

# CONTRIBUTIONS TO THE MINERALOGY OF NORWAY

## No. 15. Gahnite in the Bleikvassli ore

By

F. M. VOKES

(Mineralogisk-Geologisk Museum, Oslo.)

### Introduction

The zinc spinel, gahnite, has previously been reported, briefly, from only one locality in Norway, the pegmatite at Thors gruve, Øvre Vats, near Haugesund, (SØRBYE, 1950). The mineral has now been found in the Palæozoic pyritic lead-zinc ore at Bleikvassli in Nordland. The following note presents a description of the occurrence of the mineral, its physical properties and a complete chemical analysis.

The mode of occurrence of gahnite is quite varied, it appears as a constituent of crystalline schists, granite pegmatites and contact metamorphic limestones. Its occurrence in ore deposits is by no means uncommon, some of the most abundant occurrences being in the Swedish deposits at Falun and Ridderhyttan, and in the contact-metamorphic ores of Franklin Furnace and Sterling Hill, New Jersey. SEGNIĆ (1961) has recently mentioned the occurrence of gahnite in the crystalline schists of the Broken Hill, N.S.W., ore bodies, an environment which appears to be very similar to that at Bleikvassli. Gahnite is a widespread and at times abundant (up to 20 percent) constituent of cassiterite and sulphide bearing chlorite-sericite-(almandine) schists on the northern slopes of the Iser mountains in Lower Silesia (HARANCZYK and SKIBA, 1961). These occurrences are also of interest because of the presence of cassiterite in the Bleikvassli ore zone (VOKES, 1960). Other occurrences of gahnite in ore deposits which may be mentioned are those at Ore Knob, North Carolina and Carrol County, Maryland.

Following the identification and investigation of the Bleikvassli gahnite, a few grains of the mineral were identified in specimens collected by Dr. H. Neumann and the writer from the zinc-lead deposits of Villdalsfjell and Niingen in the Bogen area, Ofoten. It seems quite likely that further occurrences of the mineral can be expected in deposits of a similar geological nature when the detailed study of their mineralogy is undertaken.

### Description of occurrence

Gahnite is quite a ubiquitous minor constituent of the gangue of the Bleikvassli ore. Normally it occurs as small (less than 2 mm.) anhedral to subhedral grains apparently randomly distributed. The mineral was first recognised and identified in heavy fractions of the mill tailings where it is always present as clear, emerald-green fragments. A particular concentration of the gahnite occurred in the wide lens of very massive ore in the southern part of the mine between the 380 and 330 m levels. It was from here that megascopically visible gahnite was first noticed *in situ* and collected.

The most striking occurrence of the mineral was in a concordant zone of quartz-rich muscovite schist and vein quartz situated at about the centre line of the ore body, here about 7 m thick. (See sketch, fig. 1). Several subhedral crystals of dark green to black gahnite occurred along this zone, either in the quartz patches, in the schist, or in the solid sulphides. The majority of the crystals ranged in size from 0.5 to about 3 cm, the largest ones occurring in the schist and in the quartz patches. (Photo, fig. 2). Some crystals showed octahedral faces but mainly they were subrounded in outlines.

The gahnite crystals normally show a poikilitic texture, with numerous inclusions of other minerals, mainly quartz and pyrite. This texture indicates that the gahnite has grown simultaneously with the other components of the ore, or somewhat later, blastically.

Several of the gahnites show a marked, but sometimes discontinuous rim of light-brown, very fine-grained sphalerite. These rims are of the order of 1 mm thick and in them the sphalerite grains appear to be arranged in fibrous aggregates with the long axes of the fibres at right angles to the crystal surfaces of the gahnite. The sphalerite rims are developed preferentially, but not universally, where the

