Zinc-bearing chromite (donathite?) from Norway: a second look

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SUMMARY. Electron-microprobe analyses of chromites from the Helgeland area, Norway, show that they are all low in zinc. Many chromites show physical properties identical with donathite (anisotropism; polar magnetism) but have cubic lattices. One exception, from Rødøya, shows an unusual deviation from cubic symmetry and that there may exist complex intergrowths of two different tetragonal lattices and a cubic lattice. The similarity between the chromites studied and donathite suggests that the chemistry and crystallography of that mineral may be more complex than is currently accepted.

DONATH (1931) reported that chromites from Ramberget, Hestmona (= Hestmannøy) and Værnes, in the north Helgeland area of west Norway, contained zinc as a major component. This report, which included two analyses of chromites with ZnO contents of 2·62 and 2·21 %, has since been referred to in a number of standard textbooks on mineralogy and in recent publications (Thayer *et al.*, 1964; Weiser, 1967). Seeliger and Mücke (1969) on the basis of these original analyses and their own X-ray powder photographs have defined this as a new mineral, Donathite (see also Fleischer, 1969), which they found to be tetragonal with a c/a ratio of 0·9956. The mineral is found in a deposit regarded by Donath (1931) as a 'standard type' and the presence of considerable zinc is all the more surprising since the host ultramafic rocks are those in which the geochemical environment is low in zinc (Goles, 1967). The only other reports of zinc-bearing chromites of which I am aware are those dealing with the Outokumpu deposits, Finland (Thayer *et al.*, 1964; Weiser, 1967). Where chromites from other areas have been analysed for zinc it has commonly been found in small amounts, usually less than 0·5 per cent by weight of ZnO.

As part of a programme involving studies of ultramafic rocks in the Norwegian Caledonides a large number of chromites have been analysed by electron microprobe. Because those from the north Helgeland islands showed similar physical properties to the sample described by Donath (1931) and Seeliger and Mücke (1969) analyses included a check for zinc. Analyses were carried out on an ARL-EMX electron microprobe at Sentral Institutt for Industriell Forskning, Oslo, using 15 kv accelerating voltage and a sample current of between 0·05 μamp (minor elements) and 0·025 μamp (major elements). The standards were natural minerals and matrix corrections were made by the method of Bence and Albee (1968).

Results. In spite of the similarity in physical properties and origin of the chromites analysed by electron probe and the sample described by Donath (1931) the zinc content was found to be low in all samples: less than 0·3% of ZnO (by weight). Because of this a sample of the material used by Donath (sample 1069) was obtained and analysed under the same conditions. Unfortunately it has not been possible to examine the samples described by Seeliger and Mücke (1969), limited to three polished sections. The results are presented in Table I, which shows that the chromites all have low zinc contents although the values are

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TABLE I. *Electron microprobe analyses of chromites from Helgeland, Norway*

	SiO$_2$	Al$_2$O$_3$	TiO$_2$	Fe$_2$O$_3$	Cr$_2$O$_3$	MgO	FeO	MnO	CaO	NiO	ZnO	Sum
1.	0.05	4.74	0.00	41.57	26.22	10.49	15.16	0.67	0.02	n.a.	0.13	99.05
2.	0.04	2.66	0.01	10.78	57.36	6.16	22.26	0.68	0.02	n.a.	0.27	100.24
2a	0.07	3.53	0.04	14.75	51.92	6.03	22.46	0.67	0.02	n.a.	0.24	99.73
3.	0.01	11.34	0.60	22.66	34.43	6.43	22.83	0.79	0.37	0.18	0.28	99.92
4.	0.00	5.97	0.03	35.80	33.13	12.71	12.16	0.73	0.33	0.01	0.20	101.07
5.	0.01	2.54	0.49	29.68	38.52	7.06	20.53	0.76	0.25	0.08	0.22	100.14

Fe^{3+}/Fe^{2+} determined on the basis of charge balance using the structural formulae. n.a. = not analysed. K_2O in all samples is below detection limit and Na_2O is zero in all samples except 4 and 5 where it is 0.01 per cent.

