

Petrogenetic implications of Ba-sanidine in the Lionato Tuff (Colli Albani Volcanic District, Central Italy)

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ABSTRACT

A vitric fiamme containing BaO-bearing sanidine (BaO = 11 wt.%) was sampled (via di Fioranello, Rome) in the pyroclastic products of the Lower Flow Unit (LFU) belonging to the Villa Senni Eruption Unit in the Colli Albani Volcanic District (Roman Comagmatic Province, Central Italy). The fiamme of the LFU is essentially made up of glass, in which scarce phenocrysts of BaO-bearing sanidine, leucite and Al₂O₃-bearing Ca-clinopyroxene occur. In this paper the various parameters controlling barium partitioning between alkali feldspar and LFU liquid, are discussed.

KEYWORDS: Ba-sanidine, K-foidites, Alban Hills, Central Italy.

Introduction

THE pyroclastic flows of the Colli Albani Volcanic District have an unusual composition which makes these explosive volcanic products unique in the world, and as such the chemical, mineralogical and petrographic characteristics of these products have been studied since the beginning of this century (Washington, 1906). Recently, during the systematic study of the pyroclastic flows of this district (Freda *et al.*, 1997), a potassium feldspar has been analysed which has a BaO content that is unusual for analogous volcanic feldspars (Smith and Brown, 1988). The Ba-sanidine was found inside a fiamme (sample T10) in the pyroclastic unit defined by Rosa *et al.* (1993); Gaeta *et al.* (1994) and Trigila *et al.* (1995) as the 'Lower Flow Unit' (hereafter LFU) of the Villa Senni Eruptive Unit, which is also known in the literature as the Lionato Tuff (Fornaseri *et al.*, 1963). For a detailed description of the stratigraphic succession of the Colli Albani Volcanic District and the attitude and textural characteristics of the LFU, the interested reader is referred to these articles.

The aim of this paper is to describe the presence of the Ba-sanidine and to discuss the variables which control the Ba partition coefficient

(hereafter Ba-PC) between sanidine and glass. In particular, the author highlights the possible reasons for a strong increase of Ba-PC. Indeed, the Ba-PC suggested by Francalanci *et al.* (1987) for the potassium-alkaline rocks belonging to Roman Comagmatic Province is very low with respect to that found in the present work. Although, Mahood and Stimac (1990) were sceptical about Ba-PC values greater than about 10, in the case of LFU, here examined, the possible reasons for an overestimate proposed by these authors do not seem to be valid.

Materials and methods

In hand specimen the T10 fiamme is dark brown, highly irregular rectangle which is up to 3 cm in length. Microscopic and modal analyses indicate that it consists mainly of orange to honey-yellow vesicular glass (97 vol. %) and, more rarely, phenocrysts (2.5 vol.%).

Quantitative analyses (Tables 1 and 2) have been conducted using a WDS system with a Cameca SX50 microprobe equipped with five spectrometers. The qualitative compositional mapping of the Ba-sanidine was performed with an EDS Link, AN 10000 85/S system connected to a Cameca, Camebax CX827 microprobe. The variable-composition colour images (not shown)

TABLE 1. Representative microprobe analyses of glass

Sample	T10	T10	T10	T10	Average
SiO ₂	47.08	46.43	47.08	47.20	46.95 (0.20)
TiO ₂	0.95	0.81	0.84	0.75	0.84 (0.05)
Al ₂ O ₃	19.86	19.74	19.89	19.78	19.82 (0.04)
FeO ^a	7.19	7.15	6.77	6.92	7.01 (0.11)
MnO	0.16	0.25	0.17	0.19	0.19 (0.02)
MgO	1.61	1.44	1.40	1.51	1.49 (0.05)
CaO	7.83	7.64	7.77	7.74	7.74 (0.05)
Na ₂ O	4.21	3.95	4.48	4.29	4.23 (0.13)
K ₂ O	8.34	8.45	8.73	8.62	8.53 (0.10)
BaO	0.22	0.22	0.27	0.19	0.23 (0.02)
SrO	0.38	0.41	0.48	0.29	0.39 (0.05)
P ₂ O ₅	0.30	0.24	0.24	0.24	0.25 (0.02)
Cl	0.21	0.21	0.22	0.21	0.21 (0.00)
F	0.45	0.56	0.67	0.80	0.62 (0.09)
Total	98.79	97.50	99.01	98.73	98.50

Numbers in the parentheses are standard deviations
a: total Fe as FeO.

were obtained with the program DIGIPAD from Link Analytical Limited.

