Université de Liège
Faculté des Sciences
Département de Géologie
Laboratoire de Minéralogie

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

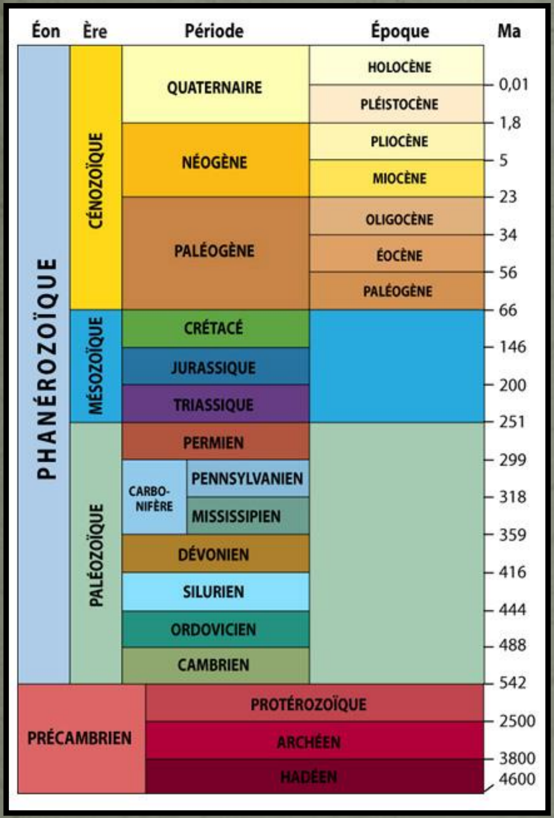
Bielawa, October 21st, 2023
Prof. Frédéric Hatert

Plan of the talk

- **Geology of the Stavelot Massif**
- **Metamorphic mineral assemblages**
- **Coticule and pseudocoticule**
- **Mineralogy of the quartz veins**

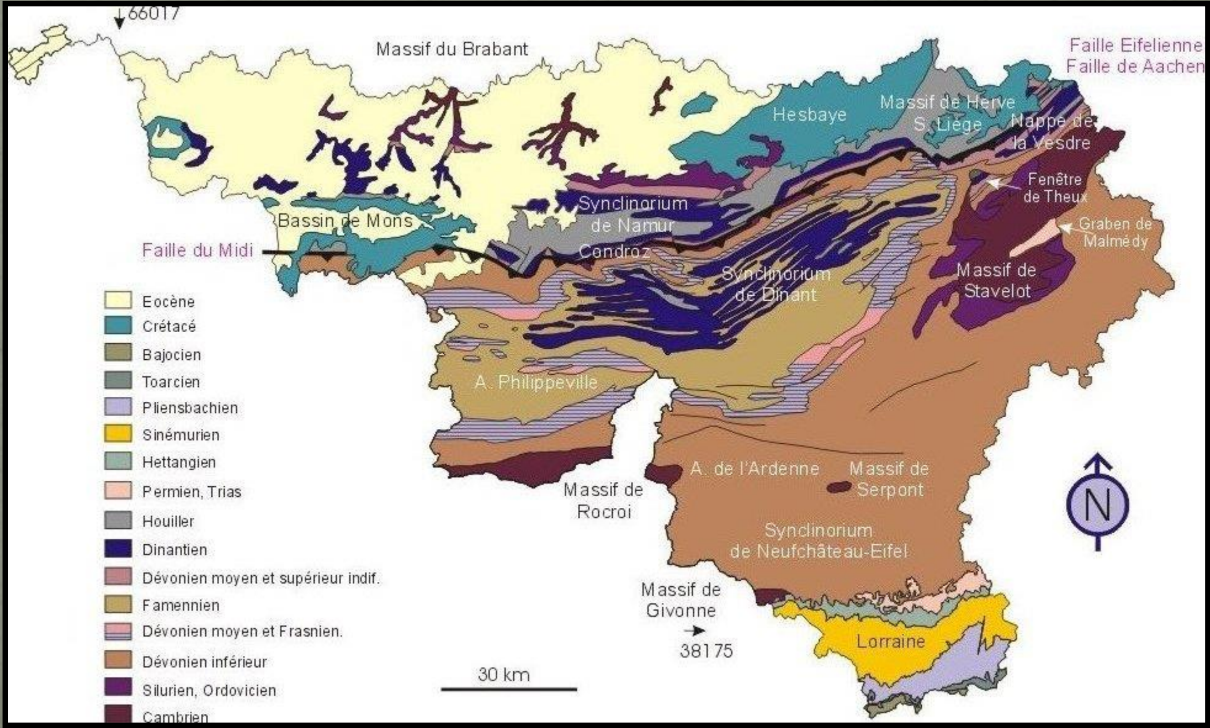
Geology | µ assemblages | Coticules | Quartz veins