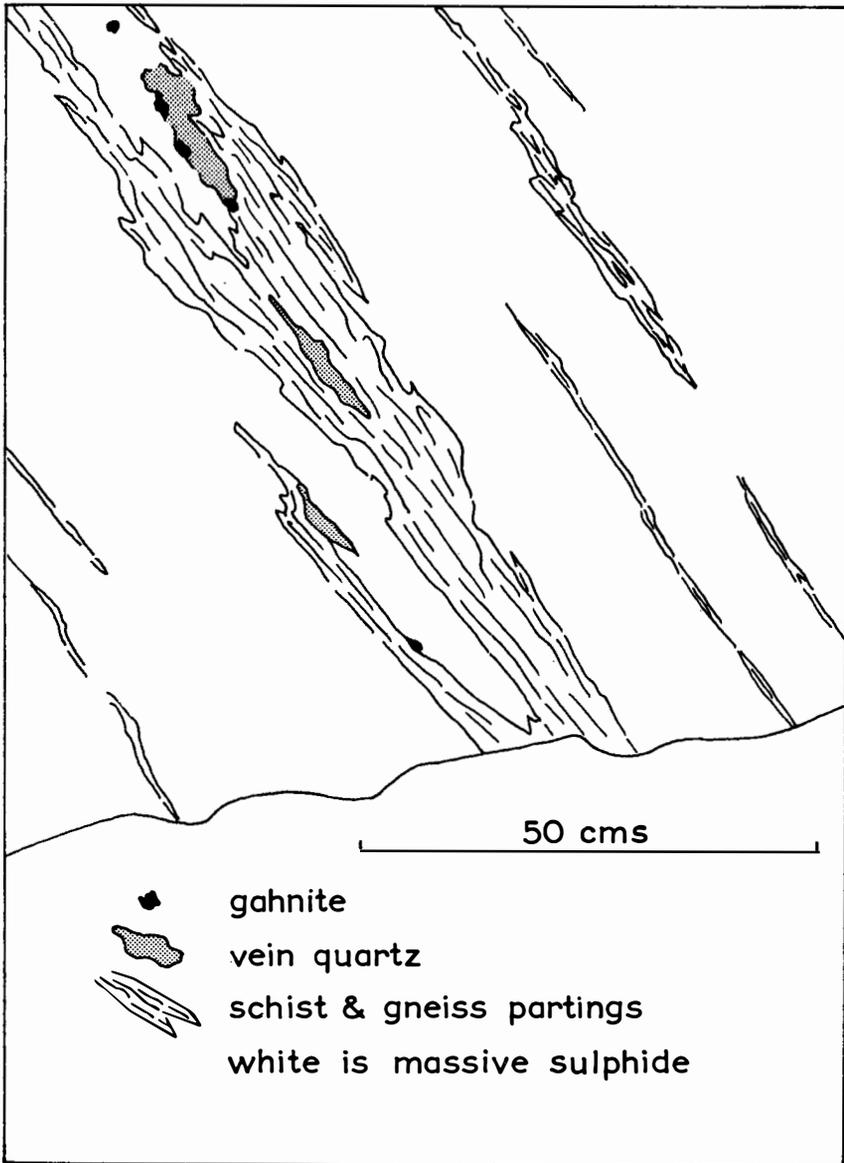


Fig. 1. Sketch of part of stope face, looking south, 330 m level south, 12.7.1960. Central schist parting in massive ore body carrying irregular quartz veins with coarsely crystalline gahnite.

