LITHOSTRATIGRAPHIC SEQUENCES IN THE CENOZOIC VOLCANIC ROCKS OF CENTRAL-SOUTHERN SARDINIA: COMPOSITIONAL VARIATIONS AND DISTRIBUTION OF ZEOLITES AND OTHERS SECONDARY MINERALS IN THE ALLAI AND ASUNI UNITS

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INTRODUCTION

The Oligo-Miocene volcano-sedimentary succession of central Sardinia is composed by five ignimbritic units, mostly emplaced in subaerial environments. These units are locally interbedded with the so-called Asuni Unit (ASU; Assorgia *et al.*, 1995), a volcano-sedimentary complex mainly emplaced in sub-aqueous environments. A similar unit is the Allai Unit (ALU; Assorgia *et al.*, 1995), which consists of several overlapping ash and pumice flows, emplaced over a short period of time in a subaerial depositional environment. Mineralogical composition of ALU is akin to that of ASU, but the welding degree is different. Both units are characterized by a zeolitization process, which leads to crystallization of mordenite + clinoptilolite (± analcime) association as main secondary phases. Recent studies have pointed out a quite widespread late zeolite crystallization affecting volcanic deposits of central Sardinia, and mostly related to a transformation process of glassy components (Cappelletti *et al.*, 2001; Brotzu *et al.*, 2006; Palomba *et al.*, 2006).

This work deals with a detailed study of the distribution of main secondary phases occurring in ASU and ALU, aimed to infer the role of different depositional environments in the minerogenetic processes. Then, 27 representative stratigraphic sequences of these units have been sampled in a NW-SE area located between the villages of Asuni and Allai.

METHODS

Detailed sampling work, carried out in different localities of the study area, has been mainly focused to zeolitized horizons within volcanic sequences. Besides, in each section, ignimbritic layers were sampled and investigated to verify the possible relationships between volcanological layering and zeolitization. Over 100 representative samples were collected for the considered sections, taking into account the best exposed areas. A preliminary petrographic study on thin sections was carried out for all samples. Then, rock mineralogy was investigated by powder X-ray powder diffraction (XRPD), using a Panalytical X'pert PRO PW 3040/60 equipped with a curved graphite diffracted-beam monocromator (Cu*K*α radiation, 40 kV, 30 mA scanning interval, step size = 0.020°, counting time 30 sec/step). Micro-morphological observations by scanning electron microscopy (SEM) and EDS microanalysis were carried out by a JEOL JSM 5310 operating at 15 kV (CISAG, University "Federico II", Napoli). Quantitative chemical data were processed by LINK AN10000 and INCA software. Natural and synthetic minerals were use as standards. Quantitative mineralogical analyses were performed using the Reference Intensity Ratio (RIR) technique, which is an evolution of the internal standard technique proposed by Chung (1974), the matrix- flushing method for quantitative multicomponent analysis, later developed and improved by Chipera & Bish (1988). In order to test the accuracy of these quantitative analyses, some samples where also analyzed by the Rietveld method, using GSAS package.

RESULTS AND DISCUSSION

The whole data set obtained by multi-analytical approach indicate as follows: 1) the strongly welded ignimbrites are unzeolitized; 2) analcime grains mostly occur within vugs and cavities; in association with well-formed quartz and k-feldspar crystals (Fig. 1a); 3) this zeolite mineral is sometimes corroded and lacking in the southern sector; (Fig. 1b) 4) clinoptilolite laths grow on cuspate shards (Fig. 1c), on cineritic matrix and often as vug filling (Fig. 1d); 5) acicular fibres of mordenite grow on both matrix (Fig. 1e) and tabular clinoptilolite crystals (Fig. 1f) and it frequently forms radiating aggregates as vug lining.

