

Columbite from the Carrock Fell tungsten deposit

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ABSTRACT. Minute crystals of columbite occur in tungstate ore in the quartz veins at Carrock Fell Mine. Accompanying wolframite crystals show pronounced niobium enrichment adjacent to growth faces. The columbite grains, however, occur as inclusions in minerals formed during metasomatic replacement of the wolframite. They are chemically variable, containing 7-18% WO_3 by weight, up to 1.9% Sc_2O_3 , and up to 4.7% TiO_2 . Tin, a common minor element in columbite, was not detected. The columbite grains are spatially associated with carbonate minerals involved in wolframite replacement, and it is suggested that their formation occurred principally when carbonate precipitation caused a reduction in the stability of dissolved niobium complexes.

THE Carrock Fell tungsten deposit, situated in the northern part of the English Lake District (fig. 1), has been mined sporadically since 1870. Wolframite and scheelite occur in north-south trending, sub-vertical quartz veins which traverse the Grainsgill granite, a cupola developed on the northern flank of the Skiddaw granite (Hitchen, 1934). This cupola intrudes Lower Ordovician slates of the Skiddaw Group immediately south of the Carrock Fell gabbro, the quartz veins extending into these country rocks as shown in fig. 1. The Grainsgill granite has undergone greisen-type alteration which is intense close to the veins (Ewart,

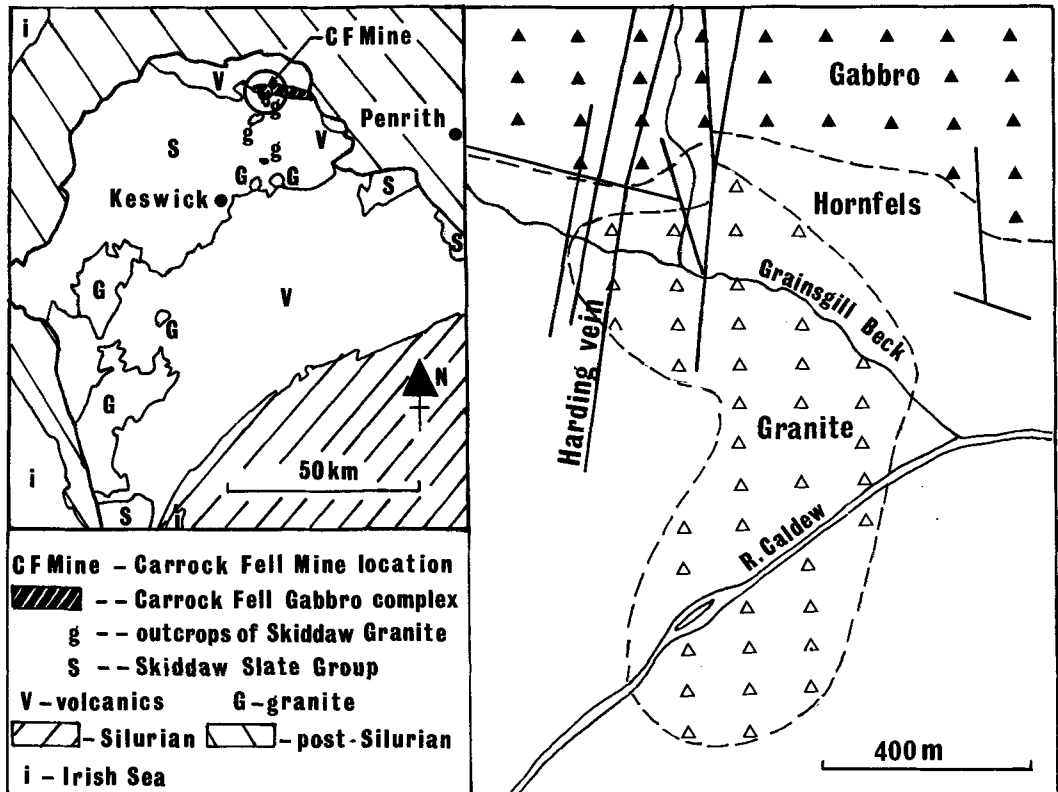


FIG. 1. (a) Location of the Carrock Fell mine. (b) Simplified geology of the mine area showing the Harding and other quartz veins.

