Phase equilibrium modelling in the KFMASH system to show the Metamorphic Evolution of the Ceán Schists (Malpica-Tui Unit, NW Iberian Massif)

Modelización del equilibrio de fases en el sistema KFMASH para mostrar la evolución metamórfica de los Esquistos de Ceán (Unidad de Malpica-Tui, NW del Macizo Ibérico)

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RESUMEN

Para complementar los resultados obtenidos mediante termobarometría convencional (termómetro granate-moscovita y barómetros GRIPS y GASP) en los Esquistos de Ceán (López-Carmona et al., 2008) se ha construido una pseudosección P-T en el sistema químico KFMASH para una composición media de estas metapelitas [SiO_2:71.42; Al_2O_3:13.42; MgO:4.78; FeO:7.04; K_2O:3.34]. Adicionalmente, la proyección de isopletas que reflejan el contenido en sílice de las fengitas en los diferentes campos de estabilidad de la pseudoseción, proporciona otro barómetro muy fiable. En base a los resultados obtenidos, y de acuerdo principalmente con las paragénesis naturales preservadas en los esquistos, las condiciones P-T obtenidas para el pico metamórfico son P=23-24 Kb y T=530-540 ºC, mientras que para un segundo evento metamórfico se obtuvieron valores de P=20-23 Kb y T=550-560 ºC. Los resultados proporcionados por la termobarometría convencional indican P=19-21 Kb y T=430-500 ºC para el pico y P=16-19 Kb y T=440-515 ºC cuando se emplean las composiciones de los minerales del segundo evento metamórfico.

Key words: *Malpica-Tui Unit, Blueschists facies, THERMOCALC, KFMASH system, P-T pseudosection.*

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Geological setting and Petrography

The Malpica-Tui Unit is the westernmost exposure of the Basal Units in the NW Iberian Massif. The Basal Units are considered part of the most external margin of north Gondwana, and record a late Devonian high-P metamorphism that probably reflects the subduction of this unit below the southern border of Larussia at the onset of the Variscan convergence (Martínez Catalán *et al.*, 1996, Arenas *et al.*, 1997).

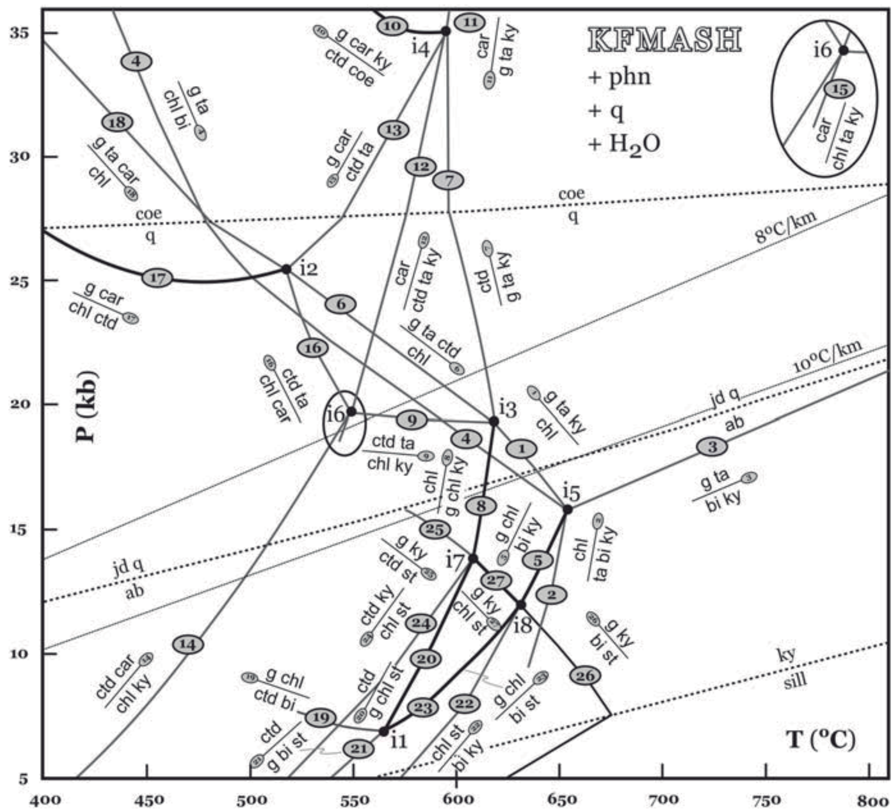

Fig. 1.- Petrogenetic grid in the KFMASH chemical system calculated for several HP metapelites. Thicker black lines represent reactions that contain stable segments for the Ceán Schists bulk rock composition. After Wei and Powell (2003).