Geology of Belgium

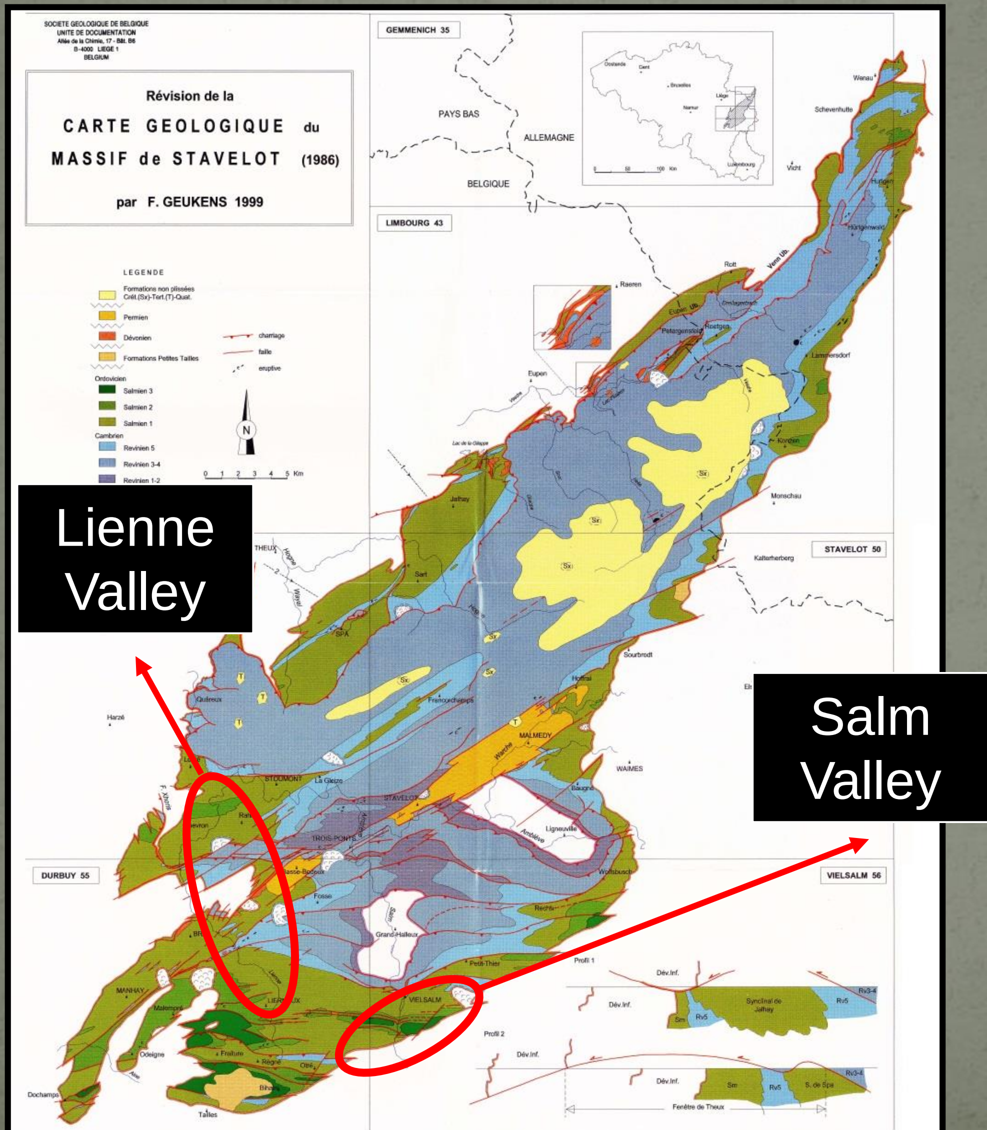


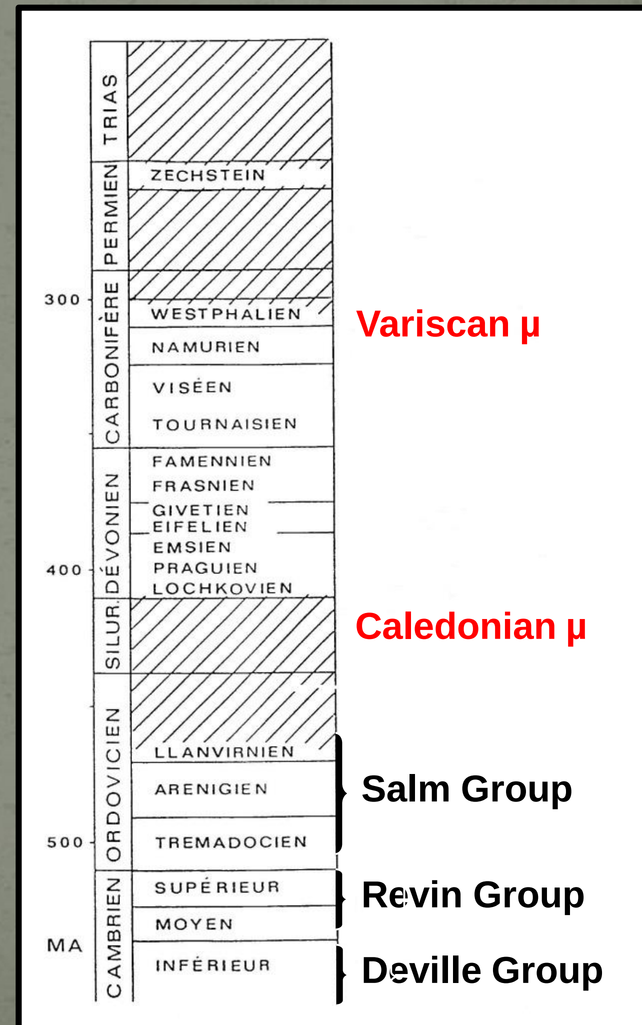
Cambro-Ordovician Massifs:

Stavelot, Rocroi, Serpont, Givonne



The Stavelot Massif





Caledonian metamorphism

- Estimated by Ferket et al. (1998)
- Fluid inclusions in quartz veins

- Age: ~ 430 My
- T = 200-350°C
- Overprinted by Variscan metamorphism

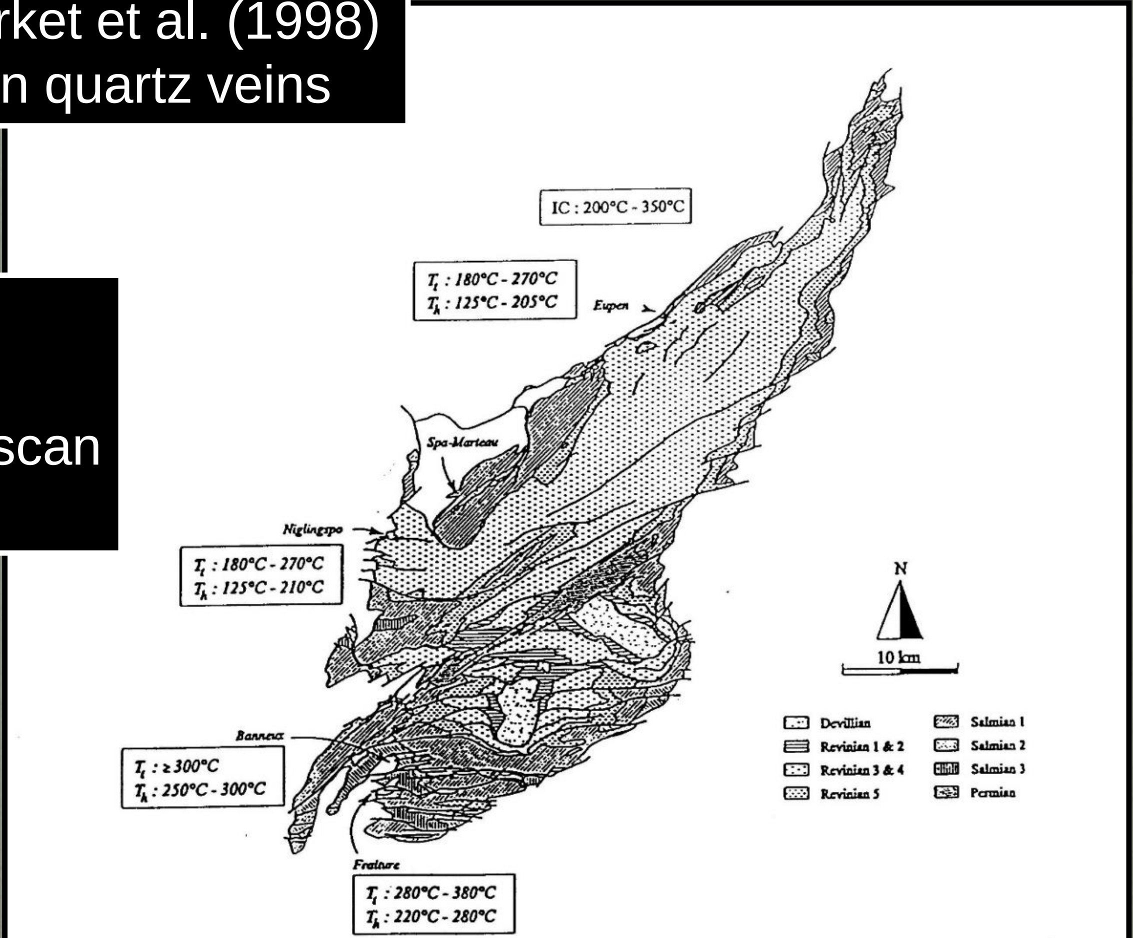
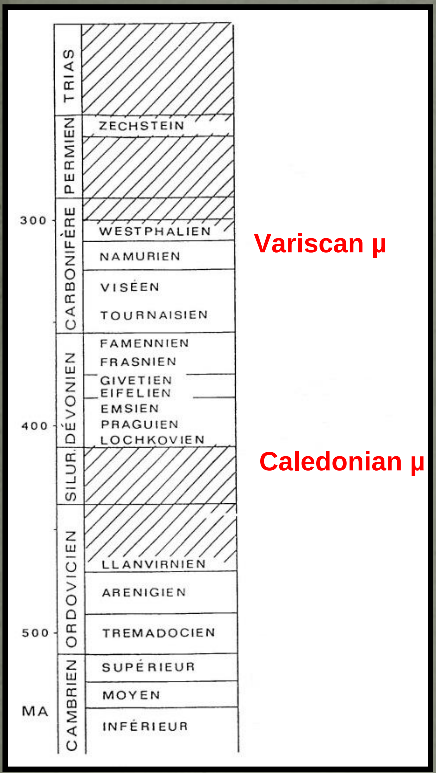


Fig. 3. Thermal conditions during the Caledonian orogeny in the Stavelot-Venn Massif. I.C.: illite crystallinity, T_h: total homogenisation temperatures of fluid inclusions, T_t: trapping temperatures of fluid inclusions.

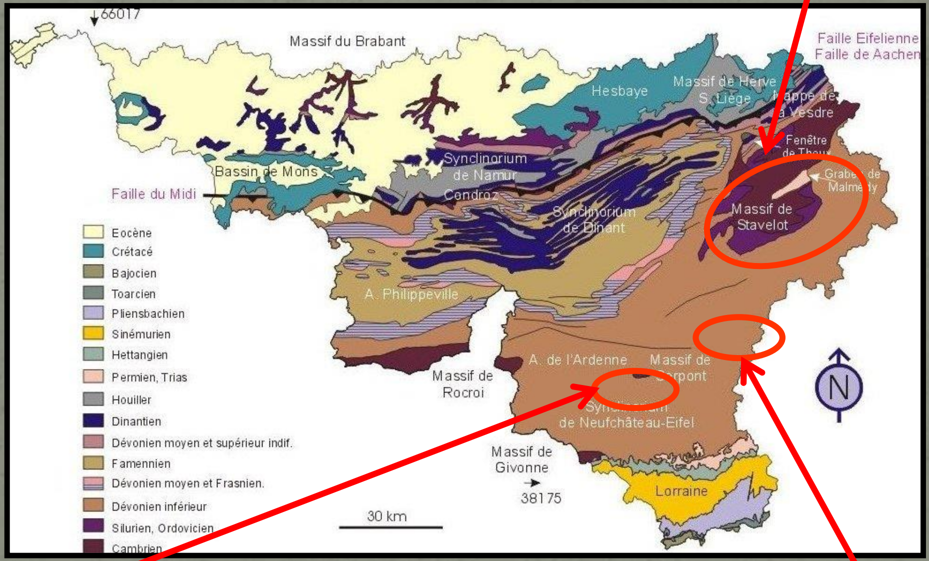
Variscan Metamorphism



Salm Valley
- Kramm et al. (1985)
- Rhodochrosite + quartz

Lienne Valley
- Theye et al. (1996)
- Carpholite

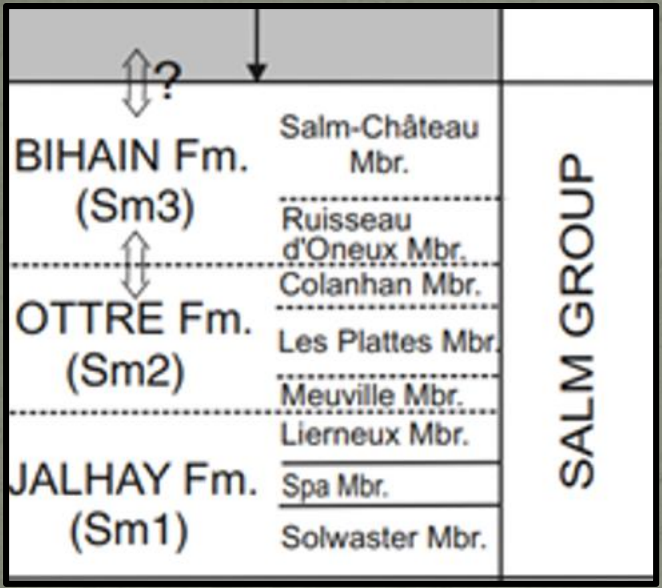
Stavelot Massif
360-420°C/2 kbar (Salm Valley)
300°C/1-2 kbar (Lienne Valley)



