SECONDARY MINERALIZATIONS IN BASALTIC ROCKS: EXAMPLES FROM THE LESSINI MOUNTS (ITALY)

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INTRODUCTION AND GEOLOGICAL SETTING

This work focus on the secondary mineralizations affecting the basaltic rocks from the Lessini Mounts (Verona Province) with the main purpose to establish a systematic of the secondary minerals that were formed in the cavities and vesicles determining the morphologies, the chemical compositions, the paragenesis and their areal distribution. Moreover, petrographic, mineralogical and geochemical investigations of volcanic host rocks have been carried out with the aim to explore possible relationships between the host rocks, their secondary minerals and the associated alteration phenomena, trying to carry a contribution to the knowledge of physico-chemical processes which are related to fluids migration through basaltic lava flows.

The Lessini Mounts can be referred to the South-Alpine Domain and a large area of its central-northern sector (now corresponding to the Veneto region) was affected by an intense magmatic activity from the late Paleocene to late Oligocene. The volcanic products related to this activity are now interbedded at various levels in South-Alpine Domain sedimentary rocks and they are described as Veneto Volcanic Province (VVP; Beccaluva *et al*., 2001; Bonadiman *et al*., 2001). On the basis of tectono-magmatic features the VVP can be divided into three main areas: the western Lessini-Southern Trentino, the Marostica hills and the eastern Lessini.

The study area is located in the eastern Lessini (Verona province) and it is bounded by the Castelvero fault to the West and the Schio-Vicenza tectonic line to the East. In this area the volcanic activity span from the late Paleocene to the late Oligocene with the emplacement of submarine to subaeral lava flows and tuffs, now interbedded in the sedimentary stratigraphic succession. The main tectonic structure of the eastern Lessini area is the Alpone-Agno *Graben*, were the volcanic succession reaches a thickness of about 400 m and represents the most significant sequence of VVP. Within this depression eight volcanic phases have been recognized, from the late Paleocene to late Oligocene (De Vecchi & Sedea, 1995). These volcanics, whose compositions range from basanites, alkali-basalts, transitional basalts to tholeiites, are often deeply weathered and show veins and vesicles frequently filled by secondary minerals.

RESULTS AND DISCUSSION

Petrography, mineral chemistry and geochemistry of the host rocks

From a petrographic point of view all of the studied samples are basaltic rocks with a fairly homogeneous composition. Their paragenesis is Ol ± Cpx ± Pl ± Opq, present in different proportions, their texture ranges from subaphyric to porphyrytic (IP from 2 to 18 wt.%) and the groundmass is oloialine to olocrystalline. Abundant disrupted olivine xenocrysts and mantle xenoliths have been observed. These rocks show variables degrees of vesiculation and alteration. Olivine phenocrysts show an average composition of $Fo_{78\text{-}84}$, with a CaO content varying between 0.22 and 0.44 wt.%, and they did not reveal the presence of minor elements such as Ni and Cr. The pyroxene shows a wide compositional variability characterized by $Wo_{41-58}En_{35-48}Fs_{2-12}$ and corresponding to the diopside field. The most significant changes are expressed by Ca (from 0.73 to 0.99 apfu) and Mg (from 0.56 to 0.88 apfu), while the TiO_2 content is between 0.33 and 4.78 wt.%; the Al is distributed mainly in the tetrahedron site (^{IV}Al 0.1-0.4 apfu, while ^{VI}Al 0-0.1 apfu). Plagioclase has a composition ranging from andesine to bytownite ($An_{47-89}Ab_{11-51}Or_{0-2}$), with the average of An_{65-75}.

According to the TAS diagram (Le Bas *et al.*, 1986), the studied volcanic host rocks are classified in order of abundances as: basanite, alkali basalts and sub-alkali basalts; K-trachibasalts, hawaiite and mugearite are very subordinate. In particular, the more basics terms show the typical characters of primitive rocks with high Mgv (> 0.5, assuming Mgv = Mg/Mg+Fe^{2+}, with Fe_2O_3/FeO = 0.15), low FeO_T/MgO (< 1.2), low Al_2O_3 (< 14 wt.%) and high Ni (176-295 ppm) and Cr (225-455 ppm).

As concerns REE, all patterns are sub-parallel with a decrease in LREE and an invariable content of HREE. In particular, the mafic rocks (basanite) have slightly higher contents of LREE compared to the relatively more evolved rocks. $(La/Lu)_N$ ratio range from 11 to 25. $(La/Yb)_N$ ratio varies from 14 for the more basic rocks, to 31 for the more evolved rocks, whereas Eu/Eu* ratio is always > 1 (1.3-2.3). Generally, all samples show a good overlap with the REE patterns of literature samples for this area.

