SERPENTINITES AND METADOLERITES FROM THE FRIDO UNIT (SOUTHERN APENNINE): GENESIS, EVOLUTION AND ENVIRONMENTAL PROBLEMS

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INTRODUCTION

The main goal of this work is to study the genesis and the evolution of serpentinites and metadolerites from the Frido Unit (Vezzani, 1969) of the Liguride Complex (Ogniben, 1969) cropping out at the Calabria-Lucanian boundary (southern Apennines). For this purpose, a petrographical-mineralogical, and microstructural study, focused mostly on the metamorphic history of these rocks in oceanic and orogenic conditions, has been carried out. Identification of mineral assemblages and their genesis is a fundamental step for the second part of this work that has been devoted to the weathering processes in ophiolitic rocks. The latter study has been carried out through a mineralogical and chemical analyses of the soils developed from serpentinites and doleritic dikes.

The presence of primary minerals, in some cases completely replaced by secondary assemblages, leads to assume that serpentinites of the Frido Unit derived from mantle lherzolitic peridotites. Metamorphic assemblages in the serpentinites allowed to recognize the environmental conditions operating during serpentinization. The mineralogical assemblages are typical of the amphibolite, greenschist-amphibolite transition and greenschist facies conditions. Serpentinites are cut by veins filled with mineralogical assemblages typical of the prehnite-pumpellyite facies likely related to the later orogenic evolution.

The geochemical features of serpentinites show differences in compositions with respect to the Primitive Upper Mantle (PUM) (Pearce & Parkinson, 1993). Metadolerite dikes are frequently intruded in serpentinites. These rocks record a polyphase metamorphic evolution, correlated with ocean-floor metamorphism and subsequent emplacement within the Liguride accretionary wedge. Mineral assemblages of ocean-floor metamorphism are typical of amphibolite and greenschist facies conditions. This event is followed by HP/LT orogenic overprint in lawsonite-glaucophane blueschist conditions (Sansone, 2006; Sansone *et al*., 2009a). Ocean-floor metamorphism is connected with significant metasomatic processes that produced Ca-rich rodingites during serpentinization (Sansone *et al*., 2009a; Sansone & Rizzo, 2009a, 2009b). The HP/LT orogenic metamorphism is related to the underplating of the ophiolitic rocks at the base of Liguride accretionary wedge during subduction of the western Tethys. Later prehnite-pumpellyite facies, recorded in veins cutting through metadolerites, developed in the accretionary wedge during the final stages of its tectonic evolution. Bulk-rock chemistry of metadolerites suggests that protoliths of the mafic rocks have a N-MORB-type affinity. Ca-rich metadolerites are affected by ocean-floor rodingitic alteration, whereas Na-rich metadolerites show a spilitic alteration (Sansone *et al*., 2009a). The product of mineral weathering in the serpentinites and metadolerites has been studied through the mineral composition of soils obtained by XRD.

GEOLOGICAL SETTING

The southern Apennine chain is a fold-and thrust belt formed between the upper Oligocene and Quaternary as a result of the convergence between the African and European plates (Patacca & Scandone, 2007, and reference therein) and a simultaneous SE-directed rollback of the Ionian subducting lithospere (Doglioni *et al.*, 1999; Gueguen *et al.*, 1998; Stampfli *et al.*, 2002). The ophiolitic sequences, which are part of the Southern Apennines, are remnants of the Ligurian oceanic lithosphere pertaining to the Jurassic western Tethys. The ophiolitic sequences crop out in the north-eastern slope of the Pollino Ridge (Calabria-Lucania border zone) and are enclosed within remnants of the Liguride accretionary wedge now incorporated in the Southern Apennine chain. The Liguride Units of the Southern Apennines include sequences characterized by an HP/LT metamorphic overprint in the Frido Unit (Vezzani, 1969) and sequences lacking orogenic metamorphism in the North-Calabria Unit (Bonardi *et al.*, 1988). The ophiolitic rocks occurring in the Frido Unit include serpentinite derived from a lherzolitic to harzburgitic mantle, as suggested by microstructural and petrographical features. The serpentinites are frequently associated to tectonic slices and dykes composed of diabase and medium to high-grade metamorphic rocks such as amphibolites, gneiss, granofels as well as gabbros and basalts with a pillow structure. Mafic and ultramafic rocks, with garnet-bearing felses, amphibolites, gneiss and granitoides occur as tectonic slices within a matrix mainly composed of calcschists and phyllites (Lanzafame *et al.*, 1979; Spadea, 1982, 1994).

