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A NEW MINERAL: BREZINAITE, Cr_3S_4, AND THE *TUCSON* METEORITE

T. E. BUNCH, *Ames Research Center,*
NASA, Moffett Field, California 94035

AND

LOUIS H. FUCHS, *Argonne National Laboratory,*
Argonne, Illinois 60430.

ABSTRACT

Brezinaite, a new chromium sulphide, occurs in the metal matrix and contiguous to silicate inclusions in the *Tucson* iron meteorite. The following average composition of brezinaite was determined by the electron microprobe: Cr 48.3; Fe 3.9; V 1.61; Ti 0.96; Mn 0.86; Ni 0.08; S 45.0, sum 100.71 wt.%. The unit cell is monoclinic with $a=5.96\pm0.01$, $b=3.425\pm0.005$, and $c=11.27\pm0.015$ Å; $\beta=91°\ 32'$, $V=229.97$ Å^3. Calculated X-ray density is 4.12 g/cm^3 ($Z=2$).

Very low iron content of the silicates, presence of chromium sulphide, significant amounts of silicon in the nickel-iron, and the chalcophile behavior of vanadium indicate a very high degree of reduction in *Tucson* similar to enstatite chondrites and enstatite achondrites.

INTRODUCTION

Although first recognized as meteorites by Le Conte (1852), who saw them used as anvils by blacksmiths in the then Mexican town of Tucson, the existence of the *Tucson* irons (i.e., *Carleton* and the Ring Meteorite or Signet Iron) has been known since the seventeenth century. Their history is both interesting and somewhat confusing. Between 1851 and 1863 pieces of one of the irons, probably *Carleton* according to Fletcher (1890), were analyzed by Smith (1855), Genth (1855), and Brush (1863). Shepard (1854) was the first to recognize silicate inclusions in the iron, which he called "chladnite" (enstatite). Smith (1855) identified olivine, and Genth (1855) concluded, on the basis of residue left after acid dissolution and the presence of lime in the analysis, that labradorite was also present. Fletcher (1890) gave a summary of the history of the *Tucson* specimens up to that time and also summarized previous analytical work. He stated that "there is absolutely no doubt that the stony matter consists very largely of olivine; and that so far there is no valid proof of the presence of any other kind of silicate"; he discounted the presence of enstatite and plagioclase. He attributed Cr_2O_3 in Smith's analysis (0.21 wt.%) to chromite, although he did not actually observe this mineral, and also assigned CaO to olivine, which he called "lime-olivine." Cohen (1905) gave an excellent historical account of *Tucson*, together with a detailed description, and confirmed the identification of plagioclase by Genth.

Recent investigations by Wai and Wasson (1969) show that there are significant amounts of silicon (0.8 wt.%) in the nickel-iron, a feature that, with the exception of enstatite chondrites, is rare among meteorites. This, together with discrepancies in earlier mineral identifications, prompted us to analyze *Tucson* with the electron microprobe.

BREZINAITE

The meteorite contains small, rounded inclusions of essentially iron-free silicates (Figure 1). Forsterite is the most abundant silicate mineral occurring as rounded, sometimes euhedral, grains that range in size from 3 mm to a few microns. Small, irregular to rounded grains of enstatite, very small amounts of aluminous diopside, and irregular patches of anorthite and feldspathic glass are located near interface regions of forsterite and the nickel-iron matrix. Kamacite, taenite, schreibersite, and

