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Mg-metasomatism of metagranitoids from the Alps: genesis and possible tectonic scenarios

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ABSTRACT

Mg-metasomatic rocks (e.g., whiteschists, leucophyllites) derived from post-Variscan granitoids are common in the Alps. Previously reported field, petrological, geochemical and fluid inclusion data are combined to trace the genetic processes and the associated tectonic scenarios. Although the heterogeneous data, many common features can be recognised in all of the continental Mg-metasomatic rocks, indicating that the genetic process is likely common in the entire range of the Alps. This process assumes highly channelised fluids—derived from ultramafic rocks previously interacting with seawater—that infiltrated the continental crust along strain zones and produced chromatographic fractionation of major and trace elements. Three tectonic scenarios, involving distinct mantle sources, are proposed: rift-related ocean-continent transition, continental subduction, and continent-continent collision. All these data suggest that the Mg-metasomatism was diachronous and occurred at different structural levels during the Alpine history.

Introduction

A number of studies have been devoted to whiteschists and other Mg-rich rocks belonging to continental Units of the Alps. These widespread rocks display a simple MgO – Al_2O_3 – SiO_2 – H_2O ± K_2O mineralogy, with rare FeO and almost absent CaO and Na_2O. Originally, their genesis was ascribed to isochemical metamorphism of a sedimentary protolith (e.g. Chopin, 1981; Schertl *et al.*, 1991), but at present they are interpreted as metasomatic rocks generated by fluid-assisted exchange of elements (e.g., Demény *et al.*, 1997; Barnes *et al.*, 2004; Sharp and Barnes, 2004; Ferrando *et al.*, 2009) or by relative enrichment of MgO due to fluid-assisted removal of other components (Prochaska, 1985; Prochaska, 1991). Protoliths are usually orthogneiss/metagranitoid (e.g., Prochaska *et al.*, 1992; Sharp *et al.*, 1993; Demény *et al.*, 1997; Manatschal *et al.*, 2000; Pawling and Baumgartner, 2001; Barnes *et al.*, 2004; Ferrando *et al.*, 2009; Gabudianu Radulescu *et al.*, 2009), though, locally, volcanic rocks (Prochaska *et al.*, 1997), paragneiss (Prochaska, 1985; Prochaska, 1991; Prochaska *et al.*, 1997), and metagabbro (Prochaska *et al.*, 1997) are also described.

Only few multidisciplinary studies were devoted to the characterisation of the metasomatic fluid (Prochaska *et al.*, 1997; Manatschal *et al.*, 2000; Barnes *et al.*, 2004; Ferrando *et al.*, 2009) and the proposed sources are: a) dehydration of serpentinites (e.g. Sharp *et al.*, 1993; Demény *et al.*, 1997; Barnes *et al.*, 2004; Ferrando *et al.*, 2009); b) interaction between seawater and mantle rocks (Manatschal *et al.*, 2000); c) mixing between seawater or formation water and meteoric water (Prochaska *et al.*, 1997); d) dehydration of flysch (Selverstone *et al.*, 1991) or of evaporitic sediments (Gebauer *et al.*, 1997); e) late-magmatic hydrothermal system (Pawling and Baumgartner, 2001). Previous works are also in disagreement about the timing of metasomatism: during late-Variscan magmatic hydrothermalism (Pawling and Baumgartner, 2001), during Tethyan rifting (Gebauer *et al.*, 1997; Manatschal *et al.*, 2000), during prograde (Ferrando *et al.*, 2009), peak or early retrograde (e.g., Selverstone *et al.*, 1991; Prochaska *et al.*, 1992; Barnes *et al.*, 2004) Alpine metamorphism. However, the widespread presence of these rocks indicates that Mg-metasomatic processes were relatively diffuse in the Alps, and some authors have recently suggested the possibility of a common genesis (Demény *et al.*, 1997; Schertl and Schreyer, 2008; Ferrando *et al.*, 2009).

In this paper, the evidence for a common genesis of continental Mg-metasomatic rocks from hosting granitoids is described, the genetic process is reported, the related tectonic scenarios are proposed, and the timing of metasomatism is made part of Alpine history. These goals are obtained by integration of available data on Mg-metasomatic rocks and hosting acid igneous protoliths. Only these lithologies have been considered because: i) the characterisation of the fluid-rock chemical exchange is favoured by the extreme difference in bulk-rock compositions, ii) most of works focused on these lithologies, iii) the comparison among similar data is favoured. Kind (field, petrography, whole-rock composition, stable isotope, fluid inclusions) and amount of collected data are heterogeneous among the considered localities (Fig. 1 and Table S1) that, from SW to NE, belong to: 1) the Dora-Maira (Cadoppi, 1990; Le Bayon *et al.*, 2006; Schertl and Schreyer, 2008; Ferrando *et al.*, 2009; Grevel *et al.*, 2009), Gran Paradiso (Chopin, 1981; Le Goff and Ballèvre, 1990; Le Bayon *et al.*, 2006), and Monte Rosa (Pawling and Baumgartner, 2001; Le Bayon *et al.*, 2006) Massifs of the Briançonnais terrane (Penninic nappe), 2) the Tauern Window (Selverstone *et al.*, 1991; Barnes *et al.*, 2004) of the Sub-Penninic nappe; 3) the Lower and Middle Austroalpine of the Eastern Alps (Prochaska, 1985; Prochaska, 1991; Prochaska *et al.*, 1992; Demény *et al.*, 1997; Prochaska *et al.*, 1997; Manatschal *et al.*, 2000).

[Figure 1]

A misleading nomenclature

The Mg-metasomatic rocks from the Alps have distinct misleading names. The term “whiteschist” has a metamorphic meaning, and refers to light-coloured eclogite-facies Mg-metasomatic schists (Fettes and Desmons, 2007) characterised by the mineral assemblage talc +

kyanite, i.e. the high-pressure (H*P*) equivalent of the Mg-chlorite + quartz assemblage (Schreyer, 1968; Massonne, 1989). "Silvery micaschist" ("micascisti argentei") is a local term mainly used in Western Alps to describes H*P* silvery-coloured quartz-talc-Mg-chlorite-phengite schists (e.g., Compagnoni and Lombardo, 1974). "Leucophyllite", a local term used in Central-Eastern Alps, is a whitish-coloured quartz-muscovite-chlorite phyllite/schist metamorphosed under greenschist- or amphibolite-facies conditions (Fettes and Desmons, 2007). Less commonly, these rocks are also named "leuchtembergite (a Mg-chlorite)-bearing rocks" (Lelkes-Felvari *et al.*, 1982). In Eastern Alps, "Weißschiefer" is used to describe Mg-rich phyllonitic rocks (Prochaska *et al.*, 1992; Schertl and Schreyer, 2008 and references therein).

In this review, the generic term "Mg-metasomatic rock" is used for metasomatic lithologies belonging to the $MgO - Al_2O_3 - SiO_2 - H_2O \pm K_2O \pm FeO$ system. For this reason, a gouge occurring within metagranitoids from Err nappe (Manatschal *et al.*, 2000) has also been considered.

[Figure 2]

Geologic and *P-T-t* outline

The European Alps (Fig. 1) are a double-vergent orogen resulting from the closure, due to the convergence between Europe and Adria, of oceanic basins belonging to the Tethyan realm, i.e. the Triassic Meliata-Vardar basin (or Neotethys) and the Jurassic Piemonte-Liguria and Cretaceous Valais basins (or Alpine Tethys; Neubauer *et al.*, 1999; Schmid *et al.*, 2004, Rosenbaum and Lister, 2005; Beltrando *et al.*, 2010; Handy *et al.*, 2010; descriptions and references are deliberately not exhaustive). The Briançonnais terrane, a micro-continent located between Valais and Piemonte-Liguria basins, represented the passive continental margin of Europe before the opening of the Valais basin (Fig. 2). At present, the Alpine Orogen is constituted by several nappes characterised by distinct lithological associations and/or Alpine metamorphism. Tectonic Units constituting the axial zone of the Alps experienced a diachronous metamorphic peak from greenschist- to ultra-high pressure (UH*P*) eclogite-facies conditions (Fig. 1; Chopin, 1984; Reinecke, 1991; Frezzotti *et al.*, 2001), and a subsequent rapid exhumation.