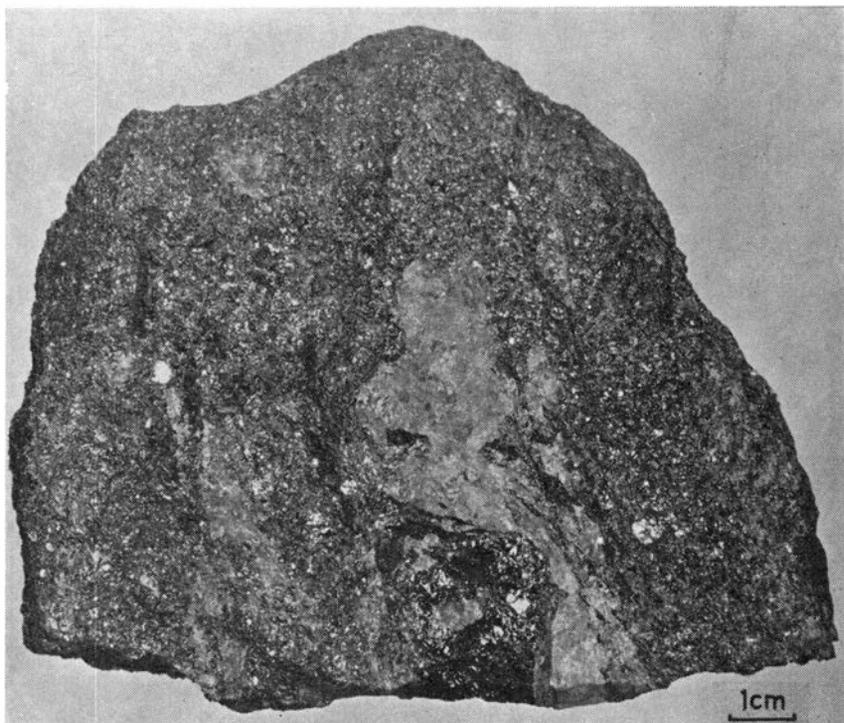


Fig. 2. Photograph of hand specimen from locality sketched in figure 1. Coarsely crystalline gahnite (black, shiny) in irregular vein quartz mass in massive pyritic ore.

gahnite lies in the vein quartz patches. HARANCZYK and SKIBA (op. cit) describe "reaction rims" of chlorite, sericite and secondary sphalerite around the gahnite grains from the Iser mountains. They ascribe these rims to diaphthoretic metamorphism. A similar action is probably responsible for the sphalerite rims round the Bleikvassli gahnite grains.

Apart from the above described large crystals, gahnite is not normally obvious in the ore in situ. One fine exception consisted of a perfect octahedron about 5 mm across which was observed sticking out of the solid ore in the back of the stope in the same general area as the large crystals. Otherwise gahnite is met with occasionally in hand specimens and thin sections, in the latter as subhedral, colourless, high-relief grains. So far the mineral has not been identified in the rocks outside the ore zone at Bleikvassli.

### Chemical composition

Approximately 3 g of gahnite were separated from pieces of ore rich in the mineral by means of heavy liquids and the Franz isodynamic separator. The analysis is given in Table 1, below.

Table 1. Chemical composition of the Bleikvassli gahnite.

	1.	2.	3.	4.
Al <sub>2</sub> O <sub>3</sub> .....	54.20	64.1	15.3	Si, Ca. Cu, Cr, V
Fe <sub>2</sub> O <sub>3</sub> .....	6.35*	4.8	1.1	
ZnO .....	35.80	26.5	6.3	
MnO .....	1.23	1.0	0.2	
MgO.....	2.43	3.6	0.9	
	<u>100.01</u>	<u>100.0</u>	8.5	

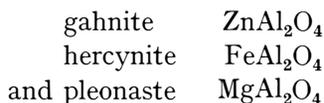
\* total iron.

1. Analysis, weight percent. Analyst, B. Bruun, Mineralogisk Museum.
2. Cation percent.
3. Atomic ratios to 32 0 atoms.
4. Other elements present in trace or minor quantities. (Spectrographically determined).

As can be seen from column 3, the cation ratios do not correspond to the theoretical ratios in gahnite. This indicates that part of the iron assigned to the bivalent positions is actually present in the trivalent positions.

The analysis results also show that, in common with the other natural gahnites which have been analysed, the Bleikvassli mineral is in reality a solid solution of mainly three spinel molecules.

viz.,



The relative amounts of these three molecules may be shown by recalculating the cation percentages Zn + (Fe+Mn) + Mg to 100 percent. In the case of the Bleikvassli material the result of such a recalculation gives

Zn ..... 74.1%, (Fe+Mn) ..... 15.3%, Mg ..... 10.6%.