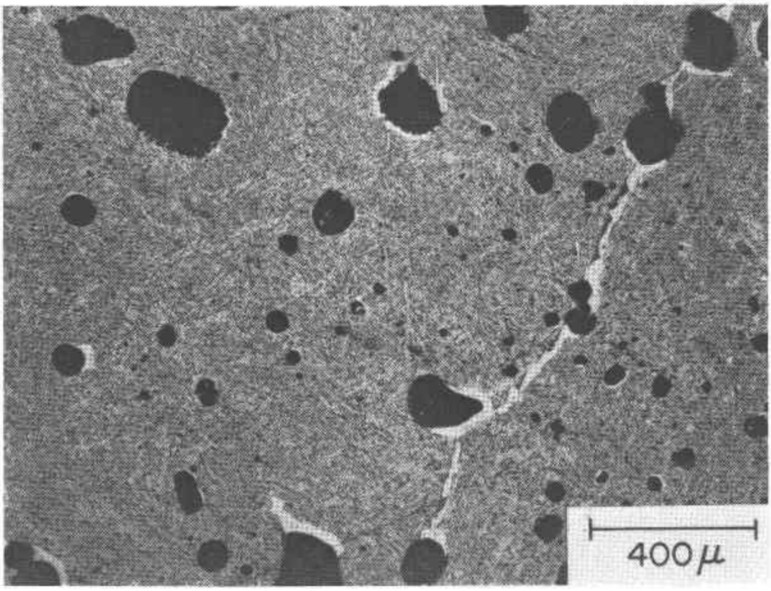

FIG. 1. Rounded silicate inclusions in the *Tucson* iron that shows residual octahedrite structure. Reflected light, nital etch.

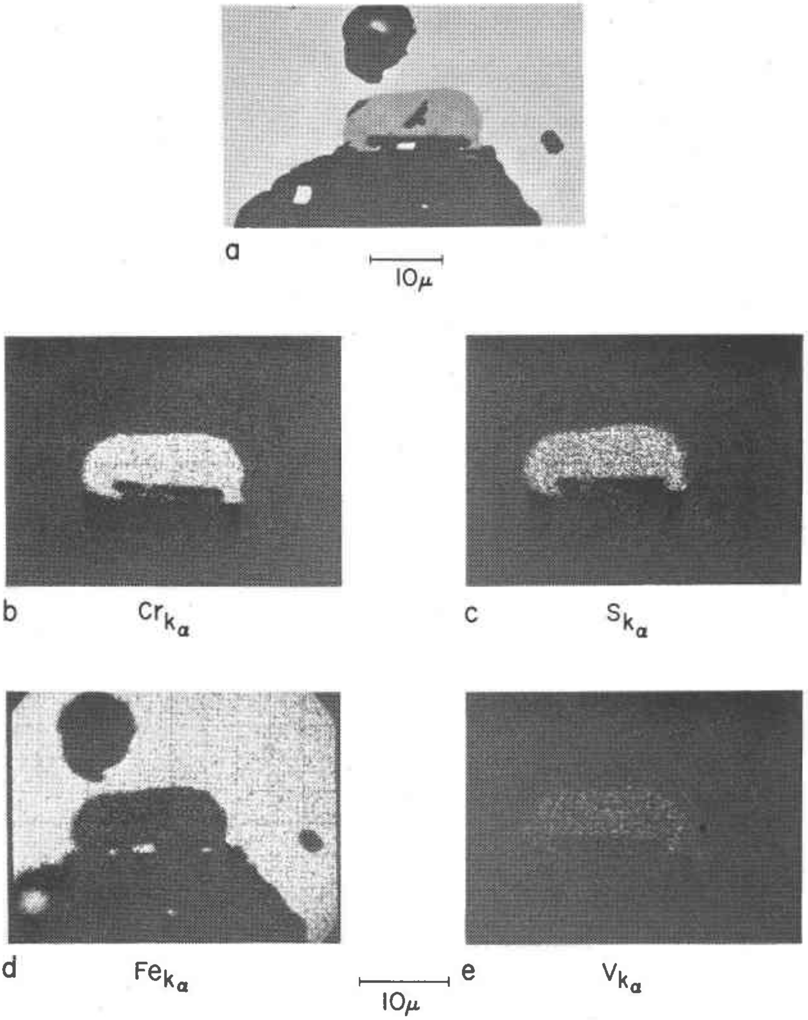

FIG. 2. Photomicrograph of brezinaite (medium gray) in reflected light (a). Electron beam scanning pictures of Cr, S, Fe, and VK_α radiation (b,c,d,e).

the new chromium sulfide, brezinaite, were the only other phases found in this study.