Structural formulae based on 24 cations.

colorimetric

	Al	Ti	Fe^{3+}	Cr	Mg	Fe^{2+}	Mn	ZnO determination
1.	1.549	0.000	8.674	5.749	4.336	3.515	0.157	0.17%
2.	0.885	0.002	2.290	12.80	2.591	5.254	0.163	—
2a	1.178	0.009	3.143	11.62	2.545	5.317	0.161	—
3.	3.652	0.123	4.659	7.437	2.619	5.216	0.183	—
4.	1.870	0.006	7.161	6.960	5.035	2.702	0.164	—
5.	0.847	0.104	6.322	8.622	2.979	4.859	0.182	0.20%

Details of analyses

1. Large chromite with chlorite inclusions from chromitite, Rødøya; magnetic and anisotropic. Non-cubic: see Table 2.

2. Small (1mm) euhedral crystal within olivine; Ramberget (Hestmona). Analysis is of core region. Apparently isotropic.

2a Same grain as in 2 but analysis of margin. Possibly weakly anisotropic.

3. Core zone of anhedral grain in chromite-rich band in carbonate-bearing dunite. Vaernes, Tjongsfjord. Weakly anisotropic and weakly magnetic. Cubic $a = 8.357$A.

4. Polygonal grains in chromite-rich band within dunite, Rødøya. Distinctly anisotropic and magnetic.

5. Aggregate of polygonal chromite crystals with olivine inclusions. Sample 1069 from Bergakademie, Freiberg, (G.D.R.), reputedly that analysed by Donath (1931) and originally from Ramberget. Strongly anisotropic and magnetic. Cubic $a = 3.375$A Cubic nature confirmed by the author, Dr. T. Rakke (Kjemisk Institut, Oslo) and Prof. A. Kato (National Science Museum, Tokyo).

TABLE II. *X-ray diffraction data*

1	2		3			1	2		3		
d(Å)	d(Å)	I	d(Å)	I	hkl	d(Å)	d(Å)	I	d(Å)	I	hkl
4.820	4.830	25	4.825	50	111	2.079	2.078	5	2.077	10	004
(4.718)*	—		—			2.070	—				
(3.551)*	—		—			—	1.709	5	—		
2.952	2.956	25	2.949	30	202	1.702	1.704	5	—		
2.936	—		—			1.605	1.608	30	1.603	30	333
2.521	2.520	100	2.514	100	311	1.597	1.597	5	—		
2.510	2.508	10	2.502	10	113	1.471	1.478	20	1.475	20	440
2.407	2.419	5	—			1.468	1.473	15	1.471	30	404
2.399	2.411	5	—			1.412	—		—		
2.085	2.088	40	2.086	60	400						

1. Magnetic chromite from Rødøya. Measurements from diffraction trace using Co-Kα radiation and graphite monochromator, University of Stellenbosch.

2. Same sample as 1. Diffractomer trace using Fe-Kα radiation and Mn filter. Prof. A. Kato, National Science Museum.

3. Donathite, after Seeliger and Mücke (1969).

* Small peaks which were present on some traces of the pure mineral but could not be identified on traces where the mineral was mixed with NaCl.

variable within a relatively narrow range. As an independent check two of the samples were analysed by the colorimetric (dithizone) method by B. Bruun (Mineralogisk-Geologisk Museum).

In view of the findings by Seeliger and Mücke (1969) some of the samples were also anaylsed using a Guinier-Wolff quadruple focusing camera and iron radiation with duplicate runs: samples alone, then mixed with $Pb(NO_3)_2$ as an internal standard. Films were measured independently by B. Nilssen and the author, neither of whom was able to identify splitting of the 311, 400, and 440 lines critical for the distinction of a tetragonal as opposed to cubic lattice. However, some diffuseness was observed in the 440 lines of some of the samples. Initially it was concluded that all of the minerals were cubic but subsequent X-ray diffraction traces, which allow for greater resolution of the peaks, have shown that one of the samples is not cubic (Table II).

