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Rare mineral assemblages in manganese-rich metasediments of the Stavelot Massif, Belgium

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Introduction and geological context

The Stavelot Massif is a large geological unit located at the East of Belgium (Fig. 1), and constituted by Cambro-Ordovician rocks. Three different lithostratigraphic groups are defined in this area: the Deville Group characterized by greenish to grey quartzites of Lower Cambrian age; the Revin Group formed by dark grey to black schists and quartzites of Middle to Upper Cambrian age; the Salm Group showing schists of Lower to Middle Ordovician age. In the middle part of the Salm Group occurs the Ottré Formation, characterized by a very unusual geochemistry dominated by iron and manganese. Depending on the oxidation degree of these rocks, as well as on their mineralogical contents, the Ottré Formation is further divided in three members: the Meuville Member showing very oxidized red schists containing manganese oxides, the Les Plattes Member with purple schists of intermediate oxidation degree and containing *coticule* layers, and the Colanhan Member characterized by weakly-oxidized grey chloritoid-bearing schists.

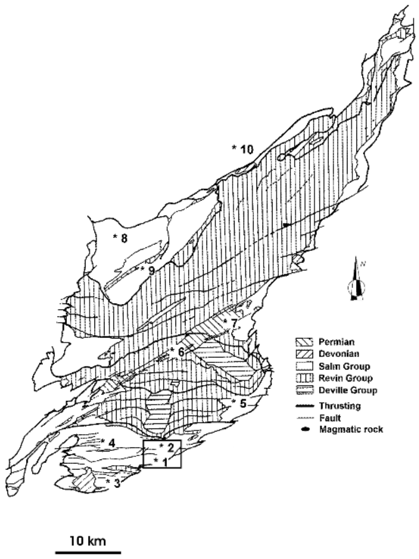


Fig. 1. Simplified geological map of the Stavelot Massif. (1) Salmchâteau, (2) Vielsalm, (3) Bihain, (4) Lierneux, (5) Recht, (6) Stavelot, (7) Malmedy, (8) Theux, (9) Spa, (10) Eupen.

The term *coticule* has been defined in the area to designate a whetstone constituted by tiny spessartine crystals (ca. 5-10 µm in diameter) enclosed in a matrix of phyllosilicates. These rocks occur in the Les Plattes Member (Fig. 2A), where it was mined for centuries, but very similar rocks named *pseudocoticules* occur in the Colanhan Member (Baijot *et al.*, 2011; Fig. 2B). These *pseudocoticules* also show spessartine grains, but of larger size (up to 50 µm in diameter), and enclosed in a matrix of quartz.

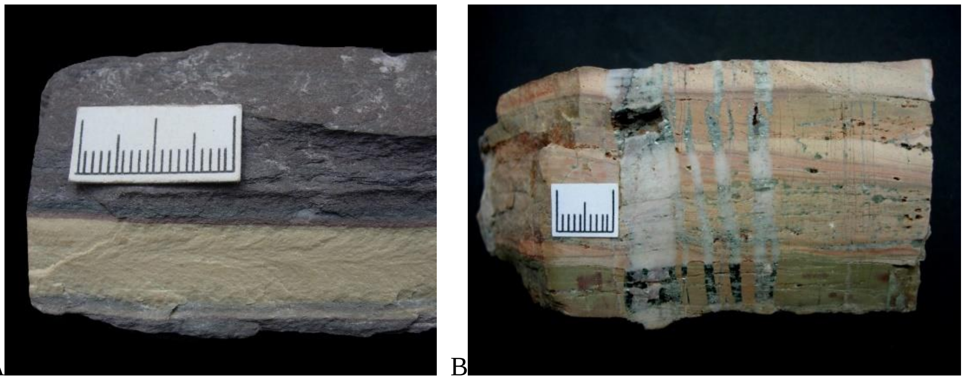


Fig. 2. A. Coticule layer (yellow) occurring in the red schists of the Les Plattes Member. B. Layer of pinkish pseudocoticule found in the Colanhan Member, and crosscuted by quartz veins.

Variscan metamorphism in the Southern part of the Stavelot Massif

Mineral assemblages occurring in the rocks of the Ottré Formation allowed to estimate the metamorphic conditions prevailing in the Southern border of the Stavelot Massif. These rocks outcrop mainly in two valleys: the Salm valley, with the localities of Vielsalm, Salmchâteau, Bihain, Ottré, Sart, and Regné, and the Lienne valley with the localities of Lierneux, Chevron, Bierleux, and Moët-Fontaine.

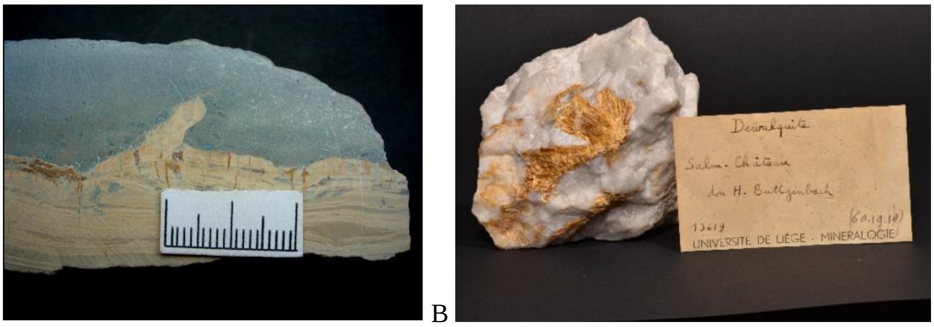
In the Salm valley, the Ottré Formation is well exposed, and the three different members can easily be distinguished. The presence of the rhodochrosite + quartz assemblage, as well as the absence of rhodonite, indicate temperature and pressure conditions of 360-420°C / 2 kbar (Kramm, 1982). These conditions produced several metamorphic minerals, as for example spessartine, chlorite, hematite, andalusite, and Mn-rich chloritoïd sometimes approaching the ottrelite end-member.

