

# Dypingite, my first new mineral – forty-two years later

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## Introduction

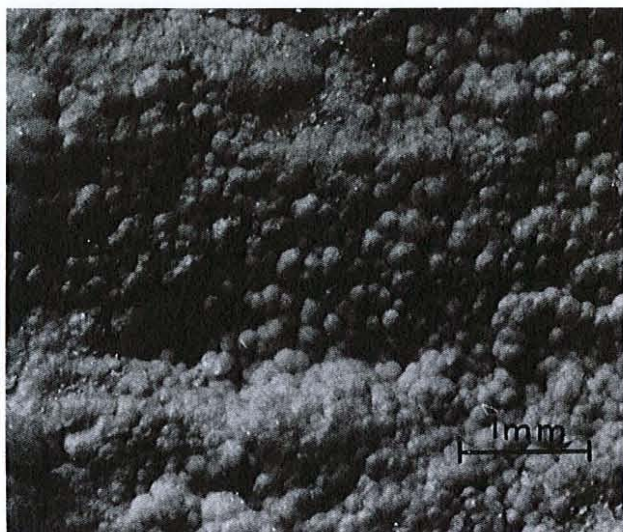
The author has up to now been involved in the description of 17 new mineral species. The first of them was dypingite (Raade 1970). It was approved by the Commission on New Minerals and Mineral Names (CNMMN) of the IMA by a vote of 12-3 (for and against). At that time, those voting negatively were not required to give their reasons for doing so. Owing to the nature of the mineral, occurring as a thin coating of tiny, globular aggregates, it was not possible to obtain a complete set of data to fully characterize the mineral. The reported data were: chemical formula obtained by wet-chemical analysis, an unindexed X-ray powder-diffraction pattern, infrared absorption data, differential thermal and thermogravimetric analyses and refractive indices. Clearly missing are crystal system (probably monoclinic), cell parameters, space group, crystal-structure refinement and measured density. I wonder if this mineral had been approved today by the present Commission on New Minerals, Nomenclature and Classification (CNMNC). It cannot be excluded. The crucial point in the description was that dypingite,  $\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 5\text{H}_2\text{O}$ , transformed to hydromagnesite,  $\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$  upon heating at  $150^\circ\text{C}$ , as could be shown by the change in X-ray powder-diffraction pattern.

Dypingite is one of my four self-collected new mineral species. It was found on a collecting trip to the serpentine-magnesite deposit at Dypingdal, Snarum, Buskerud, on 20 May 1961. I was 17 years old at the time and was accompanied by a schoolmate, Bjørn Tore Larsen, who also became a geologist. We had our tent camp at the north shore of the Dypingen lake (from which the mineral name is derived), where there was ample material dumped from the magnesite mining activities. A large block of serpentine with a white coating at one corner caught my eyes, and I cut off a piece. On 23 February 1965, I performed microchemical tests that revealed carbonate and magnesium as the main constituents. An X-ray powder film, recorded 31 March 1965, showed an unknown pattern, indicating that this was a new species. A detailed investigation of the mineral was undertaken in 1969. Most of the material on the original specimen had to be sacrificed for the investigations. At the time of description, two other specimens were available, of which only one contained the new mineral (Raade 1996). A large number of specimens with white crusts were collected at a later date and X-rayed, but they all turned out to be hydromagnesite. Dypingite from this locality occurs as well-formed globular aggregates (Fig. 1), as opposed to the more indistinct hydromagnesite.

The reviewer of the manuscript I submitted to *American Mineralogist* remarked: "The present paper is rather short of hard, reliable data, and the journal runs some risk of finding later that this was a well-intentioned but erroneous identification". The paper was accepted because the mineral was approved by the CNMMN. I am glad to state that my first new mineral has so far stood the test of time. It is easily identified by its distinctive X-ray powder diagram, and it has in the intervening years been reported from a number of localities worldwide (see below).

Dypingite and other magnesium carbonate minerals have recently been of interest as  $\text{CO}_2$ -trapping phases at ultramafic-hosted mine sites, which may have implications

for large-scale geo-sequestration of so-called greenhouse gases. I am pleased to see that my 1970 paper has been frequently referred to since its publication. The purpose of the present article is to review some of the ensuing literature dealing with dypingite.



