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The Macusani glasses, SE Peru: evidence of chemical fractionation in peraluminous magmas

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Abstract—The Pliocene non-hydrated obsidian glasses from Macusani, SE Peru, are associated with felsic peraluminous ash–flow tuffs of crustal origin. Several glasses have been analysed for their major, trace (37 elements) and isotopic compositions ($^{87}Sr/^{86}Sr$, $^{18}O/^{16}O$, D/H). They have a unique composition for obsidian glasses, similar to some rare-element pegmatites. The glasses represent a rare example of the preservation of lithophile-rich peraluminous melts as quenched glasses. The major element composition is characterized by moderately high SiO_2 ($\sim$72 weight percent), very high Al_2O_3 ($\sim$16 weight percent), high alkalies and particularly elevated concentrations in F ($\geq$1.3 weight percent), B_2O_3 (0.6 weight percent), Li_2O (0.7 weight percent) and P_2O_5 (0.5 weight percent). CaO, FeO_t, MgO and TiO_2 are very low. Trace elements show marked enrichments in Rb, Ta, U, As, Sn, Sb, W, Cs and also marked depletions in Sr, Ba, Pb, Mo, Th, LREE, Eu, Zr, Hf, Y. Two groups of glasses can be defined on the basis of field relations, major/trace elements and Sr and O isotopes. The Rb–Sr isochron age (4.9 Ma, initial $^{87}Sr/^{86}Sr$ about 0.7309, Chilcuno Chico samples) is in agreement with K–Ar and fission-track ages. Oxygen isotopic compositions are tightly grouped between 11.9 and 12.4‰. Hydrogen isotopic compositions (δD between -140 and -155‰) and their low H_2O^+ ($\leq$0.4 weight percent) suggest degassing. The discovery of inclusions of glasses in the ash–flow tuffs, the nearly identical mineralogy and mineral chemistry between tuffs and glasses and the chemical and isotopic data demonstrate a genetic filiation between these two rocks.

Experimental data in the Qz–Ab–Or system with added F, B and Li suggest that the glasses are residual liquids from the fractional crystallization of the tuffs. Enrichment/depletion patterns between tuffs and glasses are for the most part consistent with crystal fractionation of the observed phenocrysts. However, the behaviour of Al and P is unusual and relates to the specific structure of strongly peraluminous, F–, B–, P–, and H_2O–rich melts. The role of these elements in the formation of complexes in the liquid and in promoting depolymerization is emphasized.

INTRODUCTION

THE PRESENT DEBATE about chemical fractionation in felsic magmas is dominated by examples taken from the peralkaline and metaluminous series (*e.g.*, HILDRETH, 1979; BACON *et al.*, 1981; CRECRAFT *et al.*, 1981; MAHOOD, 1981; MICHAEL, 1983; CHRISTIANSEN *et al.*, 1984) with very few examples from peraluminous series (MITTLEFEHLDT and MILLER, 1983; PRICE, 1983; WHALEN, 1983; MICHAEL, 1984). However, felsic peraluminous rocks, such as the two-mica granites, are known for their markedly fractionated and distinctive chemical signatures, with enrichments in B, F, Li and trace elements Sn, W, U (*e.g.*, PICHAVANT and MANNING, 1984). Because most of these magmas crystallized as plutonic rocks, mechanisms and trends of fractionation patterns in felsic peraluminous magmas are not well defined. This situation could be significantly improved by studying felsic peraluminous volcanic series because they may provide naturally quenched eruption products (phenocrysts and glasses) that have not suffered postmagmatic alteration. Obsidian glasses are particularly interesting as they furnish relatively direct information regarding the composition of the silicate liquid in the magma chamber.

The Macusani volcanics, from SE Peru, are a rare example of a felsic peraluminous volcanic series. Here, we concentrate on the Macusani glasses (or macusanites). These are obsidian glasses spatially associated with the Pliocene ash–flow tuffs of the Macusani area. Although considered earlier as tektites (*e.g.*, LINCK, 1926 and discussion in BARNES *et al.*, 1970), recent studies have provided evidence of the volcanic origin of these glasses and of a close link with the ash–flow tuffs (BARNES *et al.*, 1970; FRENCH and MEYER, 1970; FRENCH *et al.*, 1978; KONTAK *et al.*, 1984b; NOBLE *et al.*, 1984; VALENCIA HERRERA *et al.*, 1984). The aim of this paper is to discuss the genetic relation between the ash–flow tuffs and the glasses. The following questions are specifically addressed: 1) are the ash–flow tuffs and the Macusani glasses comagmatic? 2) by what magmatic fractionation process are the glasses derived? 3) what are the implications for chemical fractionation in silicic magmas? The discussion is based on a comprehensive set of chemical data obtained on several glass samples, and on new field and mineralogical data.

THE MACUSANI GLASSES

The existence of the Macusani glasses (or macusanites) has been known for over half a century (BARNES *et al.*, 1970 and references therein; FRENCH and MEYER, 1970; FRENCH *et al.*, 1978; KONTAK *et al.*, 1984b; NOBLE *et al.*, 1984; VALENCIA HERRERA *et al.*, 1984). Because they were considered as possible tektites up to the late fifties, they have been principally discussed in the tektite literature (see *Geochim. Cosmochim. Acta,* 14, n° 4, 1958, *Special Issue on Tektites;* TAYLOR and EPSTEIN, 1962).

Macusanite occurrences are restricted to the region near Macusani, SE Peru. LINCK's (1926) "Paucartambo glass" probably comes from the Macusani area (see MARTIN and DE SITTER-KOOMANS, 1955). Geologically, the area belongs to the Western Cordillera in the Central Andes and forms part of the Inner Arc environment (CLARK *et al.*, 1984). This area differs from the Main Arc system because its magmatism is of dominantly crustal origin (CLARK *et al.*, 1984; KONTAK *et al.*, 1984a). In particular, the Western Cordillera experienced Miocene–Pliocene volcanic activity that produced peraluminous ash–flow tuffs deposited in three small tectonic basins: Macusani, Crucero and Ananea (LAUBACHER, 1978; see also BARNES *et al.*, 1970; NOBLE *et al.*, 1984; VALENCIA HERRERA *et al.*, 1984; PICHAVANT *et al.*, in prep.). BARNES *et al.* (1970) first suggested a field relation between the glass pebbles and the tuffs from the Macusani basin.

There are two main glass deposits, Caluyo Mayo and Chilcuno Chico, both of which lie at the eastern edge of the Macusani volcanic field. The first is localized within glacial moraine deposits (see map in BARNES *et al.*, 1970), whereas the second is situated in the tuff outcrop area. These two deposits are about 10 km apart. In both localities, macusanites are found as *pebbles* in stream gravels without any clear relation with the neighbouring tuffs. However, we have discovered for the first time several *inclusions* of macusanite in ash–flow tuffs from different localities. One of these inclusions was collected in a boulder of tuff near Chilcuno Chico (VALENCIA HERRERA, 1982, unpublished). Several other inclusions (Figure 1) have been found *in situ* in tuffs from the Chapi area, about 30 km from Chilcuno Chico, in the northwestern part of the volcanic field (BRIQUEU *et al.*, 1985, unpublished). These inclusions have been thus far discovered only in tuffs that belong to the upper cooling units. The glasses occupy small cavities lined with a white, kaolinite–rich layer (Figure 1).

