, Ti ranges from 27.5 to 29.6 wt percent and S ranges from 43.7 to 46.1 wt percent. The range in Cr content with the exception of one grain is less than 0.1 wt percent. In addition to Fe,

Ti, Cr, and S, the phase also contains about 200 ppm Mn and less than 0.5 wt percent Mg. One grain should be termed chromian heideite; it contains 7.9 wt percent Cr and is correspondingly deficient in Fe with respect to other heideite grains. This suggests that heideite may be part of a solid solution series towards brezinaite (Cr_3S_4).

It is clear from Table 3 that in order to maintain the charge balance, Ti must be trivalent and Cr must be divalent. Such valence states are consistent with the highly reduced conditions under which enstatite achondrites have formed (e.g., Keil, 1969).

We considered that the formula of heideite may be of the type $(Ti, Fe, Cr)_{1-x}S$, and be an extremely Ti-rich pyrrhotite solid solution, but rejected this possibility for the following reasons:

(1) x in the above formula is 0.21 for heideite and is thus higher than for natural or synthetic pyrrhotite. Such cation deficiency would be highly unlikely, especially for a phase apparently formed in the presence of metallic iron.

(2) Experimental work by Viaene, Kullerud, and Taylor (1971) indicates a compositional gap between $(Fe, Ti)_{1-x}S$ solid solution and $FeTi_2S_4$ solid solution. A similar gap is seen between Ti-rich troilite and heideite in Bustee (Fig. 1).

TABLE 2. Selected Compositions of Daubreelite (1, 2), Alabandite (3), and Troilite (4-12) in Bustee as Obtained by Electron Microprobe Techniques

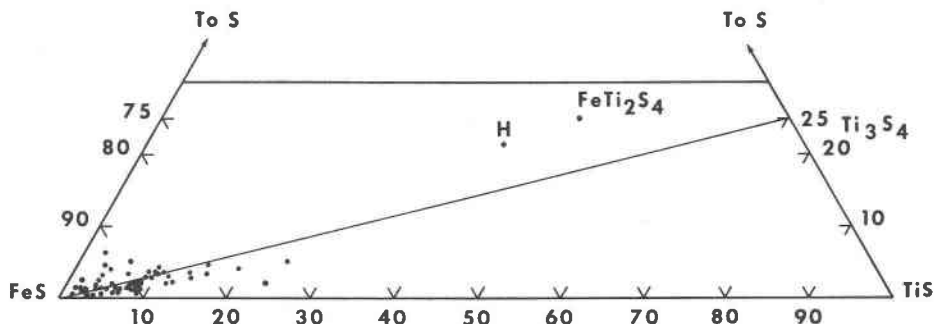|	1	2	3	4	5	6	7	8	9	10	11	12
Ti	0.07	0.36	0.01	14.1	13.9	7.8	5.93	4.83	3.57	2.87	1.48	0.20
Fe	16.3	7.4	16.2	44.7	43.7	52.0	55.9	56.2	56.2	57.8	59.4	63.0
Cr	35.4	35.1	0.18	0.78	0.91	0.82	0.46	0.55	0.47	0.31	1.40	0.42
Mn	2.0	10.3	41.6	0.49	0.01	0.01	0.04	0.02	0.04	0.01	0.06	0.02
Mg	0.27	0.45	1.75	0.32	0.38	0.38	0.35	0.34	0.26	0.36	0.38	0.29
S	45.1	45.2	38.2	40.2	40.3	38.7	38.7	36.8	37.7	36.6	36.5	36.5
Total	99.1	98.8	97.9	100.6	99.2	99.7	100.4	98.9	98.7	98.0	99.2	100.4

FIG. 1. Plot of TiS contents of Bustee troilites (mole percent). H is composition of natural heideite, if Cr is recalculated as Fe.

Phase Equilibria

We have synthesized heideite from elemental Ti, Fe, and S in evacuated silica glass tubes held at 650°C for 2 weeks (Table 3). The synthesized material has identical optical properties to natural heideite and gives a similar X-ray powder pattern (Table 4). Synthetic heideite is not attracted to a hand magnet.

Etch tests of 4 minutes duration on the polished surface of synthetic heideite using standard etch reagents gave the following results: HNO_3 (1:1), effervescence, iridescent blue etch; HCl (1:1), negative; KOH (40%, by wt.), negative; KCN (20%, by wt.), negative; $HgCl_2$ (5% by wt.), iridescent blue-to-brown tarnish; $FeCl_3$ (20% by wt.), iridescent brown-to-blue tarnish.