Strictly a fourth molecule, that of franklinite, ZnFe<sub>2</sub>O<sub>4</sub>, must

also be present as indicated by the necessity of having some ferric iron present along with the aluminium in the trivalent positions.

If one recalculates the analysis to 8 cations in the two-valent positions (i.e. the excess 0.5 cation is regarded as three-valent Fe), the following grouping as arrived at:

Zn	6.3	75.75%
Fe'' + Mn	0.8	10.00%
Mg	0.9	11.25%
	8.0	

Thus the formula of the Bleikvassli gahnite may be given as:



However, since it is not always clear from the published analyses what proportion of the iron is present as Fe<sup>3+</sup>, the first grouping will be adhered to in the following. It has also the advantage that it can be used to represent the "gahnite" compositions on a triangular diagram. (See also PEHRMANN, 1948, p. 333). Such a triangular diagram is presented as Figure 3. On it the Bleikvassli analysis is represented by the point 1. The recalculated published analyses for ten other gahnites are also plotted for purposes of comparison.

VON KNORRING and DEARNLEY (1960, p. 375) suggest that the iron contents in gahnites may be a function of the temperature of formation in the same way as is the iron content of sphalerite. They cite figures for the gahnite and sphalerite from the Rosendal pegmatite, Kimito, Finland, which show that the respective Zn:Fe ratios in the gahnite and sphalerite are 5.4 and 5.6. In order to test this hypothesis in the case of the Bleikvassli occurrence, sphalerite was separated from the material remaining after the removal of the gahnite and was carefully cleaned on the Franz separator and in Clerici solution. The analysis figures for this sphalerite are



The Zn:Fe ratio is therefore 7.7, while the corresponding figure for the gahnite is 6.5. These figures are thus not in agreement as are the Rosendal ones and do not support the contention that the iron content of the gahnite is a function of the temperature of crystallization in a quantitatively parallel manner to that of the iron con-

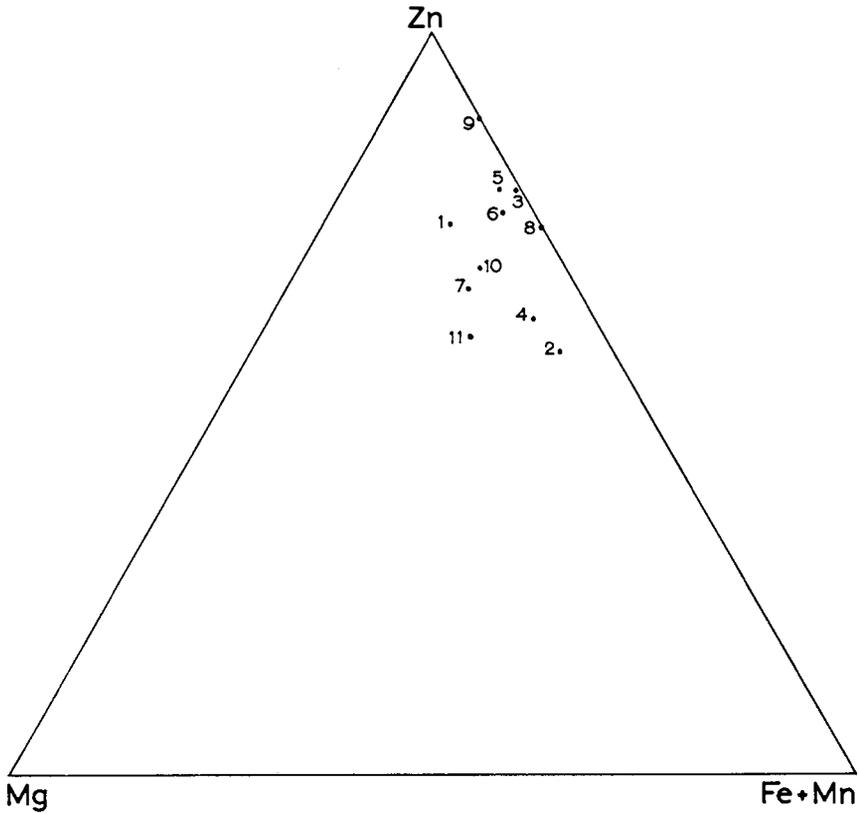


Fig. 3. Triangular diagram representing the composition of eleven analysed natural gahnites in terms of the cation percentages  $Zn + (Fe + Mn) + Mg = 100$ .