Mg-metasomatic rocks are recognised in Units belonging to both European and Adriatic domains (see also Table S1). The Dora-Maira (sites 1 and 2), Gran Paradiso (site 3), and Monte Rosa (site 4) Massifs (i.e., the Internal Crystalline Massifs) represent part of the continental Briançonnais terrane surrounded by the oceanic Piemonte-Liguria terrane, both belonging to the Penninic nappe of the Western Alps (Figs. 1 and 2). The structure is similar for all of the Massifs and consists of a Variscan amphibolite-facies basement intruded by Permian (267–279 Ma; Bussy and Cadoppi, 1996; Gebauer *et al.*, 1997; Bertrand *et al.*, 2000) granitoids, mainly converted to orthogneiss during Alpine orogeny (43-34 Ma; Scaillet *et al.*, 1990; Gebauer *et al.*, 1997; Meffan-Main *et al.*, 2004; Lapen *et al.*, 2007; Gabudianu *et al.*, 2009). Mg-metasomatic rocks from Dora-Maira occur in the *Brossasco-Isasca Unit* (Compagnoni *et al.*, 1995; site 1)—that recorded UH*P* metamorphism (730 °C and 4.0–4.5 GPa; Castelli *et al.*, 2007; Ferrando *et al.*, 2009; Table S1) followed by retrograde recrystallisation up to greenschist-facies conditions (Hermann, 2003)—and in the *Upper Complex* (Cadoppi *et al.*, 2002; site 2), that experienced H*P* metamorphism at 500 ± 50 °C and 0.9–1.5 GPa (Pognante and Sandrone, 1989; Cadoppi, 1990; Table S1). Samples from Gran Paradiso Massif come from the northern area (Fig. 1), where an Alpine metamorphic peak at 515–600°C and 1.9–2.7 GPa (Table S1; Gabudianu *et al.*, 2009) is recorded. Samples from Monte Rosa Massif (Fig. 1) experienced a metamorphic peak at T = 480–570 °C and $1.3 < P < 2.5$ GPa (Table S1; Pawling and Buamgartner, 2001; Lapen *et al.*, 2007 and references therein).

In the Eastern Alps, Penninic and Sub-Penninic nappes are exposed in tectonic windows within the Eastern Austroalpine basement (Schmid *et al.*, 2004). The *Tauern Window* (site 5) is the largest one (Fig. 1) and consists of oceanic crust (the Upper Schieferhülle), belonging to the Piemonte-Liguria (the Glockner nappe) or Valais (the Matrei zone) basins (e.g., Kurz *et al.*, 2008), and of an underlying continental crust (Dal Piaz *et al.*, 2003). This is composed of a pre-Alpine metamorphic complex (the Lower Schieferhülle) intruded by Carboniferous (~ 315 Ma) tonalites and granodiorites, now forming the so called Zentralgneis (e.g., Selverstone *et al.*, 1991). Mg-metasomatic rocks occur in the western area, where the Alpine (~ 30 Ma; e.g., Christensen *et al.*, 1994) metamorphic peak reached 1.0 GPa and 550°C (Barnes *et al.*, 2004 and references therein; Table S1).

The Eastern Austroalpine is a pile of basement and cover nappes which extend from the Swiss/Austrian border to the Pannonian basin. In the Austrian literature, it is subdivided into three main nappes (Lower, Middle and Upper Austroalpine; e.g. Prochaska *et al.*, 1992). From E to W (Fig. 1), the Mg-metasomatic rocks considered in this paper occur in the Err nappe (Lower Austroalpine), in the Gleinalmkristallin Complex (Middle Austroalpine), and in the Grobgneis Complex (Lower Austroalpine), all of them consisting of Variscan basement, intruded by post-Variscan (300 - 340 Ma; Thöni (1999); Nagy *et al.*, 2002) granites. According to Manatschal (1999), Manatschal and Bernoulli (1999) and Manatschal *et al.* (2000), the Lower Austroalpine *Err nappe* (site 6; Fig. 1) remarkably preserves remnants of the distal Adriatic margin of the Piemonte-Liguria basin (Fig. 2), and records Alpine conditions up to lowermost greenschist-facies (Table S1). On the contrary, Alpine (~ 75- 80 Ma; Prochaska *et al.*, 1992; Hoinkes *et al.*, 1999; Nagy *et al.*, 2002) metamorphic peak occurred at T = 460–480 °C and P > 0.4–0.5 GPa (Table S1; Prochaska *et al.*, 1992) in the Middle Austroalpine *Gleinalmkristallin Complex* (site 7), and at T = 500–600 °C and P = 0.8–1.3 GPa (Table S1; Moine *et al.*, 1989; Demény *et al.*, 1997) in the Lower Austroalpine *Grobgneis Complex* (sites 8-11; Fig. 1).

[Figure 3]

Mg-metasomatic rocks: evidence for a common genesis

The Mg-metasomatic rocks of the Alps considered in this work show similar field, petrographic, geochemical and fluid inclusion features.

Field relationships

In all of the localities, the Mg-metasomatic rocks occur in the centre of shear zones within metagranitoid/orthogneiss. Differences in tectono-metamorphic conditions are reflected on differences in the involved lithologies—e.g, cataclasite and gauges (Piz d'Err – Piz Bial area; Manatschal *et al.*, 2000) *vs* orthogneiss and schist (other localities; e.g., Cadoppi, 1990; Selverstone *et al.*, 1991; Prochaska *et al.*, 1992; Demény *et al.*, 1997; Pawling and Baumgartner, 2001; Schertl and Schreyer, 2008)—and in the field relationships—e.g., continuous layers (Piz d'Err – Piz Bial area, Eastern Alps; e.g., Selverstone *et al.*, 1991; Prochaska *et al.*, 1992; Demény *et al.*, 1997; Manatschal *et al.*, 2000) *vs* lens-like bodies (Western Alps; e.g., Cadoppi, 1990; Pawling and Baumgartner, 2001; Schertl and Schreyer, 2008)—as schematised in Fig. 3 and Table S1. As it approaches to the centre of shear zone, the hosting metagranitoid appears progressively enriched in micas and, then, in Mg-rich minerals (Fig. 3 and Table S1; e.g., Cadoppi, 1990; Selverstone *et al.*, 1991; Prochaska *et al.*, 1992; Demény *et al.*, 1997; Pawling and Baumgartner, 2001; Schertl and Schreyer, 2008).

[Figure 4]

Classes of metasomatism

Previous data on field occurrence, petrography, and bulk-rock chemical composition (major and, subordinately, trace elements) allow to define four homogeneous metasomatic classes, representative for a progressive increase in Mg-metasomatism, starting from the wallrock (class 0) to the centre of the shear zone (class 3). To compare homogeneous data, rocks from Tauern Window are described separately because generated from a granodioritic and not granitic protolith. Table S2 summarises petrographic and geochemical information for all of the localities, whereas Tables S4-S7 reports the whole-rock data plotted in Figs. 4-6.

Class 0 represents the hosting protolith constituted by peraluminous metagranitoids (CIPW norm) or orthogneisses/augengneisses. In sub-Units more involved in the Alpine metamorphism, only the igneous K-feldspar is still preserved, whereas H*P*-UH*P* minerals replaces the magmatic ones (Table S2; Cadoppi, 1990; Compagnoni *et al.*, 1995; Pawling and Baumgartner, 2001). Granitic rocks show (Na_2O + K_2O + CaO) and MgO contents mainly ranging from 7 to 10 wt% and from 0.2 to 1.5 wt%, respectively (Fig. 4). All of the samples have similar trace-element pattern (Fig. 5a), characterised by moderate enrichments in Cs, Rb, Th, Pb, U, K—the lower values collected in the Lower Austroalpine—and by moderate-to-strong depletions in Cr, Ni, Sr, Ti, Ba with respect to the average continental crust (Rudnik and Gao, 2005). These patterns match with that of Crd granite from the Lachlan Fold Belt (LFB), for which an origin from mixed sources (mantle-derived magmas and older crustal rocks) has been proposed (Kemp and Hawkesworth, 2005).

Class 1 consists of the transition rocks (Table S2) located between protolith and metasomatic rocks (Prochaska *et al.*, 1992; Demény *et al.*, 1997; Prochaska *et al.*, 1997; Manatschal *et al.*, 2000; Pawling and Baumgartner, 2001; Schertl and Scheryer, 2008). They are schists (Dora-Maira Massif), gneisses (Monte Rosa Massif; Middle and Lower Austroalpine) or cataclasites (Piz d'Err - Piz Bial area) characterised by the presence of white mica (phengite or muscovite) or illite (in the cataclasite; Table S2). These rocks show (Na_2O + K_2O + CaO) and MgO contents mainly from 5.5 to 8 wt% and from 0.4 to 4 wt%, respectively (Fig. 4). The trace-element pattern (Fig. 5b) is similar to that of class 0 rocks, indicating their genetic relationship. A positive anomaly of Pb is observed in some samples from Err. The evident variations in Rb, Ba, K, Sr and P—from strongly enriched to strongly depleted with respect to the average continental crust (Rudnik and Gao, 2005)—should be related to different amounts of Ca- and K-rich minerals.

