Driving forces for metamorphic vein filling during bauxite dehydration: insights from Li and Al transfer illustrated by LIBS compositional profiles (Western Alps)

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In subduction zones, the significant amounts of aqueous fluid released in the course of the successive dehydration reactions occurring during prograde metamorphism are expected to strongly influence the rock rheology, as well as kinetics of metamorphic reactions and mass transfer efficiency. Mineralized veins, ubiquitous in metamorphic rocks, can be seen as preserved witnesses of fluid and mass redistribution that partly accommodate the rock deformation (lateral segregation). However, the driving forces and mechanisms of mass transfer towards fluid-filled open spaces remain somewhat unclear. The aim of this study is to investigate the vein-forming processes and the modalities of mass transfer during local fluid-rock interactions, and their links with fluid production and rock deformation, with new insights from Laser Induced Breakdown Spectroscopy (LIBS) profiles.

This study focuses on karstic pockets (metre scale) of Triassic metabauxites embedded in thick carbonate units, that have been isolated from large-scale fluid flow during HP-LT Alpine metamorphism (W. Vanoise, French Alps). These rocks display several generations of metamorphic veins containing various Al-bearing minerals, which give particular insights into mass transfer processes.

It is proposed that the internally-derived fluid (∼13 vol% produced by successive dehydration reactions) has promoted the opening of fluid-filled open spaces (euhedral habits of vein minerals) and served as medium for diffusive mass transfer from rock to vein. Based on mineralogical and textural features, two vein types can be distinguished: (1) some veins are filled with newly formed products of either prograde (chloritoid) or retrograde (chlorite) metamorphic reactions; in this case, fluid-filled open spaces seem to offer energetically favourable nucleation/growth sites; (2) the second vein type is filled with cookeite (Li-Al-rich chlorite) or pyrophyllite, which were present in the host-rock prior to the vein formation. In this closed chemical system, mass transfer from rock to vein was achieved through the fluid, in a dissolution-transport-precipitation process.

To investigate the modalities of mass transfer towards this second vein type, LIBS profiles were performed in the host-rock, taking Li concentration as a proxy for cookeite distribution. Cookeite is highly concentrated (45-65 vol%) in regularly spaced veins, and the LIBS profiles show that cookeite is evenly distributed in the host-rock comprised between two veins. The absence of diffusion profiles suggests that the characteristic diffusion distance for Li, Al and Si is greater than or equal to the distance separating two cookeite veins (2-4 cm). This is in agreement with characteristic diffusion lengths calculated from both grain boundary and pore fluid diffusion coefficients, for the estimated duration of the peak of metamorphism. Which driving forces are responsible for cookeite selective transfer towards veins? Chemical potential gradients between host-rock pores and veins may have developed in response to either (1) a stress difference: thermochemical calculations show that pressure-solution processes may affect preferentially cookeite and pyrophyllite; (2) a difference in interfacial energy, phyllosilicates showing very different morphologies in host-rocks (fibers) compared to veins (euhedral crystals); fluid-mineral interfacial energy may be maximal in the small host-rock pores, which can maintain higher cookeite solubility than large fluid-filled open spaces (i.e. veins).