CHROMIAN ALLANITE FROM OUTOKUMPU, FINLAND

PETER J. TRELOAR*

Department of Geology and Physical Sciences, Oxford Polytechnic, Oxford, England 0X3 0BP

NORMAN R. CHARNLEY

Department of Earth Sciences, Oxford University, Oxford, England 0X1 3PR

ABSTRACT

A Cr-rich allanite containing up to 5.7 wt.% of Cr_2O_3 occurs in mica- and spinel-rich layers in a mica schist exposed in the Vuonos open pit in the Outokumpu mining district of Finnish Karelia. The Cr-rich allanite is part of a solid-solution series between allanite and a Cr-epidote of composition $Ca_4Cr_2Al_4Si_6O_{24}(OH)_2$. In view of documented site-preferences, the probable substitutions involved are *REE* for Ca on the *A* site, Al for Cr dominantly on the octahedral *M*1 site, and R^{2+} for Al on the *M*3 and *M*2 sites. This is the first recorded example of such a phase; it is an important addition to the exotic suite of Cr-rich minerals already described from Outokumpu.

Keywords: chromian allanite, Cr-minerals, solid solution, microprobe data, Outokumpu, Finland.

SOMMAIRE

Une allanite riche en chrome (jusqu'à 5.7% de Cr_2O_3 en poids) est présente dans les niveaux riches en mica et en spinelle d'un schiste micacé qui affleure dans la mine à ciel ouvert de Vuonos, dans le camp minier d'Outokumpu en Karélie finlandaise. L'allanite chromifère fait partie d'une solution solide entre l'allanite et une épidote chromifère de composition $Ca_4Cr_2Al_4Si_6O_{24}(OH)_2$. A la suite des préférences documentées parmi les sites, on propose un remplacement du Ca par les terres rares sur le site *A*, et de l'aluminium par le chrome sur les sites octaédriques *M*1 et par des cations R^{2+} sur les sites *M*3 et *M*2. C'est le premier indice d'une telle espèce minérale, qui vient s'ajouter à la suite de minéraux exotiques chromifères déjà connue à Outokumpu.

(Traduit par la Rédaction)

Mots-clés: allanite chromifère, minéraux de Cr, solution solide, données chimiques (microsonde électronique), Outokumpu, Finlande.

INTRODUCTION

The Outokumpu district of Finnish Karelia (Fig. 1) is dominated by a number of Cu–Co–Zn-bearing stratiform massive-sulfide bodies. Unusually for such deposits, both the ores and the country rocks con-

tain anomalously high concentrations of Cr. This stabilizes a wide range of unusual Cr-bearing silicate and oxide phases within both the orebodies and the country rocks. Cr-bearing diopside, tremolite, garnet, epidote, muscovite, biotite, chlorite, staurolite, tourmaline and spinel have all been described from the region (Eskola 1933, Thayer *et al.* 1964, Peltola *et al.* 1968, Vuorelainen *et al.* 1968, Treloar *et al.* 1981, Park 1983). The oxide phase eskolaite Cr_2O_3 was first documented at Outokumpu (Kuovo & Vuorelainen 1958). Most of these phases show unusually high Cr-contents, far in excess of anything reported elsewhere. Cr contents of up to 3.15% Cr_2O_3 in diopside, 3.74% in tremolite, 27.5% in garnet, 8.6% in biotite, 24.6% in muscovite, 5.2% in chlorite, 15.4% in epidote, 2.8% in staurolite and 9.6% in tourmaline have been recorded (Treloar 1985). This note records the occurrence of a Cr-bearing allanite and is the first reported occurrence anywhere of significant substitution of Cr for Al in allanite.

The massive-sulfide ores at Outokumpu are an integral part of the Outokumpu Association. The Association comprises serpentinite at the base, succeeded upward by dolomite, chert and a graphitic black schist. Intercalated within the sedimentary sequence is a series of pillowed flows, basalts and komatiitic volcanic rocks, together with occasional thin layers of heavy-mineral-rich schists. The orebodies are hosted within the chert horizons. The whole sequence, with serpentinite, pillow lavas and generally reduced sediments associated with the ore units, is consistent with a sea-floor volcanogenic origin for the massive sulfides. The rocks, which were deformed during the Svecokarelian orogeny, are tectonically enclosed within a regionally developed mica schist. Metamorphic conditions were about 600 ± 50°C at 3.5 ± 1 kbar (Treloar *et al.* 1981).

