



# Igneous and sedimentary carbonates of the Cabezo Segura Volcano (Calatrava Volcanic Field)

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# **INTRODUCTION**

The Calatrava Volcanic Field (CVF, Ciudad Real province, Spain) constitutes an alkaline, continental intraplate volcanic region formed by ~ 200 volcanoes dispersed over an area of 5000 km<sup>2</sup>. The volcanic activity was effusive and explosive with emission of alkali basic and ultrabasic lavas from ca. 8 to 1 Ma. The existence of carbonatitic rocks in the CVF is a matter of discussion. Several authors interpreted as extrusive carbonatites the carbonates within tephras of some volcanoes, or as mantle-derived the Ca-carbonate inclusions in olivine crystals. Others interpreted the same materials as sedimentary carbonates or, accepting the existence of igneous calcite in some cases, discarded that of carbonatites s. str. (cf. Carracedo Sánchez et al., 2016 and references therein). To shed light on the problem, we present textural and chemical data for: (i) carbonates included in an ultrabasic feeder dyke, (ii) carbonate-rich layers within cone deposits, and (iii) basement limestones. The samples studied are from the Cabezo Segura volcano, which was built up onto lacustrinepalustrine biomicritic limestones rich in macroscopic fossils. This volcano emitted lavas with compositions of picrobasalts, basanites and olivine nephelinites. The eruptive styles included Hawaiian-, Strombolian-, violent Strombolian- and phreatomagmatic-phases.

# Carbonates within the feeder dyke

This composite feeder dyke attests to several magmatic pulses and cuts the cone pyroclastic deposits. It is made of porphyritic rocks with micro- to cryptocrystalline, globular groundmass. Phenocrysts are of olivine and clinopyroxene. The groundmass is composed of olivine, clinopyroxene, opaque minerals, nepheline and calcite  $\pm$  melilite. The calcite crystals are subrounded to subangular with sizes up to 2 mm, often with palagonite rims (Fig. 1). Some carbonate-bearing globules display

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textural features that point to unmixing of a silicatecarbonate melt, like well defined curved meniscus towards the silicate portion, and ameboid and protrusion shapes. In cases, the carbonate is accompanied by pyroxenes and/or nepheline thus forming globules of carbonate-bearing micro-urtite to micro-melteigite in composition. Carbonates may also occur as xeno- to hypidiomorphic interstitial crystals within the groundmass.



Fig 1. Detail of palagonite rim on calcite crystal of the feeder dyke in the Cabezo Segura volcano. Scale bar 0.1mm.



Fig 3. Homogeneous carbonate layer gradually passing into carbonatecemented lapilli.

#### Carbonates within pyroclastic deposits

Carbonates occur irregularly distributed in the cone deposits. They may exhibit a massive structure and define in some places discrete beds > 15 m long with variable dip and trend. The carbonate deposits appear as aggregates of powdered aspect, poorly consolidated and

enclosing variable amounts of pyroclasts. Carbonates generally exhibit a crystalline texture and may appear rather massive or as coatings/infills of ultramafic pyroclasts, acting as cement that consolidated the original volcanic tephra (Fig. 2). In some places, they also appear as ooidal aggregates. These rocks present a groundmass of micrite and microesparite, which may preserve biogenic microstructures (algae lamination, bioclastic fragments) and ooids. Sr, Ba, REE, Zr-rich phases (e.g., garnet, apatite, perovskite) or xenocrystic olivine, phlogopite and diopside are absent.

# Whole rock element geochemistry

The dyke is composed of ultrabasic rocks (SiO<sub>2</sub> 35.6-39.4 wt %) with CaO 15.6-18.8 wt % and LOIs of 4.2-10 wt %. They are classified in the TAS diagrams as foidites. Trace element contents diagnostic of carbonatites are fairly high: Sr 1069-1554 ppm, Ba 364-497 ppm, Zr 574-625 ppm and La 177-197 ppm. Carbonate beds within pyroclastic deposits have variable contents of SiO<sub>2</sub> (2.2-7 wt %), Cao (36.6-51.9 wt %) and MgO (2.2-13.9 wt %), which reflects variable incorporation of igneous silicate components. They are poor in Ba (73-96 ppm) and La (46-78 ppm), with variable contents of Sr (586-1646 ppm).

#### Mineral element and isotope geochemistry

Electron microprobe analyses have shown that carbonates from the feeder dyke and cone beds are rich in CaO (53-61 wt %) with low amounts of FeOt (0-0.4 wt %), MgO (0-1.7 wt %), Na<sub>2</sub>O (0-0.2 wt %) and K<sub>2</sub>O (0-0.2 wt %).

Q-ICP-MS laser-ablation elemental analysis allow for a better discrimination of the different types of carbonates and moreover reveal two types of calcite within globular inclusions in the dyke. One type is rich in Sr with up to 4 wt % SrO while the other type has maximum contents of 0.2 wt %. The first type (group I) is very poor in Mg and Rb while the second type (group II) has MgO contents up to 1.3 wt % and 30-60 ppm of Rb. All of them being relatively poor in Ba and Zr. Carbonates in the carbonate-rich levels intercalated within the pyroclastic deposits (group III) are very poor in Sr ( $\leq 0.35$  wt %), Ba ( $\leq 0.06$  ppm) and Zr ( $\leq 0.05$  ppm) with MgO contents up to 1.7 wt % and up to 80 ppm of Rb.

MC-ICP-MS laser ablation Sr isotope analysis yielded fairly good results for the Sr-rich type of globular calcite (group I, Fig. 3) with (<sup>87</sup>Sr/<sup>86</sup>Sr)i ratios of 0.703-0.707, which are comparable to the values of 0.703-0.706 obtained for the lavas of this area (Cebriá, 1992). Sr isotope ratios for the Sr poor calcites of the dyke (group II) or for those in the pyroclastic deposits (group III) could not be reliably determined due to their low Sr contents (cf. error bars in Fig. 3).

# Oxygen and carbon isotope geochemistry

Oxygen and carbon isotope values obtained for the carbonate beds in the volcanic cone and for palustrine limestones of the basement attest to light carbon ( $\partial^{13}C_{PDB} < -7.92$  ‰) and relatively heavy oxygen isotopic compositions ( $\partial^{18}O_{SMOW} > +25.38$  ‰), that is, far from those of primary carbonaties and close to those of carbonates in equilibrium with meteoric water.



Fig 3. MC-ICP-MS laser ablation Sr isotope composition of carbonates from groups I, II and III of the Cabezo Segura volcano.

# **CONCLUSIONS**

Sr-rich calcites within globules of the feeder dyke at Cabezo Segura show textural and geochemical features that allow for an interpretation of them as of primary magmatic origin. Yet, those calcites account for less than 30 % of the analysed calcites in the dyke, which rather prevents that, even accumulated, would form true carbonatites, that is, rocks with more than 50 % magmatic carbonate. The Sr-poor calcites within the same feeder dyke bear chemical characteristics close to those of massive carbonates in beds of the volcanic cone, which, according to their petrography, mineral chemistry and O-C isotope ratios are sedimentary in origin and might have been precipitated from meteoric water.

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