Several petrographic descriptions of the Macusani glasses have been published (*e.g.*, MARTIN and DE SITTER–KOOMANS, 1955; BARNES *et al.*, 1970). The pebbles from the stream gravels have an ellipsoidal shape and are most frequently rounded. They have a variable but limited size and samples larger than 10 × 5 cm have not been found. One of the striking petrographical features of the Macusani glasses is their etched surface, which led to the confusion with tektites (see BARNES *et al.*, 1970). The glasses are either translucent–green, opaque milky–green or opaque red–brown in colour. In the opaque milky–green varieties, opacity is due to the presence of abundant fluid inclusions of strongly irregular shape. The red–brown varieties consist of a dense arrangement of red spots irregularly dispersed in a translucent green matrix. These red spots contain numerous minute opaque phases (size less than 1 μm), presumably Fe-oxides. Stratified specimens, with either red or milky–green bands and streaks in a translucent green matrix have been encountered. The inclusions found in the tuffs are similar in shape to the pebbles, although of generally smaller size ($\leq$2 cm). They also display a finely etched surface and are all of the translucent–green variety.

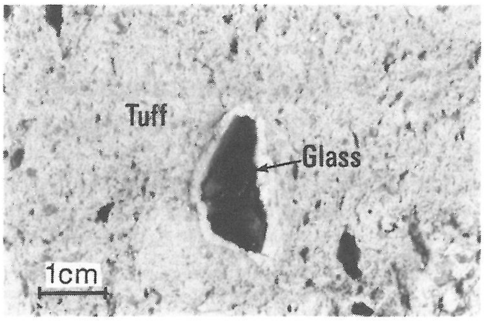

FIG. 1. Glass inclusion (sample CH0) in an ash–flow tuff, Chapi area. Note the kaolinite–rich white layer lining the cavity.

The Macusani glasses can be defined as non-hydrated obsidians (ROSS and SMITH, 1955). Although nearly aphyric, the amount of crystalline phases varies both within and between samples. All the glass pebbles studied contain a homogeneous distribution of andalusite needles (up to 3 mm long). The andalusite is euhedral, prismatic, pleochroic (colourless-pink) and optically and chemically is similar to that present in the ash–flow tuffs (BARNES *et al.*, 1970; KONTAK *et al.*, 1984b; NOBLE *et al.*, 1984; VALENCIA HERRERA *et al.*, 1984). Its modal abundance is low (a few crystals per thin section). Additional phases have been reported to occur (LINCK, 1926; FRENCH and MEYER, 1970; FRENCH *et al.*, 1978). All are discrete microphenocrysts (a few tens to hundred μm.). The andalusites, the microphenocrysts and the fluid inclusions define a flow banding parallel to the stratification of the stratified specimens. Although we have not attempted to determine the complete mineralogy of the glasses, the presence of virgilite (FRENCH *et al.*, 1978), quartz, sanidine ($Or_{68-71}Ab_{32-29}$), plagioclase ($Ab_{83-84}An_{11}Or_{5-6}$), and biotite (Al–, Fe– and F–rich) has been confirmed (detailed analyses in PICHAVANT *et al.*, in preparation). Sillimanite, ilmenite, zircon and monazite are mainly found as inclusions in the andalusites. The mineralogy of the glasses is nearly identical to that of the tuffs (KONTAK *et al.*, 1984b; NOBLE *et al.*, 1984; VALENCIA HERRERA *et al.*, 1984). In particular, there is a close similarity between the compositions of sanidines, biotites and andalusites in the glasses and in the tuffs. The plagioclase composition in the glasses is identical to the composition of the latest plagioclase phenocrysts in the tuffs. The glass inclusions in the tuffs are generally poorer in microphenocrysts than the pebbles; no andalusite has been found in our glass inclusions.

A consistent age of 4.3 Ma has been obtained for the Macusani glasses, both by K–Ar on the Caluyo Mayo samples (BARNES *et al.*, 1970, recalculated to new constants), and by the fission–track method (FLEISCHER and PRICE, 1964). Therefore, the Macusani glasses mark one of the younger volcanic events in the area because K–Ar dates of the tuffs (BARNES *et al.*, 1970; KONTAK *et al.*, 1984a; NOBLE *et al.*, 1984) indicate continuous (or semi-continuous) volcanic activity from about 10 Ma to 4 Ma. The young ages found for the glasses agree with the discovery of macusanite inclusions in tuffs from the upper units.

The most comprehensive analytical work has been carried out on two pebbles from Chilcuno Chico, JV1 of the translucent–green variety and JV2 of the opaque milky-green variety. CC2 is an additional sample (red variety) from the same deposit. JV3 is the glass inclusion in the tuff collected in the same district. Samples from the Caluyo Mayo deposit are CM1 (translucent–green), CM2 (red) and VB1 and VB2 (both of the translucent–green varieties, kindly provided by V. E. Barnes). CH0 and CH1 are two of the glass inclusions found in the Chapi area.

ANALYTICAL TECHNIQUES

Electron microprobe analyses were performed with a Camebax electron microprobe (University of Nancy I). Analytical conditions are: acceleration voltage 15 KV, sample current 6–8 nA, counting time on peak 6 sec., beam defocussed to 12–15 μm., silicate crystals as standards, and ZAF correction procedures. Because of the problem of loss of alkalies, Na_2O and K_2O were corrected slightly upwards. The correction factors were determined by analysing synthetic glasses of comparable compositions and volatile contents (PICHAVANT, 1984). Fluorine was analysed separately with longer counting time (10 sec. on peak) and higher sample current (40 nA) than for the major elements. To avoid complex ZAF corrections procedures for light elements, the raw counts for a given sample were averaged (usually from between 5 and 10 spots), then plotted against a calibration curve constructed from two standards (glass JV1 and an F-apatite) and the concentrations thus determined.

Several wet-chemical techniques, used routinely at the Centre de Recherches Pétrographiques et Géochimiques (CRPG), Nancy (CRPG Annual Report, 1984–1985), were employed for major elements, for Li (analytical error 1%), B (5%), F (2%) and for a number of trace elements, including Be (2%), Sn (3%), Zn (8%), Rb (3%), Cs (3%), Mo (25%), W (5%), As (4%), Cl (6%), and S (20%).

The instrumental neutron activation analyses were carried out at the Groupe des Sciences de la Terre, Laboratoire P. Sue, Saclay for Sc, Rb, Sb, Cs, Hf, Ta, W, Th, U, La (CHAYLA *et al.*, 1973; JORON, 1974, accuracy 5%). V, Cr, Co, Ni, Cu, Ba (microwave plasma emission spectroscopy, GOVINDARAJU *et al.*, 1976, accuracy 10%), Y, U, Th and the REE (ICP, GOVINDARAJU and MEVELLE, unpublished, 1983–1986, accuracy 10%) were analysed at CRPG. Ga was analysed by arc-emission spectroscopy at the Ecole Nationale de Géologie de Nancy (ENSG) (ROUILLIER, unpublished, accuracy 30%). Zn, Zr, Nb, Sn, W, Pb, were analysed by XRF at the University of Lyon (GERMANIQUE, unpublished, accuracy 5%).

Rb and Sr concentrations and Sr isotopic compositions were determined at CRPG (samples JV1, JV2, VB2) and at the University of Monpellier (samples CH0 and CH1). Details about techniques and accuracies can be found in ALIBERT *et al.* (1983), JUTEAU *et al.* (1984), and BRIQUEU and LANCELOT (1977).

Oxygen and hydrogen isotopic compositions were also determined at CRPG. Oxygen was extracted using the BrF_5 method with the conversion of the liberated oxygen to CO_2 gas. The data are reported as $\delta^{18}O$ values relative to SMOW. Reproductibility is better than 0.2‰. NBS-28 gives 9.60‰. The H_2O^+ content of the sample is derived from the manometrically measured yield of H_2 released after the removal of adsorbed water (*e.g.*, SHEPPARD and HAR-RIS, 1985). For the hydrogen isotopic compositions, reproducibility is better than 2‰.