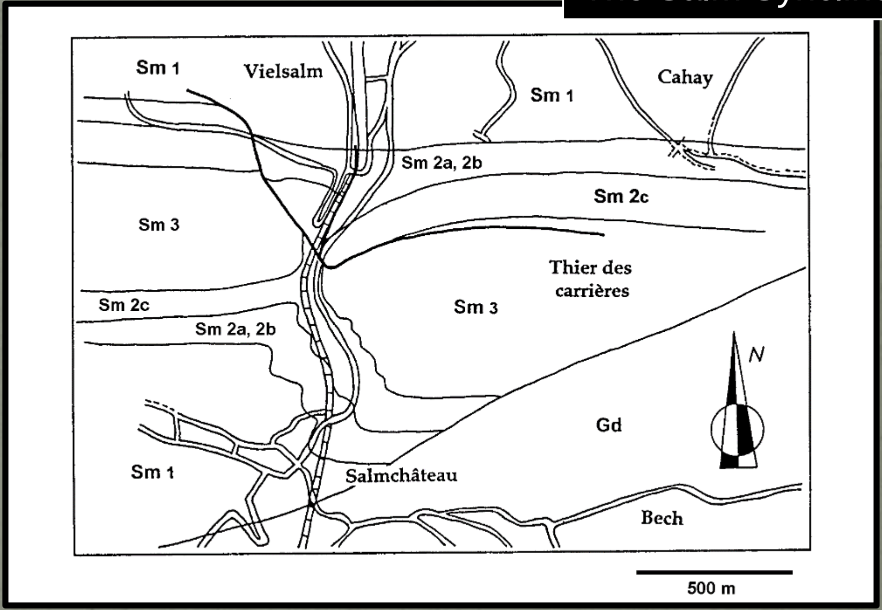
Libramont zone
500°C/3-4 kbar

Bastogne zone
400°C/2 kbar

Lithostratigraphy



The Salm Syncline

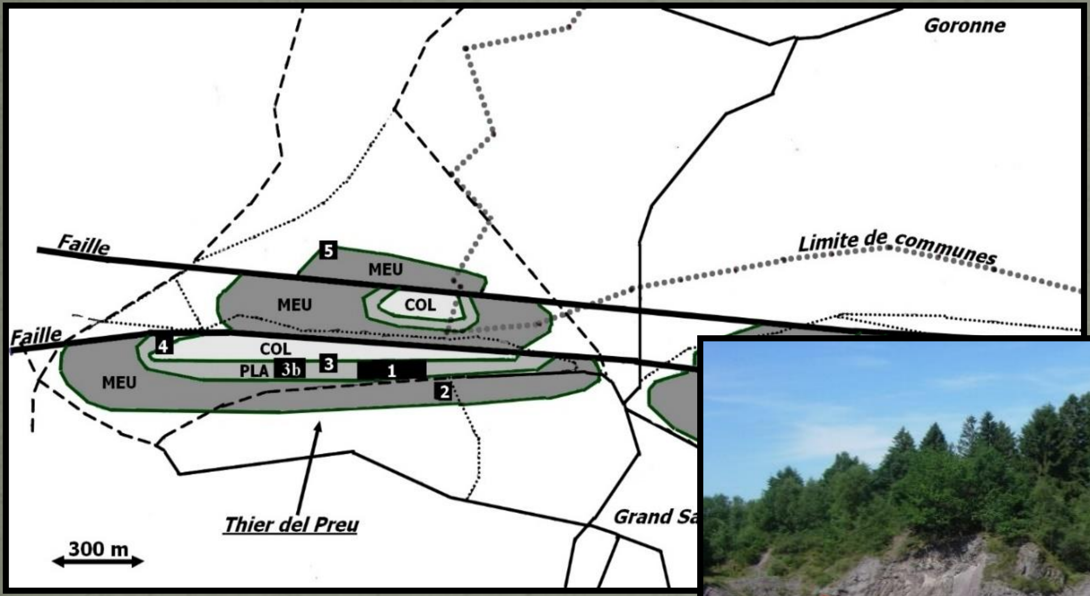


Sm2b
Les Plattes Member
Purple schists with coticule layers

Sm2a
Meuville Member
Red schists with Mn oxides

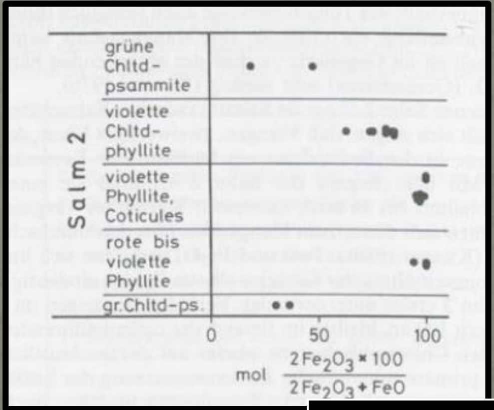
Sm2c
Colanhan Member
Gray to green schists with chloritoid
Veins with copper sulfides

The Ottré Formation

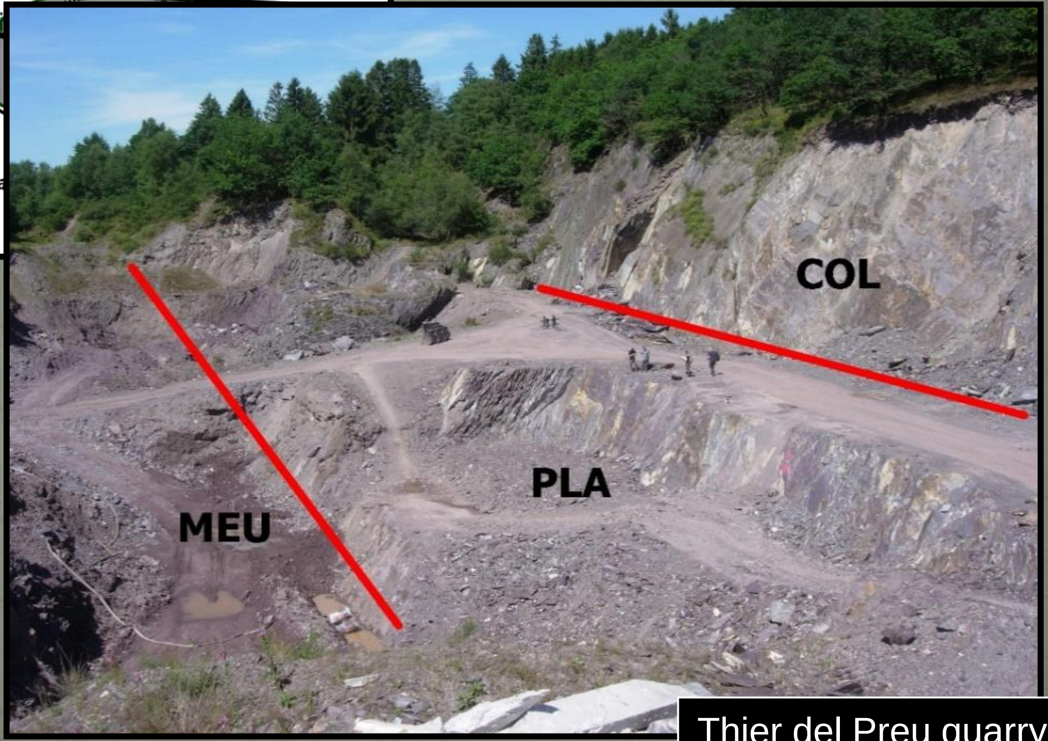


Die Metamorphose des Venn-Stavelot-Massivs, nordwestliches Rheinisches Schiefergebirge: Grad, Alter und Ursache