THE OCCURRENCE OF ALLANITE

The allanite occurs in a biotite-bearing schist exposed on the northeast face of the disused open pit at Vuonos, 5 km to the northeast of Outokumpu itself (Fig. 1). The rock type forms a minor component of the Outokumpu Assemblage (Koistinen 1981); it displays a well-marked schistosity defined

---

*Present Address: Department of Geology, Imperial College, Prince Consort Road, London, England SW7 2B9.
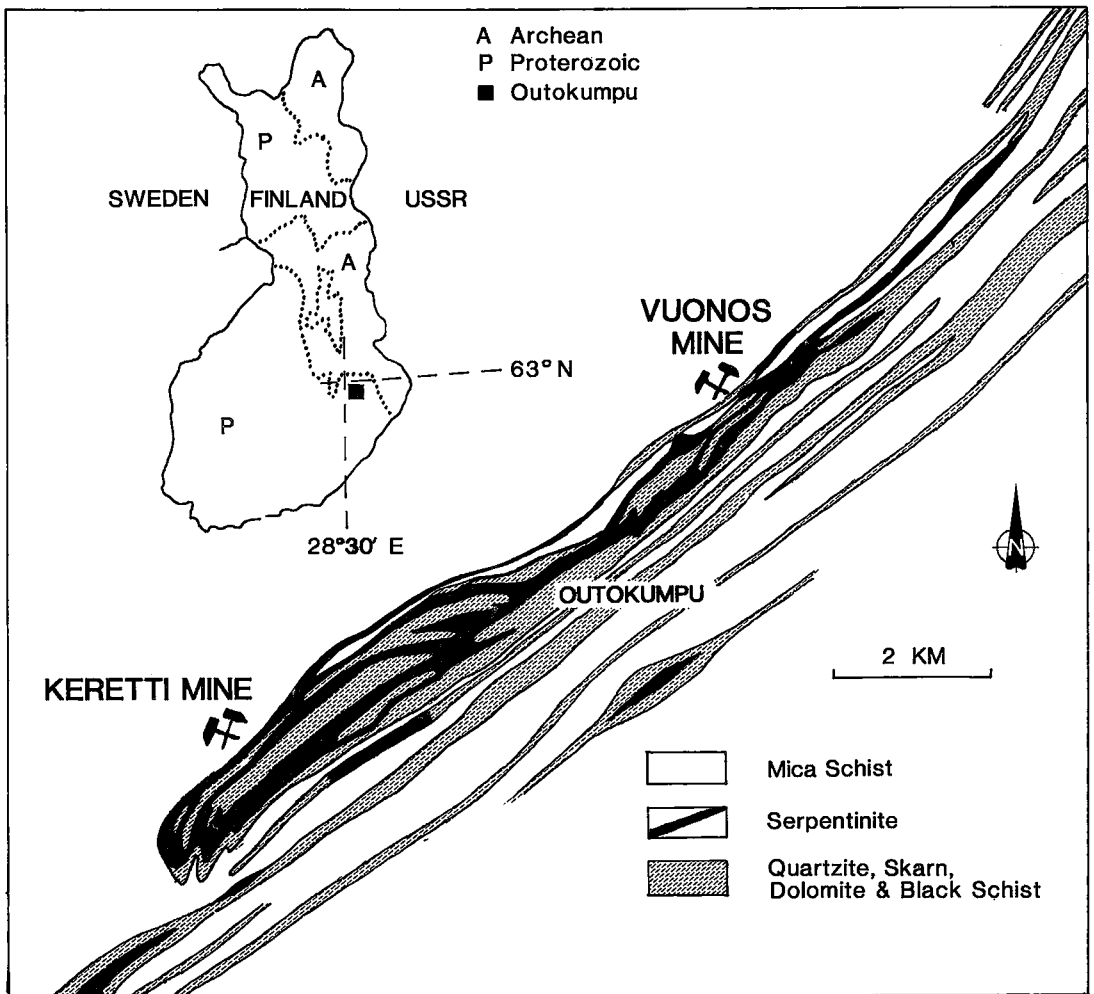
FIG. 1. Sketch map of the Outokumpu district to show the locality of the Keretti and Vuonos mines. The location of Outokumpu is shown by the square on the inset map of Finland.

