

Magma evolution within the accretionary mafic basement of Quaternary Chimborazo and associated volcanos (Western Ecuador)

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ABSTRACT

Miocene to Holocene volcanic rocks of Chimborazo and associated volcanos in the Western Cordillera of Ecuador range in composition from basaltic andesite to rhyolite. They were erupted through Cretaceous accretionary mafic basement. Three calc-alkaline magmatic trends can be distinguished in the Pleistocene and Holocene volcanic rocks. They are interpreted to reflect magma evolution within the immature continental crust. Early Pleistocene and Late Pleistocene volcanic rocks range in composition from basaltic andesite to dacite and are characterized by a moderate increase in alkalinity and little variation in the K/Rb, Ba/La, Th/Ta, and Sr/Y ratios. They show distinct geochemical differences that are attributed to variable proportions of lower crustal melts in the mafic end members. Volcanic rocks have lower $^{143}\text{Nd}/^{144}\text{Nd}$ ratios (0.5128 to 0.5129) than the basement, suggesting an origin of this isotopic characteristics from subduction modified mantle. Chemical modelling suggests that Late Pleistocene basalts may contain about 12% more of a lower crustal melt than Early Pleistocene parental melts. The development within both magmatic suites is explained by shallow level magma evolution. Other medium-K to high-K Pleistocene andesites may have been produced by mixing of a low-K basaltic melt generated from subduction-modified mantle and a high silica partial melt from the lower crust containing rutile and garnet. Partial melting of lower crust is supported by high Sr/Y (~200), Th/Ta (~42), and La/Yb ratios (~60) in the high-K andesites. $^{143}\text{Nd}/^{144}\text{Nd}$ ratios (0.51292) and $\delta^{18}\text{O}$ values (~+9‰) in the high-K andesites are indistinguishable from those in Cretaceous accretionary basement and support a genetic relationship.

Key words: Northern Andes, Ecuador, Crustal magma contamination, Quaternary, Volcanism, Geochemistry, Isotopic data, Continental margin, Magma mixing, AFC process.

RESUMEN

La evolución magmática dentro del basamento acrecionario máfico del volcán Chimborazo y volcanes asociados del Cuaternario (Ecuador Occidental). Las rocas volcánicas miocenas a holocenas del Chimborazo y volcanes asociados en la Cordillera Occidental del Ecuador varían en composición de andesita basáltica a riolita. Fueron extruidas a través de un basamento acrecionario máfico cretácico. Se distinguen tres tendencias de diferenciación magmática calco-alkalina en las rocas volcánicas pleistocenas y holocenas. Se las interpreta como indicativas de evolución magmática dentro de la corteza continental inmadura. Las rocas volcánicas del Pleistoceno temprano y tardío varían en composición de andesita basáltica a dacita, y están caracterizadas por un moderado

incremento de alcalinidad y una pequeña variación de las razones K/Rb, Ba/La, Th/Ta y Sr/Y. Muestran diferencias geoquímicas distintivas que se atribuyen a proporciones variables de fundidos de la corteza inferior en los miembros extremos máficos. Las rocas volcánicas tienen razones de $^{143}\text{Nd}/^{144}\text{Nd}$ (0.5128 a 0.5129) menores que el basamento, lo que sugiere que el origen de esta característica isotópica reside en un manto modificado por subducción. El modelamiento químico sugiere que los basaltos del Pleistoceno tardío pueden contener cerca de 12% más de fundidos de la corteza inferior que aquéllos del Pleistoceno temprano. El desarrollo de ambas series magmáticas se explica por evolución magmática a niveles poco profundos. Otras andesitas pleistocenas de mediano a alto K pueden haberse producido por mezcla de un fundido basáltico de bajo K generado en un manto modificado por subducción, y un fundido parcial rico en sílice de corteza inferior que contenga rutilo y granate. La fusión parcial de corteza inferior está apoyada por altas razones de Sr/Y (~200), de Th/Ta (~42), y de La/Yb (~60) en las andesitas de alto K. Las razones de $^{143}\text{Nd}/^{144}\text{Nd}$ (~0.51292) y los valores de $\delta^{18}\text{O}$ (+9‰) en las andesitas de alto K, son indistinguibles de aquéllas del basamento acrecionario cretácico, y sugieren una relación genética entre ellas.