**Fig. 1.** Photomicrograph of dypingite from Dypingdal, Snarum, Modum (the original type specimen). The picture was intended for the 1970 dypingite paper but was refused by American Mineralogist.

### **Worldwide dypingite localities**

A large number of dypingite occurrences are listed on the Internet site *mindat.org*. They are quoted here with localities given in an abbreviated form and mostly without references (just the year of publication):

#### Antarctica

Vestfold Hills, East Antarctica (2000) [The original reference is Gore et al. (1996)]

#### Australia

Lord Brassey mine, Heazlewood, Tasmania (2002)

#### Austria

Gmünd, Hohe Tauern, Carinthia (1995)

Stubach Valley, Hohe Tauern, Salzburg (1989)

Fishbacher Alpen, Styria (2005)

Kraubath, Leoben, Styria (1993) [The original reference is Postl (1975)]

#### Belgium

Plombières, Liège (1979) [Formed on zinc and lead smelter slag (Van Tassel 1979); see Fig. 3A]

Sclaigneau, Namur [Also a slag locality (Van Tassel 1979)]

#### Canada

Rapid Creek, Big Fish River, Yukon Territory [Reference is missing]

#### France

Ste Marie-aux-Mines, Alsace (1997)

#### Germany

Recklinghausen, Ruhr coal-mining area, Rhine-Westphalia (no year)

Letmathe, Iserlohn, Sauerland, Rhine-Westphalia (1994) [Slag locality]

Eiserfeld, Siegerland, Rhine-Westphalia (2008)

Rosenberg mine, Braubach, Bad Ems, Rhineland-Palatinate [1991] [Formed on slag]

Ronneburg, Gera, Thuringia (1998)

Garnsdorf, Saalfeld, Thuringia (1995)

#### Greece

Lavrion district [No reference]

#### Hungary

Recsk, Mátra (1993) [Additional reference: Kiss & Janosi (1993)]

#### Italy

Corchia mine, Berceto, Emilia-Romagna (1997)

Borzoli, Genova, Liguria (2006)

Brosso mine, Canavese, Torino, Piedmont (2001) [First mentioned by Ferraris et al. (1978); see Fig. 3B]

Gadoni, Sardinia (1999)

#### Japan

Yoshikawa, Aichi Prefecture, Honshu Island (1973) ["Yoshikawaite". Suzuki & Ito (1973 and 1974), Suzuki et al. (1975)]

#### Norway

Dypingdal, Snarum, Modum, Buskerud (1970) [Raade (1970)]

Sørdalen mine, Hellevika, Fjaler, Sogn og Fjordane [Not officially published; from G. Raade (1993) in *Interne Notater (Geologisk Museum, Oslo)*, 188-189]

Feragen, Røros, Sør-Trøndelag (collected by Knut Eldjarn 1973) [Photo by Atle Michalsen: [www.nags.net/nags/mineraler/bilder/dypingite.htm](http://www.nags.net/nags/mineraler/bilder/dypingite.htm)]

#### Russia

Tolbachik volcano, Kamchatka Oblast' (no reference, no year)

Chelyabinsk coal basin, southern Urals (1998)

#### USA

Clear Creek area, New Idria District, San Benito Co., California (1977)

Robinson Gulch pegmatite, Clear Creek, Jefferson Co., Colorado (1997)

Sterling Hill, Ogdensburg, Sussex Co., New Jersey (1995)

Here are some additional localities:

#### France

Basalt cave at Restivalgues, Auvergne, Massif Central (Oustrière et al. 1980); see Fig. 3A.

#### Germany

Gottesbelohnungs-Hütte, Hettstedt, Saxony-Anhalt (Knoll 2004) [Slag formation]

#### Great Britain

Hagdale, Unst, Shetland Islands, Scotland [From Handbook of Mineralogy; no reference is given]

Alston Block of the Northern Pennine Orefield, northern England (Green & Young 2006)

#### Romania

Budureasa-Pietroasa area, Bihor Mts (Ionescu & Ghergari 1999)

Dypingite mainly occurs in weathered ultramafic rocks, particularly serpentinites, and also in dump material and excavations at various ore deposits, in cave assemblages and in slag material.