Opaque, anhedral grains of brezinaite (5–80 μm across), are contiguous to silicate inclusions (Figure 2) or, less commonly, are isolated in the nickel-iron matrix. In polished sections, under reflected light, brezinaite is brownish gray in color in air. Synthetic brezinaite is dull gray; the color depends on the composition and type of polish.

Composition. Analyses of brezinaite and other phases were carried out with an ARL-EMX electron microprobe with an accelerating voltage of 20 kV and 0.04 μA sample current. Corrections were made for detector and amplifier deadtime, drift, background, mass absorption, fluorescence, and atomic number. For brezinaite, analyzed chromite (GS-2 and 53 IN 8, provided by E. D. Jackson) was used as standards for Cr, V, Ti, Fe and Mn; pyrite and troilite were used for S. Synthetic Cr_3S_4 was later used to check the accuracy of the corrected analyses for Cr and S. The results proved to be in good agreement. For silicate phases, both synthetic and natural wet-chemically analyzed minerals (forsterite, diopside, enstatite and anorthite), similar in composition to the unknowns, were used as standards.

The average composition determined by the microprobe on 26 grains of brezinaite is given in Table 1. Compositional variability between different grains is minimal for elements other than Fe, Ti, and Mn, which show a fair degree of variation. Within-grain compositional variabilities are small. The idealized structural formula is Cr_3S_4 and the actual formula is $(Cr_{2.65}Fe_{0.20}V_{0.09}Ti_{0.06}Mn_{0.04})S_4$. The metal to sulfur ratio of 0.76 is within the range of 0.76 to 0.79 as reported by Jellinek (1957) for the Cr_3S_4 phase.

TABLE 1. ELECTRON MICROPROBE ANALYSES OF BREZINAITE

	Average	Range
Cr	48.3	47.3–49.8
Fe	3.9	1.4–4.8
V	1.61	1.56–1.64
Ti	0.96	0.10–1.12
Mn	0.86	0.54–0.95
Ni	0.08	0.05–0.28
S	45.0	43.3–46.0
Total	100.71	

X-ray data. X-ray diffraction powder data for natural brezinaite and synthetic Cr_3S_4 (Jellinek, 1957) are given in Table 2. Differences in intensities and line spacing between brezinaite and synthetic Cr_3S_4 may be attributable to the minor element content of brezinaite. The powder pattern was indexed according to Jellinek on a monoclinic cell with: $a = 5.96 \pm 0.01$ Å, $b = 3.425 \pm 0.005$ Å, and $c = 11.27 \pm 0.015$ Å; $\beta = 91°32'$. Calculated X-ray density ($Z = 2$) is 4.12 g/cm^3 and the unit cell volume is 229.97 Å^3.

TABLE 2. X-RAY POWDER DIFFRACTION DATA FOR BREZINAITE COMPARED TO THAT FOR $Cr_{0.76}S$[a]

hkl[b]	$Cr_{0.76}S$[c]		Brezinaite		
	d, Å(calc.)	Intensity	*d*, Å(obs.)[d]	Intensity (visual)	*d*, Å(calc.)[e]
002	5.62	80	5.67	70	5.63
$\bar{1}01$	5.33	25	5.34	10	5.33
101	5.20	60	5.23	40	5.21
011	3.28	20	3.27	15	3.28
$\bar{1}03$	3.215	15	3.219	10	3.216
103	3.133	20	3.156	10	3.139
200	2.979	30	2.978	65	2.979
110	2.971	55			2.969
004	2.812	5	—	—	—
$\bar{2}02$	2.664	15	2.644	100	2.663
$\bar{1}12$	2.642	100			2.641
112	2.611	5	2.606 B	60	2.612
202	2.602	65			2.605
013	2.530	20	2.536	30	2.531
211	2.196	5	2.194	10	2.196
$\bar{2}04$	2.075	30	2.073	15	2.075
$\bar{1}14$	2.057	85	2.056	70	2.057
114	2.028	60	2.028	40	2.030
204	2.016	35	2.022	20	2.020
$\bar{3}01$	1.965	2	—	—	—
$\bar{2}13$, 301	1.947	15	1.946	30	1.947
213	1.910	5	—	—	—
$\bar{3}03$	1.776	10	1.773	30	1.775
310	1.718	40	1.716 B	70	1.718
020	1.713	30			1.713
$\bar{3}12$	1.655	2	—	—	—
022	1.639	2	1.640	5	1.638
$\bar{2}15$, $\bar{2}06$	1.608	5	1.608	10	1.608
116	1.575	10	1.576	20	1.577
$\bar{1}07$	1.563	5	—	—	—
220	1.485	2	—	—	—
017	1.455	3	—	—	—
$\bar{4}02$	1.450	2	—	—	—
222	1.441	2	—	—	—
222, 402	1.430	5	1.429	10	1.431
008	1.406	5	1.412	15	1.408
411	1.352	2	—	—	—
$\bar{4}04$	1.332	5	—	—	—
$\bar{2}24$, $\bar{2}17$	1.321	5	1.319	10	1.321
224	1.306	10	1.305	15	1.306
318, $\bar{1}32$	1.102	5	1.100 B	15	1.102
512, 422	1.098	1			1.098
028	1.087	5	1.089	10	1.088
318	1.075	5	1.078	5	1.077