TABLE 1. CHEMICAL COMPOSITION OF Cr-BEARING SPINEL, BIOTITE AND EPIDOTE

	a	b	c	d		a	b	c	d
SiO_2 wt.%		40.92	37.23	38.19	Si		2.913	6.021	6.103
TiO_2		0.41	0.15						
Al_2O_3	22.89	16.40	20.26	20.41	Al	7.151	1.377	3.863	3.845
Cr_2O_3	42.13	1.84	15.37	15.12	Cr	8.826	0.104	1.965	1.910
Fe_2O_3			0.48	0.50	Fe^{3+}			0.058	0.060
V_2O_3	0.37	0.24	0.32	0.20	V	0.079	0.013	0.041	0.026
MgO	3.71	20.45			Mg	1.464	2.170		
MnO	1.50		0.11		Mn	0.336		0.015	
FeO	15.23	4.91			Fe^{2+}	3.373	0.292		
ZnO	14.09				Zn	2.756			
CaO			0.13	23.16	23.55	Ca		0.010	4.014	4.033
K_2O		9.17			K		0.883		
total	99.92	94.47	97.08	97.97		23.985	7.762	15.977	15.977

a   composition of spinel (average of 23 analyses) that coexists with the Cr-allanite. Stoichiometry and Fe^{2+}/Fe^{3+} ratio are calculated on the basis of 32 oxygen atoms. b   composition of biotite (average of 3 analyses) that coexists with the Cr-allanite. All iron expressed as FeO. Stoichiometry is calculated on the basis of 11 oxygen atoms. c,d composition of Cr-epidote with X^{Cr}_{oct} = 0.33. All iron expressed as Fe^{3+}. Stoichiometry calculated on the basis of 25 oxygen atoms (Treloar 1987). All analyses were obtained on the EDS electron microprobe housed in the Department of Earth Sciences, University of Cambridge, UK. The analytical conditions are as outlined in Treloar et al. (1981).

by dimensionally aligned mica flakes and, in some places, expressed as a domainal alternation of quartzofeldspathic layers up to 6 mm wide and micaceous layers up to 4 mm in width. These layers probably reflect a primary lithological layering. The micaceous layers are dominated by biotite, often slightly chloritized and containing up to 1.94% Cr_2O_3, and a ruby-red Cr–Zn-bearing spinel. Biotite and spinel compositions are listed in Table 1. Textural relationships imply that the appearance of spinel predates the growth of the biotite fabric. It is probable that the spinel reflects heavy-mineral bands of sedimentary origin and that its composition was only slightly modified during metamorphism.

Allanite occurs as small grains within the micaceous layers. Individual crystals rarely exceed 250 µm
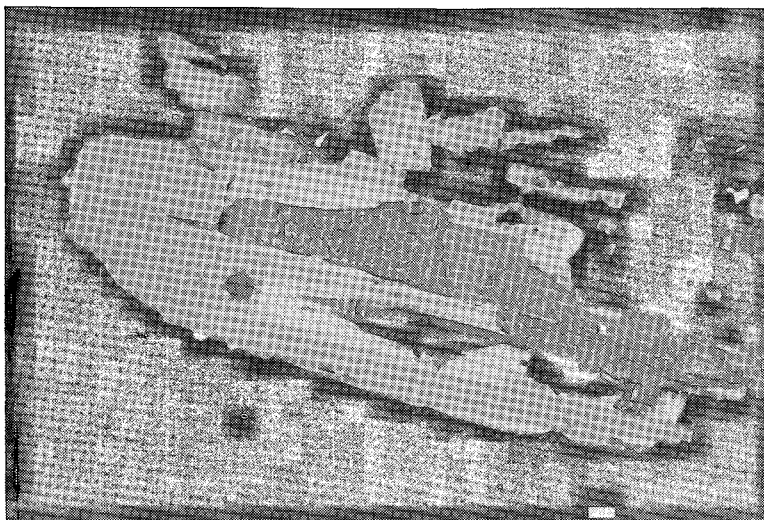
FIG. 2. Backscattered-electron image of chromian allanite. Lighter-colored areas are richer in the rare-earth elements. The pitted dark central areas have been hydrated and were not analyzed. Bright specks on the grain boundary are a rare-earth- and thorium-bearing phosphate. Scale bar: 10 μm.

