

Figure 5: A non-polarised, room-temperature Vis-NIR spectrum of the apatite shows features typically produced by rare-earth elements, in particular Nd3+. The path length of the beam was about 7.5-8.0 mm.

Gemmological textbooks (e.g. Anderson 1980) mention that the characteristic 'didymium' absorption spectrum of apatite is due to the presence of rare-earth elements (REE), in particular neodymium (Nd) and praseodymium (Pr). Although these elements were not detected by energy-dispersive X-ray fluorescence (EDXRF) spectroscopy with an EDAX Orbis Micro-XRF Analyzer, REE can be present at very low concentrations (below 100 ppmw) yet still be detectable with absorption spectroscopy and luminescence techniques. The multiple peaks seen in the Vis-NIR spectrum are typically due to the presence of trivalent rare-earth ions. In particular, the absorption bands centred at around 740 and 800 nm (Figure 5) can be attributed to Nd3+, the intense photoluminescence in the red region (Figure 6) is due to the presence of Pr3+, and the weak fluorescence to short-wave UV might indicate the presence of Ce3+ (Cantelar et al. 2001).

> Dr J. C. (Hanco) Zwaan FGA (hanco.zwaan@naturalis.nl) Netherlands Gemmological Laboratory National Museum of Natural History 'Naturalis' Leiden, The Netherlands

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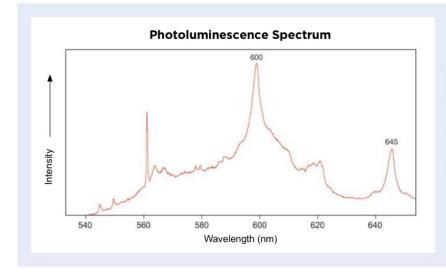


Figure 6: Strong photoluminescence in the red region, excited by a green laser, can be attributed to the presence of Pr3+ Sharp Raman bands of fluorapatite are present in the 540-580 region.

## Cobaltocalcite or Cobaltoan Calcite: A Swiss Answer

Switzerland is not known for its gem production, but rather as an important platform for trading, auctioning and certifying gems. However, at the May 2019 GemGenève fair (Geneva International Gem and Jewellery Show), a new Swiss gem material debuted in the designer area. Geneva-based art jeweller Grégoire Maret (Pierre d'Alexis S.A.) presented pink to purplish pink cobaltoan calcite from Switzerland—marketed as 'Rose of Mine'—in his handmade jewellery creations (e.g. Figure 7).

Cobaltoan calcite, (Ca,Co)CO<sub>3</sub>, is rarely seen in high-end jewellery, and is rather unusual in its nature and geological origin. It is coloured by traces of Co<sup>2+</sup> in octahedral coordination within the calcite structure (Fritsch & Rossman 1987), and may show variations in saturation and hue. The Swiss rough material, previously described by Meisser (1999), is sporadically extracted from abandoned coal mines situated near the village of Isérables in the canton of Valais in south-west Switzerland. The gemmy material is polished *en cabochon*, and so far approximately 30 stones have been cut, ranging from 5 to 35 ct.

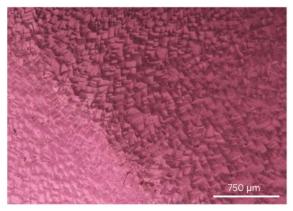
This attractively coloured calcite variety formed under unique conditions. Following the cessation of coal mining in 1943, surface waters interacted with the surrounding rocks, and the cobaltoan calcite crystallised at ambient temperature and pressure through the percolation of fluids enriched with Co, Ni and Zn (Meisser 1999), forming speleothems on black shale host rock (Figure 8) in the moist darkness of the abandoned coal mines.



**Figure 7:** A free-form cabochon of translucent cobaltoan calcite from Switzerland is set in this pendant (5 cm long) by Grégoire Maret (Pierre d'Alexis S.A.), which is called 'L'Inattendue'. In the background is a piece of the rough speleothem on the host rock. Photo by David Fraga.



**Figure 8:** A speleothem (3 cm tall) of Swiss cobaltoan calcite is shown on its black shale host rock. (The white material in bottom-centre is a later generation of calcite.) Photo by Alain Pitteloud.



**Figure 9:** Aggregates of trigonal crystals are seen on the surface of the rough cobaltoan calcite. Photomicrograph by F. Notari.

Standard gemmological testing of this strongly birefringent polycrystalline material revealed RIs of 1.49–1.66 and a hydrostatic SG value of approximately 2.70. Only a very weak purplish luminescence was observed with long-wave UV radiation and the material was inert to short-wave UV. Under magnification, it showed a granular to fibrous appearance and columnar growth with inhomogeneous colour distribution resulting from the presence of remnants of the black shale host rock. The surface of the piece of uncut rough material we examined exhibited trigonal prismatic crystals without preferential orientation (Figure 9), resulting in a generally botryoidal form and making it tougher than monocrystalline calcite.

We identified the material as calcite (rather than aragonite) using infrared specular reflectance. The UV-Vis-NIR

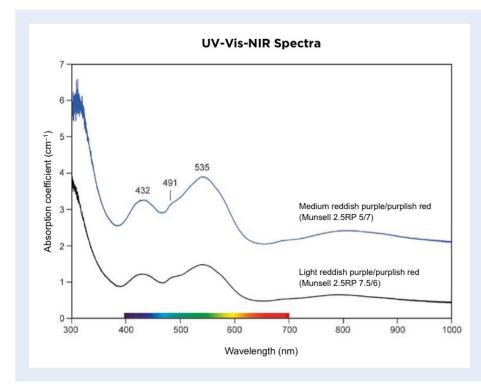


Figure 10: UV-Vis-NIR spectra taken at room temperature of two samples of cobaltoan calcite with different colouration reveal typical absorptions of Co<sup>2+</sup>, consisting of two broad bands at about 535 and 432 nm and a smaller one at about 491 nm (present as a shoulder; position calculated at 77 K) of unknown attribution.

spectra (Figure 10) exhibited absorptions at about 535 and 432 nm associated with the presence of Co<sup>2+</sup>. Semi-quantitative analysis of trace elements was measured on zones with different colour saturations using EDXRF spectroscopy (Thermo Fisher Scientific ARL Quant'X), and indicated the presence of about 850–1,400 ppmw Co—with higher amounts corresponding to deeper colouration—and up to about 220 ppmw Ni, as well as detectable levels of Zn. Pink colour in calcite is also known to be due to Mn, but this element was not detected in the Swiss samples by EDXRF analysis, in contrast to the cobaltoan calcite from an unspecified locality that was studied by Siritheerakul and Sangsawong (2015).

There is confusion between the names *cobaltocalcite* and *cobaltoan calcite*. *Cobaltocalcite* was introduced by

Palache *et al.* (1951) for CoCO<sub>3</sub> (a carbonate of cobalt), but was refused by the International Mineralogical Association and replaced by *spherocobaltite*. The material described here is a variety of calcite in which some Ca is replaced by Co—(Ca,Co)CO<sub>3</sub>—and therefore should be called cobaltoan calcite since it does not contain cobalt as a main component.

Dr Eric May (eric.may@ggtl-lab.org) and Franck Notari GGTL Laboratories Les Acacias, Switzerland

> Dr Nicolas Meisser Musée Cantonal de Géologie Lausanne, Switzerland

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