1. Bleikvassli, Norway.
2. Stewart I., New Zealand (Hutton, 1957).
3. Chiapaval, South Harris (von Knorring and Dearnley, 1960).
4. Träskböle, Finland (Eskola, 1914).
5. Rosendal, Kimito, Finland (Pehrman, 1948).
6. Malånäs, Västerbotten, Sweden (Gavelin, 1940).
7. Goyamin Pool, W. Australia (Simpson, 1937).
8. Altyn Taou, Kyzyl Kumy central, U.S.S.R. (Sosedko, 1932).
9. Greenbushes, W. Australia (Simpson, 1931).
10. Gillingara, W. Australia (Simpson, 1930).
11. Gierczyn, Lower Silesia (Haranczyk and Skiba, 1961).

tent of the coexisting sphalerite. There does, however, seem to be a more qualitative parallel. The temperature of formation of the sample of Bleikvassli sphalerite as indicated by the ZnS-FeS geother-

momenter is approximately 435°C, which is about 100°C lower than that quoted for the Rosendal sphalerite. Since the Rosendal gahnite is richer in iron than the Bleikvassli gahnite (6.14% as against 4.44%) the probability seems to be present that, like sphalerite, gahnite does form with higher iron contents at elevated temperatures. It may perhaps be pointed out here that the Bleikvassli gahnite contains considerably more Mg (2.43%) than does the Rosendal gahnite (0.19%) so that the two minerals are perhaps not strictly comparable for purposes of geothermometry.

### Physical properties of the gahnite

*Refractive Index.* The refractive index of the Bleikvassli gahnite was determined by means of immersion liquids to be

$$1.793 \pm 0.003.$$

Table 2 shows that the range of refractive indices for eight of the analysed gahnites plotted in figure 3 is from 1.78 to 1.82, which range covers most or all of the other gahnites reported in the literature. The figures show fairly convincingly that increase in refractive index is accompanied by a general increase in the proportion of the gahnite molecule, i.e., in Zn, and a decrease in the proportion of the pleonaste molecule, i.e., in Mg.

Table 2. Showing relation of R. I. to chemical composition of natural gahnites. (Tabulated in order of increasing R. I.)

Locality	Zn	Fe + Mn	Mg	R. I.
Gillingara .....	68.3	21.6	10.1	1.782
Bleikvassli .....	74.1	15.3	10.6	1.793
Stewart I. ....	57.1	36.4	6.5	1.793–1.795
Chiapaval .....	78.7	20.8	0.5	1.795
Gierczyn .....	59.0	25.0	16.0	1.80
Träskböle .....	61.3	31.3	7.4	1.81
Rosendal .....	79.0	18.5	2.5	1.810
Greenbushes .....	88.2	11.8	0.0	1.818

These trends have been previously pointed out in the literature, for example, ANDERSEN and PAYNE (1937) showed that there was a linear relation between the refractive index and the Zn:Mg ratio in

natural spinels. For synthetic material in the series gahnite-pleonaste, KORDES and BECKE (1949) showed a linear relation between refractive index and composition from  $n=1.714$  for pure  $MgAl_2O_4$  to  $n=1.795$  for pure  $ZnAl_2O_4$ . PALACHE, BERMAN and FRONDEL (1954, p. 690) report a value of 1.719 for pure artificial Mg-spinel (RINNE, 1928) and 1.805 for pure artificial Zn-spinel (LARSEN and BERMAN, 1934).

The influence of the hercynite molecule on the refractive indices of natural gahnites is negligible, as would be expected since the refractive index of hercynite (1.800) approaches very nearly that of gahnite and thus variations in composition along the gahnite-hercynite join have next to no effect on the refractive index of the natural mineral.