A very special case is the report of biologically induced precipitation of dypingite by cyanobacteria (*Lyngbya* sp.) from an alkaline wetland near Atlin, British Columbia, Canada (Power et al. 2007). The wetland is part of a larger hydromagnesite playa. It is concluded that this biochemical process represents an important link between the biosphere and the inorganic carbon pool. Magnesium isotope fractionation during inorganic and cyanobacteria-induced precipitation of dypingite was studied by Mavromatis et al. (2010). The presence of active *Gloeocapsa* sp. bacteria significantly modified the chemical composition of the growth solution, and the culture medium became progressively enriched in the heavier Mg isotopes, with respect to an inorganic control experiment. This implies a preferential incorporation of lighter Mg

isotopes in 'bio-dypingite', and the authors conclude that biological activity may have affected significantly the Mg isotopic composition of carbonates in the geological record.

### New data

Dypingite was erroneously described by me as having a fibrous texture, based on its appearance in a powder mount. It is actually platy, as shown by subsequently obtained SEM images (Fig. 2). This has also been observed for dypingite from other localities (Fig. 3). Another matter that can be clarified at this point is that two of the X-ray reflections reported for dypingite, at 7.37 and 3.68 Å, are due to contamination by chrysotile.

Without being aware of my dypingite paper, Suzuki & Ito (1973) published data on an alleged new magnesium carbonate mineral from Yoshikawa, Aichi Prefecture, Japan, with formula  $Mg_5(CO_3)_4(OH)_2 \cdot 8H_2O$ . Its X-ray powder-diffraction data are similar to those of dypingite, except for a relatively strong basal reflection at 33.2 Å. For dypingite, it was not possible to record such low-angle reflections with the instrumentation at my disposal. The name "yoshikawaite" was unfortunately used for this mineral in two subsequent publications (Suzuki & Ito, 1974; Suzuki et al. 1975), although the mineral had not been approved by the CNMMN. Also this mineral converted to hydromagnesite on heating at 150°C. I was contacted by Professor Giovanni Ferraris in 1977 regarding a dypingite-like mineral he had observed from the Brosso mine while working on the new mineral canavesite. Actually, his results were closer to those given for "yoshikawaite" regarding water content and a basal reflection at 32.5 Å (pers. comm. April 1977; Ferraris et al. 1978). The status of "yoshikawaite" is unclear; it is generally regarded as identical to dypingite.

Giorgiosite is a very poorly described basic magnesium carbonate from Santorini Island, Greece. For my description of dypingite, I had obtained type material of giorgiosite kindly provided by Muséum National d'Histoire Naturelle in Paris. The X-ray powder-diffraction data, never published before and very distinct from those of dypingite, were included in my paper. Clearly, the mineral was not identical to dypingite. A basic magnesium carbonate with the same powder pattern was synthesized by Friedel (1975) It was found, quite surprisingly, to have the same chemical formula as dypingite,  $Mg_5(CO_3)_4(OH)_2 \cdot 5H_2O$ . However, Canterford et al. (1984) have adjusted the formula to  $Mg_5(CO_3)_4(OH)_2 \cdot 6H_2O$ . Both synthetic and natural giorgiosite occurs as needles, mostly in globular aggregates. The *mindat.org* website lists seven worldwide localities for giorgiosite, including a Norwegian one at Sørvalen mine, Hellevika, Fjaler, Sogn og Fjordane [Not officially published; from G. Raade (1993) in *Interne Notater (Geologisk Museum, Oslo)*, 188-189]. Further discussion of giorgiosite and its localities is outside the scope of this article.

My published infrared spectra of dypingite and hydromagnesite were remarkably similar, and I feared in the past that something was wrong with my data. However, the same results have been obtained by others (e.g. Jones & Jackson 1993), and testify of course to the close structural similarities that must exist between the two minerals. The IR spectrum of synthetic dypingite presented by Canterford et al. (1984) looks more like the hydromagnesite spectrum to me.

A Raman spectroscopic study has been undertaken of dypingite, "yoshikawaite" and artinite, mainly as a tool for characterising minerals that are important for understanding geo-sequestration of carbon dioxide (Frost et al. 2009). There are some small divergences in the spectra of dypingite and "yoshikawaite": Raman bands occur at 1713, 1751 and 1767  $cm^{-1}$  for the latter, indicating structural differences in hydrogen-bonded water.

Roush (1996) used Fresnel reflectance and dispersion analysis to derive the real and imaginary indices of refraction of dypingite (actually "yoshikawaite") in the mid-infrared wavelength region. To quote the author: "These indices are useful for theoretical modelling of the radiative transfer that occurs within atmospheres of planets and particulate surfaces of solid bodies in the solar system".

