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ON THE OCCURRENCE OF SIDEROTIL IN THAMES RIVER GRAVEL

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Thames river gravels consist mainly of flint, but commonly pyrite occurs as an accessory constituent (Midgley, 1958). One sample of such a gravel from Chertsey, Surrey, left to weather at the Building Research Station was found to contain a high proportion of pyrite pebbles, which were covered with a white crystalline powder. This powder under the microscope consisted of very small equant grains with a refractive index of about 1.535. A powder *x*-ray diffraction pattern obtained on a 10 cm diameter cylindrical camera with filtered cobalt K_α radiation suggested by reference to the A.S.T.M. index (1960) that the mineral was $FeSO_4 \cdot 5H_2O$ (Table 1, ii, iv).

An electron microscopic examination of the mineral showed it was composed of aggregates of small tabular crystals of about 0.05×0.15 micron (Fig. 2), or aggregates of crystals, 0.1×0.01 micron, in which the crystals were commonly arranged to give a "boat-shaped" outline (Fig. 3).

TABLE 1

(i) Siderotil Chertsey		(ii) Siderotil Chertsey		(iii) Synthetic $FeSO_4.4H_2O$ (Kossenberg and Cooke, 1961)		(iv) Synthetic $FeSO_4.4H_2O$ (A.S.T.M., 1960)		(v) Rozenite (=siderotil) (Kubisz, 1961)	
dÅ	I	dÅ	I	dÅ	I	dÅ	I	dÅ	I
6.89	27	6.85	7	6.60	19	6.9	38	6.893	5
5.69	4			5.72	6				
5.51	85	5.46	9	5.31	67	5.5	100	5.483	9
		5.15[2]	1					5.179	1
4.77	34	4.75	2	4.73	43			4.762	3
4.50	100	4.48	10	4.37	100	4.49	100	4.498	10
3.98	47	3.97	8	3.90	72	3.99	75	3.979	8
								3.840	1
3.62	9	3.60	2			3.60	3	3.682	2
3.43	40	3.40	8	3.35	56	3.40	50	3.410	8
3.30[1]	23	3.28[1]	3					3.295	2
3.235	30	3.22	7	3.20	45	3.24	50	3.239	7
2.994	24							2.993	7
2.970	22	2.97	6	2.93	72	2.97	75	2.973	8
2.915	7	2.91	1					2.899	1
2.775	6	2.767	2			2.75	20	2.738	4
2.735	9			2.71	30				
2.584	24	2.573	6	2.56	48	2.58	38	2.579	7
2.481	14	2.465	2					2.478	1
2.3795	11	2.426	6	2.40	39	2.43	38	2.436	7
2.364	8	2.367	5	2.34	48			2.381	7
								2.327	7
2.295	4	2.253	4					2.293	1
2.271	20			2.24	44	2.27	38	2.272	6
2.247	6	2.24	1					2.247	1
								2.223	1
		2.181	1			2.18	3	2.188	1
		2.144	1					2.148	2
		2.113	1	2.10	39	2.11	8	2.116	1
		2.049	1			2.04	3	2.0577	1
1.973	12	1.967	4			1.97	38	1.9731	5
								1.9520	2
1.899	6	1.895	4	1.88	35	1.89	20	1.8999	3
								1.8757	2
								1.8627	2
1.802	5	1.815	1					1.8248	1
1.788	4	1.796	4	1.78	22	1.80	18	1.7975	5
		1.755	3			1.76	8	1.7592	3
1.729	5					1.72	10	1.7278	3
Diffractometer Cu K_α I peak height (I 4.50Å = 100)		Cylindrical camera 10 cm dia Co K_α I arbitrary		Camera Co K_α I photometer		Camera Mo K_α I calibrated strips		Data not given	

[1] Quartz.
[2] Melanterite.

The refractive index and appearance of the crystals indicated that the mineral resembled siderotil (Schrauf, 1892; Larsen, 1921; Palache *et al.*, 1951; Spencer, 1897). This mineral was first described by Schrauf (1892) on a sample from Idria, Italy as $FeSO_4 \cdot 5H_2O$. The authors of this note have not been able to see the original paper. Palache *et al.* (1951) quote an analysis by Schrauf as: FeO 30.0, SO_3 34.3, H_2O 34.0, on a sample of a few milligrams. They also suggest that the mineral may in fact be the tetrahydrate.

Kubisz (1960) described a new mineral, "rozenite" which is also $FeSO_4 \cdot 4H_2O$, but, as Fleischer (1961) pointed out in his evaluation of the paper, this mineral should be described as siderotil.

The sample from the Thames river gravel was sufficient in quantity for separation of the white crystals from the pyrite by means of heavy liquid flotation, about 2 gm of the white crystals being obtained.

