



Olivine compositional changes in primitive magmatic skarn environments: A reassessment of divalent cation partitioning models to quantify the effect of carbonate assimilation

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ABSTRACT

The geochemical evolution of olivine from primitive magmatic skarn environments has been studied by atmospheric pressure experiments carried out at 1250, 1200, and 1150 °C under QFM oxygen buffering conditions. The starting materials were three synthetic basalts (i.e., ^{melt}Mg#₇₈, ^{melt}Mg#₇₅, and ^{melt}Mg#₇₂) doped with variable amounts of CaCO₃, in order to reproduce the natural concentration levels of CaO-rich magmas interacting with the skarn rock shells. Results from decarbonation experiments evidence that the crystallization of Fo-CaO-rich, NiO-poor olivines is more favored at higher temperatures when primitive basaltic magmas assimilate increasing amounts of carbonate materials. The number of large size Ca cations entering olivine crystal lattice is proportional to the amount of Ca-O-Si bonds available in the melt. Due to differences between Fe²⁺ and Mg cation radii, the Ca-Fe²⁺ substitutions into M2 crystallographic site are more facilitated than Ca-Mg ones, thus enhancing the forsterite component in olivine. The partitioning behavior of Ni, Mg, Fe²⁺, Mn, and Ca between olivine and melt has been also investigated to better understand cation redistribution mechanisms at the magma carbonate reaction zone. In this context, some partitioning models from the literature have been refined to more accurately quantify the geochemical evolution of primitive skarn systems. Under the effect of CaCO₃ assimilation, the partitioning of divalent cations, can be parameterized as a function of temperature, bulk composition (mostly, CaO and MgO contents in both olivine and melt) and melt structure (expressed as the number of non-bridging oxygens per tetrahedrally coordinated cations). Conversely, the exchange partition coefficients between Fe²⁺/Ca/Mn/Ni and Mg do not vary significantly as a function of temperature and ^{melt}Mg#, due to the limited influence of these parameters on the melt structure. In turn, cation exchange reactions are primarily controlled by the strong depolymerizing effect of CaCO₃ assimilation that increases the number of structural sites critically important to accommodating network-modifying cations in the melt phase. The comparison between cumulates and magmatic skarns from the Colli Albani Volcanic District (Italy) and experiments from this study provides quantitative constraints on the geochemical evolution of olivine phenocrysts and their melt inclusions as a function of carbonate assimilation.

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1. Introduction

Crustal contamination may significantly contribute to the differentiation path of magma (Barnes et al. 2005; Del Bello et al. 2014; DePaolo 1981; Foland et al. 1993; Mollo et al. 2011; Patiño Douce 1999; Spera and Bohron 2001, 2004). This is particularly true during magma carbonate interaction which is characterized as a multi-stage

reaction zone advancing from the carbonate wall-rock towards the innermost part of the magma chamber (Di Rocco et al. 2012; Gaeta et al. 2009; Mollo et al. 2010; Mollo and Vona 2014; Wenzel et al. 2002). The interaction mechanism is generally associated with the formation of three distinct skarn domains (Di Rocco et al. 2012): (1) exoskarns i.e., thermometamorphic rocks derived by decarbonation of the protolith, (2) endoskarns i.e., magmatic rocks derived by crystallization and desilication phenomena at the exoskarn-magma interface, and (3) cumulates i.e., highly crystalline rocks derived by magma contamination and crystal accumulation at the endoskarn-magma interface. The principal products of carbonate thermal decomposition are the formation

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of CaO-rich melts and the release of CO₂ (Deegan et al. 2010; Freda et al. 2011; Mollo et al. 2010, 2011, 2013a). This latter has important implications for anomalously high CO₂ degassing rates currently estimated at several continental arc volcanoes. Indeed, in mature continental arcs reworking of crustal limestone by hot mafic magmas may be an important source of CO₂ flux (Mason et al. 2017). For example, Carter and Dasgupta (2015) have shown that magma-induced upper plate decarbonation alone may potentially contribute to the excess of CO₂ released into the atmosphere (i.e., up to ~3% of the current global arc CO₂ flux may be crustally derived). Further experimental data have also illustrated that melt composition and melt fraction are effective controlling factors in the transition from assimilation to skarnification, and that both heat and aqueous fluids released from an intruding magma may enhance significantly CO₂ degassing (Carter and Dasgupta 2016).