Synthetic preparations of hydromagnesite and dypingite have been made and their thermal stabilities studied because these substances may have several practical applications in addition to fixation of atmospheric CO<sub>2</sub>. They can be used in pharmaceuticals as an inert vehicle and an absorbent; in cosmetic manufacturing as a carrier and retainer of perfumes, due to fine texture and high absorbency; in the rubber industry as a reinforcing agent; as an extender for titanium dioxide in paint; and as a flame retardant (Botha & Strydom 2001).

It was shown by Davies & Bubela (1973) that synthetic nesquehonite, Mg(HCO<sub>3</sub>)(OH)·2H<sub>2</sub>O, can be readily altered to hydromagnesite via an intermediate phase that exhibits an X-ray pattern similar to that of dypingite. The phase was provisionally named "protohydromagnesite" because it formed curved flakes, whereas dypingite had been described by me as fibrous (erroneously as it turned out, see above). Synthetic dypingite was prepared and described in some detail by Canterford et al. (1984). The X-ray powder data showed a strong reflection at 31.0 Å. An SEM investigation revealed a flaky texture of the substance, and they noticed that it had a fibrous appearance in thin section, just like I did. They show that the published analysis of "protohydromagnesite" by Davies and Bubela (1973) yields a highly hydrated composition near Mg<sub>5</sub>(CO<sub>3</sub>)<sub>4</sub>(OH)<sub>2</sub>·11H<sub>2</sub>O.

Hopkinson et al. (2008) studied the transformation of nesquehonite to hydromagnesite in the system CaO-MgO-H<sub>2</sub>O-CO<sub>2</sub> by Raman and FT-IR spectroscopy. At 52°C, hydromagnesite and dypingite occurred with abundant quantities of a transitory magnesium carbonate hydrate (TMHC). Additional heating at 60°C resulted in the loss of TMHC and formation of an assemblage rich in dypingite and hydromagnesite. By sparging CO<sub>2</sub> through an Mg(OH)<sub>2</sub> slurry at ambient temperature and drying the product above 100°C, Botha & Strydom (2001) reported to have prepared hydromagnesite or dypingite, depending on the drying time allowed. It is somewhat disturbing that the X-ray diffraction traces of hydromagnesite and dypingite shown in their Fig. 1 are almost identical above 10° 2θ. They also discovered an unidentified product with a total mass loss of 64.6%, higher than that of dypingite. It shows a distinct X-ray powder pattern.

Frost et al. (2008) studied the thermal stability of dypingite by a combination of thermogravimetry and evolved gas mass spectrometry, using dypingite from Clear Creek, California, and "yoshikawaite" from Japan. They found that dehydration took place at 213°C with a total weight loss of only 8%, tentatively ascribed to impurities in the sample [Mg<sub>5</sub>(CO<sub>3</sub>)<sub>4</sub>(OH)<sub>2</sub>·5H<sub>2</sub>O contains 22.3 wt% H<sub>2</sub>O]. It is not stated which sample was used for obtaining the results shown in their Figs. 3 and 4, and they are not in accordance with the results of Raade (1970), Suzuki & Ito (1973) and Canterford et al. (1984). The data presented in those papers are not referred to by Frost et al. (2008), who state: "To the best of the authors' knowledge there have been few reported thermal analyses of dypingite as compared with some other magnesium carbonate minerals". I am amazed that this paper has been published. It starts with the brilliant sentence: "The ability to be able to easily and readily detect minerals is of importance".

The crystal structure of dypingite has not yet been solved, and the unit-cell parameters are not known. In Dana's New Mineralogy (Gaines et al. 1997) it is described with cell parameters  $a = 32.6$ ,  $b = 23.8$  and  $c = 9.45$  Å, although it is designated as monoclinic, and with  $Z = 8$ ,  $D = 2.15$  [g/cm<sup>3</sup>]. Since there is no reference, it is a mystery how and by whom these cell data were derived. The data provided are not internally consistent, as they give  $D = 0.88$  g/cm<sup>3</sup>. I have once tried to index the X-ray powder pattern of dypingite with the programs TREOR and ITO but without success.