*Density.* A determination of the density of the sample of gahnite used for the chemical analysis given above was made by the pyknometer method. Three separate determinations gave the following average value,

$$4.492 \pm 0.004$$

The density calculated from the value for the unit cell (see below) and the chemical analysis is 4.444.

Table 3 shows the range of densities for ten of the analysed gahnites plotted in figure 3. This table shows that there is a range from 4.38 to 4.788, but that there is no clear trend of any of the component molecules with increasing density.

Table 3. Showing relation of density to chemical composition of natural gahnites.  
(Tabulated in order of increasing density)

Locality	Zn	Fe + Mn	Mg	density
Gillingara .....	68.3	21.6	10.1	4.38
Goyaminpool .....	65.4	21.8	12.8	4.38
Gierczyn .....	59.0	25.0	16.0	4.44
Stewart I .....	57.1	36.4	6.5	4.46
Träskböle .....	61.3	31.3	7.4	4.478
Altyn Taou .....	73.7	26.3	—	4.49
Bleikvassli .....	74.1	15.3	10.6	4.492
Greenbushes .....	88.2	11.8	—	4.57
Chiapaval .....	78.7	20.8	10.5	4.55
Rosendal .....	79.0	18.5	2.5	4.788

As regards the densities of the pure molecules, the following data are available. CLARK et al (1931) give a value of 4.615 for pure  $\text{ZnAl}_2\text{O}_4$ , while PALACHE, BERMAN and FRONDEL (op.cit., p. 690) report a similar figure of 4.62. For pure artificial hercynite and pleonaste this last source reports values of 4.39 and 3.55 respectively. Thus the maximum density of natural spinels consisting dominantly of the above three molecules should be that of gahnite i.e., 4.62. As can be seen, all but one of the measured densities reproduced in table 3 fall below this figure. The exception is the gahnite from the Rosendal pegmatite, which has a reported value of 4.788. On the face of it, it would not seem possible for a spinel of this type to have a higher density than that of pure  $\text{ZnAl}_2\text{O}_4$ . The anomaly might be explained if a considerable part of the iron present is in the trivalent positions, substituting for part of the aluminium. Meanwhile, the analysis figures for the Rosendal gahnite do not support this supposition and the anomalously high density does not seem explicable.

*Unit cell.* The unit cell of the Bleikvassli gahnite was determined by measurements of an X-ray powder film of the mineral. (9 cm camera Fe radiation). A graphical method (Taylor, Sinclair, Nelson and Riley extrapolation) was used to obtain the most correct value (see AZAROFF and BUERGER, 1958, p. 238). This can be given with considerable confidence as

$$8.099 \pm 0.001. \text{ \AA.}$$

KORDES and BECKE (op.cit.) investigated synthetically the system  $\text{MgAl}_2\text{O}_4 - \text{ZnAl}_2\text{O}_4$  and found that, although refractive index and density show a linear relationship with density, (see above) the unit cell remains constant at a value of 8.067 Å. CLARK et al (op.cit.) give the values for the unit cells of the pure end-members gahnite and hercynite and pleonaste as, respectively,  $8.062 \pm 0.001$  Å,  $8.119 \pm 0.002$  Å, and  $8.086 \pm 0.002$  Å. There is thus a slight difference in the values for pure gahnite obtained by the two groups of workers, and an even greater disagreement in the values for the Mg-end member. Clark's et al value is, however, quoted by PALACHE, BERMAN and FRONDEL (op.cit).

The unit cells of natural gahnites would thus be expected to fall between the values of, approximately, 8.06 Å and 8.12 Å and the few determinations available show this to be so. In addition to the

value for the Bleikvassli gahnite given above, von KNORRING and DEARNLEY (op. cit.) found a value of 8.10 Å for the gahnite from the Chiapaval pegmatite, while HUTTON (1957) gives  $8.104 \pm 0.003$  Å as the unit cell size for this mineral from Stewart Island, New Zealand. HUTTON (op.cit.) also gives a value of  $8.097 \pm 0.004$  Å for an unanalysed gahnite from Japan. HARANCZYK and SKIBA (op.cit.) report a value of 8.155 Å for the Gierczyn gahnite.

