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Fluid circulations, chemical mass-transfer and volume change across chemically contrasted boundaries: examples from metacarbonate septa in the Quérigut granite (Eastern Pyrénées, France)

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Chemical mass-transfers associated with fluid circulations are an important research topic in metamorphism. Numerous interrogations remain concerning chemical transfer mechanisms (diffusion or fluid percolation), nature and origin of fluids (CO_2, H_2O, magmatic or metamorphic), fluid/rock ratios and circulation pathways. Chemically reactive fluid flow and metasomatism play an important role during contact metamorphism and, especially, during skarn development and the associated mineralogical, chemical and isotopic evolutions. In this study, we focus on the understanding of chemical-mass transfer and fluid flow at the contact between granitic rocks and metacarbonate septa entirely enclosed inside the magmatic rocks.

The sampling consists of perpendicular profiles made along the contact in both granitic rocks and metacarbonates. A petrological evolution appears at the contact: (1) in granitic rocks, a cm to dm-sized wide leucocratic endoskarn with Kfs, Qtz and Aug and (2) in metacarbonates, a mm to cm-sized wide exoskarn with a Di, Grt, Wo, Ves and Czo metamorphic assemblage. The initial chemical compositions of metacarbonate and granitoid protoliths are defined far from the skarn contacts. Carbonates show a decrease in CaO and CO_2content, while other elements concentrations increase, toward the contact. Granitoids show chemical modification with respect to the magmatic trend and are mainly characterized by enrichment in K_2O and Rb. These petrological and geochemical evolutions imply chemical mass-transfer during the contact meta-

morphism.

A stable isotope study was achieved to constrain the fluid regime which occurs during the contact metamorphism at septa contacts. For metacarbonates, δ^{18}O values of calcite progressively decrease toward the contact from about 24 ‰ (close to unaltered primary values) down to 14.8 ‰. Within granitoids, δ^{18}O values of whole rocks increase toward the contact from 9.2 ‰ to 13.4 ‰. The δ^{18}O values define sigmoid profiles typical of diffusion processes between two contrasted chemical rocks. Displacement of the profile inflection point into metacarbonates emphasizes limited input of magmatic fluid into metacarbonates. The evolution of δ^{13}C calcite values is only explained by dissolution and decarbonation processes. Thus, septa contacts behave like a closed system with respect to external fluids with only diffusion process between metacarbonates and granitic rocks.

Mass-balance calculations were achieved to constrain mass-transfer processes and volume changes. In granitoids, results show that chemical mass-transfers are limited on few decimetres close to the contact, with an increase in the K_2O, Rb, Y, Ce, Nb and Ba contents, in the white feldspathic zone. The most probable origin for potassium and the other mobile elements is the granitic intrusion itself. This process does not necessary imply volume change. In metacarbonate septa, chemical mass-transfers are more important with a strong decrease in the CaO, Sr and CO_2 contents (about 80 to 90%) and are characterized by an important volume loss of about 80%. These chemical mass-transfers are progressive and appear in the two last meters to the contact zone with the granitic intrusion. The observed volume loss in metacarbonates implies passive concentration of immobile chemical elements by release of CO_2 and CaO during calcite dissolution and decarbonation reactions (without important input from the granitic protolith).

In the Quérigut complex, important chemical mass-transfers appear during contact metamorphism between metacarbonate septa and granitoids in a closed system to external fluid input but an open system to CaO and CO_2 output, corresponding to the strong calcite and volume losses in metacarbonates.