Ulrich Kramm



Kramm (1982)



Thier del Preu quarry

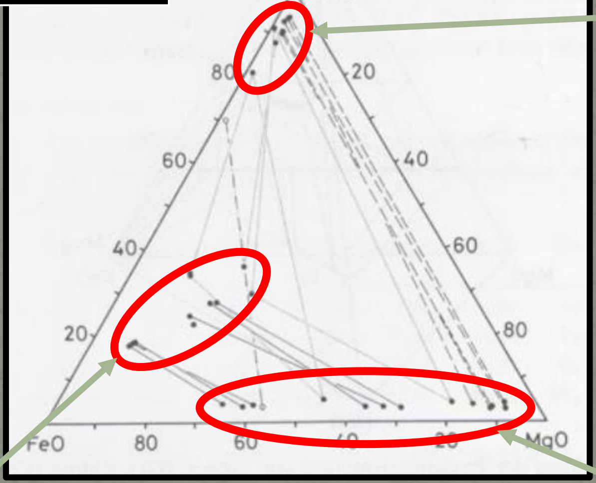
Green schists of the Colanhan Member

Mica + Quartz + Chlorite + Chloritoid + Spessartine

Low oxygen fugacity

Fe^{2+} and Mn^{2+}

Kramm (1982)



Spessartine, Salmchâteau

Chloritoid, Vielsalm

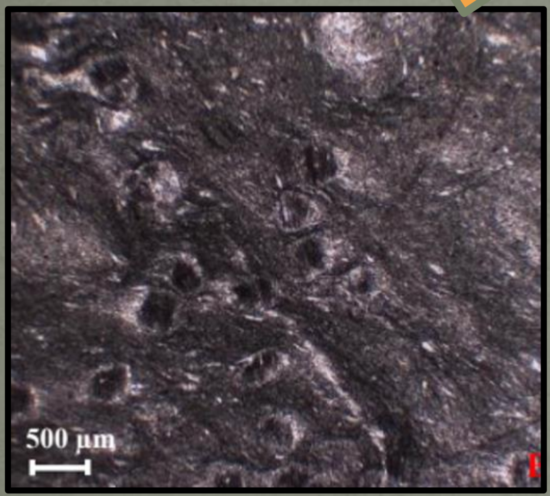
Chlorite, Thier del Preu

Chloritoid:
$Fe^{2+}Al_2O[SiO_4](OH)_2$
Spessartine:
$Mn^{2+}{}_3Al_2[SiO_4]_3$

Purple schists of the Les Plattes Member

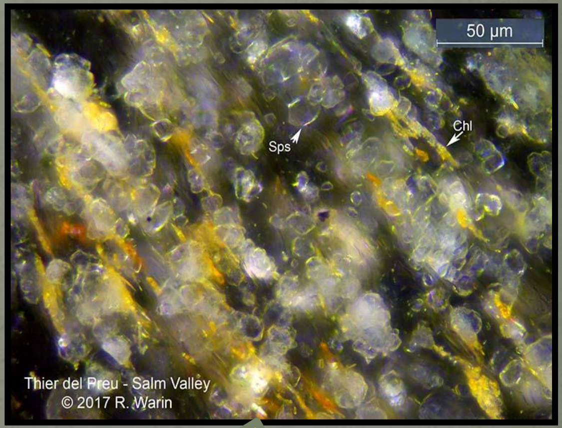
Medium oxygen fugacity

Fe^{3+} and Mn^{2+}



Coticules

Mica + Quartz + Chlorite + Spessartine



Purple schists

Mica + Quartz + Chlorite + Andalusite + Hematite

$$Fe^{2+}Al_2O[SiO_4](OH)_2 + \tfrac{1}{4}\,O_2 = Al_2O[SiO_4] + \tfrac{1}{2}\,Fe_2O_3 + H_2O$$

Red schists of the Meuville Member

High oxygen fugacity

Fe^{3+} and $Mn^{3+/4+}$

Red schists

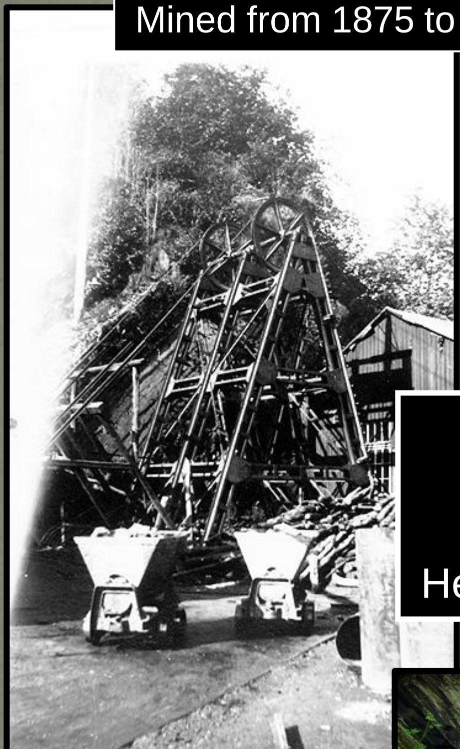
Mica + Quartz + Chlorite + Hematite + Mn oxides

Cryptomelane/lithiophorite in a quartz vein

Cryptomelane: $KMn^{3+}Mn^{4+}_7O_{16}$

The Lienne Valley

Mined from 1875 to 1934



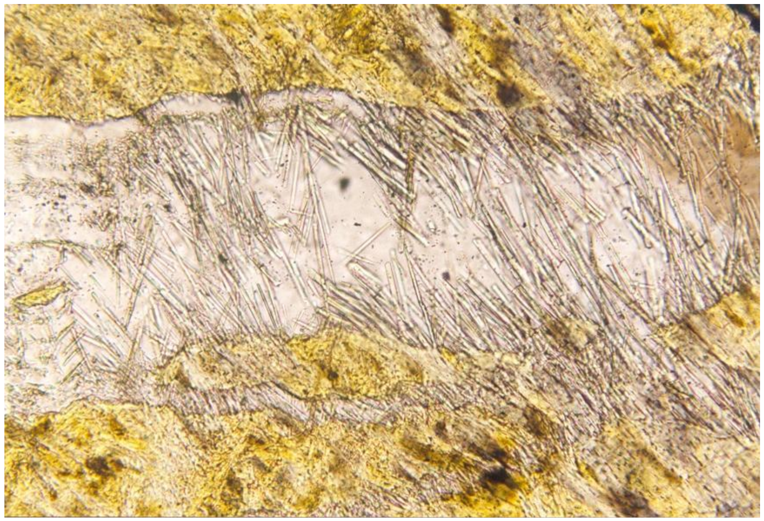
Rhodochrosite
$MnCO_3$

Red schists

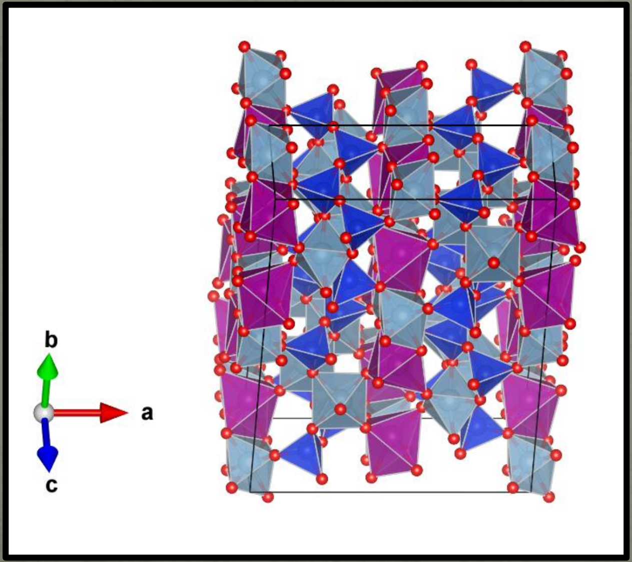
Mica + Quartz + Chlorite + Hematite + Mn oxides + Rhodochrosite

Pyrolusite
MnO_2

Carpholite



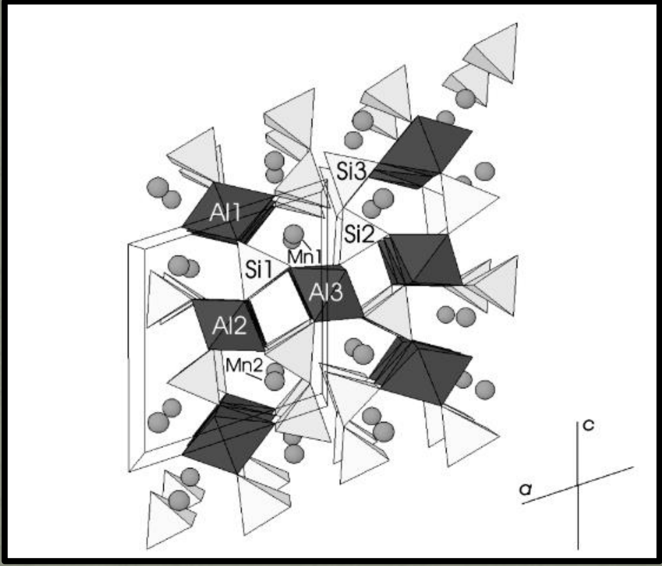
T = 300°C
P = 1-2 kbar
(Theye *et al*. 1996)



