Zeolites in hydromagmatic volcanoes. A case study of montaña Escachada (Tenerife)

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ABSTRACT

The different types of zeolites occurring in the hydromagmatic volcano called Montaña Escachada or Montaña Pelada (Southern Tenerife), have been studied. The instrumental techniques of study include X-ray diffraction, scanning electron microscopy, X-ray fluorescence and microprobe analysis. Phillipsite and analcime were detected in amounts inversely proportional from the basis (more phillipsite) to the top (more analcime) of the volcano. A selective enrichment of the phillipsite in potassium and of the analcime in sodium was also observed. The abundance and the genesis of these zeolites are related to the eruptive mechanism and the physico-chemical conditions of the zone. Their formation is, in high degree, irrespective of the composition of the parent magma.

Key words: .*Montaña Escachada, hydromagmatism, zeolites, phillipsite, analcime*

RESUMEN

En este trabajo se estudian los tipos de zeolitas en el edificio hidromagmático de la Montaña Escachada o Pelada (Sur de la isla de Tenerife). Las técnicas de estudio abarcan la difracción de rayos X, microscopía electrónica de barrido, fluorescencia de rayos X y microsonda. Se han detectado filipsita y analcima, cuyas proporciones varían inversamente desde filipsita dominante en la base del edificio y analcima en proporción creciente hacia la parte superior. Asimismo, se observa un enriquecimiento selectivo de potasio en la filipsita y de sodio en la analcima. La abundancia y el origen de estas zeolitas se asocia al mecanismo eruptivo y a las condiciones físico-químicas del medio siendo su formación, en buena medida, independiente de la composición del magma emitido.

Palabras clave: *Montaña Escachada, hidromagmatismo, zeolitas, filipsita, analcima.*

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Introduction

Most of the papers dealing with hydromagmatic volcanoes of the Canary Islands have focused so far on the study of eruptive mechanisms, volcanostratigraphy, and geochemistry of the magmatic material (Martí and Colombo, 1989; Rodríguez Losada *et al.*, 1989; De la Nuez *et al.*, 1993, among many others). Such volcanoes are in association with recent volcanic series, are placed in coastal zones and their emission centers are perfectly conserved. All of them are basaltic or trachybasaltic, except for Caldera del Rey (Southern Tenerife) which has phonolitic composition (Paradas and Fernández Santín, 1984). One of the coastal hydromagmatic basaltic volcanoes is Montaña Escachada (or Montaña Pelada).

Few studies on weathering and crystallization processes of autigenic minerals (zeolites) in such hydromagmatic volcanoes have been made so far. In Tenerife, zeolites have been well characterized in pyroclastic salic deposits, not associated with coastal hydromagmatic processes (García Hernández *et al.*, 1993), provided their higher relative abundance and their possible utilization with agricultural or industrial purposes. However, the study of the zeolites occuring in hydromagmatic volcanoes shows two points of interest. On the one hand, it could give some light on the processes of mineral formation in environments not considered yet and, on the other hand, it could be useful to the study of the formation of the volcano itself.

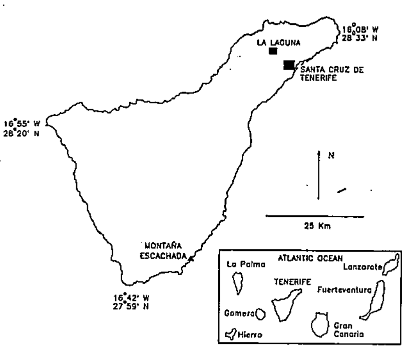

Fig. 1.- Location of Montaña Escachada

Fig. 1.- Situación de la Montaña escachada

Therefore, the main targets of this work focuse on the study of the different zeolite species existing at Montaña Escachada, as well as the main causes that determine their crystal chemistry and their relative abundance. In addition, these data will be related to the conditions in which the volcano was formed.

Experimental

Samples were taken in each level of the volcano, that in turn were recognizable by colour changes, including transition zones between two consecutive levels (if present). X-ray patterns were acquired in a Phillips PW-1720 diffractometer. Scanning micrographs were taken in a SEM Hitachi 450S and in a

JEOL 6400 coupled with a microanalysis detector Link LZ-5, operated at 20 KeV.

Results and discussion

General aspects.- Montaña Escachada is placed in southern Tenerife (Fig. 1). It shows two emission centers, aligned according to a NNW-SSE direction. The older is placed 500 m to the south, and it is almost completely eroded. Its characteristics (type of volcano, stratigraphic aspects and chemistry of the co-magmatic glass) have been studied in detail by De la Nuez *et al.*, (1993).

Montaña Escachada is a tuff-ring made up of many deposits of surge type. The lower levels are wet-surges in which there would have had high proportions of water vapor during the eruption. In contrast, the upper levels are dry-surge type. A purely magmatic (strombolian) level can be found at the top of the volcano.

