Annales de la Société Géologique de Belgique, T. 100, 1977, pp. 199-201

GAHNITE OF THE VENN-STAVELOT MASSIF AND ITS PETROLOGIC SIGNIFICANCE (*)

by U. KRAMM, Köln (**)

ABSTRACT.- In the Salm valley, 1,8 km south of Vielsalm, Luxemburg province, Belgium, low-grade metamorphic rocks with a viridine-braunite-muscovite-quartz paragenesis contain gahnite with a composition of gahnite₈₈ -Mg-spinel₁₀-galaxite₂. This spinel is the richest in zinc, known thus far from quartz-bearing slates. It is assumed for the stability of spinel-quartz assemblages that under decreasing métamorphic conditions increasing zinc contents of the spinel are necessary.

RESUME.- Dans la vallée de Salm 1,8 km au sud de Vielsalm, Prov. Luxembourg, Belgique, des roches à paragenèse viridine-braunite-muscovite-quartz contiennent de la gahnite dont la composition est gahnite₈₈-Mg-spinelle₁₀ -galaxite₂. Ce spinelle est le plus riche en zinc connu jusqu'à présent dans des schistes métamorphiques contenant du quartz. On prétend que, pour la stabilité de la paragenèse spinelle-quartz, dans des conditions métamorphiques décroissantes, un contenu croissant en zinc du spinelle est indispensable.

OCCURRENCE, MINERALOGY AND CHEMISTRY

South of Vielsalm, Prov. Luxemburg, Belgium, the valley of river Salm cuts an Ordovician syncline of manganese rich low-grade metamorphic slates (estimated metamorphic conditions : 2 kb, 400° C). Here, in the lower part of the Upper Salmian stratigraphical sequence (Salm 2), gahnite bearing viridine rocks are exposed. The outcrops are confined to the western slope of the Salm valley, 350 m N of the church of Salmchâteau (1 : 25000 map : No. 56/5-6, Bovigny – Thommen, Lambert coordinates : 259620-107710). As far as known, this is the first locality of the Venn-Stavelot Massif, from where gahnite is recorded.

The green zinc spinel forms idiomorphic octahedra, which are always included in the viridine porphyroblasts. The grains have sizes of $8 - 10 \ \mu\text{m}$. Despite of its scarcity, up to now there were found only 8 grains in 3 polished thin sections, the mineral is easy

- (*) Communication présentée et manuscrit déposé le 7 juin 1977.
- (**) Mineralogisch-Petrographisches Institut der Universität, D 5 Köln-1, Zülpicher Str. 49, Germany.

to find by its excellent bright red fluorescence color. The chemistry of the spinel, determined by microprobe analysis (ARL-microprobe EMX, operating conditions : 15 KV, beam current - time integration, corrections for mass absorption and secondary fluorescence after ALBEE & RAY, 1970), indicates a solid solution between pure Zn-spinel and Mg-spinel (Table 1). According to the general oxidation state of the rocks iron in the spinel is assumed to be in its trivalent state. Manganese, in contrast, is assumed to be in its divalent state in the gahnite thus forming a small amount of galaxite molecule. In the rock, manganese is present both in its di- and trivalent state as demonstrated by the presence of braunite (HERBOSCH, 1967). Since, however, braunite is involved in the viridine formation (KRAMM, 1973) according to the reaction and since there are no large scale oxidation

kaolinite + braunite = viridine + spessartine + quartz

 $+ H_2 0$

effects in the rocks, there is an excess amount of divalent manganese during the viridine formation, which, in part, is used for a simultaneous spessartine formation. A small amount of this divalent manganese is assumed to be present in the spinel phase.

Shape and distribution of the gahnite within the viridine grains show that this mineral is a metamorphic new formation. Its growth can be discussed together with the viridine formation. Assuming a zinc ontent of the sedimentary starting materials of the viridine, braunite and kaolinite, this element was not incorporated into the reaction products, either quartz or viridine. Thus, after zinc enrichment, it was possible to form gahnite out of this zinc and additional alumina, e.g. of the kaolinite. Such a reaction results in an additional quartz formation :

Zn-content + kaolinite = gahnite + quartz + H_20 .

According to this type of formation gahnite is compatible with the whole viridine assemblage including phengite, paragonite, chlorite, garnet, hematite, braunite, rutile and especially quartz although it is isolated in the viridine now.

TABLE 1.- Chemical composition of gahnite

	Ethinis	Number of cations on the basis of 16 oxygens	
, ZnO	39.70	Zn	3.515
Mn0	0.76	Mn	0.077
Mg0	2.32	Mg	0.415
Co0	++		
NiO	+		4.007
Al_20_3	55.74	Al	7.875
Fe ₂ 0 ₃	1.32	Fett	0.119
			
	99.84		7.994

GEOCHEMICAL ENVIRONMENT

A zinc content of the host rocks is the necessary condition for the formation of a zinc spinel. Most occurrences of gahnite in metamorphic schists are connected to zinc ore deposits (NEMEC, 1973), where zinc is available in excess amounts. This, however, is not necessary for the formation of gahnite as is demonstrated by the viridine rocks investigated. They contain 50 ppm Zn and hence are the rocks with the lowest zinc content so far recorded for the Upper salmian Series of the Venn-Stavelot Massif (Table 2). Similar or higher amounts of zinc can be found in nearly all pelitic sediments. Since, on the other hand, gahnite is a very rare component in metamorphic shales there must be factors others than the zinc content that rule the spinel formation. Beside a high and easily available alumina content, usually present by large amounts of clay minerals, the restricted substitution of zinc in other phases seems to be of main importance.