Thus the value obtained for the unit cell of the Bleikvassli gahnite agrees well with these values and with those for the pure end-members. ANDERSEN and PAYNE (op.cit.) analysed a spinel from Ceylon which on recalculation can be seen to have following cation percentages:

Fe + Mn . . . . . 3.6, Zn . . . . . 33.3, Mg . . . . . 63.1.

The mineral is therefore predominantly a mixed crystal in the pleonaste-gahnite series and as such would be expected to have a unit cell approaching the value for pure Mg spinel given above. The value obtained by Hutton for this material was in fact  $8.086 \pm 0.003$  Å.

### The origin of the gahnite

The mode of occurrence of the gahnite in the Bleikvassli ore strongly suggests that it is a metamorphic mineral, formed by crystallisation during the Caledonian orogeny. There is no suggestion that it is an originally detrital mineral, introduced into the sediments which gave rise to the metamorphic rocks of the area. Nor is there any evidence to suggest that the gahnite is a late hydrothermal introduction into the ore. The metamorphic rocks included in, and forming the country rocks to, the ore are rich in aluminium minerals, most of them aluminium silicates, comprising micas of several different types, lesser plagioclase and microcline feldspars, garnets, minerals of the zoisite group, and minor staurolite and kyanite.

In such an aluminous environment the formation of aluminates such as minerals of the spinel group is to be expected and is indeed a fairly common occurrence. The formation of a zinc spinel is no doubt governed by the extremely zinc-rich milieu represented by the Bleikvassli ore-body, which has zinc content of between 5 and 10 percent. Practically all this zinc is bound up in sphalerite, a zinc-iron sulphide having approximately 12 percent FeS. The amount of zinc combined in the spinel mineral is minute in comparison with that

combined as a sulphide. The distribution ratio Zn (sulphide) to Zn (oxide) must be of the order of several hundreds of thousands.

Granted that the formation of the spinel is a natural consequence of the regional metamorphism of the aluminous sediments of the area and that enough zinc is available, the entry of the element into this particular mineral may be explained by a consideration of its bonding characteristics. NEUMANN (1949) has explained the mineralogical and geochemical behaviour of zinc by showing that the element practically always occurs in minerals in four coordination due to its tendency to form covalent bonds which are directed in space towards the corners of a tetrahedron. In sphalerite each zinc atom is bound tetrahedrally to four sulphur atoms, while in gahnite the bonding occurs between zinc and four tetrahedrally arranged oxygen atoms. Thus the occurrence of the oxide zinc in the spinel mineral is in accordance with the bonding requirements of the element. Of the other minerals (oxides and silicates) present there are no others in which Zn could take part and still satisfy its bonding characteristics. For example, garnet is quite an abundant mineral in places closely associated with the ore and occasionally forming part of the gangue of the ore. If purely ionic considerations were applicable one would expect the Zn (ionic radius 0.83 Å) to substitute for Fe<sup>2+</sup> (ionic radius 0.83 Å) and perhaps Mn<sup>2+</sup> (ionic radius 0.91 Å) and thus to be completely camouflaged in the garnet. That zinc does not enter the garnet structure to more than a trace extent has been demonstrated by von KNORRING (1946) for the case of the Rosendal pegmatite where garnet occurs completely enclosed in sphalerite. This behaviour is explained by the bonding considerations since Fe and Mn in garnet occur in six-coordination.

If the above explanation of the occurrence of gahnite in the Bleikvassli ore holds, one would expect the mineral in other zinc-rich ore zones in similar metamorphic terrains in northern Norway. One area in which zinc-rich deposits occur in highly aluminous schists in a similar grade of metamorphism is the Håfjell-Bogen district on either side of Ofoten fjord in northern Nordland. As already mentioned, gahnite has been observed in specimens of ore from two deposits in this area and it is to be expected in others as these are examined in detail, a task which is now being undertaken.