Carpholite
$MnAl_2Si_2O_6(OH)_4$

Sursassite

Sursassite
$Mn_2Al_3(SiO_4)(Si_2O_7)(OH)_3$



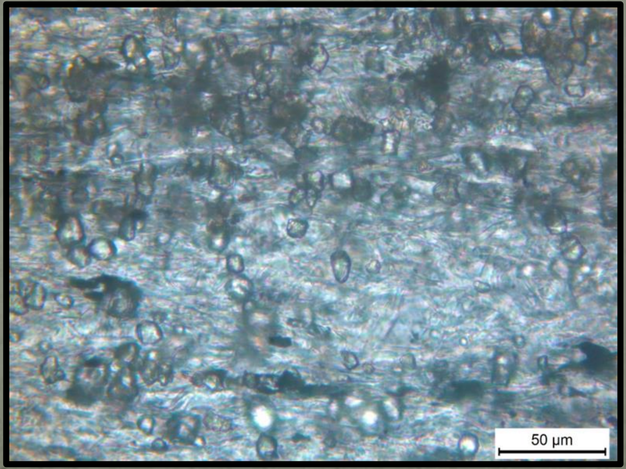
The crystal structure of sursassite from the Lienne Valley, Stavelot Massif, Belgium

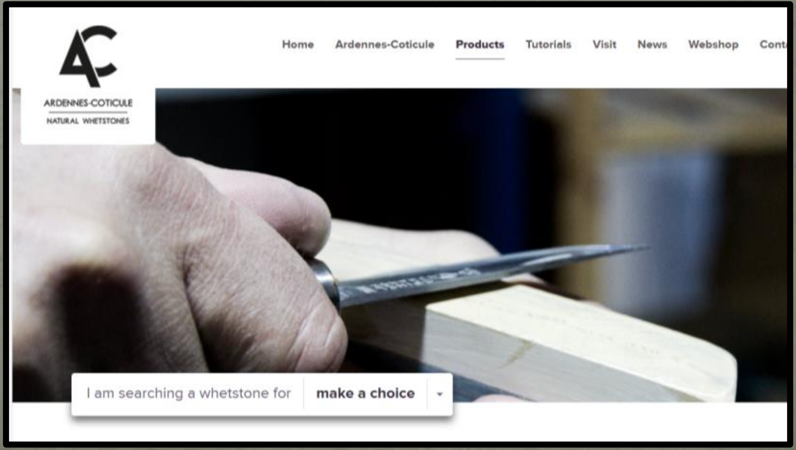
FRÉDÉRIC HATERT[1,*], ANDRE-MATHIEU FRANSOLET[1], JOHAN WOUTERS[2] and HEINZ-JÜRGEN BERNHARDT[3]

The coticule

- Whitish layers in purple schists (Les Plattes Member)
- Mainly mica, chlorite, and spessartine

- Tiny spessartine grains (< 10 µm)
- Matrix of phyllosilicates
- Mined for whetstone manufacturing





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Genesis of coticule: volcanic ashes?

Contrib. Mineral. Petrol. 56, 135–155 (1976)

Contributions to Mineralogy and Petrology

The Coticule Rocks (Spessartine Quartzites) of the Venn-Stavelot Massif, Ardennes, a Volcanoclastic Metasediment?

Ulrich Kramm

Mineralogisch-Petrographisches Institut der Universität Köln, Zülpicher Straße 49, D-5000 Köln

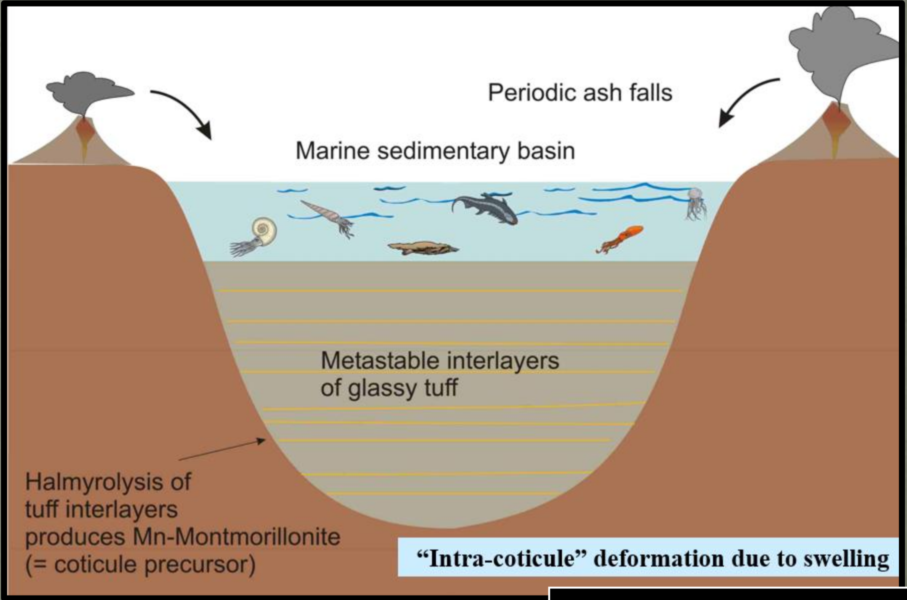
Kramm (1976)

Mn montmorillonite ⇌

spessartine + paragonite + chlorite + kaolinite + quartz + water

(high oxidation ratio assemblage)

Abstract. Thin spessartine-quartzite layers (coticules) are interstratified with Ordovician (Salmian) shales of the Venn-Stavelot Massif, Ardennes. These coticules indicate sudden interruptions in the sedimentation process of the shales. The lower contact of the coticules represents an abrupt change in the chemical composition from the underlying shales. In contrast, the upper limit of the coticules is chemically more diffuse. Phase relations of the phengite-bearing spessartine-quartzites including paragonite, chlorite, and chloritoid or kaolinite as subordinate phases give evidence for a manganese-montmorillonitic source material of the coticules. This is in good agreement with the internal structures observed in the coticule layers (swelling and sliding effects, Liesegang structures). Since there is a positive correlation between the oxidation ratio of the enclosing shales and the chemical composition of the coticules, it is proposed that the source material of the coticules developed in situ by halmyrolysis out of tuffs. High oxidation ratios of the shales with iron fixed in the trivalent state but with divalent and thus mobile manganese led to the



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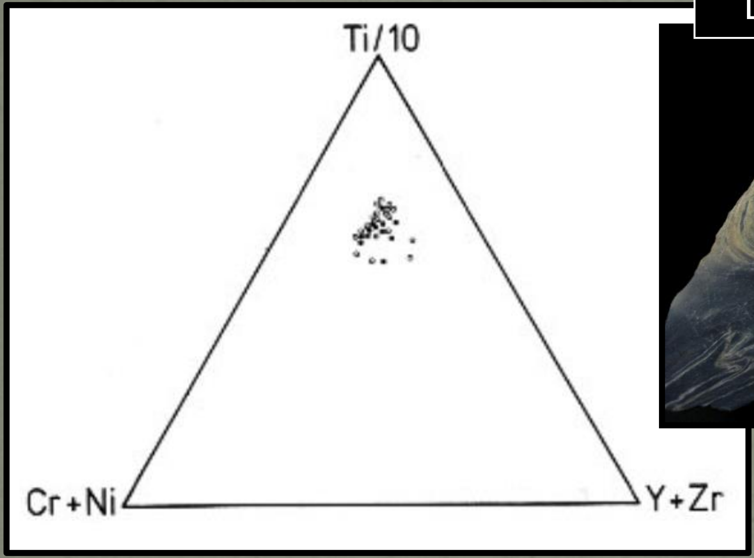
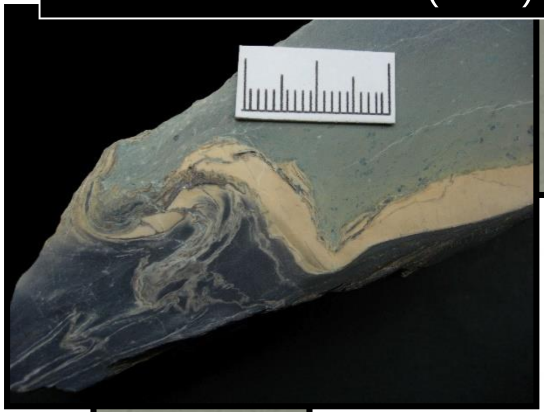
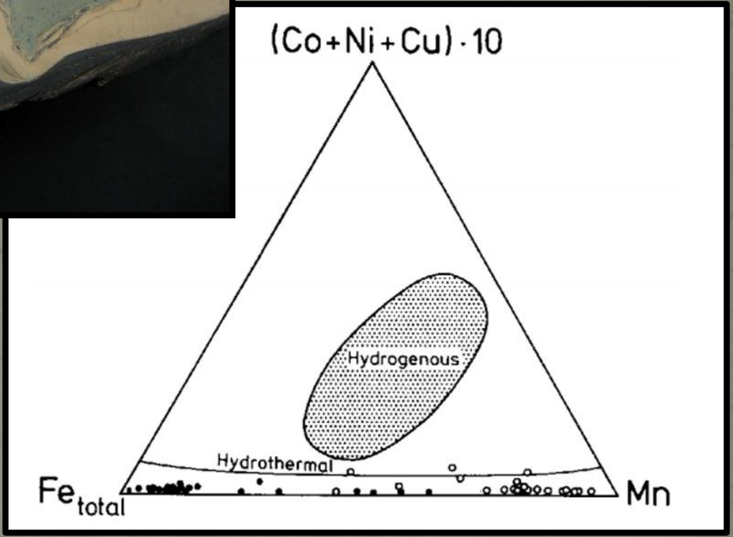
Krosse & Schreyer (1993)



