# From local equilibria to fluid channelization in low-grade shear zones: evidence from the link between chloritization mechanisms at the nanoscale and compositional heterogeneities at micron scale

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Fluid percolation in low-grade shear zones is often accompanied by the growth of phyllosilicates, which influence rock strength and strain localisation. The composition of these phyllosilicates is frequently used for pressure-temperature-time constrains of deformation events, although it is often highly heterogeneous, even in mylonites. This study investigates the reactions producing phyllosilicates (chlorite in particular) in a low-grade shear zone of the Variscan Bielsa granitoid (Axial Zone, Pyrenees). Chlorite compositional heterogeneities at micrometer scale, including iron speciation obtained by XANES-STXM and EELS, is compared to nanostructures observed by transmission electron microscopy in increasingly-strained samples and related to fluid percolation mechanisms. The undeformed but altered Bielsa granitoid exhibits local equilibria, pseudomorphic replacement of amphibole and biotite and high compositional heterogeneities (included $Fe^{3+}$) in late Variscan chlorite. This is due to variable chloritization reaction mechanisms at nanoscale (dissolution-reprecipitation and layer-by-layer substitution), each of them related to different element supply and to the formation of poorly connected nanoporosity (as ripplocation or nanopores). Such features point to a fluid limited to local reservoirs in undeformed rocks. In samples with discrete mm-sized fractures, high fluid/rock ratio triggers the precipitation of Alpine chlorites in fractures from a free channelized fluid, with no re-equilibration of late Variscan ones outside the fractures walls, down to the nanoscale. In mylonites, fluid percolates in micro and nanocracks mainly located at the rims of chlorite crystallites, bended and partially dissolved. This promotes pervasive compositional replacement (included $Fe^{3+}$) of late Variscan chlorites by Alpine ones at micrometer scale. However, chlorite replacement remains incomplete in mylonites, despite the high strain and the grain size reduction. Therefore, in the studied shear zone, local equilibria and high compositional heterogeneities in chlorite are preserved according to matrix-fracture porosity contrasts, the location and connection of nanoporosity between crystallites of chlorite and the size of cracks enhancing pervasive fluid percolation.

**Key words :** Greenschist-facies shear zone, XFe3+, chloritization reactions, TEM, Bielsa, Pyrenees

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