1962). Comparable alteration is also developed in the hornfelsed slates and gabbro adjacent to the veins. Shepherd *et al.* (1976) gave K-Ar ages of 392 ± 4 Ma for unaltered granite, and 387 ± 4 Ma for hydrothermal muscovite.

In addition to the tungstate ore the quartz veins contain apatite, fluorite, and a variety of sulphide and other minerals (Hitchen, 1934). Ferroan dolomite, ankerite, and calcite are common in the quartz veins and disseminated in the wallrocks. They also form carbonate veins including a prominent Pb- and Zn-bearing cross-vein which displaces the quartz veins at one point.

The paragenesis of the veins appears to have been a progression with decreasing temperature from separate early quartz and orthoclase veinlets through a quartz plus apatite and wolframite stage and a barren quartz stage, to scheelite followed by sulphides and other minerals. The carbonate cross-veins may be considerably younger than the main mineralization, possibly Permian or later (Ineson and Mitchell, 1974). Fluid-inclusion data (Shepherd *et al.*, 1976; T. J. Shepherd pers. comm.) suggest that the vein quartz formed at $275\text{--}95^\circ\text{C}$, whilst apatite associated with wolframite formed at slightly higher temperatures (probably $\geq 300^\circ\text{C}$),

but fluorite in vugs within quartz crystallized at considerably lower temperatures ($100\text{--}120^\circ\text{C}$).

Wolframite zonation. Wolframite occurs as elongate bladed crystals often several centimetres long and typically in clusters developed on sites at the edges of the veins. Its euhedral habit suggests formation free of growth interference from the enclosing coarse quartz crystals which are believed to have formed slightly later. Microprobe analysis of wolframite grains (Table I) shows that Nb enrichment occurs in zones close to primary crystal faces suggesting original growth zoning.

The quartz gangue contains vugs, many of which occur near the margins of the veins. Although their formation seems to have postdated the wolframite, and thus not to have controlled the latter's development, their distribution often appears to be related to the wolframite clusters, and they have clearly exerted a major control over the distribution of the later minerals. Wolframite blades adjacent to vugs tend to be veined and replaced by scheelite, arsenopyrite, pyrite, carbonate minerals and, more unusually, by quartz. However, no concentration of Nb in wolframite immediately adjacent to phases replacing it was observed, ruling out any secondary origin for the Nb distribution in wolframite.

TABLE I. *Electron-probe analyses of coexisting wolframite and scheelite*

Wt%	1A	1B	2	3A	3B	4	5	6
CaO	n.d.	n.d.	18.87	n.d.	n.d.	18.56	0.01	18.89
MnO	8.15	7.89	0.03	8.03	7.78	0.05	9.31	0.02
FeO*	13.96	14.37	0.04	14.12	14.05	n.d.	12.76	0.02
Sc ₂ O ₃	n.d.	n.d.	n.d.	0.03	0.02	n.d.	0.016	0.003
TiO ₂	0.08	0.06	0.03	0.03	0.04	0.04	0.053	0.031
Nb ₂ O ₅	0.36	0.10	n.d.	0.98	0.67	n.d.	0.280	n.d.
WO ₃	75.87	76.22	80.15	77.58	77.24	80.51	76.73	80.98
Total	98.48	98.66	99.09	100.72	99.85	99.13	99.06	99.94
Atomic formulae based on 4 oxygens								
Ca	0.000	0.000	0.976	0.000	0.000	0.964	0.000	0.972
Mn	0.354	0.343	0.001	0.340	0.333	0.002	0.402	0.001
Fe	0.598	0.616	0.002	0.590	0.593	0.000	0.543	0.001
Sc	0.000	0.000	0.000	0.002	0.001	0.000	0.001	0.000
Ti	0.003	0.003	0.002	0.001	0.002	0.002	0.002	0.001
Nb	0.008	0.002	0.000	0.022	0.015	0.000	0.006	0.000
W	1.008	1.012	1.006	1.005	1.011	1.011	1.011	1.008
A	0.952	0.959	0.982	0.932	0.927	0.966	0.946	0.974
B	1.019	1.017	1.006	1.027	1.028	1.031	1.019	1.009
H/F	0.59	0.56		0.58	0.56		0.74	