Fig. 1.- Red petrogenética en el sistema químico KFMASH calculada para varias metapelitas de AP. Las líneas resaltadas en negro señalan las reacciones que contienen segmentos estables para la composición de los Esquistos de Ceán. Modificado de Wei y Powell (2003).

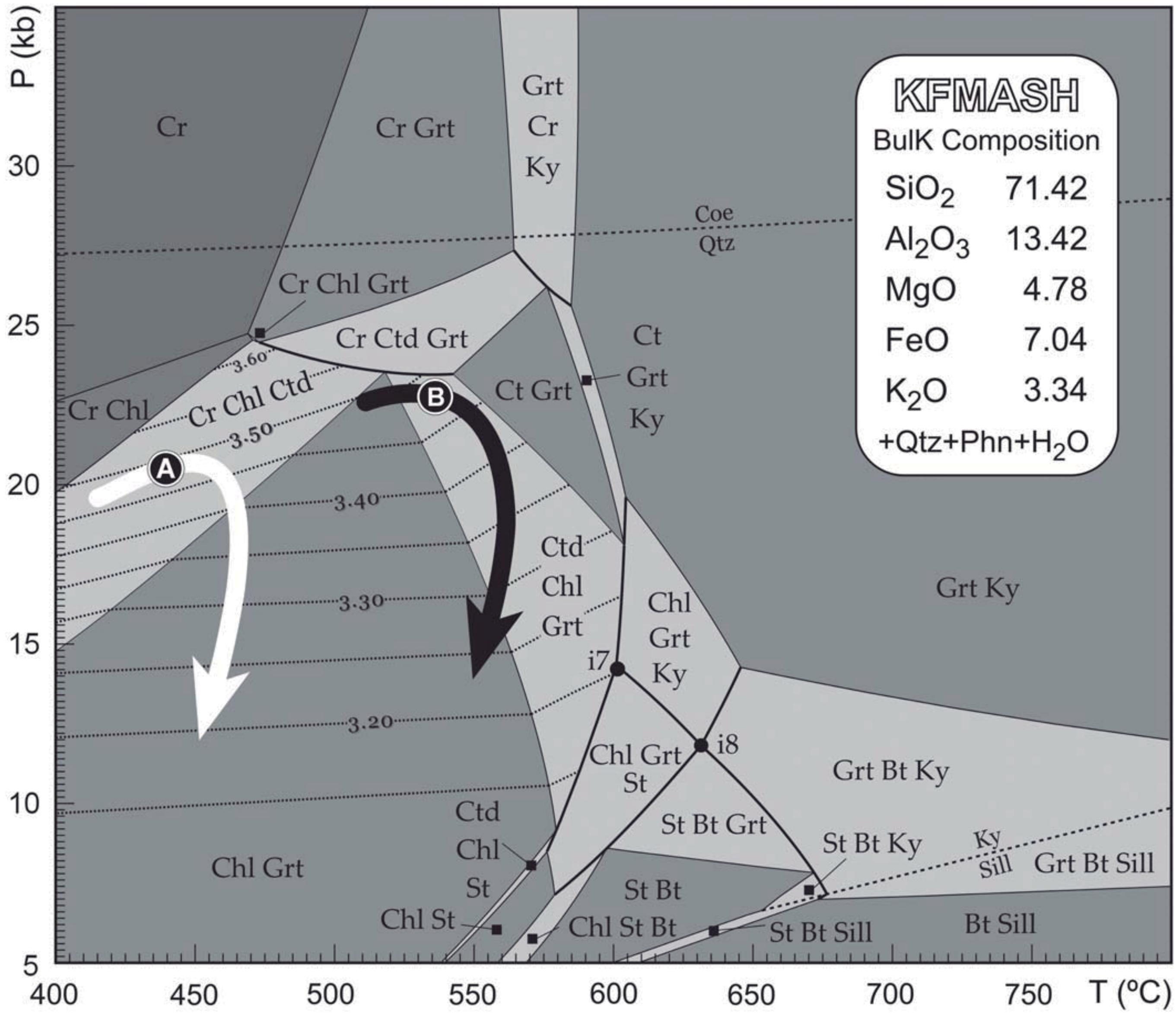

Fig. 2.- P-T pseudosection in the KFMASH system calculated for the mean bulk rock composition of the Ceán Schists. The black dashed lines are silica isopleths (values calculated in cations per formula unit). Path A has been obtained from conventional thermobarometry calculations. Path B has been deduced graphically. Light grey fields are divariant. Increasing variance is shown with progressively darker shades of grey.

Fig. 2.- Pseudosección P-T en el sistema químico KFMASH calculada para una composición media de los Esquistos de Ceán. Las líneas negras discontinuas representan las isopletas de la sílice expresadas en cationes por fórmula unidad. La trayectoria A se ha obtenido mediante termobarometría convencional. La trayectoria B ha sido deducida gráficamente.

Therefore, constraints on the P-T paths of rocks from these terrains are essential to understand the characteristics and mechanisms of the subduction of this margin.

