ELECTRONIC SUPPLEMENTARY INFORMATION FOR

Iron oxidation state in garnet from a subduction setting: a micro-XANES and electron microprobe ("flank method") comparative study

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Sample description

The studied sample OF2727 is a fine-grained eclogitized metagabbro from the Monviso meta-ophiolite (western Alps), consisting of omphacite, garnet and rutile with minor blue amphibole and very minor lawsonite, talc and jadeite, as described by Groppo and Castelli.[1] Garnet occurs as small idioblasts (up to 0.5 mm in diameter) set in a matrix mainly consisting of omphacite. Garnet cores (1a-1e in Fig. S1) are crowded of very small inclusions mostly of omphacite, whereas garnet rims (2a-2c in Fig. S1) are almost free of inclusions. Both SEM-EDS and EMP analytical techniques have been used to analyze the major element concentrations across garnet crystals. Garnet is strongly zoned, showing a Mn and Ca decrease toward the rim, counterbalanced by a Fe and Mg increase (Fig. S1).

$Fe^{3+}/\Sigma Fe$ variations in garnet as monitor of dehydration-redox reactions during subduction

The studied eclogitized metagabbro extraordinarily well preserves evidence of a prograde P-T evolution during subduction to ca. 80 km depth at very-low geothermal gradients (7-9°C/km). The prograde P-T path of this sample has been already investigated in detail[1] (Fig. S2a), as well as the main dehydration reactions occurring during subduction and responsible for the breakdown of lawsonite and chlorite.

Thermodynamic modeling shows that the dehydration-redox equilibria involving changes in both garnet and omphacite compositions are of the type (Fig. S2b):

$$Qtz+Lws+Chl_{ss}+Omp1_{ss}+Grt1_{ss}= Omp2_{ss}+Grt2_{ss}+ H_2O+O_2 \qquad (1),$$

with molar amounts of both $Grt1_{ss}$ and $Omp1_{ss}$ lower than those of $Grt2_{ss}$ and $Omp2_{ss}$ (the reaction equation is written such that the high-T assemblage is on the right side; ss = solid solution). Crossing this equilibrium up-T, both garnet and omphacite change their composition, with the $Fe^{3+}/\Sigma Fe$ ratio decreasing in both the minerals (Fig. S2b). For 1 mole of lawsonite + chlorite consumed, about 2.0-2.5 moles of H_2O are released on average, and for 1 mole of garnet + omphacite produced, about 0.25 moles of oxygen are released on average (e.g. $0.02Qtz + 0.04Lws + 0.01Chl_{ss} + 0.29Omp1_{ss} + 0.75Grt1_{ss} = 0.77Grt2_{ss} + 0.31Omp2_{ss} + 0.11H_2O + 0.01O_2$).

The breakdown of lawsonite and chlorite combined with the progressive growth of omphacite and garnet up-T thus allow the release of O_2, counterbalanced by a significant chemical re-equilibration