## REFERENCES

- ANDERSEN, B. W. and C. J. PAYNE, 1937. Magnesium-zinc Spinel from Ceylon. *Min. Mag.* 24, 547—554.
- AZAROFF, L. V. and M. J. BUEGER, 1958. The powder method in X-ray crystallography. New York. McGraw Hill Co. Inc.
- CLARK, G. L., A. ALLEY and A. E. BADGER, 1931. The lattice dimensions of spinels. *Am. Journ. Sci.*, 22, 539—546.
- ESKOLA, P., 1914. An occurrence of gahnite in pegmatites near Träskböle in Pernio, Finland. *Geol. Fören. i Stockholm förh.*, XXXVI, 1, 25—30.
- GAVELIN, S., 1939. Geology and ores of the Malänäs district, Västerbotten, Sweden. *Sveriges geol. unders.*, Ser. C, No. 424, (Årbok 33, No. 4), 68.
- HARANCZYK, C. and M. SKIBA, 1961. Gahnite from the Tin-bearing zone of Krobica-Gierczyn-Przecznica in Lower Silesia. *Bull. acad. polon. sci.*, IX, 3 149—154.
- HUTTON, C. O., 1957. Contributions to the mineralogy of New Zealand, Part IV. *Trans. Roy. Soc. N.Z.*, 84, 791—803.
- KNORRING, O. VON, 1946. On a manganese garnet enclosed in sphalerite from Kimito in S. W. Finland. *Comp. Rend. Soc. Geol. Finlande*, 19, 77—87.
- KNORRING, O. VON and R. DEARNLEY, 1960. The Lewisian pegmatites of South Harris, Outer Hebrides. *Min. Mag.*, 32, 248, 366—378.
- KORDES, E. and H. BECKER, 1949. Spinellmischkristalle des Systems  $MgAl_2O_4$  —  $ZnAl_2O_4$ . *Zeitschr. anorg. Chemie*, 258, 227—237.
- NEUMANN, H., 1949. Notes on the mineralogy and geochemistry of zinc. *Min. Mag.*, 27, 205, 575—581.
- PALACHE, C., H. BERMAN and C. FRONDEL, 1944. Dana's System of Mineralogy. Seventh Edition. Volume I. New York. John Wiley & Sons.
- PEHRMAN, G., 1948. Gahnit von Rosendal auf Kimito, SW Finland. *Bull. Geol. Inst. Univ. Upsala*. XXXII, 329—336.
- RINNE, F., 1928. Morphologisch und physikalisch-chemische Untersuchungen an synthetischen Spinellen als Beispiel unstöchiometrisch zusammengesetzter Stoff. *Neues Jhrb. Min. Beilage*, 58, Abt. A, 43—108.
- SEGNIT, E. R., 1961. The petrology of the zinc lode, New Broken Hill Consolidated Ltd., Broken Hill, N.S.W. *Proc. Aust. Inst. Min. Met.* 199.
- SIMPSON, E. S., 1930. Contributions to the mineralogy of Western Australia. Series V. *Journ. Roy. Soc. W. Aust.*, 16, 25—40.
- 1931. Contributions, etc. Series VI. *ibid*, 17, 137—148.
- 1937. Contributions, etc. Series X. *ibid*, 23, 17—35.
- SOSEDKO, A. F., 1932. Les pegmatites d'Altyn Taou (Kyzyl-Kumy central). *Comp. Rend. Acad. Sci. URSS*. 1932, 251—259.
- SØRBYE, R. C., (1950) Geological Studies in the northeastern part of the Hauge-sund peninsula, Western Norway. *Universitetet i Bergen, Årbok* 1948, naturvit. rekke, No. 6, p. 59.
- VOKES, F. M., 1960. Contributions to the mineralogy of Norway. No. 7. Cassiterite in the Bleikvassli ore. *Norsk Geol. tidss.* 40, 193—201.

Accepted for publication June 1962.

Printed December 1962.