RESULTS

Major elements

The new whole–rock analyses for two glass pebbles (Table 1) are more complete and also more accurate than previous analyses (BARNES *et al.*, 1970; ELLIOTT and MOSS, 1965; see also MARTIN and DE SITTER–KOOMANS, 1955 and LINCK, 1926). The older analyses, however, are relatively similar to our results. The two new whole–rock analyses are identical within analytical error. The electron microprobe analysis of JV1 (Table 2) is also in good agreement with the whole–rock data. All of the analysed glass pebbles, from either Chilcuno Chico or Caluyo Mayo yielded essentially identical electron microprobe results within error, except for the opaque red–brown varieties (Table 2). In the latter glasses, the translucent–green zones are compositionally similar to the other pebbles (Table 2, columns 2 and 4). However, the red spots show an important, though variable increase of FeO_t relative to the other oxides (Table 2, column 5), interpreted to result from variable contamination of the glass because of the heterogeneous distribution of the opaque phases. Apart from these red patches, all of the glass pebbles define a chemically homogeneous population, both at the macroscopic and microscopic scale.

The composition of the analysed glass inclusions (Table 2) contrasts with that of the pebbles. JV3 is only slightly different (lower SiO_2, FeO_t, higher Al_2O_3, Na_2O, F, Table 2, column 6), but the compositions of the two glass inclusions from Chapi (Table 2, column 7 and 8) are markedly distinct from all the other analysed glasses (including pebbles and JV3), principally by their higher (K_2O + Na_2O), lower molar $Al_2O_3/(CaO + Na_2O + K_2O)$, or A/CNK, and their variable (and generally higher) F contents. In addition, there are marked differences between the composition of CH0 and CH1 (reversed Na_2O/K_2O ratio, different F contents).

Taken as a whole, the major element composition of the Macusani glasses are characterized by moderate to low SiO_2, high to very high Al_2O_3, high alkalies, F, Li, B, P, and low FeO_t, MgO, TiO_2, CaO,

Table 1. Whole-rock analyses (weight percent)

	JV1[1] pebble	JV2[1] pebble	3[2] pebble	4[3] pebble	MH3[4] tuff
SiO_2	72.26	72.32	72.8	71.6	73.43
Al_2O_3	15.83	15.85	16.3	16.7	14.35
Fe_2O_3	0.04	0.05	0.29	—	—
FeO	0.57	0.56	0.30	0.6[5]	1.13[5]
MnO	0.06	0.06	0.04	0.05	0.04
MgO	0.02	0.02	0.00	tr.	0.20
CaO	0.22	0.21	0.16	0.4	0.50
Na_2O	4.14	4.13	4.1	4.7	3.37
K_2O	3.66	3.64	3.7	3.6	4.54
TiO_2	0.04	0.04	0.02	0.04	0.13
P_2O_5	0.53	0.53	0.55	0.4	0.36
B_2O_3[6]	0.62	0.60	—	0.4	0.031
Li_2O[7]	0.74	0.74	0.8	—	0.17
F[8]	1.33	1.30	—	1.4	0.41
CO_2	0.09	0.06	0.10	—	1.51
H_2O^+	0.46	0.40	0.70	0.2	
H_2O^-			0.00	—	
Total	100.61	100.51	99.06	100.89	100.17
O ≡ F	0.56	0.55	—	0.59	0.17
Total	100.05	99.96	—	100.30	100.00

[1] New analyses; average of two duplicates–Glasses from Chilcuno Chico.

[2] From BARNES *et al.* (1970)–Glass from Caluyo Mayo.

[3] From ELLIOTT and MOSS (1965)—Glass of unspecified provenance.

[4] From PICHAVANT *et al.* (in preparation).

[5] Total Fe as FeO.

[6] For VB1, B_2O_3 = 0.63 weight percent; for VB2, B_2O_3 = 0.62 weight percent.

[7] For VB1, Li_2O = 0.73 weight percent; for VB2, Li_2O = 0.75 weight percent.

[8] For VB1 and VB2, F = 1.30 weight percent.

Table 2. Electron microprobe analyses of the Macusani glasses (weight percent)

	JV1[1] pebble	CC2[2] pebble	CM1[3] pebble	CM2[4] pebble	CM2[5] pebble	JV3[6] inclusion	CH0[7] inclusion	CH1[8] inclusion
SiO_2	72.26(0.51)	72.69(0.25)	72.29(0.46)	72.31(0.20)	71.95	70.54(0.36)	70.38(0.20)	69.69(0.23)
Al_2O_3	15.79(0.22)	16.00(0.16)	15.92(0.05)	15.75(0.05)	15.62	16.31(0.04)	16.26(0.06)	16.30(0.13)
FeO	0.54(0.05)	0.56(0.04)	0.59(0.05)	0.47(0.02)	2.75	0.38(0.03)	0.30(0.05)	0.38(0.06)
MnO	0.03(0.03)	0.03(0.03)	0.08(0.08)	0.04(0.03)	0.12	n.d.	n.d.	0.09(0.05)
MgO	0.02(0.03)	0.01(0.00)	0.02(0.01)	0.01(0.01)	0.03	0.02(0.01)	0.01(0.01)	0.00(0.01)
CaO	0.19(0.03)	0.10(0.10)	0.19(0.03)	0.15(0.01)	0.26	0.17(0.02)	0.14(0.02)	0.14(0.02)
Na_2O	4.29(0.14)	4.30(0.09)	4.32(0.04)	4.27(0.14)	3.93	4.42(0.05)	5.15(0.05)	4.63(0.08)
K_2O	3.83(0.06)	3.77(0.01)	3.74(0.09)	3.88(0.01)	3.56	3.70(0.03)	4.41(0.06)	5.36(0.09)
TiO_2	0.07(0.06)	0.00(0.00)	0.02(0.01)	0.04(0.01)	0.00	0.01(0.02)	0.02(0.02)	0.00(0.01)
F[10]	1.33[9]	1.27(0.03)	1.35(0.02)	1.33(0.02)	1.27(0.03)	1.92(0.04)	1.88(0.04)	1.68(0.06)
Total	98.35	98.73	98.52	98.25	99.49	97.47	98.55	98.27
O ≡ F	0.56	0.53	0.57	0.55	0.53	0.81	0.79	0.71
Total	97.79	98.20	97.95	97.70	98.96	96.66	97.76	97.56

[1] Average of 5 spots. Translucent green glass from Chilcuno Chico.

[2] Average of 2 spots. Opaque red-brown glass from Chilcuno Chico, preserved green zones.

[3] Average of 2 spots. Translucent-green glass from Caluyo Mayo.

[4] Average of 2 spots. Opaque red-brown glass from Caluyo Mayo, preserved green zones.

[5] Red zone. Same glass as[4].

[6] Average of 4 spots. Glass inclusion in ash-flow tuff, Chilcuno Chico area.

[7] Average of 4 spots. Glass inclusion in ash-flow tuff, Chapi area.

[8] Average of 5 spots. Glass inclusion in ash-flow tuff, Chapi area.

[9] From Table 1.

[10] Analyzed separately (see text). Average of between 5 and 10 spots per sample.

Fe_2O_3/FeO. Also note the low FeO_t/MnO ratio and the $Na_2O/K_2O > 1$ (CH1 being excepted). Such a composition resembles that of a felsic, strongly peraluminous, volatile–rich granitic magma, similar to some leucogranites (*e.g.*, LE FORT, 1981; PICHAVANT and MANNING, 1984; BENARD *et al.*, 1985) and granitic pegmatites (STEWART, 1978; CERNY, 1982). The felsic character of the macusanites is best evidenced by their CIPW composition (more than 90 weight percent normative Qz + Ab + Or). Normative corundum (Co) reaches 5 weight percent with only a very small part accounted for by the presence of andalusite phenocrysts.