Notes: 1—Wolframite; A = margin, B = interior. 2—Scheelite replacing wolframite 1. 3—Wolframite; A = margin, B = interior. 4—Scheelite replacing wolframite 3. 5—Average wolframite. 6—Average scheelite. H/F = Mn/Fe or huebnerite/ferberite ratio in wolframite. * Total Fe as FeO. n.d. = below detection level (0.01–0.02% wt; Ta and Mo were below detection in both minerals).

Total variation in the Mn/Fe (the huebnerite/ferberite or H/F) ratio of wolframite crystals analysed to date from the Harding vein is from 0.5 to 1.22. Nb-enrichment is most pronounced in relatively ferberitic crystals. Some comparative analyses from individual grains suggest that increasing Nb corresponds with slight increases in H/F (see Table I), though in other grains examined H/F showed no significant variation.

Columbite. Use of the X-ray scanning facility on the microprobe (Cambridge Instruments Microscan 5) revealed a number of minute grains containing major Nb. Quantitative chemical analyses (Table II) and an X-ray diffraction identification of separated grains showed them to be columbite containing varying amounts of tungsten. The distribution of this phase is illustrated by figs. 2 and 3 which are mineralogical and textural maps compiled from photomicrographs and Nb-L α X-ray scans.

Fig. 2 shows a large wolframite crystal displaying a planar crystal face towards enclosing quartz, and which is extensively replaced by scheelite and locally by Mn-rich ankerite. Late quartz also invades or replaces wolframite in an irregular vein-like fashion. An arsenopyrite crystal exhibits planar crystal faces against quartz, and an irregular

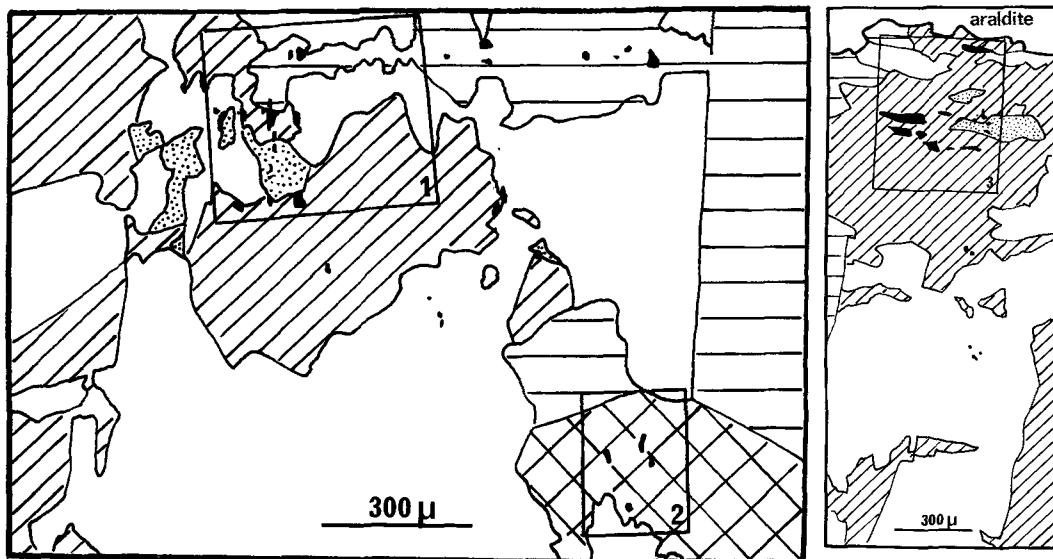
interface where it has apparently replaced wolframite. In the area figured, columbite occurs as minute grains included in minerals replacing wolframite. Many grains also occur at mineral boundaries and the small grains apparently included in wolframite are in fact related to a thin fracture. Nowhere has a columbite grain been seen totally isolated in wolframite. The densest concentration of columbite grains in the area of fig. 2 is in the ankeritic area shown in more detail in fig. 4a. Here columbite crystals form a linear swarm that appears to be a continuation of the line of columbite grains developed axially along the irregular quartz vein. This feature is suggestive of columbite formation controlled by the movement of fluid along a linear vein or channel which has subsequently annealed. Inclusions of columbite are also present in the arsenopyrite (figs. 2 and 4b), one displaying a good prismatic form while the others are less regular. This texture suggests columbite formed before arsenopyrite. Fig. 3 reveals a similar pattern with conspicuously larger bladed columbite grains included in scheelite but spatially associated with ankerite patches, which in turn host a number of smaller columbite grains. The large grains (fig. 4c) tend to lie parallel each other, which may indicate control by scheelite cleavage planes or by fractures

