ULTRAPOTASSIC LAVA FLOWS FROM COLLI ALBANI VOLCANIC DISTRICT SHED LIGHT ON THE ORIGIN OF CALCITE-BEARING MAGMAS

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INTRODUCTION

This work reports a detailed petrological, geochemical and experimental study of lava flows belonging to the whole eruptive activity of the Colli Albani Volcanic District (central Italy). Colli Albani lava flows are particularly intriguing due to the occurrence of calcite crystals in the groundmass of some of these products. By exploring still unclear aspects of the origin of the investigated lava flows, the study aims at shedding light on the origin of calcite-bearing magmas at Colli Albani, thus providing inferences on carbonate-bearing magmas from other magmatic systems worldwide.

Calcite crystals in intrusive rocks are commonly reported in hypoabyssal (*e.g.*, Galliski *et al.*, 2004; Ibrahim *et al.*, 2010) and in kimberlitic rocks (*e.g.*, Sparks *et al.*, 2009 and references therein). In contrast, calcite crystals in effusive rocks are rarely documented, mainly occurring in alkaline lava flows (*e.g.*, Kjarsgaard & Peterson, 1991; Berger *et al.*, 2009). The presence of calcite in volcanic rocks is usually related to "mantle-derived" carbonate (*i.e.*, carbonatite component; Martin *et al.*, 2012 and references therein) but rarely to magma-crustal carbonate interaction (*e.g.*, Demeny & Harangi, 1996 and references therein).

In central Italy, carbonate-bearing volcanic rocks occur in several small monogenic centres along the Apennines chain (*i.e.*, Intra-Apennine Province; Peccerillo, 1998, 2005; Barker, 2007) and with significant volumes in the Colli Albani volcanic district (Fornaseri & Turi, 1969; Freda *et al.*, 2011). The origin of these carbonated effusive rocks is still controversial. One hypothesis interprets them as magmatic carbonatites formed by liquid immiscibility between a primitive magma and a mantle-derived carbonatite melt (Stoppa *et al.*, 2005). An alternative hypothesis considers the carbonate fraction as reworked crustal carbonates (Peccerillo, 2005; Freda *et al.*, 2011).

The Colli Albani Volcanic District (hereafter CAVD) rocks are quite peculiar because of their low SiO_2 content (as low as 42 wt.%) even in highly differentiated products (Trigila *et al.*, 1995). In particular, the K-foiditic composition of the differentiated products evidences that silica-undersaturated magmas may evolve towards minimum melt compositions even more silica-undersaturated than phonolite (*e.g.*, Freda *et al.*, 2011 and references therein). The magmatic plumbing system of CAVD is hosted by a thick carbonate sequence (Bianchi *et al.*, 2008); on the basis of geochemical and experimental data, previous studies have demonstrated the central role of magma-carbonate interaction on the unusual liquid line of descent of CAVD magmas as well as on the eruptive style (Freda *et al.*, 1997, 2008, 2011; Dallai *et al.*, 2004; Gaeta *et al.*, 2006, 2009; Mollo *et al.*, 2010; Peccerillo *et al.*, 2010).

One of the most interesting features of the CAVD is the occurrence of calcite crystals in the groundmass of some lava flows. Although such calcite crystals in the groundmass have been frequently observed and reported by many authors, the petrological meaning is still under debate (Fornaseri *et al.*, 1963; Fornaseri & Turi 1969; Peccerillo *et al.*, 1984; Ferrara *et al.*, 1985; Boari *et al.*, 2009). Recently, Freda *et al.* (2011) suggested a "magmatic" origin, meaning that calcite crystallized above the solidus conditions of the considered system contemporaneously with silicate mineral phases. High temperature crystallization is actually corroborated by the occurrence of calcite crystals in CAVD cumulates as well (Freda *et al.*, 2006; Gaeta *et al.*, 2006; Di Rocco *et al.*, 2012).

