The clusters of accessory minerals in Grenville marble crystallized from globules of melt

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We live in proximity of the Central Metasedimentary Belt (CMB) of western Quebec and eastern Ontario, part of the Grenville Province, one of the major collisional orogens of the world. Graphite-bearing white marble is a regionally important unit in the CMB; the coeval migmatitic gneissic rocks have been dated in the Otter Lake area (Quebec), 75 km northwest of Ottawa, at *ca.* 1230 Ma. Temperatures and pressures of metamorphism are estimated to have reached 700–750°C and 7–8 kilobars. We focused our attention on examples of varicoloured marble that have been transformed in some way.

We first describe the blue marble along Autoroute 5, close to Wakefield, Quebec. Polished thin sections were imaged with a Zeiss Sigma HDVP SEM using the novel large-area imaging module Atlas 5. Overview image mosaics with the BSE and CL signals were acquired at a resolution of 150 nm/pixel and 90 nm/pixel. In addition, regions of interest were imaged at 15 nm/pixel. Samples devoid of visible inclusions were found to contain numerous sets of micrometric to nanometric inclusions, locally aligned. Euhedral baryte and subhedral anhydrite crystallites ~200 nm to 540 μm across occur as single inclusions. Polymineralic inclusions, from 50 to 700 μm across, contain 1) enstatite, diopside, orthoclase, albite, titanite, and phlogopite, or 2) pyrrhotite + chalcopyrite + magnetite + galena. The minerals that coexist in such polymineralic inclusions grew together, as they fit together like pieces of a jigsaw puzzle.

Some specimens contain lemon-yellow inclusions in a matrix of blue calcite. These consist of enstatite decorated with a cathodoluminescent outer boundary that is As-rich; other crystals are green, and consist of sulphate-bearing apatite. The enstatite and apatite inclusions are roundish, possibly accumulated, and range from 234 μm to 3.6 mm in size. Some enstatite crystals contain globules of calcite that are accompanied by a small (5 to 25 μm) crystal of baryte. Rare specimens of blue calcite contain euhedral crystals of wollastonite with prominent globular inclusions of calcite, with diopside, julgoldite-(Fe^{3+}), baryte, pyrrhotite, pyrite, and a quaternary apatite-group mineral containing phosphate, sulphate, silicate and carbonate groups.

Sinaei-Esfahami (2013) reported values of $\delta^{18}O$ of 20.8, 25.3 and 25.9‰ (SMOW) for the blue calcite, in the same range as the regionally developed white calcite. We still have not pinpointed the cause of the blue color, which fades in some samples that are kept out of direct sunlight. The textural evidence indicates that marble has melted. The baryte, anhydrite, apatite, enstatite and, lastly, calcite crystallized directly from the carbonate + sulfate + phosphate + arsenate melt. As the enstatite nucleated in this melt, it systematically rejected As until it was forced to accept it. Globules of the two melts, one silicate + “others” and one sulfide + oxide, must represent material left over after the removal of discrete minerals from the early melt.

We report results of a comparative study of orange calcite at the Otter Lake locality (Quebec). The calcite dykes there host impressive crystals of fluorapatite up to 30 cm in length, as well as diopside, titanite, meionite, phlogopite, allanite-(Ce), orthoclase, fluorite, thorite and thorianite. All of these except the fluorite form euhedral crystals and contain globular inclusions of calcite. The fluorapatite contains a bewildering array of globular, polymineralic micro-inclusions. These range from <1 to 700 μm across, and contain some or all of the following: quartz, fluorite, calcite, hematite, julgoldite-(Fe^{3+}), diopside, allanite-(Ce), thorite, cerite-(Ce), parisite-(Ce) and synchysite-(Ce), baryte, and anhydrite. The large globules of orange calcite themselves also contain monomineralic and polymineralic inclusions. Anhydrite primarily occurs as monomineralic inclusions in orange calcite, but was also observed together with cerite-(Ce). The polymineralic inclusions contain quartz, apatite, hematite, baryte, and xenotime-(Y).

As in the previous example, the macroscopic and microscopic inclusions, polymineralic or monomineralic in nature, formed in a fluxed silicocarbonatitic melt. Crystallization of the euhedral crystals in the low-viscosity melt likely was rapid, probably because of degassing of the melt upon its emplacement as dykes and sills. Once trapped, the domains of melt produced imbricated primary crystals. The assemblages then continued to evolve in the subsolidus realm by reacting with an oxygenated aqueous fluid. We have not encountered globules of the sulphide + oxide melt at Otter Lake.

Dykes of granitic pegmatite contains xenoliths of marble containing calcite + fluorite. Thus anatectic reactions seem to have produced coeval carbonatitic and silicate melts. The assemblage has been interpreted as a skarn, but our observations rule out a contact-metasomatic origin.

Calcite does melt in the presence of H_2O and F at the ambient conditions of P and T. Such a carbonate melt is expected to react aggressively with silicate assemblages along its contacts, and to digest them efficiently. We believe that the phosphorus and fluorine needed to crystallize the prominent fluorapatite prisms were at one time constituents of the gneisses associated with the marble. Thus is born a silicocarbonatitic melt of crustal origin. The $\delta^{18}O$ value (12.4‰, SMOW) shows that the orange calcite at Otter Lake is of crustal origin, but possibly modified by rising mantle-derived fluids responsible for the addition of the rare earths, thorium and uranium.

Kennedy *et al.* (2010) have dated two crystals of titanite (U–Pb TIMS, concordia ages): 1014.8 ± 2.0 Ma (2σ) and 998.0 ± 4.5 Ma (2σ; SHRIMP data). At the time of emplacement, at roughly 1 Ga, the Grenville system was in a state of relaxation after a major collision (the Ottawan event). We believe than an asthenospheric mantle rising in response to the detachment of a slab of lower crust at the Rigolet stage provided sufficient heat and fluids to melt units of marble as well as gneiss in the lower crust.

These two case-studies show that marble can melt in granulite-grade settings. The resulting rocks satisfy the definition of a carbonatite (>50 vol. % of primary carbonate), but are of a lineage distinct from mantle-derived carbonatites. How does one prove that there was a crustal silicocarbonatitic melt? The globules of imbricated accessory minerals constitute a very important criterion. The innovative Atlas 5 imaging software has yielded incredible detail about assemblages and textures. We are now acquiring $\delta^{18}O$ data for the euhedral minerals that crystallized early in the melt. We show that anatexis can produce three coeval melts: granitic, silicocarbonatitic, and sulphidic.

References:

Kennedy AK, Kamo SL, Nasdala, L., Timms, NE (2010): Grenville skarn titanite: potential reference material for SIMS U–Th–Pb analysis. Can Mineral 48:1423-1443

Sinaei-Esfahani F (2013) Localized metasomatism of Grenvillian marble leading to its melting, Autoroute 5 near Old Chelsea, Quebec. M.Sc. thesis, McGill University, Montreal, Canada