Niccolite-magnetite mineralization from Upper Teesdale, North Pennines

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ABSTRACT. Niccolite and other nickel-bearing minerals have been found in magnetite-rich ore at Lady's Rake Mine [NY 8063 3414] in the North Pennines 5.5 km NW of Langdon Beck, Teesdale, Co. Durham. Associated ore minerals include galena, sphalerite, chalcopyrite, pyrite, and pyrrhotite. Similar magnetite-rich ores, in places bearing ugrandite garnets, have been located at two nearby localities, though without nickel minerals. Petrographic study indicates that this unusual assemblage developed in a skarn environment, probably related to the intrusion of the Whin Sill. Field evidence suggests an association with the Teesdale Fault system. Electron microprobe analyses show that Lady's Rake niccolite is near to end-member composition: analyses of other North Pennine niccolites show up to 25 at. % substitution of S and Sb for As.

KEYWORDS: niccolite, magnetite, ullmannite, gersdorffite, Teesdale, Pennines, England

NICCOLITE has only been recorded from two localities other than Lady's Rake in the North Pennine Orefield (fig. 1). It was found, accompanied by ullmannite, in the witherite vein at Settlingstones Mine [NY 842 683] near Hexham: about half a ton of niccolite was raised from this mine (Russell, 1927). Niccolite, accompanied by gersdorffite, millerite, and annabergite, has been described by Bridges (1982) from Hilton Mine [NY 763 226] near Appleby. Other records of nickel minerals from the area are those of ullmannite from New Brancepeth Colliery [NZ 223 420] (Spencer, 1910); millerite in a borehole at Greens Farm [NZ 228 602] (Anderson and Smythe, 1942), Boldon Colliery [NZ 36234 60484], Walker Colliery [NZ 295 640], Boltsburn Mine, Rookhope [NZ 937 427] and Cowgreen Mine, Teesdale [NY 810 305] (Dearman and Jones, 1967).

In 1981 D. B. Smith found millerite in an underground borehole at Blackhall Colliery [NZ 4979 4104]. Gersdorffite and ullmanite occur as microscopic inclusions in sulphide ores from several North Pennine localities (Ixer *et al.*, 1979; Vaughan and Ixer, 1980). Brief accounts of the geology and history of Lady's Rake Mine have been given by Dunham (1948) and Beadle (1977).

Geological setting. The Harwood Valley, in which Lady's Rake lies, is cut in Yoredale beds of the Alston Group (Viséan), into which the quartz



FIG. 1. Locality map showing nickel mineral occurrences mentioned in the text: 1. Settlingstones Mine; 2. Green's Farm Borehole; 3. Walker Colliery; 4. Boldon Colliery;
5. Boltsburn Mine; 6. New Brancepeth Colliery; 7. Blackhall Colliery; 8. Cowgreen Mine; 9. Hilton Mine.

dolerite of the Whin Sill is intruded. The sill, which crops out beneath boulder clay approximately 1 km SE of Lady's Rake Mine, extends beneath the mine workings. This point is discussed more fully below, together with evidence for related 'whin' dykes occupying the Teesdale Fault both here and at the head of the valley. Structurally the valley is dominated by, and its course possibly determined by, the NW-SE trending Teesdale Fault (fig. 2). This is one of the major faults of the Alston Block and may be traced for approximately 20 km from near Alston to Middleton-in-Teesdale: the fault is mineralized locally in Teesdale and also in the South Tyne Valley. South-west of the Teesdale Fault, and forming a branch from it, is the Teesdale-Winterhush Vein, which at Lady's Rake is probably a single vein formed by the coalescence of the separate Teesdale and Winterhush Veins of the Cowgreen area to the south (Dunham, 1948). This vein may continue a short way north-east of the Teesdale Fault.