The structure of dypingite is likely to be based on the hydromagnesite structure, which was described by Akao et al. (1974) and Akao & Iwai (1977). It is monoclinic but with a strong pseudo-orthorhombic character. Corner-shared MgO<sub>6</sub> octahedra and carbonate triangles form a corrugated framework. Modelling of the dypingite structure, based on the hydromagnesite parent structure, is presently being undertaken (Mills et al. 2010; Stuart Mills, pers. comm. April 2012).

### **Carbon dioxide sequestration**

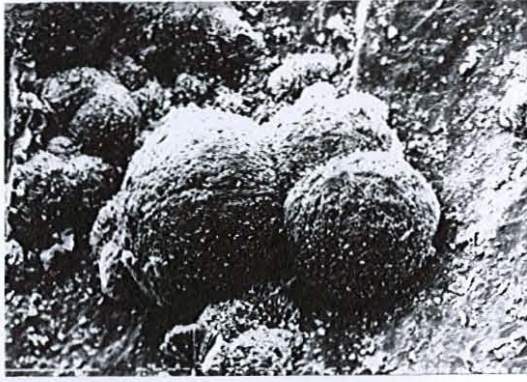
Fixation of atmospheric CO<sub>2</sub> during neo-formation of hydrated magnesium carbonate minerals like lansfordite, nesquehonite, hydromagnesite and dypingite has attracted a great deal of interest lately. Sequestration of CO<sub>2</sub> by such minerals in ultramafic mine tailings from active and abandoned mining operations has been demonstrated (Wilson et al. 2005 and 2006, Dipple et al. 2009), in particular in the case of chrysotile mine tailings at Clinton Creek (Yukon) and Cassiar (British Columbia) (Wilson et al. 2005 and 2009).

An atmospheric source of CO<sub>2</sub> in neo-formed hydrated magnesium carbonates has been confirmed with carbon and oxygen isotope techniques (Wilson et al. 2005 and 2009). A method for separation and isotopic analysis of primary and secondary carbonate minerals from ultramafic mine tailings was described by Barker et al. (2009). Bedrock carbonate minerals contained zero atmospheric CO<sub>2</sub>, whereas secondary phases contained between 30 and 99% modern atmospheric CO<sub>2</sub>.

Tailings rich in serpentine and olivine are produced by many types of mining, including chrysotile, chromium, nickel, platinum and diamond. According to Wilson et al. (2005), the global scale of these mining activities has a sequestration capacity on the order of 100 million tonnes of carbon per year, and widespread implementation of CO<sub>2</sub> sequestration in mine tailings is potentially able to render large mining operations greenhouse gas neutral and significantly reduce CO<sub>2</sub> emissions on a global scale.

Based on granulated serpentinite from localities in Slovakia, Tuček et al. (2009) demonstrated that products of carbonatization (nesquehonite, hydromagnesite with less dypingite and barringtonite) could be produced in relatively short times of several hours by reaction at specific P-T conditions.

There seems to be a realistic potential for using magnesium-rich rocks for geo-sequestration of the greenhouse gas CO<sub>2</sub>, dependent on the formation of magnesium carbonate minerals like hydromagnesite and dypingite. The latter is likely to decompose to the more stable hydromagnesite structure, which in turn may further decompose to magnesite, MgCO<sub>3</sub>, one of the most stable mineral traps for CO<sub>2</sub>. Greenhouse gases might be removed by pumping liquefied CO<sub>2</sub> several kilometres below the ground in a suitable rock type. It shall be interesting to watch further developments in this field.