We performed differential thermal analysis on synthetic heideite in evacuated silica glass tubes using the method of Kullerud (1971). Heating and cooling rates were 5°C/minute. The temperature range of the experiments was from room temperature to 900°C. No exothermic or endothermic reactions were observed. N. Morimoto and S. Nakajima (written communication, 1973) find that high and low temperature polymorphs exist for $FeTi_2S_4$. Either heideite is sufficiently removed compositionally from $FeTi_2S_4$ that these polymorphs do not occur, or any transitions that occur are too sluggish or have ΔH too small to be recorded at the heating and cooling rates used.

Hahn, Harder, and Brockmüller (1956) made runs in the system $FeS-TiS-TiS_2$ at 600°C and found a solid solution field that extended from FeS to about 45 mole percent TiS and at least to 10 mole percent TiS_2. Their runs were exploratory, however, and no phase boundaries can be drawn. Viaene, Kullerud, and Taylor (1971) found an extensive monosulfide solid solution between $Fe_{1-x}S$ and $Ti_{1-x}S$ at 800°C. They found that a ternary solid solution, which includes $FeTi_2S_4$ and presumably heideite, extends towards the FeS join.

Structure

On the basis of X-ray powder diffraction studies, Hahn, Harder, and Brockmüller (1956) state that synthetic $FeTi_2S_4$ prepared at 600°C has a NiAs structure (Table 4). Plovnick, Vlasse, and Wold (1968) found that $FeTi_2S_4$ prepared over a range of temperatures as high as 300°C has the Cr_3S_4 structure which is a monoclinic defect NiAs structure (space group $I2/m$). This structure has cation layers with ordered vacancies alternating with completely filled cation layers. Plovnick, Vlasse, and Wold show that there is a limited compositional range for the ordered structure. Appreciable deviation from the $FeTi_2S_4$ composition results in formation of a disordered structure with trigonal symmetry ($\bar{3}m$). Plovnick, Vlasse, and Wold state that no disorder occurs in $FeTi_2S_4$ up to about 1000°, unless decomposition and lack of stoichiometry occur. Nakajima, Horinchi, and Morimoto (1972) confirm the structure of Plovnick, Vlasse, and Wold (1968). The filled cation layers contain Ti atoms; the layers with vacancies contain Fe. With increase of Fe/Ti, Fe occupies

TABLE 3. Composition (wt percent) and Formula for Heideite and Composition of Synthetic Heideite*

	1	2	Formula and charges for Heideite
Ti	28.5	29.5	$(Fe^{2+}_{0.99} Cr^{2+}_{0.16}) (Ti^{3+}_{1.70} Fe^{2+}_{0.30}) S_4$
Fe	25.1	25.1	
Cr	2.9	--	$1.98 + 0.32 + 5.10 + 0.60 = 8.00$
S	44.9	45.2	
Total	101.4	99.8	

* 1: *Heideite; average of 5 grains analyzed.*
2: *Synthetic heideite; -- = not detected.*

TABLE 4. d-Values in Å of Natural and Synthetic Heideite and Synthetic FeTi$_2$S$_4$*

hkl	Natural heideite			Synthetic heideite			FeTi$_2$S$_4$ **		
	d$_{obs}$	d$_{calc}$	I	d$_{obs}$	d$_{calc}$	I	d$_{obs}$	d$_{calc}$	I
002	5.71	5.703	20	5.743	5.743	2	5.72	5.746	m-strong
101	5.28	5.280	25	5.302	5.277	2	--	--	----
110	2.97	2.970	50	2.975	2.975	15	2.97	2.976	weak
112	2.64	2.636	75	2.644	2.643	90	2.63	2.641	strong
104	2.57	2.570	5	--	--	--	--	--	----
114	2.06	2.055	100	2.068	2.067	100	2.05$_5$	2.066	v. strong
$\overline{2}$13	1.94	1.940	5	--	--	--	--	--	----
015	--	--	--	--	--	--	1.90	1.911	v. weak
020	1.72	1.711	75	1.719	1.719	50	1.71	1.716	m. strong
312	--	--	--	--	--	--	1.64	1.643	v. weak
$\overline{1}$16, $\overline{1}$16, 206	1.60	1.603	5	1.609	1.609	2	1.60	1.612	m. strong
222	1.44	1.436	10	1.445	1.440	10	1.42	1.440	m. strong
$\overline{2}$17, 404, $\overline{4}$04, $\overline{2}$24, 217, 018, 224	1.32	1.32	5	--	--	--	1.31	1.318	medium
$\overline{2}$08, $\overline{3}$21, $\overline{4}$13, 321, $\overline{1}$18, 413, 208, $\overline{1}$18	1.29	1.29	5	--	--	--	1.28	1.295	weak
415	--	--	--	--	--	--	1.17	1.177	strong-med
14 possible reflections	1.10	1.10	5	--	--	--	1.10	1.105	v. strong
231	--	--	--	--	--	--	1.06$_5$	1.065	medium
417	1.05	1.046	5	1.051	1.049	5	--	--	----
514	--	--	--	--	--	--	1.04	1.045	medium
129	--	--	--	1.010	1.010	5	--	--	----