A unique feature is the concentration of F, B, Li and P. The glass pebbles, from either Chilcuno Chico or Caluyo Mayo, are homogeneous in terms of F, B and Li. The F contents reach 1.3 weight percent in the pebbles (Tables 1 and 2) and increases up to 1.9 weight percent (Table 2) in the glass inclusions, a range similar to those found for some ongonites (KOVALENKO and KOVALENKO, 1976), topaz rhyolites (CHRISTIANSEN *et al.*, 1983; 1984), topaz granites (PICHAVANT and MANNING, 1984) and rare–element pegmatites (*e.g.*, CERNY, 1982). The Li_2O contents (0.73–0.75 weight percent, Table 1) are only available for 5 glass pebbles; they are in a range comparable to the rare–element pegmatites (STEWART, 1978; CERNY, 1982; CERNY *et al.*, 1985). The Macusani glasses (data for 5 pebbles) have the highest B_2O_3 content ever reported for a natural glass (0.60–0.63 weight percent, Table 1). Elevated, though lower, B_2O_3 concentrations are found in tourmaline granites, aplites and pegmatites (*e.g.*, NEMEC, 1978; PICHAVANT and MANNING, 1984; CERNY, 1982). The very high P_2O_5 (0.53 weight percent, Table 1) is comparable to that found in topaz granites (PICHAVANT and MANNING, 1984), and rare–element pegmatites (CERNY, 1982; LONDON, 1987) and exceeds the amount of CaO (about 0.2 weight percent). On the other hand, the H_2O content (H_2O^+: 0.23 weight percent, FRIEDMAN, 1958; 0.16 to 0.40 weight percent, Table 5; H_2O_t: 0.40–0.46 weight percent, Table 1) is low, in agreement with that expected for a non–hydrated obsidian (ROSS and SMITH, 1955). LONDON (1987 and written communication) reports higher H_2O contents (1.1 weight percent) for a translucent–green glass analysed by ion microprobe.

As pointed out by previous workers (BARNES *et al.*, 1970; NOBLE *et al.*, 1984; VALENCIA HERRERA *et al.*, 1984), the major element composition of the adjacent ash–flow tuffs (Table 1) compares in many aspects with that of the macusanites: moderate SiO_2, very high Al_2O_3, high alkali, Li, B, F and P, low FeO_t, MgO, TiO_2, and CaO. However, significant differences appear (inversion of the Na_2O/K_2O ratio from the tuffs to the glasses). The ash–flow tuffs (data from PICHAVANT *et al.*, in preparation) and the glasses (Tables 1 and 2) plot in separate fields on a Qz–Ab–Or diagram (Figure 2).

Trace elements

The new analyses (Tables 3, 4 and 5) present a nearly complete trace element data base. Where available, earlier data (BARNES *et al.*, 1970) are also reported for comparison. Except for a few elements, the agreement between the two sets of data is rather poor. In the present study, several elements (Zn, Rb, Sn, Cs, W, Th, U) have been duplicated or triplicated with good agreement among the various techniques.

The analysed glass pebbles yield strikingly similar values (Tables 3, 4 and 5). A further check of the homogeneity of these glass pebbles is provided by the Rb data; the high values all lie within a narrow bracket (Table 5). In contrast, Rb analyses of two glass inclusions from Chapi yielded distinctly higher values (Table 5).

Compared to normal silicic rocks (*e.g.*, low–Ca granites, TUREKIAN and WEDEPOHL, 1961), the macusanites are enriched in As, Rb, Sn, Sb, Cs, Ta, W, Zn, Nb, U, Be, Ga, and are in the same range

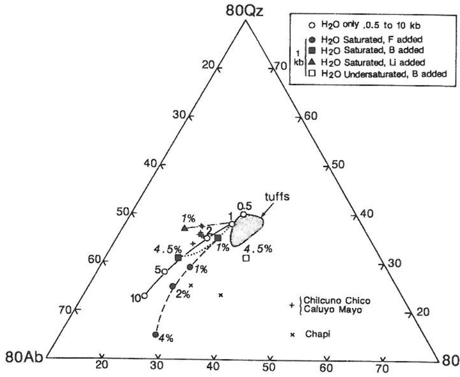

FIG. 2. CIPW normative composition of the Macusani glasses (+ : samples from Chilcuno Chico and Caluyo Mayo; × : samples from Chapi). The CIPW normative compositions of the tuffs (stippled field) are shown for comparison (data from PICHAVANT *et al.*, in preparation). For the glasses, both whole-rock (Table 1) and electron microprobe data (Table 2) have been plotted. Minima and eutectic compositions in the Qz–Ab–Or system taken from LUTH (1976), MANNING (1981), MARTIN (1983), PICHAVANT (1984), PICHAVANT and RAMBOZ (1985a,b). The experimental points for H_2O only (LUTH, 1976) are labelled with pressure from 0.5 to 10 kbar. All the other experimental points are labelled with concentrations (weight percent) of either F, Li_2O, or B_2O_3 in the melt.

Table 3. Trace element composition (ppm)

	JV1 pebble	JV2 pebble	3[7] pebble	MH3[8] tuff	1[9] tuff
Be	41.1[1]	41.3[1]	—	—	37
S	60[1]	70[1]	—	80	—
Cl	427[1]	446[1]	—	49	—
Sc	2.2[2]	2.4[2]	<3	3.0	2.76
V	<10[3]	14[3]	—	13	4.5
Cr	<10[3]	<10[3]	10	<10	15–1.7
Co	0.71[2]	0.71[2]	—	1.5	1.13
Ni	<10[3]	<10[3]	—	<10	—
Cu	<10[3]	<10[3]	4	<10	3.7
Zn	92[4]–97[1]	96[4]–95[1]	80	69	111–83
Ga	42.4[5]	43.0[5]	45	—	40
As	314[1]	325[1]	130	—	73
Rb	see Table 5	see Table 5	890	549	488
Sr	see Table 5	see Table 5	—	88	115
Y	5.16[6]	4.89[6]	—	8.89	—
Zr	39[4]	34[4]	15	72	23
Nb	44[4]	47[4]	—	20	—
Mo	0.4[1]	0.4[1]	<5	0.2	2–<1
Ag	—	—	0.17	—	—
Sn	155[4]–194[1]	203[4]–202[1]	—	46	45–60
Sb	3.6[2]	3.5[2]	—	0.66	2.0
Cs	566[1]–516[2]	571[1]–524[2]	400	91.8	118
Ba	<10[3]	<10[3]	<50	246	340–270
Hf	<2[2]	<2[2]	—	2.7	2.99
Ta	26.9[2]	26.7[2]	—	5.1	6.28
W	62[4]—73[1]–59[2]	69[4]–73[1]–60[2]	—	9.3	<4
Tl	—	—	18	—	2.0
Pb	7[4]	10[4]	14	30	52–35
Bi	—	—	1	—	<5
Th	2.3[6]–0.064[2]	1.7[6]–0.11[2]	—	9.1–8.6	14.6–11
U	18.8[6]–23.1[2]	20.3[6]—31.7[2]	—	6–11.3	10.2

[1] Wet chemical techniques.
[2] Instrumental neutron activation.
[3] Microwave plasma emission spectroscopy.
[4] X-ray fluorescence.
[5] Arc emission spectrometry.
[6] Inductively coupled plasma emission spectroscopy.
[7] From Barnes *et al.* (1970).
[8] From Pichavant *et al.* (in preparation).
[9] From Noble *et al.* (1984).

