

An occurrence of ϵ -FeOOH in a black shale

FERRUGINOUS sediments are now known to contain a variety of iron oxides and hydrated iron oxides in addition to such well-known forms as hematite and goethite. Minerals such as maghemite (γ -Fe₂O₃) and lepidocrocite (γ -FeOOH) may be identified by ore microscopy (Craig and Vaughan, 1981) but phases such as ferrihydrite 5Fe₂O₃·9H₂O and ferroxhyte (disordered δ -FeOOH) require more elaborate procedures, especially electron microscopy and select area electron diffraction (Chukhrov and Gorshkov, 1981). In addition to these naturally occurring minerals there exists a variety of synthetic phases, including β -FeOOH (akaganéite), green rust (x Fe(OH)₂· y FeOCl· z H₂O), hydrohematite Fe₂O₃· x H₂O, and ϵ -FeOOH, all recently discussed by Murray (1979), the occurrence of which in the natural environment is practically unknown. The present note describes an occurrence of one of these, ϵ -FeOOH, in a Proterozoic carbonaceous black shale.

ϵ -FeOOH was first reported by Bendeliani *et al.* (1972) as a new polymorph of FeOOH, synthesized at 90 kbar and 400 °C. This phase was found to be isostructural with manganite, and to have a monoclinic space group $P2_1/c$, with $a = 8.721$, $b = 5.164$, and $c = 5.680$ Å, $\beta = 90^\circ$. Its X-ray diffraction spacings and relative intensities distinguish it from the other common and rare iron oxides (Murray, 1979).

The phase was identified on the basis of this X-ray pattern in a specimen of NW Western Australia (Pilbara area) ferruginous black shale, the Mt McRae shale of the Brockman Iron Formation, Hamersley Group (Trendall and Blockley, 1970). Trendall (1983) notes the existence of two varieties of this shale: a very fine-grained, soft, poorly laminated shale containing pyrite and free carbon and a greenish, finely laminated shale containing chert and volcanic ash. The specimen described here comes from the first category.

Using back-scattered electron (BSE) techniques on polished sections of shale (Kransley *et al.*, 1983) it was possible to detect quartz, illite and an iron oxide phase as the chief components of the shale. Chemical analysis indicated the presence of free carbon as well as carbonate. The latter was identified by X-ray diffraction as siderite. Under these circumstances the 'd' spacings of the iron oxide, estimated on the basis of the SEM analysis to occupy at least 40% by volume of the shale, were examined.

TABLE I. X-ray diffraction data on synthetic ϵ -FeOOH and Mt McRae shale iron oxide

ϵ -FeOOH		Iron oxide	
d (Å)	I	d (Å)	I
3.335	100	3.34†	§
2.56	50	2.56†	§
2.488	80	2.49	s
2.22	50	2.22	m
2.162	30	n.d.	—
1.750	70	1.76‡	§
1.689	80	1.69	m
1.655	50	1.65	w
1.541	30	1.54	§
1.50	30	n.r.	—
1.447	50	n.r.	—
1.369*	50	n.r.	—

* numerous other weaker lines; † also a quartz line; ‡ also an illite line; § relative insensitivities of the iron oxide could not be determined; s = strong; m = moderate; w = weak; n.d. = not detected; n.r. = not recorded.

X-ray diffraction data on ϵ -FeOOH (from Bendeliani *et al.*, 1972) and data on the shale mineral are given in Table I. It will be seen that the shale diffraction pattern contains lines which are essentially those of ϵ -FeOOH, and lines where the d spacings of quartz, illite, and the iron oxide overlap, making identification more difficult. Moreover, these lines do not fit any other of the thirteen iron oxides listed by Murray (1979). Thus there is a definite possibility that ϵ -FeOOH may occur in the natural environment.

Electron probe microanalyses, fully ZAF corrected and non-normalized, on the ϵ -FeOOH indicated 88.7–90.2 wt. % Fe₂O₃, with 11.3–9.8 wt. % H₂O by difference. This is close to the theoretical composition FeO·OH. Traces of TiO₂, perhaps indicating inclusions of ilmenite or rutile occurred in some grains.

The shale samples examined often showed an alteration zone of light-brown colouration in contact with the black shale. An X-ray analysis showed that the pale-coloured shale contained the same illite and quartz as the black shale, but no siderite and the iron oxide was hematite. The bleaching in colour thus appears to be a result of oxidation, making siderite unstable (Garrels and Christ, 1965),

oxidising free carbon and apparently converting ϵ -FeOOH to hematite.

REFERENCE

- Bendeliani, N. A., Baneyeva, M. I., and Poryvkin, D. S. (1972) *Geochem. Int.* **9**, 589-90.
 Chukrov, F. V., and Gorshkov, A. I. (1981) *Trans. R. Soc. Edinburgh, Earth Sci.* **72**, 195-200.
 Craig, J. R., and Vaughan, D. J. (1981) *Ore Microscopy and Ore Petrography*. John Wiley & Sons, 406 pp.
 Garrels, R. M., and Christ, C. C. (1965) *Solutions, Minerals and Equilibria*. Freeman, Cooper & Co., 450 pp.