[Figure 5]

Class 2 consists of Mg-bearing rocks (whiteschists, Prp quartzite, gouge, Ms-Qtz-phyllonite, leucophyllite) located in (or near) the centre of the shear zone. Mineral assemblage and, consequently, structure are related to experienced *P-T* conditions (Table S2). Variable amounts of quartz/coesite, Mg-rich minerals (Mg-chlorite, Mg-chloritoid, talc, pyrope, ellenbergerite, Mg-dumortierite, bearthite, wagnerite), and K-rich minerals (illite, muscovite, biotite, phlogopite, phengite) have been observed even in small outcrops (e.g., Prochaska *et al.*, 1992; Compagnoni *et al.*, 1995; Bussy and Cadoppi, 1996; Demény *et al.*, 1997; Prochaska *et al.*, 1997; Manatschal *et al.*, 2000; Pawling and Baumgartner, 2001; Gabudianu *et al.*, 2009). These rocks usually show high MgO (from 2.0 to 8.0 wt%) and low ($Na_2O + K_2O + CaO$) contents (from 1.5 to 6.0 wt%; Table S6). With respect to the average continental crust (Rudnik and Gao, 2005), trace-element patterns show little enrichments in Rb, Th, U, Ta, and depletion in Sr, Cr, Ni and Ti (Fig. 5c), other elements ranging from enriched to depleted. The evident variations in Pb, P and, locally, HFSE, Y and HREE are probably due to different modal amounts of relative compatible minerals (e.g., apatite, garnet).

Class 3 comprises rocks, located in the centre of the strain zone, showing the highest Mg content. They are almost monomineralic and consist of Mg-chlorite or garnet, depending on *P-T* conditions (Table S2). Minor amounts of other Mg-rich minerals (e.g., talc, chloritoid) and kyanite are usually present, whereas quartz/coesite and micas are subordinate or absent (e.g., Chopin, 1981; Prochaska *et al.*, 1992; Pawling and Baumgartner, 2001; Schertl and Scheryer, 2008). In the Monte Rosa Massif, calcite is also present (Pawling and Baumgartner, 2001). Class 3 rocks show a very low ($Na_2O + K_2O + CaO$) content (< 1 wt%) and a very high (from 20 to 30 wt%) MgO content (Fig. 4). With respect to the average continental crust (Rudnik and Gao, 2005), the trace-element pattern shows moderate to strong depletion in K, Sr, Sm, Ba, Rb, LREE and MREE, and small enrichment in Nb, Zr, Y, and Th. Ni vary from depleted to enriched (Fig. 5d).

In Tauern Window, protoliths (class 0) are peraluminous granodiorites (CIPW norm; Table S2; Selverstone *et al.*, 1991) in which ($Na_2O + K_2O + CaO$) and MgO contents range from 6.69 to 8.04 wt% and from 2.18 to 2.93 wt%, respectively. Weak enrichments in Rb, Ba, Nb, and depletions in Ti, Cr and Ni (Fig. 6b) are observed with respect to the average continental crust (Rudnik and Gao, 2005). Also in this case, the patterns match with those from the Lachlan Fold

Belt (Hbl granite; Kemp and Hawkesworth, 2005). Rocks belonging to class 1 are Bt-Phg schists, and those belonging to class 2 and 3 are Grt-Chl-St schists (Table S2; Selverstone *et al.*, 1991; Barnes *et al.*, 2004). Bt-Phg schists show (Na_2O + K_2O + CaO) and MgO contents from 6 to 10 wt% and from 6.5 to 11 wt%, respectively (Fig. 6a). Enrichments in Rb, K, Ba, Nb, P, and depletions in Cr, Ni, Sr (Fig. 6c) are recorded with respect to the average continental crust (Rudnik and Gao, 2005). The rocks from class 2 show (Na_2O + K_2O + CaO) and MgO contents from 4.5 to 5.5. wt% and from 13 to 14 wt%, respectively (Fig. 6a), and enrichments in Rb, K, Nb, P and depletions in Ni and Sr (Fig. 6c) with respect to the average continental crust (Rudnik and Gao, 2005). The only sample belonging to class 3 shows very low (Na_2O + K_2O + CaO) content (< 2 wt%), high MgO content (about 13 wt%; Fig. 6a), enrichments in Nb and P and depletions in Rb, Ba, K, Sr, Zr, Cr (Fig. 6c) with respect to the average continental crust (Rudnik and Gao, 2005).

[Figure 6]

Chemical composition of metasomatic fluids and their isotopic signature

In all of the localities, the chemical composition of metasomatic fluids is achievable by indirect (mass transfer) and/or direct (fluid inclusions) methods. The use of isocon diagrams (Grant, 1986) should be the correct way to evaluate element gain and loss among the classes of metasomatism (e.g., Selverstone *et al.*, 1991; Demény *et al.*, 1997; Manatschal *et al.*, 2000; Pawling and Baumgartner, 2001), but the lack of data from many samples prevent its use in this work. Because samples belonging to the same metasomatic class show similar major- and trace-element composition, the average of element concentrations for each class can be considered, in first approximation, representative for all of the samples. In Fig. 3, plot of the average of element concentrations in classes 1, 2 and 3 relative to class 0 is shown (see also Table S3). Data from Tauern Window are reported separately and are locally too scarce and, maybe, affected by anomalous modal concentration of minerals (e.g., apatite) to be always representative. Fig. 3 reveals a chromatographic fractionation of some major and trace elements from class 0 to class 3. A progressive decrease in Na, Ca and Sr contents from class 1 to class 3 is evident. The K and Rb contents increase in class 2 and strongly decrease in class 3, whereas the Si content usually remains constant up to class 2 and always decreases in class 3, in agreement with the modal variations of micas and quartz/coesite, respectively. A progressive increase in Mg, Ni and H_2O is evident toward the centre of the strain zones, and a minor increase in Fe and Cr is also probable (Fig. 3). These data indicate that the metasomatic fluid was an aqueous fluid releasing Mg, Ni, Fe, Cr and incorporating alkalis, Ca, Si and LILE.

A direct way to obtain the chemical composition of the fluid is by fluid inclusion study. Ferrando *et al.* (2009) demonstrate that the metasomatic fluid generating the UH*P* whiteschists of the Brossasco-Isasca Unit was a Mg-Cl-rich (up to 28 $NaCl_{eq}$ in wt%) aqueous fluid containing minor amounts of dissolved cations (Na, Al, Si). In some localities of the Lower Austroalpine, Prochaska *et al.* (1997) propose a metasomatic aqueous fluid containing Mg—but also Ca and minor Na, Al and Fe—and showing an increase of salinity (up to 35 $NaCl_{eq}$ in wt%) from top to bottom of the Unit. In conclusion, mass transfer and fluid inclusions data point to a high-salinity Si-undersaturated aqueous fluid containing Mg, but probably also Ni, Fe, and Cr. All of the metasomatic rocks were generated by progressive release of Mg, Ni, Fe, Cr and incorporation of alkalis, Ca, Si and LILE from the metasomatic fluid. The hypothesis of a relative enrichment of MgO due to removal of the other components (e.g., Prochaska, 1985) seems to be unconvincing because it would imply an unlikely metasomatic fluid only able to remove, but not to release, elements.

Stable isotope data ($\delta^{18}O$ and δD; Table S8 and Fig. 3) collected on mineral-separates and/or whole-rock from 7 of 10 localities (Prochaska *et al.*, 1992; Sharp *et al.*, 1993; Demény *et al.*, 1997; Prochaska *et al.*, 1997; Manatschal *et al.*, 2000; Barnes *et al.*, 2004) are similar. The least-altered granitic samples of class 0 shows values close to 11‰, confirming the crustal anatectic origin suggested by the trace-element pattern (Demény *et al.*, 1997; Manatschal *et al.*, 2000; Barnes *et al.*, 2004), whereas other samples show isotope disequilibrium due to the metasomatic process (Sharp *et al.*, 1993; Demény *et al.*, 1997). Transition rocks (class 1) from Tauern (Barnes *et al.*, 2004) and Sopron (Demény *et al.*, 1997) show high δD values, suggesting an isotopic re-equilibration during metasomatism. This re-equilibration, observed also in the Middle Austroalpine (Prochaska *et al.*, 1992), is not recorded in Err, where $\delta^{18}O$ values of protolith are still preserved (Manatschal *et al.*, 2000). Where measured, $\delta^{18}O$ and δD data from Mg-metasomatic rocks (classes 2 and 3) are relatively consistent and show an increase in δD values and a decrease in $\delta^{18}O$ values with respect to the corresponding samples from classes 0 and 1 (Prochaska *et al.*, 1992; Sharp *et al.*, 1993; Demény *et al.*, 1997; Manatschal *et al.*, 2000; Barnes *et al.*, 2004). All of the authors interpret these variations as the evidence for an isotopic re-equilibration due to influx of metasomatic fluids characterised by low $\delta^{18}O$ and high δD values, typical marks for seawater. Interaction with meteoric water is negligible and only locally observed in Lower Austroalpine (Prochaska *et al.*, 1997) and Tauern Window (Barnes *et al.*, 2004).