A well-defined characteristic of the volcano is the contrast in the colour of the strata, pale brown and yellowish at the lower levels and greyish at the upper ones. These changes are also recognizable by side transitions at a given stratigraphic level, from brownish tones at the center to yellowish at the periphery. Thus, all the central and lower zone of the volcano shows prevalence of brownish tones, whose limit with the upper (greyish) zone tends to follow approximately the shape of the volcano.

Crystal chemistry of zeolites.- The microanalyses of phillipsite and analcime previously detected by X-ray diffraction and scanning electron microscopy are shown in tables 1 and 2, respectively. The chemical composition of their respective unit-cells has been calculated assuming the theoretical water content for each zeolite species. Both zeolites show a relative enrichment in Si and Al and a depletion of Fe with regard to the parent material. Iron has been completely excluded from the analcime framework. In phillipsite, the sum Si + Al is never higher than the theoretical value (16), whereby it is expected that Fe may be part of the phillipsite framework. Such a fact could be explained from palagonitization processes of volcanic glass, where Fe and Mn are significantly (but not completely) excluded from those elements composing the autigenic minerals, such as Si, Al, Ca, Mg, Na and K (Honnorez, 1978).

There are some outstanding features concerning the alkali and alkaline earth (non-framework) cations in zeolites. Thus, the sodium and the potassium content are extremely different from one species to the other: phillipsite is mainly K-rich, and it shows small amounts of Na, whereas analcime completely lacks K and only in some cases shows smalls amounts of Ca, being Na the main cation. Magnesium is a minor cation in phillipsite and it is completely absent in analcime. All of these facts are in good agreement with data reported in literature.

The K content in the phillipsite is very close to the maximum limits described by Gottardi and Galli (1985). Although Passaglia et al. (1990) have already evidenced the selectivity of phillipsite towards this cation, those phillipsites formed in hydrologically closed systems where sodium exceeds potassium (as in these case) are usually Na-rich, rather than K-rich. This fact suggests that Na was depleted from the fluid phase prior to the phillipsite formation, thus leading to K-rich phillipsite. Otherwise, the results obtained by microprobe analysis could not be explained. As a matter of fact, experimental synthesis of phillipsite can be easily achieved by oxide mixtures including K and Na and/or Ca (Gottardi and Galli, 1985). Both the relationship between the Si:Al ratio and the alkali cation content approach these phillipsites to those described by Stonecipher (1978) in deep-sea environments.

	ME2	ME23	ME3
Si	10.99	11.18	11.09
Al	4.41	4.30	3.95
Fe	0.26	0.07	0.26
Ca	0.51	1.02	0.24
Mg	0.21	0.00	0.00
Na	1.65	0.99	1.63
K	2.75	3.12	4.88
Ti	0.05	0.00	0.00
H_2O	12.00	12.00	12.00

Table 1.- Unit-cell composition of phillipsites (Based upon 32 oxygen atoms)

Tabla 1.- Composición de la celdilla unidad en las filipsitas (basado en 32 oxigenos)

As far as the analcime is concerned, no significant deviations from the theoretical stoichiometric formula of this mineral have been observed. Only in one case Fe was detected in the microanalyses but, unlike phillipsite, the Si+Al content in the unit cell leave no place to other framework-building cations, so Fe should be regarded as an impurity. Potassium has been completely excluded from the network, as stated above, which only in some cases shows small amounts of Ca together with Na, the most significant non-framework cation. Analcime is not infrequent in marine environments, where it occurs in association with basaltic glasses or basaltic-like materials (Gottardi and Galli, 1985). Moreover, Höller (1970) demonstrated the viability of analcime synthesis in autoclave from basaltic glass and NaOH solutions.

	ME3	ME4
Si	32.97	32.11
Al	15.30	15.57
Fe	0.00	0.49
Ca	0.00	0.49
Na	14.22	14.41
H_2O	16.00	16.00

Table 2.- Unit-cell composition of analcimes (Based upon 96 oxygen atons)

Tabla 2.- Composición de la celdilla unidad en las analcimas (basado en 96 oxígenos)

Distribution of zeolites.- The X-ray patterns corresponding to the different levels of Montaña Escachada are shown in Figure 2, from the basis to the top of the volcano. The lowest level (ME1) is entirely composed by glass, with no crystalline phases at all. However, crystalline minerals were detected from the transition to the second level (ME12). In the ME12 sample, as well as in the upper levels (ME2 and ME23) phillipsite is the only zeolite species. Further X-ray quantitative analyses (Chung, 1974) revealed that the phillipsite amount in each of these levels is small and never higher than 10% (in weight). Analcime only occurs in the two uppermost levels, especially in the last one (ME4), and the occurrence of analcime implies a decrease in the phillipsite content up to limits close to the sensitivity level of the quantitative analysis employed (5% in weight). Except in the lowest level, feldspars (sanidine or plagioclase) were also detected by this technique.