Table 4. REE composition (ppm)

	JV1 pebble	JV2 pebble	MH3[3] tuff	1[4] tuff
La	1.92[1]–1.3[2]	1.21[1]–1.7[2]	14.45	19.8
Ce[1]	4.52	3.06	29.57	—
Sm[1]	0.86	0.51	2.95	3.47
Eu[1]	0.02	0.03	0.41	0.62
Gd[1]	0.72	0.63	2.35	—
Dy[1]	0.79	0.85	1.66	—
Er[1]	0.35	0.40	0.87	—
Yb[1]	0.39	0.40	0.70	0.81
Lu[1]	0.06	0.06	0.11	—

[1] Inductively coupled plasma emission spectrometry.
[2] Instrumental neutron activation.
[3] From Pichavant *et al.* (in preparation).
[4] From Noble *et al.* (1984).

or depleted in Cl, Y, V, Cr, Ni, Cu, Mo, S, Sr, Zr, Ba, Hf, Pb, Th. The data of Barnes *et al.* (1970 and Table 3) also suggest enrichments in Ag, Tl and Bi. Cohen (1960) found a concentration of 5 ppm Ge for a Macusani glass which also implies a Ge enrichment compared to normal silicic rocks.

The Rb, Ta (26–27 ppm, same value given by Noble *et al.*, 1984), U (18–32 ppm, 18 ppm according to Friedman, 1958), Ga (42–43 ppm) and Be (41–42 ppm) values (Table 3) are in the range found for some of the most differentiated silicic rocks on Earth such as ongonites (Kovalenko and Kovalenko, 1976), topaz rhyolites (Christiansen *et al.*, 1983, 1984) and rare-element pegmatites (Cerny *et al.*, 1985). The Nb (44–47 ppm) and Zn (92–97 ppm) both lie in the lower range of values

Table 5. Rb, Sr concentrations and isotopic compositions

	JV1 pebble	JV2 pebble	VB1 pebble	VB2 pebble	CM2 pebble	CH0 inclusion	CH1 inclusion	Qtz[1]
Rb (ppm)	1151[2]–1177[3]–1166[4]	1153[2]–1168[3]–1171[4]	1166[4]	1179[2]–1179[4]	—	1424[2]	1377[2]	—
Sr (ppm)	1.62[2]	1.30[2]	—	1.41[2]	—	4.13[2]	3.97[2]	—
$^{87}Sr/^{86}Sr$	0.87356 ± 6	0.91060 ± 9.5	—	088260 ± 6	—	0.76875 ± 5	0.76928 ± 24	—
$\delta^{18}O$ (‰)	12.2 ± 0.2	12.1	12.4 ± 0.1	—	11.9	12.1 ± 0.1	—	12.7 ± 0.1
H_2O^+ (weight percent)	0.22	0.16	0.40	—	—	—	—	—
δD (‰)	−155 ± 6	−143	−140 ± 3	—	—	—	—	—

[1] Quartz separated from the tuff hosting the glass inclusion CH0.
[2] Isotopic dilution.
[3] Instrumental neutron activation.
[4] Wet chemical techniques.

for ongonites or topaz rhyolites but remain lower than in peralkaline rhyolites (*e.g.*, NICHOLLS and CARMICHAEL, 1969; BARBERI *et al.*, 1975; MAHOOD, 1981). The As (310–330 ppm), Sn (150–200 ppm range), Sb (3–4 ppm), Cs (510–570 ppm, 500–540 ppm, NOBLE *et al.*, 1984), and W (60–90 ppm range) all display values well above those found in topaz rhyolites and ongonites; some of these elements are in the range found in rare-element pegmatites (CERNY, 1982; CERNY *et al.*, 1985).

Unlike the above elements, Sr (1–2 ppm for the pebbles, about 4 ppm for the Chapi inclusions), Ba (<10 ppm), Pb (7–10 ppm), Sc (2–3 ppm), Y (4–6 ppm) as well as Co, V, Cr, Ni and Cu (Table 3) are all depleted to levels similar to those found in ongonites, topaz rhyolites and peralkaline rhyolites. The S content (60–70 ppm) is very low, and the Cl content (420–450 ppm) is not as high as expected from the F contents; it is in the range found for ongonites (KOVALENKO and KOVALENKO, 1976) and calc–alkaline rhyolites (HILDRETH, 1979) but remains lower than in topaz rhyolites (CHRISTIANSEN *et al.*, 1984). The Cl is one order of magnitude lower than in peralkaline rhyolites (*e.g.*, CARMICHAEL, 1962). The Mo (0.4 ppm), Th (1–3 ppm), Zr (30–40 ppm) and Hf (<2 ppm) all are depleted in the macusanites compared to the ongonites, topaz rhyolites, calc–alkaline rhyolites (Bishop Tuff) and peralkaline rhyolites. In particular, the behaviour of Mo contrasts with that of W. F/Cl (30–40), Rb/Sr (1000), and W/Mo (150–225) are markedly elevated while Nb/Ta (1.7), Th/U (0.03–0.1) and Zr/Hf (17–20) are notably low.

The chondrite–normalized REE patterns (Table 4) are shown on figure 3 where they are compared with an ash-flow tuff (MH3, Table 4), a topaz rhyolite (CHRISTIANSEN *et al.*, 1984), and an aplite from the Manaslu leucogranite massif (VIDAL *et al.*, 1982). The two analysed glass pebbles have very low total REE (below 10 × chondrites) and their normalized patterns are similar. They are flat (La/Lu = 2–4) and have a marked Eu anomaly (Eu/Eu* = 0.08–0.16). Such a pattern is similar to the Manaslu aplite but contrasts with both the topaz rhyolites (higher total REE, lower Eu/Eu*) and the Macusani tuffs (higher total REE, Eu/Eu* and La/Lu).

Patterns of chemical fractionation between the tuffs and the glasses have been calculated by dividing the concentration in JV1 by the corresponding concentration in MH3 or 1 (Tables 1, 3 and 4). This is a somewhat arbitrary method as the tuffs probably are not exactly representative of their parental magma. Nevertheless, major element ratios calculated from two glasses (JV3/JV1) conform with

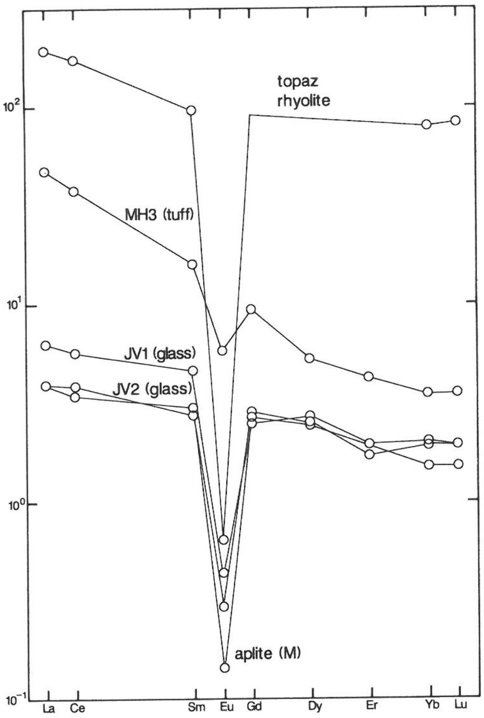

FIG. 3. REE composition of two Macusani glasses (Table 4), compared to a topaz rhyolite (CHRISTIANSEN *et al.*, 1984) and a Manaslu aplite (VIDAL *et al.*, 1982). Concentrations are normalized to 0.83 Leedey chondrite.

those calculated from JV1/MH3. Such patterns (Figure 4) show both marked similarities and differences with those defined for calc–alkaline rhyolites (Bishop Tuff, HILDRETH, 1979) and topaz rhyolites (CHRISTIANSEN *et al.*, 1984). Elements that conform to the variations observed in calc–alkaline and topaz rhyolites include Li, B, F, Cl, Be, Na, Mn, Rb, Nb, Sn, Sb, Cs, Ta, W, Mo, U (enriched), and Mg, K, Ca, Ti, Fe, Co, Sr, Zr, Ba, LREE, Eu and Hf (depleted). On the other hand, Al and P (enriched), Y, Th and the HREE (depleted) are reversed compared to both Bishop Tuff and topaz rhyolites. The Sc and Pb are depleted in Macusani glasses (also Sc in topaz rhyolites) whereas they are enriched in the Bishop Tuff. The Zn appears slightly enriched in the Macusani glasses as opposed to the Bishop Tuff. Thus, fractionation patterns are, for most elements, identical in the peraluminous Macusani volcanics and in the calc–alkaline and topaz rhyolites. However, there is poor agreement (Figure 4) in the relative enrichments (see for example Be, Cl, Nb, Sn, Ta, W, U), whereas there is good agreement in the relative depletions; in the three example considered, Sr, Ba and Eu are the most depleted trace elements. As noted previously for the Bishop Tuff (HILDRETH, 1979) and for the topaz rhyolites (CHRISTIANSEN *et al.*, 1984), the peraluminous Macusani volcanics show large enrichments or depletions in the trace elements but only very minor changes in the major elements.