[Figure 7]

Genesis of Mg-metasomatic rocks and possible tectonic scenarios

The continental Mg-metasomatic rocks considered in this work show similar field, petrographic, geochemical and fluid inclusion features, indicating that their genetic process is likely the same in the entire range of the Alps. This process, as already proposed by some authors (Sharp *et al.*, 1993; Demény *et al.*, 1997; Manatschal *et al.*, 2000; Barnes *et al.*, 2004; Sharp and Barnes, 2004; Ferrando *et al.*, 2009), must assume i) highly channelised metasomatic fluids infiltrating the continental crust and ii) chromatographic fractionation of major and trace elements. The fluid composition (a Si-undersaturated Ni-Mg-rich brine with Fe and Cr) and its “oceanic” (seawater) signature suggest an origin from serpentinised ultramafics. An evaporitic source (Gebauer *et al.*, 1997) can be excluded because the generated fluids should be Mg-K-rich aqueous fluids with high

$\delta^{18}O$ signature and containing high amounts of F, Li and B, and lacking Ni and Cr (Moine *et al.*, 1981; Moore and Waters, 1990). Also a late-magmatic hydrothermal source (Pawling and Baumgartner, 2001) should be excluded because the hydrothermal alteration of a granite does not produce Mg enrichments (Parneix and Petit, 1991; Nishimoto and Yoshida, 2010).

Fig. 7 schematises the possible process generating the Mg-metasomatic rocks. Extensive dehydration of oceanic serpentinites releases Si-undersaturated Ni-Mg-rich brines characterised by high δD values. These metasomatic fluids infiltrate continental crust along high-permeability conduits (i.e., strain zones) and are channelized over significant distances. It is noteworthy that the flux of the channelised fluid could even have been similar to that observed in high-level hydrothermal systems (McCaig, 1997). Along the flow path, ion exchange between fluid and granitoid modifies the fluid composition through progressive precipitation of Mg, Ni, Fe and Cr, and dissolution of alkalis, Ca, Si and LILE toward the centre of the strain zone. Moreover, a further fractionation occurs from the ultramafic source to the continental rocks, as revealed by the increase of Ni and Cr contents in continental Mg-metasomatic rocks that occur in close spatial association with ultramafic bodies (Err: Manatschal *et al.*, 2000; Tauern Window: Selverstone *et al.*, 1991; Barnes *et al.*, 2004).

[Figure 8]

At least three tectonic scenarios can be proposed, in which this genetic process could occur along faults juxtaposing hydrated mantle with continental crust: rift-related ocean-continent transition, continental subduction, and continent-continent collision (Fig. 8). The rift-related ocean-continent transition (Fig. 8a) is characterised by large-scale, low-angle detachment faults related to thinning and break-up of continental crust and to mantle exhumation. In this geological context, marine fluids penetrate and interact with the exhumed mantle before to be channelised into the continental crust along the detachment faults (Manatschal *et al.*, 2000 and reference therein). The fluid flow is upward and its driving force is supposed to be a thermal fluid convection associated with mantle exhumation (Manatschal and Nievergelt, 1997).

At present, an univocal tectonic model for the continental subduction is lacking (e.g., Stöckhert and Gerya, 2005; Agard *et al.*, 2009) and a discussion about the cutting-edge models is beyond the aim of this work. The most important point is that all of these models assume a tectonic association between oceanic serpentinites and continental crust. During subduction, antigorite from serpentinites progressively dehydrates in a narrow range of P-T conditions (Sharp and Barnes, 2004). Part of the high amounts of produced metasomatic fluids percolates and hydrates the overlying mantle wedge, and part of them are channelised along the main convergent structures and infiltrates the subducted continental crust (Fig. 8b). Arguments on direction of channelised fluid flow and on its driving force are strictly related to the tectonic model considered. Usually, the main driving force is considered to be a high fluid pressure, that allows long-distance fluid transport along shear zones and/or induces microfractures and vein-network formation (Zack and John, 2007).

The third geological context is the continent-continent collision (and exhumation), in which oceanic, continental and mantle-wedge tectonic Units are imbricated to form the belt, and major extensional shear zones accommodate their exhumation (Fig. 8c). Dehydration of oceanic or mantle-wedge serpentinites during exhumation releases metasomatic fluids that are channelised upward along extensional shear zones. Local mixing with meteoric water percolating from the surface could occur. The temperature at which the serpentinites dehydrate affects the fluid mobility. At $T > 550$°C, large volumes of high-mobile metasomatic fluid are released and channelised, whereas at lower T low-mobile metasomatic fluids generate blackwall zones at the contacts between serpentinite and wall rock (Barnes *et al.*, 2004).

Mg-metasomatic rocks in the Alpine history

At present, the Alps comprise two orogens: an older Late Cretaceous orogen due to the closure of the Meliata-Vardar basin (Neotethys) and preserved in the Eastern Alps, and a younger Cenozoic (Eocene–Oligocene boundary) orogen due to the closure of the Piemonte-Liguria and Valais basins (Alpine Tethys) and preserved in the Western Alps (Handy *et al.*, 2010 and references therein). Mg-metasomatic rocks considered in this work become from both orogens. The age of metasomatism proposed by previous authors is different among the localities (Table S1), supporting the presence of diachronous processes in the Alps. Moreover, field and petrological data described above show variations (e.g., lacking *vs* pervasive Alpine deformation; L*P*-L*T* vs UH*P*-M*T* mineral assemblages) that can only be referred to Mg-metasomatic processes operating within different structural levels of the Alpine chain and through distinct geodynamic regimes.

[Figure 9]

A temporal sequence of the Mg-metasomatic events related to Alpine history is shown in Fig. 9. The earliest Mg-metasomatic events involving (meta)granitoids probably occurred during Tethys opening and involved portions of continental crust, belonging to both Europe and Adria (Fig. 2), along the ocean-continent transition. The sub-continental mantle exposed at the seafloor interacted with seawater and the resulting fluids were channelised into the continental crust along rift-related detachment systems (Fig. 8a). This geological event is well recorded in the Err domain (Fig. 9), where it was responsible for the genesis of gouges (Manatschal *et al.*, 2000) during the Early Jurassic (late Pliensbachian - early Toarcian) opening of the Piemonte Liguria basin.

Other Mg-metasomatic events occurred at the closure of the Tethyan basins and during the subsequent continent-continent collision and exhumation. During continental subduction, oceanic serpentinites belonging to distinct basins (Fig. 2) progressively dehydrated and part of the released fluids infiltrated the juxtaposed continental crust along main tectonic structures (Fig. 8b). During the continent-continent collision and exhumation (Fig. 8c), a further Mg-metasomatic event occurred along extensional shear zones and was promoted by fluids probably originated from portions of both oceanic crust and hydrated mantle-wedge. In the Eastern Alps, the Sopron Mg-metasomatic rocks formed though continental subduction at about 80-70 Ma (Demény *et al.*, 1997), i.e. during the Eastern Alps orogeny (Fig. 9). Likely, the oceanic serpentinites involved in this process belonged to the Meliata-Vardar basin because, at that time, the Piemonte-Liguria and Valais basins just started their closure (Handy et al., 2010; Fig. 9). During the same orogeny, the Mg-metasomatic rocks of the Austrian Lower and Middle Austroalpine formed via continent-continent collision and exhumation (Prochaska, 1985; Prochaska, 1991; Prochaska *et al.*, 1992; Prochaska *et al.*, 1997; Table S1; Fig. 9). More recently, at about 45-20 Ma (i.e., during the Western Alpine orogeny), similar Mg-metasomatic events occurred in the Western and Central Alps. In the Southern Dora-Maira (Western Alps), Mg-metasomatic rocks formed during continental subduction (Sharp and Barnes, 2004; Ferrando *et al.*, 2009; Table S1; Fig. 9), whereas in the Tauern Window (Central Alps) they formed during continent-continent collision or exhumation (Selverstone *et al.*, 1991; Barnes *et al.*, 2004; Table S1; Fig. 9).

Concerning the other localities considered in this study, current data indicate that the Mg-metasomatic rocks from Monte Rosa, Gran Paradiso, and northern Dora-Maira formed before the continent-continent collision related to the Western Alpine orogeny, although the geological context is still enigmatic (Fig. 9). Multidisciplinary studies, combining petrological, geochemical (major and trace elements, stable isotopes) geochronological and fluid inclusion data, would be necessary to discriminate between rift-related ocean-continent transition and continental subduction as possible tectonic scenarios.

Concluding remarks

Continental Mg-metasomatic rocks in metagranitoids are relatively common in the Alps and occur in the palaeogeographic realms of both Europe and Adria (Fig. 1). This review indicates that all of these lithologies generated along strain zones by influx of external fluids coming from ultramafic rocks that previously interacted with seawater. This process could have occurred during distinct geological events (Fig. 8): i) the opening of the Tethyan basins, ii) the continental subduction after the closure of these basins, iii) the collision and exhumation of the tectonic Units constituting the Alpine Orogen. In these scenarios, three kinds of ultramafic rocks could have originated the metasomatic fluid (Fig. 8): a) sub-continental ultramafic rocks hydrated during rifting, b) subducted oceanic serpentinites belonging to distinct Tethyan basins, c) mantle-wedge ultramafic rocks hydrated during subduction.

