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GREIGITE, THE THIO-SPINEL OF IRON; A NEW MINERAL

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ABSTRACT

Greigite, Fe_3S_4, occurs as tiny grains and crystals in certain clay layers of the upper part of the Tropico Group, a Tertiary lacustrine sequence in the Kramer-Four Corners area, San Bernardino County, California. Greigite is cubic, $a=9.876\pm0.002$ Å at 25° C., space group *Fd3m*, Z=8, calculated density 4.079 ± 0.003 gm/cc. The strongest x-ray powder diffraction lines are 2.980 Å(100), 1.746 Å(77), 2.469 Å(55), 3.492 Å(31.5) and 1.008 Å(31). Greigite is strongly magnetic; responding like magnetite to the hand magnet. The mineral has an ideal spinel structure and contains 8Fe in site 8*a*, $(\frac{1}{8}\,\frac{1}{8}\,\frac{1}{8})$, 16Fe in site 16*d*, $(\frac{1}{2}\,\frac{1}{2}\,\frac{1}{2})$ and 32S in site 32*e*, $(x\ x\ x)$, where $x=0.2505$ with a standard error of 0.0038. The structure parameters were refined to a reliability factor of 9.9%. Greigite is the iron member of the thiospinels, represented in nature by such well-established minerals as linnaeite, polydymite and violarite.

Greigite is named in honor of Dr. J. W. Greig, Pennsylvania State University.

INTRODUCTION

The existence of a magnetic iron sulfide with a spinel structure and a composition in the range Fe_3S_4 to Fe_2S_3 has been frequently postulated. Recent studies by Berner (1964), Yamaguchi and Katsurai (1960), and Piggott and Wilman (1958) demonstrate that a magnetic iron sulfide compound with x-ray and electron diffraction properties appropriate for a spinel can be synthesized in various ways. Authors, such as Lepp (1957) and Hutton (quoted by Berner, 1964), have prepared a phase with the necessary x-ray properties, but did not recognize the relationship to the spinel structure compounds. Freke and Tate (1961) and numerous others, have synthesized magnetic iron sulfide compounds for which analyses have indicated compositions in the range Fe_4S_5 to Fe_2S_3, but for which, unfortunately, proof of the purity of the analyzed sample by x-ray or other means was lacking.

We have discovered a magnetic iron sulfide with the formula Fe_3S_4 and a spinel structure, in drill cores from the Kramer-Four Corners area, San Bernardino County, California, and propose to name it greigite

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[1] Publication authorized by the Director, U. S. Geological Survey.

(grĕg-īt) in honor of Dr. J. W. Greig, formerly at the Geophysical Laboratory, Carnegie Institution of Washington, and now at Pennsylvania State University, in recognition of his many contributions to mineralogy and physical chemistry. The name has been approved by the Commission on New Minerals and Mineral Names, IMA.

Occurrence

Greigite was discovered in cores recovered from lacustrine sediments in three test holes drilled in the Kramer-Four Corners area, San Bernardino County, California. The location of the wells, known as Four Corners No. 3, 4, and 5, and details of the geology are given by Benda *et al.* (1960) and by Dibblee (1958). The flat-lying greigite-bearing sediments are Tertiary in age and are unconformably overlain by 650 to 800 feet of Recent alluvium. They are unconformably underlain by sandstones and conglomerates of uncertain age. The lake beds belong, stratigraphically, to the upper part of the Tropico Group of Miocene(?) and Pliocene(?) age which were deposited in a former lake about eight miles east of the well-known Kramer borate district. Although it is not known whether the former lake in the Four Corners area was part of the larger lake at Kramer, the mineralogy of the borate-bearing beds in both localities indicates that the lake waters were similar in composition. At Four Corners, the lake beds are composed of interbedded calcareous clays, silts and fine- to medium-grained arkosic sands.

Greigite is found continuously through a 120-foot section in holes 3 and 4 and through about 400 feet in hole 5. The heaviest concentrations of the mineral were noted in cores from the 1700–1701-ft interval in hole 3, 1345–1355-ft interval in hole 4, and the 1344–1348-ft interval in hole 5.