Isotopic compositions

Rb–Sr data have been obtained for both Chilcuno Chico and Caluyo Mayo pebbles and for the two Chapi inclusions (Table 5). The data can be divided into two groups. An isochron age calculated from the two pebbles from Chilcuno Chico yields 4.9 Ma (error interval 4.2–6.1 Ma, calculated with an experimental uncertainty of 2% on the $^{87}Rb/^{86}Sr$), in agreement with the 4.3 ± 1.5 Ma K–Ar age (Caluyo Mayo samples, BARNES *et al.*, 1970) and with the 4.3 ± 0.4 Ma fission track age (FLEISCHER and PRICE, 1964). There is a large error on the initial $^{87}Sr/^{86}Sr$ ratio (0.73097) due to the markedly elevated $^{87}Rb/^{86}Sr$ values. The third glass pebble (Caluyo Mayo) lies slightly outside the isochron. By assuming an initial $^{87}Sr/^{86}Sr$ ratio identical to the other pebbles, its calculated age is 4.4 Ma, in excellent agreement with the K–Ar and fission track ages. One possible hypothesis is that the glass pebbles are cogenetic, the Caluyo Mayo samples having a slightly different cooling history than the others. On the other hand, the two Chapi inclusions (nearly identical within error) plot off the isochron for the pebbles, even if account is taken of the experimental errors. Therefore, the Chapi inclusions cannot have both the same age and initial $^{87}Sr/^{86}Sr$ ratio as the pebbles. Given the field relations and the major and trace element data, it is likely that the Chapi inclusions and the Chilcuno Chico/Caluyo Mayo samples have different initial $^{87}Sr/^{86}Sr$ ratios and are not cogenetic. Preliminary Rb–Sr data on the tuffs (KONTAK *et al.*, 1984b; NOBLE *et al.*, 1984; PICHAVANT *et al.*, in preparation) indicate that they have high initial $^{87}Sr/^{86}Sr$ (0.723). Further Sr isotopic data are clearly required, for both tuffs and glasses, to constrain more tightly the genetic relation between tuffs and glasses and between the different glasses.

The oxygen isotopic composition of the glasses is listed on Table 5. The $\delta^{18}O$ values of four pebbles range from 12.4 to 12.1, mean 12.2, and the single glass inclusion at 11.9 is thus slightly less enriched in ^{18}O. These results are in agreement with an earlier analyses of a pebble ($\delta^{18}O = 12.0$, TAYLOR and EPSTEIN, 1962). Because these non-hydrated obsidians have not suffered any postmagmatic alteration, the $\delta^{18}O$ values are likely to represent the oxygen iso-

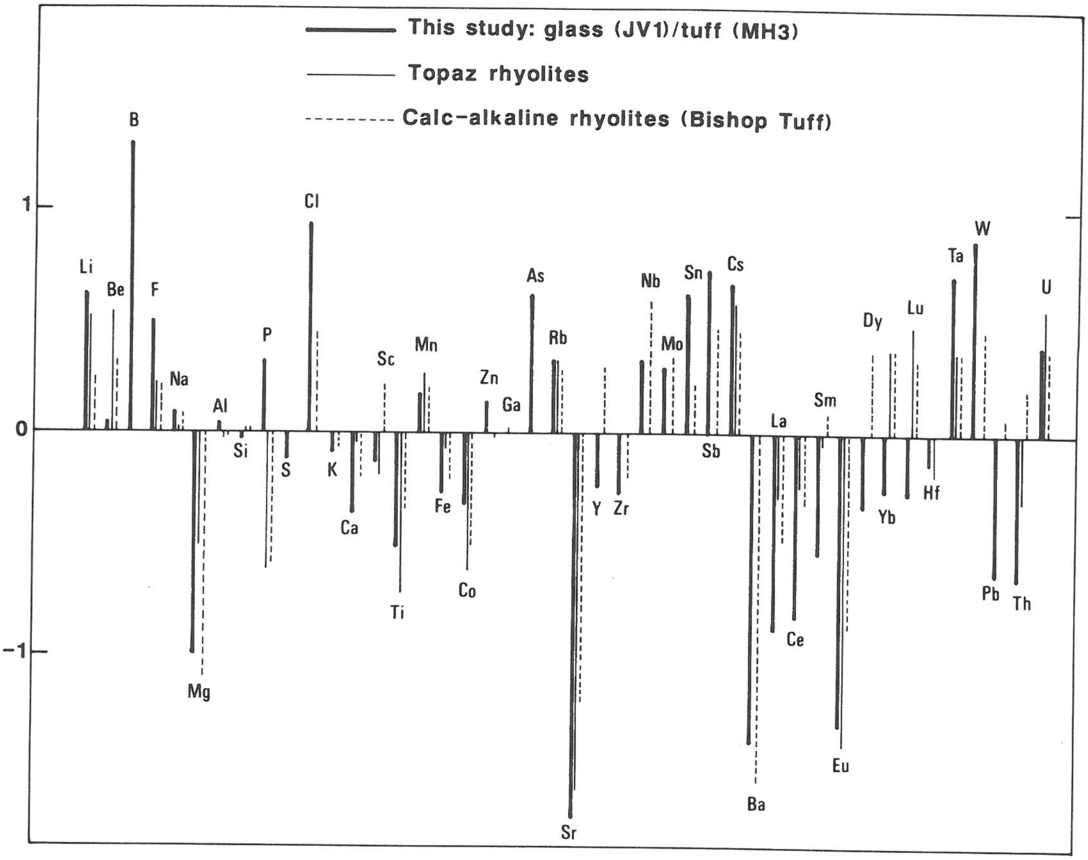

FIG. 4. Enrichment/depletion patterns for the peraluminous Macusani volcanics, calculated as log (concentration in glass JV1/concentration in tuff MH3), (data in Tables 1, 3, 4 and 5) and compared with topaz rhyolites (CHRISTIANSEN *et al.*, 1983, 1984) and calc–alkaline rhyolites (Bishop Tuff, HILDRETH, 1979).

topic composition of the parental magma. Additionally, the fractionation of oxygen isotopes between the glass inclusion and quartz from the host tuff (Table 5) is that expected if the glass parental melt and the quartz were once at equilibrium (TAYLOR, 1968; TAYLOR and TURI, 1976). Oxygen isotope analyses, reported by NOBLE *et al.* (1984), of minerals from other ash–flow tuffs in the region are similarly high in ^{18}O.

The oxygen isotope data strongly support a genetic filiation between the tuffs and glasses. However, the small difference between $\delta^{18}O$ of the pebbles and inclusion are consistent with the other chemical and isotope data that the pebbles and inclusions are not cogenetic.

