Iron Speciation of Metamorphic Silicates at Microscale

Françoise, M.[1], Dubacq, B.[1], Bourdelle, F. [1], Verlaguet A.[1]

[1] *Sorbonne Université, CY Cergy Paris Université, CNRS INSU, Institut des Sciences de la Terre de Paris, ISTeP, F-75005 Paris, France*

ABSTRACT

The crystal chemistry of metamorphic minerals allows assessing the pressure-temperature history of crustal rocks, via phase diagrams constructed with thermodynamic models. Conversely, an error or approximation in the determination of the phase chemistry can result in discrepancies in the outcomes of thermodynamic models, and to major misinterpretations of the conditions undergone by the rock.

Routinely, the chemistry of metamorphic minerals is measured with electron microprobe (EPMA) and hence considers all iron as divalent. However, silicates and in particular phyllosilicates (chlorite, mica, serpentine) may include ferric and ferrous iron, and the speciation can vary on short distances, i.e. on few micrometers. Neglecting iron speciation in these Fe-rich minerals strongly impacts their estimated temperature of crystallisation**[1,2,3]**.

The *Schistes Lustrés* complex (Western Alps) is a well-studied area**[4]** where the thermobarometry via thermodynamic models is particularly challenging. This study reports on X-ray Absorption Spectroscopy (XAS) measurements carried out at the GALAXIES beamline of SOLEIL synchrotron to determine the iron speciation of a selection of metamorphic minerals from this complex. The beamline micro-beam ($<500\ \mu m^2$) and circular polarization enabled to collect XANES at the K edge of Fe in anisotropic micrometric metamorphic minerals, following the procedure of Wilke et al. (2001)**[5]**. Iron in chlorite is mainly divalent (0-40% Fe^{3+}) but reaches non-negligible Fe^{3+} levels, while it is mainly – or even completely – trivalent in mica (40-100% Fe^{3+}). These high Fe^{3+} content greatly differ from the generally-assumed crystal chemistry, in particular for estimated octahedral vacancies in chlorite, pointing out to the importance of the di-trioctahedral substitution ($2Al^{3+}$ + vacancy $\leftrightarrow 3Mg^{2+}$), in addition to the Tschermak substitution (${}^{IV}Si^{4+} + {}^{VI}Mg^{2+} \leftrightarrow {}^{IV}Al^{3+} + {}^{VI}Al^{3+}$) and homovalent substitutions ($Al^{3+} \leftrightarrow Fe^{3+}$ and $Mg^{2+} \leftrightarrow Fe^{2+}$). These measurements will now help refining thermodynamic modelling of the di-trioctahedral substitution.

REFERENCES

1. F. Bourdelle et al., *Contribution to Mineral Petrology,* 166:423–434 (2013).
2. L. Masci et al., *American Mineralogist*, **104**, 403–417 (2019).
3. B. Dubacq and J. B. Forshaw, *European Journal of Mineralogy*, **36**, 657-685 (2024).
4. C. Herviou et al., *Tectonophysics*, **827**, 0040-1951 (2022).
5. M. Wilke et al., *American Mineralogist*, **86**, 714–730 (2001).