Discussion. The distinctive features of many, but not all, of the chromites from ultramafic rocks in the north Helgeland area is that they show polar magnetism and distinct optical anisotropism of varying intensity in reflected, polarized light. Donath (1931) attributed both of these features to the presence of zinc. However, these features are here present in chromites in which zinc is not a major component. Moreover, zinc-bearing chromites from Outokumpu may contain up to 12 % ZnO in the dark bands of zoned crystals (Weiser, 1967), yet are non-magnetic and optically isotropic.

Examination of polished sections show that possible impurities present in the chromite samples are olivine (the only impurity in sample 1069), chlorite, phlogopite, orthopyroxene, and carbonate. None of these can be responsible for the magnetism. Jenness (1959) has shown that magnetic chromites in Newfoundland owed their magnetic properties to the presence of discrete magnetite veins, which could be separated out by fine crushing. Although this is not the case for the Helgeland chromites, the calculated mineral formulae (Table I) indicate that they have a high proportion of Fe_2O_3 and it is suggested that this may be responsible for their magnetic properties. Robbins *et al.* (1971) have shown that there is an increase in the magnetic moments with increase in Fe_2O_3 in the system $FeCr_2O_4$–Fe_3O_4 ($Fe^{2+}Cr_{2-x}Fe_x^{3+}O_4$) in accordance with the substitution of Fe^{3+} in tetrahedral sites leading to *A–B* coupling (i.e. Fe^{3+}–Fe^{3+}) interaction, because $Fe^{2+}Cr_2O_4$ is a normal spinel and Fe_3O_4 is an inverse spinel. Similarly, Schmidbauer (1971) has shown experimentally that in Fe–Cr spinels with a reduced number of Fe^{3+} ions in *A* and *B* sites the strong A–B coupling is replaced by weaker interactions, thus causing a drop in the Curie temperatures.

For the chromites that have been found to be cubic, including sample 1069, the anisotropism is difficult to explain. Klemm (1962) made a detailed study of anisotropism in opaque cubic minerals, one of which was chromite. Of thirty-one chromite samples he examined twenty-nine showed anisotropism, a feature that he concluded was largely due to strain (*Tektonische anisotropism*). It would thus seem that anisotropism in chromite is not as rare as previously thought and the presence, or absence, of unusual elements or of a non-cubic lattice is not a prerequisite. Blanc and Maisonneuve (1971) concluded that the optic anisotropism in cubic garnets (ugrandites), which were strictly cubic and undeformed, could be related to the presence of magnetic ions (essentially heavy rare-earth elements) substituting for calcium. The basis for this conclusion is that in such minerals one cannot assume a value equal to unity for the magnetic permeability in the Maxwell equations for the velocity of light (electromagnetic radiation). This may provide a reasonable explanation when considering transmitted light through relatively thick sections so the influences on both the electric and magnetic vectors can be sufficiently substantial as to be observed. However, it seems unlikely that phase differences between magnetic vectors in reflected polarized light will be sufficient to cause the

marked anisotropism observed here, although there does seem to be a correlation between Fe_2O_3 content (magnetism) and optic anisotropy.

