

## Nickeloan pyroaurite from Leslie, Aberdeenshire

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**SUMMARY.** A nickel-bearing mineral belonging to the pyroaurite-sjögrenite group has been found in a serpentinite rock near the village of Leslie, Aberdeenshire. X-ray powder diffraction data and electron-probe microanalysis indicate that the mineral has a three-layer rhombohedral structure with a probable formula near  $Mg_4^{2+}Ni_2^{2+}Fe_2^{3+}(OH)_{13}CO_3 \cdot 4H_2O$ . The mineral can therefore be described as nickeloan pyroaurite. It decomposes readily in mildly acid conditions and if inherited by serpentinite-derived soils could well be an important source of plant-available nickel.

THE pyroaurite-sjögrenite group of minerals has recently been reviewed by Taylor (1973). The group has the general formula  $M_6^{2+}M_2^{3+}(OH)_{16}CO_3 \cdot 4H_2O$ , with a structure consisting of brucite-like layers alternating with layers of water and carbonate groups (Ingram and Taylor, 1967); it also has two isostructural sub-groups which have been characterized as three-layer rhombohedral (3R) and two-layer hexagonal (2H) polytypes. Most of the minerals belonging to the group show a divalent to trivalent metal cation ratio of 3:1, the best characterized polymorphs being pyroaurite and sjögrenite with  $Mg^{2+}$  and  $Fe^{3+}$ , hydrotalcite and manasseite with  $Mg^{2+}$  and  $Al^{3+}$ , and stichtite and barbertonite with  $Mg^{2+}$  and  $Cr^{3+}$ . Two other varieties have also been reported in which  $Ni^{2+}$  replaces  $Mg^{2+}$ , namely reevesite with  $Ni^{2+}$  and  $Fe^{3+}$  (White *et al.*, 1967; De Waal and Viljoen, 1971) and cardleyite with  $Ni^{2+}$  and  $Al^{3+}$  (Taylor, 1973). Several related nickeliferous hydroxide minerals with X-ray powder patterns similar to the pyroaurite-sjögrenite group are also known (Jambor and Boyle, 1964; Lapham, 1965).

The mineral reported in this paper is a previously undescribed nickel-bearing variety belonging to the pyroaurite-sjögrenite group. It appears to be a 3R polytype with approximately one out of every three  $Mg^{2+}$  replaced by  $Ni^{2+}$  and it can, therefore, be described as nickeloan pyroaurite. The occurrence of this type of mineral in serpentinite suggests that it may act as a source of available nickel in some serpentinite-derived soils.

*Experimental.* The mineral occurs in serpentinite rock exposed in a roadside quarry approximately 1 km west of the village of Leslie, Aberdeenshire (NJ/585247). It is disseminated sporadically through the rock and is also found along fracture surfaces where it occurs as soft, pale, grass-green encrustations. The mineral is intimately associated with fibrous chrysotile from which it could not be entirely separated. The serpentinite does not appear to have been affected by weathering to any great extent and the mineral probably formed during a period of hydrothermal alteration, the occurrence of which is indicated by conspicuous veining.

The mineral was hand-picked from the rock under a binocular microscope and characterized by X-ray diffraction, infrared spectroscopy, transmission and electron microscopy, and electron-probe microanalysis.

### Results

*X-ray powder pattern.* The mineral was first detected during a preliminary X-ray powder diffraction survey of the mineralogy of the serpentinites in north-east Scotland.

TABLE I. *d*-spacings,\* intensities, observed and calculated structure factors, and indexing of lines of the mineral from Leslie, Aberdeenshire, referred to 3R (pyroaurite) and 2H (sjögrenite) unit cells.