The veins formerly worked at Lady's Rake Mine [NY 8063 3414] lie within the barium zone of North Pennine mineralization: minerals previously recorded from the mine include galena, sphalerite, baryte, ankerite, and siderite (Dunham, 1948). Part of the Lady's Rake dump contains magnetite-rich rock, some of which also has niccolite together with minor amounts of ullmannite, gersdorffite, and annabergite. Magnetite-rich ore, without nickel minerals, is present on the dumps from two other workings in the valley, at the trial shaft [NY 8028 3446] approximately 427 m NW of Lady's Rake shaft, and Cadger Well Level [NY 7978 3480], at the head of the valley. Typical specimens of the ores found at these localities are described in the following section.

Petrography of magnetite-niccolite ores. Magnetite-rich ore is common on part of the Lady's Rake dump. In hand specimens the magnetite commonly forms almost pure, fine-grained, dull grey masses up to about 10 cm across. Fine to medium-grained white calcite is a common associate and in some specimens magnetite veinlets cut areas of calcite. Some specimens show streaks and round pockets up to 1 cm across of greenishwhite phyllosilicates which include talc, chlorite, and smectite. Niccolite occurs sparingly in the magnetite-rich rock; it usually occurs as irregular spots and patches up to 1 cm across embedded in both magnetite and calcite. It is generally fresh and unaltered with a bright metallic lustre on newly broken surfaces: thin encrustations of pale green annabergite are present on the outer surface of



FIG. 2. Veins and mine workings in the Harwood Valley.

some fragments and in places along fractures in the niccolite. Ullmannite and gersdorffite are visible only under the microscope.

A polished thin section (E 57541)* of niccolitebearing ore was found to be composed largely of calcite and magnetite with lesser amounts of dispersed pyrite up to 0.5 mm in size. Niccolite occurs in discrete stringers and is usually fine grained $(100-200 \ \mu m)$. It is associated with pyrrhotite and much lesser amounts of ullmannite and a few isolated grains of gersdorffite. In some places pyrrhotite occurs as thin lamellae within ullmannite grains and less commonly pyrrhotite may comprise the greater portion of the grain where the intergrowth of the two minerals is less regular. The exact origin of this relationship is not clear but it appears that ullmannite has been replaced by pyrrhotite rather than the latter occurring as exsolution lamellae. Other magnetite-rich specimens show a few scattered grains of galena, sphalerite, chalcopyrite, pyrite, and pyrrhotite.

A poikiloblastic intergrowth of calcite and magnetite was noted in one section (E 57557). Several stages of magnetite-calcite development can be distinguished in this specimen. An early, comparatively fine-grained, calcite mosaic shows a poorly defined fenestrate fabric outlined by small $(4-10 \ \mu m)$ magnetite grains. This is, in part, overgrown by coarser calcite containing fewer, larger (40 μ m) commonly euhedral magnetite grains. Cutting these two phases is a vein or zone (7-10 mm wide) of recrystallization in which subhedral magnetite displays a wide range of grain sizes (up to 100 μ m) and is accompanied by pyrite (40-100 μ m) and segregations of yellowish phyllosilicates. Another specimen (E 57558) shows a calcite matrix retaining a ghost fabric of magnetite granules clearly outlining the shape of a calcareous alga; the rock is obviously a metamorphosed limestone. It is cut by veins of yellowish green chlorite and smectite with minor calcite and accessory pyrite. Strongly orientated strain extinction is characteristic of much of the calcite, which in some specimens is accompanied by minor dolomite, ankerite, and locally, siderite veinlets; quartz is a subordinate component in these and all other magnetite-rich rocks discussed in this paper.

Magnetite is abundant in specimens from the dump of the trial shaft [NY 8028 3446] NW of Lady's Rake Mine, though no Ni-bearing minerals have been identified. Specimens from there show magnetite forming anastomosing dendritic to reticulate aggregates permeating a groundmass of coarse calcite and subordinate segregations of

* Figures shown thus refer to sections in the BGS English sliced rock collection.

quartz and siderite (E 57559). Galena is abundant in many specimens from this dump and in one thin section (E 57561) anhedra of galena up to several millimetres across are set in a groundmass of calcite. This assemblage is intimately cross-cut by veins of calcite, quartz, and magnetite with minor amounts of galena, possibly redistributed from the preceding stage of crystallization.