RESULTS AND DISCUSSION

On the basis of the microtextural features, the studied lava flows have been divided into two groups: *a*) calcite-bearing leucitites and *b*) calcite-free leucitites. The first group is characterized by foiditic lava flows with calcite crystals in the groundmass. The second group divides into phonotephritic lava flows with olivine phenocrysts, named olivine leucitites, and foiditic lava flows with rare phenocrysts of leucite and clinopyroxene, named leucitites *sensu stricto*.

Calcite occurs in the groundmass of CAVD lava flows with peculiar microtextural (Fig. 1) and geochemical features that give insights on the genetic processes leading to its crystallization.
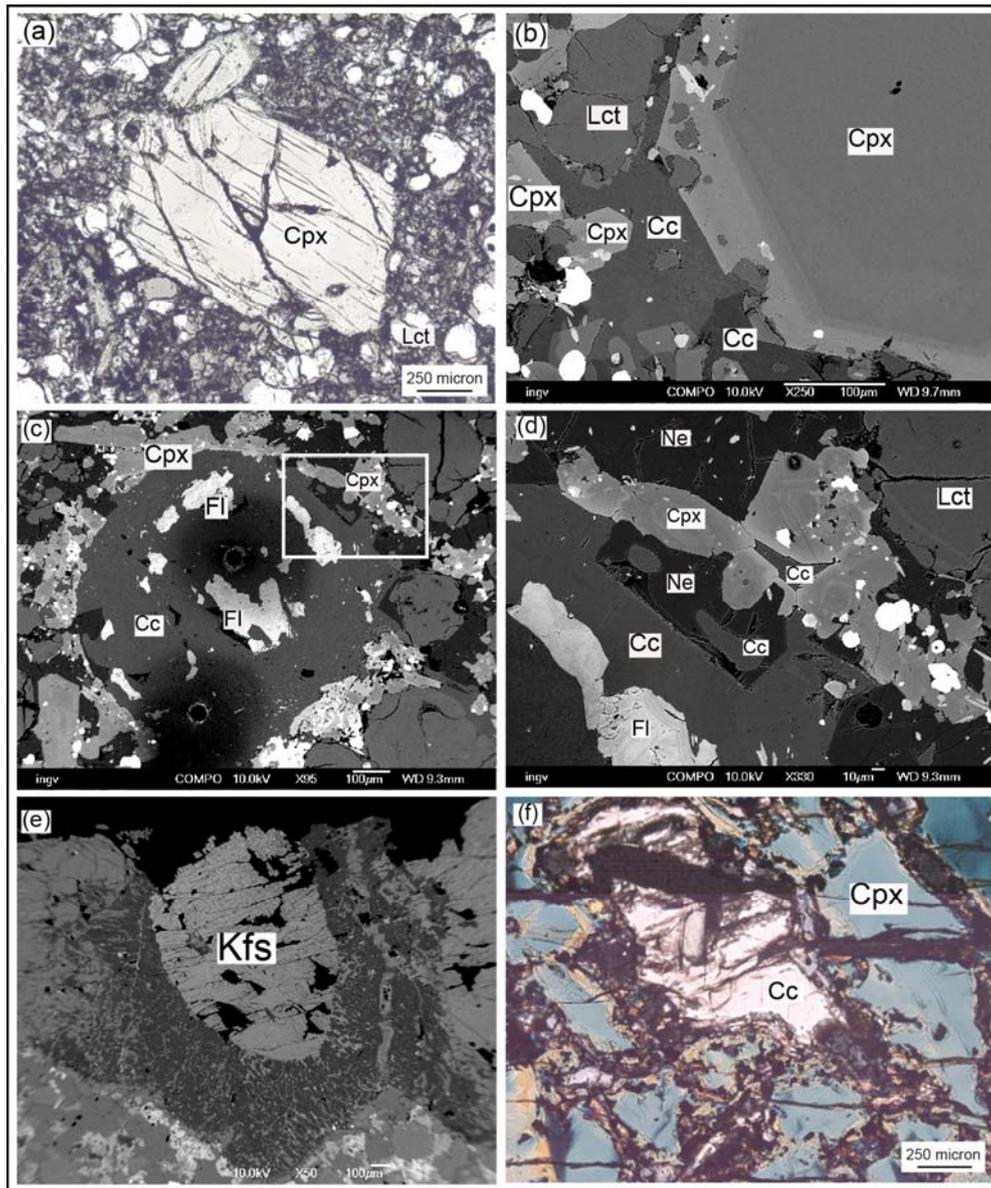

