

However, evidence (e.g. Thompson *et al.*, 1984; Wolff, 1984) is gradually accumulating that such ratios may alter systematically during post-magmatic processes, generally as a result of crystal-liquid equilibria involving minor or accessory phases with non-chondritic element ratios. Clearly, crystallization of zirconolite could rapidly and progressively change the existing ratios of these element pairs in a melt with which it is in equilibrium. At Glen Dessarry, extreme and variable Zr/Hf ratios have been recorded (Fowler, 1985), particularly in pegmatites formed by filter pressing, which represent an evolved melt composition (Zr/Hf = 69.4 to less than 11.8). Since the Zr/Hf ratio in zirconolite from Glen Dessarry is relatively high (88.8), the low values for the whole-rock might record the previous extraction of zirconolite, while the high values might represent its accumulation. Thus zirconolite is another example to add to a rapidly increasing list of minor phases whose potential effects during crystal fractionation should not be overlooked in petrogenetic studies, especially of 'evolved' magma types.

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Department of Mineralogy, British Museum (Natural History), London SW7 5BD

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V-bearing derbylite from the Buca della Vena mine, Apuan Alps, Italy

DERBYLITE is an iron, titanium, and antimony oxide, first described by Hussak and Prior (1897). Derbylite has a closed-packed (...*chh*...) oxide structure (Moore and Araki, 1976) and has ideal crystal-chemical formula $\text{Fe}_4^{3+}\text{Ti}_3^{4+}\text{Sb}^{3+}\text{O}_{13}\text{OH}$.

Based on Moore and Araki's results, Mellini *et al.* (1983) interpreted the actual chemical data for derbylite by the formula $\text{Fe}_x^{2+}\text{Fe}_{4-2x}^{3+}\text{Ti}_3^{4+}\text{Sb}^{3+}\text{O}_{13}\text{OH}$. Several chemical variants might result from substitution of suitable octahedral cations for

M. B. FOWLER

C. T. WILLIAMS

Fe and Ti, and of pseudo-tetrahedral cations for Sb. A possible case is realized in tomichite, $\text{Fe}^{3+}\text{V}_3^{3+}\text{Ti}_3^{4+}\text{As}^{3+}\text{O}_{13}\text{OH}$, which is the vanadium and arsenic analogue of derbylite (Nickel and Grey, 1979). In this communication new chemical data for vanadium-bearing derbylite are reported and the possible existence of a derbylite-tomachite solid solution is discussed.

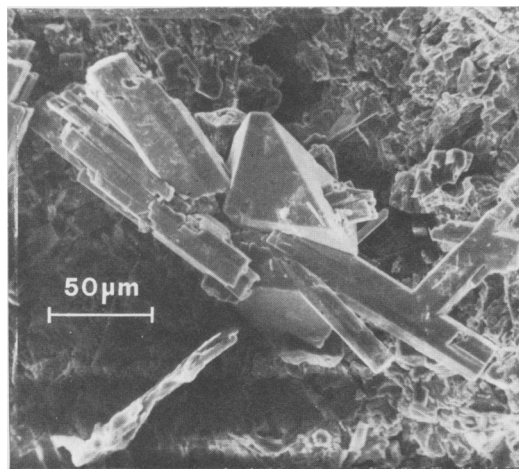


FIG. 1. SEM micrograph of V-rich derbylite (prismatic) and anatase (bipyramidal).

The new specimens of V-bearing derbylite occur in the Buca della Vena mine, Apuan Alps, Italy. This is the same ore deposit from which V-free derbylite has already been reported (Mellini *et al.*, 1983). V-free derbylite and V-bearing derbylite are very easily distinguished by their different habits. Whereas V-free derbylite usually forms squat prismatic crystals and twins consisting of two or three individuals, the V-bearing crystals show a more elongated prismatic habit (fig. 1). They are rather small in size, usually less than a millimetre long and always occur together with black bipyramidal anatase, and commonly with yellow prismatic

vanadinite and green platy stibivanite. A distinctive feature of V-bearing derbylite is the association with black anatase, metallic in lustre and showing an unusual {113} bipyramidal form, together with dolomite crystals which are black owing to V-bearing derbylite and anatase inclusions. The X-ray powder diffraction patterns of V-free and V-bearing derbylite are virtually identical, owing to the close similarity of the unit-cell parameters. Table I gives the refined cell parameters, obtained by least squares fitting of the powder pattern; the accuracy is lower in the case of V-bearing derbylite, as these patterns were obtained using a Gandolfi camera.