Results

On the basis of the TAS classification system (Le Bas *et al.*, 1986) the T10 glass has a K-foid composition (Table 1 and Fig. 1) which is in agreement with the general chemistry of the glass in other LFU fiammes. For comparative purposes the average T10-glass analyses are plotted on a TAS diagram (Fig. 1), along with those of other flamme-glass samples collected from the LFU (Freda *et al.*, 1997). The representative point analyses of sample T10 glass reported in Table 1 show the unique chemical composition of this rock, which is characterised by a low SiO₂ and MgO content and an elevated Al₂O₃ and K₂O content; note that the low analytical sums are due to the lack of H₂O and because Fe is given as FeO. Due to the low MgO value (<2%) the LFU glass cannot be considered as a primitive ultrapotassic lithotype (Foley *et al.*, 1987). The average BaO content in the T10 glass is about 0.23 wt.% (Table 1) corresponding to 2060 ppm of Ba, which is slightly lower than that measured in the glasses of other LFU scorias.

The clinopyroxene of sample T10 (Freda *et al.*, 1997) is submillimetre in size, light green,

TABLE 2. Representative microprobe analyses of Ba-sanidine

Sample	T10	T10	T10	T10	T10
SiO ₂	54.07	53.12	54.04	54.37	54.74
Al ₂ O ₃	21.55	21.82	21.79	21.55	21.65
K ₂ O	10.11	9.87	9.89	9.85	9.64
Na ₂ O	1.34	1.37	1.24	1.21	1.25
BaO	11.33	11.57	11.77	11.40	11.78
SrO	1.22	1.02	1.05	1.54	1.28
Total	99.62	98.77	99.78	99.92	100.34
Cations					
Si	2.712	2.685	2.706	2.718	2.721
Al	1.274	1.300	1.286	1.269	1.268
K	0.647	0.636	0.632	0.628	0.611
Na	0.130	0.134	0.120	0.117	0.120
Ba	0.223	0.229	0.231	0.223	0.229
Sr	0.035	0.030	0.030	0.045	0.037
Total	5.021	5.014	5.005	5.000	4.986

Formula computed on the basis of 8 O.

ehedral, has a diopsidic composition which lacks zonation, is enriched in CaO, Al₂O₃, TiO₂ and FeO, is impoverished in SiO₂ and MgO, and has Cr₂O₃ values which are less than the analytical standard deviation. These compositional characteristics indicate crystallisation from a differentiated, potassium-alkaline magma.

Leucite is submillimetre in size, subhedral, has an almost stoichiometric composition (Freda *et al.*, 1997), a low Na₂O content and a slight SiO₂ deficiency. The SiO₂ deficiency is likely compensated by Fe³⁺ in the tetrahedral site which balances the bivalent Ba and Sr cations present in the alkaline ion sites.

In thin-section the Ba-K-feldspar is colourless, subhedral, of the order of 1 mm, and has one set of distinct cleavages with another, less well-defined set at approximately 90°. The position of the optic axis plane with respect to the two cleavage directions and the optic angle value of 2V_x ≈ 40–50° indicates that this is a high-temperature phase which can be defined, on a strictly optical basis, as normal symmetrical sanidine. The electron photomicrograph shown in Fig. 2, taken with Backscattered Secondary Electrons (BSE), shows the clear colour contrast between the feldspars and the glass. This contrast is due to the difference in the average atomic number of the elements in the two phases, which