Greigite occurs in laminae of grayish-black-colored sulfide-bearing clays and fine silts which are interlaminated with sulfide-free clays, silts, and sands. The laminae average 0.8 mm in thickness, but the greigite-bearing layers range from 0.02 mm to 12 mm in thickness. Greigite is restricted to clay and fine silt layers, being completely absent from the sands and other coarse-grained material.

Minerals associated with greigite are montmorillonite, chlorite, calcite, colemanite, veatchite, orpiment, and realgar. The greigite sample concentrated for analysis, from hole 5, also contained a small amount of marcasite in close association. It is noteworthy that the only other iron sulfide observed in the drill cores was a small amount of pyrite occurring as disseminated crystals in the interval 843–874 feet from hole 3. Greigite was not directly associated with the pyrite, and was not observed in hole 3 above 1622 feet.

Greigite has also been found in the Kramer borate district as tiny inclusions in crystals of kernite on the B-level of the Mudd (old Western Borax) mine in the southern part of the district. Associated as included minerals are montmorillonite, chlorite, biotite, and single euhedral crystals of dolomite, calcite and searlesite. In contrast to the widespread occurrence in the Four Corners area, greigite has been positively identified only from this single occurrence in the Kramer borate district.

ORIGIN

The alternation of sulfide-bearing and sulfide-free laminae in the greigite-bearing sediments suggests varves and may represent seasonal variations in the composition and physical conditions of the lake waters. Additional studies of the cores to confirm an annual periodicity have not been made.

Freke and Tate (1961) demonstrated that greigite, together with other iron sulfides, can be synthesized by using a culture of the bacteria *Desulphibrio desulphuricans* to reduce iron solutions. The importance of bacteria in the formation of sedimentary iron sulfides is widely accepted and, considering the geological occurrence in the Four Corners area, it seems probable that greigite was formed by bacterial reduction of iron-bearing waters in essentially anaerobic bottom sediments of an alkaline lake. With the exception that laminae containing iron hydroxide are absent, the appearance of the greigite-bearing core is quite similar to the sedimentary section (Oppenheimer, 1960, Fig. 8, p. 258) from a marine environment showing color banding due to bacterial activity.

In the Kramer district, greigite appears to have formed with borax in the temperature range 25° to 35° C. (Christ and Garrels, 1959), and to have remained as a stable or metastable phase after conversion of the borax to kernite, which occurs at $58° \pm 5°$ C. and a depth of 2500 ± 500 feet, according to Christ and Garrels (1959).

CONCENTRATION AND CHEMICAL ANALYSIS

Greigite occurs as tiny grains and crystals evenly dispersed throughout the host clay, to an estimated content of 5% by weight. A partial concentration of the sulfide was effected by dispersing the clay in water or acetone and using a magnet to draw the particles away from the nonmagnetic clay minerals. A further concentration was obtained by a heavy liquid separation, but again, a clean separation was not obtained. In both cases, considerable quantities of clay minerals and chlorite were trapped with the magnetic grains. Following Neuerburg (1961), we were most successful in concentrating greigite by an initial magnetic concentration followed by treatments with HF and dilute HCl. *X*-ray and optical examination of the final concentrate showed that it contained about 7% marcasite as the only crystalline contaminant to the greigite. Careful measurement of the *x*-ray patterns before and after the concentration process did not reveal any physical changes in the sulfides.

Initial analytic studies to develop suitable microanalytical methods and to determine the elements to be analyzed were conducted on a carefully purified concentrate. Microspectrochemical analysis (Table 1) revealed the presence of Fe as a major element with Al as a significant but lesser constituent. No other elements were detected in amounts greater than 0.5%.