- Krinsley, D. H., Pye, K., and Kearsley, A. T. (1983) *Geol. Mag.* **120**, 109-14.
 Murray, J. W. (1979) In *Marine Minerals* (Burns, R., ed.) Mineral. Soc. Am. Short Course Notes, **6**, 47-98.
 Trendall, A. F. (1983) In *Iron Formation: Facts and Problems* (A. F. Trendall and R. C. Morris eds.) Elsevier, 69-123.
 — and Blockley, J. G. (1970) *West. Austral. Geol. Survey Bull.* 119.

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Powder X-ray diffraction data of rossite

In a review of the literature for the Mineral Powder Diffraction File by Bayliss *et al.* (1980), powder X-ray diffraction data could not be found of the mineral rossite, $\text{CaV}_2\text{O}_6 \cdot 4\text{H}_2\text{O}$. With the crystal structure parameters of rossite determined by

Ahmed and Barnes (1963), a powder X-ray diffraction pattern was calculated with the programme of Langhof, Physikalische Chemie Institute, Darmstadt. Since the powder data of synthetic $\text{CaV}_2\text{O}_6 \cdot 4\text{H}_2\text{O}$ prepared by Kovgan and Nakhodnova

TABLE I. Powder X-ray diffraction data of rossite

<i>hkl</i>	d_{calc}	d_{obs}	I/I_1	I_{calc}	<i>hkl</i>	d_{calc}	d_{obs}	I/I_1	I_{calc}
100	7.249	7.260	90	87	$\bar{2}03$	2.290	2.287	5	5
$\bar{1}10$	6.630	6.636	95	100	130	2.223	2.224	3	1
001	5.999	6.017	50	53	$\bar{3}30$	2.210	2.209	10	3
110	4.578	4.599	10	13	031	2.149	2.148	15	9
020	3.927	3.934	25	26	$\bar{2}23$	2.134	2.132	5	3
$\bar{2}10$	3.853	3.860	100	86	$\bar{2}13$	2.109	2.111	5	3
$\bar{1}02$	3.430	3.432	60	12	$\bar{1}40$	2.092	2.092	25	14
$\bar{1}12$	3.428				$\bar{3}13$	2.090	2.092	25	
$\bar{2}20$	3.315	3.320	25	17	$\bar{2}32$	2.077	2.077	10	5
012	3.182	3.186	3	6	$\bar{2}22$	2.062	2.061	5	5
$\bar{2}21$	3.128	3.127	6	7	$\bar{3}13$	2.042	2.038	3	4
$\bar{1}20$	3.031	3.033	55	37	040	1.964	1.965	3	5
$\bar{2}12$	3.022				420	1.9266	1.9266	10	8
002	2.999	3.000	50	33	$\bar{4}12$	1.9158	1.9155	5	9
$\bar{2}10$	2.920	2.921	40	6	$\bar{2}41$	1.9056	1.9046	15	7
$\bar{1}12$	2.919				$\bar{3}40$	1.8873	1.8871	25	7
$\bar{1}22$	2.916	16	11	$\bar{1}23$	1.8540	1.8581	2	3	
$\bar{2}11$	2.817	2.818	15	12	$\bar{4}11$	1.8451	1.8447	2	5
$\bar{1}30$	2.801	2.804	15	12	230	1.8353	1.8332	3	4
131	2.723	2.725	6	5	320	1.7932	1.7941	5	5
$\bar{3}02$	2.609	2.613	15	12	$\bar{4}32$	1.7767	1.7755	8	6
$\bar{3}10$	2.582	2.586	20	14	$\bar{2}14$	1.7568	1.7564	25	14
$\bar{3}12$	2.546	2.550	10	5	311	1.7283	1.7275	10	5
$\bar{1}22$	2.516	2.520	6	4	032	1.7079	1.7089	12	6
$\bar{2}22$	2.432	2.431	15	15	$\bar{1}24$	1.6935	1.6926	10	9
$\bar{3}11$	2.421	2.420	25	9	$\bar{2}50$	1.6749	1.6749	10	7
032	2.417				$\bar{2}51$	1.6715	1.6706	10	4
300	2.416	8	312	1.6483	1.6472	5	7		
$\bar{2}31$	2.376	2.375	5	5	$\bar{2}14$	1.6044	1.6039	12	4
$\bar{1}32$	2.341	2.342	10	4	$\bar{3}50$	1.6030	1.6030	12	3
$\bar{1}13$	2.312	2.309	15	6	$\bar{4}14$	1.5878	1.5868	10	1
$\bar{1}21$	2.307				$\bar{1}52$	1.5625	1.5618	10	5