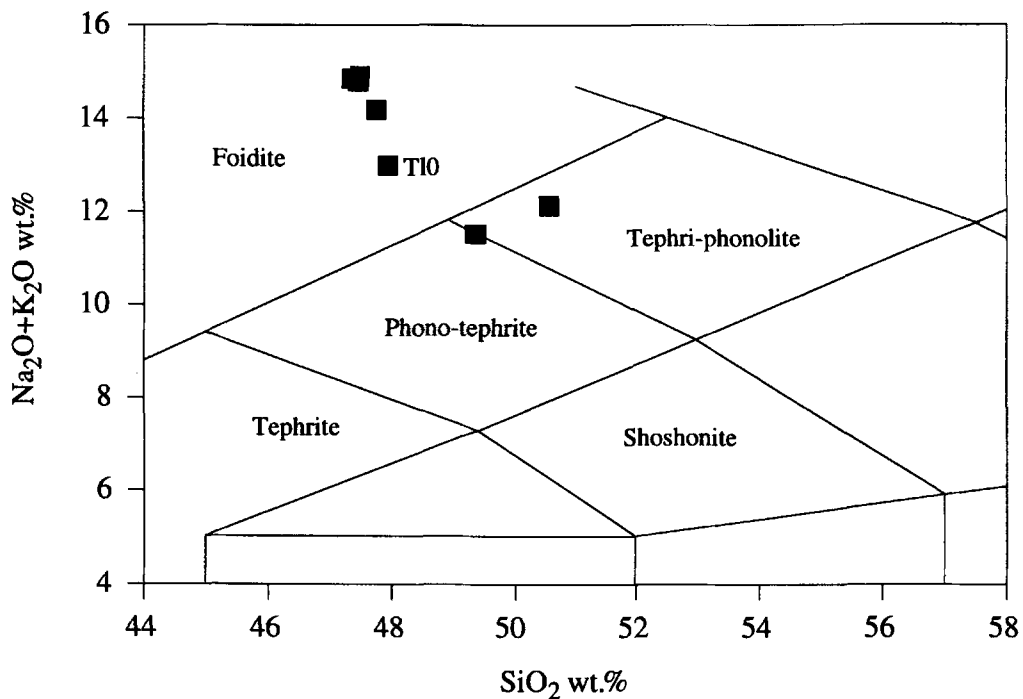


FIG. 1. Average T10-glass analyses plotted on a TAS diagram (Le Bas *et al.*, 1986), along with those of other fiamme-glass samples collected from the LFU (after Freda *et al.*, 1997).

is principally the result of the significant BaO content in the crystals. The qualitative spatial analyses of the amount of BaO and other oxides in the Ba-sanidine have shown the phase to be homogeneous, in agreement with the quantitative point analyses reported in Table 2. In addition, the microprobe analyses always gave CaO, FeO and MgO concentrations which were less than the analytical standard deviation. Based on a unit cell containing 8 oxygen atoms (Table 2), this feldspar is a solid solution having an average formula of $\text{Or}_{63}\text{Ab}_{12}\text{Cn}_{25}$. The Ba content of the sanidine in sample T10 is above the range reported by Smith and Brown (1988; Fig. 14.26) for volcanic alkaline feldspars; however, it is closer to that given for ultrapotassic-volcanic alkaline feldspars (Cundari, 1979; Holm, 1982; Van Kooten, 1980).

Discussion

The interpretation of Ba distribution between phenocrysts and groundmass is, in general, problematic due to the wide range of values often found in the same rock. In this study it should be pointed out that the rarity of alkali

feldspars in the pre-LFU hypabyssal rocks, lava flows and pyroclastic deposits of the Colli Albani

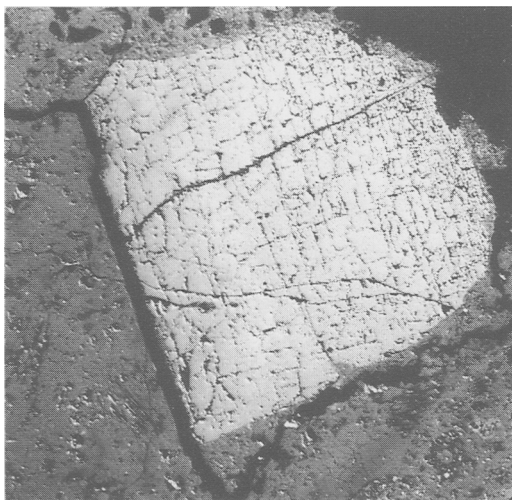


FIG. 2. Ba-sanidine electron photomicrograph, taken with BSE (horizontal field of view is 2 mm).

Volcanic District excludes the possibility that the Ba-sanidine found in the LFU fiamme is a xenocryst. Another indication of the equilibrium between the Ba-rich alkali feldspar and the glass of sample T10 comes from the comparison of the Ba content in sample T10 glass with that in other LFU fiamme glasses, which are (as already mentioned) systematically enriched in Ba (Freda *et al.*, 1997). On this basis, the knowledge of the BaO content in the Ba-sanidine and glass of sample T10 can give more information, with respect to that already discussed in the literature (Mahood and Hildreth, 1983; Guo and Green, 1989; Mahood and Stimac, 1990), on the variables that influence the Ba partition coefficient between alkali feldspars and glass. Characteristics which favour an accurate Ba-PC determination include the very low porphyricity of the T10 fiamme and, above all, the absence of compositional zoning in the Ba-sanidine.

Although the sample T10 has only a low percentage of phenocrysts and the feldspar lacks trace element zoning, the Ba-PC has the very high value of about 50. This value could not be related to the temperature (topic discussed by Guo and Green, 1989), to the melt polymerisation, or to the $(\text{Na}_2\text{O}+\text{K}_2\text{O})/\text{Al}_2\text{O}_3$ ratio (topics discussed respectively by Mahood and Hildreth, 1983; Mahood and Stimac, 1990). Indeed, the values of these parameters in the LFU could not explain the high Ba-PC because the LFU is a high-temperature liquidus with intermediate degree of polymerisation and a $(\text{Na}_2\text{O}+\text{K}_2\text{O})/\text{Al}_2\text{O}_3$ ratio below unity.