TABLE 2. REPRESENTATIVE CHEMICAL COMPOSITIONS OF Cr-BEARING ALLANITE

SiO_2	32.94	33.63	34.39	34.87	34.59	34.37	35.04	34.40	34.90	34.40	34.70
Al_2O_3	18.19	17.89	18.55	18.37	18.58	18.47	18.64	18.83	18.89	18.31	18.81
Cr_2O_3	4.04	5.40	4.91	5.22	4.82	5.22	5.10	5.05	4.95	5.39	4.77
FeO	1.47	2.07	2.84	2.46	2.43	2.58	2.82	2.67	2.70	2.76	2.49
MgO	4.69	3.64	3.01	3.03	3.30	2.98	2.93	3.00	2.92	2.69	3.01
Y_2O_3	0.30	0.22	0.14	0.14	0.18	0.13	0.17	0.13	0.16	0.21	0.16
Ce_2O_3	12.30	10.72	9.43	9.41	9.38	9.03	9.29	9.05	9.08	8.81	8.37
La_2O_3	11.10	10.10	9.24	9.14	9.25	9.46	9.22	9.18	9.21	8.69	8.30
Nd_2O_3	1.79	1.51	1.29	1.51	1.23	1.26	1.33	1.27	1.31	1.33	1.33
Sm_2O_3	0.34	0.31	0.24	0.26	0.23	0.25	0.23	0.17	0.24	0.29	0.29
CaO	10.82	12.09	13.95	14.25	13.85	14.08	14.01	13.75	14.19	14.30	14.16
Total	97.98	97.58	97.99	98.66	97.84	97.83	98.78	97.40	98.55	97.18	96.39
Si	6.015	6.092	6.122	6.159	6.145	6.121	6.169	6.114	6.147	6.149	6.185
Al	3.915	3.819	3.893	3.825	3.891	3.878	3.868	3.957	3.923	3.857	3.952
Cr	0.583	0.774	0.691	0.728	0.677	0.735	0.710	0.712	0.690	0.761	0.673
Fe	0.224	0.314	0.422	0.363	0.361	0.385	0.416	0.398	0.397	0.412	0.371
Mg	1.276	0.982	0.780	0.797	0.873	0.791	0.769	0.796	0.768	0.717	0.800
Y	0.029	0.022	0.014	0.014	0.017	0.012	0.016	0.012	0.015	0.020	0.015
Ce	0.822	0.711	0.615	0.609	0.610	0.589	0.599	0.591	0.586	0.577	0.546
La	0.748	0.675	0.607	0.596	0.606	0.622	0.599	0.604	0.598	0.573	0.546
Nd	0.117	0.098	0.082	0.096	0.078	0.080	0.084	0.081	0.082	0.085	0.085
Sm	0.022	0.020	0.015	0.016	0.014	0.016	0.014	0.011	0.015	0.018	0.018
Ca	2.117	2.346	2.662	2.698	2.636	2.687	2.644	2.626	2.678	2.738	2.705
Tot	15.868	15.853	15.903	15.901	15.908	15.916	15.888	15.902	15.899	15.907	15.896
Si+Al	9.930	9.911	10.015	9.984	10.036	9.999	10.037	10.071	10.070	10.006	10.137
Al+Cr+Fe+Mg	5.998	5.889	5.786	5.713	5.802	5.789	5.763	5.863	5.778	5.747	5.796
Cr+Fe+Mg	2.083	2.070	1.893	1.888	1.911	1.911	1.895	1.906	1.855	1.890	1.844
Fe+Mg	1.500	1.296	1.202	1.160	1.234	1.176	1.185	1.194	1.165	1.129	1.171
Ca+REE	3.855	3.872	3.995	4.029	3.961	4.006	3.956	3.925	3.974	4.011	3.915
REE	1.738	1.526	1.333	1.331	1.325	1.319	1.312	1.299	1.296	1.273	1.210

Stoichiometry is calculated on the basis of 25 oxygen atoms. All iron expressed as FeO. The analytical method is outlined in the text.