A chemical analysis of the separated material gave (wt. per cent): SO_3 34.85, FeO 29.9, Fe_2O_3 absent or trace, other sulfur compounds absent or trace, water (Karl Fischer method) 30.5, matter insoluble in water (SiO_2) (*ca.*) 4.75. The analysis of the soluble portion gives the following ratios: FeO 1, SO_3 1.04, H_2O 4.06. This shows that siderotil is the ferrous sulfate tetrahydrate ($FeSO_4 \cdot 4H_2O$).

Kubisz (1960) gives: FeO 31.13, MgO 0.97, MnO 0.06, SO_3 36.29, H_2O 32.98, total 101.43; (FeO.MgO) 1., SO_3 0.99, H_2O 4.00, for what must be another example of siderotil.

A more careful x-ray examination of the separated siderotil from the Thames gravel was made using a counter diffractometer, set at 40 Kv., 20 ma., $\frac{1}{4}$°/min., $\frac{1}{2}$° scatter slit, 0.1 receiving slit, rate 8, time const. 8. The result is given in Table 1, ii.

A comparison with the data for rozenite (siderotil) from "Staszie" mine (Kubisz, 1960), for synthetic $FeSO_4 \cdot 4H_2O$ (Kossenberg and Cooke, 1961), A.S.T.M. index (1960) and siderotil from Chertsey is given in Table 1. The data show the identity of siderotil and synthetic $FeSO_4 \cdot 4H_2O$, the only differences being in the weaker reflections, their presence or absence depending on the method of recording. The natural minerals may be contaminated by traces of melanterite ($FeSO_4 \cdot 7H_2O$) and quartz.

A D.T.A. record of siderotil from Chertsey gave endotherms at 74°, 114°, 555° and 700° C., and exotherms at 275° and 400° C. (Fig. 1). This is in agreement with the thermogram quoted by Kubisz (1960) as Fig. 1, with the addition of a low temperature endotherm at 74° C., due probably to adsorbed moisture and an exotherm at 275° C. due to the oxidation of a small trace of pyrite.

Single crystal electron diffraction patterns (Fig. 4) were obtained from the tablets (Fig. 2) on an A.E.I. E.M.6 electron microscope, and cali-

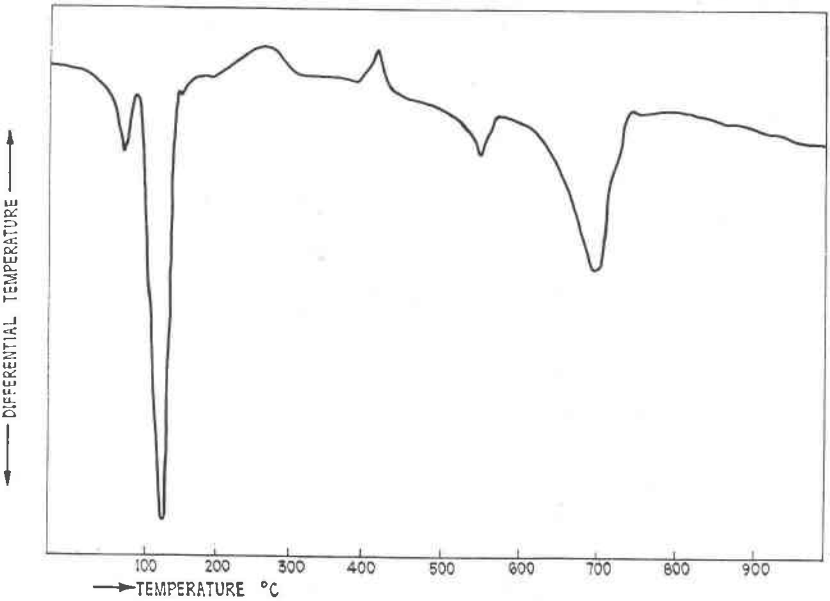

FIG. 1. Differential thermal analysis of siderotil from Thames River gravel.

brated with carbon and MgO, using an accelerating voltage of 100 Kv. These tablets were lying on the basal pinacoid and gave a diffraction pattern of the a.b. plane. From the diffraction pattern the parameters 7.0 and 11.75 Å were obtained.