Palabras claves: Andes del norte, Ecuador, Contaminación magmática cortical, Cuaternario, Volcanismo, Geoquímica, Datos isotópicos, Margen continental, Mezcla de magmas, Procesos AFC.

INTRODUCTION

Since the Miocene recurrent magmatic arc activity has formed various volcanic rock suites in the Andes of Ecuador (Barberi *et al.*, 1988; Harmon *et al.*, 1984; Hörmann and Pichler, 1982; Kilian and Pichler, 1989; Vanek *et al.*, 1994). The volcanic rocks range in composition from basaltic andesite to rhyolite with low K to high K content. There is little or no information on the specific magmatic processes which produced the chemical variations of these volcanic rock suites.

In general, chemical and isotopic characteristics of volcanic rocks from destructive plate margins are controlled by metasomatic and magmatic processes in the mantle wedge. Intra-crustal processes, including fractional crystallization and crustal assimilation (AFC process) or magma mixing between mantle and crustal derived melts, may produce additional chemical and isotopic variations. The authors have investigated volcanic rocks from Chimborazo and other volcanos that were erupted on Cretaceous

basement, which has been interpreted as juvenile crust, due to its uniform basaltic to low-K andesitic composition and its mantle-like Sr and Nd isotopic data. This contrasts with Andean crust from the Central and Southern Andes, which is chemically very heterogeneous.

To study the different possible magmatic processes within the accretionary crust, the authors investigated the petrography, the trace element, and O, Sr and Nd isotopic compositions of a selected suite of volcanic rocks from Western Ecuador. The aim of this study is to constrain processes responsible for the chemical and isotopic variations in the volcanic rock suites. Since all Miocene to Holocene volcanic rocks of the Western Cordillera of Ecuador are variably fractionated (Harmon *et al.*, 1984), the authors tried to recalculate a primary basalt composition and to infer the mineralogy and chemical composition of the magma source.

GEOLOGICAL AND TECTONIC SETTING

The Andes of Ecuador are part of a 7,000 km long destructive plate margin along the South American continent. They consist of two mountain ranges, the Western Cordillera and the Eastern Cordillera which are separated by the Intra-Andean Valley (Fig. 1). Chimborazo and associated volcanos in the Western Cordillera of Ecuador are produced through the subduction of the Nazca Plate. The Benioff plane is located approximately 80-100 km below the inves-

tigated volcanos (Hall and Wood, 1985). The Nazca Plate is subducted with a dip of 30-35° and a velocity of ~9 cm/yr. Its age at the trench is about 15-20 Ma (Barazangi and Isacks, 1976; Bevis and Isacks, 1984; Minster and Jordan, 1978; Nur and Ben Avraham, 1981; Pennington, 1981; Pilger, 1984). The crustal thickness below the studied area is around 35-40 km (Case *et al.*, 1973). The coastal range, the Western Cordillera and the Intra-Andean

Valley consist of Cretaceous accretionary mafic units (Feininger and Bristow, 1980; Hegner *et al.*, 1995; Lebrat *et al.*, 1986; Wallrabe-Adams, 1987,

1991) which are also displaced northwards along a fault zone (Fig. 1; Dewey and Lamb, 1992; Feininger and Seguin, 1983; Winter and Lavenue, 1989).