[a] Copper radiation, Ni filter, Norelco powder camera (diam. 11.45 cm).

[b] Indexing after Jellinek (1957).

[c] *d* calculated from published cell constants of Jellinek's Cr_3S_4: $a=5.960 \pm 0.003$ Å, $b=3.427 \pm 0.002$ Å, $c=11.253 \pm 0.006$ Å, $\beta=91$ deg. 38′. Intensities were calculated by multiplying the tabulated values of F_0^2p (table 3 e of above reference) by the Lorentz polarization factors (powder). Intensities given on the XRDF card 11-8 are incorrect as they were obtained by applying polarization factors for single crystals to Jellinek's powder data.

[d] Abbreviation B = broad.

[e] *d* calculated for monoclinic cell. $a=5.96 \pm 0.01$ Å, $b=3.425 \pm 0.005$ Å, $c=11.27 \pm 0.015$ Å, $\beta=91.54° \pm 0.03°$.

Name and type material. The mineral is named for Aristides Brezina (1848–1909), past director of the mineralogy-petrography section of the Natural History Museum, Vienna, Austria, for his contributions to mineralogy and meteoritics. Brezinaite has been found only in *Tucson.* The main mass of both *Carleton* and Ring specimens is in the meteorite collection of the United States National Museum, Washington, D. C. The name has been approved by the commission on New Minerals and Mineral Names, I.M.A.

SILICATE PHASES

Compositions. Forsterite and enstatite are remarkably simple in composition; no detectable amounts of Cr, Ti, Mn, Ni, V (<200 ppm) and Na and K (<300 ppm) were found in either of these silicates (analyses of all silicate phases are given in Table 3). Diopside contains 7.3 weight percent Al_2O_3, which is rare among meteoritic calcium-rich pyroxenes; only

TABLE 3. ELECTRON MICROPROBE ANALYSES OF SILICATE PHASES IN TUCSON

	Olivine	Orthopyroxene	Clinopyroxene	Plagioclase	Glass
SiO_2	42.8	59.2	51.0	44.9	52.4
Al_2O_3	<0.03	<0.03	7.3	35.2	28.1
Cr_2O_3	<0.02	<0.02	<0.02	<0.02	<0.02
TiO_2	<0.02	<0.02	0.25	<0.02	<0.02
FeO	0.23	0.27	0.31	<0.02	<0.02
MgO	56.7	39.8	19.1	<0.02	<0.02
CaO	0.11	0.36	21.7	20.2	19.8
MnO	<0.02	<0.02	<0.02	<0.02	<0.02
Na_2O	<0.03	<0.03	<0.03	<0.03	<0.03
K_2O	<0.03	<0.03	<0.03	<0.03	<0.03
Total	99.84	99.63	99.66	100.3	100.3
			Cation Fractions		
Si	1.003	1.990	1.828	7.996	
Al	—	—	0.308	8.004	
Ti	—	—	—	—	
Fe	0.005	0.008	0.009	—	
Mg	1.981	1.994	1.021	—	
Ca	0.003	0.013	0.833	4.000	
Total cations	2.992	4.005	3.999	16.000	
Theoretical	3.000	4.000	4.000	16.000	
			Component Percent		
	Fo 99.8	En 99.0	En 54.8	An 100	
	Fa 0.2	Fs 0.4	Fs 0.5	Ab 0	
		Wo 0.6	Wo 44.7	Or 0	