1			2			3				
<i>d</i>	<i>I</i>	<i>F</i> <sub>obs</sub>	<i>hkl</i>	<i>d</i> <sub>calc</sub>	<i>F</i> <sub>calc</sub>	<i>F</i> <sub>obs</sub>	<i>hkl</i>	<i>d</i> <sub>calc</sub>	<i>F</i> <sub>calc</sub>	<i>F</i> <sub>obs</sub>
7.68 Å	not measured	—	0003	7.68 Å	—	—	0002	7.68 Å	—	—
3.83	0.7803	0.1460	0006	3.84	60.79	62.87	0004	3.84	41.67	24.36
2.65	not measured	—	1011	2.667	—	—	1011	2.645	—	—
2.611	0.2263	0.1152	0112	2.615	57.58	49.61	0006	2.56	2.35	19.22
2.435	0.0555	0.0573	1014	2.433	18.89	24.68	1013	2.534	16.87	9.56
2.316	0.2036	0.1231	0115	2.320	58.40	53.01	?	—	—	—
2.100	0.0590	0.0730	1017	2.080	14.41	31.44	?	—	—	—
1.961	0.1793	0.1362	0118	1.964	73.98	58.65	1015	2.022	19.01	22.72
1.920	not measured	—	0.0.0.12	1.920	—	—	0008	1.920	—	—
1.746	0.0885	0.1071	1.0.1.10	1.748	49.60	46.17	0009	1.707	0.0	17.89
1.649	0.0700	0.1008	0.1.1.11	1.651	37.69	43.41	1017	1.699	3.01	16.82
1.548	0.0794	0.1140	1.1.1.0	1.550	56.61	49.09	1.1.1.0	1.549	38.30	19.02
1.503	0.893	0.1243	1.1.1.2.3	1.519	44.51	53.53	1.1.1.2.2	1.519	29.12	20.74

1. *d* spacings and intensities of X-ray powder pattern. The line at 7.68 Å is too intense and those at 2.65 and 1.92 Å too weak for accurate measurement.

2. Indexing of lines and calculated structure factors referred to the 3R (pyroaurite) unit cell with  $a = 3.1$ ,  $c = 23.04$  Å. The *F*<sub>obs</sub> values are those of column 1 scaled by the factor  $K = \sum F_{calc} / \sum F_{obs}$ .

3. As in column 2 referred to the 2H (sjögrenite) unit cell with  $a = 3.1$ ,  $c = 15.36$  Å.

\* Philips camera of 57.3 mm radius, Co- $K\alpha$  radiation.

It yields a strong reflection at about 7.7 Å, which can easily be distinguished from the strong, first order basal reflection of the serpentine minerals at 7.3 to 7.4 Å and, after deletion of the chrysotile reflections, the powder pattern (see Table I) agrees well with those of pyroaurite, of the nickeliferous mineral described by Lapham (1965), and of reevesite (White *et al.*, 1967). The mineral appears to be thermally unstable, as heating at 300 °C results in the elimination of the entire powder pattern.

In order to determine the polytype, the powder pattern was indexed using unit cells of 3R and 2H types (Table I). Indexing of the powder lines suggests that the mineral is a 3R polytype, a conclusion that is supported by the average values of the discrepancies between calculated and observed *d* spacings.

To confirm this designation and to test the hypothesis that the mineral has the same structure as pyroaurite with nickel (which is later shown to be an important constituent) replacing some magnesium, the intensities of the strong lines of the powder pattern were measured on two microphotometers and compared with calculated data.

Intensities were converted to structure factors,  $F_{\text{obs}}$ , using Lorentz and polarization factors for a randomly oriented powder. Structure factors  $F_{\text{calc}}$  were calculated for the reflections assuming that Ni replaces one-third of the Mg atoms. The observed structure factors were then scaled to those calculated using the scale factor  $K = \Sigma F_{\text{calc}} / \Sigma F_{\text{obs}}$ . The resulting values for the two polytypes are shown in Table I. Using indexed lines only, the  $R$  factors, where  $R = \frac{\sum \{|F_{\text{obs}}| - |F_{\text{calc}}|\}}{\sum |F_{\text{obs}}|}$ , for the 3R and 2H models are 0.168 and 0.70 respectively. The structure factor agreement is thus sufficiently good to confirm that the mineral is a 3R rather than a 2H polytype.