of both omphacite and garnet, resulting in a progressive decrease of their $Fe^{3+}/\Sigma Fe$ ratio toward the rim. The predictions of equilibrium (1) are perfectly in agreement with the observed and measured mineral zoning, thus confirming the validity of the thermodynamic modelling and suggesting that dehydration-redox reactions occurring at least in some lithologies of the subducting slab may act as effectively oxidizing agents for the mantle wedge.
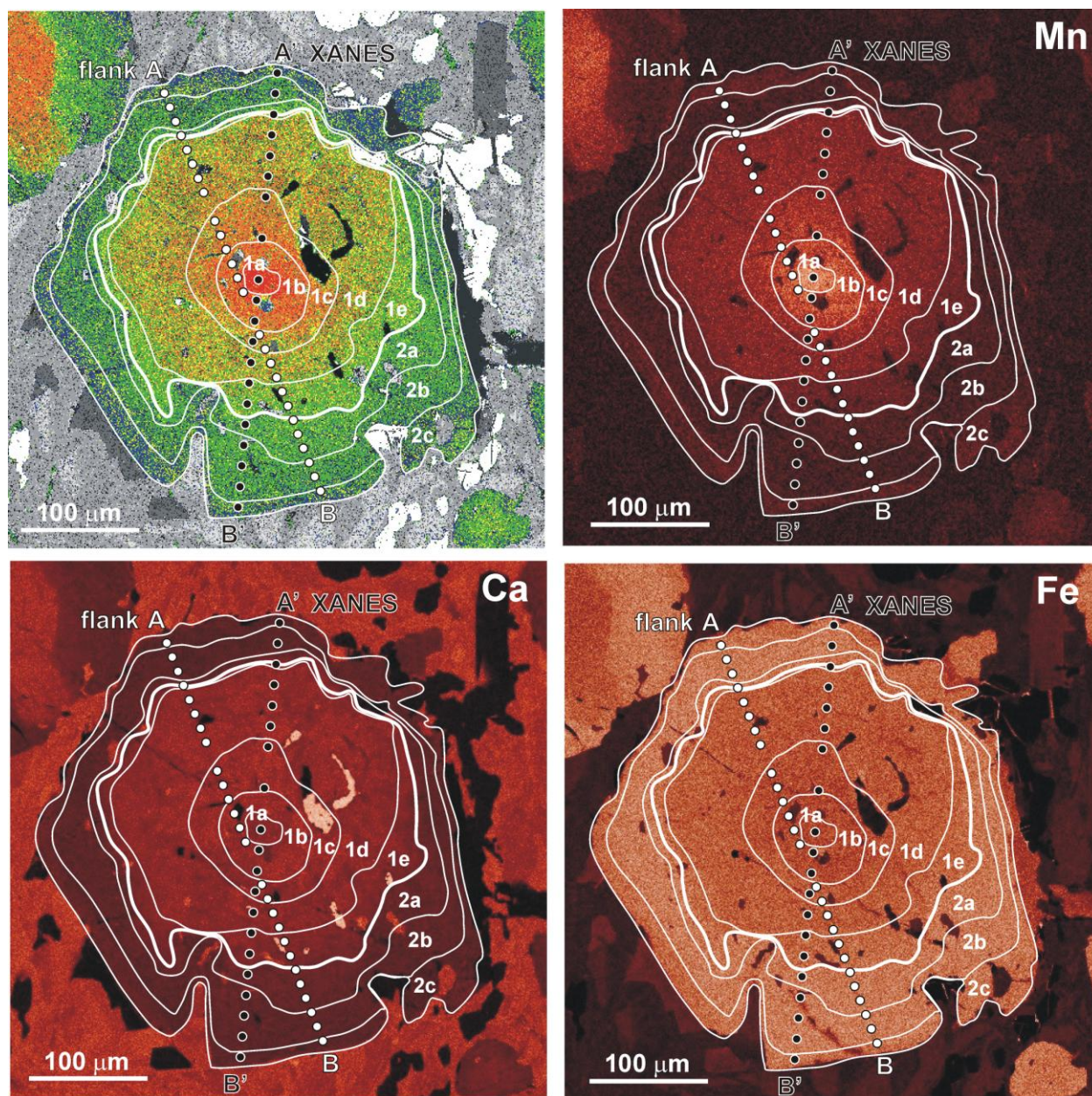