Lamens & Geukens (1984)





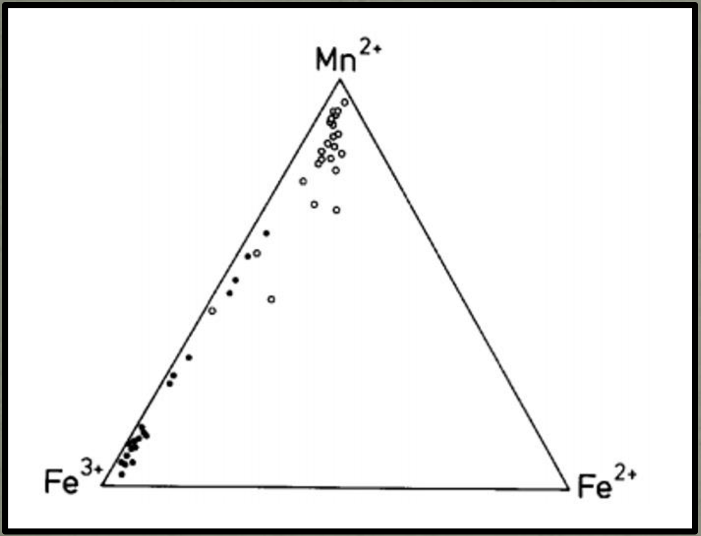
Trace element fingerprints identical for coticules and red schists

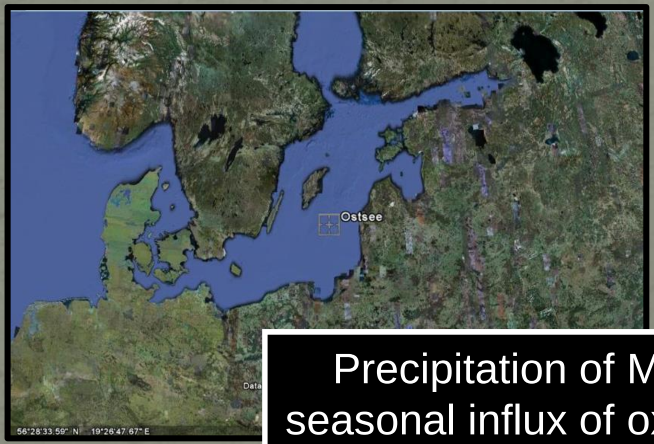
Same origin for Fe and Mn
NOT A VOLCANIC TUFF!

Fe and Mn produced by hydrothermal processes

Exhalations on the oceanic floor, linked to a magmatic rock

The Baltic See model

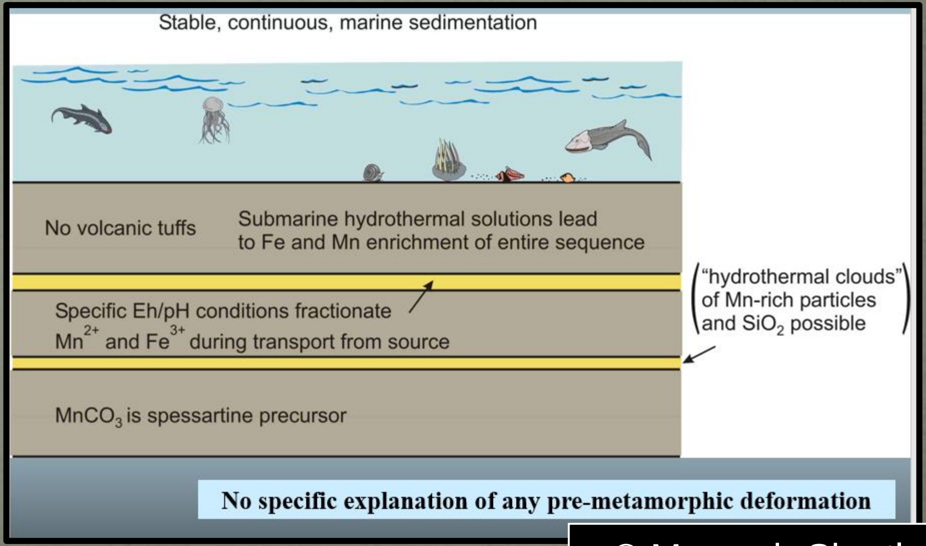




Precipitation of MnO_2 due to the seasonal influx of oxygen-rich waters

Fe and Mn separated between coticule and the red schists

Variations of Eh-pH conditions ?



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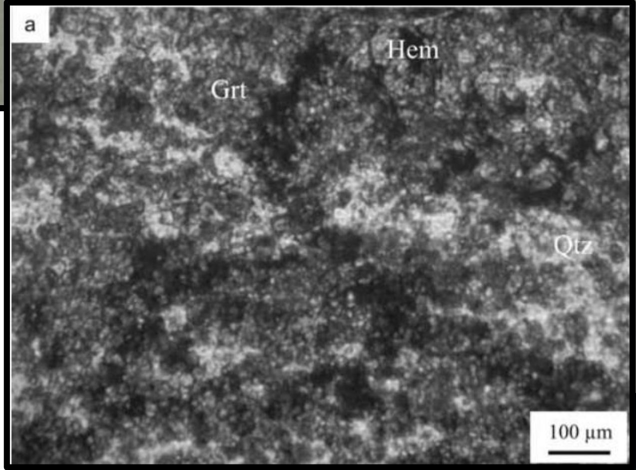
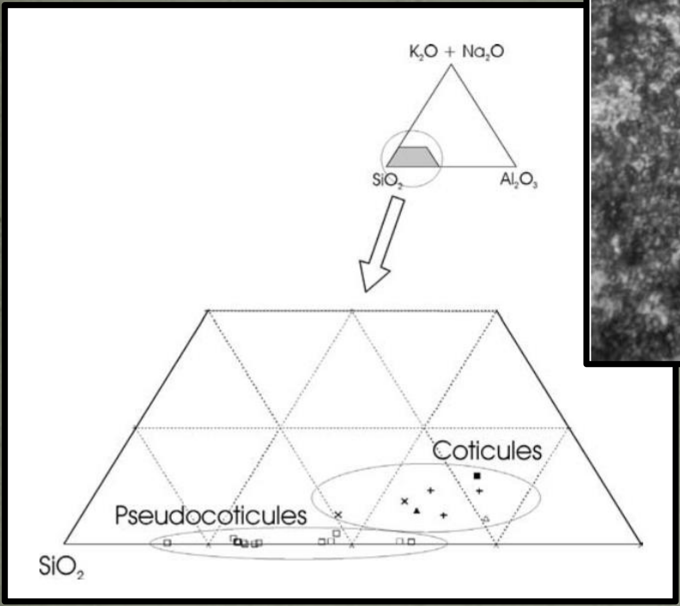
The pseudocoticule



- Large spessartine grains (> 50 µm)
- Matrix of quartz
- Presence of hematite (pink colour)
- Very bad whetstone



In the Colanhan Member

Low amount of phyllosilicates

Low ($Na_2O + K_2O$) content, compared to coticules

Mineralogical and geochemical study of pseudocoticule from the Stavelot Massif, Ardennes (Belgium), and redefinition of coticule

MAXIME BAIJOT, FRÉDÉRIC HATERT* and ANDRÉ-MATHIEU FRANSOLET

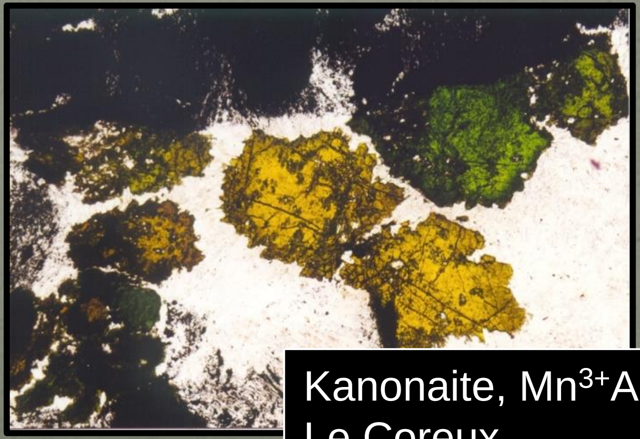
Manganese oxide veins – Meuville Member

Braunite, $Mn^{2+}Mn^{3+}_6O_8(SiO_4)$
Le Coreux

Hollandite-strontiomélane, $(Ba,Sr)(Mn^{4+}_6Mn^{3+}_2)O_{16}$
Le Coreux

La viridine et la braunite de Salm-Château,

par A. HERBOSCH,
Stagiaire de Recherches au F.N.R.S.