Qualitative analysis by energy dispersive X-ray spectrometry in a scanning electron microscope shows the presence of Ti, Fe, Sb, V, As, and minor, sporadic Cr; no other element with $Z > 11$ was detected. A quantitative wavelength-dispersive analysis was carried out using an ARL-SEMQ fully automated electron-microprobe analyser, with 15 kV accelerating voltage, and a beam diameter of approximately 5 μm . Natural ilmenite, synthetic As_2S_3 , metallic V, Sb, and Cr were used as standards. The raw data were corrected by the MAGIC IV program (Table II); possible interference effects, as determined by complete analysis of the standard materials, were also taken into account. No significant chemical variations were found within the individual grains. The formulae for V-bearing derbylite were calculated assuming eight cations per unit-formula, with the Fe^{2+} and Fe^{3+} contents based on 13 (O) + (OH) (i.e. sum of cation charges = 27). The $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio calculated for V-bearing derbylite fits the value we previously determined by analytical methods for V-free derbylite (Mellini *et al.*, 1983) and supports the validity of our computational approach since similar $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratios would be expected for minerals formed under similar conditions. The four derbylite specimens have fairly similar Ti contents. The V content is variable, from 0 to 7.01 wt. %, and is negatively correlated with the Fe content. As may substitute for Sb.

The crystal-chemical data for derbylite and tomichite can be plotted within a tetrahedron,

Table I. Unit cell parameters for derbylite and tomichite

		a	b	c	β
V-bearing derbylite	413	7.20(1)	14.32(1)	4.973(3)	104.3(1)
V-bearing derbylite	560	7.14(1)	14.35(3)	4.97(1)	105.1(1)
V-free derbylite		7.156(2)	14.354(4)	4.980(1)	104.69(2)
Tomichite		7.119(3)	14.176(5)	4.992(2)	105.05(1)

Table II. Chemical analyses for derbylite and tomichite

	V-free derbylite (Mellini et al. 1983)	V-bearing derbylite 560	V-bearing derbylite 413	V-bearing derbylite 420	Tomichite (Nickel and Grey, 1979)
TiO ₂	40.20	38.54	38.73	37.87	37.42
FeO	4.44	4.48	4.81	3.11	-
Fe ₂ O ₃	31.83	31.63	27.50	28.09	11.39
V ₂ O ₃	-	2.00	4.03	7.01	34.92
Cr ₂ O ₃	-	-	-	0.46	-
Sb ₂ O ₃	19.80	18.11	18.96	18.40	1.22
As ₂ O ₃	-	1.55	1.05	0.24	11.31
H ₂ O	1.24	1.25	1.23	1.24	1.36
	97.51	97.56	96.31	97.42	97.83
Ti	3.66	3.48	3.55	3.43	3.10
Fe ²⁺	0.45	0.45	0.49	0.31	-
Fe ³⁺	2.90	2.86	2.52	2.52	0.94
V ³⁺	-	0.19	0.39	0.68	3.08
Cr ³⁺	-	-	-	0.04	-
Sb ³⁺	0.99	0.90	0.95	0.96	0.06
As ³⁺	-	0.11	0.08	0.02	0.76
H	1.00	1.00	1.00	1.00	1.00

defined by the Ti, Fe, V, and Sb contents. The distinction between As and Sb can be neglected for the sake of simplicity since $As = 1 - Sb$ independently of the other cations. This is equivalent to projecting the whole tetrahedral space on to the Ti-V-Fe face (fig. 2). The compositional space for the two minerals can be further restricted by imposing suitable boundary conditions such as charge balance. In particular, when derbylite and tomichite are represented by the formula $Fe_x^{2+}M_{4-2x}^{3+}Ti_{3+x}^{4+}\psi O_{13}OH$, with M representing