TABLE 2.- Zn-contents of Upper Salmian rocks

Viridine schist	Salm valley	50 ppm Zn
Green ottrelite schist	Vielsalm	109 ppm Zn
Violet ottrelite schist	Ottré	134 ppm Zn
Andalusite schist	Regné	123 ppm Zn
Andalusite schist	Recht	89 ppm Zn
Ottrelite schist	Recht	150 ppm Zn
Blue hematite schist	Konzen/Germany	139 ppm Zn
Green ottrelite schist	Konzen/Germany	199 ppm Zn

PETROLOGIC SIGNIFICANCE

Spinels can be formed under low as well as under high grade metamorphic conditions. There are no p -T stability limits. Assemblages of Mg-Spinel - hercynite solid solutions with quartz, however, are only compatible under granulite type conditions. Yet, this rigorous restriction of the assemblage is cancelled if zinc is introduced into the spinel phase. Obviously zinc has a stabilizing effect here (FROST, 1973). In regional metamorphic zinc ores and their neighboring gneisses or quartz bearing schists gahnite is not uncommon (FROST, 1973, NEMEC, 1973). Comparing the chemistry of these gahnites the zinc spinel of the Venn-Stavelot Massif is by far the richest in zinc and the poorest in total iron (Fig. 1). It is assumed that this extreme chemistry can be interpreted by the very low-grade formation conditions of gahnite in the area of Vielsalm. The lowest formed gannite so far known with its highest zinc content implies that the continuation of the compatibility relation between quartz and spinel under decreasing p - T conditions is possible only by increasing incorporation of gannite molecule into the spinel phase.

The importance of the hercynite molecule and especially its absence in the gahnites of the Venn-Stavelot Massif cannot be discussed in detail since only little is known about the distribution of iron among its di- and trivalent state in the zinc spinels of the high-grade metamorphic schists and gneisses. Experimental investigations under high-grade metamorphic conditions show that the presence of quartz stabilizes the almandine – sillimanite assemblage of the reaction

Hercynite + quartz = almandine + sillimanite



FIGURE 1.- Chemical composition of zinc containing spinels. After NEMEC (1973) total iron is calculated to Fe0 to form a hercynite molecule. Genetical types : open circles – pegmatites, filled circles – quartz free basic metamorphic rocks of skarn type, open squares – marbles, open triangles – rich zinc ores in acid regional metamorphic rocks, filled triangle – viridine rock of the Venn-Stavelot Massif. Figure after NEMEC (1973).

(RICHARDSON, 1968). It can be supposed that, under decreasing metamorphic conditions, a spinel – quartz assemblage can continue its compatibility only by decreasing the amount of hercynite molecule in the spinel phase.

Galaxite, the manganese equivalent of gahnite, cannot be expected to be discovered in the rocks of the Venn-Stavelot Massif, since quartz, which is always present, and galaxite are incompatible under the metamorphic conditions realized (DASGUPTA et al. 1974). Instead of this assemblage there can be found quartz assemblages with carpholite or ottrelite, both of which lie on the join quartz – galaxite assuming excess water contents. Beyond that the viridine rocks give a chance to find Mn-cordierite, another phase on the join quartz – galaxite under excess water. Up to now this mineral, which is stable only up to 400° C/ 1kb, is not known from natural occurrences (DAS-GUPTA et al. 1974).

REFERENCES

- ALBEE, A.L., RAY, L. (1970) Correction factors of electron probe microanalysis of silicates, oxides, carbonates, phosphates and sulphates. Anal. Chem. 42, 1408 – 1414.
- DASGUPTA, H.C., SEIFERT, F., SCHREYER, W. (1974)
 Stability of manganocordierite and related phase equilibria in part of the system Mn0 Al₂O₃ SiO₂ H₂O. Contr. Mineral. Petrol. 43, 275 294.
- FROST, B.R. (1973) Ferroan gahnite from quartz-biotitealmandine schist, Wind River Mountains, Wyoming. Am. Mineralogist 58, 831 - 834.
- HERBOSCH, A. (1967) La viridine et la braunite de Salm-Chateau. Bull. Soc. belge Géol., 74, 183 – 202.
- KRAMM, U. (1973) Chloritoid stability in manganese rich low-grade metamorphic rocks, Venn-Stavelot Massif, Ardennes. Contr. Mineral. Petrol. 41, 179 - 196.
- NEMEC, D. (1973) Das Vorkommen der Zn-Spinelle in der Böhmischen Masse. Tschermaks Min. Petr. Mitt. 19, 95 - 109.
- RICHARDSON, S.W. (1968) Staurolite stability in a part of the system Fe - Al - Si - 0 - H. J. Petrology 9, 467 - 488.

ACKNOWLEDGEMENT

I am very grateful to Dr. A.-M. FRANSOLET, Liège, who critically read the manuscript.