Metapelitic schists from the upper structural levels of the Malpica-Tui Unit contain an initial blueschist facies mineral assemblage formed by garnet (Grt), phengite (Phn), glaucophane (Gln), chloritoid (Cld), chlorite (Chl), epidote (Ep), albite (Ab), rutile (Rt) and quartz (Qtz) (abbreviations after Kretz, 1983). These minerals appear mainly preserved as micro-inclusions in garnet, albite and chloritoid porphyroblasts defining a fine internal foliation (Si=S_1) that frequently shows cross-cutting relationships with the external foliation (Se=S_2). The main foliation (S_2) represents an evolution of the S_1 to slightly higher temperature and lower pressure, but still in blue-schist facies conditions, indicated by a paragenesis formed by Grt, Phn-Pg, Cld, Chl, Ep-Czo, Ab, Rt-Ill, and Qtz. Post-S_2 deformation includes restricted development of spaced C' shear bands, tight and straight D_3 folds and, a later, gentle sub-horizontal crenulation. Thus, according to the petrographic observations, three metamorphic events have been established for the metamorphic evolution of the Ceán Schists, but only the first two could be quantified.

Thermobarometry

Garnet-Phengite thermometry (Hynes and Forest, 1988) and GRIPS (Bohlen and Liotta, 1986) and GASP (Koziol, 1989, Holdaway, 2001) barometry calculations using micro-inclusion compositions indicate peak conditions around P=19-21 Kbar and