Previous studies on Montaña Escachada evidenced that the chemical composition of the entire volcano is trachybasaltic (although very close to the basaltic compositional

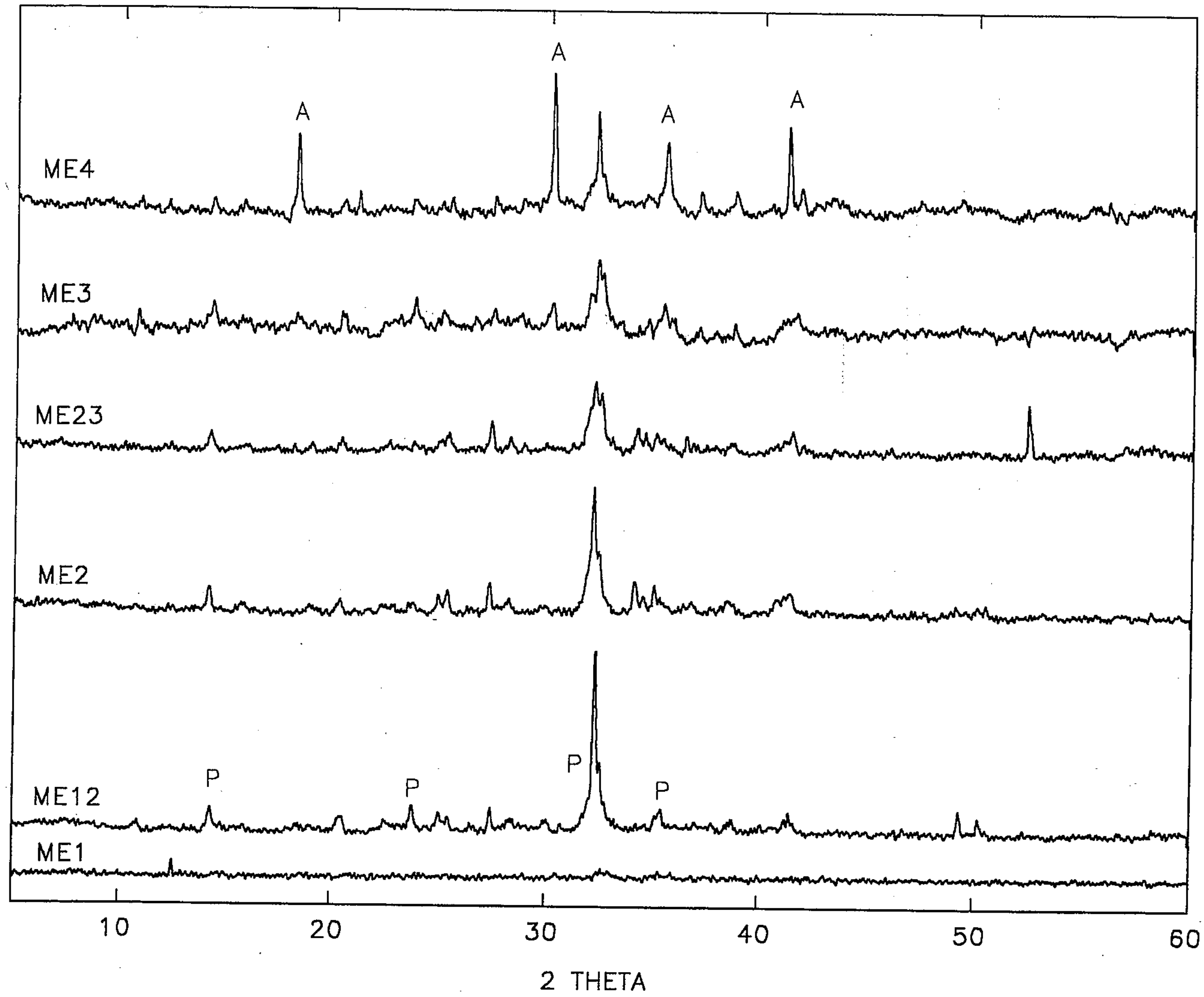

Fig. 2.- X-ray patterns of samples taken in each level of Montaña Escachada from the basis (ME1) to the top (ME4), including transition levels if present (ME12 and ME23). The uppermost level corresponding to the strombolian phase has not been considered. A and P denote characteristic X-ray lines for analcime and phillipsite, respectively.

Fig. 2.- Difractogramas de rayos X de las muestras tomadas en cada nivel de Montaña Escachada desde la base (ME1) hasta el nivel superior. El nivel más lato correspondiente a la fase estromboliana no se ha tenido en cuenta. A y P denotan picos de rayos X característicos de la analcima y la filipsita, respectivamente.

range), so that the distribution of zeolites cannot be attributed to differences in the chemistry of the parent material. Zonality is one of the most frequent features in hydrothermal weathering processes, as it has been widely demonstrated both by field evidences and laboratory simulation experiments. In our case, and in principle, this phenomenon may be explained on the basis of local variations of the physicochemical conditions during the genesis of zeolites.