Figure S1. Processed (a) and unprocessed (b, c, d) major elements (Mn, Ca and Fe) X-ray maps of $Grt_{\#11}$ showing the eight growth shells (1a-2c) discussed by Groppo and Castelli.[1] Colours in (a) have been obtained combining the Mn, Ca and Fe X-ray maps. In (b, c, d), brighter colours (from black to red and yellow) imply higher concentrations. The profiles A-B and A'-B' locate the two sections analysed using the "flank method" and the micro-XANES technique, respectively. The boundary between the outer garnet core shell (1e) and the inner garnet rim shell (2a) is outlined by a thicker white line.
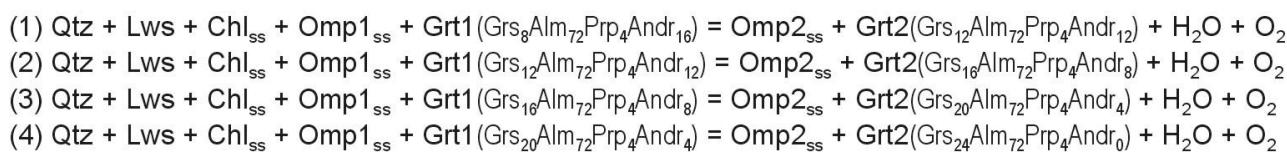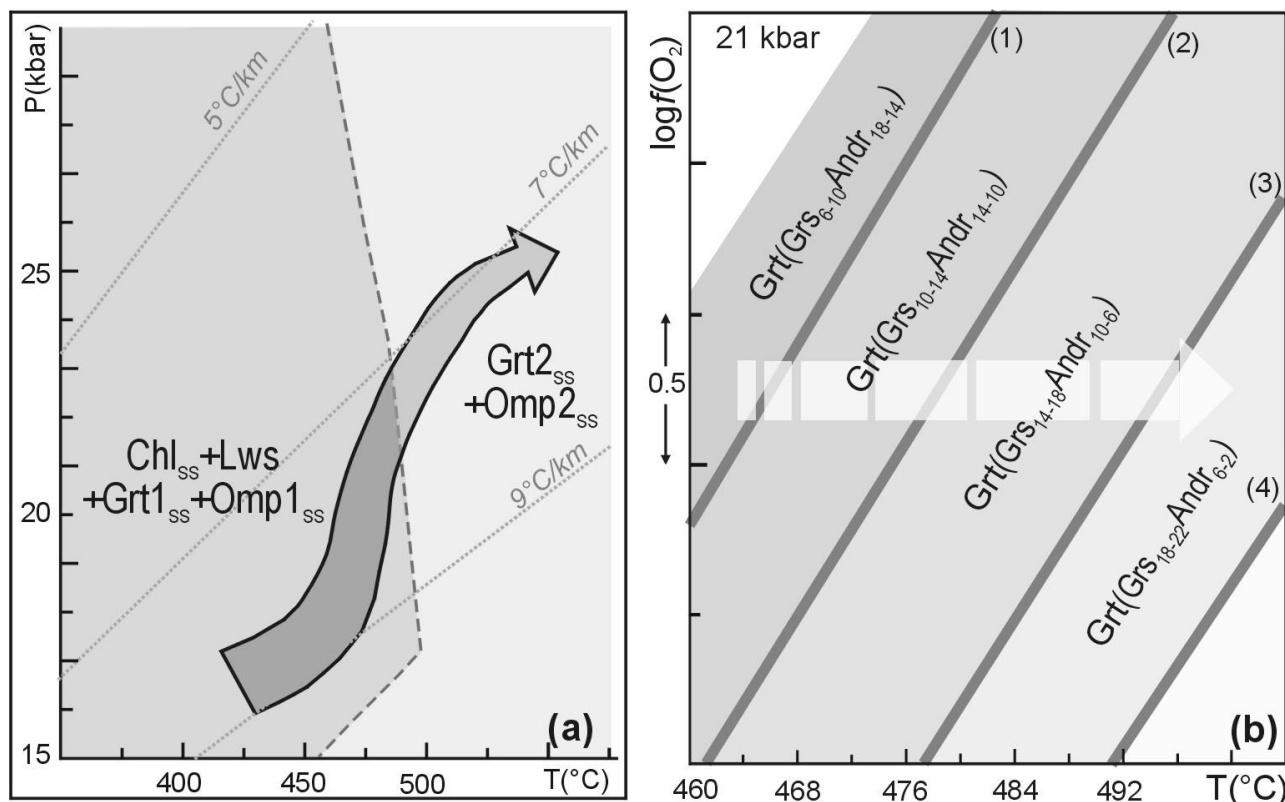
(1) $Qtz + Lws + Chl_{ss} + Omp1_{ss} + Grt1(Grs_8Alm_{72}Prp_4Andr_{16}) = Omp2_{ss} + Grt2(Grs_{12}Alm_{72}Prp_4Andr_{12}) + H_2O + O_2$
(2) $Qtz + Lws + Chl_{ss} + Omp1_{ss} + Grt1(Grs_{12}Alm_{72}Prp_4Andr_{12}) = Omp2_{ss} + Grt2(Grs_{16}Alm_{72}Prp_4Andr_8) + H_2O + O_2$
(3) $Qtz + Lws + Chl_{ss} + Omp1_{ss} + Grt1(Grs_{16}Alm_{72}Prp_4Andr_8) = Omp2_{ss} + Grt2(Grs_{20}Alm_{72}Prp_4Andr_4) + H_2O + O_2$
(4) $Qtz + Lws + Chl_{ss} + Omp1_{ss} + Grt1(Grs_{20}Alm_{72}Prp_4Andr_4) = Omp2_{ss} + Grt2(Grs_{24}Alm_{72}Prp_4Andr_0) + H_2O + O_2$