titanaugite in *Angra dos Reis* (Mason, 1968) and aluminous diopside in *Colomera* (Bunch *et al.*, 1969) are known to contain large amounts of Al. The moderately high Al^{VI}/Al^{IV} ratio of 0.72 suggests a crystallization environment of moderate pressures and high temperatures; the calcium-poor pyroxene, however, contains <0.03 weight percent Al_2O_3 and is thus inconsistent with a moderate to high pressure origin (Boyd and England, 1960). Plagioclase glass is present in very small amounts and its composition approaches that of anorthite (Table 1). Individual grains are too small for optical or X-ray diffraction study. The assumption that this phase is glass is based on its nonstoichometric plagioclase composition and the tendency to decay more rapidly than anorthite under the electron beam.

The nickel-iron matrix has two distinctly different textures: (1) Partially recrystallized finest octahedrite structure (very fine mixture of kamacite and taenite) whose average composition is Fe 87.4; Ni 10.6; Si 0.75; Co 0.40; and Cr 0.23 weight percent.[1] (2) Narrow, continuous, irregular bands of kamacite (Fe 90.5; Ni 7.5; Si 0.78; Co 0.39; and Cr 0.26 wt.%) with small inclusions of taenite (Fe 80.3; Ni 17.8; Si 0.77; Co 0.37; and Cr 0.25 wt.%). Variation of minor element contents in the above phases is within the analytical error.

Luminescence. Another notable feature of the silicates is their characteristic luminescence under electron bombardment. Enstatite displays a pale blue luminescence under electron bombardment; forsterite, bright blue; diopside, very pale violet; and anorthite, bright purple. Other investigators have shown that enstatite from enstatite achondrites (Derham and Geake, 1964; Derham *et al.*, 1964; and Reid *et al.*, 1964), and enstatite chondrites (Keil, 1968) luminesce under X-ray, proton, or electron bombardment. A correlation between color or luminescence and manganese content of enstatite has been suggested by Derham *et al.* (1964), Garlick (1964), and Reid and Cohen (1967), provided that the iron content is sufficiently low to prohibit a "quenching effect." Reid and Cohen (1967) found that Mn content of less than 350 ppm gives a bright blue luminescence and changes to red at higher manganese contents (900–1200 ppm) Results obtained here for low manganese-bearing enstatite (<200 ppm) are in good agreement with the findings by Reid and Cohen and support their conclusion that luminescence in enstatite is a sensitive indicator of manganese content within certain concentrations.

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[1] Bulk Ni (9.45 wt.%) and Cr (0.17 wt.%) were determined colorimetrically by K. Jensen, Chemistry Division, Argonne National Laboratory (personal communication). Bulk Ni (9.68 wt.%), Co (0.43 wt.%), Cr (0.22 wt.%), and P (0.06 wt.%) have been determined by Carleton Moore (personal communication).

DISCUSSION

The above results show that tentative identifications of enstatite by Shepard (1854) and plagioclase by Genth (1855) were correct, although their reasoning may have been in error, as argued by Fletcher (1890). Chromium content in *Tucson* is not attributable to the presence of chromite as Fletcher stated; rather, it is present in brezinaite (Cr_3S_4) and in solid solution with nickel-iron. *Tucson* has been classified as an ataxite (Cohen, 1905) because of its apparent lack of octahedrite structure. Close inspection of several etched, polished sections, however, reveals a faint residual Widmanstätten pattern, which has been mostly destroyed by reheating (Figure 1). Accurate measurement of band widths is not possible; an estimation of band width (<0.2 mm) suggests, however, that *Tucson* originally formed as a finest octahedrite. It is not clear whether reheating was natural or artificial, but because the large-scale texture is homogeneous and lacks sharp compositional gradients and textures typical of artificial reheating, it would appear that reheating was natural and probably preterrestrial.