in length (Fig. 2) and show a faint yellow color. The allanite grains are variably altered, the core regions in particular being extensively hydrated. A patchy incipient hydration throughout the grain is reflected by systematically low analytical totals, together with an increased level of Si in the structural formula. The allanite crystals are zoned with respect to Ce, La and Cr, with both the rare earths enriched in the core with respect to the rim. The sharp zonation-boundaries on the BSE image are apparently crystallographically controlled and may reflect a two-stage period of growth, with an early *REE*-rich phase being subsequently overgrown by a slightly less *REE*-rich one. Occasional pockets of high rare-earth con-
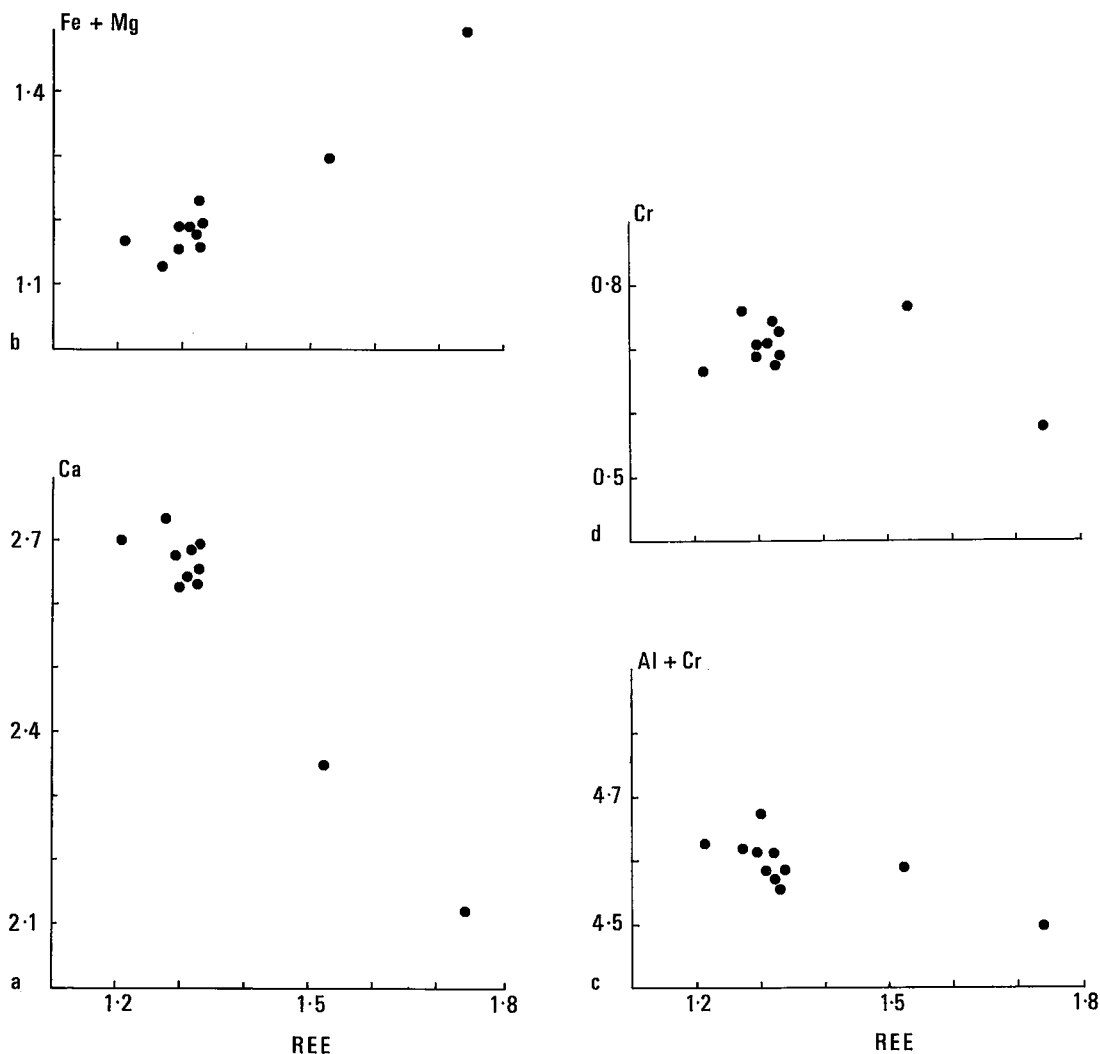
FIG. 3. Plots of concentration of Ca (a), Fe + Mg (b), Al + Cr (c) and Cr (d) against the sum of rare-earth-element concentrations (atoms per formula unit) in chromian allanite.

centration at isolated spots adjacent to the rim probably reflect localized near-rim concentrations of a rare-earth-bearing phosphate.