Fig. 1 - Selected photomicrographs and FESEM images of the calcite-bearing leucitites. (a) Subhedral clinopyroxene and leucite phenocrysts. (b) Back-scattered electron image of the groundmass of calcite-bearing lava flows with the presence of interstitial calcite; noteworthy is the euhedral shape of clinopyroxene at the edge with calcite. (c) Back-scattered electron image of a spherical *ocellus* of calcite and fluorite with tangentially arranged clinopyroxenes (holes were produced by LAM measurements). (d) Particle of calcite-nepheline intergrowth at the edge of *ocellus*. (e) Xenocrysts of K-feldspar with coronitic texture. (f) Calcite inclusion in clinopyroxene xenocryst. Cpx, clinopyroxene; Lct, leucite; Ne; nepheline; Cc, calcite; Fl, fluorite; Kfs, K-feldspar.

i) The spherical outline of the *ocelli* excludes an origin via filling of vesicles by hydrothermal fluids, as vesicles in a lava flow are usually elongated shaped. Notably, the absense of calcite-filled veins also exclude the hydrothermal origin. Other microtextural features, such as the sharp edge, and the occurrence of nepheline crystallized across the *ocellus*-lava boundary, indicate that *ocelli* represent globules of immiscible carbonate liquid formed by *in situ* immiscibility (Roedder, 1979; Bogoch & Magaritz, 1983; Demeny & Harangi, 1996). The tangential arrangement of clinopyroxene crystals around the *ocelli* reveals the surface tension of the carbonate liquid preventing the penetration of clinopyroxenes (Philpotts, 1972; Phillips, 1973). This indicates that calcite crystallized when the groundmass was still partially molten, *i.e.* above the solidus temperature of the lava flow.

ii) The inhomogeneous spatial distribution of calcite in the lava flow groundmass is in accordance with the limited carbonate melt mobility when hosted in a silicate melt (Minarik, 1998).

iii) Calcite-nepheline intergrowths are likely due to a simultaneous crystallization of carbonate and silicate phases.

iv) the leucite + clinopyroxene + calcite + mica + nepheline + analcime corona textures observed around K-feldspar xenocrysts highlights magma-carbonate interaction at syn-eruptive conditions.

v) The Sr contents measured in calcite crystals (up to 1 wt.%) are consistent with crystallization at high temperature (Barker 2007; Rosatelli *et al.*, 2010).

Although it has been experimentally demonstrated that, under dry conditions, the minimum pressure for calcite crystallization is 4 MPa at 1240 °C (Wyllie & Tuttle, 1960), all the above-mentioned features imply that calcite crystallized from a molten carbonate in the groundmass of the calcite-bearing leucitites (*i.e.*, at atmospheric pressure), above the solidus temperature of the hosting lava. Actually, it has been demonstrated that the occurrence of small percentages of fluorine ($\leq$ 5 wt.%) in the system allows calcite crystallization even at atmospheric pressure and temperature of about 1000 °C (Gittins & Jago, 1991; Jago & Gittins, 1991). Furthermore, if fluorine is available in the form of CaF_2, the $CaCO_3$ melting temperature decreases down to 880 °C (Gorzkowska *et al.*, 1998a, 1998b).

High activity of fluorine in the CAVD lava groundmass has been already suggested (Gaeta & Freda, 2001) and is here confirmed by the presence of fluorine-rich phases (*e.g.* mica, amphibole and fluorite) as well as of high-polymerised crystals (Si-rich, Al-poor clinopyroxenes. The crystallization of the latter, in particular, is favoured by the enhancement of melt polymerization as a consequence of the fluorine aptitude to form complexes with networking modifier cations (Foley *et al.*, 1986; Veksler *et al.*, 1998; Bartels *et al.*, 2012). Notably, fluorite and Si-rich, Al-poor clinopyroxenes occur only in the calcite-bearing lava flows, corroborating the assumption of very high calcium and fluorine activity in the melt.

