Modelling metamorphic rocks in complex systems: present-day developments in high pressure experimental petrology

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ABSTRACT. — Metamorphic processes at subduction zones are strictly related to the transfer and release of water via dehydration reactions from the subducting slab toward the mantle wedge. Results and present-day developments in high pressure experimental petrology in the laboratory of Milano are presented here, dealing with lithologies which are expected to be subducted, i.e. mainly mafics and ultramafics. Particular emphasis will be given to hydrate-bearing assemblages.

Experiments performed in mafic rocks at pressures of up to 5 GPa show that phase relationships are controlled by amphibole s.s. to 2.5 GPa and by epidote group minerals and lawsonite at higher pressure. Phase relationships point out to strong sensitivity of assemblages from continuous reactions and therefore from bulk composition considered.

In ultramafics, at temperatures between 680 and 800°C, amphibole and chlorite are the major hydrous phases able to transport water deep into the Earth's Mantle. At pressure > 4.8 GPa, a hydrous silicate with a 10Å phase structure forms at the expense of chlorite, providing a «carrier» by which water might be transported down to 200 km depth. The interaction between alkali-rich fluids and mantle peridotites lead to the occurrence of potassic hydrous phases such as phlogopite. Experiments on K-peridotite suggest a pressure dependent relevance of a «talc» component in phlogopites.

RIASSUNTO. — I processi metamorfici presso margini convergenti sono strettamente connessi con il trasporto e rilascio di acqua dalla placca subducente verso il cuneo di mantello. Nel presente lavoro vengono presentati risultati ottenuti presso il laboratorio di Petrologia Sperimentale di Milano.

Gli esperimenti condotti in composizioni mafiche (fino a pressioni di 5 GPa) mostrano che le relazioni di fase sono controllate dall'anfibolo s.s. fino a 2.5 GPa, e da epidoto e lawsonite a pressioni superiori.

In composizioni ultramafiche, a temperature comprese tra 680 e 800°C, anfibolo e clorite rappresentano le principali fasi idrate capaci di trasportare acqua in profondità. A pressioni > 4.8 GPa, un silicato idrato con una struttura tipo fase 10Å si forma a spese della clorite. Tale fase idrata rappresenta un ottimo candidato per il trasporto di acqua fino a 200 km di profondità. Le interazioni tra fluidi ricchi in alcali e peridotiti di mantello intruse all'interno della crosta continentale subdotta portano alla formazione di fasi idrate potassiche quali la flogopite. Esperimenti in K-peridotiti suggeriscono che al crescere della pressione la rilevanza del componente «talco» nelle flogopiti aumenta.

KEY WORDS: *High pressure metamorphism, subduction zones, hydrous phases, water transport and release.*

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In the last decades, the world-wide occurrence of high pressure metamorphic terrains (Liou *et al.*, 1998) equilibrated at pressures > 5 GPa, have led to an increasing interest in petrological tools to be used to unravel the P-T evolution of convergent plates boundaries. Among such tools, experimental petrology represents a direct approach, able to model geological processes, phase relationships and metamorphic equilibria along the subducting slab from greenschist to eclogite facies. Particular emphasis has been given to the identification of equilibria involving volatiles-bearing phases, responsible for most of geological processes occurring at subduction zones, where volatiles recycle deep into the Earth's Mantle.

Although there has been a relevant amount of experimental work in simple model systems, mainly devoted to define the maximum stability field of high pressure phases, information on phase relationships in more complex systems, Fe-bearing, approaching natural compositions are still fragmentary. Most natural systems are actually characterized by a large number of independent chemical components, therefore complex continuous reactions are expected to control phase relationships.

This contribution focuses mainly on experimental studies performed in the laboratory of the University of Milano on complex model systems and on compositions close to real rocks expected to be subducted, namely of mafic and ultramafic compositions, taking into account the key role played by aqueous fluids in subduction zones environments. This contribution also draws on previous reviews by Poli and Fumagalli (2003), and Poli and Schmidt (2002).

