ECLOGITE-FACIES SEA-FLOOR HYDROTHERMALLY-ALTERED ROCKS: CALCULATED PHASE EQUILIBRIA FOR AN EXAMPLE FROM THE WESTERN ALPS AT SERVETTE

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ABSTRACT

In the St. Marcel Valley at Servette in the Western Alps metabasic rocks crop out that were variably altered in a sea-floor hydrothermal system. Successively, they were metamorphosed to eclogite facies. This was used as an opportunity to explore the range of eclogite-facies mineral assemblages that can develop in such altered rocks. The continuum is represented qualitatively by a series of rock-types: eclogite, glaucophanite, talc schist and chlorite schist, with increasing alteration, supposed to all have involved eclogite-facies mineral assemblages. Later, they were variably retrogressed under greenschist-facies conditions. The eclogite-facies mineral assemblages developed from the broad alteration trend represented by the four rock-types have been forward-modelled in terms of three composition vectors. P-T pseudo-sections for the compositions used to represent the rock-types suggest that a P-T of about 22 kbar and 600°C is consistent for the conditions of formation of the rock-types. T-X pseudo-sections along the composition vectors are used to represent the alteration continuum showing the way the mineral assemblages are affected by the degree of alteration.

INTRODUCTION

In a convergent margin, rocks in the upper part of the slab that are subducted and enter the eclogite-facies environment are commonly not of standard MORB composition. This is because at ocean ridges the upper ocean floor levels have been extensively chemically modified by post-solidification hydrothermal systems. These systems, involving massive fluid circulation and ore formation, commonly give rise to rocks of very varied composition, juxtaposed to each other, although all derived from parent MORB lithologies. The Servette region comprises such a sequence of rocks that has undergone eclogite-facies metamorphism. We investigate the phase equilibria in the very wide range of rock compositions found at Servette in terms of a simple approximating trend through the geochemical data.

GEOLOGY AND PETROGRAPHY AT SERVETTE

The Servette rocks represent a fossil hydrothermal system metamorphosed at eclogite facies, it has been described in detail by Martin et al. (2008), and earlier by Tartarotti et al. (1986) and Martin and Tartarotti (1989). Here we outline briefly the main features of the rock types observed. The hydrothermal system developed in the ophiolites of the Zermatt-Saas unit, which is here overlain by the Austroalpine Mt. Emilius klippe (Fig. 1). The rocks underwent a polymetamorphic evolution from an oceanic hydrothermal alteration stage, through a prograde blueschist-facies metamorphism (as reflected by inclusions in garnet), to a peak eclogite-facies metamorphism at 550±60°C and of 2.1±0.3 GPa, according to Martin et al. (2008). Angiboust et al. (2009), suggested that these rocks reached peak conditions within the lawsonite stability field, due to the presence of lawsonite pseudomorphs in glaucophanites, and proposed P-T-peak conditions of 23.4 kbar and 530°C. This metamorphism occurred in Eocene times (45 ± 2.8 Ma, by Rb/Sr on white mica; $44-47\pm1.5$ Ma, by 40 Ar/ 39 Ar, Dal Piaz et al., 2001).

Regarding the peak metamorphic mineral assemblage, minor eclogite occurs with interbanded glaucophanite, talc schist and chlorite schist, associated with sulphide-bearing quartzite, metagabbro and felsic gneiss. This series, from eclogite through glaucophanite, talc schist to chlorite schist represents increasing alteration of the original hydrothermal system. The peak metamorphic mineral assemblages are variably retrogressed to greenschist-facies. The rocks experienced at least three Alpine deformation events, each developing a foliation. The oldest one is only found as relicts in garnet cores and as S planes in chlorite schist. The second one is characterised by isoclinal folds, a pervasive foliation and glaucophane lineation. The first deformation is likely to be prograde, while the second developed at peak metamorphic conditions. The last deformation event involves open folding and greenschist-facies shear zones, and is most strongly developed at the contact with the overlying Mt. Emilius nappe (see the geological map of Fig. 2 in Martin et al., 2008).