The *infrared spectrum* of the mineral is similar to those of related minerals such as sjögrenite and hydrocalcite (Mumpton *et al.*, 1965) and also resembles that of reevesite (De Waal and Viljoen, 1971). It is characterized by intense absorption near  $3440 \text{ cm}^{-1}$  indicating relatively strongly hydrogen-bonded OH. There are also moderately strong bands at  $1355 \text{ cm}^{-1}$  and  $1626 \text{ cm}^{-1}$ , which are associated with hydrated basic carbonate. Spectral changes brought about by heating the sample are similar to those described by Mumpton *et al.* (1965) for coalingite and may be interpreted in terms of loss of hydration water and structural modification of the basic carbonate at  $100^\circ\text{C}$ , followed by progressive loss of structural OH up to  $300^\circ\text{C}$  to give an anhydrous carbonate phase. Other features of the infrared spectrum were obscured by bands associated with admixed chrysotile.

*Electron diffraction.* Hand-picked fragments were dispersed ultrasonically in distilled water and a drop of the resulting suspension dried on a carbon support film on a transmission-electron-microscope grid. Electron microscopy revealed that the bulk of the sample consists of fibres giving a typical chrysotile electron-diffraction pattern. Although many large electron-dense particles were aggregates of fibres, some had a platy morphology (fig. 1a) and yielded a hexagonal electron diffraction pattern (fig. 1b) very similar to that given by brucite crystals with (0001) normal to the beam. The pattern can be interpreted, therefore, as a section of the reciprocal lattice normal to  $c$  consisting of  $hkio$  reflections only. Accurate measurement of the  $d$  spacings in patterns from two crystals gave  $d_{110} 1.555 \pm 0.0015 \text{ \AA}$  for one and  $1.545 \pm 0.004 \text{ \AA}$  for the other, corresponding to  $a 3.11 \pm 0.01 \text{ \AA}$  and  $3.09 \pm 0.01 \text{ \AA}$ , respectively. This overall variation in  $a$  is rather greater than would be expected from errors in measurement and may indicate some variation in chemical composition between crystals. Electron diffraction measurements are in good agreement with X-ray results except that the 10 $\bar{1}0$  reflection was absent on the X-ray pattern, an observation consistent with rhombohedral structure. Its appearance on the electron diffraction pattern can be accounted for by super-lattice effects arising from cation ordering—as proposed for sjögrenite and pyroaurite by Taylor (1969). These effects may also explain the presence of additional weak spots on some patterns (arrowed in fig. 1c), which together with the stronger ones lie on a hexagonal lattice of  $a$  parameter  $\sqrt{3} \times 3.1$ .

*Electron-probe microanalysis.* The Stereoscan stage was modified so that transmission-electron-microscope specimen grids could be examined in scanning transmission mode with simultaneous X-ray analysis. In practice only particles  $> 2 \mu\text{m}$  gave a reasonable X-ray count and analysis can only be approximate. The platy

particles that yield the hexagonal electron-diffraction patterns mentioned above contain magnesium, nickel, and iron, with a small amount of silicon due to some adhering chrysotile. Two platy particles gave counts indicating Mg:Ni:Fe ratios of 1.0:2.5:4.9 and 1.0:3.6:5.0. The fibrous chrysotile contains little or no nickel but there appears to be a little iron. As the amount of X-rays generated depends greatly on

