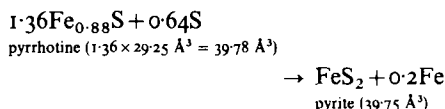removal of some of the sulphur from the site of alteration. Nevertheless, the general pattern of elemental gain or loss during alteration is probably portrayed reasonably well by the equations. A feature common to all equations is that the alteration requires an over-all addition of iron. The metals released (nickel and manganese), however, appear to be accommodated in the alteration assemblage. Nickel released by the alteration of pentlandite is probably consumed by the formation of nickelian mackinawite from alabandine. Manganese released from the alteration of alabandine is probably consumed by the precipitation of the carbonate phase. The volumetric proportions of the alteration products empirically suggest that the expelled nickel and manganese are mainly redistributed locally without net removal from the system. It seems likely therefore that alteration is induced by high iron activity but postulation of a mechanism for concentrating iron under these conditions remains a problem.

The unusual mode of occurrence of the pyrite and pyrrhotine in this deposit could perhaps be significant. There is good evidence to suggest that the pyrrhotine monosulphide was derived from pre-existing pyrite by contact metamorphism. Much of the pyrrhotine so formed is thought to have been subsequently re-pyritized. Where areas of pyrrhotine are pervasively replaced by pyrite, the

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overall sulphide fabrics are identical. There is certainly no evidence for an expansion of the rock mass. In this respect, it is interesting to note that the formation of pyrite from pyrrhotine at constant volume theoretically requires the release of some iron:

$$1 \cdot 36 Fe_{0 \cdot 88}S + 0 \cdot 64 S$$
pyrrhotine ($1 \cdot 36 \times 29 \cdot 25$ Å^3 = $39 \cdot 78$ Å^3)

$$\rightarrow FeS_2 + 0 \cdot 2 Fe$$
pyrite ($39 \cdot 75$ Å^3)

The relatively common association of pyrite with the alteration, especially in the specific case of cross-cutting veinlets, leads to the speculation that the concentration of iron required for this alteration process may result from the pyritization of pyrrhotine.

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C. F. BLAIN

Microprobe analyses of cadmium-rich tetrahedrites from Tyndrum, Perthshire, Scotland

CADMIUM-RICH tetrahedrites were analysed in a sample from the Tyndrum mining district, Scotland. It is the first occurrence of this variety of the mineral.

The mineralization at Tyndrum occurs in northeast-south-west trending fractures associated with the Tyndrum-Glen-Fyne fault. The mineral assemblage is mainly galena and sphalerite in quartz gangue with minor chalcopyrite, pyrite, baryte, and pyrargyrite. Tetrahedrite inclusions were observed in many galena samples from the area, but were most abundant in fine-grained massive galena from the 'Hard Vein' of the main mine where the largest inclusions attained a size of

100 microns. Inclusions from various samples were analysed.

The analyses were performed on a Cambridge Microscan 5 microprobe at the Grant Institute of Geology, Edinburgh. The general formula of the tetrahedrite-tennantite series is (Cu, Ag)$_{10}$(Zn, Fe)$_2$(Sb, As)$_4$S$_{13}$, but Hg and Bi and, very rarely, Pb and Te have been recorded as major elements in the mineral. The inclusions were analysed for fifteen elements: Cu, Ag, Au, Ni, Co, Mn, Zn, Fe, Cd, and Bi using pure metal standards; Pb, Hg, and S using galena, cinnabar, and pyrite; and Sb and As using GaSb and GaAs. Te was also checked and found to be absent. Some difficulty was encountered in

resolving Cd and Ag peaks using the microprobe because of the closeness of the $Ag-L\beta_1$ peak to the $Cd-L\alpha$ peak. The closeness of these peaks could mean that Cd has been overlooked in some previous tetrahedrite analyses.

The Tyndrum analyses are shown as wt% in Table I and as the number of atoms in the tetrahedrite formula in Table II. Many of the inclusions from normal samples (e.g. TY 1G and TY 3D) are typical tetrahedrites and have about 30 wt% Cu (Table I) with the predominant divalent element being Zn. These inclusions are pale

grey and often sub-idiomorphic. All the inclusions analysed contain little or no As and are essentially end-member tetrahedrites.

Inclusions from the Cd-rich sample (TY 9) have high Ag values with some over 20 wt% Ag (Table I) and these can be considered as freibergites (Riley, 1974). Cd values in inclusions from this sample range up to 11·70 wt% (TY 9XJ, Table I) and are often over 5·0 wt%. Previously only trace amounts of Cd have been recorded in tetrahedrites notably by Bernard (1955) and up to 1500 ppm by Schroll and Azer Ibrahim (1959), both using spectro-