The Macusani glasses belong to TAYLOR's (1968) high ^{18}O HH–group of igneous rocks and such values are characteristic of peraluminous magmas (SHEPPARD, 1986). Although there are relatively few published studies on high ^{18}O volcanic rocks, comparable or higher oxygen isotopic compositions are known in rhyolites/rhyodacites from the Tuscan volcanic province (TAYLOR and TURI, 1976), in the Banda Arc (MAGARITZ *et al.*, 1978) and in the Neogene volcanics from SE Spain (MUNKSGAARD, 1984).

Hydrogen isotope compositions are listed in Table 5. The δD values are very low and cover a range between −140 and −155‰. FRIEDMAN's (1958) value of 0.0127 mole percent D converts to a δD value of about −175‰ with a large uncertainty. Macusanites have not experienced any hydration by meteoric water as in perlites. Consequently, the δD numbers apply to magmatic water held in solution within the glass. Similarly low δD values in obsidians have been reported by TAYLOR *et al.* (1983) and were attributed to the degassing of the magma prior to and during the eruption. This interpretation is consistent with the very low H_2O^+ contents found for the Macusani glasses and mineralogical evidence that the H_2O^+ content of the parental magmas were higher (see below).

DISCUSSION

The discovery of inclusions of macusanites in ash–flow tuffs and the nearly identical mineralogy and mineral chemistry between coexisting tuffs and glasses, based on the comprehensive set of chemical and isotopic data presented here, lead us to conclude that 1) the tuffs and their glass inclusion are cogenetic, and 2) all the glass pebbles and inclusions, although not cogenetic, have shared a common magmatic evolution with the tuffs. Similar but less rigorously constrained conclusions were reached by BARNES *et al.* (1970) who suggested that the Macusani glass pebbles and ash–flow tuffs originated during the same volcanic episode, on the basis of similarities in age, chemical composition and mineralogy (*e.g.*, presence of andalusite in both rocks) and by NOBLE *et al.* (1984) who also related the glass pebbles to the tuffs that they studied. We now concentrate on fractionation processes that relate the glasses and the tuffs.

Application of experimental data in the Qz–Ab–Or system

Phase relations in the haplogranite system Qz–Ab–Or strongly depend on bulk chemical composition. The Macusani glasses contain elevated concentrations of components such as F, Li, B, Al, P that may change the phase relations in the Qz–Ab–Or system. The presence of F, Li, B can be taken into account as the individual effect of these components are known experimentally (MANNING, 1981; MARTIN, 1983; PICHAVANT, 1984; PICHAVANT and RAMBOZ, 1985a,b). Concentrations of Al_2O_3 in large excess of that required to form feldspars shift the minimum liquidus compositions towards the quartz apex (BURNHAM and NEKVASIL, 1986). In addition, rocks with high normative corundum can give misleading plots in the Qz–Ab–Or system (too low in normative quartz). On the other hand, the role of P can not be evaluated due to the lack of experimental data. Nevertheless, the low FeO_t, MgO, TiO_2 and CaO contents of the macusanites make the use of the Qz–Ab–Or system particularly appropriate.

An unknown when trying to apply the experimental data is the H_2O content of the macusanite parental liquid. The hydrogen isotope data imply that degassing occurred. This is consistent with the presence of fluid inclusions which indicate that vesiculation of the liquid took place. The red spots and streaks (oriented parallel to the planes of fluid inclusions) are zones of localized oxidation that may possibly be related to the exsolution of vapour phase (CANDELA, 1986). The rim of whitish material around the glass inclusions (Figure 1) suggests that degassing continued after the deposition. Therefore, the low H_2O contents (Tables 1 and 5) are considered to be unrepresentative of the H_2O contents during magmatic evolution. The H_2O contents were quite high as indicated by the presence of muscovite phenocrysts in the ash–flow tuffs (KONTAK *et al.*, 1984b; NOBLE *et al.*, 1984; VALENCIA HERRERA *et al.*, 1984).

Another problem is that the individual effect of H_2O on phase relations in the Qz–Ab–Or system is not well known. Phase relations in this system have been determined for various pressures mostly under H_2O–saturated conditions (TUTTLE and BOWEN, 1958; LUTH *et al.*, 1964; LUTH, 1976). Thus, the effect of H_2O on phase relations cannot be separated from that of pressure. There is only a limited number of experiments carried out in that system under H_2O–undersaturated conditions (STEINER *et al.*, 1975; PICHAVANT and RAMBOZ, 1985a,b); they consistently show that an isobaric reduction of the melt H_2O content shifts the minimum liquidus compositions at approximately constant Qz contents towards the Qz–Or side of the diagram. In contrast, calculations indicate a displacement of these minima towards the feldspar join (BURNHAM and NEKVASIL, 1986; NEKVASIL and BURNHAM, 1987).

In spite of these restrictions, several conclusions arise from the Qz–Ab–Or diagram (Figure 2). The tuffs cluster near and below the low-pressure H_2O–saturated minima. In contrast, the Chilcuno Chico and Caluyo Mayo glasses are shifted towards the Ab corner, the more marked shift being for the more F-rich glass (JV3, Table 2, Figure 2). This displacement reflects the progressive increase of F, Li and B in the liquid, and the combined effects of these components on phase relations in the Qz–Ab–Or system. Starting from a magma compositionally similar to the tuffs, fractional crystallization of quartz and feldspar phases is able to produce liquid compositions similar to the macusanites in Figure 2. This fractionation is associated with a reduction of the liquidus temperatures, in accord with the nearly aphyric character of the glasses and in contrast with the crystal-rich nature of the tuffs (40–50 volume percent, PICHAVANT *et al.*, in preparation). Mineralogical evidence (PICHAVANT *et al.*, in preparation) also shows that the glasses quenched a lower-temperature phenocryst assemblage than in the tuffs. The Chapi inclusions (Figure 2) are different. They are significantly less peraluminous (3 weight percent normative corundum) than the other glasses. They have variable F contents and their Li and B concentrations are not known. CH0 plots close to the 2 weight percent added F minimum point; its position is compatible with fractional crystallization from a magma with the composition of the tuffs, as suggested previously. However, CH1 plots distinctly away from CH0 toward the Qz–Or side. One plausible explanation to this peculiar composition is that the H_2O contents of CH0 and CH1, like the F contents, were significantly different during the magmatic evolution. An isobaric reduction of the melt H_2O content between CH0 and CH1 would account for their relative position in Figure 2.

Origin of the Macusani glasses

The details of the mechanisms that led to the segregation and collection of the residual melts are not known, mainly because of limited field information on the relations between the tuffs and the glasses. The field relations, major elements, trace elements, Sr and O isotopes show that the investigated macusanites can be divided into two groups (the Chilcuno Chico and Caluyo Mayo samples on one hand and the Chapi inclusions on the other hand). It is likely that each group was derived from a different magma (the ash–flow tuffs are not cogenetic, even if generated in a closely similar way, see NOBLE *et al.,* 1984). Within each group, there is some indication of chemical heterogeneity [compare the F content of JV3 with the other glass pebbles (Tables 1, 2); also CH0 and CH1]. However, given the limited field information, it is not possible to relate these chemical variations with the relative position in the magma chamber. During crystallization in the magma chamber, low viscosities, as promoted by the presence of F in the residual liquids (DINGWELL *et al.,* 1985; DINGWELL, 1987) would greatly enhance their segregation and collection. These residual liquids were not simply quenched at the top of the chamber but were complexly degassed, prior to and during eruption. Pieces of the residual liquid were erupted as clasts and were air-quenched, as indicated by their shape and etched surface. The quenched glasses were included by compaction within the air-fall tephra. Later, essentially mechanical (alluvial and glacial) alteration eventually separated the inclusions from their host tuff, yielding the pebbles.

