

1. Research activity (max 1.000 words)

This study of cation exchange reactions between olivine, clinopyroxene, plagioclase and melt is a useful tool to better understand the most important physicochemical changes of crystallizing systems during magma dynamics. This project can be schematized into four points: (1) quantitative assessment of cation redistributions in olivine growing from CaO-rich basaltic melts, (2) rare earth element partitioning between olivine and basaltic melts as a function of carbonate assimilation, (3) transition elements partitioning between olivine and decarbonated melts, and (4) REE-in-plagioclase-clinopyroxene thermobarometry of natural eruptive products.

The geochemical evolution of olivine from primitive skarn environments has been studied by atmospheric pressure experiments carried out at 1,250, 1,200, and 1,150 °C under QFM oxygen buffering conditions. The starting materials were three synthetic basalts (i.e., $^{\text{melt}}\text{Mg}\#_{78}$, $^{\text{melt}}\text{Mg}\#_{75}$, and $^{\text{melt}}\text{Mg}\#_{72}$) doped with variable amounts of CaCO_3 , 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 Fe^{2+} and Mg cation radii, the Ca- Fe^{2+} 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, Fe^{2+} , 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 CaCO_3 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 partitioning of REE, Y and Sc (R³⁺) between olivine and melt has been investigated through the same basalt-carbonate interaction experiments. Results show regular relationships between the ionic radius and the partition coefficient, in agreement with classical Onuma parabolic trends. D³⁺ values are weakly dependent on temperature, whereas they drastically decrease with increasing CaCO₃ assimilation. From the point of view of the lattice strain theory, the optimum ionic radius decreases as Ca cations are preferentially accommodated into the expanded M2 site of olivine. This is counterbalanced by a higher number of Mg cations entering into the small M1 site, favoring the crystallization of forsterite-rich olivine from decarbonated melts. Ca entering olivine is also proportional to the number of Si and Ca atoms available in the melt structure. Consequently, the Young modulus is anticorrelated either with Ca in olivine or the activity of CaO in the melt. The strain-free partition coefficient scales with the degree of melt depolymerization during basalt-carbonate interaction. R³⁺ cations behave as network modifiers and the increasing abundance of non-bridging oxygens enhances the solubility of R³⁺ cations in the melt. However, the crystal chemistry (Fo and Al contents) exercises also a strong influence on the substitution of R³⁺ cations into the crystal structure. It is found that the accommodation of R³⁺ cations requires maintenance of local charge-balance by the generation of vacancies, in accord with a paired substitution of R³⁺ and a vacancy for Mg cations in octahedral sites.

2. Research products

- a) No
- b) No

- c) Olivine compositional changes in primitive skarn environments: A reassessment of divalent cation partitioning models to quantify the effect of carbonate assimilation (Submitted)
- d) No

N.B. I dottorandi del primo anno al punto 1 possono inserire il riassunto del progetto di ricerca (max 1.000 parole)