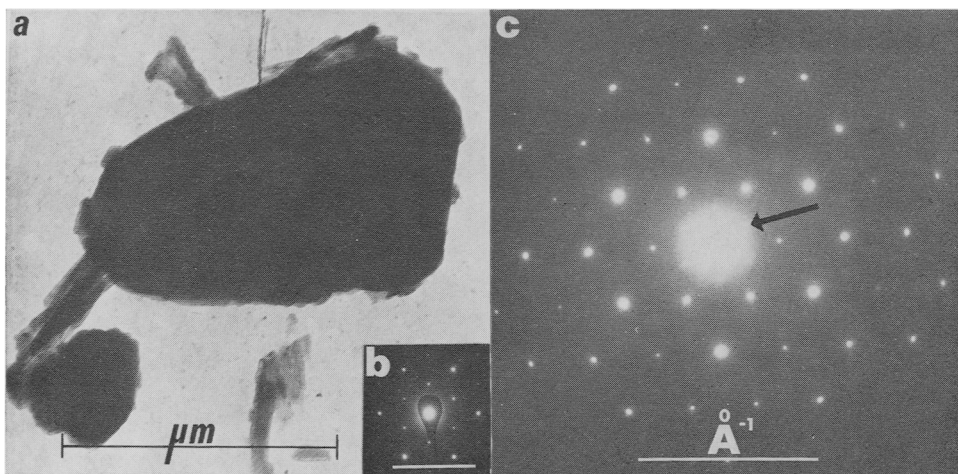


FIG. 1a. Electron micrograph of pyroaurite-like mineral showing platy morphology. b. Electron-diffraction pattern from particle in fig. 1a. c. Electron-diffraction pattern of a pyroaurite-like particle showing additional weak spots, one of which is arrowed.

TABLE II. *Metallic ions extracted at different pH values from serpentinite rock containing pyroaurite-like mineral (expressed as ppm in < 2 mm crushed rock).*

	Ni	Fe	Co	Cr	Mg
Total content	2400	46000	170	1960	220000
2.5% acetic acid (pH 2.5)	1950	2400	42	21	5500
1N ammonium acetate/acetic acid (pH 4.5)	1690	2300	22	5.5	3600
1N ammonium acetate (pH 7.0)	30	29	0.54	0.13	560

particle thickness, quantitative analysis is not possible but comparison of the count rates of magnesium, nickel, and iron with those for appropriate standards indicates that these elements are present in the platy mineral in the approximate atomic proportion 2:1:1.

*Acid extraction of serpentinite rock.* The serpentinite rock was crushed to fragments less than 2 mm in diameter and extracted with acetic acid (pH 2.5), ammonium acetate/acetic acid (pH 4.5), and ammonium acetate (pH 7.0). Over 80 % of the total nickel of the rock is mobilized by a single acetic acid treatment (Table II), and significant amounts of iron and cobalt are also released. Extraction at pH 4.5 removes 70 % of the total nickel but at pH 7.0 only a minor amount is extracted. X-ray diffraction

traces of < 0.5 mm fraction of the crushed serpentinite demonstrate that the nickel-bearing pyroaurite-like mineral is completely decomposed at pH 2.5 and 4.5 and it seems reasonable to conclude that most, if not all, of the nickel extracted in these relatively mild conditions is associated with this phase. It may be noted that although the ratio of nickel to iron is 1:20 in the rock the three different extractants always remove these metals in an approximate 1:1 ratio. This suggests that there is a similar nickel:iron ratio in the mineral decomposed—which is consistent with the results obtained by electron-probe microanalysis. It is clear that should this type of mineral occur in serpentinite-derived soils it would quickly break down under acid pedogenic conditions to release appreciable amounts of mobile nickel and iron.

*Conclusions.* The X-ray powder data and the infrared spectrum indicate that the mineral has a pyroaurite-type structure, although its composition differs from that of pyroaurite in that it contains nickel as well as magnesium and iron. In view of the fact that most minerals in the pyroaurite-sjögrenite group have a divalent to trivalent metal : cation ratio of 3:1, the most likely structural formula of the mineral is  $Mg_4^{2+}Ni_2^{2+}Fe_3^{2+}(OH)_{16}CO_3 \cdot 4H_2O$ . The mineral can therefore be best described as nickeloan pyroaurite.

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