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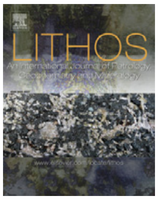

The geochemical evolution of clinopyroxene in the Roman Province: A window on decarbonation from wall-rocks to magma

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ABSTRACT

We present results from magma–carbonate interaction experiments designed to shed light on the geochemical evolution of clinopyroxene in the Roman Province (central Italy). Atmospheric pressure experiments were performed at 1140, 1160 and 1180 °C under NNO, MH and air oxygen buffering conditions. The starting materials were a shoshonite and a phonotephrite doped with different amounts of CaO and CaO + MgO whose stoichiometric proportions reproduced the assimilation by magmas of calcite and dolomite, respectively. The results show that clinopyroxenes, spinels and residual glasses are ubiquitous phases in all run-products. Calcite-doped runs crystallize more clinopyroxene than dolomite-doped runs at the same conditions. This leads to the formation of strong desilicated CaO-rich melts showing compositions comparable to those of magmatic skarns. During magma–carbonate interaction, the content of Fe^{3+} in clinopyroxene increases with increasing fO_2 promoting the substitution of Al for Si in tetrahedral site. Local charge imbalances are also compensated by the incorporation of highly charged cations, such as Ti, into the crystal lattice. According to this cation substitution, Al–Ca–Fe^{3+}–Ti-rich clinopyroxenes of the skarn environment testify to continuous CO_2 fluxes produced by the thermal decomposition of carbonate wall-rocks. Nevertheless, the oxidative capacity of CO_2 progressively decreases from the skarn shells towards the interior of the magma chamber driving the crystallization of Si–Fe^{2+}–Mg-rich clinopyroxenes.

1. Introduction

Both early and recent investigations have emphasized that assimilation of carbonate by magmas is an important crustal process controlling the geochemical signature of magmatic systems (Baker and Black, 1980; Barnes et al., 2003, 2005; Chadwick et al., 2007; Coulson et al., 2007; Dallai et al., 2011; Daly, 1910; Deegan et al., 2010; Doroshkevich et al., 2012; Spandler et al., 2012; Troll et al., 2012, 2013; Wenzel et al., 2002). Among the alkaline igneous provinces in the world, the Roman Province (central Italy; Fig. 1S published online) is a natural laboratory in which magma–carbonate interaction has been documented for more than two decades (e.g., Dallai et al., 2004; Di Rocco et al., 2012; Freda et al., 1997, 2010; Gaeta et al., 2006, 2009; Gozzi et al., 2013). According to Peccerillo (2005), the Roman Province includes the large volcanic complexes of Monti Vulsini, Vico, Monti Sabatini and Colli Albani (Fig. 1S). The products consist of large-volume pyroclastic deposits and lava flows that are mostly ultrapotassic and undersaturated in silica; minor amounts of silica-saturated to oversaturated potassic rocks also occur in some volcanic complexes (Fig. 1S).

It has been demonstrated that carbonate assimilation controls the liquid line of descent of magmas at the Colli Albani Volcanic District (CAVD) and Montefiascone Volcanic Complex (MVC) belonging to the Monti Vulsini district (Conte et al., 2009; Freda et al., 2008). Lava flows and pyroclastic rocks at the CAVD have silica-undersaturated ultrapotassic compositions ranging from tephrite to foidite (leucitite) and tephriphonolite (Fig. 1S); conversely, volcanic rocks at the MVC are leucitites, leucite tephrites, leucite basanites to leucite phonolites of the High-Potassium Series (HKS), and trachybasalts to trachytes of the Potassic Series (KS) (Civetta et al., 1984; Coltorti et al., 1991; Di Battistini et al., 1998, 2001; Trigila et al., 1995). The occurrence of skarn ejecta in the CAVD and MVC products documents the strong interaction of magmas with carbonate host rocks (Conte et al., 2009; Dallai et al., 2004; Di Filippo et al., 1999; Federico and Peccerillo, 2002; Federico et al., 1994; Gaeta et al., 2000, 2006).