During magma carbonate interaction, the exoskarn domain is characterized by low temperature, metamorphic/metasomatic reactions where the oxidative capacity of CO₂-rich fluids ($X_{\text{CO}_2} > 0.99$) leads to high oxidation conditions (\geq MH buffer; Di Rocco et al. 2012). The endoskarn domain is governed by significant magma cooling and differentiation under moderate-to-high oxidation conditions (\geq NNO buffer; Wenzel et al. 2002). The abundant crystallization of CaTs-rich clinopyroxene phenocrysts (Carter and Dasgupta 2015; Mollo et al. 2010) produces silica-poor, alkali-rich magmas typical of ultrapotassic volcanism (Gaeta et al. 2009). The cumulate domain represents the primitive skarn environment where high temperature, less oxidized (\sim QFM buffer), primitive magmas fractionate Fo-rich olivine phenocrysts accumulating at the base and periphery of the magma chamber (Di Rocco et al. 2012). Considering the temporal and spatial relationships between exoskarns, endoskarns, and cumulates, the occurrence of olivine as liquidus phase and its compositional evolution are strictly dependent on the progressive advancement of the magma-skarn interface, the thermal (differentiation) path of the system, and the degree of CaO contamination (Barnes et al. 2005; Chadwick et al. 2007; Coulson et al. 2007; Di Rocco et al. 2012; Freda et al. 2008; Gaeta et al. 2009; Iacono Marziano et al. 2008; Jolis et al. 2015; Wenzel et al. 2002). In this scenario, the overall skarn environment acts as a continuous source of CO₂ gas phase and CaO-rich melts that variably interact with primitive basaltic magmas, thus controlling their geochemical evolution under olivine-saturated to olivine+clinopyroxene-cosaturated to clinopyroxene-saturated conditions (cf. Gaeta et al. 2009).

The purpose of this study is to experimentally investigate the early stage of carbonate assimilation when high temperature, primitive basaltic magmas assimilate variable amounts of carbonate material and then equilibrate with olivine phenocrysts. These experimental data allow to better constrain the effect of CaO contamination on the evolutionary behavior of the primitive magmatic skarn environment that is represented by the endoskarn domain. The partitioning of divalent cations (i.e., Ni, Mg, Fe, Mn, and Ca) between olivine and melt has been also investigated due to its importance in estimating the solidification temperature of rocks (e.g., Hart and Davis 1978; Ford et al. 1983; Beattie 1993; Putirka 2005, 2008; Putirka et al. 2007, 2011; Wang and Gaetani 2008; Li and Ripley 2010; Matzen et al. 2013; Pu et al. 2017), in ascertaining the equilibrium condition of minerals (e.g., Filiberto and Dasgupta 2011; Leeman and Scheidegger 1977; Putirka 2005, 2016; Roeder and Emslie 1970; Snyder and Carmichael 1992; Toplis 2005), and in understanding magmatic processes (e.g., Danyushevsky and Plechov 2011; Mollo et al. 2015). In this context, several olivine-melt partitioning equations published over the last decades have been collected and integrated all together into an Excel spreadsheet submitted online as supplementary material (Beattie 1993; Beattie et al. 1991; Hart and Davis 1978; Jones 1995, 2016; Libourel 1999; Pu et al. 2017; Putirka 2005, 2016; Putirka et al. 2007, 2011; Snyder and Carmichael 1992; Toplis 2005; Wang and Gaetani 2008). The equations more suitable for modeling decarbonation data from this study have been selected, discussed and reappraised in terms of temperature and

compositional variations during magma carbonate interaction. More specifically, the predictive ability of these equations has been improved by including compositional parameters that more accurately describe the variance of the data obtained from decarbonation experiments.

