

# Chlorite chemical adjustment in the Gréixer vein: effects on thermometry

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## INTRODUCTION

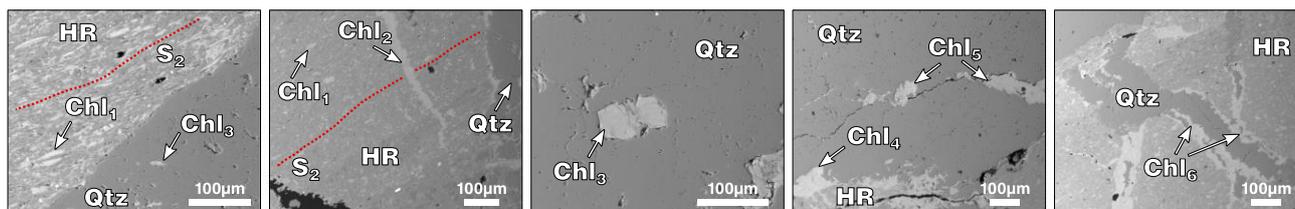
Chlorite is a common mineral formed during low-medium temperature metamorphism, diagenesis and/or hydrothermalism. Its chemistry depends on the host rock composition and its physicochemical conditions of growth (e.g., T, P and  $fO_2$ ; e.g. Inoue et al., 2009). Thus, chlorite composition has been widely used as a geothermometer, first through empirical equations based on their  $Al^{3+}$ ,  $Fe^T$  or  $Mg^{2+}$  contents (see a review in De Caritat et al., 1993), and more recently by thermodynamic and semi-empirical approaches (e.g., Bourdelle et al., 2013; Lanari et al., 2014; Inoue et al., 2009; 2018). The latter methods, based on a combination of chlorite end-members, often come near to formation conditions for low-temperature chlorites. However, they do not always reflect the real temperatures, in part due to the usual lack of information about the  $Fe^{3+}$  content of chlorites (e.g., González-Esvertit et al., 2020).

In the Pyrenees, an Alpine fold and thrust belt, several metric to kilometric, SE-NW to SW-NE oriented massive quartz bodies are hosted in the Variscan and Pre-Variscan basement, which includes a metasedimentary succession, Variscan gneisses derived from Ordovician magmatic rocks and Late-Variscan granitoids. Phyllosilicates (mainly chlorite) are common in these veins. The Gréixer vein, in the southern slope of the Canigó Massif, is hosted in Cambrian-Ordovician metasandstones and shales. The vein consists of a discontinuous SW-NE quartz body, ~8-10m width and ~600m length. In this work, we compare the chemistry and thermometry of different chlorite types, which were distinguished according their petrographic characteristics and relationships with quartz microstructures forming the Gréixer vein. Thermometric analysis by using their  $Fe^{3+}/Fe^T$  ratio (Inoue et al., 2009; Lanari et al., 2014 (Chl1)) and not considering them (Bourdelle et al., 2013; Lanari et al., 2014 (Chl2); Inoue et al., 2018) are used to understand the differences between the calculated temperatures. Moreover, we discuss the origin of the variations in chlorite compositions in relation to their location.

## RESULTS AND DISCUSSION

Petrographic, microstructural and Electron Probe Microanalysis (EPMA) from 6 vein samples allow to distinguish, in most of the 31 studied thin sections, 6 types of chlorites. EPMA analyses were filtered to consider only those without smectite-vermiculite interlayers ( $Na+Ca+K<0.1apfu$ ) and octahedral sites below 5.95apfu ( $n=737$ ). The chlorite types are shown in Figure 1 and their characteristics are: Chl<sub>1</sub>, crystals growing within the host-rock coevally with regional foliation ( $S_2$ ); Chl<sub>2</sub>, micrometric veinlets crosscutting the  $S_2$ ; Chl<sub>3</sub>, isolated crystals within the quartz; Chl<sub>4</sub>, crystals growing from hostrocks towards the quartz; Chl<sub>5</sub>, crystals close to stylolites; Chl<sub>6</sub>, crystals in the walls of quartz micrometric veinlets that crosscut the hostrocks. Thus, Chl<sub>1,2</sub> grew within the hosting rocks and Chl<sub>3-6</sub> are located within the quartz, although Chl<sub>3</sub> are the only chlorite type spatially unlinked from the host rocks.

Statistically, Chl<sub>1</sub> is the most chemically homogeneous with the lowest  $Si^{4+}$  and  $Al^{VI}$  and the highest  $Al^{IV}$  and  $Fe^T$  content. Conversely, Chl<sub>3</sub> shows the lowest  $Al^{IV}$  and  $Fe^T$  and the highest  $Si^{4+}$  and  $Al^{VI}$  values. Types Chl<sub>2,4-6</sub> show a wide range of composition between Chl<sub>1</sub> and Chl<sub>3</sub>, and are those with higher standard deviations regarding their  $Si^{4+}$ ,  $Al^{3+(IV,VI)}$ ,  $Fe^T$  and  $Mg^{2+}$  contents.



**Fig 1.** Back-scattered images of chlorites from the Gréixer vein. Abbreviations: HR, host rock; Chl, chlorite; Qtz, quartz; S<sub>2</sub>, regional foliation.

If Chl<sub>1</sub> could have registered the temperature of regional foliation and Chl<sub>3</sub> the quartz formation conditions, it is proposed that types Chl<sub>2,4,6</sub> represent discrete steps of the chemical difference between Chl<sub>1</sub> and Chl<sub>3</sub>. The Si<sup>4+</sup> enrichment in Chl<sub>3</sub> leads to an Al<sup>3+</sup> decrease in the tetrahedral layer and an Al<sup>3+</sup> increase in the octahedral position.

Calculated temperatures using the Verdecchia et al. (2019) spreadsheet reflect the aforementioned variations on the chlorite composition, and a temperature gradation between Chl<sub>1</sub> (310-370°C) and Chl<sub>3</sub> (140-180°C) for Chl<sub>2,4,6</sub> chlorites. These temperatures have been obtained using approaches that do not consider the Fe<sup>3+</sup>/Fe<sup>T</sup> ratio (Bourdelle et al., 2013; Lanari et al., 2014 (Chl<sub>2</sub>); Inoue et al., 2018).

The Fe<sup>3+</sup>/Fe<sup>T</sup> ratios of the Gréixer chlorites are unknown. However, we applied the Lanari et al. (2014) (Chl<sub>1</sub>) and Inoue et al. (2009) methods considering a suitable range of Fe<sup>3+</sup>/Fe<sup>T</sup> values (from 0.05 to 0.4, by intervals of 0.05; González-Esvertit et al., 2020). Results show that the calculated temperatures vary significantly (up to 100°C) when different Fe<sup>3+</sup>/Fe<sup>T</sup> values for each chlorite type are considered. Therefore, calculated temperatures for Chl<sub>1</sub> could match within a ±30°C interval (the typical error of the applied methods) with the Chl<sub>2,4,6</sub> types. Similarly, Chl<sub>3</sub> and Chl<sub>2,4,6</sub> temperatures also could match.

Interestingly, there is no ±30°C coincidence field between Chl<sub>1</sub> and Chl<sub>3</sub> whatever Fe<sup>3+</sup>/Fe<sup>T</sup> is chosen, pointing to different physicochemical formation conditions for these two chlorites. Thus, we propose a sort of progressive “chlorite refinement” during the quartz formation that involves changes in the texture and chemistry of chlorites.

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