The non-cubic chromite (Table II) is very similar to donathite of Seeliger and Mücke (1969), which is described as being tetragonal. However, the X-ray diffraction trace indicates the presence of more peaks than can be accounted for by a tetragonal lattice. Part of the problem in interpretation is that the lattice is very close to cubic and the peak-splitting is so fine that $K\alpha_1$ and $K\alpha_2$ peaks partially overlap. The specimen is not suitable for single-crystal work as it consists of a polycrystalline aggregate of intimately intergrown grains less than 0·5 mm in size. However, Dr. G. Gafner (written pers. comm.) was able to obtain a fragment that was close enough to single to give meaningful results and an extremely odd deviation from cubic symmetry was found. Using a Philips PW 1100 four-circle single-crystal diffracto-meter he reported that the $Mo–K\alpha_1$ and $K\alpha_2$ components of the 16.0.0, $\overline{16}$.0.0, 0.0.16, and 0.0.$\overline{16}$ spots appear at 42·74 and 43·05° with 0·01° accuracy, respectively, giving a cell constant of 8·36 Å. The expected ratio of 2:1 is found for the $K\alpha_1$ and $K\alpha_2$ components. The 0.16.0 beam and its Friedel partner are quite different in that four peaks are found at 42·47, 42·78, 43·07, and 43·37° with heights of 20, 15, 20, and 9 respectively. If these were nearer 20, 10, 20, 10 it would be a clear case of two tetragonal cells present with third axes of 8·40 and 8·31 Å. Due to the unexpected height of the 42·78° peak, it would seem that a little of the arrangement giving the other two axes is also present. The best conclusion is thus that the *one* crystal looked at carefully consists of about 45 % of a tetragonal species with cell constants of $a = b = 8·36$, $c = 8·40$ Å, a further 45 % of another tetragonal species with cell constants of $a = b = 8·36$, $c = 8·31$ Å, and 10 % of a cubic component with constants of 8·36 Å. Further work is in progress.

Conclusions. Analyses of a large number of chromites from the north Helgeland area of Norway, including Rødøya, Værnes, and Hestmona, the type locality[1] for donathite (Seeliger and Mücke, 1969), have failed to reveal the presence of zinc in amounts greater than traces (approximately 0·3 % ZnO). Analyses of a sample of the original material described by Donath (1931) have given similar results. It is not possible to state whether donathite is the same mineral as the unusual, non-cubic chromite described here from Rødøya without further examination of the type material. However, the similarities between the two samples appear to be very close and it is therefore suggested that the crystallography and chemistry of donathite may be more complex than is currently accepted.

Other than the Outokumpu deposits of zoned zinc-bearing chromites (Thayer *et al.*, 1964; Weiser, 1967), I am not aware of any other reports of chromites in which zinc is present other than in minor amounts. Those from Woods Mines (Pearre and Heyl, 1960) contain 0·52 wt. % ZnO, which is unusually large for chromites from serpentinite but *is* still not a major component. Evans and Frost (1975) have reported chromites from a phlogopite–talc–enstatite-olivine rock, Central Alps of Switzerland, with a ZnO content of 0·77 %. The rarity of naturally occurring zinc-rich chromites is the result of the geochemical environment rather than any crystallographic control. The Outokumpu deposits are very unusual and involve special circumstances in which strongly zoned chromites are possibly formed at a late stage by hydrothermal activity involving both chrome-bearing serpentinite and spatially associated zinc-bearing sulphide deposits (Vähätalo, 1953). The chromites from north Helgeland are found in carbonate-bearing harzburgites (sagvandites) and metaperidotites in which serpentine minerals are rare and which are not associated with any zinc minerals.

The X-ray powder photographs and diffraction traces have shown that while some of the

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[1] Hestmona is the current official name of the locality formerly known as Hestmannøy; Hestmandöy of Seeliger and Mücke is a variant spelling.

magnetic and optically anisotropic chromites are cubic, at least one is not and gives a diffraction pattern similar to donathite, but with significant differences suggesting a lattice that is not tetragonal (Table II). There is a tendency for the 440 peak of one of the cubic chromites to split into two peaks (Professor Kato, pers. comm.) indicating that a gradation in lattice type may exist between the cubic and non-cubic chromites. At this stage it is not certain as to the cause of the change but it may be a function of tectonic distortion.

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Errata: Table I, Details of analyses:
   3. *For* 8.357A *read* 8.357Å.
   5, last line, *for* Institut, *read* Institutt,