EXPERIMENTAL TECHNIQUES

In order to experimentally investigate metamorphic equilibria at pressures > 1 GPa,

the facilities available include internally heated solid media pressure vessels such as the piston cylinders, both single stage and end-loaded, and the multianvil apparatus. The single stage piston cylinder typically runs up to 2.5 GPa and pressure is controlled by an automated hydraulic system where the load is measured directly by a load cell. Because of the relatively low temperatures investigated in subsolidus experiments, low-friction assemblies can be used profiting of NaCl pressure media. At higher pressure, up to ca. 4 GPa, end-loading has to be applied to the vessel, configuring the so-called Boyd and England type piston cylinder. The end-loaded piston cylinder module can be mounted on a 1000-ton uniaxial press and can be readily interchanged with multianvil modules.

Pressures > 4 GPa are generated by multianvil apparatus, mounted on a 1000 ton uniaxial press, driven by a hydraulic system. High-resolution pressure control is usually obtained by an electronically driven screw worm jack. WC cubic anvils of 32 mm of edge and with 4, 8, 11, and 17 mm of Truncation Edge Length (TEL) are available. The smaller is the TEL, the higher pressure is achieved, e.g. 4 mm TEL can be used up to 20 GPa. Pressure cells are made of prefabricated MgO octahedra with 10 (10M), 14 (14M), 18 (18M), 25 mm (25M) edge length, to be used with cubes of 4, 8, 11 and 17 mm of TEL respectively.

Assemblies are constituted of furnaces, ceramic spacers and noble metal or graphite capsules containing the sample. Furnaces are prepared with graphite or lanthanum chromate depending on the pressure-temperature conditions to be achieved. Axial thermocouples are placed in direct contact with the capsule, choosing the type as a function of temperatures attained. Depending on the pressure cell used, namely on experimental pressure and temperature chosen, assemblies may differ one respect to the other mainly by sizes and by the presence of a zirconia sleeve, used to improve the thermal and mechanical properties of the assembly.

MAFIC SYSTEMS

Even though garnet and clinopyroxene often constitute more than 90% of the mode of mafic eclogites, minor and accessory phases are as important as major minerals because of their influence on a variety of geological processes. As examples, we know that physical and chemical properties of rocks, including brittle failure and creep, initiation of melting, generation of volatile-rich magmas responsible for explosive volcanism, geochemical signatures, etc., are mostly influenced by the presence of minor (typically hydrates and carbonates) and accessory phases (typically rutile, allanite, zircon, phosphates, ellembergerite). Despite their importance, most reactions involving minor and accessory minerals are still in a state of preliminary investigation, because a clear gap exists between the chemical complexity of real rocks and the model systems studied in the laboratory.

Phase Relationships in H₂O-bearing Systems

Phase Relationships in H_2O-bearing Systems

Because of the large number of independent chemical components present in mafic rocks, continuous reactions are the relevant mechanism controlling the appearance and the abundance of mineral phases. Hence, phase transitions observed in MORB+H$_2$O cannot be extrapolated to the universe of gabbroic rocks found in crustal sections (continental or oceanic), often recorded in high pressure terrains, due to the strong effects of variable bulk compositions.

Fig. 1 displays current knowledge to pressures of about 6 GPa. Most experimental studies are substantially consistent and apparent discrepancies (e.g. epidote, Na-amphibole and Mg-chloritoid stabilities) can be ascribed to differences in experimental setups and bulk compositions adopted.

All of the experimental studies agree that amphibole breakdown is located at approximately 2.5 GPa at 700-750°C in the system MORB+H$_2$O, both in a simplified

chemical composition (Poli, 1993; Poli and Schmidt, 1995; Schmidt and Poli, 1998) and in natural starting materials (Pawley and Holloway, 1993; Liu *et al.*, 1996; Forneris and Holloway, 2003). On the contrary, at lower temperatures the experimental results obtained recently by Forneris and Holloway (2003) significantly differ from the previous studies. Glaucophane was found up to 3 GPa at 625°C, lawsonite and epidote stability fields were reduced by ca. 50 °C, and Mg-chloritoid was suggested to be a metastable phase in high-pressure phase assemblages in MORB compositions.