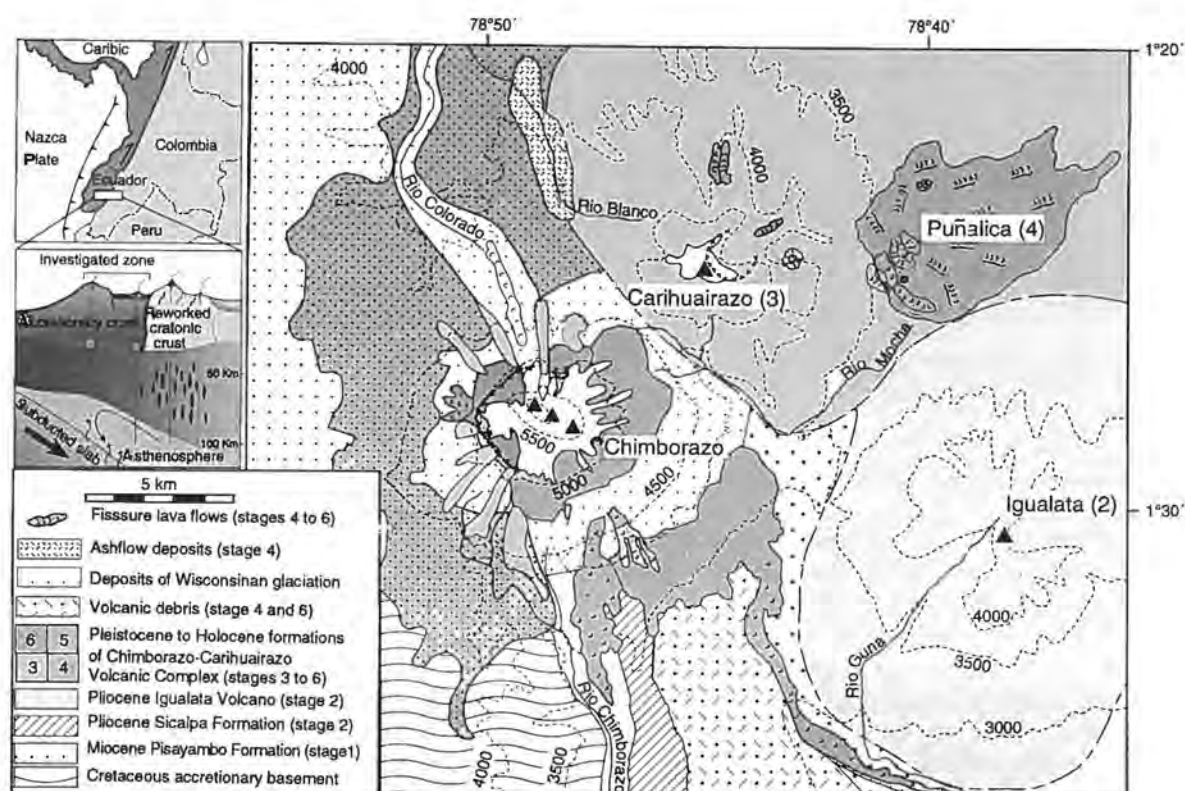


FIG. 1. The Northern Andes of South America (left upper corner) and the investigated area in the Western Cordillera and Intra-Andean Valley of Ecuador related to Cretaceous accretionary basement (left: schematic cross section). Stratigraphy and radiometric dating suggests six different volcanic units (stages 1- 6).

STRATIGRAPHY

The geographic and stratigraphic relationship of the investigated volcanoes are illustrated in figures 1 and 2. Six stages of volcanic activity are distinguished:

- Extended ignimbrite sheets and caldera-like structures were formed during the Miocene (volcanic stage 1) in the Western Cordillera of Ecuador and are underlying the Chimborazo volcano. K-Ar dates constrain a time interval between 7.9 and 12.5 Ma for this volcanic stage (Kilian, 1987a, b; Lavenue *et al.*, 1992).

- The Igualata volcano (volcanic stage 2) was formed later in the Intra-Andean Valley, probably during the Early Pliocene. This age can be inferred from other volcanoes in the Intra-Andean Valley showing similar stages of erosion, and having K-Ar ages in the range of 2.7 to 4.8 Ma (Lavenue *et al.*, 1992; Kilian, 1987b).