The dumps from the Cadger Well Level [NY 7978 3480] contain small quantities of magnetitebearing rock similar to that at Lady's Rake with, in addition, garnets, though without nickel or other ore minerals. X-ray diffraction reveals that a yellowish garnet in section E 57552 is of the ugrandite type. It occurs typically as granular aggregates and subhedral crystals (up to 0.5 mm) in garnet-rich selvages which separate magnetite-rich and calcite-rich portions of the rock, though minor amounts of this garnet also occur with both the magnetite and calcite. Interstitial chlorite locally accompanies the calcite. Hydrogrossular was proved by X-ray diffraction to accompany the ugrandite in one section (E 57553). No garnet was found in any of the rocks analysed by electron microprobe. Fragments of quartz dolerite of typical Whin Sill type were also found on the same part of the dump. A thin section of this (E 57554) shows that many of the ferro-magnesian constituents exhibit strong chlorite-smectite alteration.

Mineral composition at Lady's Rake, Hilton, and Settlingstones. Niccolite from Lady's Rake, Hilton, and Settlingstones mines has been analysed by electron microprobe using an energy-dispersive X-ray analyser. Elements of atomic no. 11 (Na) and greater can be detected and the limit of detection is around 0.1 wt. % element. The electron beam was focused to approximately 5 μ m diameter.

The niccolite from Lady's Rake Mine (Table I) is close to end-member niccolite, with only traces of substitution of Fe for Ni and only a 2-3 at. % substitution of Sb and sporadically S for As. In contrast the niccolite from Settlingstones has around 25 at. % substitution for As with more S than Sb. Niccolite from Hilton Mine falls between the niccolites from the other two localities with around 10 at. % substitution and a slight preference for Sb over S.

Analyses of the minerals associated with niccolite at Lady's Rake are given in Table II. Ullmannite shows 10-20 at. % substitution of As for Sb and gersdorffite shows around 40 at. % substitution of Sb for As. Both pyrrhotite and pyrite contain small amounts of Ni and As. Magnetite is fairly pure with minor substitution by Mn. Analyses of galena, sphalerite, pyrrhotite, and chalcopyrite are all close to end-member compositions.

TABLE I SLECTRON NICROPROBE ANALYSES OF NEC MEMORY (or ")

	1	Z	3	4	5	6
۹i	43.83	0,75	44.82	0,76	45.30	1,53
Fe	0.31	0.05	-	-	-	~
As	53.48	1,17	47,93	1.43	42.34	2,32
Sb	2,25	1.04	6.07	1.67	9,46	3.30
s	0,20	0.11	0.89	0.52	4.10	0.59
					101 00	
Total	100.07		99.71		101,20	
	letected	atoms o	99.71 m basis	of 1 (· · · ·	
	letected	atoms o		of 1 ()	· · · ·	
- not d	No. of	atoms o	m basis	of 1 ()	As+Sb+S)	
- not d	No. of	atoms o	m basis 1.06	of 1 ()	As+Sb+S) 1.00	
- not d Ni Fe	No. of 1.01 0.01	atoms o	n basis 1.06	of 1 ()	As+Sb+S) 1.00	

1. Lady's Rake Mine niccolite (mean of 8).

Standard deviation.

Hilton Mine niccolite (mean of 5). з.

Standard deviation.

5. Settlingstones Mine niccolite (mean of 8).

6. Standard deviation.

Table III shows analyses of minerals associated with niccolite at Settlingstones. Here the ullmannite shows 10 at. % substitution of As for Sb, less than at Lady's Rake, and similarly gersdorffite, recorded for the first time at Settlingstones, shows around 25 at. % substitution of Sb for As, and S, again less than at Lady's Rake.