suitable octahedral cations such as Fe or V, and ψ representing As or Sb, charge balance requires $0 \leq x \leq 2$. As a consequence, the compositional space is defined by the three end-member compositions Fe_4Ti_3 , V_4Ti_3 , and Fe_2Ti_5 . Any x displacement from Fe_4Ti_3 or V_4Ti_3 towards Fe_2Ti_5 represents also the bivalent cation content x and the trivalent cation content $4-2x$. In such an approach, holotype tomichite would not be an end-member, as still more V-rich compositions, approaching V_4Ti_3 , might be expected. The actual data for derbylite deviate from the nearest end-member, Fe_4Ti_3 , in having excess Ti cations and a corresponding reduction of Fe^{3+} to Fe^{2+} . Furthermore, the data for derbylite do not cluster at any given point, but lie approximately along the tie-line that joins V-free derbylite and tomichite. At present there are too few analyses of derbylite and tomichite to confirm or refute the possibility of complete solid solution between them. However, it seems possible that, as more derbylite crystals are analysed, a wider compositional range may also be expected around the holotype tomichite composition. No crystal-chemical reason seems to hinder the complete occupancy of the composi-

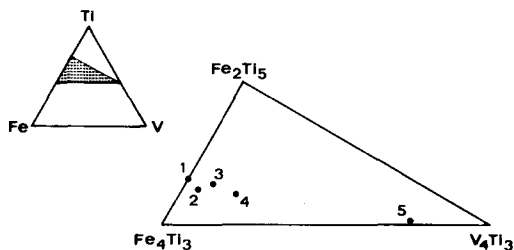


FIG. 2. Ternary compositional diagram for derbylite and chite: 1 V-free derbylite; 2, 3, 4 V-rich derbylite no. 560,413,420; 5 tomichite.

tional space we defined and limits, if any, are probably to be found in the particular geochemical environment.

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*Dipartimento di Scienze della Terra, Università di Pisa, and C.N.R.,
 C.S. Geologia Strutturale e Dinamica dell' Appennino, via S. Maria 53,
 56100 Pisa, Italy*

M. MELLINI
 P. ORLANDI

*Istituto di Mineralogia e Petrologia, Università di Modena,
 via S. Eufemia 19, 41100 Modena, Italy*

G. VEZZALINI

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On the shapes of dissolved crystals

DISSOLUTION often produces crystal morphologies quite different from those of growth. The normal (or pole) to a face on a growth form corresponds to a direction of slow growth. Despite statements to the contrary (Donaldson, 1985, quoting Bagdasarov *et al.*, 1974), the same direction should also be one of slow etch; and if dissolution has proceeded far enough, a vertex may be expected. Thus (I) faces in growth become vertices in dissolution.

A vertex on a growth form, however, results from factors involving the growth rates of several different crystallographic orientations, notably the normals to the three or more facets which meet at the vertex. The statement (II) that vertices on growth forms become faces in dissolution is not generally true. Donaldson (1985) is incorrect in suggesting that statements (I) and (II) are just different ways of saying the same thing.

If (I) and (II) were *both* true—faces becoming vertices and vertices becoming faces—then growth and dissolution forms would be dual figures. For example, the eight faces of the octahedron would become the eight vertices of the cube, and the six octahedral vertices would become the six cube faces. This is seldom observed in practice. For example, natural diamonds of octahedral habit become rounded rhombic dodecahedra by geologi-

cal dissolution (Moore and Lang, 1974). Here the propagation of kinks along $\langle 110 \rangle$ edges on $\{111\}$ monolayers seems to be the shape-determining process. The twelve edges of the octahedron eventually become the twelve (rounded) faces of the dodecahedral dissolution body. The eight octahedral growth faces do indeed become eight of the vertices of the rhombic dodecahedron, but note that the six vertices of the octahedron remain as vertices for the dodecahedron. Growth and dissolution forms are not necessarily dual figures (Moore, 1973).

Now the dual of the rhombic dodecahedron is the cubo-octahedron. Whilst it is true that the cubo-octahedron is a common growth form for *synthetic* diamond (Bovenkerk *et al.*, 1959; Litvin and Butuzov, 1969; Strong and Wentorf, 1972), it is rare for natural diamond (Moore, 1979, and for a general review of diamond morphology see Moore, 1985). When diamonds of combined cubic and octahedral habits are made in the laboratory, the relative development of the two forms can be varied by changing the temperature (Bovenkerk, 1961). The cubo-octahedron (of six square and eight triangular faces, and only twelve corners) is particularly favoured for sawing applications. This is a unique morphology between the cube and octahedron, in the middle of the spectrum of shapes