Eclogite is rare at Servette, and often retrogressed to greenschist-facies conditions, but rarely eclogite-facies mineral assemblages with garnet, omphacite and rutile are preserved; minor glaucophane is found. Glaucophanite is the most abundant rock type, followed by chlorite schist and talc schist, the rocks being named after the most abundant mineral constituents (see Table 1 of Martin et al., 2008). Glaucophanite has, besides glaucophane, garnet (up to 1 cm in diameter) and chloritoid (up to 2 cm long), subsets of epidote, talc, phengite, magnetite, ilmenite, rutile and quartz. Pseudomorphs after lawsonite, deformed in D₂, are locally abundant. Paragonite, chlorite, barroisite, talc and albite may also be present as a consequence of retrogression. Glaucophanite with disseminated sulphide is found near the sulphide ore deposit. The transition from glaucophanite to talc schist is commonly gradual, but sharp boundaries at a high angle to the pervasive S_2 foliation can be observed.

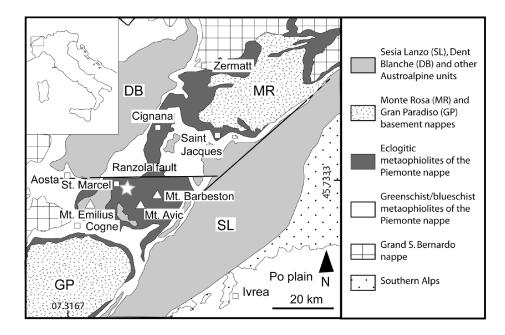


Fig. 1 - Simplified tectonic map of the Aosta Valley. The star indicates the location of the St. Marcel Valley (redrawn after Martin et al., 2008).

Table 1 - Mineral Compositions used for pseudosection modelling (in moles %).

name	SiO ₂	Al ₂ O ₃	CaO	MgO	FeO	K ₂ O	Na₂O	TiO ₂	0
eclogite	54.78	8.84	13.76	8.94	7.73	0.1	6	0.39	1
glaucophanite	53.25	9.89	2.73	16.67	10.02	0.1	4.2	1.86	1.27
talc schist	45.68	9.84	1.34	20.78	10.09	0.01	0.06	1.45	2.75
chlorite schist	27.3	13.26	1.17	20.67	28.86	0.08	0.39	2.42	5.85

Talc schists contain up to 70% talc, commonly with chloritoid and garnet porphyroblasts, rutile, and with occasional epidote and quartz. They are often interlayered with quartzite and may have dispersed sulphide minerals. Lawsonite pseudomorphs are locally abundant (see Angiboust and Agard, 2010). The presence of lawsonite alone is not enough to constrain peak temperatures, as it is essential to define whether it is prograde or retrograde on the basis of textures (see Tsujimori et al., 2006 and references therein).

Chlorite schist may have, besides chlorite, which may form up to 90% of the rock, garnet, chloritoid, talc as well as glaucophane, epidote, paragonite, hematite, rutile and dispersed sulphide near mineralization.

GEOCHEMISTRY OF ALTERATION

Hydrothermal alteration of oceanic crust has been widely studied in the past years, on the large collections of samples acquired by ODP (for instance in hole 406B) and by extensive studies conducted on ocean ridge and off-axis oceanic metamorphic rocks, as well as in ophiolites (Pineau et al., 1976; Alt and Honnorez, 1984; Alt et al., 1986; Lowell et al., 1995; Miller and Cartwright, 2000). The patterns of alteration of rocks due to hydrothermal circulation of fluids are very varied, depending on, among other things, the temperature of the fluids, depth in the crust, type of rock, pH, and many other factors. Even with such a great variability, researchers have identified some major alteration trends, both in the recharge and the discharge zones of hydrothermal systems (for references see IODP publications http://www-odp.tamu.edu/publications/), especially for holes 504B and 735B (Thompson, 1991; Alt, 1995; Honnorez et al., 1998; Juteau and Maury, 2008) as follows:

i) sea-floor weathering, which takes place at low T (< 70° C) and shallow depths, causing enrichment in alkalis and oxidation. It also includes the palagonitisation of basaltic glass, with loss of Ca, Mg and Si, and gain of K, Mn and Na;

ii) intermediate T alteration (70-350°C) at depths of 300-500 m, causing reduction, increase in Mg, precipitation of anhydrite and loss of alkalis;

iii) higher T alteration (T > 350° C, at depths of 1.5-2 km), causing complex patterns of alteration dependent upon T, fluid composition and type of circulation, amongst others. When the discharge is focussed, so as to produce black smokers on the sea floor itself, "metasomatic rocks" such as epidosites may form. When the discharge is diffuse, the mixing of high T and low T fluids produces precipitation of disseminated polymetallic sulphides and quartz in the altered oceanic rocks.