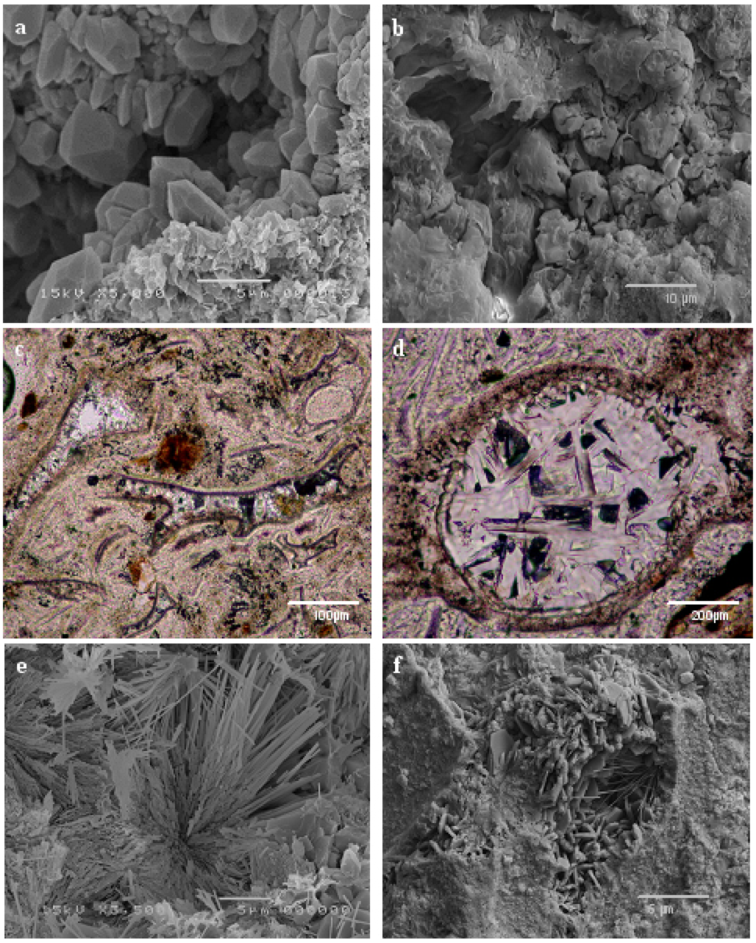

Fig 1 - (a) Analcime crystals associated with K-feldspar and bipiramidal quartz; (b) corroded analcime in vugs; (c) tabular clinoptilolite growing in a glass shard, and (d) in a subsferical cavity; (e) fibres mordenite growing on matrix, and (f) on clinoptilolite crystals.

As regards ALU, the extraframework cation variations of clinoptilolitic zeolite are plotted in Fig. 2a. Clinoptilolite is a Ca-rich variety with average contents of Na, Ca+Mg, and K equal to 23, 56, and 21 afu , respectively. Mordenite fibres, plotted in Fig. 2b, show a distinct sodic feature with mean amounts of Na, Ca+Mg, and K of 46, 42, and 2 afu, respectively. It is worth to note that, with the exception of few samples, narrow compositional variation is observed between the clinoptilolite and mordenite growing on cuspate shards and those occurring in vugs. On the basis of RIR and Rietveld quantitative analysis, a wide variation in the content of newly-formed phases can be emphasized. Anyway a clear mineral zoning does not appear in the sections sampled for this work. In several levels, clinoptilolite content often is higher than 30 wt.%, and the maximum mordenite amount is 31 wt.%. Smectite content is on average lower than 5 wt.%, analcime amount is lower than 21 wt.%.

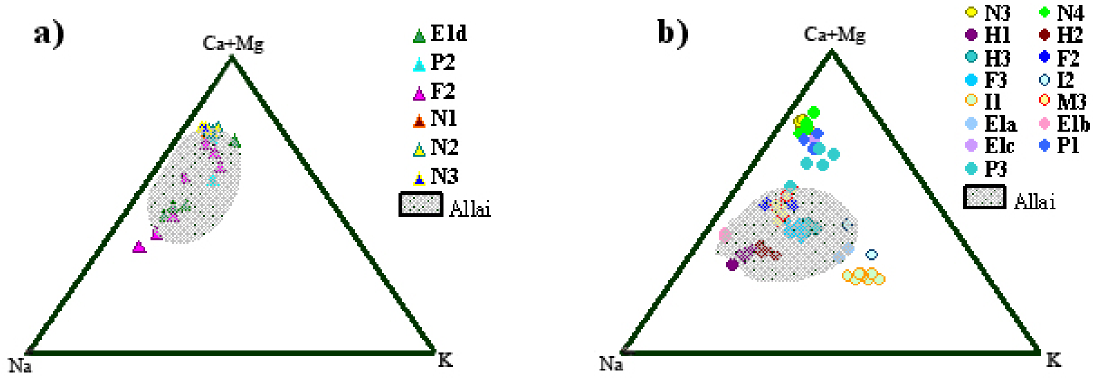

Fig. 2 - (a) Extraframework cations of clinoptilolite, and (b) mordenite plotted in (Ca+Mg)-Na-K ternary diagram for Asuni Unit. The grey area represents the clinoptilolite and mordenite compositional variation for Allai Unit.

ASU is formed by several and diversified lithologies ranging from variably welded ash and pumice pyroclastic flows to epiclastic and laminated levels mainly formed by volcanic materials with carbonized and silicified vegetal remnants. The main authigenic phases are represented by mordenite, clinoptilolite and smectite. As regards vertical distribution of secondary phases in twelve sequences studied here, any sharp vertical mineral zonation can be recognized. Comparative analyses between different lithologies demonstrate that the overall textural feature is similar to that observed in ALU. On average, chemical composition of tabular clinoptilolite shows Na, Ca+Mg, and K amounts of 28, 58, and 4 afu, respectively (Fig. 2a). Mordenite is a Ca-Na-K- rich variety, with Na equal to 32 afu, Ca+Mg equal to 45 afu, and K equal to 23 afu (Fig. 2b)

Only in few samples, quantitative analyses display high mordenite and clinoptilolite contents (over 28 wt.% in zeolite content).

CONCLUSIONS

The vertical distribution of the authigenic minerals recognized in two volcanic and volcano-sedimentary units from central Sardinia cannot be interpreted according to a single genetic model. Taking into account a likely similar starting materials (*i.e.* rhyolitic glass), peculiar physical and chemical conditions are required to promote the observed newly-formed phases and to cause large differences in alteration degree of volcanic products immediately after their emplacement. In particular, regarding local temperature differences, ALU is characterized by mineral parageneses testifying higher temperature than ASU; this is perfectly in line with the geological evidence that ALU is more close to the emission sector. The wide chemical compositional variation of ASU zeolites is probably related to the presence of a transitional fluid. These data, together with differences in fluids/glass quantitative ratios, may explain the observed scenario.

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