A careful evaluation of the bulk compositions used and of the fO_2 conditions fixed might explain discrepancies with previous experimental studies. Unusually low Mg number (Mg# = 47.5) in the basaltic composition used by Forneris and Holloway (2003), compared to Mg# 56 in most other studies, might account for the reduced stability of chloritoid, as chloritoid is recorded in nature mostly in Mg-gabbros. Similarly, assuming that normative anothite (An) is representative of the potential amount of epidote present, it is
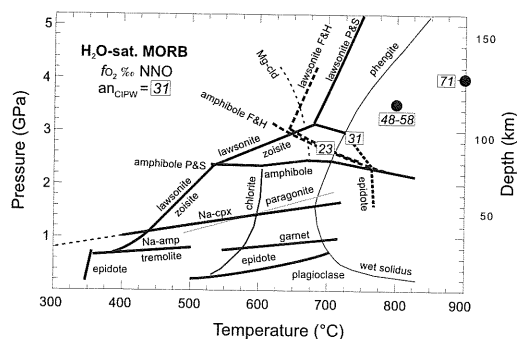

Fig. 1 – Phase stabilities in hydrated MORB compositions based on Poli and Schmidt (1995, 2002) (P&S) and Schmidt and Poli (1998). Numbers indicate normative anorthite content in weight percent from studies that synthesized epidote (circles; An = 48-58: Thompson and Ellis 1994; An = 71: Wittenberg *et al.* 2003) or defined an epidote-out reaction (An = 31: Poli and Schmidt 1995; Schmidt and Poli 1998; An = 23: Forneris and Holloway, 2003, broken line, F&H). Note the systematic increase in normative anorthite content with increasing pressure.

expected that plagioclase-rich compositions might show epidote over a much larger pressure range than An-depleted compositions. Forneris and Holloway (2003) found epidote breakdown at ca. 2.7 GPa, 700°C in a bulk composition containing 23% An. Poli and Schmidt (1995) determined the breakdown of epidote in an average MORB with 31% An at ca. 3.1 GPa, 700°, whereas Thompson and Ellis (1994) and Wittenberg *et al.* (2003) were able to synthesize epidote-bearing assemblages at 3.5 GPa, 800°C and 4 GPa 900°C-1000°C in synthetic mafic bulk compositions having 48-58% and 71% An, respectively, though both these studies did not reach the upper pressure limit of epidote in their compositions. Furthermore, uncertainties in oxygen fugacity in the order of ±1.3 log unit, as reported in Forneris and Holloway (2003), can be critical for epidote stability and related phase relationships (Liou 1973).

The temperature region < 600°C is essentially unexplored, and probably unexplorable, because, despite the presence of a free fluid, even experiments as long as one month do not show appreciable approach to equilibrium. As a consequence we have only a very rough idea of reactions involving chlorite. Nevertheless, because most mafic compositions at high pressure are silica-saturated, as a result of the albite breakdown to form jadeite component and quartz, chlorite breakdown should be located at pressures comparable to amphibole breakdown, and it is not expected to reach the ultra high pressure field. On the contrary olivine-saturated compositions might show a completely different pattern for chlorite (see section devoted to ultramafic systems).

Lawsonite and epidote-group minerals, which have been known as typical hydrous minerals for relatively shallow hydrothermal conditions, show some of the most interesting relationships in the high pressure metamorphism. Even though there has been some skepticism about the actual presence of lawsonite in ultra high pressure eclogites, recent findings of coesite in the famous lawsonite-eclogite xenoliths from the Four-

Corner Region (Colorado Plateau, Usui *et al.* 2003) demonstrate the relevance of these minerals even in tectonic settings which are not expected to be the most suitable for such low temperature assemblages. The importance of lawsonite is also related to the very high amount of H_2O stored in its structure, which makes it of primary interest for geophysicists and geochemists modelling the geodynamics of subduction zone environments.

Talc, though not ubiquitous in experimental products, is expected to play an important role in differentiated gabbros and, again, it is expected to be sensitive to the bulk Mg/(Mg+Fe) in the system. The fate of talc with pressure is closely related to the stability of the 10Å phase, chemically analogous to talc, which is discussed in more detail below.

Finally, we mention the occurrence of Mg-staurolite in various high pressure studies at conditions close to the wet solidus of mafic systems at ca. 2.5-3.0 GPa. Despite the apparent rarity of Mg-staurolite in natural rocks, it is worth noting its frequency in quite different experimental configuration which might suggest that this mineral has been overlooked in nature.