Figure S2. (a) Prograde P-T path inferred for the studied FeTi-oxide metagabbro.[1] The light and dark grey fields correspond to the more oxidized lawsonite + chlorite + garnet core (Grt_1) + omphacite core (Omp_1) assemblage and to the more reduced garnet rim (Grt_2) + omphacite rim (Omp_2) assemblage, respectively. The dashed line marks the lawsonite breakdown.[1] The dotted curves are thermal gradients. (b) Qualitative isobaric T-log$f(O_2)$ section in the NCFMASHO system at P-T conditions immediately preceding the lawsonite and chlorite breakdown (T=460-500°C, P=21 kbar; Fig. S2a). Each of the thick grey line corresponds to several pseudo-univariant redox equilibria of the general type reported in the lower portion of the figure (equilibria 1 to 4), grouped together for simplicity. Along each of these pseudo-univariant redox equilibria the composition of garnet does not change, whereas chlorite and omphacite compositions progressively change as a function of T and log$f(O_2)$, approximately in the range $Daph_{58}Clin_{42}$ to $Daph_{42}Clin_{58}$ for chlorite and $Di_{20}Jd_{30}Aeg_{28}Hed_{22}$ to $Di_{30}Jd_{20}Aeg_{28}Hed_{22}$ for omphacite. Crossing equilibria (1) to (4) up-T (white arrow), a progressive variation in the garnet composition is observed: fields reported with different grey tones correspond to the stability field of garnets with different compositions (i.e. $Fe^{3+}/\Sigma Fe$ ratio decreases up-T). The step-like variation of garnet composition is due to the modeling of the continuous variation in the solid-solution compositions by discrete steps following the pseudocompounds approximation.[2] Solid-solution compositions: Grs=grossular, Alm=almandine; Prp=pyrope; Andr=andradite for garnet; Di=diopside, Jd=jadeite, Aeg=aegirine (hedenbergite as difference to 100) for omphacite; Daph=daphnite (clinochlore as difference to 100) for chlorite. The isobaric T-log$f(O_2)$ projection has been calculated at P = 21 kbar and T = 460-500°C in the system NCFMASHO, using the approach of Connolly[3, 4] (Perple_X version 6.6.5.5, updated March 2011). The internally consistent thermodynamic dataset and equation of state for H_2O of Holland and Powell[5] were used. The minerals considered in the calculation were: garnet, omphacite, chlorite, lawsonite and quartz and the following solid solution models were considered: garnet (ideal model, modified from Engi and Wersin[6]; restricted compositional range: Grs_{13-20}, Alm_{72-82}, Prp_{4-8}), omphacite[7] (restricted compositional range: Di_{20-30}, Jd_{20-30}, Aeg_{28-34}) and chlorite[5] (restricted compositional range: $Daph_{42-68}$).

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