TABLE 1. MICROSPECTROCHEMICAL ANALYSIS OF A CONCENTRATE CONTAINING APPROXIMATELY 75% GREIGITE, 10% MARCASITE, AND 15% ORGANIC MATTER

Constituent	Percentage
Fe	Major
Al	3
Cu	0.1
Co	0.03
Mg	0.1
Mn	<0.002
Na	0.1
K	<0.01
Ni	<0.05
Si	<0.01
Ti	<0.001
F	<0.5

No other elements were detected.
Analyst, C. L. Waring

From the previously gained experience, approximately 5 mg. of a carefully prepared concentrate, which had been repeatedly digested in warm HF and 5% HCl, followed by repeated washings in acetone, was quantitatively analyzed by microchemical techniques. The chemical treatment insured the removal of significant amounts of silicate, fluoride, oxide and sulfur phases as well as any pyrrhotite that might have been present.

Marcasite was isolated by heating the concentrate for 20 hours in (3+2) HCl to dissolve the greigite.[1] The sulfur in the marcasite was determined turbidimetrically as $BaSO_4$ and subtracted from the total sulfur in the concentrate, determined gravimetrically as $BaSO_4$. Organic matter was calculated as the difference between HCl acid insoluble and

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[1] Tests under identical conditions on marcasite ground to an impalpable powder showed that 1 to $1\frac{1}{2}$% of the marcasite dissolved on heating for 20 hours in (3+2) HCl.

the sum of marcasite plus the ignited aqua regia insoluble. Aluminum was determined colorimetrically with alizarin and iron colorimetrically with o-phenanthroline, to yield the results given in Table 2.

The organic matter, acid insolubles, and soluble Al_2O_3 reported in Table 2 do not reveal their presence in *x*-ray diffraction photographs of the initial concentrate and are therefore presumably amorphous. The form of the soluble Al_2O_3 is not known but it is clearly not incorporated in the greigite because the content of soluble Al_2O_3 was found to vary between samples, being least in the most carefully prepared concentrates. The formula of the sulfide, deduced from the soluble Fe and soluble S, is $Fe_{3.000}S_{4.006}$, indistinguishable in the present study from Fe_3S_4. The relative error in the iron determination is estimated as $\pm 0.3\%$ and of sulfur as $\pm 0.4\%$. If both of these errors should work in the same direction, the maximum composition range indicated is only $Fe_{3.00}S_{4.00\pm 0.07}$.

TABLE 2. CHEMICAL ANALYSIS OF A 5 MG SAMPLE OF GREIGITE

FeS_2	7.2%		
Acid insoluble, Ignited	5.8	SiO_2	none
		Fe_2O_3	0.3
Organic matter	13.0	Al_2O_3	3.2
		CaO	0.5
Soluble[1] Fe	40.3	MgO	0.5
Soluble S	30.9		
Soluble Al_2O_3	1.2		
Soluble CaO	<0.5		
Soluble MgO	<0.5		
Total[2]	98.4		

[1] Soluble when digested on a steam bath in (3+2) HCl for 20 hours. Ratio Fe/S $=1:1.335=3.000:4.006$.

[2] Taking soluble CaO+MgO as zero.

Analyst, Frank S. Grimaldi.

PROPERTIES

Physical and optical properties. A concentrated powder of greigite is sooty black in color, strongly magnetic and apparently quite stable in air. Because of the small grain size and lack of coherency in the clay matrix, we were not successful in obtaining a good polished surface of greigite within its matrix, but a greigite concentrate was readily mounted and polished in cold setting plastic medium. The concentrate contained individual crystals ranging from 0.0004 mm to 0.0045 mm in diameter, the median being about 0.0015 mm. Irregular clots and intergrown groupings of crystals and grains ranged up to 0.015 mm in diameter.

The small grain size precluded a determination of cleavage, relative hardness and specific gravity. The calculated density, based on *x*-ray diffraction measurements, is 4.079±0.003 gm/cc.

In vertically reflected light greigite is opaque with a pale creamy white color. Against marcasite it is less yellow and more pink colored; against pyrrhotite it is distinctly whiter and less pink. Greigite is completely isotropic in reflected light. The polishing hardness of greigite is about the same as that for marcasite, but apparently slightly greater than that for pyrrhotite. A sharpened steel needle just scratched greigite, but the test must be considered inconclusive because of the small size of the grains on which the test was made.