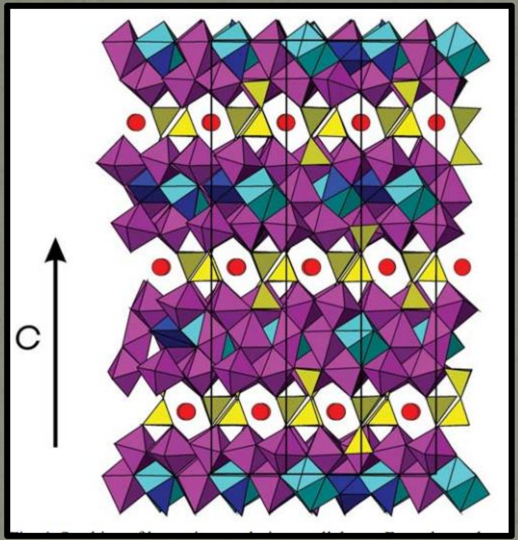


Kanonaite, $Mn^{3+}AlO(SiO_4)$
Le Coreux

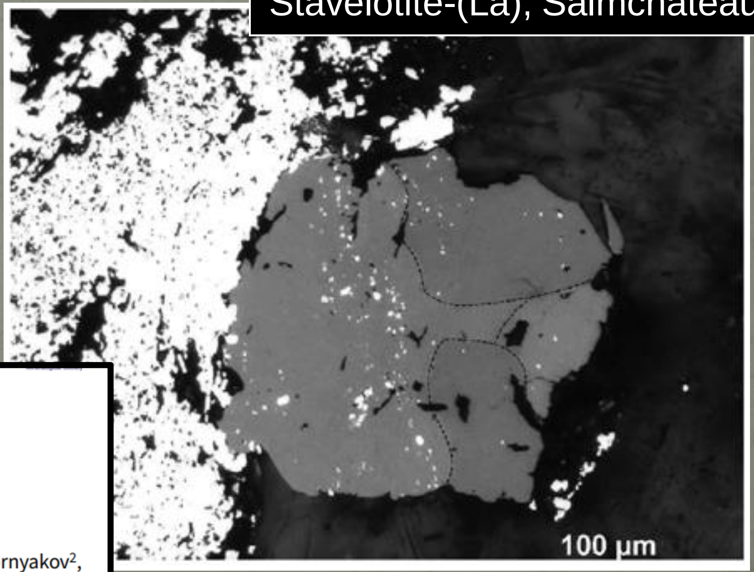
Stavelotite-(La)

Stavelotite-(La)
$La_3(Mn^{2+})_3Cu^{2+}(Mn^{3+},Fe^{3+},Mn^{4+})_{26}(Si_2O_7)_6O_{30}$

According to Krivovichev et al. (2013), 10th more complex crystal structure of the Mineral kingdom



Stavelotite-(La), Salmchâteau



Review

Structural and chemical complexity of minerals: an update

Sergey V. Krivovichev[1,2*], Vladimir G. Krivovichev[2], Robert M. Hazen[3], Sergey M. Aksenov[1], Margarita S. Avdontceva[2], Alexander M. Banaru[1,4], Liudmila A. Gorelova[2], Rezeda M. Ismagilova[2], Ilya V. Kornyakov[2], Ivan V. Kuporev[2], Shaunna M. Morrison[3], Taras L. Panikorovskii[1,2] and Galina L. Starova[2]

Andalusite quartz veins – Les Plattes Member

Green colour due to small amounts of Mn^{3+}

Green andalusite
Thier del Preu

Hematite, Fe_2O_3
Thier del Preu

Andalusite + pyrophyllite
Thier del Preu

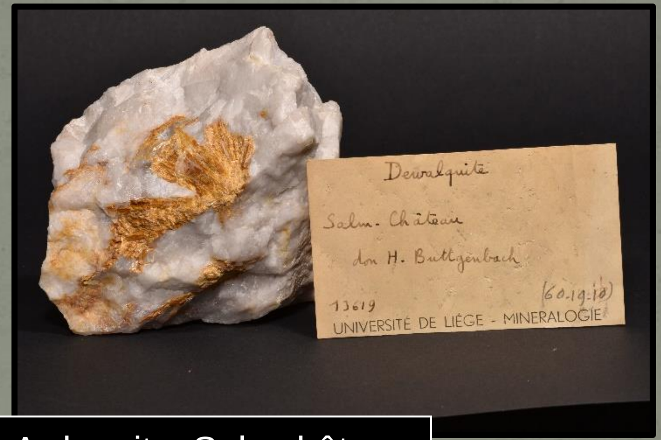
Ardennite

$Mn_4(AlMg)Al_4[Si_5(As,V)]O_{22}(OH)_6$

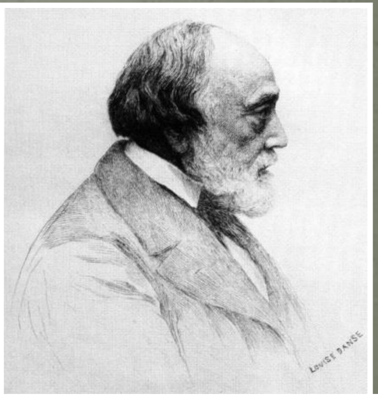
Dewalquite (Pisani, 1872)

↓

Ardennite (von Lasaulx, 1872)

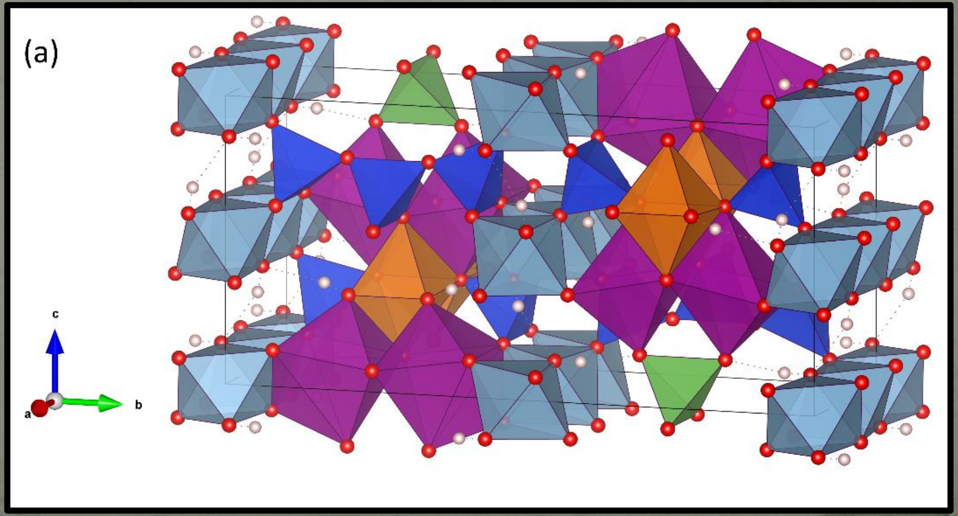


Ardennite, Salmchâteau



Gustave Dewalque (1828-1905)

