Harmotome within Coatings of Basanitic Tephra from Cabeza Parda Volcano (Calatrava Volcanic Field)

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INTRODUCTION

The Calatrava Volcanic Field (CVF) is located in the Ciudad Real province of Spain and includes more than 300 volcanoes dispersed in an area of 5000 km^2. The volcanic activity was effusive and explosive with emission of alkali basic and ultrabasic lavas (alkali basalt, basanite, nephelinite, melilitite and leucitite) between the Miocene (8.7–6.4 Ma) and Plio-Quaternary (3.7–1.75 Ma; e.g., Ancochea, 2004). Vesicles of the volcanic deposits (lava flows, pyroclastic rocks, tephras, dykes and plugs) appear often partially to totally filled by calcite, sulfate minerals like ettringite and thaumasite, and zeolites, particularly phillipsite, gonnardite, gismondine, and stilbite (e.g., Calvo et al., 2010).

This contribution reports the first evidence on the presence of a particular and rare zeolite, the harmotome, within the coatings of basanitic lapilli tephras that constitute part of the scoria cone of the Cabeza Parda volcano in the CVF.

Harmotome (e.g., Coombs et al., 1997) is an aluminium- and barium-bearing hydrated silicate mineral that usually forms monoclinic crystals, frequently twinned; the proposed empirical formula is $(Ba_{0.5},Ca_{0.5},K,Na)_5(H_2O)_{12}[Al_5Si_{11}O_{32}]$. The harmotome defines a continuous series with calcic phillipsite $(Ca_{0.5},Na,K)_x(H_2O)_{12}[Al_xSi_{16-x}O_{32}]$, where x = 4.1–6.8. Harmotome has been synthesized from gels with appropriate composition at atmospheric pressure and variable temperature between 95 and 250 ºC (Barrer and Marshall, 1964; Perrotta, 1976).

THE CABEZA PARDA VOLCANO

The Cabeza Parda volcano is located next to the Ciudad Real airport (Don Quijote airport) in the central area of the CVF (longitude 38º52'46.79''; latitude 3º59'52.34''). This is a scoria cone essentially constituted by lapilli- to bomb-sized pyroclasts, minor ash-tuffs, and small lava flows, the latter practically confined to the volcanic cone area. The volcanic edifice was built onto limestone deposits that fill the Tertiary palustrine–lacustrine sedimentary basin of Cañada de Calatrava. The lava flows consist of alkali basalts and basanites, compositionally close to nephelinites.

The reddish tephras of Cabeza Parda volcano

At the top of the volcanic sequence and exposed in the quarry located south of the Cabeza Parda volcanic cone, there outcrop some reddish, massive lapilli tephras. These lapilli show hyalocrystalline microporphyritic texture with a variable vesicular microlithic groundmass. The microphenocrystals and microliths are of olivine, clinopyroxene and opaque minerals, whereas the glass may vary from tachylitic to sideromelanic in the same clast. Sideromalene appears frequently altered to palagonite. The lavic clasts include quartzite xenoliths/xenocrystals.

The pyroclasts are coated as shown in Figure 1 by a thin (≤ 1–2 mm) coat of an isotrope, not coherent material with powdery aspect and reddish colour, which appears speckled by microliths, microphenocrystals and crystal fragments of clinopyroxene, olivine, and quartz. Also, among them, stand out sparse, up to 200 µm in size, white coloured euhedral crystals that are nearly transparent to translucent, show a vitreous lustre and are often twinned. The optical characteristics of these white crystals, like habit, colour, relief, cleavage and twins, suggest that they may correspond to some type of zeolite. Yet, their small crystal size required the

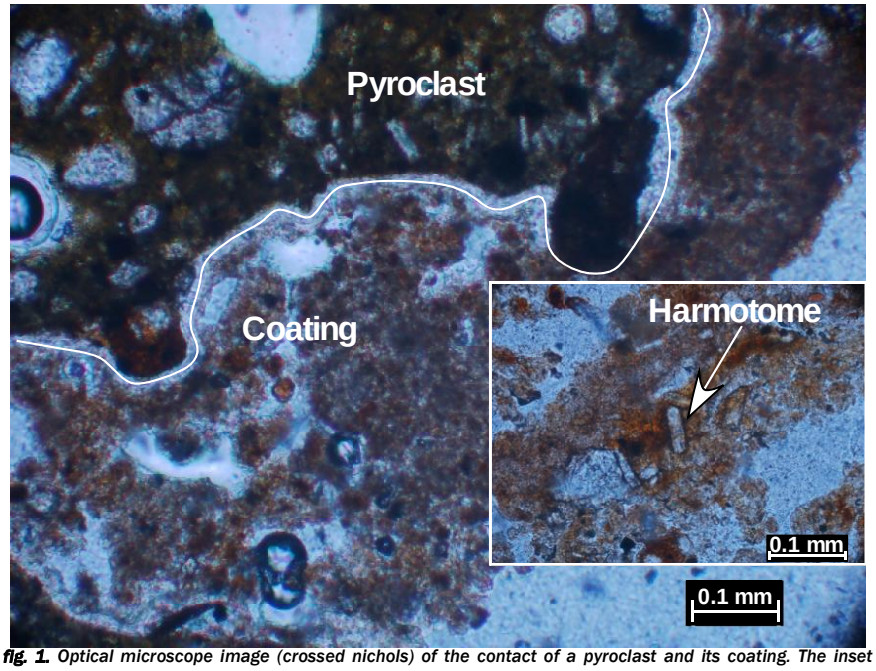

fig. 1. *Optical microscope image (crossed nichols) of the contact of a pyroclast and its coating. The inset picture shows a detail of one harmotome crystal within the coating.*

palabras clave: Harmotoma, Zeolita, Cabeza Parda, Calatrava.
key words: Harmotome, Zeolite, Cabeza Parda, Calatrava.