SERPENTINITES

The studied serpentinites of the Frido Unit show mesh, xenomorphic and mylonitic texture. Primary mantle minerals are represented by olivine, orthopyroxene, clinopyroxene and spinel. Pseudomorphic minerals are serpentine, magnetite and tremolite. Olivine is replaced by serpentine forming a mesh texture; orthopyroxene is mostly altered to bastite and in some cases shows exsolution lamellae of clinopyroxene and kink bands. Clinopyroxene is armoured by a tremolite rim. Spinel shows a holly-leaf habit (Mercier & Nicolas, 1975) and is often armoured by a corona of Cr-chlorite. The core of the analyzed spinel has a Cr-Al spinel composition corresponding to chromite (Al_2O_3 = 29-31 wt.%; Cr_2O_3 = 28-37 wt.%), whereas the rim has a Fe-Cr spinel composition corresponding to ferritchromite (Al_2O_3 = 1-2 wt.%; Cr_2O_3 = 28-30 wt.%). The Cr-Al spinel/ferritchromite ratio may be various in different spinel porphyroclasts. Serpentine has a fibrous stretched subidiomorphic habit, it is colourless or pale green. Tremolite is present as nematoblasts associated with orthopyroxene. Magnetite replaces spinel or occurs within the mesh textured serpentine. The metamorphic assemblages in the Frido Unit serpentinites allowed to infer the physical conditions operating during serpentinization (Sansone *et al.*, 2010a, 2010b). The mineralogical assemblages found are typical of the amphibolite facies, greenschist-amphibolite transition and greenschist facies conditions. Serpentinites are cut by veins filled with mineralogical assemblages typical of prehnite-pumpellyite facies likely related to the late orogenic Apennine evolution. The geochemical features of serpentinites show differences in compositions with respect to the Primitive Upper Mantle (PUM). These are likely related to serpentinization processes, since elements normalized to PUM show different trends, comparable to Residual MORB Mantle and to Primitive Upper Mantle respectively. HP/LT metamorphic conditions can be documented in mafic dykes enclosed in serpentinites, but similar conditions are not recorded in serpentinites.

METADOLERITES

Metadolerites occur as dikes cutting through serpentinized peridotites. Metadolerites have different kinds of texture reflecting various degrees of crystallinity and strain: porphyritic or aphyric, intersertal/intergranular, blastophitic, cataclastic to mylonitic. In all metadolerites primary plagioclase and clinopyroxene can be observed. The metamorphic mineral assemblage consists of brown amphibole, green amphibole, chlorite, blue amphibole, pumpellyite, prehnite, quartz, epidote, white mica, lawsonite and plagioclase (Pl2 and Pl3). Accessory phases are opaque minerals, Fe-hydroxides and zircon. Metadolerites are cross- cut by veins filled with pumpellyite, chlorite, prehnite, tremolite, plagioclase, white, mica, quartz, lawsonite, epidote and zircon (Sansone & Rizzo, 2008, 2009c). The veins are straight, a few millimetres in thickness and occur isolated or in closely spaced sets. The vein morphology ranges from planar to sinuous and irregular (Sansone & Rizzo, 2008, 2009c). On the basis of metamorphic mineral phases three different types of metadolerite can be distinguished: i) rocks with a high content of prehnite crystals in cataclastic-mylonitic bands, exhibiting an intersertal or a blastophitic texture or a mylonitic fabric and in some cases a seriate texture; ii) rocks with brown horneblende showing an intersertal or a blastophitic texture or a partially blastophitic and foliate texture in one specimen; iii) rocks with brown horneblende and blue amphibole with an intersertal or a blastophitic texture. Primary clinopyroxene is replaced by brown and green amphiboles interpreted as being of oceanic origin; brown amphiboles show Mg-hastingsite, edenite, pargasite, Fe-hastingsite, Mg-horneblende and tschermakite compositions, whereas green amphiboles show Mg-hastingsite, hastingsite, edenite, Mg-horneblende, tschermakite and Fe-tschermakite compositions. Other minerals developed in the amphibolite facies conditions are: oligoclase, titanite and apatite. The blue amphiboles have a winchite and barrowisite composition and are interpreted as being originated during the early stages of the orogenic metamorphism, since they rim the oceanic brown and green amphiboles. The mineral assemblage of orogenic metamorphism is typical of the LT-blueschist facies conditions and consists of glaucophane, Mg-riebekite, lawsonite, phengite, pumpellyite and aegerin-augite (Sansone *et al*., 2010c). Bulk-rock chemistry of metadolerites suggests that protoliths of the mafic rock have a N-MORB-type affinity (Sansone *et al*., 2009a). Ca-rich metadolerites are affected by ocean-floor rodingitic alteration, whereas Na-rich metadolerites show a spilitic alteration. The study of metadolerites from Frido Unit shows evidence of the entire evolution from their origin in the ocean floor to their emplacement in the accretionary wedge. Textural and mineralogical observations suggest that the metadolerites of the Frido Unit have been affected by both ocean-floor metamorphism in the amphibolite to greenschist facies and subsequent orogenic metamorphism under relatively HP/LT conditions (Sansone *et al*., 2009a, 2010c). The HP/LT orogenic metamorphism reflecting underplating of the ophiolitic suite at the base of the Liguride accretionary wedge during subduction produced mineral assemblages typical of the lawsonite-glaucophane facies. Such polyphase metamorphic evolution has been entirely preserved in the metadolerites probably in response to inhomogeneous deformation within the Apennine accretionary wedge.