Stable isotope values measured in the studied samples give insights into the nature of the carbonate melt producing calcite crystals in the groundmass (Fig. 2; see also Fornaseri & Turi, 1969). In particular, the $\delta^{18}O$ values of calcites overlap those measured in limestone and are significantly higher than those typical of mantle carbonate. The $\delta^{13}C$ values range from -18 to +5‰ PDB, whereas typical mantle values are around -7‰ PDB (see also Fornaseri & Turi, 1969). Therefore, the origin of calcite crystals is related to the interaction between the differentiated magma and the limestone wall-rock at shallow level rather than to primitive magmas and mantle-originated carbonatite component at deep level.

It is generally accepted that the interaction between magma and carbonate wall-rock may result in *i*) decarbonation of carbonate wall-rock with consequent CO_2 addition to the magma (*e.g.*, Behrens *et al.*, 2009; Deegan *et al.*, 2010; Dallai *et al.*, 2011), *ii*) assimilation of carbonate wall-rock with consequent addition of CO_2 and CaO-rich melt to the magma (*e.g.*, Fulignati *et al.*, 2001; Chadwick *et al.*, 2007; Gaeta *et al.*, 2009; Troll *et al.*, 2012), *iii*) melting of carbonate wall-rock (*e.g.*, Lenz, 1999; Wenzel *et al.*, 2002; Barnes *et al.*, 2005). Moreover, it has been demonstrated that carbonate assimilation causes a decrease in the SiO_2 content of alkaline magmas, driving the differentiation towards foidite compositions (Daly, 1910; Shand, 1930; Freda *et al.*, 2008 and reference therein). It is worthwhile stressing out that among CAVD lava flows, the calcite-bearing leucitites

show the lowest SiO_2 bulk contents, the most CaO-enriched groundmass olivines (see also Melluso *et al.*, 2010) and the highest $\delta^{18}O$ values in phenocrysts. Moreover, the rough negative correlation between SiO_2 and CaO contents of whole rocks suggests a process occurring progressively. These features highlight the significant interaction between magmas and carbonates during the solidification of calcite-bearing leucitites.
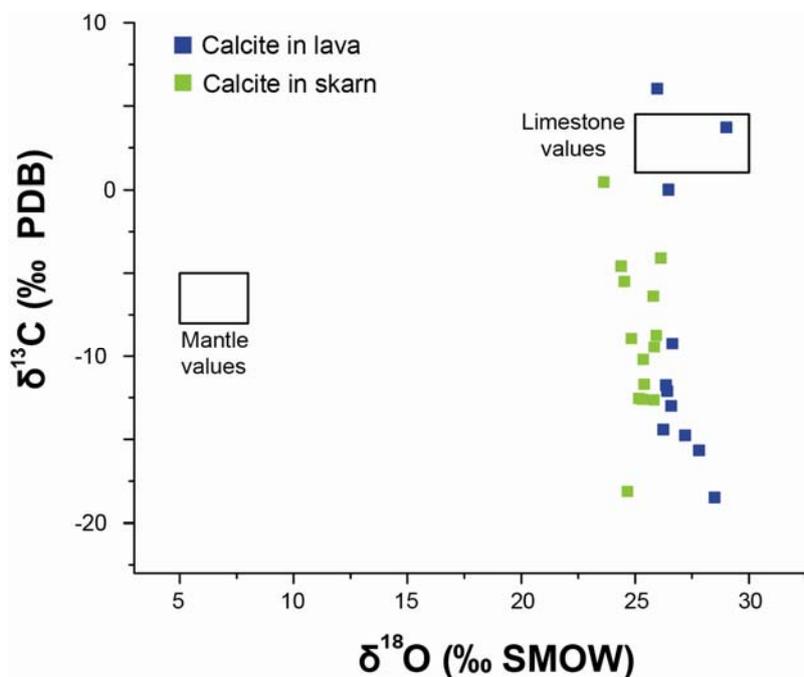

Fig. 2 - $\delta^{18}O$ *vs.* $\delta^{13}C$ diagram showing stable isotope composition of calcite in lava groundmass, compared with calcite in CAVD skarn rocks (data from Di Rocco *et al.*, 2012). Mantle and limestone sediment data from Taylor *et al.* (1967) and Keller & Hoefs (1995).