In addition, in fossil hydrothermal systems, effects of the different styles of alteration may be superimposed on each other as the hydrothermal system waxed and waned. The chemical variations observed at Servette are compared with those recorded for ODP holes 504B and 735B (Alt and Emmermann, 1983; Alt and Honnorez, 1984; Alt et al., 1986; referred to as ODP) and in the GERM ocean floor basalt compilation (Sun and McDonough, 1989; Bach et al., 2001; referred to as GERM) in Fig. 2. In a general way, the Na-Al relationships are comparable in that Na decreases as a consequence of alteration, although the eclogites are more sodic than both the ODP and GERM rocks. In addition, the alteration found at Servette becomes more extreme, with nearly complete loss of Na, and eventually increase of Al from talc

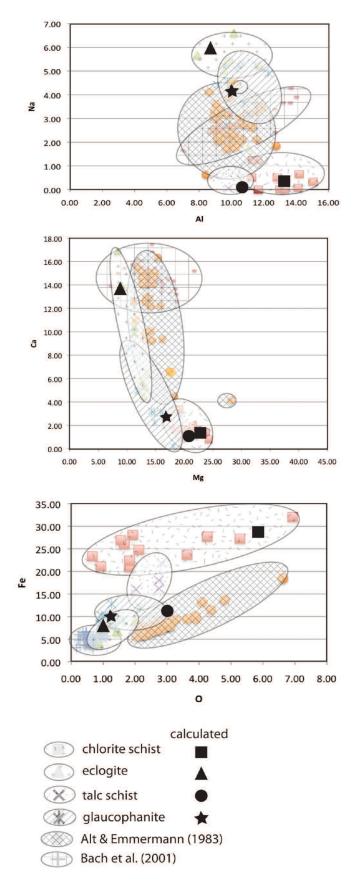


Fig. 2 - Plots of whole rock data from the Servette rocks (Martin et al., 2008), and present-day ocean-floor rocks (Alt and Emmermann, 1983; Bach et al., 2001). All data are represented as mole% oxides. Analyses have been normalised to the 10 oxides being considered (NCKFMASHTO system). Symbols represent the 4 compositions used for the calculations, with different patterned fields representing the range% and how overlapping the natural rocks compositions are.

schist to chlorite schist. Similarly the key chemical variations of Ca and Mg are similar but displaced to slightly lower Mg, becoming more extreme than ODP and GERM in the talc schist and chlorite schist. The Fe-O relationships show that the range of oxidation state for the chlorite schist is similar to that in GERM, but that the FeO content is higher.

The range of chemical variation in the Servette rocks is considerable, and not just in a simple way, e.g., in the decrease of Na and Ca with alteration, presumably due to the complexity of the different processes that must have operated in the hydrothermal system, superimposed on possible variability of the original compositions. For example, some of the metabasics may derive from gabbroic protoliths, thus explaining some of the differences in composition with the oceanic metabasaltic examples. The chemical variation introduces a considerable difficulty in phase equilibria modeling of the rock compositions, as there are so many different composition dimensions that would need to be covered in order to have a thorough consideration of the phase equilibria.

Therefore our approach was to choose four compositions that represent the main lithologies observed at Servette (eclogite, glaucophanite, talc schist and chlorite schist) and then link them with a line through the multicomponent space in order to represent a simple "alteration trend" and to consider the effect of varying contemporaneously the proportions of 10 oxides on the assemblages observed at equal P-T conditions. Although this can only give a rough indication of the dependence of mineral assemblage development on alteration, it allows the trend of alteration to be represented in a relatively small number of pseudo-sections. Many more such diagrams would be needed, based on much more analytical work on rock composition in a tightly controlled field context, if the original alteration story is to be pulled apart in more detail, and then what happened during the eclogite facies metamorphism established. Already the choice of the four composition required a simplification, as we tried to account for the fact that they represent also a trend of Fe and O enrichment, while also trying to exclude those rocks that contain the ores (as the presence of sulphides would change the composition to be considered, as much Fe is bound in sulphide minerals).

The chosen bulk compositions used to represent the eclogites, glaucophanites, talc schists and chlorite schists in mole% are reported in Table 1. As stated above, they do not represent compositions of actual samples and have been chosen to show a trend that simplifies the complex compositional changes observed in hydrothermal systems.