Höller and Wirsching (1978) carried out experiments of zeolite synthesis in autoclave from volcanic glasses of different compositional type, modifying the treatment solution, the weathering conditions and the temperature. When using basaltic glass, they observed the appearance of analcime, both in the presence of deionized water and 0.01M NaOH, whenever the temperature was higher than 200 ºC. If the temperature value during the experiment was lower than 200 ºC, phillipsite was obtained instead of analcime and, in some cases, small amounts of chabazite. The application of these results to our case suggests a close relationship between the temperature of the different strata that compose the volcano and the genesis and distribution of zeolites. In other words, the occurrence of one or another zeolite suggests differences in the physicochemical conditions during the formation of zeolites, especially dealing with the temperature.

Eruptive mechanism and zeolite genesis.- There are two main factors to consider about Montaña Escachada. The first one, already commented above, deals with the existence of two zones in the volcano, distinguishable by changes of colour from yellowish-brown to grey, being the transition between them not gradual but abrupt. The second factor is the gradual zeolite distribution from the basis to the top of the volcano, also related to such changes in colours. Prior to any discussion concerning these factors, it is worth pointing out that the uppermost levels (strombolian phases) are not affected by colour changes or zeolitization processes. Also, and even though Montaña Escachada is a volcano with a double point of emission, it should be born in mind that the marks from the older point have been partially masked by the materials from the other eruption, which are perfectly conserved. Because of this, the effects observed now are due to the most recent eruption.

With regard to the first factor, that is, the colour changes between two zones clearly separated, there is a similar and equally significant case: Caldera del Golfo (Lanzarote). According to Marti *et al.*, (1989), the yellowish to brown zones existing there are indicative of palagonitization processes characterized by the occurrence of smectites, Fe oxides and zeolites, whereas the greyish upper zones correspond to non weathered or weakly weathered levels. The uppermost zone is greater and, according to the authors, this could be due to particular factors linked to the eruptive mechanism; however, the existence of a thermal gradient in the volcano during the eruption was not considered due to the absence of a gradual transition from the more weathered to the less weathered zones. Therefore, the palagonitization process would be the result of the reaction between the fluid phase trapped inside the pores of the material (mainly water vapour) and the basaltic glass.

The eruptive mechanisms described for Caldera del Golfo can be perfectly applied to Montaña Escachada, with a lower zone in the volcano whose pores, saturated by the fluid phase trapped inside them, point the more palagonitized zone with regard to the rest of the volcano, where the loss of the fluid phase determines the appearance of greyish colours.

However, the zeolite distribution in Montaña Escachada seems to obey not only to colour changes, but also to an inverse thermal gradient in the volcano, that determined the zeolite genesis, as suggested above. The prevalence of phillipsite in the lower part of the volcano and of analcime in the upper one, the temperatures in which each species forms, and the gradual variation of zeolites from the basis to the top, clearly points towards the existence of an inverse thermal gradient (higher temperature towards the upper levels) in Montaña Escachada that gave place to the occurrence of phillipsite in the lower (and cooler) zone and analcime in the upper (and hotter) one. The establishment of such gradient can be explained by the cooling effect of the fluid phase in the lower part of the volcano, where wet surges prevail. Moreover, the higher size of glasses in dry surges deposits lends them a lesser surface area, whereby their cooling during the eruption is slower with regard to the pyroclastic glasses of the lower levels, which are smaller. All these factor will contribute to a inverse thermal gradient, after the multiple eruptive phases in Montaña Escachada, which in turn will determine the formation of zeolites.

The high K content of phillipsites could also be related to the thermal gradient. The formation of phillipsite should take place from a sodic solution (like sea water), whereby Na should be the most abundant non-framework cation in the unit cell. The reality, however, is different so we would have to consider the possibility of a relative Na depletion of the fluid phase in the lower levels of the volcano. The causes of this phenomenon would be beyond the aim of this paper and will require our attention in further researchs. In spite of this, a Na migration towards the upper levels should not be discarded, as it would be favoured by the inverse thermal gradient. That would lead to K-rich phillipsites in the basis of the volcano and analcimes at the upper zones from a Na-rich solution, and a selective exclusion of K by the remaining phillipsite.

Conclusions

The results obtained in this paper open a new perspective to the study of hydromagmatic phenomena in which the zeolite formation is involved. Although further work on this subject is undoubtely necessary, it has been clearly demonstrated that the study of zeolites may give very useful information on the processes that followed the eruption at Montaña Escachada, and vice versa.

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