When enough potassium is present in the system (e.g. in altered oceanic basalts or impure mafic rocks derived from sedimentary sequences) phengite is a characteristic high pressure mineral. Schmidt (1995) and Schmidt and Poli (1998) described the stability of phengite in both mafic and intermediate systems where the celadonite buffering assemblages is garnet + omphacite + silica. For such an assemblage a progressive increase in Si with pressure and decrease with temperature is observed. Celadonite endmember composition is achieved at ca. 9 GPa close to phengite s.s. breakdown to K-hollandite. Phengite is the hydrous mineral with the largest stability field observed in mafic systems. Because it is also the only hydrate on the solidus above the epidote breakdown, phengite controls melting and the geochemical signatures of first melts. Unfortunately, despite considerable effort performed both in model (e.g. Massonne and

Szpurka 1997; Hermann 2002) and in more complex systems (Schmidt and Poli 1998, Schmidt 1996, Okamoto and Maruyama 1998), there is still no complete formulation of a phengite geothermobarometer available for mafic eclogites at high pressure conditions.

ULTRAMAFICS

The hydration of peridotites along mid-ocean ridges has been widely accepted. Many efforts have been devoted to unravelling phase relations in hydrated peridotites, where hydrous minerals such as antigorite, chlorite, amphibole, and a variety of Dense Hydrous Magnesium Silicates (DHMS) may persist under subsolidus conditions at high and ultra high pressure. It is far beyond the goal of this short contribution to review the huge amount of experimental work performed in the model chemical systems MgO-SiO_2-H_2O (MSH) and MgO-Al_2O_3-SiO_2-H_2O (MASH). Source for literature can be found in Ulmer and Trommsdorff (1995, 1999), Frost (1999), Wunder *et al.* (2001), Bromiley and Pawley (2003), and Pawley (2003). We therefore focus here on phase relationships on complex chemical systems approaching natural peridotites, with emphasis on «post-antigorite» phase assemblages.

Experimentally investigated peridotite compositions are mainly derived from variably enriched Hawaiian xenoliths (spinel and garnet lherzolites, Mysen and Boettcher, 1975), fertile spinel lherzolites (KLB-1; Hirose and Kushiro, 1993) and peridotites which are depleted in incompatible elements, but not in Ca and Al (Tinaquillo lherzolite; Robinson and Wood, 1998). Green (1973) calculated a model peridotite composition, the MORB-pyrolite, combining a primitive basalt with a harzburgite residue and used such a pyrolitic composition as starting material to investigate the amphibole stability at subsolidus and near solidus conditions (Niida and Green, 1999). The MORB-pyrolite is an intermediate member between fertile lherzolites (Hawaiian xenoliths)

and the Tinaquillo lherzolite. It is worth noting that serpentinized ocean floor peridotites are generally strongly depleted in Ca during hydrothermal activity shifting bulk compositions toward low CaO/Al_2O_3.

Mantle metasomatism, due to the interaction between ultramafics and alkali rich fluids, has also received a worldwide attention. In particular, in order to investigate the effect of potassium in mantle petrology, natural bulk compositions have been doped with phlogopite or K-amphibole (Mengel and Green, 1989; Konzett and Ulmer, 1999; Konzett and Fei, 2000; Fumagalli, 2003).

Here follow the results on phase relations in both the peridotite+H_2O and peridotite+K_2O systems from subsolidus high pressure experiments (T<800°C).

The Peridotite + H_2O System

Although many experimental studies have been devoted to investigate near solidus and supersolidus phase relations, knowledge on subsolidus equilibria is still fragmentary. In order to unravel the complex reactions involving hydrates such as amphibole and chlorite at temperature < 800°C, we performed subsolidus experiments in the system Na_2O-CaO-FeO-MgO-Al_2O_3-SiO_2-H_2O (NCFMASH) using multianvil and piston cylinder apparata at the Dipartimento di Scienze della Terra, Milan. Gels were used as starting material with bulk compositions corresponding to the Tinaquillo lherzolite (LZ) and a hawaiian pyroxenite nodule (PX). In order to favour crystals growth, a mixture of seeds constituted of natural clinochlore (34.58%), natural pyrope (7.44%), synthetic diopside (36.94%) and synthetic forsterite (Fo80, 21.04%) was added to gels in variable proportions depending on the bulk composition (1.26% in the LZ and 10.0% in the PX). Experiments were performed at pressure ranging from 2.0 to 6.5 GPa and temperature from 650°C and 800°C (Fumagalli 2000; Fumagalli and Poli, *submitted* 2004). Runs lasted up to 2 months. All experiments were