TABLE 3. RESULTS OF HEATING EXPERIMENTS ON GREIGITE. CHARGES WERE SEALED IN EVACUATED SILICA GLASS TUBES

Temperature, ° C.	Time of heating, Hours	Results
105	90	No change
148	65	No change
198	170	No change
238	165	No change
282	148	Approximately 5% had broken down to pyrrhotite plus S vapor
320	504	Complete breakdown to pyrrhotite+pyrite
395	17	Complete breakdown to pyrrhotite+pyrite

Greigite has magnetic properties similar to those of magnetite. The tendency of grains to form clumps and aggregates during separation procedures probably is due to the magnetic properties.

Thermal properties. The thermal stability of greigite was tested by heating small fractions of the concentrate in sealed, evacuated silica glass tubes, the heated product being examined by *x*-ray and optical means. The results are presented in Table 3. No change occurred in runs up to 238° C. and the first evidence of a breakdown occurred at 282° C. in a 148-hour run, where a small amount of the greigite had broken down to pyrrhotite. Because no pyrite was intergrown with the pyrrhotite breakdown product, it was assumed that the excess sulfur generated from the breakdown was present as a tenuous vapor phase in the free space of the silica glass tube. Runs at 320° C. for 504 hours and at 295° C. for 17 hours showed a complete breakdown of the greigite to pyrrhotite plus pyrite.

These results cannot be considered conclusive evidence for an upper thermal stability between 238° C. and 282° C. Clearly there is a kinetic problem involved and many more runs, and runs of longer duration, would be necessary to satisfactorily determine the thermal stability and the temperature dependence of the breakdown rate. The results suggest, however, that greigite, once formed, may exist for long periods under many natural conditions, provided that it is in an environment shielded from oxidizing agents and fluids in which it is soluble. It is probable, therefore, that greigite may be found well back into the geologic column in suitable environments.

Chemical properties. Greigite is very slowly soluble in HF and in warm (3+2) HCl. A dried concentrate of greigite is apparently quite stable in air, showing no tendency to oxidize or decompose. Although its stability in water has not been specifically determined, it was observed that a sample left in contact with water for three days developed a brown tarnish, indicating partial oxidization. Although the drill cores were damp when first obtained, owing to the circulating muds used in drilling, the absence of all solution effects on the associated borate minerals indicated that the enclosing sediments were effectively sealed off from contact with ground water by the abundant clay in the section. Some of the greigite developed a coating of iron oxides after prolonged exposure to surface humidity, but the bulk of the greigite in the cores has shown no sign of oxidation during the six-year period since the cores were first obtained.

Etch reaction on the polished surface, using standard etch reagents, gave the following results:

HNO_3, 1:1	Slight etching after 4 minutes. A few grains tarnished light brown.
HCl, 1:1	Slight etching of grain boundaries after 2 minutes. Drop turned pale yellow. No tarnish.
KOH, 40% (by weight)	Negative, 4 minutes.
KCN, 20% (by weight)	Negative, 4 minutes.
$HgCl_2$, 5% (by weight)	Negative, 4 minutes.
$FeCl_3$, 20% (by weight)	Negative, 4 minutes.

CRYSTALLOGRAPHY

Morphology. A few grains showed some external crystal morphology, but were too small to be separated for individual morphological study. In polished section about five per cent of the grains have four-sided out-lines suggestive of sections cut through octahedra. Unpolished aggregates of grains examined in reflected light showed only triangular reflecting surfaces suggesting either tetrahedra or octahedra. Electron micrographs revealed forms suggesting both octahedra and, infrequently, cubes. Thus, although the morphological form cannot be identified with certainty, the evidence suggests very strongly that the predominant crystal form is the octahedron.

X-ray powder diffraction data. The small grain size prevented any successful attempt to study greigite by single crystal *x*-ray techniques, but made it an ideal substance for powder techniques. No grinding or further handling was necessary to reduce the grain size of the initial concentrate.