The tectonic scenarios proposed in this study point to a metasomatic process more extended (in space and time) than previously believed. The continental tectonic Units most involved in the Alpine history (e.g., Dora-Maira, Gran Paradiso, Monte Rosa) could have experienced more than a single Mg-metasomatic event and the fluid should have originated, from time to time, from distinct mantle sources. Moreover, similar tectonic scenarios could be invoked also for other Mg-metasomatic products widespread in continental, but also oceanic, Units of the Alps, such as: Mg-metasomatic rocks observed in other lithologies (e.g., volcanic rocks, paragneiss and metagabbro; Lelkes-Felvari *et al.*, 1982; Prochaska, 1985; Prochaska, 1991; Prochaska *et al.*, 1997; Scambelluri and Rampone, 1999), Cr-Ni-Mg-rich veins (e.g., Spandler *et al.*, 2011) and some deposits of Mg-rich mineral (talc, magnesite, dolomite, emerald; e.g., Prochaska, 1989; Kiesl *et al.*, 1990; Sandrone *et al.*, 1990; Ferrini *et al.*, 1991 and references therein) which origin is still debated.

A multidisciplinary approach is useful to test these hypotheses. Meso- and micro-structural observations, *P-T-t* data, whole-rock trace element contents (in particular Cr, Ni, Li, B, F), stable isotope data ($\delta^{18}O$, δD, $\delta^{37}Cl$, $\delta^{11}B$, $\delta^{7}Li$), and fluid inclusion data could allow to distinguish distinct metasomatic events, to trace the source of the metasomatic fluid and its chromatographic fractionation during infiltration in the continental crust, and to define the timing of metasomatism and its possible diachronous distribution in the orogenic evolution.

Finally, Mg-metasomatic rocks probably have a crucial role in large scale tectonic events (not only Alpine) because on their rheological behaviour. In Mg-rich rocks (class 3) along shear zones, it is possible that the occurrence of talc (and maybe also of Mg-chlorite and other phyllosilicates) instead of pyrope could reduce fault strength and induce stable sliding (e.g., Soda and Takagi, 2010; Moore and Lockner, 2011).

However, to improve the knowledge on Mg-metasomatism in continental and oceanic rocks and on its role in mechanical properties of faults, further studies on fluid/mineral element partitioning, on physical-chemical parameters (*P-T-X*) affecting composition and mobility of the metasomatic fluid, on rheological behaviour of Mg-metasomatic rocks, and on other genetic tectonic scenarios (e.g., oceanic subduction, accretionary prism) are needed.

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Figure and table captions

Fig. 1.

Tectonic sketch map of the Alps modified from Prochaska (1989), Neubauer *et al.* (1999), Pohl and Belocky (1999), Dal Piaz *et al.* (2003); Ferrando *et al.* (2004), Schmid *et al.* (2004), Handy *et al.* (2010). The occurrences of the studied Mg-metasomatic rocks is reported: (1) Valle Po-Val Varaita (Le Bayon *et al.*, 2006; Schertl and Schreyer, 2008; Ferrando *et al.*, 2009; Grevel *et al.*, 2009); (2) Val di Susa (Cadoppi, 1990); (3) Valnontey-Valleille-Bardoney area (Chopin, 1981; Le Goff and Ballèvre, 1990; Le Bayon *et al.*, 2006); (4) Val d'Ayas (Pawling and Baumgartner, 2001; Le Bayon *et al.*, 2006); (5) Pifisch region (Selverstone *et al.*, 1991; Barnes *et al.*, 2004); (6) Err nappe (Manatschal *et al.*, 2000); (7) Weißkirchen (Prochaska, 1985; Prochaska *et al.*, 1992); (8) Hollersgraben, Außberegg, S-Pacher, Ratten, Vorau (Prochaska *et al.*, 1997); (9) Klingfurth (Prochaska *et al.*, 1997); (10) Sopron (Demény *et al.*, 1997; Prochaska *et al.*, 1997). Occurrence of diamond and/or coesite is shown with a star symbol.

Fig. 2.

Early Cretaceous reconstruction of the Alps. Modified after Rosenbaum and Lister (2005). Where necessary, the name of the corresponding Alpine nappe is reported in brackets.

Fig. 3.

Schematic sketch showing field relationships of hosting and Mg-metasomatic rocks, from wallrock to the centre of the shear zone (arbitrary scale of outcrops). Stable isotope ($\delta^{18}O$ and δD) data ranges for each classes and average of element concentrations in classes 1, 2 and 3 relative to class 0 for granitic and granodioritic protoliths (note the different Y scale) are also reported. VL*P*: very-low pressure rocks (gouges from Err); UH*P*: ultra-high pressure rocks (pyrope-whiteschists from Dora-Maira); M*P*-H*P*: medium-to-high pressure rocks (Mg-metasomatic rocks from other localities). Toward the centre of the strain zones, an increase in Mg, Ni, H_2O, δD—and, maybe, in Fe—and a decrease in Na, K, Rb, Ba, Ca, Sr, Si and $\delta^{18}O$ is evident.

Fig. 4.

Diagram showing the (Na_2O + K_2O + CaO) content vs. the MgO content for samples with granitic protolith and belonging to the four classes of metasomatism. A progressive increase in MgO and decrease in (Na_2O + K_2O + CaO) contents is evident from class 0 to class 3.

Fig. 5.

Trace-element pattern of rocks of granitic protoliths and belonging to class 0 (a), class 1 (1), class 2 (c), and class 3 (d) of metasomatism. Patterns are normalised to the average continental crust (Rudnick and Gao, 2005). In Fig. 5a, trace-element composition of Crd granite from the Lachlan Fold Belt (LFB; Kemp and Hawkesworth, 2005) is reported for comparison.

Fig. 6.

Major- (a) and trace-element (b, c) diagrams of rocks from Tauern Window (granodioritic protolith) belonging to classes 0-3. Trace-element patterns are normalised to the average continental crust (Rudnick and Gao, 2005). In Fig. 6b, trace-element composition of Hbl granite from the Lachlan Fold Belt (LFB; Kemp and Hawkesworth, 2005) is reported for comparison.

Fig. 7.

Schematic sketch showing the genetic process of the Mg-metasomatic rocks. This process, assumes highly channelised fluids—derived from ultramafic rocks that has previously interacted with seawater—infiltrating the continental crust along strain zones and producing chromatographic fractionation of major and trace elements. Font-size of elements is qualitatively related to their amount released or incorporated by the fluid.

Fig. 8.

Tectonic models for fluid flow along faults juxtaposing hydrated mantle and continental crust. (a) Rift-related ocean-continent transition: seawater fluids interact with mantle rocks before to be channelised along large-scale detachments. Modified from Manatschal *et al.* (2000). (b) Continental subduction: part of fluids released during H*P*/UH*P* dehydration of tectonically associated oceanic serpentinites are channelised along main convergent structures. Modified from Agard *et al.* (2009). (c) Continent-continent collision: fluid generated by local dehydration of serpentinites are channelised along major extensional shear zones. Modified from Agard *et al.* (2009).

Fig. 9.

Timetable, related to Alpine history, of the Mg-metasomatic events recorded in the localities considered in this work (see text for details). The Eastern Alps orogeny (Late Cretaceous), due to the closure of the Meliata-Vardar basin, and the Western Alps orogeny (Cenozoic), due to the closure of the Piemonte-Liguria and Valais basins, are well distinguishable.

Supplementary material

Table S1

Summary of geologic, metamorphic, and field data referring to the localities considered in this work. The number of the locality refers to that reported in Fig. 1.

Table S2

Summary of petrographic and geochemical data that refer to rocks belonging to class 0 of metasomatism (i.e., protolith). The number of the locality refers to that reported in Fig. 1. Mineral abbreviation after Fettes and Desmons (2007). Amp: amphibole; Bea: bearthite; Ell: ellenbergerite; Mg-Dum: Mg-dumortierite; Opm: opaque mineral; Wag: Wagnerite.

Table S3

Average (in ppm, except LOI in wt%) of some major- and trace-element concentrations in samples belonging to the four classes of metasomatism.

Table S4

Major- (wt% oxide) and trace-element (ppm) compositions of rocks belonging to class 0 of metasomatism (protolith). mg# = MgO/(MgO+FeO_{TOT}); a: Ferrando *et al.* (2009); b: Schertl and Schreyer (2008); c: Grevel *et al.* (2009); d: Cadoppi (1990); e: Le Goff and Ballèvre (1990); f: Pawling and Baumgartner (2001); g: Barnes *et al.* (2004); h: Selverstone *et al.* (1991); i:

Manatschal *et al.* (2000); j: Prochaska *et al.* (1992); k: Prochaska *et al.* (1997); l: Demény *et al.* (1997).

Table S5

Major- (wt% oxide) and trace-element (ppm) compositions of rocks belonging to class 1 of metasomatism (transition rocks). mg# = MgO/(MgO+FeO_{TOT}); a: Schertl and Schreyer (2008); b: Pawling and Baumgartner (2001); c: Barnes *et al.* (2004); d: Selverstone *et al.* (1991); e: Manatschal *et al.* (2000); f: Prochaska *et al.* (1992); g: Prochaska *et al.* (1997); h: Demény *et al.* (1997).