Primordial mantle-normalized (McDonough *et al*., 1992) diagrams for Lessini volcanic host-rocks show sub-parallel patterns characterized by an increase from Rb to Nb (only for basic rocks), a significantly decrease in U and a more regularly decreases from Nb to the couple Tb-Y. A small trough can be seen at Hf. Primitive mantle-normalized (Sun & McDonough, 1989) diagrams for selected Lessini mafic rocks show smooth patterns characterized by a slight concavity downwards with positive peaks at Ba, Nb and La, while Th, U, Pb and K are negative peaks. All the analyzed rocks show patterns resembling that of the literature for this area. The only differences rest on negative Th, U, Pb, and Sm anomalies, which are significantly lower in the studied samples.

On the basis of petrology and chemical characters all the studied rocks are related to alkaline or moderately alkaline magma series, with $Na_2O > K_2O$ and low SiO_2 content (< 46 wt.%), features similar to OIB mantle sources. The data display typical within-plate geochemical signature and the multi-element diagrams show patterns which resemble those of magmas derived from a depleted mantle, similar to MORB or HIMU-type basalts, with the exception of some negative Th, U and Pb anomalies. However, in spite of their similar whole geochemistry, the studied samples evidence significant differences in particular geochemical characters. Elements such as Hf, La and Nb, for example, do not show any correlation with Zr, as it should be in the case of comagmatic rocks. Moreover, some element ratios such as Ba/Nb and Ba/La show no correlation with Zr.

These data seem to indicate that the Lessini volcanics are likely to be generated from substantially similar mantle sources, as suggested by the subparallel incompatible element patterns. However, some geochemical characters suggest that the deepest mantle sources, with an HIMU signature, were probably not homogeneously enriched by metasomatic fluids prior to and/or melting processes, as also well evidenced by recent isotope systematics (Beccaluva *et al*., 2007). The HIMU metasomatizing agents may possibly be related to a convecting mantle plume that is thought to extend from the eastern Atlantic to Europe (Macera *et al*., 2003; Piromallo & Morelli, 2003; Beccaluva *et al*., 2007).

Secondary mineralizations in the Lessini basalts

Vesicles and cavities in the Lessini basalts were partly to completely filled with secondary minerals. The zeolite group constitutes about ~ 90% of the total mineral species and it is represented mainly by analcime, harmotomo, chabazite, gmelinite, phillipsite and natrolite whereas erionite, offretite, heulandite and stilbite are less common. In some samples very rare zeolites as yugawaralite and willhendersonite were also found, and this the first discovery in VVP. Zeolite minerals are often associated with other silicates as apophyllite, gyrolite, prehnite, pectolite and smectite (*e.g.* saponite, Fe-saponite) and non-silicates as carbonates (calcite, aragonite), sulphates (celestine) and oxides (quartz, tridimite).

Regarding the zeolite group, analcime, gmelinite and natrolite show macroscopic features, optical properties and chemical compositions comparable with the same minerals already described in the literature for other areas of the Lessini Mounts (Vicenza province) as well as other locations (Gottardi & Galli, 1985; Tschernich, 1992; Bish & Ming, 2001). Phillipsite and harmotomo are consistent with the literature data for macroscopic features and optical properties, while in terms of chemical composition, they are predominantly phillipsite-Ca, with subordinate phillipsite-K and very rare phillipsite-Na. These data show a well compositional range between Ba and K contents which significantly extends the miscibility between the two end-members phillipsite and harmotome. The chabazite shows a wide range of morphologies and can also be found with very rare habits. One of them, never seen before in Lessini Mounts, is the result of a geometrically regular growth of lamellae with pseudo-hexagonal shape. Its optical properties are consistent with those of the literature and, with respect to chemical compositions, the studied chabazite is a predominantly chabazite-Ca, whereas chabazite-K is very rare and chabazite-Na is absent. In particular, a significant amount of Sr has been detected in some chabazites and this seems to be systematically related to some unusual morphologies. Among the other zeolites heulandite and stilbite are easily recognizable and their characteristics are consistent with the literature data, whereas erionite and offretite show very similar morphologies and their distinction is only possible through accurate chemical and diffraction analysis. Macroscopic characters, optical properties and chemical compositions are comparable with the literature data; in particular, in the Verona Province, only erionite-Ca and Ca-rich offretite have been found, while erionite-Na and erionite-K are absent or very subordinate. Yugawaralite and willhendersonite are rare in Lessini basalts, but their low spread in other parts of the world makes their presence particularly significant. Moreover, this is the first discovery of these zeolites in the Veneto Volcanic Province.

As regards the other silicates (apophyllite, gyrolite, prehnite, pectolite, pectolite-larimar) and non-silicates (celestine, calcite, aragonite, quartz and tridimite) their distribution is very limited and the analyzed samples show coherent characteristics in terms of macroscopic features, optical and chemical compositions if compared to the literature data.