Comparison of the *x*-ray powder diffraction data with those of Berner (1964) for a synthetic magnetic iron sulfide (Table 4) leaves no doubt that Berner's material and greigite are the same compound. The close similarity between the *x*-ray pattern for greigite and that for the cobalt thio-spinel, linnaeite, Co_3S_4, has already been pointed out by Yamaguchi and Katsurai (1960) and Berner (1964). Table 4 lists, for comparison, the *x*-ray data for linnaeite and magnetite (Fe_3O_4) quoted by Berry and Thompson (1962). Although greigite has a considerably larger unit cell than either linnaeite or magnetite, the direct correspondence of indexed lines and similarity of intensities serves to emphasize the close correspondence between greigite and the spinels. The increased cell edge of greigite relative to linnaeite is analogous to, and the same magnitude as, the difference between the cell edges of the corresponding oxy-spinels, magnetite and Co_3O_4.

Crystal structure. On the assumption that linnaeite and magnetite (space group *Fd3m*) are isostructural with greigite, the entire powder pattern can be indexed on a cubic cell with $a = 9.876$ Å (Table 4), which compared favorably with the 9.870 Å value observed by Berner (1963) for his synthetic material.

Diffraction intensities were recorded with a diffractometer by mounting the sample in a welled quartz holder and making repeated oscillations along the peaks at a traverse speed of $\frac{1}{8}°$ 2θ per minute. The intensities were determined from planimetric measurements of the areas under the diffraction maxima. The reproducibility of measurement, between different mounts, was 4%. This good reproducibility, together with the small grain size, lack of obvious cleavage and equant shape of the grains, suggests that strong preferred orientation was not present and hence that the observed intensities can be used for structure calculations with considerable confidence.

Correcting the observed powder intensities for multiplicity and apply-

TABLE 4. *X*-RAY POWDER DIFFRACTION DATA FOR GREIGITE COMPARED WITH THOSE FOR SYNTHETIC Fe_3S_4 (BERNER, 1964), LINNAEITE AND MAGNETITE (BERRY AND THOMPSON, 1962)

d_{calc} for a cubic cell with $a = 9.876$ Å. Measurements made in FeKα radiation, intensities measured planimetrically as described in the text. Intensities of synthetic Fe_3S_4 linnaeite and magnetite were reported as relative intensities by visual estimation. N.O. = not observed.

hkl	Greigite			Synthetic, Fe_3S_4		Linnaeite, Co_3S_4		Magnetite, Fe_3O_4	
	d_{calc}	d_{obs}	I	d_{obs}	I	d_{obs}	I	d_{obs}	I
111	5.702	5.720	8.0	5.70	4	5.47	2	4.84	3
220	3.492	3.498	31.5	3.48	6	3.34	4	2.96	6
311	2.978	2.980	100.0	2.97	10	2.83	10	2.53	10
222	2.851	2.855	3.9	2.85	2	—	—	2.42	1
400	2.469	2.470	54.8	2.465	8	2.36	7	2.09	7
331	2.266	2.260	1.2	—	—	—	—	—	—
422	2.016	2.017	9.2	2.012	3	1.926	3	1.712	4
333, 511	1.901	1.901	28.6	1.899	6	1.815	6	1.611	8
440	1.746	1.746	76.8	1.745	9	1.670	8	1.481	9
531	1.669	1.671	0.9	—	—	—	—	1.416	$\frac{1}{2}$
442	1.646	—	N.O.	—	—	—	—	—	—
620	1.5615	1.5625	4.2	1.561	2	1.493	1	1.327	2
533	1.5061	1.5058	9.8	1.505	3	1.439	2	1.280	4
622	1.4889	1.4883	1.5	—	—	—	—	1.264	1
444	1.4255	1.4253	8.6	1.425	5	1.362	2	1.211	2
711, 551	1.3829	1.3826	0.7	—	—	1.321	1	1.175	$\frac{1}{2}$
642	1.3197	1.3204	3.6	1.319	2	1.260	2	1.122	4
731, 553	1.2857	1.2859	12.8	1.285	6	1.227	3	1.094	8
800	1.2345	1.2349	9.2	1.234	5	1.179	3	1.050	5
733	1.2065	1.2097	0.3	—	—	—	—	—	—
644	1.1982	1.1975	0.2	—	—	—	—	—	—
822, 660	1.1639	1.1640	0.3	—	—	1.112	2	0.990	4
751, 555	1.1404	1.1401	1.8	1.140	5	1.090	4	No more lines reported	
662	1.1329	—	N.O.	—	—	—	—		
840	1.1042	1.1051	16.4	1.104	7	1.055	4		
753, 911	1.0840	1.0844	0.6	—	—	1.036	$\frac{1}{2}$		
842	1.0776	—	N.O.	—	—	—	—		
664	1.0528	1.0544	2.1	—	—	1.005	$\frac{1}{2}$		
931	1.0353	1.0351	7.1	1.035	3	0.988	5		
844	1.0080	1.0080	30.9	1.007	8	No more lines reported			