CHEMICAL COMPOSITION

Analytical data for allanite from Outokumpu are listed in Table 2. All analyses were carried out on the Cambridge Instruments Microscan Mark 9 electron microprobe in the Department of Earth Sciences at Oxford University using a 20 kV accelerating voltage, with rare earths calibrated against the standard glasses of Drake & Weill (1972). All iron is tabulated as FeO, and stoichiometries were calculated on the hydroxyl-free basis of 25 oxygen atoms. Total abun-

dances of the rare-earth elements range between 1.21 and 1.74 atoms per formula unit. Individual rare-earth elements show the following range in concentrations: Ce, 8.37 to 12.30 wt.% Ce_2O_3 (0.546 to 0.822 atoms); La, 8.30 to 11.10% La_2O_3 (0.546 to 0.748 atoms); Nd, 1.23 to 2.65% Nd_2O_3 (0.078 to 0.167 atoms); Sm, 0.17 to 0.34% Sm_2O_3 (0.011 to 0.022 atoms). In addition, Y contents range from 0.13 to 0.30% Y_2O_3 (0.012 to 0.029 atoms). Cr contents similarly show a range, from 3.63 to 5.40% Cr_2O_3, corresponding to 0.508 to 0.774 atoms per formula unit. The maximum extent of substitution of REE on the A site and of Cr on the octahedral sites is indicated by the relationships $X_{REE}^A = 0.45$ and $X_{Cr}^{oct} = 0.13$. REE concentrations have been

plotted against the concentration of a variety of other elements (Fig. 3). The plots show possible correlations of decreasing Ca, decreasing $Al^{3+} + Cr^{3+}$, and increasing $Fe^{2+} + Mg^{2+}$ with increasing concentration of the *REE*.

DISCUSSION

The composition of allanite may be considered within the framework of the general epidote-clinozoisite formula $A_4M_6Si_6O_{24}(OH)_2$ (Dollase 1971), in which trivalent *REE* atoms substitute for Ca on the A site, with charge balance maintained by the coupled substitution of divalent Fe and Mg for trivalent Al on the octahedrally co-ordinated M sites. This gives as general formula for allanite:

$$(Ca_{4-n}, REE_n)_4[(Fe^{2+}, Mg^{2+})_n(Fe^{3+}, Al^{3+}]_{2-n})_2(Al^{3+})_4 \\ Si_6O_{24}(OH)_2$$
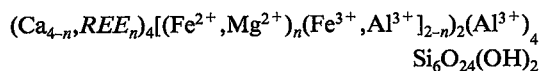
where n is between 1.2 and 2.0 (Deer *et al.* 1962). Where n equals 2, there will be an equal number of Ca and *REE* atoms on the A site, and the ratio of divalent to trivalent atoms on the octahedral M sites will be 1:2.

In the Outokumpu allanite, the octahedrally co-ordinated atoms Cr^{3+}, Fe^{2+} and Mg^{2+} contribute an approximate 2 atoms to the formula unit. These non-Al octahedral atoms therefore occupy a constant one third of the octahedral sites $[X^{oct}_{(Cr+Fe^{2+}+Mg)} = 0.33]$, and yield a general formula for the allanite from Outokumpu of:

$$(Ca, REE)_4(Cr^{3+}, Fe^{2+}, Mg^{2+})_2(Al^{3+})_4Si_6O_{24}(OH)_2.$$

There is a slight Si excess (Si > 6 atoms per formula unit) in all the analyzed points, which probably reflects a two-stage process of alteration involving an initial incipient metamictization of the crystal structure, followed by a slight leaching, preferentially of atoms other than silicon, during the patchy hydrothermal alteration mentioned above. The compositions listed in Table 2 do not completely charge-balance, as in each case there is a slight excess of trivalent *REE* over divalent Fe^{2+} and Mg^{2+} (1.74 to 1.21 atoms of *REE* are balanced by 1.50 to 1.13 atoms of Fe^{2+} and Mg^{2+}). This charge imbalance might be reduced if some of the chromium is present in its divalent rather than trivalent state.