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use of additional analytical techniques for a proper determination.

RESULTS AND DISCUSSION

Harmotome determination

Precise mineral identification of the suspected zeolite has been carried out by applying common techniques in this kind of studies, namely: (1) X–ray powder diffraction (XRD), and (2) Scanning Electron Microscopy (SEM) combined with spot chemical analysis by means of SEM–EDX methods. These determinations where carried out at the SGIker-facility of the University of the Basque Country UPV-EHU.

XRD was performed on material obtained through ultrasonic immersion and scratching of the surface of coatings developed in the lapilli clasts. The results obtained indicate that besides the orthomagmatic phases typical of this kind of lavas, i.e., pyroxene, olivine, and glass, and the quartz present as xenolith/xenocryst, in the pyroclasts, there exists a mineral of the harmotome–phillipsite series; some smectite was also found as an accessory phase.

SEM images of the surface coating of the lapilli clasts (Fig. 2) reveal that it is constituted by an aggregate of micro-, to nano-spheres (isotrope under optical microscope), crystals and crystal fragments of olivine, clinopyroxene and quartz dispersed into this aggregate, and, notably, euhedral crystals up to 200 µm long, with monoclinic symmetry and commonly twinned, whose crystal shape and twin features are characteristic of the harmotome–phillipsite series (Fig. 2).

SEM–EDX data for the isotrope micro- to nano-spheres indicate that they have an Al-rich silicate composition with minor amounts of Mg, K, Ca, Ti, Mn and Fe.

Euhedral crystals of the presumed zeolites analized by SEM–EDX indicate that they are also Al-rich silicates but with K, Ca, Ba and some Mg, while displaying marked variations in Ca, K and Ba contents (Table 1). The chemical data suggest that these zeolite crystals are compositionally intermediate between end member terms harmotome (Ba) and phillipsite (Ca, K). Yet, Ba contents markedly higher than K and Ca would imply that they might effectively be regarded as harmotome rather than Ba-bearing phillipsite (e.g., Passaglia and Sheppard, 2001).

CONCLUSIONS

X–Ray diffraction data, SEM imagery, and semi-quantitative SEM–EDX chemical analysis have allowed us to identify harmotome zeolite in the coatings of reddish tephra clasts from the Cabeza Parda volcano of the CVF. Harmotome appears as euhedral crystals, generally twined, dispersed into an aggregate of glassy silicate micro- to nano-spherules that cover the pyroclasts of the tephra.

Element	*Crystal*		
Weight %	*#1*	*#2*	*#3*
Mg	0.2	0.58	0.53
Al	11.10	8.43	8.00
Si	28.70	20.30	24.32
K	2.29	3.32	3.92
Ca	3.19	6.99	5.34
Ba	9.01	23.20	17.73
O	45.50	37.18	40.16

Table 1. *SEM-EDX analyses of harmotome within coatings of reddish tephra from the Cabeza Parda volcano.*

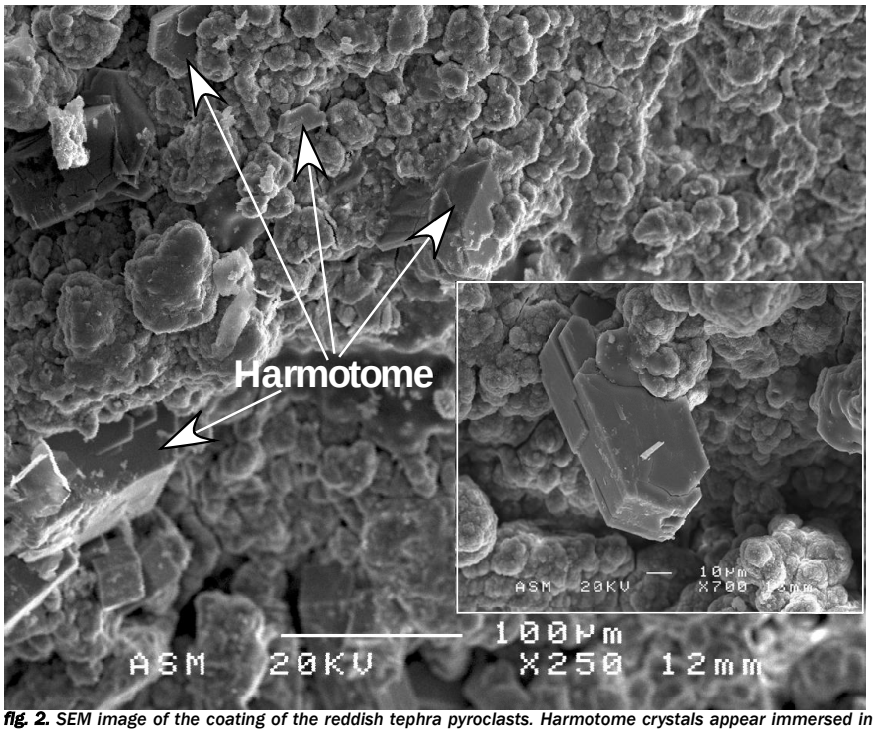

fig. 2. *SEM image of the coating of the reddish tephra pyroclasts. Harmotome crystals appear immersed in an isotrope aggregate of aluminosilicate micro-, nano-spherules. Inset picture: euhedral shape of one harmotome crystal.*

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