The $\delta^{18}O$ values of calcites are significantly dissimilar from those measured in silicate phases, implying that carbonate and silicate phases had not enough time to equilibrate (Perkins *et al.*, 2006). This suggests that crustal carbonate might have been entrapped in the lava flow shortly before the eruption. In this frame, I infer that crustal calcite-bearing fragments (*e.g.*, limestone) entrapped in fluorine-bearing lava flows, produced a $CaCO_3$ melt, in turn, producing the calcite crystals documented in the groundmass (*i.e.*, in the *ocelli* and as interstitial phase).

The entrapment of crustal fragments is actually recorded by the occurrence of thermo-metamorphosed limestone xenoliths in the lava flows. However, even though trace element patterns measured in calcites (Fig. 3) mirror the typical pattern of Apennines Meso-Cenozoic limestone (Di Battistini *et al.*, 2001), their abundances are significantly different. Trace element abundances in calcites, indeed, are generally higher than in limestone with the exception of HFSE (Ta, Nd, Zr, and Hf) and Rb that are instead significantly lower. The fractionation of trace elements between limestone and calcite suggests that the molten carbonate (eventually crystallizing into groundmass calcite) resulted from a complex, multi-steps process. In particular, trace element abundances measured in calcites, are higher than those typical of limestone, suggesting variable degrees of melting of the crustal fragments and preferential partitioning of trace elements into the melt phase.

To quantify this process, I have calculated the theoretical trace element abundances in carbonate melts formed after increasing the degrees of melting of a limestone. As input data, I have used the calcite solid/melt K_d values (Ionov & Harmer, 2002) and the trace element abundances of the Meso-Cenozoic limestone. Results from calculations (Fig. 3) show that the highest trace element abundances, *i.e.*, in the Vallerano lava flow, reflect partial melting of the limestone of 10 wt.%. However, according to the calculations, all trace elements should concentrate in the first aliquot of the melt and then decrease as the degree of melting is increased. Differently, in groundmass calcites, it is observed a significant decrease of HFSE and Rb in all studied lava flow samples. The behavior of HFSE can be explained by considering that liquid-liquid trace element partition coefficients in a

carbonate-silicate system lead HFSE to strongly concentrate into the silicate phase (Veksler *et al.*, 2012). The Rb depletion is, instead, explained taking into account the intergrowth crystallization of nepheline and calcite.
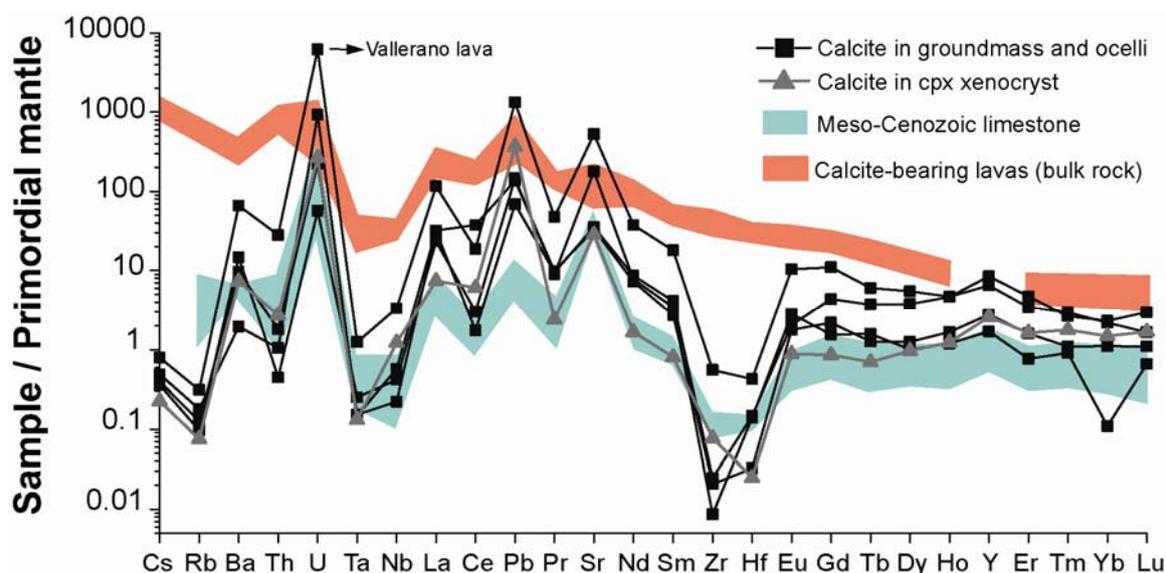