performed at fluid saturated conditions and oxygen fugacity in iron bearing systems was constrained by the presence of graphite.

Due to the relatively low temperatures investigated, the assessment of equilibrium of phase assemblages obtained as run products has to be taken into account. Several petrological tools, both chemical and textural, are often of help to accomplish this scope. As an example, Fe-Mg partitioning between coexisting phases has been considered and compared with both previous experimental results and calculated curves at temperatures of 600 and 800°C by means of available calibrations (e.g. olivine/orthopyroxene, Fonarev, 1981; Koch-Mueller *et al.*, 1992; von Seckendorff and O'Neill, 1993; Brey and Khöler, 1990; Medaris, 1969). Although the Fe-Mg fractionation between olivine and orthopyroxene is unsuitable as geothermometer (Taylor, 1998; Perkins and Vielzeuf, 1992), experimental data are useful to evaluate whether or not these minerals are in equilibrium. Our data are in agreement with Taylor (1998), Niida and Green (1999), and Brey *et al.* (1990), suggesting that experimental olivines and orthopyroxenes are in equilibrium. Furthermore, growth of relatively large, euhedral crystals even at temperatures as low as 650°C reveal approach to textural equilibrium (Fig. 2).

Fig. 3 shows a summary of H_2O-saturated phase relations in ultramafic rocks as resulted by combining available experimental data. Antigorite dominates the low temperature field up to a pressure of 6.0 GPa (Ulmer and Tromsdorff, 1999).

Amphibole is stable in a wide temperature range and it shows a temperature dependent mineral chemistry: a calcic amphibole occurs at low temperatures, a relatively Al-poor, tremolitic amphibole coexists with chlorite and, as temperature further increases, above the thermal stability of chlorite (750-800°C), a Na,Al-rich pargasitic amphibole is stable up to the solidus (Niida and Green, 1999). Amphibole pressure stability is dependent on bulk compositions, mainly on the Na and Ca bulk content, i.e. on the fertility (Mysen and Boettcher, 1975; Wallace and Green, 1991; Niida and Green, 1999). Niida and Green (1999) also showed that the maximum temperature stability expands from 1025 to 1150°C with increasing bulk alkali contents, the higher temperature being related to the higher potassium content (as in the Northern Hessian Depression peridotite modified with 1.5% phlogopite, $K_2O = 0.43$ wt.%) which would stabilizes amphibole to higher temperature.

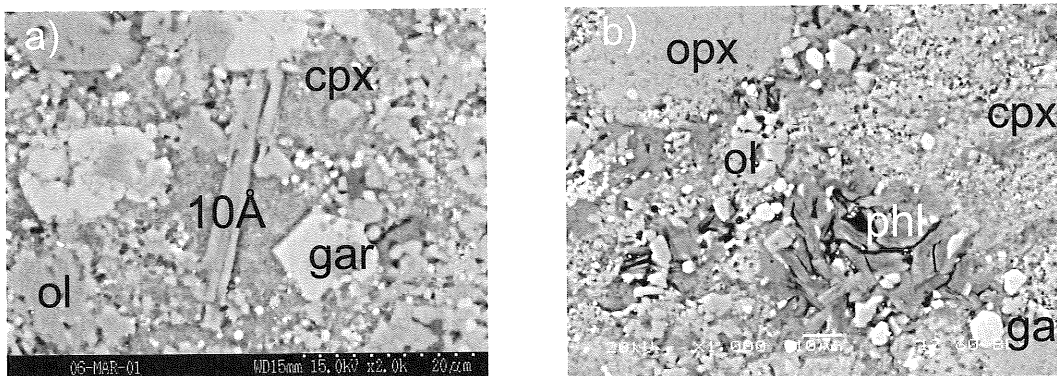Niida and Green (1999) investigated systematically the composition of amphibole