- The oldest rocks of Chimborazo volcano (CH-I) were formed during the Late Pliocene and the Early Pleistocene (K-Ar ages of 1.7-1.8 Ma; Kilian, 1987b) and represent volcanic stage 3. The basal unit of

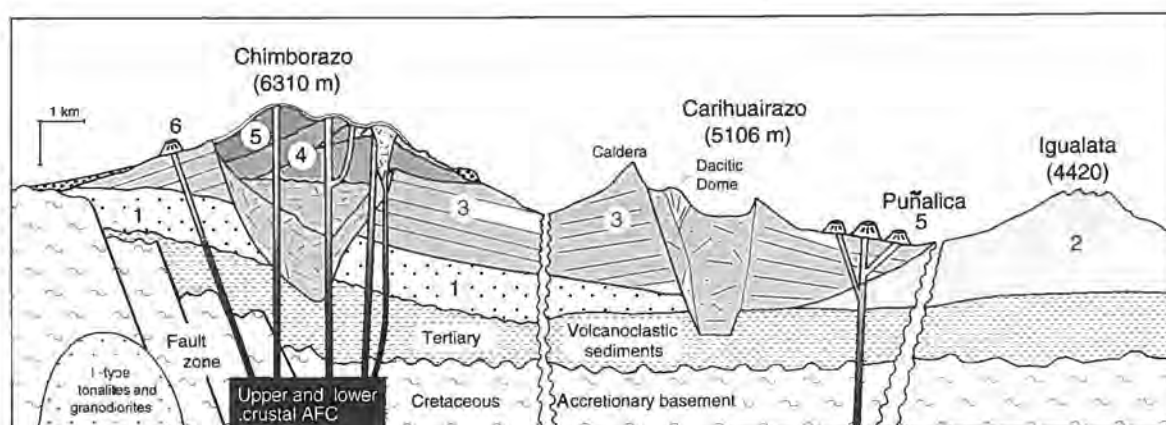


FIG. 2. Cross section of the investigated Miocene to Holocene volcanos (stages 1-6; Fig. 1) located in the Western Cordillera and Intra-Andean Valley of Ecuador.

nearby Carhuairazo volcano was formed in the same period.

- Volcanic stage 4 is represented by Late Pleistocene volcanic cores and fissure lava flows ranging in composition from basaltic andesite to dacite. The volcanic rocks are pyroclastic flows and volcanic domes of andesitic to dacitic compositions. Two western cones of Chimborazo volcano (CH-II-A and CH-II-B) belong to this volcanic stage (Fig. 2). In the same time interval extensive debris layers and ash-flows were deposited to the north of Chimborazo volcano in the Río Ambato valley, and to the south

in the Ríobamba depression (Fig. 1). Carbonized tree trunks in an ash-flow north of Chimborazo volcano gave ^{14}C ages of 35,000 and 38,000 y B.P. (Kilian, 1987b).

- Cones west and east of Chimborazo (CH-III) and the Puñalica volcano (to the east of Carhuairazo) may have formed during the Wisconsin glaciation (volcanic stage 5).
- Post glacial lava flows (volcanic stage 6) were erupted at the eastern and southern slopes of the Chimborazo volcano and at Puñalica volcano (Clapperton, 1990).

PETROGRAPHY

Phenocryst assemblages of the investigated volcanic rocks of the Western Cordillera in Ecuador show crude correlations with the SiO_2 content (Fig. 3). The mafic volcanic rocks of Puñalica and Chimborazo III volcanos are basaltic andesites ($\text{SiO}_2=52$ to 54 wt %) and contain olivine phenocrysts with core to rim zonations of Mg# from 86 to 65. Clinopyroxene (Mg# 78-72) occurs as phenocrysts. Plagioclase (An_{75-50}) was formed only as part of the groundmass (Fig. 4).