The Cr-bearing allanite is not the first Cr-rich epidote-group mineral to have been described from Outokumpu. A Cr-rich epidote, tawmawite, with 9.6% Cr_2O_3, was described by Eskola (1933); recently, Treloar (1987) has shown that the degree of substitution of Cr for Al in epidote may reach the equivalent of 2 atoms per formula unit (Table 1). The general formula of the Outokumpu chromian

allanite shows a constant ratio between $Cr^{3+} + Fe^{2+} + Mg^{2+}$ and Al^{3+} that is approximately equal to 1:2, and a complete absence of Fe^{3+}. Consequently, the phase chemistry may be viewed solely in terms of two theoretical end-members: the chrome-epidote $Ca_4Cr_2Al_4Si_6O_{24}(OH)_2$ (Table 1), with $X^{oct}_{Cr} = 0.33$, which has recently been described from Outokumpu (Treloar 1987), and pure allanite $Ca_2REE_2R^{2+}_2Al_4Si_6O_{24}(OH)_2$.

These two phases may be linked by a balanced substitution: $Ca + Cr \rightleftharpoons REE + R^{2+}$. The tabulated compositions indicate that there is at least limited solid-solution between the two end-members.

Whereas Ca and the rare-earth elements substitute for each other on the A site, the site (or sites) on which Cr and the R^{2+} atoms substitute is (or are) not so clear. Mössbauer spectral analysis, site-occupancy refinement (Dollase 1971) and polarized absorption spectroscopy (Burns & Strens 1967) show strong site-preferences for substitutions of Cr, Fe and Mn for Al. The $M2$ site is dominated by aluminum atoms, with the non-Al octahedral atoms partitioning into the $M3$ and $M1$ sites (Dollase 1971). Ferric iron, for instance, goes dominantly into the $M3$ site. The phase $Ca_4Fe^{3+}_2Al_4Si_6O_{14}(OH)_2$ marks the Fe-rich end of the clinozoisite–epidote solid-solution series; with its complete occupancy of $M3$ sites by Fe^{3+} (Dollase 1971), it has appreciable crystal-chemical significance. Cr^{3+} shows a strong site-preference for $M1$ (Burns & Strens 1967); the recognition of a Cr-epidote with $X^{oct}_{Cr} = 0.33$ (Treloar 1987) may have a similar crystal chemical significance. Site preferences for the divalent atoms are less clear. Dollase (1971) indicated a strong site-preference of Fe^{2+} for $M3$, although Mg may prefer the more ordered $M2$ site.

In the case of the chromian allanite from Outokumpu, the above site-preferences, if fully obeyed, would imply that the solid-solution series from chromian allanite to Cr-epidote involves substitution of R^{2+} atoms for Al on the $M3$ and $M2$ sites, and substitution of Al for Cr on the $M1$ site. The former would maintain the charge-balance requirement of the Ca-for-*REE* substitution on the A site, whereas the latter maintains $X^{oct}_{Al} = 0.67$ and $X^{oct}_{(Cr+Fe^{2+}+Mg)} = 0.33$. It is possible that this last relationship has crystal-chemical significance, all the non-Al octahedral atoms being limited to just one site, which, given the strong crystal-field effects of chromium, may be $M1$. The substitutions are, however, likely to be disordered to some extent over all three octahedral sites, with Cr dominantly, though not exclusively, on the $M1$ site, and Fe^{2+} dominantly on the $M3$ site, and so on.

The recognition of substantial substitution of Cr for Al in allanite is not surprising in crystal-chemical terms. Cr has been shown to substitute readily for octahedral Al in a number of phases in which Al is normally an essential component (Burns & Burns 1975). Treloar (1987) has shown that Cr may enter the clinozoisite

structure through Cr–Al solid solution, to a value of $X_{Cr}^{oct} = 0.33$. Even in phases such as pyroxene and amphibole, in which Al, though not an essential component, commonly occurs on both octahedral and tetrahedral sites, Cr has been shown to mimic Al in substituting for octahedral Fe^{2+} and Mg^{2+} (Burns & Burns 1975).