Fig. 2 – Back Scattered Electron images of experimental charges. a) 6.0 GPa, 680°C, lherzolite composition; b) 4.8 GPa, 680°C, K-doped lherzolite. Ol:olivine; opx: orthopyroxene; cpx: clinopyroxene; gar: garnet; phl: phlogopite.
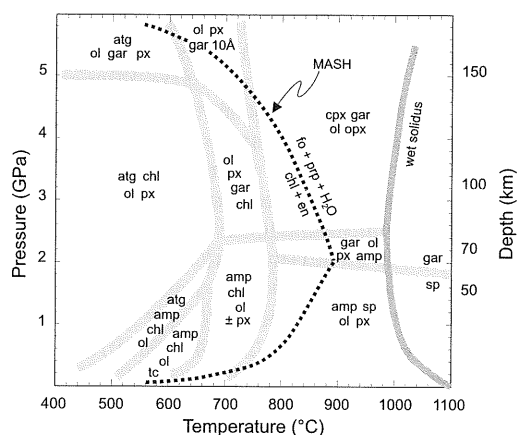
Fig. 3 – Phase assemblages in pyroxenite (squares), lherzolite (circles), and harzburgite (diamonds) compositions at fluid-saturated conditions as a function of pressure and temperature. Phase relationships involving antigorite (ant) are from Ulmer & Trommsdorff (1999); topology of amphibole breakdown reactions from Schmidt & Poli (1998). Dotted lines represent the location of chlorite breakdown reactions in the MASH system (Pawley, 2003); chl = chlorite, amp = amphibole, ol = olivine, cpx = clinopyroxene, opx = orthopyroxene, gar = garnet, 10Å = 10Å phase, sp = spinel, tc = talc (after Fumagalli and Poli, *submitted* 2004).
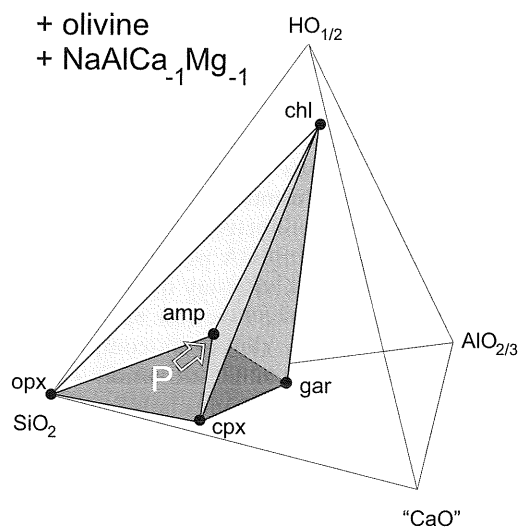
Fig. 4 – Chemographic representation of amphibole-bearing assemblages in pyroxenite composition at 700°C and 2.2 GPa. The arrow (P) shows schematically the shift in amphibole composition with pressure toward the plane chlorite-clinopyroxene-orthopyroxene.

and coexisting phases in a constant bulk composition, the MORB pyrolite, from 0.4 to 3.0 GPa and between 925 and 1100°C and found that amphibole breaks down through complex continuous reactions. The synthetic amphiboles we obtained at temperatures lower than 800°C are mainly Mg-hornblendes and show compositional variations as shown in the chemography of fig. 4. At 2.0 GPa, 700°C amphibole lies above the chemographic plane chlorite-clinopyroxene-orthopyroxene. As pressure increases, amphibole composition is moving toward this plane, suggesting a coplanarity among amphibole, chlorite, orthopyroxene, clinopyroxene. It follows that, while at temperature higher than 800°C a dehydration reaction governs the amphibole breakdown, at temperature lower than 800°C, its pressure stability is controlled by the degenerate H_2O-conserving reaction:

amphibole + olivine =
= orthopyroxene + clinopyroxene + chlorite.
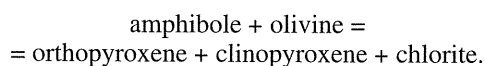
In terms of H_2O budget, such a result implies that major variations of H_2O contents in amphibole-bearing assemblages are within its stability field and not at its breakdown. The latter governs a transfer of the H_2O component to chlorite-bearing assemblages with no release of free fluid.