Ardennite, Regné

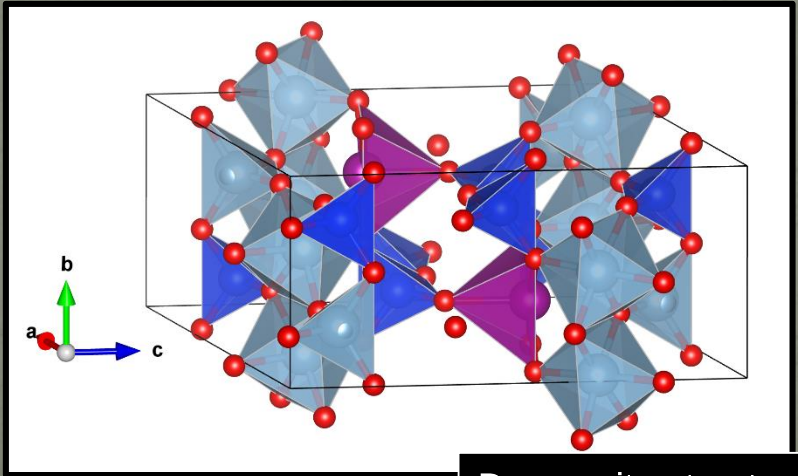


Davreuxite

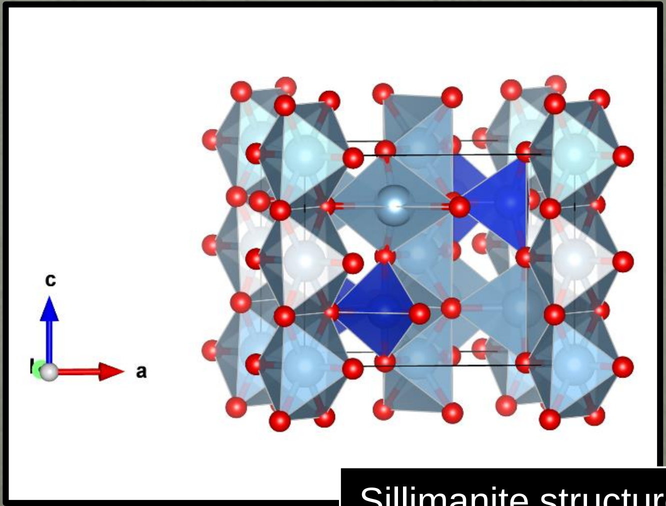
Davreuxite, Salmchâteau

Davreuxite
$MnAl_6Si_4O_{17}(OH)_2$

Charles-Joseph Davreux (1800-1863)
Chimiste et naturaliste, Liège



Davreuxite structure



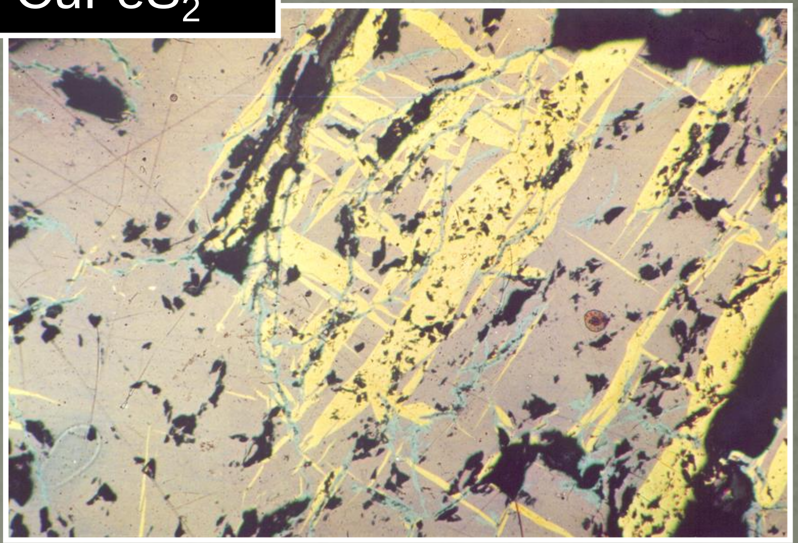
Sillimanite structure

Copper sulfides – Colanhan Member

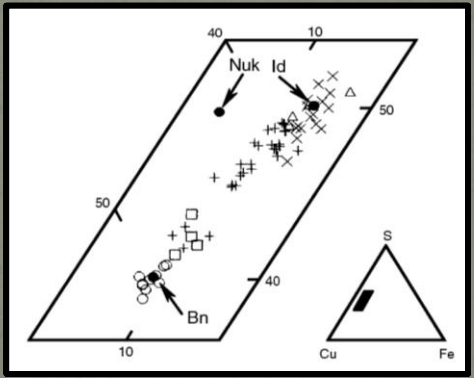
Bornite
Cu_5FeS_4

Chalcocite
Cu_2S

Chalcopyrite
$CuFeS_2$



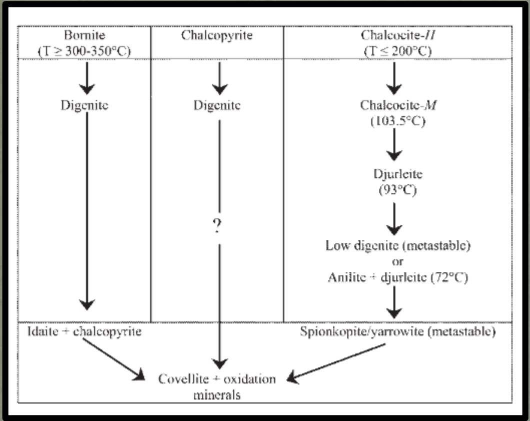
Idaite
Cu_3FeS_4



Occurrence of sulphides on the bornite-idaite join from Vielsalm, Stavelot Massif, Belgium

FRÉDÉRIC HATERT

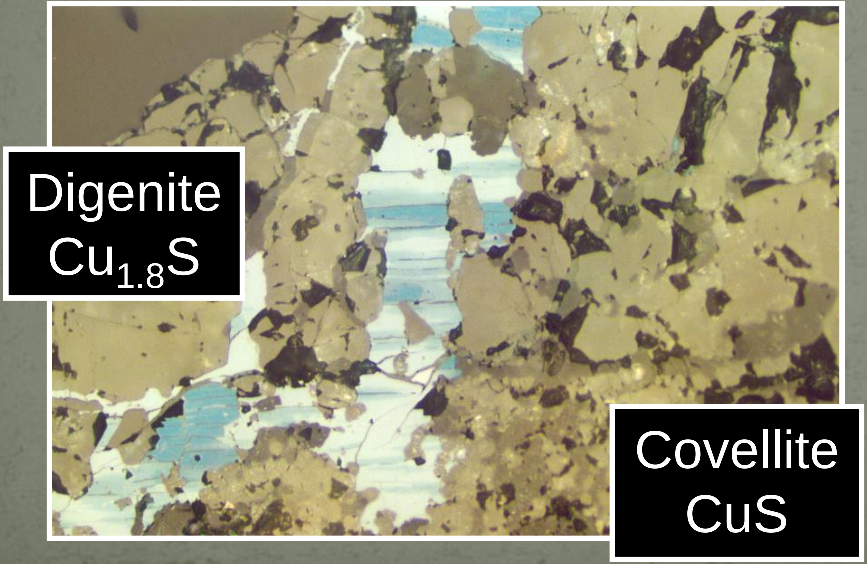
Genetical sequences of copper sulfides

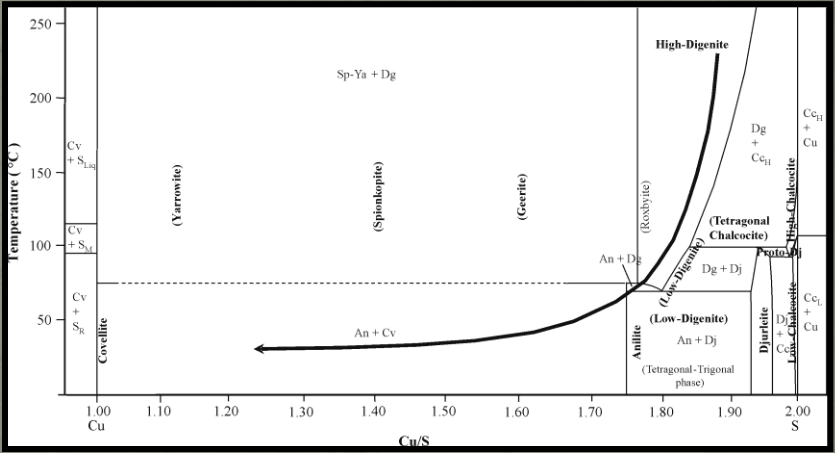


The Canadian Mineralogist
Vol. 43, pp. 623-635 (2005)

TRANSFORMATION SEQUENCES OF COPPER SULFIDES AT VIELSALM, STAVELOT MASSIF, BELGIUM

FRÉDÉRIC HATERT[§]





Conclusions

- Ordovician rocks of the Ottré Formation in the Stavelot Massif show a very exotic geochemistry
- Hydrothermal submarine exhalations are responsible for an enrichment of the sediments in Fe and Mn, but also in Cu, Te, Bi, Be, Au, U….
- The low-grade Variscan metamorphism (max. 420°C) produced a plethora of rare minerals, as for example ardennite, davreuxite, stavelotite-(La), carpholite, and sursassite
- The crystallisation of tiny spessartine grains, in a fine matrix of phyllosilicates, produced coticule, a rare rock mined for centuries as a whetstone.