# *First-principle partitioning and disequilibrium of chromium in garnet - clinopyroxene assemblage*

BENOÎT DUBACQ\*, SARAH FIGOWY\*, YVES NOËL, PHILIPPE D'ARCO



CNRS-INSU, Sorbonne Université, Institut des Sciences de la Terre de Paris, ISTeP UMR 7193, F 75005 Paris, France

\*correspondence: Benoit.Dubacq@sorbonne-universite.fr Sarah.Figowy@sorbonne-universite.fr





# AIM: partitioning of Cr to test equilibrium between garnet and clinopyroxene

## **CONTEXT OF THE STUDY**

Using partition coefficients is extremely useful to model melting processes and fluid-rock interactions. However, partition coefficients values remain scarce in regard of their sensitivity to mineral composition and to the variability of mineral composition.

In addition, the inferred equilibrium between phases is not necessarily reached, even in high-grade metamorphic conditions associated to melting. *Disequilibrium may dramatically hamper the effective* mobility of species and lead to element distribution far from the predicted values.

This contribution aims at estimating partition coefficients for chromium (Cr) between garnet and clinopyroxene, and testing them in natural rocks of various metamorphic grades. As a poorly mobile trivalent element, *Cr* is chosen as a proxy to rare earth elements.

#### **A COMBINED APPROACH**

**Theoretical partition coefficients for Cr between garnet and clinopyroxene are calculated ab initio** from structures where Cr<sup>3+</sup> is modelled as a defect in Al<sup>3+</sup> sites using CRYSTAL17 (Dovesi et al., 2009, 2018) and the thermodynamic description of Dubacq and Plunder (2018).

The distribution of Cr in natural samples is measured with electron microprobe (EPMA) in garnet-clinopyroxene assemblages containing 10s to 10 000s of ppm of Cr. Element mapping is crucial for correct interpretation of zoning.

*Comparison between predicted and measured partition coefficients allows estimating the deviation from equilibrium.* 

For more, check out: Figowy et al., Partitioning of chromium between garnet and clinopyroxene: first principles *modelling versus metamorphic assemblages,* accepted with minor revisions in *European Journal of Mineralogy* 

# Ab initio modelling of Cr in garnet and clinopyroxene

#### **Structures and strain**



#### **Pyroxene end-members**

Kosmochlor (Kos) Jadeite (Jd)



**Figure 1: Crystal structures of grossular and jadeite.**  $Cr^{3+}$  substitutes with  $Al^{3+}$  in  $AlO_6^{9-}$  octahedra in both grossular and jadeite.



#### **Gibbs free energy of reactions**



**Defect energy? energy difference before and after defect** 

#### A fundamental difficulty...

**Trace element content implies non-interacting defects,** which may only be reproduced with large systems! Here large systems allow representative dilution of Cr (Fig. 4).



Figure 4: Schematic drawing of increasing system size (and therefore computing time) with decreasing Cr content.

incorporation and relaxation!





activity product



### **Conclusions (1)**

- computations highlight the role of crystal-chemistry over the strain field around point defects, controlling the dynamics of the  $Cr^{3+} = Al^{3+}$  exchange

- the partitioning of Cr between garnet and clinopyroxene depends strongly on the grossular and pyrope content

Cr incorporates grossular preferentially to jadeite ( $\Delta G_r^{\circ}_1 = 22 \text{ kJ.mol-1}$ ) Cr incorporates jadeite preferentially to pyrope ( $\Delta G_r^{\circ}_2 = 7 \text{ kJ.mol-1}$ )

## **APPLICATION:** Mapping trace and minor Cr content shows disequilibrium Computed vs. measured "apparent" partition coefficients ( $D_{theo}$ vs $D_{app}$ )

**PARTITIONING... vs. DISEQUILIBRIUM** 





Figure 7: EPMA composition maps for SE1416B. Crystallization: 7 kbar, 650 °C (Soret et al., 2017)  $\langle 1 \land D_{app} = 6.5 \langle 2 \land D_{app} = 24 \langle 3 \land D_{app} = 4.1 \rangle$ vs.  $D_{theo} = 146$ : far from equilibrium



**Figure 5: Optical microscope images of the samples. A-B-C:** sample L3515; D: sample SE1416B; E: sample MA1438.



Figure 6: Garnet and clinopyroxene compositions.

#### **REFERENCES**

Dovesi et al. (2009) Z. für Kristallographie - Crystalline Materials, 220(5/6), 571–573 doi: 10.1524/zkri.220.5.571.65065 Dovesi et al. (2018) WIREs Computational Molecular Science, 8(4), e1360, doi:10.1002/wcms.1360 Dubacq and Plunder (2018) J. of Petrology, 59(2), 233–256, doi: 10.1093/petrology/egy027 Dubacq et al. (2019) Lithos, 334–335, 161–179, doi: 10.1016/j.lithos.2019.03.019 Locatelli et al. (2018) Lithos, 320-321, 378 - 402, doi: 10.1016/j.lithos.2018.09.028 Soret et al. (2017) J. of Metamorphic Geology, 35(9), 1051–1080, doi:10.1111/jmg.12267



**Figure 8: EPMA composition maps for L3515. Crystallization: 10 kbar, 850 °C (Dubacq et al., 2019)**  $\langle 1 ] D_{app} = 3.6 \langle 2 ] D_{app} = 1.6 \langle 3 ] D_{app} = 6.8$ vs *D*<sub>theo</sub> = 1.6 : only partial equilibrium!

Sectorial, non-radial zoning

*Impact of kinetics!* 

**Figure 9: EPMA composition maps for L3515.** Crystallization: 26 kbar, 550 °C (Locatelli et al., 2018)  $\langle 1 ] D_{app} = 39 \ \langle 2 ] D_{app} = 7.9 \ \langle 3 ] D_{app} = 1.3$ vs  $D_{theo} = 0.3$ : far from equilibrium

### **Conclusions (2)**

- disequilibrium is evidenced even for samples metamorphosed around 850°C

- it is attributed to slow diffusivity of Cr in fluid and at grain boundaries during crystal growth, leading to interface-coupled dissolution-precipitation.

- measuring the distribution of trace elements when possible appears **safer for correct interpretation**, especially in thermobarometry-based studies