SOILS

The mineralogical composition of the soils includes serpentine (chrysotile, antigorite and lizardite), amphiboles (tremolite and actinolite), chlorite and chlorite/smectite mixed-layers (C/S). C/S can be interpreted as a neoformation mineral (Sansone *et al*., 2009b). The relative abundance of the mineralogical phases in soil samples was obtained from the peak area ratio. By these means the different amount of minerals in various soil levels was calculated. The top and bottom levels of weathered profile, developed from massive serpentinites, are serpentine-rich; whereas middle levels are serpentine-poor. Tremolite only occurs in the top level of the weathered profile developed from massive serpentinites. Large amounts of C/S can be found in the middle levels of the weathered profile developed from massive serpentinites. C/S show an inverse correlation with the amount of chlorite, thus suggesting that C/S are mainly formed from chlorite alteration. In the weathered profile developed from cataclastic serpentinites, amphiboles and chlorite show a similar variation in different soil levels yet tending to increase at the base of the soil section. It is here suggested that chlorite/smectite mixed-layers are generated by serpentine alteration (Sansone *et al*., 2009b). The geochemical study of the soils shows that they are enriched in Ti, Al, Fe, Ca, Na, K, V, Nb, Y, Sr, Zr, Cu and Rb with respect to the unweathered rocks. During weathering processes Ti, P and Mn are immobile, whereas trace elements have been mobilized. Element mobility has been evaluated through mass-balance calculations.

CONCLUSIONS

The geodynamical setting in which the Frido-Unit ophiolitic rocks formed can be compared with slow-spreading Mid-ocean ridges such as the Mid-Atlantic Ridge.

The serpentinites of the Frido Unit derive from an oceanic lherzolitic mantle for the occurrence of primary minerals such as olivine + orthopyroxene + clinopyroxene and holly-leaf spinel typical of a porphyroclastic oceanic mantle.

The geochemical features of serpentinites are different from the Primitive Upper Mantle and are related to serpentinization processes, which cause compositional changes.

The petrological study of metadolerites made it possible to recognize the polyphase metamorphic evolution connected both to an ocean-floor metamorphism, which often occurs together with the metasomatic processes, and a subsequent orogenic overprint developed during the emplacement of these rocks within the Liguride accretionary wedge.

The geochemical features of metadolerites show a N-MORB affinity, Ca-rich metadolerites show a rodingitic alteration, whereas Na-rich metadolerites are affected by spilitic alteration.

The geochemical features of serpentinites and metadolerites suggest that metadolerite dykes are intruded into serpentinites before they are affected by serpentinization processes which produce Ca-poor serpentinites and metadolerites affected by a rodingitic alteration during serpentinization.

The mineralogical study of soils shows that serpentine (chrysotile, lizardite and antigorite), amphiboles (tremolite and actinolite) and chlorite are primary minerals, whereas clorite/smectite mixed-layers (C/S) are neoformation minerals.

The geochemical study of soils show that they are enriched in Ca, Na, K, Ti, Al, V, Nb, Y, Sr, Zr, Cu, Rb with respect to the unweathered rocks due to presence of weathering-resistant minerals or minerals showing little alteration and containing these elements.

The environmental risk factors at the Calabria-Lucanian boundary are due to the occurrence of serpentine and amphiboles in rocks and soils as well as to the Cr mobility observed in the soils.

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