

Nakauriite from Unst, Shetland

NAKAURIITE was described by Suzuki *et al.* (1976) as a new mineral, with formula $(\text{Cu,Ni,Mn})_8(\text{SO}_4)_4\text{CO}_3(\text{OH})_6 \cdot 48\text{H}_2\text{O}$ found intimately mixed with chrysotile from fracture fillings in a brucite-bearing serpentinite at Nakauri, Aichi Prefecture, Japan, and has been reported on a similar matrix from an abandoned brucite pit at Basic Refractories mine, near Gabbs, Nye County, Nevada (Oswald and Crook, 1979; cf. Peacor *et al.*, 1982).

In 1975 Mr Tony Ellis of Liverpool presented one of the authors with some specimens which he had collected at about that time in the Shetland Islands, and similar material was subsequently presented by Mr Hilary Corke who had also collected in the area. Among this material were specimens of chromitite from Hagdale quarry, Unst, showing occasional pentlandite and heazlewoodite grains embedded in pale green chrysotile (Bish and Livingstone, 1981), some with thin films of colourful alteration products. These include a golden-brown lustrous platy hydrated carbonate near pyroaurite (IR 3450(s,br), 1630(m,br), 1500(sh), 1370(s,br), 960(w,br), 580(w,br) cm^{-1} and XRD 7.91(m), 7.42(w), 4.04-4.64(w,br), 3.94(w), 2.70(m), 2.64(ms), 2.35(s), 1.99(w), 1.57(s), 1.53(w), 1.52(w), 1.30(w) Å), white, sometimes radiating crusts of hydromagnesite (IR 3650(m,sp), 3520(s), 3440(s), 1515(sh), 1470(s), 1420(s), 1112(mw), 882(m,sp), 878(sh), 853(m,sp), 798(m), 760(mw), 740(w), 712(w), 590(m), 480(sh), 430(s) cm^{-1}), pink massive to indistinctly crystallized clinocllore ('kämmererite') (IR 3680(sh), 3590(s,br), 3440(m,br), 1640(w,vbr), 1060(sh), 1000(vs), 960(s), 815(w), 645(s), 520(sh), 460(s), 440(sh), 415(sh) cm^{-1}) and small amounts of deep green translucent theophrastite giving an X-ray powder diffraction pattern close to that of reagent grade nickel hydroxide and the values quoted by Livingstone and Bish (1982), with IR $\nu_{\text{O-H}}$ 3640 cm^{-1} , and n 1.65, near Livingstone and Bish's value of 1.66, whereas Marcopoulos and Economou (1981) quote anomalously high values of n_{ω} 1.759 and n_z 1.760 for their theophrastite. Associated with these alteration products are small amounts of a pale blue fibrous mineral interbedded with the chrysotile. Samples of this blue material were carefully separated from its associates, using a binocular microscope, and its infra-red spectrum measured. Despite the care in separation, the resulting spectra are dominated by absorptions due to chrysotile, but also show a strong broad absorp-

tion due to the ν_3 asymmetrical stretching vibration of the CO_3^{2-} ion with maximum near 1360 cm^{-1} and another near 3500 cm^{-1} due to a hydrogen-bonded O-H stretching vibration. These extra absorptions are also present in the spectrum of a nakauriite (RSWB 80-40) from Nakauri, Japan, which has a very similar appearance to the Hagdale material, and is from a closely related mineral association. The SO_4^{2-} anion absorbs strongly in the infra-red near 1100 cm^{-1} (strong, broad band, due to the ν_3 asymmetrical stretching vibration) and near 600 cm^{-1} (due to the ν_4 asymmetrical bending vibration), and if the anion is distorted also near 980 and 450 cm^{-1} (see, for example, S. D. Ross in Farmer, 1974). Unfortunately chrysotile has absorption bands in all these regions, but some of the stronger sulphate absorptions might be expected to distort the profiles of the corresponding chrysotile bands. No such distortions are noticeable in our spectra or those reported by Suzuki *et al.* (1976). According to Peacor *et al.* (1982) electron microprobe analyses of nakauriite from Japan and from Nevada show little or no sulphur to be present. Microchemical tests on very small samples of our nakauriite confirmed the presence of Cu(II), CO_3^{2-} and some Fe(III), and the absence of Zn(II) and Co(II); traces of Ni(II) and SO_4^{2-} were just detectable. Nakauriite needs to be reanalysed in order to determine its true composition.