A typical phenocryst assemblage of basaltic andesites is olivine (<25 vol%), clinopyroxene (45 vol%), orthopyroxene (17 vol%), plagioclase (10 vol%), and Ti-Fe-oxides (3 vol%). Basaltic andesites and andesites commonly contain glomerophyres of clinopyroxene (Mg# 77-68) and orthopyroxene ($\sigma=$

0.5-3 mm). Evolved andesites are characterized by plagioclase phenocrysts ($\sigma=1-3$ mm) with normal and complex zonations in the anorthite content (An_{55-75}). Corroded olivine occurs occasionally in andesites with SiO_2 contents up to 58 wt% and may have formed in a more mafic melt. Compared to basaltic andesites, andesites have a lower content of olivine (~3 vol%), clinopyroxene (~30%), and Fe-Ti-oxides (~2 vol%), and a higher content of orthopyroxene (32 vol%) and plagioclase (~30 vol%).

Phenocryst assemblages in the dacites are dominated by plagioclase (66 vol % of the phenocrysts), showing complex zonations in the anorthite content (An_{50-31}). Mafic minerals are mainly hypersthene and amphibole. Apatite and Fe-Ti-oxides are typical minor phases.

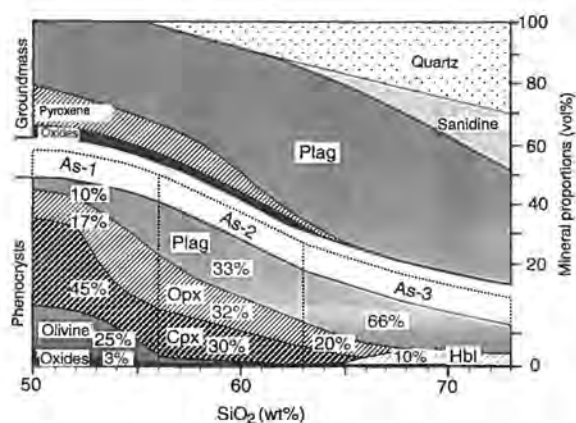


FIG. 3. Phenocryst and groundmass mineral assemblages of the investigated volcanic rocks related to the SiO_2 range from 50 to 73 wt%. Three phenocryst proportions and assemblages (As-1 to As-3) were distinguished for the ranges of basaltic andesites, acid andesites and dacites. These were used in the trace element models of AFC processes.

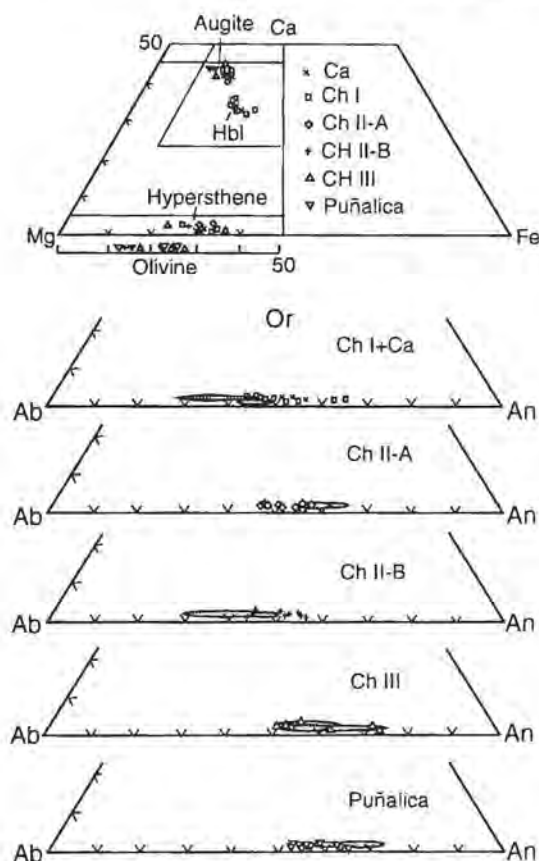


FIG. 4. Olivine and pyroxene (Ca, Fe, Mg triangle) as well as plagioclase compositions (Or, Ab, An triangles) for Pliocene to Holocene volcanic rocks of the Chimborazo-Carhuairazo Volcanic Complex.

