



Low Ni olivine in silica-undersaturated ultrapotassic igneous rocks as evidence for carbonate metasomatism in the mantle



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ABSTRACT

Subduction drags a large amount of CO₂ into the Earth's interior, which is partly returned to the atmosphere by arc volcanism. Processes involved in the recycling of subducted carbon within the upper mantle are mainly related to mineralogical transformation. Subducted CO₂ may dramatically affect the equilibria among peridotitic minerals (olivine vs. pyroxenes) changing their stability fields and hence their modal abundances. This process is accompanied by a subduction-induced change in the budget of some incompatible trace and major elements (e.g., K, Ca, HFSE), whereas it has a minimal effect on the mass balance of compatible elements (e.g., Ni). We report trace elements in olivine in subduction-related mafic alkaline ultrapotassic rocks from Italy, which are used as a proxy to define mantle wedge mineralogy and metasomatic processes. Minor element concentrations, and in particular the high Li and low Ti of all the olivines, confirm a major role for recycled sediment in the generation of Italian ultrapotassic magmas. The distinct contents of Ni, Mn, and Ca in olivine reflect the bimodal character of silica-rich and silica-poor ultrapotassic Italian rocks and constrain two distinct mineralogical reactions between metasomatic agents and peridotite. Olivine chemistry from silica-saturated rocks reflects the reaction of silicate melts with the ambient mantle, with consequent consumption of olivine in favour of orthopyroxene. In contrast, the low-Ni, high-Mn/Fe of olivine crystallised from silica-undersaturated leucitites require a mantle source enriched in olivine (and clinopyroxene) compared to orthopyroxene, as a result of the interaction between the ambient peridotitic mantle and CaCO₃-rich metasomatic agents. The change from silica-oversaturated lamproites to silica-undersaturated leucitites and thus the difference in the olivine composition is due to a change in composition of the subducting sediment from pelitic to carbonate-rich. The results of this study provide new insights into how CO₂ is recycled via subduction processes deep into the mantle.

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1. Introduction

The fate of carbonate-rich sediments recycled at destructive plate margins is a key issue for constraining the budget of deep CO₂ supplied to the atmosphere by volcanism (Burton et al., 2013). Carbonatite-like metasomatic liquids (fluids and/or melts) are thought to be freed at destructive plate margins by decarbonation and partial melting of carbonate-pelitic sediments (e.g., Ague and Nicolescu, 2014; Dasgupta and Hirschmann, 2010; Grassi and Schmidt, 2011; Mallik et al., 2015; Kerrick and Connolly, 2001; Thomsen and Schmidt, 2008; Tumati et al., 2013). Recent exper-

imental studies have shown that Ca-rich hydrous carbonatitic liquids can form within a P–T range corresponding to shallow depths of just 120 km beneath the subduction zone in volcanic arcs in warm thermal regimes (Poli, 2015). These are extremely mobile and reactive melts that can flow through the mantle and react with either fertile (lherzolite) or depleted peridotite (harzburgite) to form a new mineralogical, metasomatic, assemblage (Yaxley et al., 1991).

Trace elements in olivine emerged as a key tool for recognising the nature and evolution of the mantle source of magmas (De Hoog et al., 2010; Foley et al., 2013; Herzberg, 2011; Sobolev et al., 2005, 2007). Olivine is the most abundant mineral phase in the upper mantle and it is usually the first silicate phase to crystallise from mantle derived melts in equilibrium with their source. Hence, forsterite-rich [Fo = 100*Mg/(Fe + Mg) molar] olivine in mafic volcanic rocks provides information about the mineralogy

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of the mantle source in which magmas equilibrated. The concentration of some compatible trace elements (e.g., Ni, Mn, Cr, Co) depends critically upon the modal abundance of olivine in the residual mantle source (De Hoog et al., 2010; Sobolev et al., 2005, 2007; Straub et al., 2008). On the other hand, the distribution of other trace elements (e.g., Ca, Li, Ti) in olivine is mainly determined by their original abundance in the mantle source and can thus provide important constraints on the nature of the metasomatic agent (Foley et al., 2011, 2013; Prelević et al., 2013).

Several studies have interpreted the high Ni content of highly forsteritic olivines measured in ocean island basalts (OIB) and continental within-plate igneous mafic rocks as evidence for an olivine-poor (and pyroxene-rich) mantle source generated by the interaction between peridotitic mantle and silica-rich melts (e.g., Sobolev et al., 2005, 2007). Other studies have interpreted the same chemical features as due to temperature- and pressure-related variations of the partition coefficient of nickel in olivine (Matzen et al., 2013; Niu et al., 2011). High-Ni olivines have also been reported for igneous rocks from subduction-related geodynamic settings (Foley et al., 2013; Prelević et al., 2013; Straub et al., 2008); the high Ni contents were ascribed to the same olivine-consuming reaction, in this case as a response to the addition of a wide range of fluids and silica-rich melts released by the subducting slab into the peridotitic mantle wedge (Foley et al., 2013; Straub et al., 2008). On the contrary, low Ni contents in forsterite-rich olivines are seldom reported in the literature (Kamenetsky et al., 1997) and mainly for MORB.