X-ray powder diffraction photographs were taken of the Hagdale material, nakauriite from Nakauri and of chrysotile from Nakauri. The diffraction patterns of the Hagdale material and of the Japanese nakauriite were found to be almost identical. This result was subsequently confirmed by Miss E. E. Fejer of the British Museum (Natural History). Comparison of our values with those reported by Suzuki *et al.* (1976) for 'Type I' nakauriite and by Peacor *et al.* (1982) shows good agreement, particularly with the latter. The absence from our photographs of the 7.8 Å line reported by Suzuki *et al.* (1976) for some nakauriite samples ('Type II') supports the conclusions of Peacor *et al.* (1982) that it is due to impurity. All our X-ray powder diffraction photographs of nakauriites and those reported in the literature show lines due to chrysotile.

This is the first reported find of nakauriite from the British Isles, and the third in the world.

Infra-red spectra were recorded in Nujol and hexachlorobutadiene mulls between KBr plates over the 400–4000 cm^{-1} range, using a Perkin-Elmer 397 precision grating spectrophotometer, each spectrum being calibrated against polystyrene. X-ray powder diffraction photographs were taken using an IRDAB XDC 700 Guinier camera employing Cu-K α radiation, the samples being mounted on adhesive tape. For the values quoted, s = strong, m = medium, w = weak, v = very, sp = sharp, sh = shoulder, br = broad.

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Melanosiderite is siliceous ferrihydrite

MELANOSIDERITE was claimed to be a new mineral species by Cooke (1875). It was found in a clay bed near a serpentinite outcrop at Mineral Hill, Delaware County, Pennsylvania, and was described as a hydrated basic ferric silicate with the following average analysis: Fe₂O₃ 75.12, Al₂O₃ 4.34, SiO₂ 7.42, H₂O 13.83, total 100.72%. The mineral is compact and brittle, has a conchoidal fracture and a vitreous lustre inclining to resinous. It is black in colour and yields a brownish red to brick red streak. Hardness is 4.5 and specific gravity is 3.39. Melanosiderite was thought to be a true silicate because of its vitreous lustre, its fusibility, its definite composition and because it gelatinizes in acids. Palache *et al.* (1944), on the other hand, state that melanosiderite is without doubt a mixture of a hydrous oxide of iron with colloidal silica or a silicate, but so far, this has never actually been proved.

A sample of melanosiderite from the type locality was kindly supplied from the British Museum (Natural History) mineral collection (BM 66908, obtained in 1891 from J. R. Gregory); its general description is in good agreement with that of the material described by Cooke. Typical shiny black fragments were examined using a Philips Debye-Scherrer camera of 11.48 cm radius with Co-K α radiation. The X-ray diffraction patterns obtained from both rotated and stationary fragments consist

of eight rather broad lines that, with the exception of a broad line at 4.26 Å which can probably be attributed to goethite, are in excellent agreement with the pattern of ferrihydrite (Table I).

Frequently associated with the black melanosiderite are patches of rusty weathering material, the powder pattern of which is identical with that

TABLE I. X-ray data for (1) melanosiderite and (2) synthetic ferrihydrite

(1)		(2)	
dÅ	I	dÅ	I
4.26	40(b)	—	—
2.55	75(b)	2.54	100
2.45	20	2.46	25
2.24	100	2.24	90
1.980	30	1.977	40
1.719	30	1.727	20
1.512	40	1.512	50
1.471	60	1.469	80

- (1) Melanosiderite, shiny black fragment, Middleton, Delaware County, Pennsylvania, BM No. 66908. (b) = broad line.
 (2) Synthetic ferrihydrite, Brown (1980).