GEOCHEMISTRY

Chemical and isotopic investigations were performed on pristine samples. Below, chemical characteristics and trends of Miocene to Holocene vol-

canic rocks from the Chimborazo and associated volcanos are described in stratigraphic order.

Miocene volcanic rocks of the Western Cordille-

ra (volcanic stage 1) range in composition from basaltic andesites to dacites with medium-K to high-K content (Fig. 5). It is not possible to establish geochemical trends due to uncertainty in the stratigraphy. Volcanic rocks show large variations in the concentrations of large ion lithophile (LIL) elements, *e.g.*, Rb (22-71 ppm), Ba (319-1,350 ppm) and Sr (412-1,500 ppm). The concentrations of other trace elements, *e.g.*, Y (7-21 ppm), Yb (1.1-2.2 ppm) and Nb (2-10 ppm), also vary significantly. Most of the Miocene medium-K andesites overlap chemically with samples of Pliocene Pasochoa volcano (4.2 Ma; Kilian *et al.*, 1987a). Volcanic products of the Pliocene Igualata volcano (volcanic stage 2) have

higher K_2O contents than those of the Pasochoa volcano, but plot in the cluster of the Miocene volcanic rocks. Some andesites have low concentrations of Y (<10 ppm) and Yb (<1.1 ppm), and high Sr/Y (>60) ratios, suggesting derivation from a garnet-amphibolitic source (Drummond and Defant, 1990). $^{87}Sr/^{86}Sr$ (0.7039-0.7041), $^{143}Nd/^{144}Nd$ ratios (-0.51287) and $\delta^{18}O$ values (+7.7 to +7.8‰) of two medium-K andesites of Miocene ignimbrites show less depleted isotopic composition than N-MORB and the accretionary basement (Hegner *et al.*, 1995). All Miocene and Pliocene volcanic rocks have very low Rb/Sr ratios (<0.002) implying that the Sr isotopic evolution since the Miocene is negligible.