CALCULATED PHASE EQUILIBRIA

The calculated phase equilibria were undertaken using THERMOCALC (Powell et al., 1998, with recent upgrade, tc335i) and the internally-consistent thermodynamic dataset (Holland and Powell, 1998; upgrade tc-ds55.txt from Nov. 2003). The amphibole and pyroxene activity-composition models are those of Diener et al. (2007) and Green et al. (2007), with the revisions in Diener and Powell (2012). The white mica model (for muscovite and paragonite *sensu lato*) is from Smye et al., (2010). The biotite, garnet and Fe-Ti oxide models are from White et al., (2007) (but with the garnet asymmetry involving a(gr) = a(andr) = 3 not 9). For chlorite and talc, preliminary versions of new ferric-bearing non-equipartition models are used in order to properly model these minerals in the full NCKFMASHTO system. The

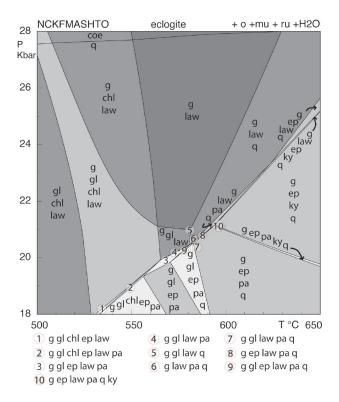


Fig. 3 - Calculated P-T pseudosection based on the eclogite composition (see Table 1), which is: $SiO_2 = 54.78$; $Al_2O_3 = 8.84$; CaO = 13.76; MgO = 8.94; FeO = 7.73; $K_2O = 0.10$; $Na_2O = 6.00$; $TiO_2 = 0.39$; O = 1.00 (mole%) in NCKFMASHTO using THERMOCALC. This figure involves additionally H₂O in excess. Omphacite, muscovite and rutile are present in all fields. Abbreviations: g- garnet; gl- glaucophane; ctd- chloritoid; law-lawsonite; ep- epidote; chl- chlorite; pa- paragonite; mu- muscovite; ky-kyanite; q- quartz.

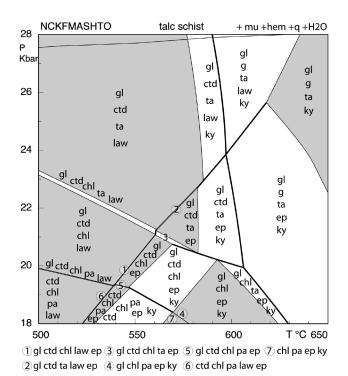


Fig. 5 - Calculated P-T pseudosection based on talc schist composition (see Table 1), which is: $SiO_2 = 45.68$; $Al_2O_3 = 9.84$; CaO = 1.34; MgO = 20.78; FeO = 10.09; $K_2O = 0.01$; $Na_2O = 0.06$; $TiO_2 = 1.45$; O = 2.75 (mol. %) in NCKFMASHTO using THERMOCALC. This figure involves additionally H_2O in excess. Hematite, muscovite and quartz are present in all fields. Abbreviations, see captions for Figs. 3-4; additionally: hem-hematite.

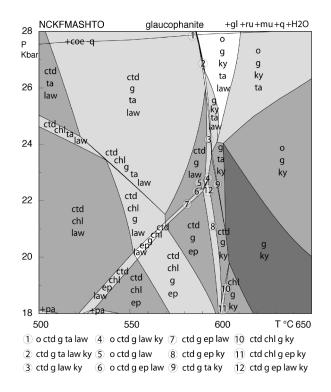


Fig. 4 - Calculated P-T pseudosection based on glaucophanite composition (see Table 1), which is: $SiO_2 = 53.25$; $Al_2O_3 = 9.89$; CaO = 2.73; MgO = 16.67; FeO = 10.02; $K_2O = 0.10$; $Na_2O = 4.20$; $TiO_2 = 1.86$; O = 1.27 (mole%) in NCKFMASHTO using THERMOCALC. This figure involves additionally H_2O in excess. Glaucophane, muscovite, rutile and quartz are present in all fields. For abbreviations, see caption for Fig. 3; additionally: o- omphacite; ta- talc; ky- kyanite.