Ultrapotassic mafic rocks are particularly suitable to investigate metasomatic processes in the mantle. Their extreme enrichment in K and related incompatible trace elements, and their typical isotopic crustal signatures require the highest contribution from recycled sediments, accommodated in their mantle sources, ever recorded among subduction-related igneous rocks (e.g., Avanzinelli et al., 2008, 2009; Conticelli and Peccerillo, 1992). Different types of high-Mg ultrapotassic rocks, are related with strongly but differently metasomatised mantle sources (Foley et al., 1987). Central Italy is the unique site on Earth where different types of ultrapotassic rocks, namely silica-saturated (lamproite-like) and silica-undersaturated (leucitites), occur closely associated in space, and with only a slight shift in time (Conticelli et al., 2015). Both are strongly enriched in K, with the former relatively depleted in Ca, Al, and Na with respect to the latter. Lamproite and leucitites are plagioclase-free and -bearing ultrapotassic igneous rocks, respectively (Foley et al., 1987). The magmas are produced via partial melting of differently metasomatised lithospheric upper mantle sources. In the Italian case, the metasomatic components of lamproitic and leucitic primary melts are thought to be generated by recycled sediments that are enriched and depleted in carbonate component, respectively (e.g., Conticelli and Peccerillo, 1992; Conticelli et al., 2002, 2013, 2015; Mallik et al., 2015; Kamenetsky et al., 1995). This induces variable CO_2 content during partial melting that is responsible for the observed differences between lamproitic and leucitic ultrapotassic mafic rocks in the degree of silica saturation, and also it explains the variations in Sr and Nd isotopic compositions and in trace element contents (Avanzinelli et al., 2008; Conticelli et al., 2013, 2015; Peccerillo and Frezzotti, 2015). Hence, Italian ultrapotassic mafic rocks represent a unique opportunity to compare and contrast the effect of recycling different crust-derived melts within the mantle wedge.

In this study, we describe the occurrence of low Ni contents in highly forsteritic olivine from silica-undersaturated ultrapotassic rocks (leucitites) from Central Italy (Roman Magmatic Province). These data are compared with high-Ni olivines from silica-saturated ultrapotassic rocks (lamproites), which are closely associated in space and time to leucitites. The major and minor element contents of olivine are discussed in relation to the com-

position of their host rocks, and to the processes of recycling of carbonate-rich sediment in the mantle wedge through subduction processes. We propose a model that helps to clarify the complex mantle processes operating under the Italian peninsula that controlled lava compositions, showing that olivine phenocrysts can be used to identify carbonate-affected sources of magma.

2. The Central Italian potassic and ultrapotassic magmatism

The present day geological setting of the Mediterranean region is the result of a complex geodynamic history of convergence between the African and Eurasian plates over at least 30–35 million years. The geodynamic evolution of the area is related to the differential trench retreat of the Ionian–Adriatic slab (e.g., Faccenna et al., 2001), which is also responsible for the formation of the Liguro-Provençal and Tyrrhenian back arc basins and the eastward migration of Apennine deformation and magmatism.

The Italian Peninsula is the site of intense subduction-related ultrapotassic magmatism with bimodal character in terms of silica activity, associated with variably K-enriched shoshonitic to calc-alkaline igneous rocks (Conticelli et al., 2015). The most extreme ultrapotassic end-members are represented by Ca-poor silica-saturated lamproite-like rocks (Tuscan province), and by Ca-rich strongly silica-undersaturated leucitites and kamafugites (Roman Province). Lamproitic magmas were employed in the early phases of magmatic activity (ca. 4.1–0.8 Ma) mostly confined to the northernmost portion of the Italian Peninsula (Fig. 1), and strictly associated with shoshonites and high-K calc-alkaline products (e.g., Avanzinelli et al., 2009; Conticelli, 1998; Conticelli et al., 1992, 2011, 2013). Leucitic and minor kamafugitic magmas, also associated with shoshonites to high-K calc-alkaline ones, were erupted starting from Pleistocene (0.4 Ma-present) to form a volcanic belt along the Tyrrhenian side of the Italian Peninsula (Conticelli and Peccerillo, 1992). Roman shoshonites to high-K calc-alkaline rocks, often referred to as low-K series (KS), are generally younger than leucite-bearing ones, which often referred to as high-K series (HKS; Conticelli and Peccerillo, 1992; Conticelli et al., 2009; Kamenetsky et al., 1995; Nikogosian and van Bergen, 2010; Peccerillo and Frezzotti, 2015).

Lamproitic and leucitic primary magmas are generated in the sub-continental lithospheric mantle at the destructive plate margin under contrasting partial melting conditions of low and high X_{CO_2} ($\text{CO}_2/\text{CO}_2 + \text{H}_2\text{O}$), respectively (Foley, 1993). The different levels of CaO in magmas and the contrasting X_{CO_2} have been interpreted as due to recycling of subducting sediments with increasing amounts of carbonate (Avanzinelli et al., 2008, 2009; Conticelli and Peccerillo, 1992; Peccerillo et al., 1988) southward. This process enriched the lithospheric mantle wedge in K and large-ion lithophile incompatible elements (LILE) with respect to high field strength elements (HFSE), and imparted a characteristic isotopic signature to the magmas. This includes contrasting behaviour of Sr isotope ratios, which are highly radiogenic in the silica-saturated lamproitic rocks (0.713–0.717), whilst remaining buffered at less radiogenic values (0.708–0.711), typical of carbonate-rich metapelites, in the silica-undersaturated leucitites (e.g., Conticelli and Peccerillo, 1992).

Alternatively, the geochemical and isotopic compositions of the ultrapotassic rocks of the Italian Peninsula have been interpreted as related to within-plate origin, possibly linked to partial melting of an uprising mantle plume (e.g., Vollmer and Hawkesworth, 1980; Bell et al., 2013). In the ‘plume-related’ model, the trace element enrichment and the ‘crustal’ isotopic signature is generally ascribed to shallow level crustal assimilation. In particular, the widespread occurrence of limestone deposits, especially in the southernmost Italian regions, has been used to suggest a major role for carbonate assimilation in determining the chemical and

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