Another unusual textural characteristic is the arrangement of silicate inclusions in a parallel or subparallel curved pattern, which is suggestive of flow. In addition, there is a tendency for the long dimension of grains to be aligned parallel to the flow direction. Observations of the residual Widmanstätten pattern suggest that, if these are indeed flow lines, they occurred before solidification, as there is no evidence of mechanical distortion of the Widmanstätten pattern. We have, however, looked at only a few small specimens and study of much larger surface areas would be more conclusive.

Occurrence of a mineral with a composition approximating Cr_3S_4 in the *Tucson* iron meteorite, to the exclusion of daubreelite and troilite, is consistent with the Fe-Cr-S system as reported by El Goresy and Kullerud (1968, 1969), if the Ni content of the meteorite is considered to have no effect. The metal in *Tucson* contains about 0.2 weight percent Cr in solid solution, and since the Cr content of brezinaite expressed in weight percent exceeds the S content, the composition of the meteorite lies close to the 100 percent Fe apex of the ternary system, with minor Cr but with lesser S. From phase relations in the Fe-Cr-S system at 600°C, the composition of the metal and sulfur of *Tucson* (when projected onto the Fe-Cr-S plane) lies in the divariant field: $(Cr,Fe)_{1-x}S+\alpha$ Fe Cr_{ss}. Brezinaite, however, has an X-ray powder pattern identical to that reported by Jellinek (1957) for Cr_3S_4, which is unlike that for $(Cr,Fe)_{1-x}S$. In this respect, therefore, the occurrence of this mineral is at variance with the equilibrium diagrams of the ternary system at 600°C and 700°C. At these temperatures, El Goresy and Kullerud (1969) found no evidence for the existence of a single phase with an X-ray pattern corresponding to Jellinek's Cr_3S_4. Moreover, even if such a compound formed along the the Cr-S join, a single phase region $(Cr,Fe)_{1-x}S$ at elevated temperatures lies between the compositions of Cr_3S_4 and that of the meteorite. Thus,the meteorite should contain a phase with the X-ray pattern of $(Cr,Fe)_{1-x}S$ instead of that observed for brezinaite, provided the mineral assemblages displayed in polished sections represent original phase relations.

Unpublished results supplied by El Goresy and Kullerud indicate that at 500°C the $(Cr,Fe)_{1-x}S$ field gradually pulls toward the Cr-S join; also, the daubreelite+$(Cr,Fe)_{1-x}S$ field narrows, so that at $425 \pm 25°C$ the invariant reaction takes place:

$$\underbrace{\text{daubreelite} + (\text{Cr,Fe})_{1-x}S + \text{vapor}}_{\substack{\text{High temperature}\\ \text{assemblage}}} \rightarrow \underbrace{\text{Cr}_{2.1}\text{S}_3 + \text{FeCr}_{ss}}_{\substack{\text{Low temperature}\\ \text{assemblage}}}$$

If the $Cr_{2.1}S_3$ composition changes to $Cr_{2.25}S_3$ at low temperatures or as a result of minor element amounts present in brezinaite, then the Cr_3S_4 phase will form. The impurities in the mineral, especially 1.6 percent V and 1.0 percent Ti, probably contribute to its stability, as shown by the fact that the mineral was readily synthesized at 800°C from a preparation of its composition and persisted as a single phase when heated to 935°C for an additional two weeks.

Wide variations in the degree of reduction occur among meteorites. The reduction process in *Tucson* has been sufficiently intense to reduce nearly all the Fe and Ni and some Si and Cr to the elemental form and to change the behavior of V and most Cr from lithophile to chalcophile. Only enstatite chondrites and enstatite achondrites have experienced a similar degree of reduction. In addition, ferromagnesian silicates in *Tucson* show a low abundance of minor elements compared to those in stony meteorites, with the exception of enstatite chondrites (Easton and Hey, 1967; Keil, 1968).

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