ing the appropriate Lorentz-polarization correction for powder measurements (Buerger, 1960), yielded the $F_{(obs)}$ in Table 5. With the linnaeite spinel structure (space group *Fd3m*) as a model we placed 8 Fe in the tetrahedral site 8*a*, $(\frac{1}{8}\ \frac{1}{8}\ \frac{1}{8})$, 16 Fe in the octahedral site 16*d*, $(\frac{1}{2},\ \frac{1}{2},\ \frac{1}{2})$ and 32 S in site 32*e*, $(x\ x\ x)$, with x approximately $\frac{1}{4}$. The x coordinate, scale factor and overall isotropic temperature factor were refined by the full matrix least squares technique. The final results are: $x=0.2505$, with a standard error of 0.0038; $B=3.2$ Å^2, with a standard error of 0.4 Å^2. These parameters yield an R factor of 9.9%, providing a convincing demonstration of the correctness of the assumed spinel structure. All bond lengths out to 5 Å are listed in Table 6.

Table 5. Comparison of Observed and Calculated Structure Factors for Greigite

(*hkl*)	F_{obs}	F_{calc}	(*hkl*)	F_{obs}	F_{calc}
111	55.6	58.1	642	75.0	−73.3
220	153.5	−164.2	553	N.M.	−122.5
311	230.8	−260.3	731	N.M.	−116.9
222	82.7	−23.2	800	340.5	342.8
400	425.6	428.9	733	N.M.	14.4
331	35.0	−34.9	644	29.9	0.1
422	111.8	118.7	660	N.M.	−59.4
333	N.M.	190.3	822	N.M.	−59.3
511	N.M.	196.5	555	N.M.	101.8
440	544.8	532.0	751	N.M.	−97.1
531	31.2	−28.4	662	N.M.	−14.4
442	0.0	0.1	840	201.7	175.2
620	101.8	92.0	753	N.M.	−13.8
533	161.9	−149.9	911	N.M.	18.1
622	63.7	−11.9	842	0.0	0.1
444	274.8	−257.9	664	45.3	48.5
551	N.M.	27.3	931	78.5	−81.7
711	N.M.	−19.4	844	200.8	234.9

N.M. = Not measured because of overlap or interference.
R = 9.9%
$B=3.2\pm0.4$ Å^2

The cell data for greigite are:

Space group:	*Fd3m*, by analogy with linnaeite
Cell dimensions:	9.876 ± 0.002 Å at 25° C.[1]
Cell volume:	963.3 ± 0.3 Å^3
Cell constants:	8 [Fe_3S_4]
Density:	4.079 ± 0.002 gm/cc

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[1] Determined by six successive oscillations across the 440 reflection of greigite and the 331 reflection of Si metal. The sample was remade between oscillations. The uncertainty is expressed as the standard deviation of each oscillation. The cell edge used for Si at 25° C. was calculated from the data of Parrish (1960).

Crystal chemistry. It is apparent that greigite is the iron member of the family of thio-spinels represented in nature by the well-established minerals linnaeite (Co_3S_4), polydymite (Ni_3S_4), seigenite $(Co, Ni)_3S_4$, violarite $FeNi_2S_4$, carrollite $CuCo_2S_4$ and daubreelite $FeCr_2S_4$.