Table S6

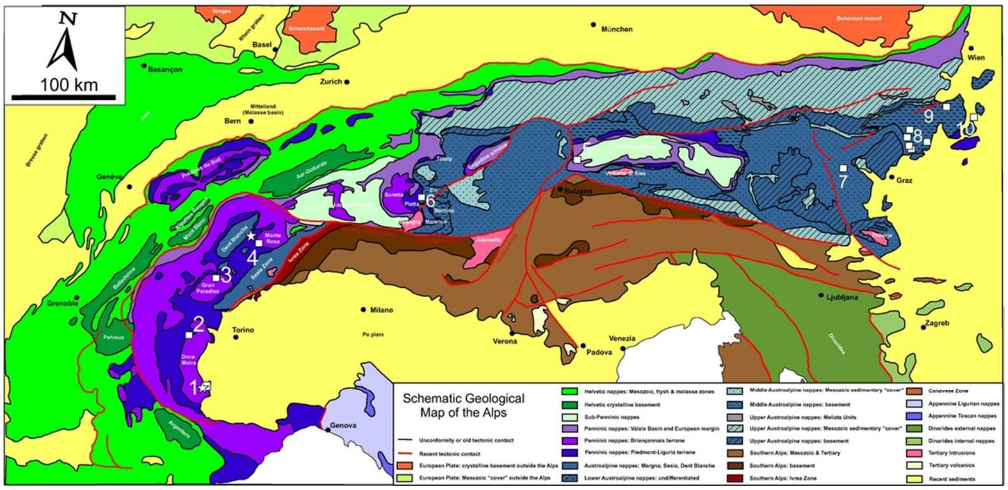
Major- (wt% oxide) and trace-element (ppm) compositions of rocks belonging to class 2 of metasomatism (Mg-bearing rocks). mg# = MgO/(MgO+FeO_{TOT}); a: Ferrando *et al.* (2009); b: Schertl and Schreyer (2008); c: Grevel *et al.* (2009); d: Le Bayon *et al.* (2006); e: Cadoppi (1990); f: Chopin (1981); g: Pawling and Baumgartner (2001); h: Selverstone *et al.* (1991); i: Manatschal *et al.* (2000); j: Prochaska *et al.* (1992); k: Prochaska (1985); l: Prochaska *et al.* (1997); m: Demény *et al.* (1997).

Table S7

Major- (wt% oxide) and trace-element (ppm) compositions of rocks belonging to class 3 of metasomatism (Mg-rich rocks). mg# = MgO/(MgO+FeO_{TOT}); a: Schertl and Schreyer (2008); b: Chopin (1981); c: Barnes *et al.* (2004); d: Prochaska *et al.* (1992); e: Prochaska (1985).

Table S8

Oxygen, hydrogen and carbon isotopic composition of mineral separates from rocks belonging to the four classes of metasomatism. *: average; a: Sharp *et al.* (1993); b: Barnes *et al.* (2004); c: Manatschal *et al.* (2000); d: Demény *et al.* (1997); e: Prochaska *et al.* (1992); f: Prochaska *et al.* (1997); g: Pawling and Baumgartner (2001).



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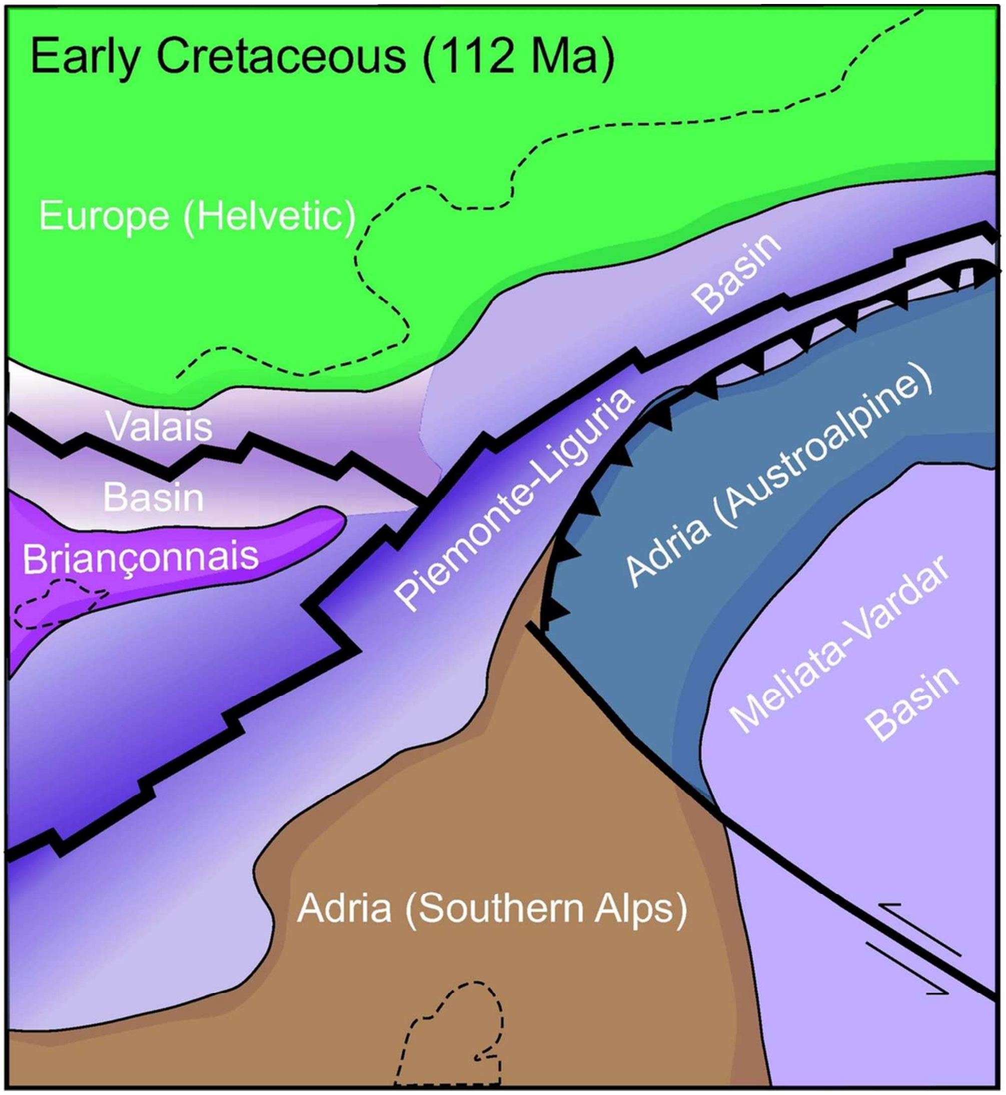

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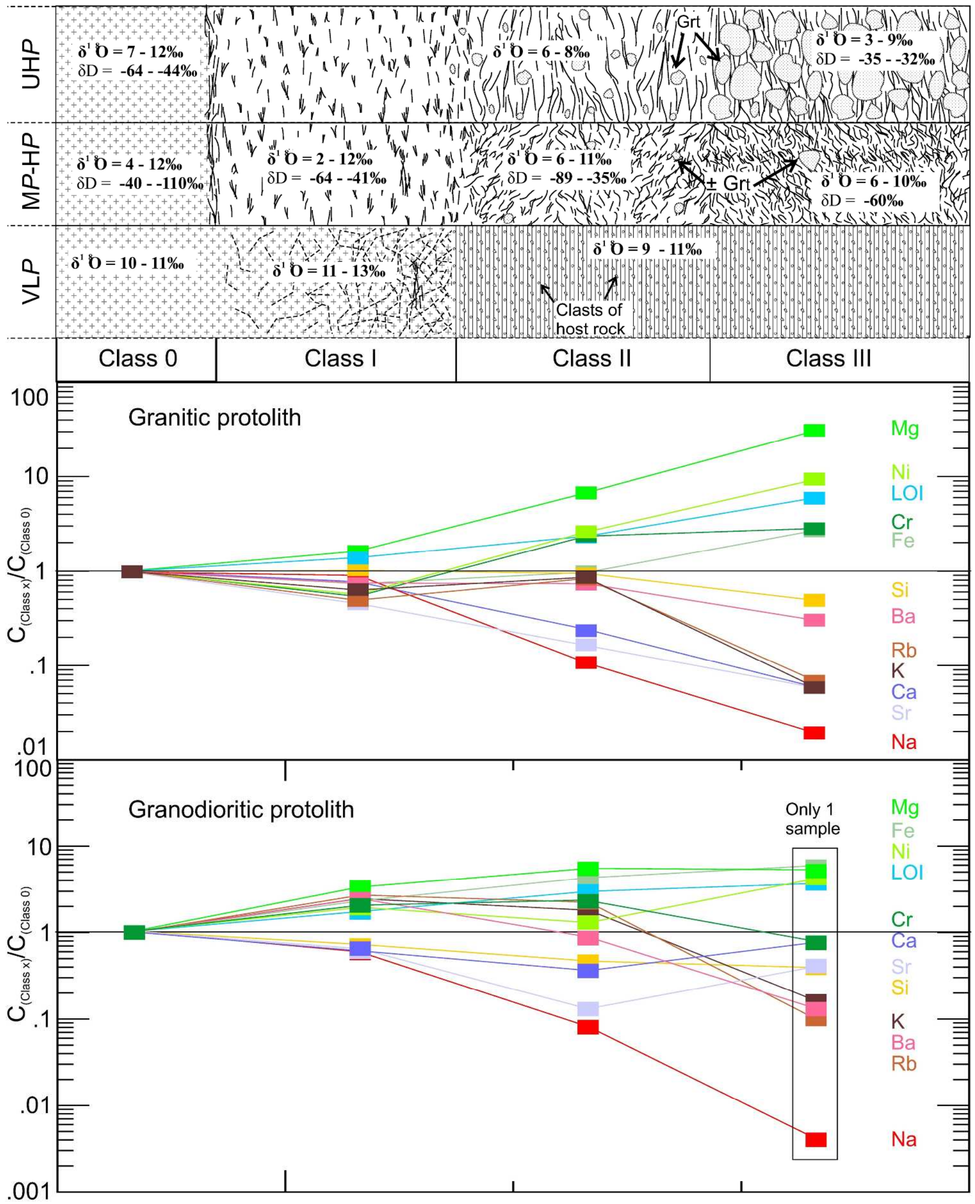