The assimilation of carbonate by magmas of the Roman Province is a multi-step process that progressively evolves from the carbonate wall-rock towards the interior of the magma chamber (Di Rocco et al., 2012). Therefore, skarns can be classified as (i) exoskarns formed by means of solid-state thermal metamorphic reactions in the carbonate protolith and (ii) endoskarns (or magmatic skarns) crystallized from magmas that have experienced strong interaction with carbonate rocks (Barnes et al., 2005; Belkin et al., 1985; Fulignati et al., 2004; Gaeta et al., 2009; Jutras et al., 2006; Mollo et al., 2010a; Peccerillo et al., 2010; Wenzel et al., 2002). We stress that the skarn rocks central to this study are magmatic skarns, in agreement with the presence of

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interstitial glass in equilibrium with high-temperature crystals as well as with the isotopic signature of individual phases. As pointed out by Gaeta et al. (2009), the skarn environment acts as a source of CaO-rich melts that are assimilated by primitive mafic magmas to produce silica-undersaturated ultrapotassic liquids. However, one of the principal products of carbonate thermal decomposition is the release of CO_2 (Mollo et al., 2010a) that strictly controls the oxygen fugacity of the system (e.g., Wenzel et al., 2002) and the degree of magmatic, metasomatic and metamorphic reactions (e.g., Barnes et al., 2005; Mollo et al., 2012a). Additionally, Dallai et al. (2011) have shown that large amounts of ^{18}O-rich (sedimentary-derived) CO_2 can flux through the magma, changing its isotopic composition at the early stage of magma–carbonate interaction. The fO_2 estimated for primitive mafic magmas and differentiated ultrapotassic liquids is generally close to the QFM (quartz–fayalite–magnetite) and NNO (nickel–nickel oxide) buffer, respectively (cf. Gaeta et al., 2009; Wenzel et al., 2002); conversely, CO_2-rich fluids with $X(CO_2)$ >0.99 produce oxygen fugacities equal to or higher than the MH (magnetite–hematite) buffer.

Magma–carbonate interaction experiments have been conducted over a broad range of pressures (0.1–1000 MPa), temperatures (1050–1300 °C) and melt-water contents (0–5 wt.% H_2O) (Conte et al., 2009; Freda et al., 2008; Iacono Marziano et al., 2007; Mollo et al., 2010a), but the role played by oxygen fugacity on the geochemical evolution of clinopyroxene in the Roman Province has been scarcely investigated (cf. Dolfi, 1996). In order to address this paucity of information, we present new magma–carbonate interaction experiments designed to simulate calcite and dolomite assimilation under variable redox conditions. The compositions of experimental clinopyroxenes are then compared with those of natural crystals in skarns and lavas of the CAVD and MVC. Our results demonstrate that clinopyroxenes in magmatic skarns crystallized under extreme oxidizing conditions due to continuous CO_2 fluxes produced by the thermal decomposition of carbonate wall-rocks. In contrast, clinopyroxenes in lavas equilibrated under more reducing conditions, as the oxidative capacity of CO_2 fluxing progressively decreased towards the interior of the magma chamber.

2. Starting materials, experiments and analyses

The starting materials used in this study were a shoshonite of the KS series (hereafter named LP) and a phonotephrite of the HKS series (hereafter named E42) from MVC. The whole-rock analyses normalized to 100 indicate that LP and E42 have virtually identical oxide contents with the exception of Na_2O and K_2O (Table 1S published online); in particular, the alkali content of E42 ($Na_2O + K_2O = 8.34$ wt.%) is higher than that of LP ($Na_2O + K_2O = 6.37$ wt.%).

Approximately 50 g of LP and E42 was reduced to a homogeneous powder in a ball mill and ground so as to pass through a #200 mesh sieve. Rock powders were then doped with two different amounts of CaO and CaO + MgO whose stoichiometric proportions reproduced the assimilation by magmas of calcite and dolomite. This strategy is justified by (i) the complete decomposition of carbonates at magmatic temperatures, (ii) the incorporation of calcium and magnesium in crystals and melts, and (iii) the preferential partitioning of CO_2 into the gaseous phase (e.g., Behrens et al., 2009). Fractional crystallization (FC) of magmas was studied by means of undoped LP and E42 powders (FC experiments). Conversely, assimilation and crystal fractionation (AFC) was investigated using LP and E42 powders doped with 8 and 18 wt.% of calcite (*8Cal*-AFC and *18Cal*-AFC experiments, respectively) and dolomite (*8Dol*-AFC and *18Dol*-AFC experiments, respectively).