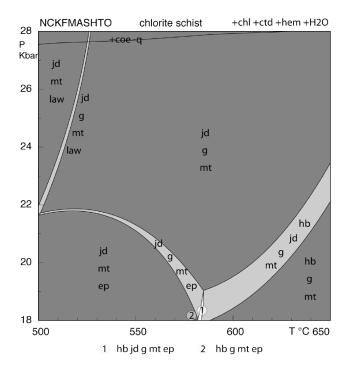


Fig. 6 - Calculated P-T pseudosection based on chlorite schist composition (see Table 1), which is: $SiO_2 = 27.30$, $Al_2O_3 = 13.26$, CaO = 1.17, MgO = 20.67, FeO = 28.86, $K_2O = 0.08$, $Na_2O = 0.39$, $TiO_2 = 2.42$, O = 5.85 (mole%) in NCKFMASHTO using THERMOCALC. This figure involves additionally H_2O in excess. Muscovite, hematite, chlorite and chloritoid are present in all fields. Abbreviations, see captions for Figs. 3-5; additionally: jd-jadeitic cpx; mt-magnetite.

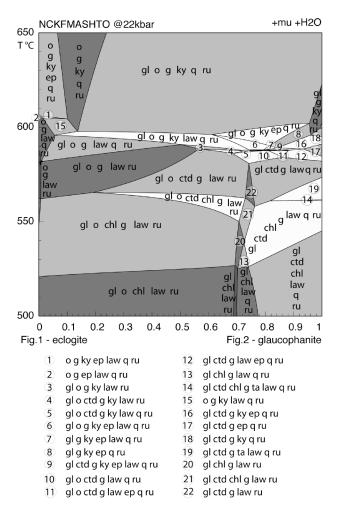


Fig. 7 - T-X pseudosection at 22 kbar, using the compositions of Fig. 3 (eclogite) and Fig. 4 (glaucophanite), as in Table 1. H_2O , muscovite and rutile are in excess. Abbreviations, see captions for Figs. 3-6.

epidote model is from Holland and Powell (1998). The other phases are pure end-members: lawsonite, kyanite, rutile, quartz, and H_2O .

Notwithstanding the strictures in Rebay et al., (2010) and Guiraud et al., (2001), the modelling was undertaken with H_2O in excess, and with the O contents in the ranges as given by the wet-chemically determined Fe_2O_3 of the samples. As a part of a wider study of the Servette rocks, the dependence of mineral assemblage on H_2O , particularly for the eclogites, and on O content, for all the rock compositions, would need to be investigated. The pseudo-sections supersede those of Martin et al., (2008), by using a larger, more appropriate chemical system to represent the rock compositions and new improved thermodynamic models of the minerals, even though, in contrast to what is done in Martin et al., (2008), they do not correspond to any actual sample.

P-T pseudo-sections are presented for the 4 chosen rock compositions in Figs. 3-6 and there are considerable phase relationship differences among them. However there are some features in common with the "backbone" CASH reaction involving the breakdown of lawsonite to kyanite and clinozoisite (Figs. 3-5). This is no longer evident for the chlorite schist (Fig. 6) which is the poorest in CaO and SiO₂, and richest in MgO, FeO and O. For the eclogite, glaucophanite and talc schist, the divariant fields increase in area, and more univariant reactions are seen. This results in

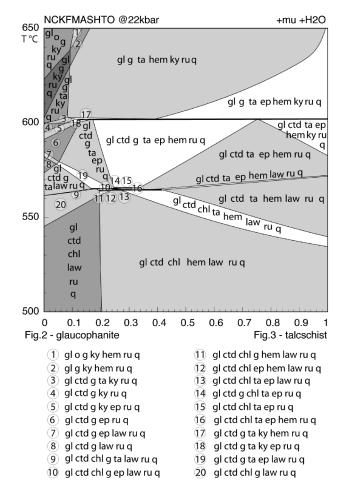
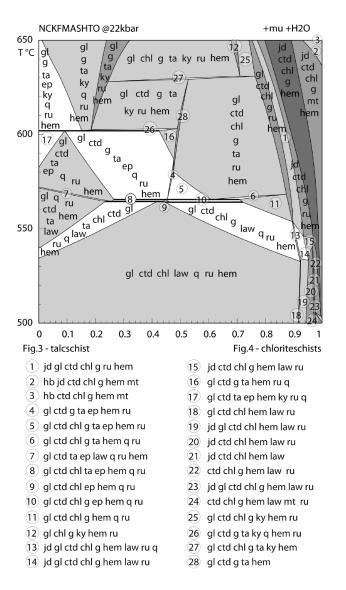