TABLE II. *Electron-probe analyses of columbite*

Wt%	1	2	3	4	5	6	7	8	A
Nb ₂ O ₅	68.10	65.86	64.33	63.05	61.41	57.82	55.81	54.25	55.91
Ta ₂ O ₅	1.87	3.08	3.54	1.95	1.72	1.87	3.17	3.47	17.01
WO ₃	7.63	7.40	8.76	9.56	11.49	14.20	14.11	18.49	3.65
TiO ₂	3.49	5.28	4.68	3.53	3.04	3.45	5.24	3.17	4.99
FeO	5.80	6.46	6.77	6.21	5.86	7.90	6.93	4.67	14.98
MnO	10.31	11.00	10.49	13.49	13.02	12.70	10.13	11.59	3.60
Sc ₂ O ₂	1.23	1.72	1.58	0.88	1.16	1.43	1.82	0.85	0.80
Total	100.43	100.80	100.15	98.67	97.70	99.37	97.21	96.49	101.05*
Atomic formulae based on 6 oxygens									
Nb	1.738	1.666	1.653	1.659	1.641	1.536	1.501	1.507	1.490
Ta	0.029	0.047	0.055	0.031	0.028	0.030	0.051	0.058	0.273
W	0.112	0.107	0.129	0.144	0.176	0.216	0.218	0.294	0.056
Ti	0.148	0.222	0.200	0.154	0.135	0.152	0.234	0.146	0.221
Fe	0.274	0.302	0.322	0.302	0.290	0.388	0.345	0.240	0.738
Mn	0.588	0.522	0.505	0.665	0.652	0.632	0.514	0.603	0.180
Sc	0.060	0.084	0.078	0.045	0.060	0.073	0.094	0.046	0.041
A	0.922	0.908	0.905	1.012	1.002	1.093	0.953	0.889	0.962
B	2.027	2.042	2.037	1.988	1.980	1.934	2.004	2.005	2.040
A + B	2.949	2.950	2.942	3.000	2.982	3.027	2.957	2.894	3.002

* Includes 0.20% SnO₂.

Note: Total Fe expressed as FeO. Analyses 1-8 from Carrock (Harding vein). Analysis A from Hodgkinson and Clark (1977).



FIGS. 2. and 3. FIG. 2 (*left*). Mineralogical map showing distribution of columbite (black) in relation to wolframite (blank), scheelite (diagonal lines), quartz (horizontal lines), ankerite (dots), and arsenopyrite (crosshatch). Boxed areas 1 and 2 refer to fig. 4*a* and *b* respectively. FIG. 3 (*right*). Mineralogical map showing large-bladed columbites. Ornamentation as for fig. 2. Boxed area 3 refers to fig. 4*c*.

along which Nb-rich and possibly CO₂-rich fluids migrated. The small grains indicated in fig. 3 as occurring within wolframite are developed in thin veins containing secondary minerals. In general, examination of a number of specimens has revealed a strong spatial association of carbonate and columbite.