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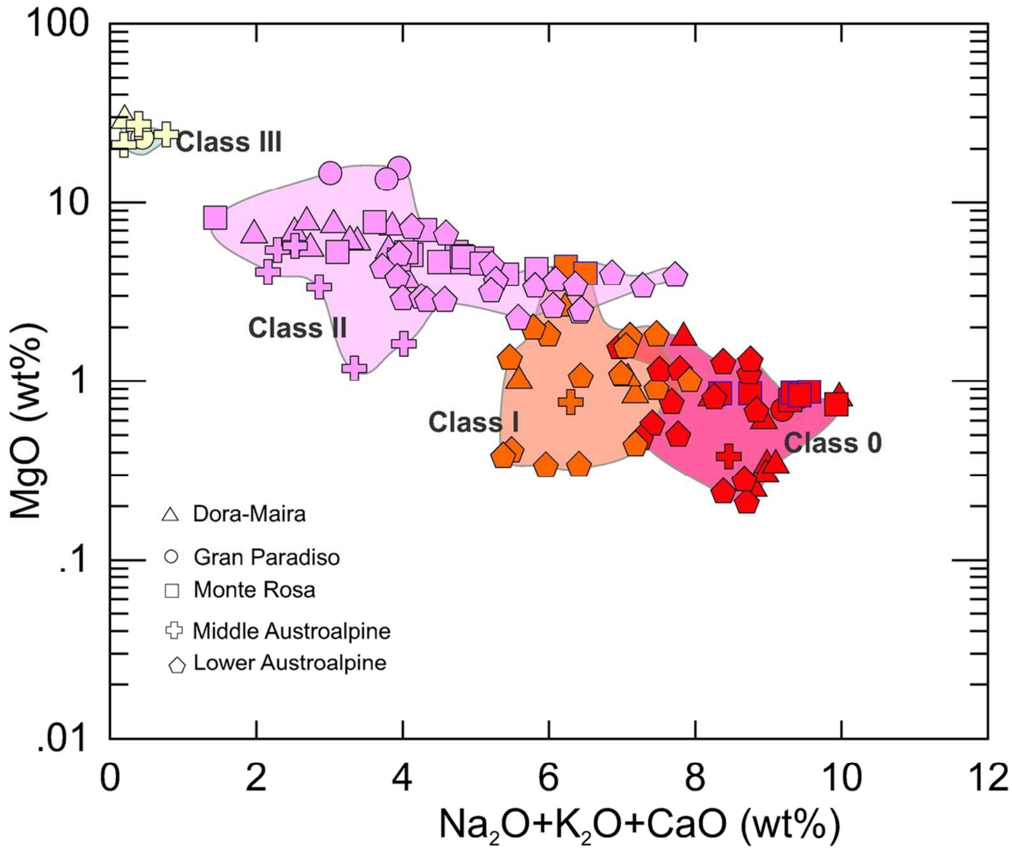
247x307mm (300 x 300 DPI)



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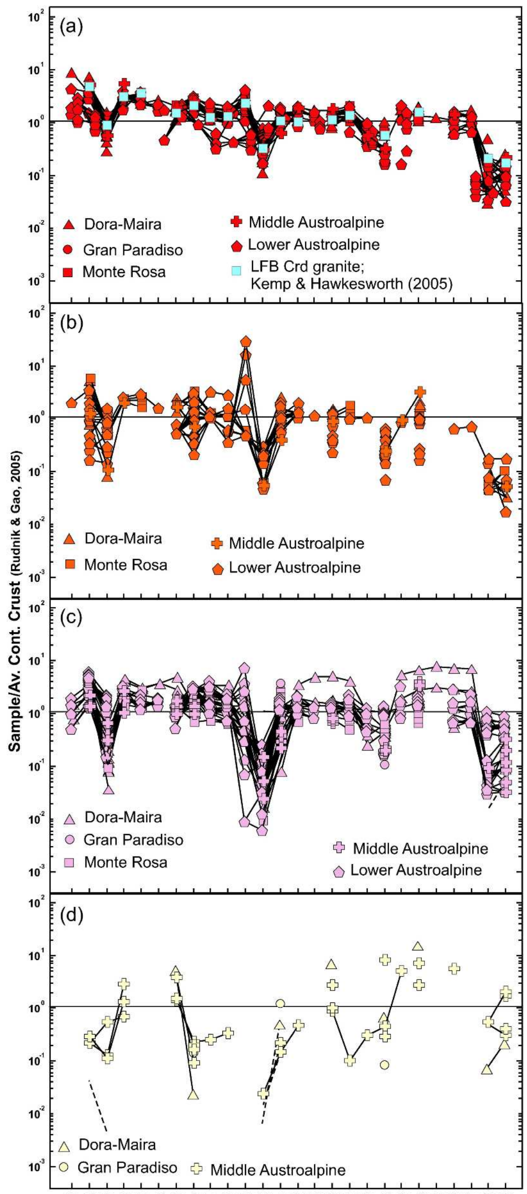
106x91mm (300 x 300 DPI)



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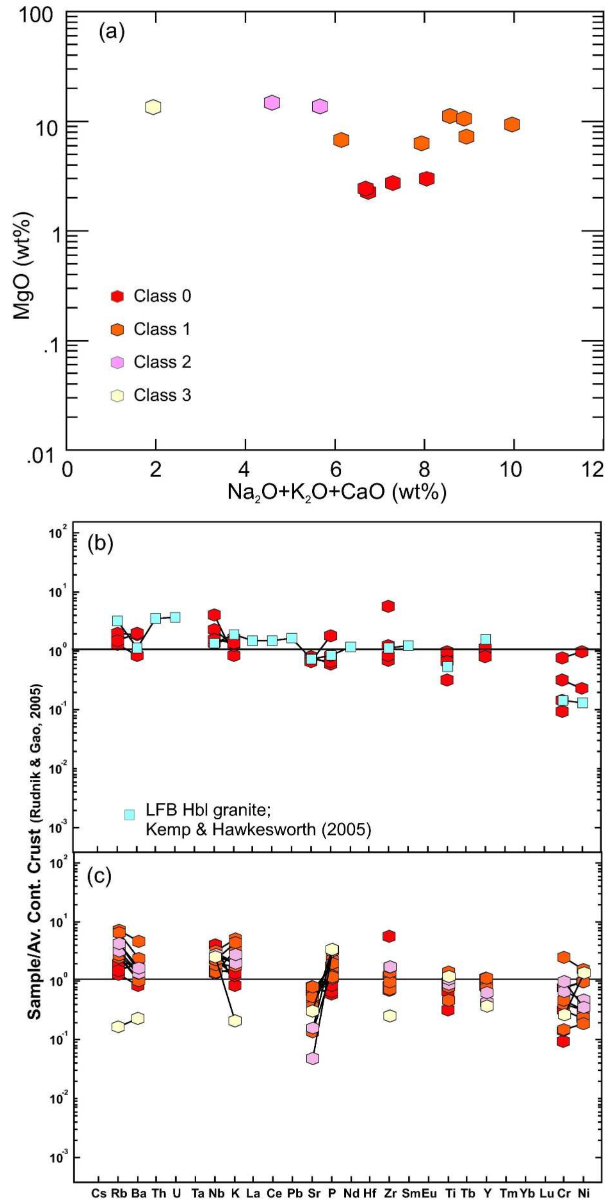
217x504mm (300 x 300 DPI)