The incorporation of Ba in the sanidine (spatial group $C2/m$, lattice constant $c \approx 7 \text{ \AA}$) — celsian (non standard spatial group $I2/c$, lattice constant $c \approx 14 \text{ \AA}$) solid solution is regulated by $\text{BaAl} \rightleftharpoons \text{KSi}$ substitution, such that an increase of the Ba content results in a higher Al/Si ratio in the feldspar. This substitution is analogous to that observed in the $\text{NaAlSi}_3\text{O}_8$ – $\text{CaAl}_2\text{Si}_2\text{O}_8$ series, whereby a complete solid solution between two different structural domains and a doubling of the anorthite lattice constant results (Carpenter and Ferry, 1984).

Considering that during crystallisation the Al/Si ratio in the feldspar is certainly influenced, within the limits of aluminium incompatibility (Loewenstein, 1954), by the silica and aluminium activity of the melt, one can hypothesise the existence of a positive correlation between Ba-PC and the liquid $\text{Al}_2\text{O}_3/\text{SiO}_2$ ratio. Although no experiments were conducted during this work on verifying this positive correlation, some indica-

tions can be derived from the previously mentioned experimental work of Guo and Green (1989). A comparison of the starting glass compositions and the Ba-PC obtained experimentally by the two authors in an isothermal (950°C) and isobaric (15 kbar) plane appears to indicate a positive correlation between the barium partition coefficient and the $\text{Al}_2\text{O}_3/\text{SiO}_2$ ratio of the initial glass (Fig. 3), although the linear correlation coefficient is relatively low ($R = 0.762$) with respect to the number of interpolated points (8). Considering, however, that the experimental glass used by Guo and Green (1989) was not made to study this specific issue (i.e. Al_2O_3 and SiO_2 concentrations occur in a relatively narrow range) and that the correlation does not necessarily have to be linear, the available data do not preclude a positive correlation between Ba-PC and the $\text{Al}_2\text{O}_3/\text{SiO}_2$ ratio in the liquid (Fig. 3). This relationship indicates that the solid/liquid partition coefficient is also dependent upon the total composition of the system.

If the correlation is considered linear as a first approximation, the regression line in Fig. 3, extrapolated to the $\text{Al}_2\text{O}_3/\text{SiO}_2$ value of sample T10 glass (0.42), yields a Ba-PC value of 42. Considering the different crystallisation pressures of the two glasses (15 kbar for the experiments of Guo and Green, 1989; around 2 kbar for the LFU glass, Freda *et al.*, 1997) and its influence on the partition coefficient, this value is very close to that obtained from the analysis of the sample T10 phases (Ba-PC ≈ 50). An analogous qualitative correlation can be obtained from the Mahood and Stimac (1990) data; however, in this case, the regression line extrapolated up to the $\text{Al}_2\text{O}_3/\text{SiO}_2$

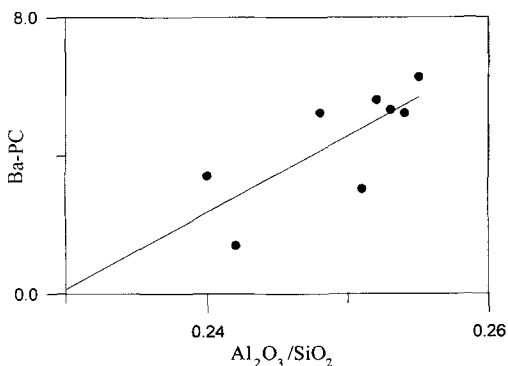


FIG. 3. Comparison of $\text{Al}_2\text{O}_3/\text{SiO}_2$ in the starting glass compositions and the Ba-PC obtained experimentally at 950°C and 15 kbar (data from Guo and Green, 1989).

value of sample T10 glass yields a Ba-PC lower than 42. This is due either to the previously-mentioned non-linear correlation or to the $(\text{Na}_2\text{O}+\text{K}_2\text{O})/\text{Al}_2\text{O}_3$ differences in the two datasets. Indeed, the compositions reported by Mahood and Stimac (1990) are strongly peralkaline; on the contrary, LFU and Guo and Green (1989) starting glasses have very similar $(\text{Na}_2\text{O}+\text{K}_2\text{O})/\text{Al}_2\text{O}_3$ ratios below unity.

Conclusions

The discovery of the Ba-sanidine in sample T10 confirms that the volcanic alkaline feldspars with the highest BaO content are associated with ultrapotassic rocks, in particular with those linked to Quaternary magmatism of Central Italy (Cundari, 1979; Holm, 1982). Aside from its primary petrological characteristics, however, this rock also has a clear negative Ba anomaly. The positive correlation between barium partition coefficient and the $\text{Al}_2\text{O}_3/\text{SiO}_2$ ratio in the liquid may give a valid explanation for this apparent contradiction, such that the highly Ba-enriched sanidine (11.5 wt.% BaO) of sample T10 could have been formed by a magma having high aluminium and low silica activity.

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