Chlorite thermal stability, related to the reaction: *chlorite + enstatite = garnet + olivine + water*, results depressed towards lower temperatures in the peridotite model system as compared to MASH system, related to the preferential partitioning of iron into garnet and to the participation of clinopyroxene in a reaction where garnet contains a grossular component (Fumagalli, 2000; Fumagalli and Poli, *submitted* 2004).

The significant quantities of Al in the bulk compositions studied lead to a wide occurrence of chlorite from greenschists to eclogite facies. The pressure stability of chlorite in complex ultramafic systems is still poorly explored and defined. Available experiments performed in the model peridotite system NCFMASH have

shown that the pressure stability of chlorite is controlled by the appearance, at temperature < 700°C, of a 10Å phase structure. The 10Å phase, first synthesized in the MgO-SiO_2-H_2O system by Sclar *et al.* (1965), is a phyllosilicate chemically analogous to talc but with excess water: the chemical formula may be represented as $Mg_3Si_4O_{10}(OH)_2 \cdot nH_2O$. In the complex ultramafic system a 10Å phase structure, identified on the basis of X-ray diffractometry, shows however, at the electron microprobe scale, a homogeneous aluminous composition (Fumagalli and Poli, 1999; Fumagalli *et al.*, 2001). The surprising coincidence in composition between this phase and the mixed-layered mineral kulkeite (clinochlore:talc=1:1; Schreyer *et al.* 1982), may suggest a structural rearrangement of chlorite intercalating Al-free 10Å phase through a continuous reaction. The thermal stability of the 10Å phase structure is governed by the reaction at T > 700°C:

$$10\text{Å phase} + \text{clinopyroxene} = \text{garnet} + \text{orthopyroxene} + H_2O.$$
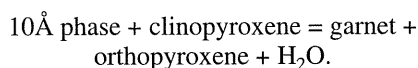
The K-peridotite System

The effect of metasomatism in peridotites is testified by xenoliths suite assigned both to shallow upper mantle (phlogopite-spinel peridotites, Nixon, 1987) and deep continental lithosphere (phlogopite-garnet peridotites). Although the relevance of metasomatic processes in subduction zones, affecting peridotites of the mantle wedge, has been recognized since long time (Gill 1980), peridotites «intruded» in subducted continental crust provide a unique petrological window on processes undergoing at the slab-mantle interface (Brueckner, 1998). Buoyancy forces are responsible for peridotite emplacement in the subducted continental crust; as a consequence devolatilization of felsic rocks and mass-transfer toward peridotite bodies are strongly enhanced. A variety of volatile-bearing phases developed in ultramafics, and recent findings of diamond, Ti-phlogopite, magnesite, dolomite, monazite as inclusions in

garnet-peridotites from Bardane (Norway) testify to the intensity of mass exchange at depth (van Roermund *et al.*, 2002). Despite the relevance of hydrous phases at relatively low temperature high pressure conditions (T < 900°C, P > 2 GPa) there is very little experimental work performed on complex systems approaching natural compositions.

Available experimental data on phase relations in potassium doped model peridotites are limited to few studies (Konzett and Ulmer, 1999; Konzett and Fei, 2000). Phase relations are governed by the occurrence of three potassic phases, which are in order of pressure stability: phlogopite, a potassic amphibole of richteritic composition, and a K-rich hydrous silicate, termed phase X ($K_{2-x}Mg_2Si_2O_7H_x$, x=0-1; Yang *et al.* 2001). K-amphibole represents the breakdown product of phlogopite bearing assemblages and phase X represents the breakdown product of K-amphibole. Most experimental efforts have been devoted to locate reactions such as the amphibole-in and -out reactions and phlogopite out reactions. Relatively simple systems and compositions were investigated by Luth (1997) and Sudo and Tatsumi (1990), who considered phlogopite alone or phlogopite plus enstatite plus diopside. Natural approaching peridotite compositions were investigated by Konzett and Ulmer (1999) and Konzett and Fei (2000).