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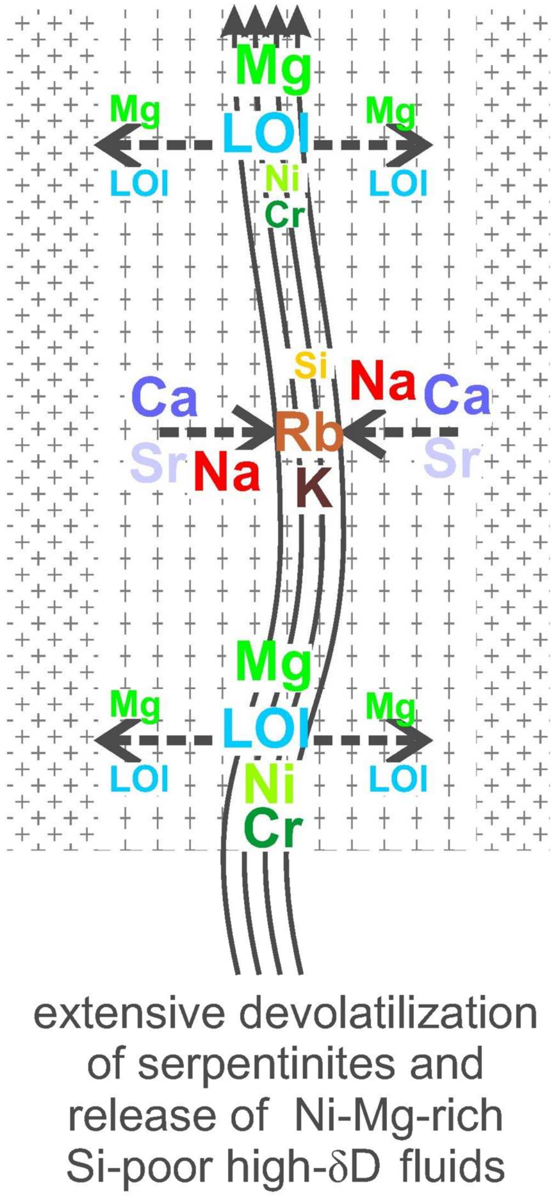

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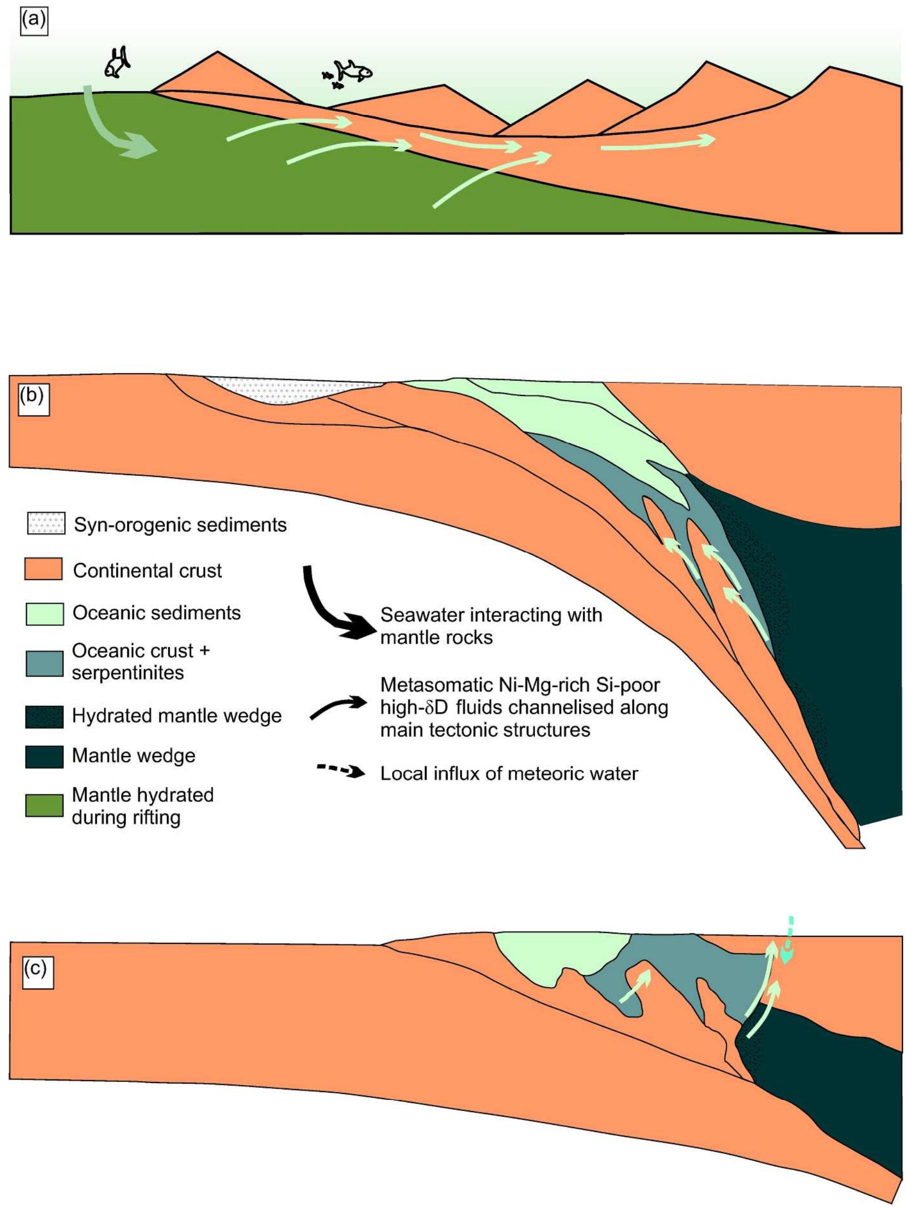

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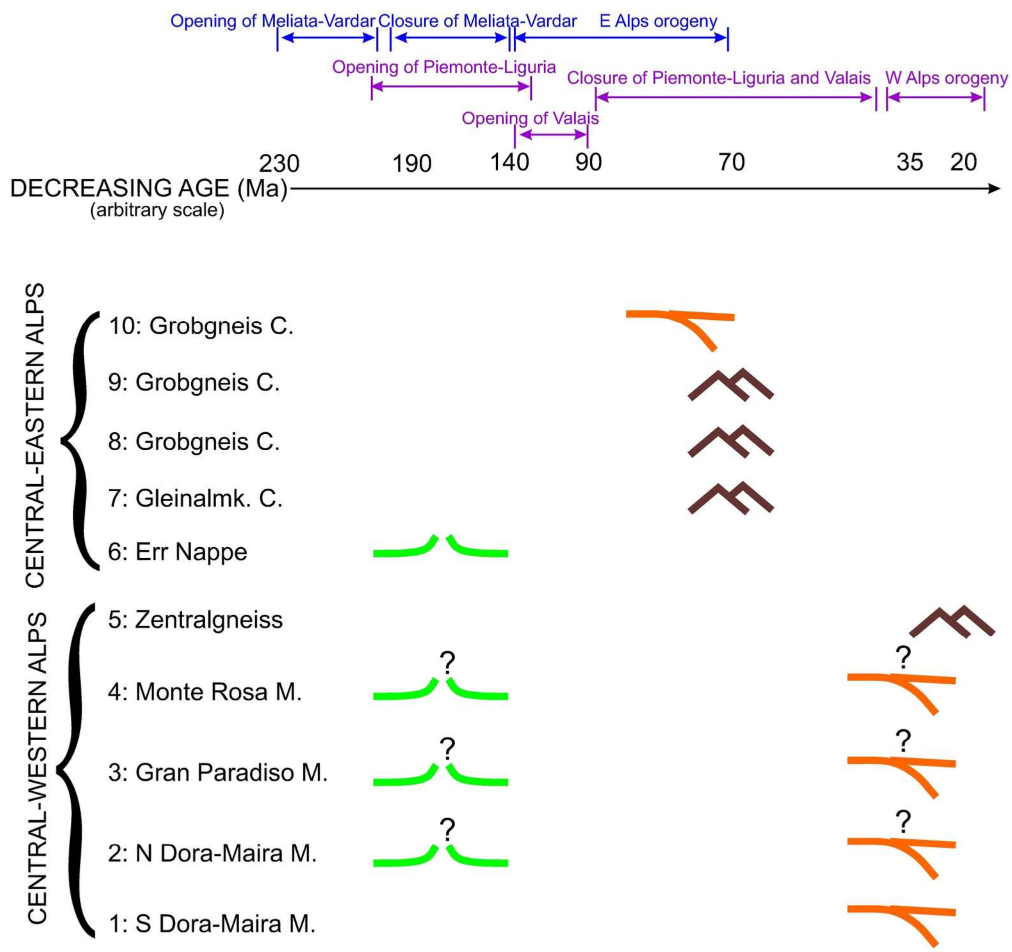
212x284mm (300 x 300 DPI)



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188x176mm (300 x 300 DPI)