The composition Fe_3S_4 makes greigite a polymorph of the recently described mineral smythite (Erd *et al.*, 1957). Smythite is rhombohedral with a structure consisting of slabs of pyrrhotite stacked on each other to give a sheet structure. The measured specific gravity of smythite is 4.06, very close to the density of 4.079 gm/cc calculated for greigite. This similarity is to be expected because sulfur atoms in both structures occur in nearly ideal closely-packed arrays—smythite as a combination of hexagonal and cubic close packing and in greigite as cubic close packing—which should lead to almost identical densities. The iron atoms in both structures are distributed between the possible sites in such a way that they do not cause any significant distortions in the closely-packed arrays.

TABLE 6. BOND LENGTHS IN GREIGITE OUT TO 5Å

From	To	Bond length Å	Multiplicity
S (0.2505, 0.2505, 0.2505)	S(0.2505, −0.0005, −0.0005)	3.50_8	3
	S(0.2505, 0.4995, 0.4995)	3.48_0	3
	S(0.0005, 0.2495, 0.5005)	3.49_4	6
	Fe(0.1250, 0.1250, 0.1250)	2.14_8	4
	Fe(−0.1250, 0.3750, 0.3750)	4.09_8	12
	Fe(0.5000, 0.2500, 0.2500)	2.46_6	6
	Fe(0.5000, 0.5000, 0.5000)	4.27_0	2
	Fe(0.5000, 0.0000, 0.0000)	4.28_2	6
Fe(0.1250, 0.1250, 0.1250)	Fe(−0.1250, −0.1250, −0.1250)	4.27_9	16
	Fe(0.5000, 0.2500, 0.2500)	4.09_7	24
Fe(0.5000, 0.5000, 0.5000)	Fe(0.5000, 0.7500, 0.7500)	3.49_4	12

DISCUSSION

Successful syntheses of a phase which is obviously greigite have been reported by Berner (1964), Hutton (quoted by Berner, 1964), Yamaguchi and Katsurai (1960), Piggott and Wilman (1958), and Lepp (1957). Probable syntheses, but lacking sufficient data to justify certain identification, have been reported by many others.

Lepp (1957) identified his synthetic product, later shown by Berner (1964) to be identical with greigite, as melnikovite. Doss (1912 a, b) originally described melnikovite as a magnetic form of FeS_2, soluble in warm dilute HCl, with a specific gravity about 4.2 to 4.3 and hardness of 2 to 3. It is possible that the type melnikovite may contain some greigite, as suggested by Berner (1964), who remarked that it was probably a "finely intergrown mixture of elemental sulfur and one or more of the following magnetic iron sulfides: pyrrhotite, smythite, or the cubic Fe_3S_4 . . . ". The original identification of melnikovite remains so uncertain, and the description so unsatisfactory and incomplete, that it is unwise to attempt to use the name for a well-defined species like greigite.

X-ray diffraction data have recently been published by Korolev (1958) and Volkov (1961) for natural materials which they called melnikovite. Korolev's material occurred as a finely dispersed iron sulfide in a Tertiary sediment. The *x*-ray pattern of this substance does not match that of any known iron sulfide, nor any mixture of known iron sulfides. Volkov's (1961) material occurred as black, magnetic iron sulfide concretions at a depth of 3.5 meters in the Black Sea sediments. Analysis of the concretions gave a composition of $FeS_{1.30}$ which is close to the $FeS_{1.33}$ of greigite. The *x*-ray diffraction pattern, as recognized by Berner (1964), indicated a mixture of tetragonal FeS (recently described as the mineral mackinawite by Evans *et al.*, 1962) and greigite, with greigite as the major phase. Volkov's observation appears to be the first unequivocal observation of the natural occurrence of greigite.