Implications for chemical fractionation in volatile–rich peraluminous magmas

We have not attempted to model quantitatively the chemical fractionation observed between the tuffs and the glasses. This is, firstly, because of uncertainties regarding the composition of the parental magma of the tuffs. Secondly, the partition coefficients are lacking for phases such as the aluminium silicates, muscovite, cordierite, and tourmaline that are major mineralogical components in the tuffs. Thirdly, partition coefficients for rhyolites are strongly dependent on the structure and composition of the liquid (MAHOOD and HILDRETH, 1983). Crystal fractionation of quartz and feldspar phases in a liquid becoming progressively enriched in F, Li and B, as proposed above, accounts for the increase in Na_2O, Al_2O_3, Na_2O/K_2O and for the depletion in SiO_2, K_2O and CaO with differentiation. Trace element data are also consistent with fractional crystallization; Sr, Ba, Pb, Eu are depleted, whereas Rb and Cs are enriched. The very low Sr and Ba contents in the glasses show that they cannot be produced directly by partial melting unless the source was nearly devoid of feldspars. Simultaneous fractionation of other major phases such as biotite also accounts for the depletions in Fe, Mg, Ti. Continuous fractionation of zircon agrees with the depletion in Zr and with the decrease of the Zr/Hf ratio. The observed depletions in Th, LREE are attributed to the removal/fractionation of restite monazites (MITTLEFEHLDT and MILLER, 1983; MONTEL, 1986). The change in the REE patterns between the tuffs and the glasses has been modelled by monazite removal/fractionation (MONTEL, 1986). Thus, there is little doubt as to the importance of crystal fractionation in these peraluminous volcanics. CHRISTIANSEN *et al.* (1984) similarly concluded that the chemical variations observed in topaz rhyolites (which have similar fractionation patterns, Figure 4) are for the most part consistent with crystal fractionation.

The behaviour of several components, however, cannot be explained by such a model. Both P and Al are enriched during differentiation (Figure 4) and their behaviour in the Macusani volcanics contrasts with calc–alkaline and topaz rhyolites. The very high P_2O_5 (0.53 weight percent) of the glasses is incompatible with apatite fractionation. Apatite is an abundant phenocryst in the tuffs (KONTAK *et al.,* 1984b; NOBLE *et al.,* 1984; VALENCIA HERRERA *et al.,* 1984). It has not been identified in the glasses. Atomic Ca/P ratios change from 1.5 to 3 in the tuffs (1.67 in apatite) to 0.4 in the glasses. In addition, many peraluminous felsic magmas have P_2O_5 higher than 0.2 weight percent (LE FORT, 1981; BENARD *et al.,* 1985; ADAM and GAGNY, 1986). Fractionation of apatite should buffer the melt P_2O_5 content to the apatite solubility value for the prevailing intensive and compositional variables. Calculation of the melt P_2O_5 concentration from apatite solubility data of HARRISON and

WATSON (1984) yields P_2O_5 = 30 ppm for a temperature of 650°C.

In the same way, values of normative corundum in the range found in the Macusani glasses (from 3 to more than 5 weight percent Co) have been attained in experimental melts only at high temperatures (800–850°C), pressures (5 kbar), H_2O contents (from 4 to 10 weight percent) and in the presence of excess sillimanite (CLEMENS and WALL, 1981). Experimental liquids saturated with aluminium silicate phases at lower temperatures and pressures have much lower normative corundum (about 2 weight percent, BURNHAM and NEKVASIL, 1986). The available experimental data therefore indicate that the normative corundum of the melt should increase mainly with temperature and possibly melt H_2O content. Thus, for a melt saturated with aluminium silicates (such as the Macusani tuffs and glasses), the normative corundum is not expected to increase significantly with differentiation (decrease in temperature, increase in melt H_2O content). Nevertheless, we record a clear increase of the normative corundum from the tuffs (average 3 weight percent Co) to the glasses (from 3 to more than 5 weight percent Co). Moreover, the more fractionated glasses (JV3) have the highest normative corundum yet they contain less andalusite. This increase of the peraluminous character of the melt during differentiation contrasts with the "restite model" (WHITE and CHAPPELL, 1977), as proposed for more mafic peraluminous series ("S-type"), which predicts less peraluminous magmas with increase in differentiation.

Another problem is the boron concentration. B_2O_3 contents as high as 0.60 weight percent in the glasses are also incompatible with the presence of tourmaline, a conspicuous early phenocryst in the tuffs (KONTAK *et al.*, 1984b; VALENCIA HERRERA *et al.*, 1984). Continuous fractionation of tourmaline should buffer the melt B_2O_3 content to very low values, as shown experimentally by BENARD *et al.* (1985).

The above difficulties clearly relate to the specific structure of peraluminous, F–, Li–, B–, P– and H_2O–rich melts. One characteristic feature of the Macusani melt is its strongly peraluminous composition. There is increasing evidence that Al behaves like a network–modifying cation in peraluminous melts (MYSEN *et al.*, 1985). H_2O solubility in melts has been found to increase in peraluminous compared to metaluminous compositions (DINGWELL *et al.*, 1984). In contradiction to some previous assumptions (*e.g.*, LUTH, 1976), liquidus temperatures are significantly lowered in peraluminous compared to metaluminous compositions (BURNHAM and NEKVASIL, 1986). Another characteristic feature is the presence of elevated concentrations of components such as F, B, Li, P and H_2O. The chemical interaction between these components and the aluminosilicate network leads to a major reorganisation of the melt structure. One important structural modification is the formation of interstitial structural units that involve cations (Al and alkalies) previously forming part of the aluminosilicate network. The existence of structural units involving F, B and the Ab–forming components of the melt is indicated by phase equilibrium studies in the H_2O–saturated Qz–Ab–Or system in the presence of either F or B (MANNING, 1981; MANNING *et al.*, 1984; PICHAVANT, 1984; MANNING and PICHAVANT, 1986; BURNHAM and NEKVASIL, 1986). In the F–bearing system, the observed changes in phase relations are interpreted to indicate the formation of interstitial aluminofluoride complexes (MANNING, 1981; MANNING *et al.*, 1984). Spectroscopic studies in the system Na_2O–Al_2O_3–SiO_2–F at 1 atm (MYSEN and VIRGO, 1985) suggest association of F with Na or Al or both. In the same way, B may coordinate with alkalies or Al, or both (MANNING *et al.*, 1984). By analogy with F and B, the observed changes in phase relations with an isobaric increase of the melt H_2O content (STEINER *et al.*, 1975; PICHAVANT and RAMBOZ, 1985a,b) suggest association of H_2O with the Ab–forming components. Complexes of Al with P have been identified spectroscopically in three-dimensional aluminosilicate melts ($AlPO_4$, MYSEN *et al.*, 1981). When complexes with Al are formed, the alkalies previously required for charge-balancing Al in tetrahedral coordination become network–modifiers. When complexes with alkalies are formed, an equivalent fraction of Al can no longer exist in tetrahedral coordination and becomes network–modifier. This results in both cases in the expulsion of Al from tetrahedral coordination and in the increased abundance of network–modifiers that will promote depolymerization of the melt. Depolymerization would be enhanced with the presence of components such as B which increase the H_2O solubility in the melt (PICHAVANT, 1981).

The preceeding discussion emphasizes the role of Al, alkalies, and of F, B, P and H_2O in the formation of complexes and in promoting depolymerization of the melt. This explains the observed increase in the peraluminous character of the melt during fractionation and also the behaviour of phosphorus in strongly peraluminous magmas. Lowering of the liquidus temperatures would allow these magmas to remain crystal-poor, even at low temperatures (600–650°C). The solubility of "refractory" minerals (*e.g.*, aluminium silicates, tourmaline, apatite) in the melt would be enhanced. The existence of Al complexes with P is consistent with the commonly observed crystallization of amblygonite ($LiAlPO_4$ (OH, F)) rather than apatite in some leucogranites and rare-element pegmatites (CUNEY *et al.*, 1986; LONDON, 1987).

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