The study of systematic and paragenesis within cavities and vesicles of the investigated samples suggest that most of the secondary minerals in the Lessini basalts were formed at relatively low temperatures, in the range of 50-150°C. Rarely, the secondary minerals and/or their paragenesis can be related to higher temperatures (> 250°C), probably linked to local situations and/or subsequent crystallization processes.

Considering that: (i) most of the cavities and vesicles is only partially filled by secondary minerals, and they crystallize from the walls toward the centre of the vesicle in which, however, there is still space available, (ii) most of the minerals gives rise to secondary crystals with well-developed morphologies observable even at macroscopic scale, (iii) the mineralization observed in the cavities and vesicles in the studied samples are related to phenomena occurring usually at low temperatures (< 150°C), (iv) this is a wide systematic of minerals mainly referred to the zeolite group, and (v) some of them are characterized by well-defined chemical compositions, so it can be concluded that these minerals may be related to hydrothermal systems. However, there may be several distinct genetic environments, all related to hydrothermal systems but slightly different with each other and probably overlapped in time and space.

In some cases the presence of low-temperature zeolite paragenesis with high variability at small-scale, connected with a strong alteration of host rocks, is consistent with hydrothermal alteration phenomena produced by high temperature fluids that locally pervade already consolidated basaltic rocks. In other cases, however, the mineralogy of the observed associations and their widespread homogeneity suggest a system characterized by the presence of massive injections of high temperature fluids pervading continuously and homogeneously (and for a long time) large masses of already consolidated volcanic rocks or only partially solidified; this feature is typical of volcanic areas with large volumes of emplaced magma. A further possibility involve the formation of secondary minerals as derived from the simple cooling of lava flows where the heat flux produced by the mass in cooling can interact with water bodies, generating high-temperature fluids which may lead to the formation of secondary minerals. In this case, the presence of gaps and/or important tectonic structures may facilitate the movement of water masses (and thus increase the possibility of interaction with magma bodies) and the increase of temperature (also for the heat generated by friction). Finally, the presence of minerals of high temperature, the absence of zeolites and the complete filling of fractures and veins of irregular shape, may indicate the existence, at least locally, of microsystems in which genetic conditions may be very near to the field of low-grade metamorphism.

The alteration of basaltic rocks can be considered as the result of very complex geological processes which probably develop at different scales and time and space. However, in the area of Lessini Mounts, is recognizable a main phase of alteration which is acting on a regional scale and it is responsible for the observed zoneography in volcanic rocks, and other secondary alteration phases, contemporary or subsequent to the main phase and of local importance, may be responsible for the considerable variability observed in terms of amounts of secondary minerals, mineralogical associations and chemical compositions.

The processes of secondary mineralization not affected systematically all the basaltic rocks of the Lessini Mounts and several variations can be recognized, suggesting the presence of significant relationships between the development of mineralizations and some geological characters such as tectonics, fracturing of rock masses and presence of levels with different degree of permeability. At a small scale, the most common mineralizations are generally located on the roof of volcanic bodies or at the contact with clay levels or compact basaltic bodies. At a large scale, however, the mineralized areas have a distribution that follows the most important tectonic structure in this area (Castelvero fault), which may have acted as surface lifts and mobilization of fluids, causing thermic anomalies. These elements suggest that the formation of secondary mineralization in basaltic rocks in the Lessini Mounts (but probably also in other similar contexts) is strongly linked to the presence of preferential pathways of movement and/or stagnation of fluid masses.

Generally cannot be observed systematic changes or specific relationships between the compositions of host rocks and the associated secondary minerals in terms of paragenesis and chemical compositions, suggesting a greater influence by the composition of circulating fluids rather than that of the host rocks. However, in restricted areas, there are significant changes in the contents of some chemical elements in both host rocks and in related secondary minerals, showing the presence of possible genetic relationship of local character.

Almost all of the secondary minerals in cavities and vesicles in the Lessini basalts are characterized by the peculiar presence of calcium as a single- or dominant-cation, as testified by the presence of phillipsite-Ca, gmelinite-Ca, chabazite-Ca, erionite-Ca, Ca-rich offretite, pure Ca-zeolites like yugawaralite, stilbite and peculiar calcium minerals as pectolite, gyrolite, calcite and aragonite. If it is considered that the volcanic rocks hosting the mineralized cavities not have high ratios Ca/(Na+K), and their primary minerals show an enrichment in calcium if compared to what should be their classical composition (*e.g.* pyroxene), it can be concluded that these rocks cannot be held as responsible for the release of calcium. Thus, the Ca cation was to be extremely abundant in the hydrothermal fluids circulating in the rock masses and its origin could be related to the presence of thick and important carbonate successions surrounding (or interbedded with) the volcanic bodies and/or the entire lava sequences of the Lessini Mounts.

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