We performed multianvil experiments at low temperature conditions (< 800 °C) on a K-doped lherzolite (Na_2O = 0.71 wt.%, CaO = 0.59 wt.%, Al_2O_3 = 4.43 wt.%; X_{Mg} (X_{Mg} = Mg/(Mg+Fe^{2+}) = 0.9; doped with 5 wt% of phlogopite) in the pressure range from 4.8 to 6.0 GPa (Fumagalli 2003): the stable phase assemblage is constituted of olivine, orthopyroxene, clinopyroxene, garnet and phlogopite. Phlogopite was preliminary identified by X-ray powder diffraction showing the basal peak at 2θ = 8.73.

Phlogopite mineral chemistry (Fig. 5) suggests a deficiency of interlayer cations, with K+Na ranging from 0.275 (at 6.0 GPa, 680°C) to 0.462 atoms/11 oxygens (at 4.8 GPa, 680°C). It should be noted however that the Na
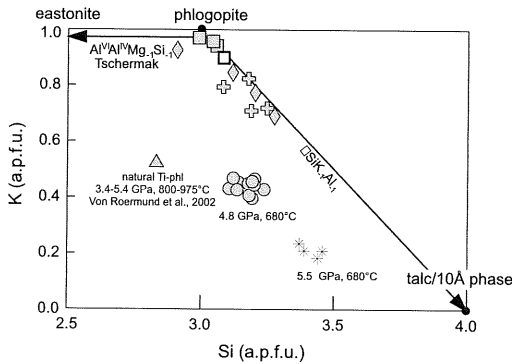
Fig. 5 – Chemistry of phlogopite. Previous experimental data are represented by crosses: 0.2-2.0 GPa, 700-800°C - Wunder and Melzer (2002), diamonds: 2.0-2.4 GPa, 780-900°C - Hermann (2002); filled squares: 6.0-6.5 GPa, 1100°C - Konzett and Ulmer (1999); open square: 6.5 GPa 800°C Konzett J., *personal communication*. Circles and stars represent phlogopite compositions obtained in experiments performed in Milan (unpublished data).

content is always lower than 0.04 a.p.f.u., being preferentially partitioned in the coexisting clinopyroxene. As a result the interlayer cations deficiency is interpreted as a K-deficiency, suggesting the occurrence of interlayer vacancies into the structure, which increase with pressure. In particular, the potassium content is combined with an increase of Si and decrease of aluminium, suggesting an exchange vector such as $Si[]Al_{-1}K_{-1}$ ([] represents vacancy), which points towards a talc like composition. The relevance in phlogopite of a «talc» component is not new both in experimental and natural phlogopites. Hermann (2002), investigating felsic rocks at pressures in the ranges 2.0-4.0 GPa and 780-900°C, found that phlogopite, with increasing pressure, preferentially forms solid solution with talc rather than with phengite. The relevance of talc component in phlogopite was also suggested by Wunder and Melzer (2003) who investigated the concentration of interlayer vacancies as a function of composition in three series of synthetic phlogopite (Rb-series, Cs-series and Ba-series) at 0.2-2.0 GPa and 700-800°C. Although they did not consider the effect of P and T conditions, they suggested an appropriate

method for identification of interlayer vacancies in phlogopites: by assigning the Infrared band at 3674-3678 cm⁻¹ to talc component they obtained results (up to 29 mole % of interlayer vacancies) comparable with independently derived Electron Microprobe Analysis data. Mineral chemistry of Ti-rich natural phlogopite, found as inclusion in diamonds of the Bardane garnet peridotite (Norway, van Roermund *et al.*, 2002), also suggests an important K deficiency of up to 0.5 a.p.f.u.. The relevance of a «talc» component, if suggested by mineral chemistry, is however not in agreement with the pressure stability of such a hydrous phase at high pressure conditions in ultramafic compositions. Nevertheless the occurrence and stability of the 10Å phase at high pressure has been experimentally reported (see above). The pressure stability of the 10Å phase together with its structural similarities with phlogopite, suggests that interlayering and/or solid solution between these two hydrous phases are reasonable. However TEM investigations are certainly needed to corroborate, at the structural scale, such a hypothesis.

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