The extensive substitution of As for Sb found in the Lady's Rake gersdorffite gave compositions almost midway between NiAsS and NiSbS. This suggests that the solid solution between these compositions is more extensive than that reported by Bayliss (1969) from experiments carried out at 550 °C, and could indicate that the Lady's Rake minerals formed at higher temperatures. The authors have been unable to find any other experimental data for the phase equilibria of minerals with the complex anion substitutions described here, from which the temperature of formation might be estimated directly.

Discussion. Magnetite-bearing ore specimens, unlike any previously described from the North Pennine Orefield, have been found at three localities in the Harwood Valley. The common factor is that the workings at each locality cut the Teesdale Fault, or associated fractures, and it is likely that this unusual assemblage is associated with this fracture system.

At Lady's Rake Mine, the Jew Limestone Level is known to have cut the Teesdale Fault near its junction with the Teesdale-Winterhush Vein. Dunham (1948) noted that the mine plans record the fault taking the form of a 12 m wide 'whin dyke' though he could not confirm the presence of

	ELECTRON HICROPROBE ANALYSES OF HINEKALS ASSOCIATED WITH NICCOLITE AT LADY'S RAKE MINE (wt \gtrsim)								
	1	2	3	4	5	6	7	8	
Ni	28,20	28.19	29,97	30,56	1.54	1.17	-	-	
Fe	0.82	0.56	2.28	1.33	59,54	45.81	88,46	87,5	
Mn	-	-		-	-	-	-	3.70	
Co	-	-	1,08	0,42	-	-	-	-	
٨s	8,52	4.65			0.41	0.40	-	-	
Sb	48.76	52.75	22.86		-	-	-	-	
s	15,39	15.26	17.31	16.71	39,42	52,55	-	-	
TOTAL	101.69	101.41	102.33	101.48	100,91	99.93	88,46	91.2	
					s of 1 (As	,			
Ni	0.48	0.49	0.46	0.49	0.02	0.01			
Fe	0,01	0.01	0.04	0.02	0.86	0.50			
Mn	-	-	-	-	-	-			
Co	-		0.02	0.01	-	-			
Λs	0.11	0.06	0.34		-	-			
SÐ	0,40	0.45	0.17	0.24					
S	0.49	0.49	0.48	0.49	1,00	1,00			

1-2 ULLMANNITE 3-4 GERSDORFFI 5 PYRRHOTITE

PYRITE

7-8 MAGNETITE (expressed as wt% Fe0 and Mn0).

dolerite here and no dolerite has been found on the Lady's Rake dumps. It is possible, however, that the hard magnetite-calcite rock could have been mistaken by the miners for dolerite or 'whin'. The rock containing a calcareous alga replaced by calcite and magnetite could well be a fragment of metamorphosed Jew Limestone. The trial shaft [NY 8028 3446] explored a continuation of the Teesdale-Winterhush Vein. A branch of the Cadger Well Level [NY 7978 3480] at the head of the valley is reported to have been driven through the Teesdale Fault into dolerite (Dunham, 1948). Here magnetitebearing rock is found on the same part of the dump as dolerite blocks.

The mineralogy of the ore specimens with abundant magnetite, calcite, and, locally, ugrandite