From fig. 4 it is evident that most of the columbite grains are generally less than 30 μm in diameter and many have submicron dimensions. The grains in fig. 4*c* which reach 180 μm in length are the largest observed and are much rarer. The form of columbite varies from irregular blebby to angular, with euhedral and prismatic forms occasionally evident. Blade-like cross-sections are also characteristic. In reflected light the columbite is grey-white and shows faint anisotropy. Its colour and reflectivity are very close to that of wolframite which makes it difficult to distinguish optically. However, its form and association with carbonate are distinctive.

The chemical analyses reported here were obtained by wavelength-dispersive electron-microprobe analysis following the procedure described by Bowles (1975) and using pure metal standards. Final oxide percentages were obtained using the ZAF correction programme of Mason *et al.* (1969). Detection levels for the minor elements are in the range 0.01–0.02%.

Table II lists eight analyses in order of Nb-

content. Atomic formulae are based on AB₂O₆ where A = Fe + Mn + Sc and B = W + Nb + Ta + Ti. Ixiolite, the disordered form of columbite-tantalite in which A and B cations are randomly distributed (Nickel *et al.*, 1963), is not ruled out by these analyses. The degree of ordering has no effect on the gross chemistry since the proportions of the cations are governed by valency considerations, as apparent from the fact that ixiolite is readily transformed to columbite upon heating (Nickel *et al.*, 1963). Unfortunately, attempts to assess the degree of disorder from the X-ray diffraction pattern gave ambiguous results due to the sparsity and small grain-size of the material.

Apart from the essential oxide constituents of columbite-tantalite, WO₄, Sc₂O₃, and TiO₂ are present in significant amounts and on an atomic basis both W and Ti occur in excess of Ta. Recent analyses have also reported these elements in varying abundances. An analysis of columbite from Cornwall (Hodkinson and Clark, 1977), included in Table II for comparison, contains similar levels of Ti and Sc to the Carrock Fell examples, but has more Ta and much less W. In addition, Hodkinson and Clark (1977) report minor SnO₂ as do other authors (Grice *et al.*, 1972; Haapala *et al.*, 1967; Khalili, 1977), whereas at Carrock Sn is below the detection level. Tin is also frequently quoted in amounts up to several percent in ixiolite (Nickel *et al.*, 1963; von Knorring *et al.*, 1969; Grice *et al.*,