Fig. 8 - T-X pseudosection at 22 kbar, using the compositions of Fig. 4 (glaucophanite) and Fig. 5 (talc schist), as in Table 1. H_2O and muscovite are in excess. Abbreviations, see captions for Figs. 3-6.

assemblages with increasing number of stable phases, and in an increase of hydrous phases and decrease of omphacite + garnet. Also whereas in eclogite the Na-bearing phase stable at lower P and higher T is paragonite, moving towards glaucophanite and talc schist the stability of paragonite shifts to lower pressures and the Na-bearing phase becomes glaucophane. The kyanite stability field also expands, reflecting the increasing Al₂O₃. Kyanite is not observed in Servette but is found in other "metabasic" rocks from the western Alps ophiolites. Chloritoid is stable in glaucophanite to chlorite schist, whereas glaucophane is not present in the chlorite schist, hornblende being the amphibole present at higher T and lower P. Finally hematite occurs instead of rutile in talc schist, and magnetite appears in chlorite schist, where quadrivariant fields prevail, and the stable pyroxene is jadeitic in composition. Hematite has not been observed in such proportions in Servette rocks but is observed in small proportion in the chlorite schists reflecting possible shortcomings in the way that ferric iron is incorporated in the minerals, or in the analysed ferric contents of the rocks. Usually a higher O content would stabilize hematite, and would change the stability fields of all phases including Fe³⁺: as we stated in the introduction an exhaustive discussion of this topic would require a paper by itself.

The Servette geology implies that it lies within a coherent tectonic unit, therefore, the Servette rocks can be assumed to



have been metamorphosed at the same P-T conditions. Thus, peak P-T should be consistent amongst the 4 rocks as shown by their pseudo-sections in Figs. 3-6. The occurrence of pseudomorphs after lawsonite in the glaucophanites suggests that these P-T conditions lie within or close to the boundary of the lawsonite stability field. Glaucophanite, containing combinations of chloritoid, talc, \pm epidote and possibly some kyanite with glaucophane and garnet constrains the P to be about 22 kbar at a temperature of around 590°C. For garnet to occur in the talc schist composition, the temperature needs to be a little higher, above 590°C, with the pressure poorly constrained (but 22 kbar is consistent). Moreover, in Fig. 5 garnet and chloritoid are not predicted to be stable together, but, when adding Mn, the garnet stability field could be enlarged towards lower temperatures. Slight changes in the bulk composition stabilize garnet and chloritoid and limit kyanite. Little constraint arises from the chlorite schist pseudo-section. In fact, a wide range of FeO and O contents is observed in chlorite schist, as shown in Fig. 2, so that the pseudo-section would change dramatically with changing the Fe and O contents of the bulk.

The eclogite pseudo-section involves hydrous minerals, epidote and/or lawsonite, evidence for which in the rocks is absent, maybe indicating that the H_2O -present assumption for the eclogite is incorrect (see Rebay et al., 2010 for a dis-

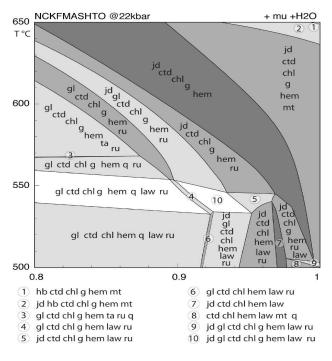


Fig. 10 - Enlargement of the right side of the T-X pseudosection at 22 kbar of Fig. 9. H_2O and hematite are in excess. Abbreviations, see captions for Fig. 3-6.

Fig. 9 - T-X pseudosection at 22 kbar, using the compositions of Fig. 5 (talc schist) and Fig. 6 (chlorite schist), as in Table 1. H_2O and muscovite are in excess. Abbreviations, see captions for Figs. 3-6.

cussion about addition of H₂O to a MORB composition).