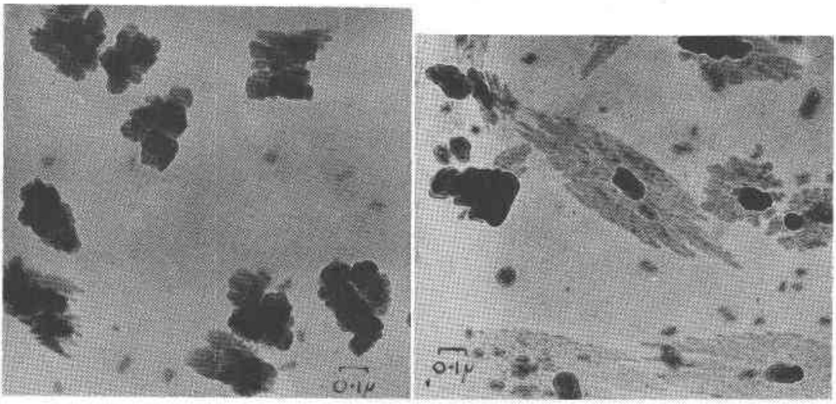

FIG. 2 FIG. 3

FIG. 2. Electron micrograph of siderotil (001) tablet.
FIG. 3. Electron micrograph of siderotil ("boat-shaped" crystal) (010) plates.

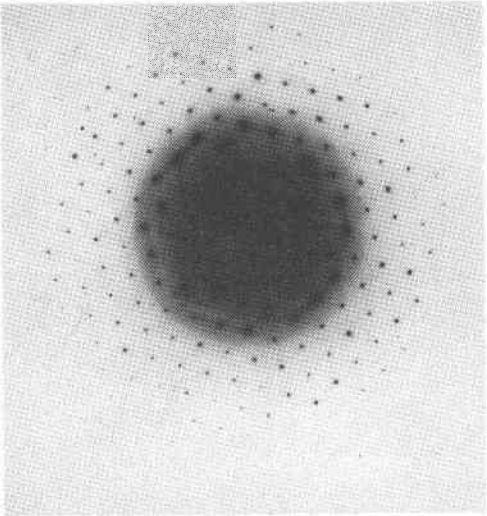

FIG. 4. Electron diffraction pattern of a *b* plane.

Single crystal electron diffraction patterns were also obtained from the "boat-shaped" crystal (Fig. 3); they were of poorer quality than those given by the a.b. plane, but they were indexed approximately, giving the parameters 11.8 and 10.2 Å, $\beta=102°$. In these patterns there was strong pseudohalving of the 10.2 Å direction, alternative layer lines being extremely weak. From these data a unit cell of approximate dimension $a=11.75$, $b=7.0$, $c=10.2$ Å, $\beta=102°$ was obtained. It was then possible to index the more accurate powder *x*-ray diffraction data and the following unit cell was obtained:

$$a = 11.82, \quad b = 14.08, \quad c = 10.96 \text{ Å}, \quad \beta = 101.9°.$$

These data suggest that siderotil is isomorphous with the $BaNi(CN)_4 \cdot 4H_2O$ group of substances, the structure of which are given by Wyckoff (1960). Kubisz (1960) suggests that $FeSO_4 \cdot 4H_2O$ is isomorphous with ilosite, $(Mn, Zn, Fe)SO_4 \cdot 4H_2O$, and leonhardite $MgSO_4 \cdot 4H_2O$.

There is no indication from the conditions of weathering why siderotil ($FeSO_4 \cdot 4H_2O$) should be formed instead of the more usual melanterite ($FeSO \cdot 7H_2O$), the stable phase at room temperature. The siderotil stored in the laboratory atmosphere remained unchanged at the end of the year.

References to the occurrence of siderotil are rare; Ross (1940) referred to it in cavities in quicksilver ore from Contra Costa County, California, which he suggests "may be derived by dehydration from melanterite

($FeSO_4 \cdot 7H_2O$), one of the more widespread and more abundant sulphates." Schaller (1940) also refers to siderotil as associated with a phosphate-sulfate of aluminum from Utah. Kubisz (1960) described a new mineral, rozenite, $FeSO \cdot 4H_2O$, from "Staszie." Siderotil is a well-established mineral name and so has precedence.

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REEXAMINATION OF CUPRORIVAITE

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Cuprorivaite was described as a new mineral from Vesuvius by Minguzzi (1938). He assigned it the formula, $2(Ca, Na)(Cu, Al)(Si, Al)_4(O, OH)_{10} \cdot H_2O$, derived from analyses of impure material after deductions for contamination. Some critics have questioned the validity of the species, and Strunz (1957, p. 366) says cuprorivaite is a mixture of wollastonite and glass. One of us (Pabst, 1959) suggested that cuprorivaite is probably the natural analogue of Egyptian blue, $CaCuSi_4O_{10}$. Our reexamination was carried out on crushed material remaining from the type specimen used by Minguzzi. No other cuprorivaite was available for study.

By means of heavy liquids, tetrabromethane diluted with toluene, followed by manual separation, one of us (F. M.) obtained about 1 cg of