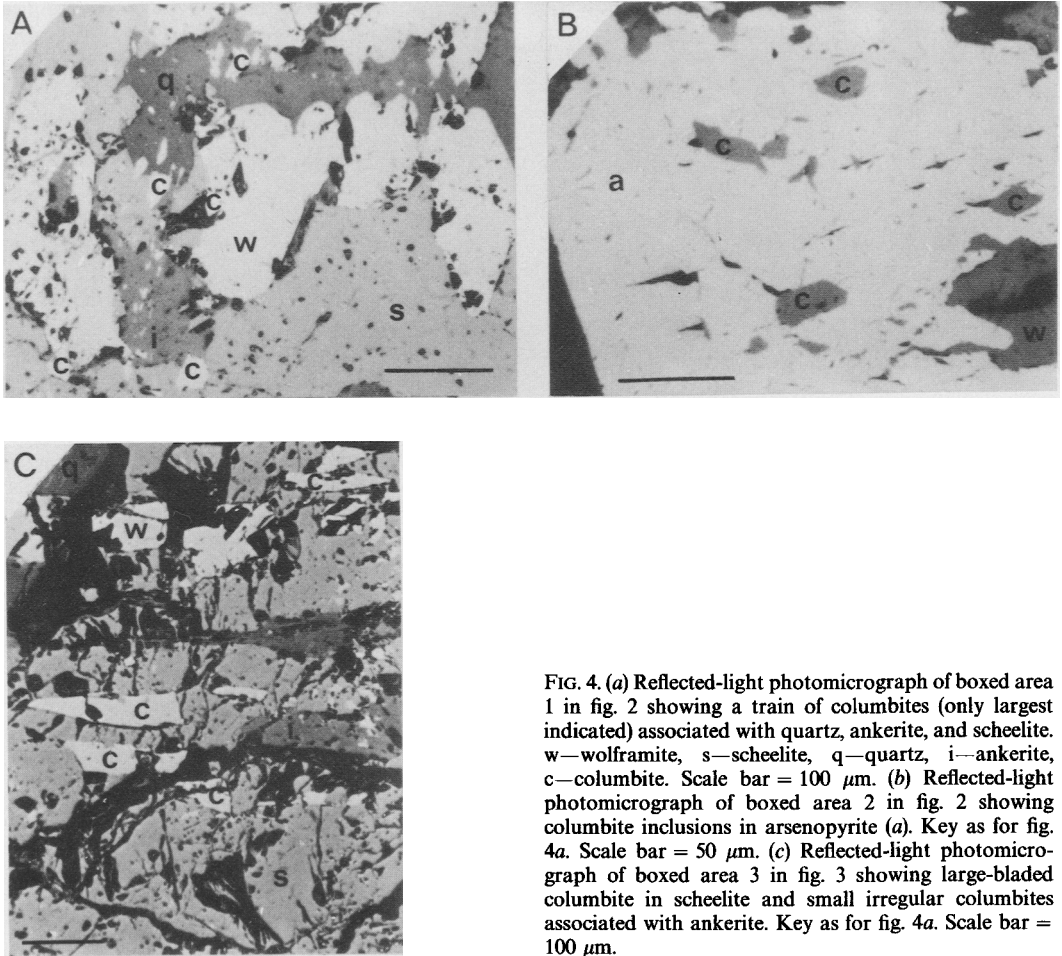
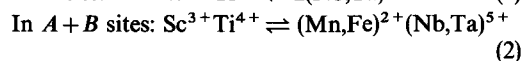
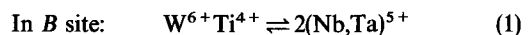


FIG. 4. (a) Reflected-light photomicrograph of boxed area 1 in fig. 2 showing a train of columbites (only largest indicated) associated with quartz, ankerite, and scheelite. w—wolframite, s—scheelite, q—quartz, i—ankerite, c—columbite. Scale bar = 100 μm . (b) Reflected-light photomicrograph of boxed area 2 in fig. 2 showing columbite inclusions in arsenopyrite (a). Key as for fig. 4a. Scale bar = 50 μm . (c) Reflected-light photomicrograph of boxed area 3 in fig. 3 showing large-bladed columbite in scheelite and small irregular columbites associated with ankerite. Key as for fig. 4a. Scale bar = 100 μm .

1972). The levels of WO_3 , up to 18% reported here, are the highest recorded to the authors' knowledge. Björlykke (1935) quotes a value of 13% WO_3 in a semi-quantitative X-ray analysis of pegmatitic columbite from southern Norway, and von Knorring (pers. comm., 1980) has analysed a columbite-tantalite from Mozambique with 7% WO_3 . Such tungsten levels are, however, in accord with experimental evidence on the solubility of Fe-Mn-tungstate in columbite (Schröcke, 1961). Scandium appears to be a common minor element in columbite (Haapala *et al.*, 1967; Hodgkinson and Clark, 1977), but it is often not included in analyses. Von Knorring *et al.* (1969) record up to 7.5% Sc_2O_3 in ixiolite, further confirming that this element is easily accommodated by the columbite or ixiolite lattice.

