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## Chloritization of granites in shear zones: an open window on fluid pathways, equilibrium length-scales and porosity formation down to nanoscale

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Strain localisation in the upper crust is strongly influenced by the presence of phyllosilicates (e.g. white mica, biotite, chlorite), systematically observed in shear zones in granites. Identifying reactions involving phyllosilicates at low-grade metamorphic conditions is crucial to understand crust mechanics and fluid-granite interactions during deformation. In the 305 Ma old basement of the Bielsa massif (Axial Zone, Pyrenees), extensive pre-orogenic (i.e. pre-Alpine) alteration related to feldspar sericitization and chloritization of biotite and amphibole occurred at temperatures of 270–350°C at 230–300 Ma. This event was followed by mylonitization and fracturing at 40–70 Ma, and fluid-rock interaction at 200–280°C marked by replacement and new crystallization of chlorite and white mica. In undeformed parts of the granite, compositional maps reveal in situ reaction, high local heterogeneities and low element mobility (migration over few  $\mu\text{m}$ ) for most elements. Transmission electron microscopy (TEM) shows disconnected reaction-induced nanoporosity in chloritized amphiboles and ripplifications in chloritized biotite. Chloritization reaction varies over tens of nanometres, indicating high variability of element availability. Equilibrium is reached locally due to isolation of fluid in pockets. In samples with fractures, both elemental maps and TEM images show two chlorite groups: alpine chlorites in fractures have homogeneous composition while pre-alpine chlorites in the matrix show patchy compositions. Channelization of fluids in fractures and sealing by chlorite prevented replacement of the matrix chlorite. High element mobility was therefore limited to fractures. In mylonites, compositional maps show secondary chlorites up to 1 mm around cracks and only partial replacement of chlorite within the matrix. This suggests fluids could percolate from cracks to the matrix along chlorite grain boundaries. TEM images show nanocracks at the boundary of chlorite crystallites where replacement is localised. Crystallites were individually replaced by dissolution-precipitation reactions and not by intra-crystallite mineral replacement, explaining the patchy compositional variations. While fracturing did not allow chlorite sheets to be progressively re-oriented, a continuous, brittle-ductile deformation in mylonites did, making preferential fluid pathways progressively change. Despite high strain, chlorite replacement was not complete even in mylonites. Replacement appears to be controlled by matrix-fracture porosity contrasts and the location and connection of nanoporosity between crystallites, criteria that may be only transiently met in space during deformation. These

mechanisms need to be taken into account when attempting to reconstruct the metamorphic history of shear zones as well as the evolution of their mechanical behaviour since they affect the scale of the thermodynamic equilibrium and the preservation of hydrothermal metamorphism in granites.