Fig. 3 - Theoretical trace element concentrations (normalized to primordial mantle; Hofmann, 1988) in a carbonate melt originated by partial melting of Meso-Cenozoic limestone outcropping in the Apennines (data from Di Battistini *et al.*, 2001). The trace element concentrations in the carbonate melt was calculated using the formula: $Cl = Cs/[K_d+F*(1-K_d)]$. As K_d values were used the solid/melt partition coefficients of calcite (Ionov & Harmer, 2002). The calculated values span from the limestone values (when the fusion process is complete, *i.e.*, F = 1) to higher values (decreasing the fusion degree down to F = 0.1).

Actually, considering the long eruptive history of the Colli Albani district (> 600 ky) and the large volume of erupted products (> 200 km³), it would be too simplistic to assume that the carbonate melt ensued from the complete fusion of single lithotype (*e.g.*, limestone). It is, instead, more reasonable to assume that crustal, carbonate-bearing fragments before being entrapped in the lava flows have experienced variable degree of fusion, as demonstrated by trace element abundances and/or carbon loss, as corroborated by the large δ¹³C variation (Di Rocco *et al.*, 2012). In this frame, calcite crystals with δ¹³C values comparable to those of Meso-Cenozoic limestones and/or high concentration of trace elements (*e.g.*, in Vallerano and Capo di Bove lava flows) would indicate the pristine nature of the entrapped fragments (*i.e.*, a negligible carbon loss and/or fusion).

Remarkably, Vallerano and Capo di Bove lava flows are rather voluminous, surely the most voluminous of the CADV (2.5 and 1 km³, respectively), and this may account for magma interaction with pristine wall rocks. On the contrary, calcites in small volume lava flows generally show low δ¹³C values in agreement with the entrapment of fragments that have experienced intense carbon loss, *i.e.*, thermo-metamorphosed exoskarns and/or endoskarns. The occurrence of thermo-metamorphosed rocks is actually recorded by the clinopyroxene xenocrysts with calcite inclusions. Moreover, the significant decrease of δ¹³C values in calcite from the bottom to the top of the Vallerano and Frascati2 lava flows, records the progressive decarbonation of entrapped carbonate-bearing fragments, confirming the efficiency and rapidity of the decarbonation process at the syn-eruptive time scale.

On one hand, as generally accepted, the assimilation of carbonate at magma chamber conditions affects the liquid line of descent of magmas as well as triggers large explosive eruptions (*e.g.*, Freda *et al.*, 2008, 2011). On the other hand, it should be now acknowledged that magma-carbonate interaction at syn-eruptive conditions can form both free CO_2 and molten carbonate (see also Chadwick *et al.*, 2007), allowing the additional

crystallization of calcite in lava flow groundmass. The *in situ* immiscibility between the carbonate liquid and the silicate melt can have been favored by the limited ability for the two liquids to mix on syn-eruptive timescales as well as to localized super-saturation due to high degree of assimilation.

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