Following completion of the present study, and while this paper was in press, the article "Melnikovite as a mineral species" by A. P. Polushkina and G. A. Sidorenko was published in *Zapiski Vses. Mineralog. Obshch.*, **92**, 547–554, 1963. The article was very generously translated for us by our colleague Michael Fleischer.

Polushkina and Sidorenko clearly established the existence of an iron sulfide mineral which is identical with greigite. We disagree with their assignment of the name melnikovite however, for the reasons outlined. The uncertainty as to the identity of Doss' original melnikovite remains, and for this reason the Commission on New Minerals and Mineral Names, International Mineralogical Association, approved the name greigite for the thio-spinel of iron.

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REFERENCES

BENDA, W. K., R. C. ERD AND W. C. SMITH, (1960) Core logs from five test holes near Kramer, California. *U. S. Geol. Survey Bull.* **1045-F**.

BERNER, R. A. (1964) Iron sulfides formed from aqueous solution at low temperatures and atmospheric pressure. *Jour. Geol.*, in press.

BERRY, L. G. AND R. M. THOMPSON (1962) X-ray powder data for ore minerals: *The Peacock Atlas, Geol. Soc. Am. Mem.* **85.**

BUERGER, M. J. (1960) *Crystal-structure Analysis.* John Wiley and Sons, N. Y.

CHRIST, C. L. AND R. M. GARRELS (1959) Relations among sodium borate hydrates at the Kramer deposit, Boron, California. *Am. Jour. Sci.* **257,** 516–528.

DIBBLEE, T. W. JR. (1958) Geologic map of the Boron Quadrangle, Kern and San Bernardino Counties, California. *U. S. Geol. Survey Mineral Invest. Field Studies Map* **MF-204.**

DOSS, BRUNO (1912a) Über die Natur und Zusammensetzung des miocänen Tonen der Gouvernements Samara auftretenden Schwefeleisens. *Neues Jahrb. Mineral., Beil. Bd., Abt. A*, **33,** 662–713.

——— (1912b) Melnikowit, ein neues Eisenbisulfid, und seine Bedeutung für Genesis der Kieslagerstätten. *Zeit. prakt. Geol.* **20,** 453–483.

ERD, R. C., H. T. EVANS, JR. AND D. H. RICHTER (1957) Smythite, a new iron sulfide, and associated pyrrhotite from Indiana. *Am. Mineral.* **42,** 309–333.

EVANS, H. T. JR., R. A. BERNER AND CHARLES MILTON (1962) Valleriite and mackinawite. *Geol. Soc. Am. Program* 1962 *Ann. Meet.*, 47a.

FREKE, A. M. AND DONALD TATE (1961) The formation of magnetic iron sulfide by bacterial reduction of iron solutions. *Jour. Biochem. and Microbiol. Techn. and Eng.* **3,** 29–39.

KOROLEV, D. F. (1958) The role of iron sulfides in the accumulation of molybdenum in sedimentary rocks of the reduced zone. Geochemistry (English translation), 1958 (4), 452–463.

LEPP, H. (1957) The synthesis and probably geologic significance of melnikovite. *Econ. Geol.* **52,** 528–535.

NEUERBURG, G. J. (1961) A method of mineral separation using hydrofluoric acid. *Am. Mineral.* **46,** 1498–1501.

OPPENHEIMER, C. H. (1960) Bacterial activity in sediments of shallow marine bays. *Geochim. Cosmochim. Acta.*, **19,** 244–260.

PARRISH, W. (1960) Results of the I. U. Cr. precision lattice-parameter project. *Acta Cryst.* **13,** 838–850.

PIGGOTT, M. R. AND H. WILMAN (1958) The sulphiding of mild steel surfaces. *Acta Cryst.* **11,** 93–97.

VOLKOV, I. I. (1961) Iron sulfides, their interdependence and transformation in the Black Sea bottom sediments. *Trudy. Inst. Okeanol. Akad. Nauk SSSR.* **50,** 68–92 (in Russian).

YAMAGUCHI, S. AND T. KATSURAI (1960) Zur Bildung des ferromagnetischen Fe_3S_4. *Kolloid Zeit.* **170,** 147–148.

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