TABLE III ELECTRON MICROPROBE ANALYSES OF

	1	2	3	4	5	6	7	8
Ni	28.55	28.08	34,13	32.43		-	-	-
Fe	-	-	-	-	-	47,44	46.13	29.75
Cu	-	-	-	-	-	0,52	-	34.00
Zn	-	-	-	-	68,51	0.78	1.07	-
Co	-	-	0.40	0.57	-	-	-	-
As	3.34	3.34	37.74	30.81	-	0.26	-	0.97
Sb	55,06	55.08	12,03	19.00	-	-	-	-
s	15.06	14.83	17,20	15.78	32,96	53.62	53.51	35.05
TOTAL	102.01	101,33	101,50	98.59	101.47	102.62	100.71	99.77
			No, atoms	on basi	s of 1 (A	s+Sb+S)		
Ni	0.50	0.50	0,51	0.52	-	-	-	-
Fe	-	-	-	-	-	0.51	0,49	0.48
Cu	-	-	-	-	-	-	-	0.49
Zn	-	-	-	-	1.02	0.01	0.01	-
Co	-	-	0.01	0.01	-	-	-	-
As	0.05	0.05	0.44	0.39	-	-	-	0.01
Sb	0.47	0.47	0.09	0.15	-	-	-	-
s	0.48	0.48	0.47	0,46	1.00	1.00	1.00	0.99

1-2 ULLMANNITE 3-4 GERSDORFFITE

SPHALERITE

6-7 PYRITE 8 CHALCOPYRITE

garnet, with in one case a remnant calcareous alga replaced by magnetite, suggests a skarn environment. Metamorphism of Viséan limestones by the Whin Sill elsewhere in Teesdale, for example at Cowgreen, has produced garnet-bearing calcsilicate rocks (Dunham, 1948). We suggest that the Whin Sill provided the heat source for the alteration seen in the magnetite-bearing ores of the Harwood Valley.

The top of the Whin Sill lies immediately beneath the Peghorn Limestone approximately 1 km SE of Lady's Rake. If this horizon is maintained beneath Lady's Rake, the top of the sill would be expected to lie approximately 50 m beneath the deepest levels of the mine. However, evidence from adjacent areas of the North Pennines suggests that the top of the sill rises towards the west. At Tynehead [NY 760 371] 5.5 km NW of Lady's Rake it lies immediately beneath the Tynebottom Limestone. It is possible therefore that the lowest workings at Lady's Rake could have reached within a few metres of the top of the sill. In addition the presence of 'whin' dykes within the Teesdale Fault, and almost certainly belonging to the Whin Sill suite, has already been mentioned at Lady's Rake and Cadger Well Level. It is possible that dolerite may have been intruded into the Teesdale Fault where reaction with limestone wall-rocks produced the magnetite-rich skarn assemblage.

The genetic association of nickel arsenides with the Nippissing diabase, a basic sill in the Cobalt-Gowganda region of Ontario has been described by Jambor (1971) and Petruk (1971). The small concentrations of nickel minerals in the Lady's Rake magnetite-rich ores could have been derived from the underlying Whin Sill. Elsewhere in the North Pennine Orefield, small concentrations of Ni minerals at Settlingstones and Hilton Mines occur in veins in which the Whin Sill formed the wall-rock or was in very close proximity to the deposit. (Very small amounts of millerite noted above from a few localities in the Durham Coalfield are probably not related to the North Pennine mineralization.) Ni contents in the Nippissing diabase vary mainly between 75 and 100 ppm (Jambor, 1971) whereas in the Whin Sill the values are mainly between 60 and 70 ppm (Dunham and Kaye, 1965). The very limited evidence available from the Ni-bearing minerals at Lady's Rake suggests a temperature of formation of 550 °C or higher. This is considerably higher than the highest temperatures proposed for the main North Pennine mineralization (e.g. Smith and Phillips, 1975, Vaughan and Ixer, 1980). The Lady's Rake magnetite-niccolite ores may therefore be the product of skarn alteration brought about by the emplacement of the Whin Sill, accompanied, or followed by, the introduction of Ni-bearing fluids emanating from the sill. Galena and sphalerite, sulphides typical of the main North Pennine mineralization, are found locally in close association with magnetite, notably on the dumps from the trial shaft. It is possible that at least some of the North Pennine mineralizing fluids were circulating in the Teesdale Fault system very shortly after the emplacement of the Whin Sill and perhaps while the latter was still hot (Dunham, pers. comm.).

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