* Calculated d-values and indexing were derived from the computer program of D. Appleman
  assuming a monoclinic cell (I2/m). Intensities were estimated visually.
** Values obtained by Hahn, Harder, and Brockmüller (1956).

sufficient sites to fill the Ti layer according to Nakajima, Horiuchi, and Morimoto (1972). Morimoto and Nakajima (written communication, 1973) have done further single crystal X-ray diffraction studies on the structure of FeTi$_2$S$_4$ and find that there is a high-temperature polymorph with NiAs structure stable above 540°C in addition to the low temperature polymorph whose structure was determined by Plovnick, Vlasse, and Wold (1968). The low form decomposes below about 300°C according to Nakajima and Morimoto. They state that decomposition is extremely sluggish.

Because all grains of heideite that we examined in Bustee are anhedral, there are no data on the external morphology of the phase. The small grain size and rarity of the phase prevented any attempt to study heideite by single-crystal X-ray techniques but X-ray diffraction films were obtained using the Debye-Scherrer technique using Ni-filtered Cu radiation. The heideite grains were mounted for electron micro-probe analysis upon completion of the diffraction studies to confirm that the diffraction pattern was, in fact, that of heideite. Due to the small amount of material available, the X-ray patterns are so poor that d-values are given only to the second decimal place (Table 4). Similarly, since we could not obtain diffractometer data, the intensity data for heideite (Table 4) are semi-quantitative only.

Debye-Scherrer data were also obtained on heideite synthesized at 650°C (Table 4) using Mn-filtered Fe radiation. Note the good agreement in d-values between natural and synthetic heideite. Synthetic FeTi$_2$S$_4$ (data from Hahn, Harder, and Brockmüller, 1956) has similar d-values (Table 4). The d-values of heideite are sufficiently similar to those of troilite to suggest that heideite probably has a distorted NiAs structure.

A computer program written by D. Appleman that indexes and calculates theoretical d-values and cell dimensions for an assumed symmetry was used to

calculate the best structure and cell dimensions from the X-ray data (Tables 4, 5). The two polymorphs of $FeTi_2S_4$ discussed above were chosen as possible structures in addition to a number of other distorted NiAs structures. The best fit of the X-ray data for heideite, synthetic heideite, and for Hahn's d-values for $FeTi_2S_4$ was obtained by assuming the low temperature polymorph of $FeTi_2S_4$ (space group $I2/m$) obtained by Morimoto and Nakajima (Table 4). The fit is by no means perfect, perhaps because of the poor X-ray data. One can positively state that heideite has a distorted NiAs structure and is probably monoclinic ($I2/m$), in which case the cell dimensions and cell volume are those listed in Table 5. This structure is the same as that of brezinaite, Cr_3S_4 (Bunch and Fuchs, 1969), which is consistent with the possible solution of heideite toward brezinaite reported above. Assuming that this structure is correct, the calculated density is 4.1 g/cc; Morimoto and Nakajima (written communication, 1973) obtain a calculated density of 3.993 g/cc for the low temperature form of $FeTi_2S_4$.

By analogy with the structure obtained for low $FeTi_2S_4$ by Nakajima, Horiuchi, and Morimoto (1972) in which Ti layers are filled, we have written the structural formula as shown in Table 3. The fact that $FeTi_2S_4$ prepared by Hahn, Harder, and Brockmüller (1956) at 600°C appears to be the low temperature form suggests that the high-low transition is rapid.

Conclusions

The following conclusions can be made concerning the conditions of formation of heideite in Bustee:

(1) The high Ti content of some troilite in Bustee suggests that the meteorite cooled rapidly from elevated temperatures—16.1 wt percent Ti is surely not stable in troilite at room temperature.