As a way to proceed, the following T-X pseudo-sections are drawn for 22 kbar, with the understanding that there is likely to be an uncertainty of at least 1 kbar on the peak metamorphic pressure. In the light of general considerations on assemblages developed in rocks at the same P-T conditions but with varying composition, T-X pseudo-sections at 22 kbar are shown in Figs. 7-10, for linear composition vectors joining the 4 rock compositions. These show dramatically the way in which the phase relationships change as the rock composition is varied along the schematic alteration trend. The stabilities of the main minerals along the schematic alteration trend are summarised in Fig. 11, in which it is evident that at 22 kbar chlorite is always stable below 560°C, but only stable in chlorite schist at higher temperatures. Quartz is interestingly not present at low temperatures in eclogite, and then it completely disappears in chlorite schist. The stable clinopyroxene is omphacitic in eclogite and jadeitic in chlorite schist, but is completely absent in intermediate compositions, where glaucophane is stable. Chloritoid is present in all compositions with Al₂O₃ content higher than 9 mole%.

A better perspective of the phase relationships along the compositional trend is seen in the modebox of Fig. 12. Here the diagnostic changes in phases occurring in large modal proportions are seen, in contrast to the pseudo-sections where they can be obscured by changes of only small proportions of other minerals. A reflection of this is evident comparing the phase relationships in the pseudo-sections at 550°C, 575°C, 600°C and 625°C with the modebox information at these temperatures in Fig. 12. Although major assemblage changes occur between 575°C and 625°C in the pseudo-sections, the modebox diagrams are remarkably similar. The only significant exceptions to this relate to garnet stability in the talc schist composition, and the increased mode of kyanite with increasing temperature at the start of the alteration trend.

In more detail, chloritoid is present only in the chlorite schist at 600°C whereas it is present also in glaucophanite and talcschist at 575°C and 625°C. Its modal abundance varies quite abruptly, from absent to 20-30%. Lawsonite is in modally significant quantities only in eclogite and glaucophanite below 575°C. Chlorite is present in all compositions at lower temperatures, except in talc schist, and it is then "replaced" by talc above 570°C in glaucophanite and talc schist, and by glaucophane in eclogites. Hematite appears in glaucophanite in very small amounts, and reaches up to 20% in talc schist and chlorite schist, no matter the temperature. In the most oxidised composition, magnetite can be up to 10%in chlorite schist. Garnet has a maximum abundance at 600°C in all lithotypes, and it is absent from talc schist for lower and higher temperatures. Jadeitic clinopyroxene is present in chlorite-schists, always in modal amount < 3%.

DISCUSSION AND CONCLUSIONS

The modeling of a full range of compositional variability, albeit strongly simplified, shows that bulk composition has a dramatic effect on the assemblages developed at specified PT, and that P-T pseudo-sections alone are not enough to account for observed mineral assemblages, but that modal compositions need to be evaluated too. Notwithstanding caution, we show that indeed forward modeling is a very powerful tool, not only in the calculation of P-T conditions, but also in constraining general processes in metamorphism.

Within the context of the finite number of pseudo-sections that can be presented in a work such as this, necessarily representing a much wider range of alteration chemistry by a piecewise linear trend, the modeling shows a satisfactory correspondence with the observations if the rocks were metamorphosed at about 22 kbar and 600°C, which is well within the P-T conditions proposed by Martin et al., (2008), i.e., 550±60°C and 2.1±0.3 Gpa. This is in the range of previous estimates but at a slightly higher temperature. The differences in P-T conditions published in the literature for rocks similar to these and coming from different parts of the Alps (Bucher et al., 2005; Angiboust et al., 2009) show that it is essential, when applying a pseudo-section approach, to have a very detailed structural-petrological analysis of the rocks studied, as determination of assemblages and their succession can have a dramatic effect on the P-T conditions. We show that fields with minimal differences in assemblages and mineral abundance and composition can have very different P-T ranges. For instance in Bucher et al. (2005) similar rocks, but containing larger amounts of sodic pyroxene, are interpreted as being stable in the coesite stability field, whereas Martin et al., (2008), and Angiboust et al., (2010) calculate for the Servette rocks P-T conditions that are quite similar, within error especially for P values, but also as far as T is concerned, when considering the differences in textural interpretation.