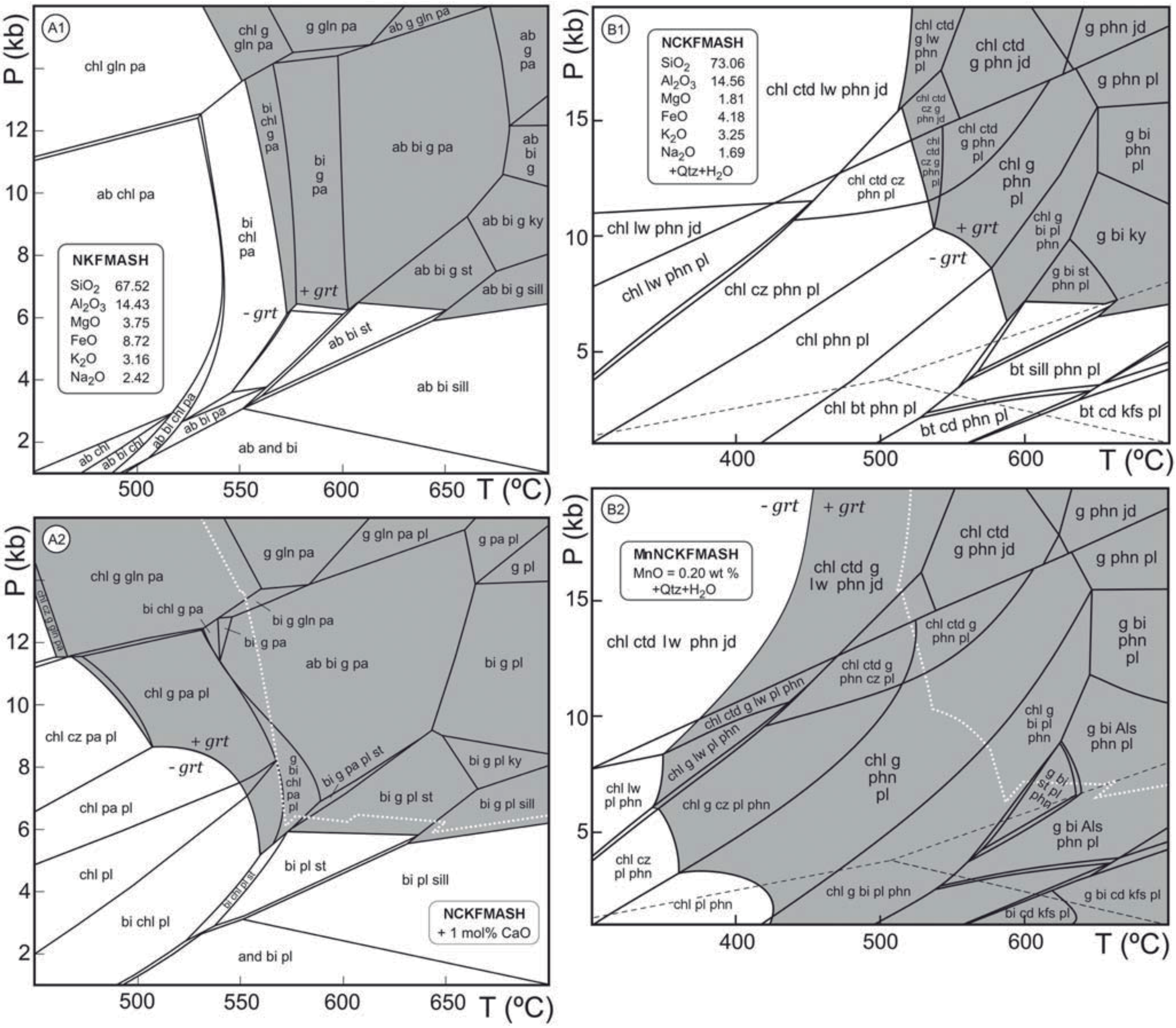

Fig. 3.- P-T pseudosections calculated in different chemical systems for HP metapelites to illustrate CaO and MnO components influence in garnet stability field. The withe dashed line in figures A2 and B2 represents garnet stability field in abstence of CaO and MnO respectively. Explanation on the text. Pseudosections A1 and A2 have been modified after Proyer (2003). Pseudosections B1 and B2 have been modified after Matsumoto et al. (2005).

Fig. 3.- Pseudosecciones P-T calculadas en diferentes sistemas químicos para metapelitas de AP con el fin de representar la influencia de los componentes CaO y MnO en la estabilidad del granate. Las líneas blancas discontinuas en las figuras A2 y B2 representan el campo de estabilidad del granate en ausencia de los componentes CaO y MnO respectivamente. Explicación en el texto. Las pseudosecciones A1 y A2 han sido modificadas de Proyer (2003). Las pseudosecciones B1 y B2 han sido modificadas de Matsumoto et al. (2005).

T=430-500 ºC. The same calculations using the S_2 fabric minerals yield values of P=16-19 Kbar and T=440-515 ºC (López-Carmona, 2007).

In order to further constrain the P-T conditions of these metamorphic events, a P-T pseudosection in the model system KFMASH has been calculated with the THERMOCALC (v. 3.25) *software* of Powell and Holland (1988) and Powell *et al.* (1998), using the internally consistent thermodynamic data set (tcds55.txt of November 2003), updated from that of Holland and Powell (1998), for a mean bulk composition of the Ceán Schists [SiO_2: 71.42; Al_2O_3: 13.42; MgO: 4.78; FeO: 7.04; K_2O: 3.34]. This pseudosection was built using the KFMASH petrogenetic grid of Wei and Powell (2003) (Fig. 1).