Atmospheric pressure experiments were performed at the University of Roma Tre using a vertical tube gas-mixing furnace. Oxygen fugacity was monitored and maintained constant by means of an yttria-doped-zirconia solid electrolyte oxygen sensor ($SIRO_2$, Ceramic Oxide Fabricators, Ltd., Australia) and two digital thermal mass flow meters for CO and CO_2. The experiments were conducted under the oxygen buffering conditions of air, MH and NNO. The experimental temperatures were 1140, 1160 and 1180 °C. For each temperature, ten Pt-loops (about 1.5 mm in diameter) were simultaneously suspended within the furnace (Fig. 2Sa published online). Each loop was charged with about 35 μg of undoped and doped LP and E42 powders. Due to the small (300 μm) diameter of the Pt-wire formed into a loop, iron loss was minimized so that it was never detected by microprobe analyses. The samples were cooled at a rate of 30 °C/h from 1300 °C down to the final target temperature that was kept constant for 48 h. According to previous investigations by Mollo et al. (2013a, 2013b), this experimental duration was sufficient to ensure the achievement of equilibrium and ferric–ferrous equilibration in alkaline magmas. The superliquidus temperature of 1300 °C was reached starting from room temperature (with a heating ramp of 30 °C/min) and it was maintained for 30 min before beginning cooling. We experimentally verified that no crystalline phases were formed during thermal treatment at 1300 °C. At the end of each experiment, samples were fast quenched by dropping the charge into a water bath.

Analyses of experimental products were performed at the CNR-Istituto di Geologia Ambientale e Geoingegneria (Rome, Italy) with a Cameca SX50 electron microprobe equipped with five wavelength-dispersive spectrometers using 15 kV accelerating voltage, 15 nA beam current, 10 μm beam diameter, and 20 s counting time. The following standards were used: wollastonite (Si and Ca), corundum (Al), diopside (Mg), andradite (Fe), rutile (Ti), orthoclase (K), jadeite (Na), and metal (Mn). Sodium and potassium were analyzed first to prevent alkali ion migration effects. Precision was better than 5% for all cations. Clinopyroxene components have been determined using the procedures reported in Putirka et al. (1996) and then slightly modified in Putirka (1999).

Image analyses were conducted at the HP–HT Laboratory of Experimental Volcanology and Geophysics (INGV, Roma) with a Jeol FE-SEM 6500F equipped with an energy dispersion microanalysis system. The crystal content was estimated by using the commercial software Image Pro Plus following the procedure reported in Iezzi et al. (2011).

3. Results

3.1. Textural features

The most important textural features of run-products can be summarized as follows: (i) clinopyroxene, spinel and glass are ubiquitous in all run-products (Fig. 2Sb), (ii) the amount of spinel is low (≤1 vol.%), (iii) rare (≤1 vol.%) leucite and plagioclase are found in FC runs of E42 and LP, respectively, (iv) clinopyroxene is the most abundant crystalline phase and its content progressively increases with increasing oxygen fugacity and carbonate assimilation (Fig. 3S published online), (v) *Cal*-AFC experiments have crystal contents higher than *Dol*-AFC ones (Fig. 3S), (vi) LP run-products are slightly more crystallized than E42 run-products (Fig. 3S), (vii) clinopyroxenes exhibit a maximum size of 600 μm (Fig. 2Sb), and (viii) significant core-to-rim crystal zoning as well as sieve-textures, which are evidence of disequilibrium, are not observed.

3.2. Glass chemistry

Despite the increasing degree of crystallization of clinopyroxene with increasing carbonate assimilation (Fig. 3S), higher CaO + MgO and CaO contents are preserved in the evolving doped liquids from *Dol*-AFC and *Cal*-AFC experiments, respectively (Table 2S published online). These melts are chemically homogeneous around clinopyroxenes suggesting equilibrium condition. Figs. 4S and 5S published online highlight that FC, *Dol*-AFC and *Cal*-AFC run-products exhibit similar differentiation trends as the temperature decreases. Accounting for the different compositions of the starting materials