Formation of the oxidized manganiferous rocks of the Les Plattes Member (Ottré Formation, Salm Group) in the Stavelot Massif: timing and weathering processes

Augustin DEKONINCK[1], Patrick MONIÉ[2], Frédéric HATERT[4], Sabine BLOCKMANS[1,3], Gaëtan ROCHEZ[1], Johan YANS[1]

1 Institute of Life-Earth-Environment (ILEE), University of Namur, 61 rue de Bruxelles B-5000, Namur Belgium.
2 Géosciences Montpellier, UMR-CNRS 5243, Université de Montpellier, Montpellier, France
3 Service géologique de Wallonie, DGO3, Service public de Wallonie, 14 Avenue Prince de Liège B-5100, Jambes, Belgium.
4 Laboratoire de Minéralogie, Université de Liège, 14 allée du six août B-4000, Liège, Belgium.

1. Introduction

Intense and long-term chemical weathering have produced numerous economic manganese deposits worldwide, which have supplied the steel industry for decades. The base of the Lower to Middle Ordovician red and purple slates of the Les Plattes Member (Ottré Formation, Salm Group) at the southern part of the Stavelot Massif are particularly enriched in manganese. These levels were mined until the first half of the 21th century, but are known worldwide for their coticule veins, a metasedimentary yellowish rock composed of fine-grained spessartine, quartz and muscovite (e.g. Baijot et al. 2011; Herbosch et al. 2016). These strata have undergone weathering processes leading to the formation of supergene Mn-oxides. The investigation proposed here focuses on the weathering processes and the timing of those sediments.

2. Geological settings

2.1. Tectonic of the Stavelot Massif

The Stavelot Massif is the largest and best-exposed lower Paleozoic inlier of Belgium and belongs to the Ardennes allochthon, which is part of the Rheno-hercynian fold-and-thrust belt. The Massif has been strongly tectonized by the Caledonian and Variscan orogenic cycles. A graben, filled by Permian conglomerates, delimits two structural domains: the southern part of the Massif records an epizonal metamorphism, when the northern part corresponds to an anchizonal zone (e.g. Herbosch et al. 2016). It has been suggested that Tertiary uplift of the Ardennes started with large scale tilting during Paleocene, after a very long period of tectonic quiescence during the Mesozoic (e.g. Demoulin et al. 2018).

2.2. Location and features of the manganiferous levels

Two locations expose the Fe-Mn-bearing strata: in the Salmchâteau syncline (epizonal zone) and the Chevron syncline (anchizonal zone). The Les Plattes Member consists of red and purple slates interbedded with coticule beds. The slates are composed of quartz grains, laminated and disseminated hematite, and variable content of spessartine in a clayey matrix. The yellowish coticule levels are devoid of hematite but contain larger amount of spessartine associated with quartz and clays (Baijot et al. 2011; Herbosch et al. 2016). Metamorphic transformations of the Ottré Formation has led to the formation of slates and quartz veins containing spessartine, rhodochrosite, Mn-chloritoïd, andalusite-kanonaite, pyrophyllite, paragonite, kaolinite and chlorite in the Salmchâteau syncline, as well as manganese oxides, manganese aluminosilcates, and copper sulphides (Hatert, 2003, 2005; Blondieau et al., 2017). Differences exist in the

Chevron syncline and are mostly attributed to the variation in metamorphic grades. Therefore, andalusite-kanonaite, pyrophyllite and kaolinite are absent in the northern area (Chevron syncline), when rhodochrosite is scarce in the Salmchâteau area (south).

3. Weathering transformations and timing

Manganese oxides are known as late weathering products of Mn-carbonates and, possibly, Mn-rich silicates. Most of these oxides are often considered together as massive botroyoidal "psilomelane" or soft fine-grained "wad" disseminated in the host slates or in quartz veins. The main Mn-oxide phases are cryptomelane and lithiophorite, which are associated with small amounts of manganite, pyrolusite and ramsdellite. Groutite, hausmannite, hollandite-strontiomelane, nsutite and todorokite have also been described (Hatert et al., 2014; Blondiau et al. 2017).

Scanning electron views show that spessartine is poorly or even non-weathered both in coticule and slates. The Mn-oxides are rather located in the clayey matrix. Some of these clay minerals could contain some Fe and Mn in their structure. However, the small amount of Mn substituted in the clayey lattice is probably not sufficient to provide large amount of Mn-oxides. The observation of nsutite by Fransolet (1979) could indicate the presence of primary Mn-carbonates, as nsutite is often associated with Mn-carbonates and results from the weathering of rhodochrosite. New $^{40}Ar/^{39}Ar$ dating of pure cryptomelane samples indicate the major weathering period(s) to be Oligocene-Miocene in age. Some older periods (Cretaceous?) cannot be excluded, as they are common in other weathered deposits of the Ardenne (e.g. Demoulin et al. 2018) and suspected in some discordant $^{40}Ar/^{39}Ar$ spectra. A recent weathering phase is also reported between 5-1 Ma and could then correspond to the current weathering of the Stavelot Massif.

References

Baijot, M., Hatert, F. & Fransolet, A.-M., 2011. Mineralogical and geochemical study of pseudocoticule from the Stavelot Massif, Ardennes (Belgium), and redefinition of coticule. European Journal of Mineralogy, 23, 633-644.

Blondieau, M., Puccio, S., Compère, P & Hatert, F., 2017. Données nouvelles sur quelques espèces minérales de Vielsalm et Salmchâteau (Province de Luxembourg, Belgique). Bulletin de la Société Royale des Sciences de Liège, 86, 1-48.

Demoulin, A., Barbier, F., Dekoninck, A., Verhaert, M., Ruffet, G., Dupuis, C. & Yans, J., 2018. Erosion Surfaces in the Ardenne–Oesling and Their Associated Kaolinic Weathering Mantle, in: Demoulin, A. (Ed.), Landscapes and Landforms of Belgium and Luxembourg. Springer International Publishing, Cham, pp. 63–84.

Fransolet, A.-M., 1979. Occurences de lithiophorite, nsutite et cryptomélane dans le massif de Stavelot, Belgique. Annales de la Société Géologique de Belgique 102, 303–312.

Hatert, F., 2003. Occurrence of sulphides on the bornite-idaite join from Vielsalm, Stavelot Massif, Belgium. European Journal of Mineralogy, 15, 1063-1068.

Hatert, F., 2005. Transformation sequences of copper sulfides at Vielsalm, Stavelot Massif, Belgium. Canadian Mineralogist, 43, 623-635.

Hatert, F., Blondieau, M., Puccio, S., Baijot, M. & Gustine, C., 2014. Le gisement de manganèse de la Vallée de la Lienne, Belgique. Le Règne Minéral, 117, 5-24.

Herbosch, A., Liégeois, J.-P. & Pin, C., 2016. Coticules of the Belgian type area (Stavelot-Venn Massif): Limy turbidites within the nascent Rheic oceanic basin. Earth-Science Reviews 159, 186–214.