2. Starting materials, experimental conditions and analytical methods

Three different basaltic starting materials were synthesized in batches of ~2 g from pure oxides and carbonates mixed by grinding under ethanol in an agate mortar for ~1 h. These mixtures were chosen in order to obtain three basalts with different primitive characters of $^{\text{melt}}\text{Mg}\#_{72}$, $^{\text{melt}}\text{Mg}\#_{75}$, and $^{\text{melt}}\text{Mg}\#_{78}$ [$^{\text{melt}}\text{Mg}\# = X_{\text{MgO}} / (X_{\text{MgO}} + X_{\text{FeO}}) \times 100$, where X_{FeO} refers to FeO recalculated at the QFM buffer, according to the formula of Kress and Carmichael 1991] (Table 1S). Ni was added to the powdered mixture as solution with nominal concentration of 1000 ppm. To guarantee obedience of Henry's Law (Mysen 2006), the Ni concentration is similar to that observed in natural basaltic rocks (cf. Mollo et al. 2013b). A Fe pre-saturated Pt-crucible containing the synthetic powder was loaded in a 1 atm vertical tube CO–CO₂ gas-mixing furnace at the quartz-fayalite-magnetite (QFM) buffer. Melting experiments were conducted at the HP-HT Laboratory of Experimental Volcanology and Geophysics of the Istituto Nazionale di Geofisica e Vulcanologia (INGV) in Rome, Italy. The temperature was kept at 900 °C for 1 h to ensure decarbonation and, then, was raised up to 1600 °C and kept for 1 h to ensure melting and to obtain glass starting material. The resulting glass was removed from the Pt-crucible and, then, powdered. Backscattered images and microprobe analyses performed on chips extracted from top, middle, and bottom of the Pt-crucible, demonstrated homogeneity and the absence of crystalline phases. In order to minimize loss of transition metals, some aliquots of the powder were previously loaded into the Pt-crucible and run for 3 h at 1600 °C to saturate the crucible (cf. Conte et al., 2006). The sample holder was then quenched and cleaned in a hot HF solution. The same approach was adopted to saturate the Pt-wire (0.1 mm in diameter) used for the equilibrium experiments conducted at 1 atm and the QFM buffer. Through this strategy, the Fe loss from the samples was kept to <5% of the initial amount. Notably, all the experiments were carried out at 1 atm on the basis of the following considerations: i) our magma carbonate interaction experiments can be more properly compared with previous studies investigating and modeling the partitioning of divalent cations between olivine and melt at ambient pressure (e.g., Beattie 1993; Hart and Davis 1978; Jones 1995, 2016; Kohn and Schofield 1994; Leeman and Scheidegger 1977; Libourel 1999; Roeder and Emslie 1970; Snyder and Carmichael 1992; Wang and Gaetani 2008), ii) olivine is always the liquidus phase and its stability field increases at the expense of clinopyroxene (Mollo et al. 2015; Snyder and Carmichael 1992), iii) cation exchange reactions in olivine do not substantially change from low to moderate crustal depths (e.g., Gee and Sack 1988; Kushiro and Mysen 2002; Matzen et al. 2011; Roeder and Emslie 1970; Sack et al. 1987; Takahashi 1978; Toplis 2005), and iv) the effect of H₂O and P_{H₂O} on olivine stability is practically negligible in primitive magmatic skarn environments due to the strong amount (~45 wt%) of CO₂ released during calcite thermal decomposition (Di Rocco et al. 2012; Wenzel et al. 2002). The equilibrium temperature was measured by a Pt–Pt₉₀Rh₁₀ thermocouple located within 1 cm of the sample chandelier holding the experimental Pt-loops (about 1.5 mm in diameter) charged with about 45 μg of powdered starting material (cf. Mollo and Vona 2014). The oxygen fugacity was monitored and maintained constant over the experimental temperatures of 1150, 1200 and 1250 °C by means of an yttria-doped-zirconia solid electrolyte oxygen sensor (SIRO₂, Ceramic Oxide Fabricators, Ltd., Australia) and two digital thermal mass flow meters (for CO and CO₂) controlled via software. The $^{\text{melt}}\text{Mg}\#_{72}$, $^{\text{melt}}\text{Mg}\#_{75}$, and $^{\text{melt}}\text{Mg}\#_{78}$ basaltic powders were also doped with 0, 10, and 20 wt% of CaCO₃ in order to obtain total CaO contents of ~11, ~16, and ~22 wt%, respectively. At a given experimental

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