Substitution of W, Ti, and Sc into columbite can

be related to the following coupled substitution reactions:



If Sc and Ti are first accounted for by reaction (2) it is found that in all but one analysis in Table II reaction (1) then leaves excess W. Tungsten might be incorporated to some extent as a wolframite-type molecule, but this would lead to an apparent cation excess in position A—the opposite of that observed. Alternatively a reaction of the sort:



might be operative leading to vacancies in A. Graham and Thornber (1974) note that cation deficiencies are not uncommon in the $\alpha\text{-PbO}_2$ structural analogues of which columbite is one. In

particular, they show that incorporation of ferric iron as $\text{Fe}_2^{3+}\text{Nb}_6\text{O}_{18}$ also leads to A-site cation deficiencies. The electron microprobe cannot distinguish the Fe species present but analyses by von Knorring *et al.* (1969), giving up to 8% Fe_2O_3 in ixiolite, indicate substantial ferric iron is possible.

Data in Table I indicate that the replacement of wolframite by scheelite will have released small quantities of Sc and Ti as well as Nb. The average proportions $\text{Nb}_2\text{O}_5:\text{TiO}_2:\text{Sc}_2\text{O}_3$ for columbite calculated from Table II are 91.6:6.0:2.1, which are close to the proportions 86.2:9.2:4.6, calculated as the difference in these oxides between wolframite and scheelite. This suggests that most if not all the Ti and Sc in columbite were probably originally contained in the wolframite. Tantalum may also follow this pattern but in both wolframite and scheelite it is less than the detection level (*c.* 0.02%). However, if Ta_2O_5 in wolframite was 0.007% greater than in scheelite, then the average abundance of this oxide could be accounted for in the same way as Nb, Sc, and Ti.

The other components of columbite are present to excess, tungsten released from wolframite mainly entering scheelite, whilst Fe and Mn are incorporated in later sulphides, hydroxides, and carbonates. The preferential tendency for Fe to form sulphides as compared to manganese is reflected in the higher Mn/Fe ratio of columbite compared to wolframite.

Discussion. It is evident that columbite-tantalite chemistry is strongly governed by the elements available and their relative abundances. The columbite structure and those of associated MO_2 compounds have the ability, as Graham and Thornber (1974) note, of incorporating a wide range of metallic cations. Thus the high WO_3 but negligible SnO_2 contents of the Carrock columbites is a direct reflection of their formation in a tungstate environment exhibiting no evidence of tin mineralization.

The persistence of Nb and other metals released during wolframite breakdown indicates that they were able to form stable soluble ionic complexes in the hydrothermal fluid. The association of columbite with carbonate minerals suggests that metal-carbonate complexes might have been important. Shepherd *et al.* (1976) have reported, in this context, significant and variable CO_2 contents in inclusions within quartz at Carrock. In addition, Higgins (1980) has stressed the importance of CO_2 -rich fluids in the movement of tungsten prior to quartz-wolframite deposition in Newfoundland.

Relatively little is known about Nb transport in hydrothermal fluids, but Aleksandrov (1967) has demonstrated that up to 6000 ppm Nb can be dissolved in carbonate-rich H_2O in the tempera-

ture range 100–200 °C. Below 100 °C Nb solubility as a carbonate-complexed metal drops sharply and above 250–300 °C Nb solubility also tends to decline. Aleksandrov (*op. cit.*) also suggests that increased pressure enhances Nb solubility. Thus it can be envisaged that as scheelite replaced wolframite at temperatures less than about 250 °C, niobium was dissolved in CO_2 -bearing hydrothermal fluids. Columbite precipitation will occur when the solubility of Nb is exceeded and this could happen in two ways. Firstly, the amount of Nb released from wolframite (up to *c.* 10 000 ppm) might locally exceed that which can be dissolved as a complex causing the excess to immediately precipitate. This mechanism could account for the less common columbites sited at scheelite-wolframite boundaries or included within scheelite or sulphide, but which are not obviously associated with carbonate. Secondly, and more importantly, columbite precipitation will occur as *P-T* and other physical changes cause carbonate minerals to crystallize, thus removing complexing agents from solution. This mechanism is suggested by Aleksandrov (1967) as the most important in explaining the association of Nb-mineralization with carbonatites, and it clearly explains the close spatial association of carbonate and columbite in late-stage veinlike replacements at Carrock Fell mine.

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