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Zirconolite, calzirtite, baddeleyite, betafite, geikielite and qandilite in skarn ejecta from Vesuvius - inferences for the magma-wallrock interactions.

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Zirconolite $CaZrTi_2O_7$, calzirtite $Ca_2Zr_5Ti_2O_{16}$, baddeleyite ZrO_2, betafite $(Ca,U,Th)_2(Ti,Nb)_2O_6(OH)_2$, perovskite, geikielite $MgTiO_3$ and qandilite Mg_2TiO_4 occur as minute crystals in a special type of finely banded skarn (forsterite-spinel/calcite), ejected by explosive eruptions of Vesuvius such as Avellino (3550 BC) and 1631. These skarns occur in contact with more-or-less contaminated magmatic rocks (pyroxenites, syenites, tephriphonolites), from which they are separated by a phlogopite reaction rim, and display mineralogical zonings that provide insights on their mode of formation.

One type of zoning is characterized by Ti-, Nb- and (U,Th)-rich oxides (Nb-perovskite, zirconolite) occurring close to ($<$ 2 mm) the phlogopite rim and the originally magmatic rock, whereas those oxides observed farther ($>$ 1cm) are Zr-rich and (Ti, Nb, U, Th)-poor or free (calzirtite, then baddeleyite). Qandilite, which occurs at some distance from the magmatic rock, is observed to result from desilication of the perovskite+forsterite association. The (Fe, Ti) contents of spinel and qandilite decrease at increasing distance from the magmatic rock. Textural relationships between minerals provide evidence for a metasomatic development of the skarn at the expense of the contaminated magmatic rock and its phlogopite boundary, through drastic leaching of K, Si, Fe, the same process being responsible for the zoning in the skarn (leaching of Fe, Si, Ti, Nb, U and Th). The banded structure of the skarn originates from

the strong volume reduction involved in the leaching, which promoted fracturation and deposition of calcite in the fractures. The direction of fluid movement as well as the chemical features of this metasomatic process indicate a source foreign to the magmatic rock.

The other type of zoning corresponds to the reworking of the same type of banded forsterite-spinel-baddeleyite-calcite skarn, close to its boundary with the magmatic rock under the influence of a magma-derived fluid, i.e., a fluid flow in the opposite direction compared to the first type. Reactions involving enrichment in incompatible elements such as Ti, Nb and actinides include the mantling and replacement of baddeleyite by zirconolite and, very close to the syenite, of zirconolite by betafite. Inputs of Fe and Ti are demonstrated by zonings of individual spinel grains. An input of silica is involved in the formation of geikielite + forsterite at the expense of qandilite, followed by the replacement of geikielite by forsterite-perovskite symplectites which indicate conditions of decreasing pressure of CO_2 and/or increasing $aSiO_2$, all consistent with the infiltration of a magma-derived fluid. A local partial melting of calcite is also observed, probably due to this fluid.

Spinel and qandilite in both types of zoned skarns have a large compositional range in response to the back-and-forth movements of components, which allows to locate the miscibilty gap in the system $MgAl_2O_4$-$MgFe_2O_4$-Mg_2TiO_4, presently only documented on the join $MgAl_2O_4$-Mg_2TiO_4. The observed compositions show that in spite of their contrasting features, both metasomatic processes took place at the same temperature, i.e., belong to one and the same overall process which probably involved carbonate anatexis by aqueous magma-derived fluids, followed by fenitization-like processes.