The surprising aspect of the occurrence is in the juxtaposition of Cr and rare-earth elements in the same phase. The enhanced levels of chromium in the sediments of the Outokumpu Association are attributed to sedimentary enrichment during derivation from a local ultramafic–volcanic substrate (Treloar 1985). The Cr was incorporated within the sediments both in a heavy-mineral fraction and by direct precipitation out of reduced seawater, involving absorption onto clay-mineral surfaces. The spinel–biotite-rich bands in which the allanite occurs, with spinel grains only slightly modified by metamorphism, are typical of sedimentary heavy-mineral bands. Spinel grains form over 20% of the bands in the particular schist examined. If the Cr represents an ultramafic source-rock, possibly of greenstone type, the rare-earth elements must represent a different, more acidic, provenance, which may be the Archean terrane to the east. It is probable that the heavy-mineral bands represent a mixed provenance, the spinel grains derived from a basic terrane being admixed with zircon (?) from a more acidic one. This unusual mixture resulted, during metamorphism, in the necessary chemical microenvironment for growth of this unusual phase.

Without doubt, as shown by the references listed above, the best documented suite of Cr-bearing minerals is that described from Outokumpu. Although this suite may well prove to be unique, it does not contain all those phases into which Cr may substitute. Others, such as sapphirine, corundum, cummingtonite and kyanite, have been described from other locations. A chromium-bearing allanite has not previously been reported, but given the potential substitution of Cr for Al within the epidote series, it is not surprising that a combination of rare-earth elements and Cr within a sediment could generate such a phase. It is perhaps appropriate that such a phase should be described first from Outokumpu, to be added to that locality's unique suite of chromian minerals.

REFERENCES

BURNS, R.G. & STRENS, R.G.J. (1967): Structural interpretation of polarised absorption spectra of the Al–Fe–Mn–Cr epidotes. *Mineral. Mag.* **36**, 204-226.

BURNS, V.M. & BURNS, R.G. (1975): Mineralogy of chromium. *Geochim. Cosmochim. Acta* **39**, 903-910.

DEER, W.A., HOWIE, R.A. & ZUSSMAN, J. (1962): *Rock-forming Minerals. 1. Orthosilicates.* Longman, London.

DOLLASE, W.A. (1971): Refinement of the crystal structure of epidote, allanite and hancockite. *Amer. Mineral.* **56**, 447-464.

DRAKE, M.J. & WEILL, D.F. (1972): New rare earth element standards for electron microprobe analysis. *Chem. Geol.* **10**, 179-181.

ESKOLA, P. (1933): On the chrome minerals of Outokumpu. *Comm. Géol. Finlande Bull.* **103**, 26-44.

KOISTINEN, T.J. (1981): Structural evolution of an early Proterozoic stratabound Cu–Co–Zn deposit, Outokumpu, Finland. *Trans. Roy. Soc. Edinburgh, Earth Sci.* **72**, 115-158.

KUOVO, O. & VUORELAINEN, Y. (1958): Eskolaite, a new chromium mineral. *Amer. Mineral.* **43**, 1098-1106.

PARK, A.F. (1983): Sequential development of metamorphic fabric and structural elements in polyphase deformed serpentinites in the Svecokarelides of eastern Finland. *Trans. Roy. Soc. Edinburgh, Earth Sci.* **74**, 33-60.

PELTOLA, E., VUORELAINEN, Y. & HÄKLI, T.A. (1968): A chromian tourmaline from Outokumpu, Finland. *Geol. Soc. Finland Bull.* **40**, 35-38.

THAYER, T.P., MILTON, C., DINNIN, J. & ROSE, H. (1964): Zincian chromite from Outokumpu, Finland. *Amer. Mineral.* **49**, 1178-1183.

TRELOAR, P.J. (1985): The chrome minerals of Outokumpu – their chemistry and significance. *J. Geol. Soc. London* **142**, 1240 (abstr.).

────── (1987): Chromian muscovites and epidotes from Outokumpu, Finland. *Mineral. Mag.* **51**, pt.3 (in press).

──────, KOISTINEN, T.J. & BOWES, D.R. (1981): Metamorphic development of cordierite-orthoamphibole rocks and mica schists in the vicinity of the Outokumpu ore-deposit. *Trans. Roy. Soc. Edinburgh, Earth Sci.* **71**, 201-215.

VUORELAINEN, Y., HÄKLI, T.A. & KATAJA, M. (1968): A hydrated oxide of chromium as a pseudomorph after eskolaite, Outokumpu, Finland. *Geol. Soc. Finland Bull.* **40**, 125-9.