Pseudosections are arguably the diagrams that best illustrate mineralogical changes in a rock as the P-T-t conditions change because they show only the relevant reactions for a particular bulk rock composition. In the case of the Ceán Schists these relevant reactions are shown in figure 1 highlighted in black. The calculated pseudosection predicts the stable mineral assemblages for the above composition at different P-T conditions. These possible parageneses are represented in different fields with their corresponding variances as seen in figure 2. Additionally, plotting of isopleths for silica content in phengite in the different stability fields of the pesudosection provides an accurate barometer that will allow us to further constrain the P-T path for the Ceán Schists.

Comparing the stability fields of the obtained pseudosection with the natural parageneses preserved in the schists and with the silica isopleth calculations, a fragment of the P-T path can be traced, with peak conditions around P=23-24 Kb and T=530-540 ºC (path B in Fig. 2). However, when the trajectory obtained by conventional thermobarometry (path A in Fig. 2) is superposed on the P-T pseudosection, it can be seen that it evolves at lower T, crossing fields that do not correspond with the actual parageneses preserved in the schists. Therefore, it is evident that the stability fields obtained with this phase diagram are not consistent with the conventional thermobarometric calculations and, considering only the mineral associations of the schists, it is clear that the calculated P-T path overestimates the temperature. However, the pressure values obtained with the silica isopleths barometer are essentially in agreement with those obtained by conventional thermobarometric calculations.

The effect of Na_2O, CaO and MnO on Ceán Schists mineral equilibria

The oxides Na_2O, CaO and MnO are not present as components of the chemical system used to calculate the P-T pseudosection. This implies that their variations in the composition of the phases will not be reflected in the phase diagram. These three components usually appear in minor proportion in metapelites, but their contents may be high enough to condition the stability of a phase, hence influencing the stability of the minerals containing such phases (e.g. albite, paragonite, glaucophane and garnet), then these minerals are either not present in the model pseudosection (Ab, Pg, Gln) or are present as a simple solid solution (Fe-Mg in garnet).

Variations in the concentration of Na_2O can affect the pressure stability and modal abundance of plagioclase (Boger and Hansen, 2004), whereas CaO and MnO remarkably influence the stability of garnet (Spear and Cheney, 1989, Symmes and Ferry, 1992, Mahar *et al.*, 1997).

Obviously, the absence of garnet in the stability fields crossed by the proposed P-T path A is inconsistent with the fact that this mineral is present in all the natural parageneses preserved in the schists, from the initial foliation up to S_2. The presence of garnet can be easily explained by the effect of these minor components in the stability fields of the pseudosection. Figure 3 shows two pseudosections proposed by Proyer (2003) for a high pressure metapelite with a composition similar to that of the Ceán Schists. In the pseudosection calculated in the NKFMASH system, the garnet stability field is reduced to the grey area in Fig. 3a. However, with the addition of CaO component, this area would shift towards lower pressures and temperatures, modifying the existing parageneses in the remaining fields (Fig. 3b). Pseudosections c and d in the same figure (Matsumoto *et al.*, 2005) illustrate how garnet would be influenced by the addition of the MnO component to a chemical system with CaO. The first one has been calculated in NCKFMASH system and the second one in the MnNCKFMASH for a bulk rock composition of a pelitic schist in the garnet zone from the Sanbagawa metamorphic belt. As in the previous example, with the addition of this component, the garnet-bearing field expands towards lower pressures and temperatures, and garnet appears as an extra phase at lower pressures.

Conclusions

The high pressure mineral associations of the Ceán Schists contain garnet, chloritoid, chlorite and phengite (KFMASH system minerals) in M_1 and M_2 metamorphic events. Therefore, the P-T path during the high pressure episode should have developed inside the divariant field Cld, Chl, Grt.

Variation of silica content in phengite allows to be more precise, indicating pressures higher than 20 kb [Si=3.5 c.p.f.u] for M_1 and an isothermal decompression with a slight increase of temperature for M_2 [Si = 3.4-3.3 c.p.f.u].

This approximation, in spite of containing significant uncertainties, is considered to be essentially valid, especially the pressure estimations obtained with the silica content in phengite barometer.

The chemical system KFMASH used to calculate the pseudosection is excessively simple when applied to these schists, mainly due to the absence of CaO and MnO components that remarkably influence the stability of garnet in the phase diagram. Furthermore Na-containing minerals such as glaucophane, paragonite and albite, relevant for these rocks, can not occur. Therefore, a pseudosection calculated for a more complex system, including these three components would be necessary to further constraint the P-T trajectory of the Céan schists.

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