a



b



c



d

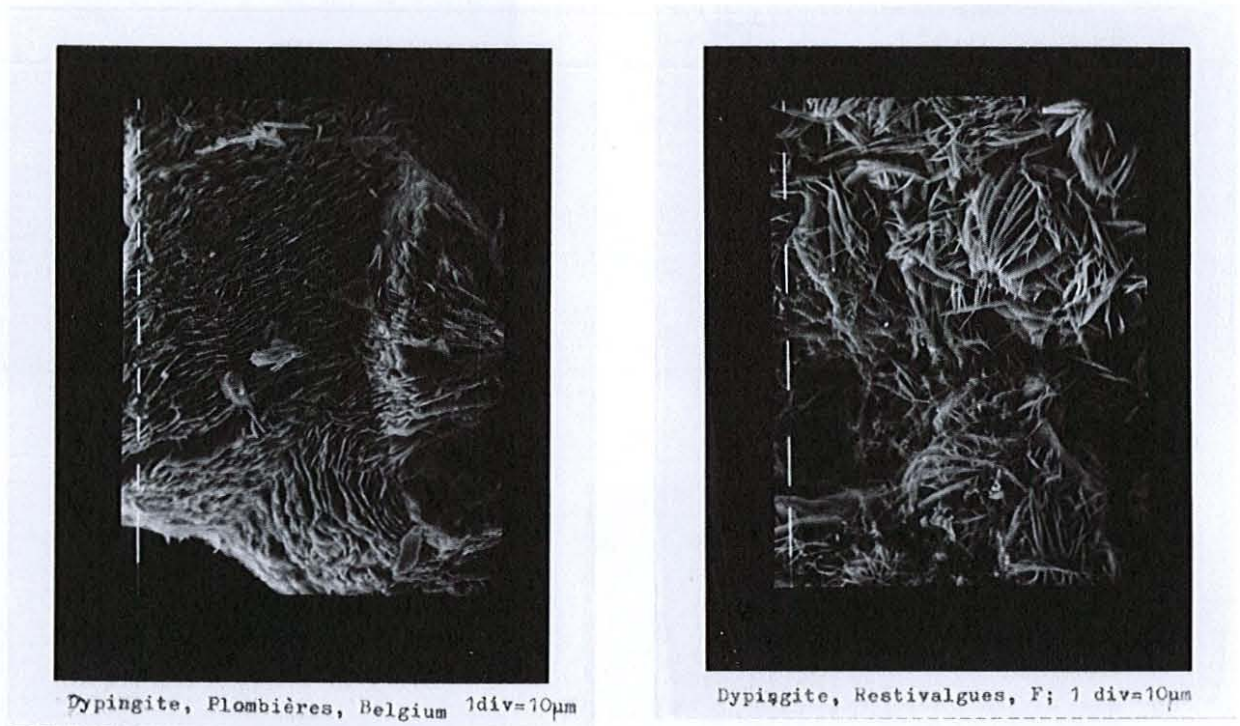


e

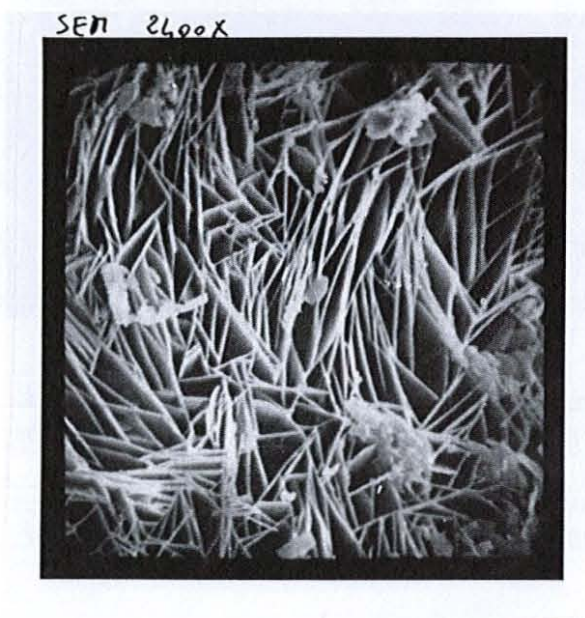


f

**Fig. 2.** Back-scattered SEM images of dypingite from Dypingdal, Snarum. Recorded at Mineralogisches Institut, Universität Karlsruhe in 1980. Images a, b and c show the globular form of the mineral; image d is an enlargement of the globule surface. The two lower images e and f show broken globules, revealing scaly texture and hollow centres. Width of images: a 0.6 mm, b and c 0.35 mm, d not recorded. The diameter of the globules in e and f is 0.13 mm.



**Fig. 3A.** SEM-BSE images of dypingite formed on slag from Plombières, Belgium (left) and from a basalt cave at Restivalgues, Auvergne, France (right). The scale bars are 10  $\mu$ m. Courtesy of Professor R. Van Tassel 1980 (images taken by Dr K. Wouters).



**Fig. 3B.** SEM-BSE image of dypingite from Brosso, Italy. The enlargement is reduced to 1650x here. Courtesy of Professor Giovanni Ferraris 1977.



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