TABLE I. *Microprobe analyses of tetrahedrites from Tyndrum, Scotland. Weight%*

Inclusion no.	Cu	Ag	Zn	Fe	Cd	Sb	As	S	Others*	Total
TY 1G	30·91	8·08	6·66	0·26	0·34	29·17	0·03	23·42	0·40	99·27
TY 3D	29·44	9·88	6·61	0·25	0·25	27·98	0·22	23·43	0·90	98·96
TY 9A	23·19	17·21	0·13	1·23	7·60	26·27	0·00	22·61	0·63	98·87
TY 9B	25·23	18·24	1·78	3·75	0·69	27·14	0·00	22·35	0·52	99·70
TY 9D	23·56	19·00	1·57	3·59	1·34	27·14	0·00	22·00	0·77	98·97
TY 9E	24·84	15·91	0·07	4·85	1·70	27·55	0·00	22·48	0·90	98·30
TY 9XA	20·34	21·96	4·66	1·64	0·32	27·32	0·06	22·24	0·41	98·95
TY 9XB	23·78	17·05	2·67	1·03	5·12	27·10	0·06	22·45	0·48	99·74
TY 9XC	22·99	19·05	2·67	1·20	5·19	27·16	0·05	22·06	0·43	100·80
TY 9XD	22·48	16·18	0·17	4·05	7·31	26·63	0·00	22·31	0·69	99·82
TY 9XE	22·53	17·80	0·40	1·40	8·31	26·67	0·04	22·20	0·60	99·95
TY 9XF	16·22	29·11	0·67	4·08	2·31	26·95	0·00	21·04	0·44	100·82
TY 9XG	22·96	18·75	2·63	0·46	5·19	26·52	0·02	21·75	0·57	98·85
TY 9XJ	30·41	6·00	0·07	0·34	11·70	27·14	1·12	22·42	0·38	99·58
TY 9BD	14·04	30·89	0·21	4·91	1·23	26·18	1·42	20·48	0·57	99·93
TY 9BJ	17·41	26·37	4·02	2·01	0·40	27·41	0·25	21·04	0·41	99·32

* Au, Ni, Co, Mn, Pb, Hg, and Bi.

TABLE II. *Microprobe analyses of tetrahedrites from Tyndrum, Scotland. Number of atoms in tetrahedrite formula calculated to 12 atoms of $Cu+Ag+Zn+Fe+Cd$, using weight% values of elements displayed*

Inclusion no.	Cu	Ag	Zn	Fe	Cd	Sb	As	S
TY 1G	8·70	1·34	1·82	0·08	0·05	4·29	0·01	13·06
TY 3D	8·39	1·66	1·83	0·08	0·04	4·16	0·05	13·23
TY 9A	7·11	3·11	0·04	0·43	1·32	4·20	0·00	13·12
TY 9B	7·15	3·04	0·49	1·21	0·11	4·01	0·00	12·55
TY 9D	6·88	3·27	0·45	1·19	0·22	4·13	0·00	12·72
TY 9E	7·31	2·76	0·02	1·63	0·28	4·23	0·00	13·12
TY 9XA	6·12	3·90	1·36	0·56	0·06	4·29	0·01	13·27
TY 9XB	7·05	2·98	0·77	0·35	0·86	4·19	0·01	13·19
TY 9XC	6·71	3·28	0·76	0·40	0·86	4·14	0·01	12·77
TY 9XD	6·60	2·79	0·05	1·35	1·21	4·08	0·00	12·97
TY 9XE	6·81	3·17	0·12	0·48	1·42	4·21	0·01	13·30
TY 9XF	4·87	5·15	0·20	1·39	0·39	4·22	0·00	12·52
TY 9XG	6·89	3·31	0·77	0·16	0·88	4·15	0·01	12·92
TY 9XJ	8·82	1·13	0·02	0·11	1·92	4·11	0·28	12·89
TY 9BD	4·35	5·64	0·06	1·73	0·22	4·23	0·37	12·58
TY 9BJ	5·31	4·74	1·20	0·70	0·07	4·36	0·06	12·71

graphic analyses. The analyses from Tyndrum show that Cd replaces Zn and Fe in the tetrahedrite structure. There are usually two atoms of divalent elements in the formula; as up to 1·92 atoms of Cd were detected (TY 9XJ, Table II), this suggests the existence of a new variety of tetrahedrite, $Cu_{10}Cd_2 Sb_4S_{13}$. Although the Cd-rich sample contains the inclusions with the highest values of Cd, Ag, and Fe, there is no simple relationship between the Cd content of the inclusions and the other substituting elements.

The Cd-rich inclusions are often very irregular in shape and sometimes resemble tennantite in appearing greenish in colour. The inclusions were rather small for reflectance or cell-size measurements, but this will be undertaken on synthetic equivalents.

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RICHARD A. D. PATTRICK

Post-growth readjustment of a cassiterite twin-boundary revealed by cathodoluminescence

A SIMPLE planar contact marking the change in crystallographic orientation of the two members of a cassiterite 'knee twin' (fig. 1) can be seen using reflected-light microscopy (fig. 2, I). However, cathodoluminescence by scanning electron microscopy (fig. 2, II, III, and IV) reveals details of growth history and provides evidence that the present twin contact must have replaced an original growth-twin contact. The observations leading to this conclusion are outlined below.

Cassiterite, SnO_2 is tetragonal ($a = 4.73$ Å and $c = 3.18$ Å), has principal refractive indices

FIG. 1. The prepared cassiterite 'knee twin'. Only natural faces (labelled 'n') belonging to the forms {100} and {110} were represented on the specimen. The two members of the twin have been termed A and B. Three of the natural faces were diamond polished (A4, A5, and A6) and three new faces normal to the (011) twin plane were manufactured by grinding and diamond polishing (A1/B1, A2/B2, and A3/B3). The mottled surface has been ground but not polished. The cross-hatched region represents the palimpsest, which appears dark in simple oblique-incident illumination. The vibration directions of all polished areas are shown. These directions represent extinction positions in reflected-light microscopy. The extraordinary-ray vibration direction is also the trace of the c-axis. This direction is that of the higher refractive index and the higher reflectance. In fact the orientation of polished sections of cassiterite, with respect to the c-axis, can be determined on small areas (50 μm) using micro-reflectance measurements and this was undertaken in order to confirm the nature of the twin using the technique outlined by K. von Gehlen (1960).