In the Lienne valley, the Ottré Formation is not so developed: the Colanhan Member seems to be absent, and the Meuville and Les Platte members are difficult to distinguish. In this area, we observe red schists that contain meter-sized layers of manganese ore, which was mined until the Second World War; at a few meters of these ores occur tiny layers of *coticule*. The presence of carpholite [$Mn^{2+}Al_2Si_2O_6(OH)_4$] in those red schists indicates metamorphic conditions lower that those occurring in the Salm valley. According to Theye *et al.* (1996), these conditions are close to 300°C and 1-2 kbar.

Genesis of coticule and pseudocoticule

Rocks of the Ottré Formation are extremely enriched in iron and manganese, and these two chemical elements occur in variable amounts. For example, *coticule* layers are particularly rich in manganese, the reason why spessartine crystals occur in these rocks. On the other hand, the red schists enclosing *coticule* layers are iron-rich, thus explaining their color produced by the presence of hematite.

The geochemical investigation by Krosse & Schreyer (1993) revealed that both sediments originated from the same source, since the trace elements occurring in the *coticules* and in the red schists show the same fingerprints. The origin of these elements is hydrothermal, indicating that probably, both iron and manganese were produced by submarine hydrothermal springs. These exhalations are certainly correlated to the magmatic rocks found in direct contact with the coticule (Fig. 3A). According to Baijot *et al.* (2011), the origin of *pseudocoticule* in the Colanhan Member is certainly comparable.



A B

Fig. 3. A. Magmatic rock (grey), occurring in direct contact with the coticule (yellow). B. Sample of ardennite-(As) (yellow fibers) included in quartz from Salmchâteau (collection ULiège n° 13619).

The reason why iron and manganese are separated in different layers is still unclear. Indeed, some authors (Lamens *et al.,* 1986) identify sedimentary textures typical of density currents, thus explaining the manganese-rich layers by turbiditic deposition processes. However, a more realistic model was developed by Krosse & Schreyer (1993), who suggested that Eh-pH variations in the sedimentary basin would lead to a periodical precipitation of manganese oxides, thus producing manganese-rich coticule layers during metamorphism. These variations of Eh-pH conditions would be produced by periodical flux and influx of water in a relatively closed sedimentary basin, as observed actually in some area of the Baltic see.

Quartz vein mineralizations

The quartz veins crosscutting rocks of the Ottré Formation show a very unusual mineralogy. Indeed, the manganese-rich sediments, coupled with a very low metamorphism that affected the area during the Variscan orogeny, produced a plethora of rare minerals. Most quartz veins show a simple mineralogy, with quartz, hematite, and chlorite. But some of them may contain other species as for example ottrélite [$Mn^{2+}{}_2Al_4(Si_2O_{10})(OH)_4$], the manganese equivalent of chloritoid which was defined in the locality of Ottré. Other rare species were first described in the quartz veins of the Stavelot Massif, as for example davreuxite [$Mn^{2+}Al_6(Si_4O_{17})(OH)_2$], a manganese aluminosilicate structurally related to sillimanite, as well as ardennite-(As) [$Mn^{2+}{}_4(Al,Mg)_6(SiO_4)_2(Si_3O_{10})[AsO_4](OH)_6$], which was named for the Ardenne mountains (Fig. 3B).

The mineralogy of the quartz veins is sometimes strictly correlated with the geochemistry of the enclosing rocks. For example, in the extremely oxidized Meuville Member occur quartz veins containing manganese oxides, as for example lithiophorite, cryptomelane, nsutite, hollandite-strontiomelane, pyrolusite, and braunite. In those quartz veins was defined stavelotite-(La) [$La_3Mn^{2+}{}_3Cu(Mn^{3+},Fe^{3+},Mn^{4+})_{26}(Si_2O_7)_6O_{30}$], a species with one of the most complex crystal structure known in the mineral kingdom (Bernhardt *et al.*, 2005).

In the Colanhan Member, characterized by a low oxidation degree, occur quartz veins mineralized with copper sulfides (Hatert, 2003, 2005). It seems that the source for copper is constituted by the pseudocoticules occurring in those rocks. The primary sulfides crystallizing in these veins are bornite, chalcocite, and chalcopyrite, but they progressively transform to supergene sulfides like covellite, idaite, digenite, djurleite, anilite, spionkopite, and yarrowite. Tiny mineral inclusions in the copper sulfides are constituted by tellurides as for example native tellurium, melonite, tellurobismuthite, and altaite. The presence of these minerals, which are generally a signature for a magmatic origin, confirm that the pseudocoticule are probably related to the hydrothermal exhalations produced by the volcanic rocks observed in the area.

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