(2) The presence of titanian troilites that do not lie on the FeS-Ti$_2$S$_3$ join, but rather in the area bounded by FeS, TiS, and Ti$_2$S$_3$ (Fig. 1) suggests that both divalent and trivalent Ti are present, thus placing constraints on the redox conditions pertaining during the cooling of the Bustee parent body.

(3) The broad range of Ti content of troilite in Bustee indicates that, at most, only conditions of local equilibrium prevailed during cooling.

(4) Skinner and Luce (1971) have determined a solvus for CaS in alabandite in equilibrium with oldhamite and troilite. Ferroan alabandite in Bustee does not co-exist with oldhamite and troilite, and any temperature obtained from the above solvus represents

TABLE 5. Unit Cell Dimensions, Cell Volume, and Calculated Density for Natural and Synthetic Heideite

	Heideite	Heideite synthetic	FeTi$_2$S$_4$*	FeTi$_2$S$_4$**
a (Å)	5.97	5.936	5.94	5.927
b (Å)	3.42	3.438	3.44	3.426
c (Å)	11.4	11.48	11.5	11.463
β (degrees)	90.2	89.5	91.0	90.0
V (cc/mole)	70.2	70.5	70.8	70.10
ρ	4.1	4.01	3.9	3.993

* FeTi$_2$S$_4$, after Hahn et al. (1956).
**Low FeTi$_2$S$_4$, after Morimoto and Nakajima, written comm. (1973). A monoclinic cell (I2/m) and Z=2 were assumed, after the work of Morimoto and Nakajima (written comm., 1973) on low FeTi$_2$S$_4$.

a minimum temperature of formation. Bustee ferroan alabandite contains from about 0.4 to 1.3 mole percent Ca; this indicates a minimum temperature of formation ranging from about 240°C to nearly 500°C, which is approximately the range obtained by Skinner and Luce (1971) for alabandite coexisting with oldhamite in enstatite chondrites.

(5) Viaene, Kullerud, and Taylor (1971) have shown that at 800°C there is an extensive solid solution which includes $FeTi_2S_4$ and compositions toward the Fe-S join. This solid solution includes heideite, and is not in equilibrium with metallic Fe. Equilibrium between metal and heideite appears to be possible at low temperatures. Either heideite was formed under disequilibrium conditions at high temperature in a parent body that cooled rapidly, or heideite formed at relatively low temperatures. It is puzzling that no heideite grains are associated with other sulfide or metal grains, and that its range of composition is small. This suggests that heideite was formed as a discrete phase at relatively low temperature that restricted the solid solution field for heideite.

Heideite is certainly a mineral of limited occurrence, but we speculate that other examples of it may be found in other enstatite achondrites.

Acknowledgments

References

Bunch, T. E., and L. H. Fuchs (1969) A new mineral: brezinaite, Cr₃S₄, and the Tucson meteorite. *Am. Mineral.* **54**, 1503–1518.

Hahn, H., B. Harder, and W. Brockmüller (1956) Untersuchungen der ternären Chalcogenide. X. Versuche zur Umsetzung von Titansulfiden mit Sulfiden zweiwretiger Übergangsmetalle. *Z. anorg. allg. Chem.* **288**, 260–268.

Keil, K. (1967) The electron microprobe x-ray analyzer and its application in mineralogy. *Fortschr. Mineral.* **44**, 4–66.

—— (1969) Titanium distribution in enstatite chondrites and achondrites and its bearing on their origin. *Earth Planet. Sci. Lett.* **7**, 243–248.

Kullerud, G. (1971) Experimental techniques in dry sulfide research. In, G. C. Ulmer, Ed., *Research Tech-niques for High Pressure and High Temperature*, Springer-Verlag, New York, Inc., p. 289–315.

Nakajima, S., H. Horiuchi, and N. Morimoto (1972) Crystal structures of (Fe,Ti)₃S₄ (abstr.). *Acta Crystallogr.* **A28**, 61.

Plovnick, R. H., M. Vlasse, and A. Wold (1968) Preparation and structural properties of some ternary chalcogenices of titanium. *Inorg. Chem.* **7**, 127–129.

Skinner, B. J., and F. D. Luce (1971) Solid solutions of the type (Ca, Mg, Mn, Fe)S and their use as geothermometers for the enstatite chondrites. *Am. Mineral.* **56**, 1269–1296.

Viaene, W., G. Kullerud, and L. A. Taylor (1971) Phase equilibria studies in the system Ti-S and Fe-Ti-S (abstr.). *Geol. Soc. Am. Abstr. Programs,* **3**, 739.