From the point of view of using pseudo-sections to repre-

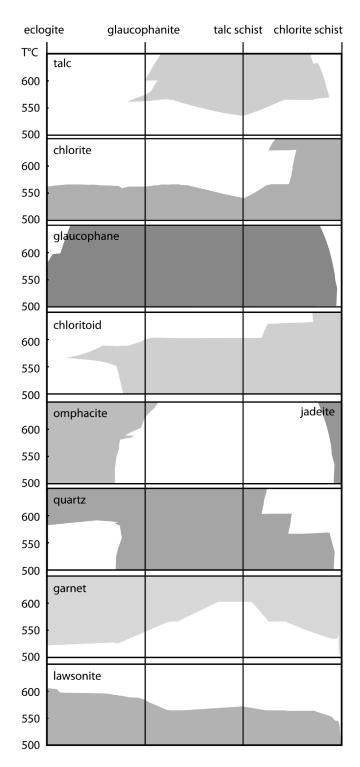


Fig. 11 - Fields of stability of talc, chlorite, glaucophane, chloritoid, cpx (omphacite or jadeite), quartz, garnet and lawsonite along the considered compositional range. Refer to Figs 7 to 10 for details on T-X pseudosections.

sent the results of phase equilibria modeling, the above results illustrate an ongoing problem that is at least in part relieved by using the modebox diagrams. That is a line on a pseudosection may reflect a major change in mineral assemblage in terms of marking the appearance (or disappearance) of a phase that becomes (or was) a significant constituent of the rock, or it may reflect only a minor change in mineral assemblage in terms of mineral proportions. In the latter case, such a minor change may in fact be significant, or it can be a

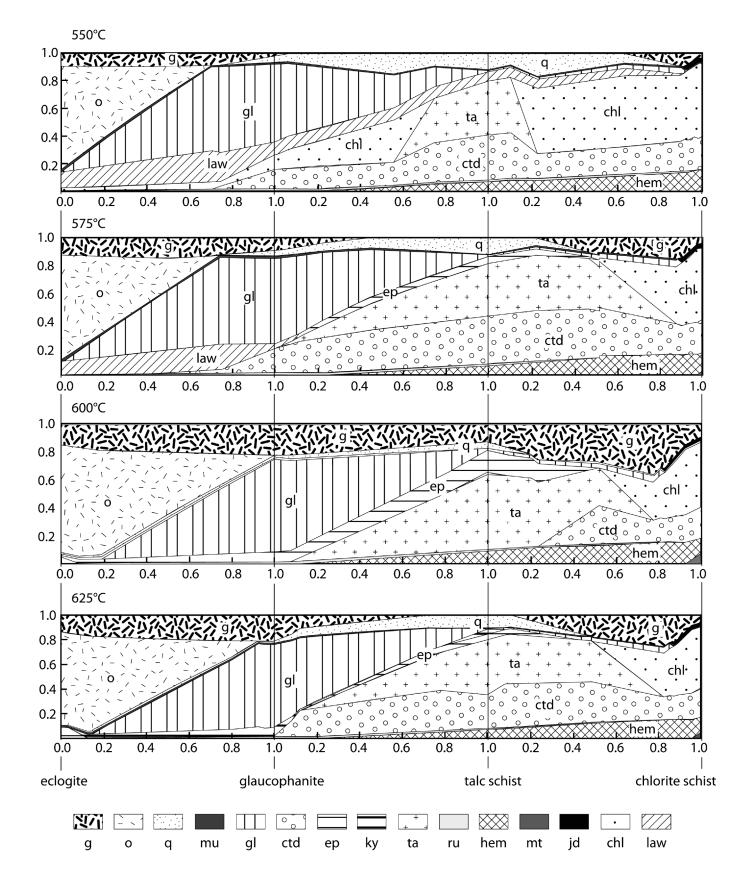


Fig. 12 - Modal composition of rocks along the compositional trend at 22 kbar and 550°C, 575°C, 600°C and 625°C respectively. Abbreviations as used in all figures, refer to Figs 7 to 10 for details on T–X pseudosections.

consequence of either a small problem in a-x models or a small shortcoming in the bulk composition used for the pseudo-section. In the presence of either or both of these difficulties, the presence or absence of a phase only ever present in small proportion may well not be significant. The result can be thought of as "noise". This is more likely to be true for oxides that are being competed for among a number of phases, like SiO₂ in the context of the presence or absence of quartz, or Al₂O₃ in the context of the presence or absence of kyanite. In contrast, TiO₂ is present in few phases so that whether it resides in rutile or hematite (i.e., ferric-rich FeTiO₃-Fe₂O₃) may be significant, even if the proportions involved are small.

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