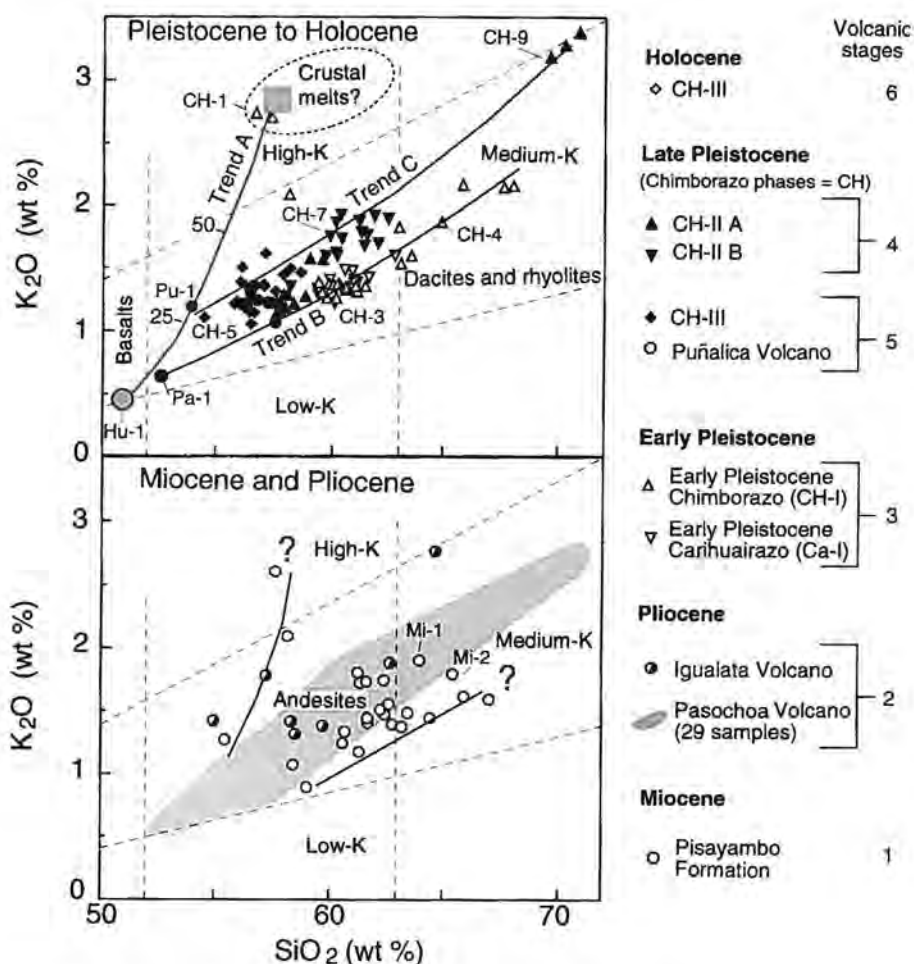


FIG. 5. K_2O versus SiO_2 diagram for Miocene and Pliocene volcanic rocks, and Pleistocene to Holocene volcanic rocks of the Western Cordillera and Intra-Andean Valley of Ecuador. Three trends (A, B, C) were distinguished. Numbered samples were taken for trace element models and investigations of Sr, Nd, and O isotopes.

The chemical characteristics of 70 volcanic rocks of the Pleistocene to Holocene Chimborazo-Carihuairazo volcanic complex (Table 1, Figs. 1, 2) are similar to those of the Miocene to Pliocene volcanic rocks (Fig. 5). Three different trends of the volcanic stages 3-6 can be distinguished and are illustrated in figures 5-7.

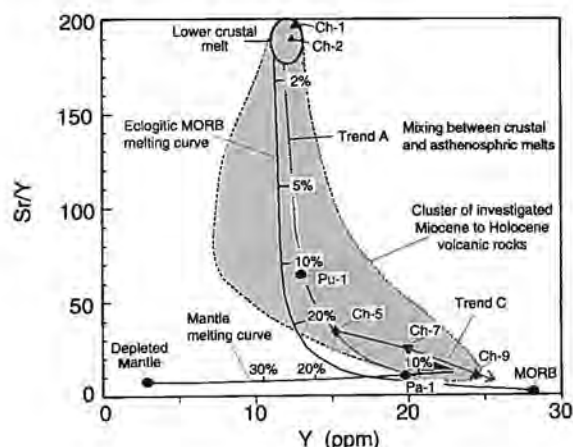


FIG. 6. Sr/Y versus Y concentrations for Miocene to Holocene volcanic rocks of the Western Cordillera and Intra-Andean Valley of Ecuador. Partial melting lines for an asthenospheric mantle source and a MORB-like garnet-amphibolitic source as well as a mixture between a crustal (Ch-1) and mantle melt (Hu-1) are illustrated. The AFC path of the Late Pleistocene starting from sample Ch-7 is shown.

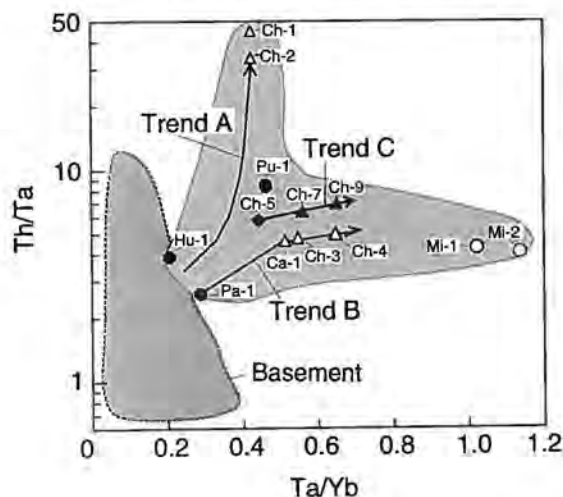


FIG. 7. Th/Ta versus Ta/Yb ratios for the investigated volcanic rocks (grey cluster) of Ecuador, and for the Cretaceous accretionary basement (dark grey cluster). The Trends A, B, and C are illustrated.

Trend A represents Pleistocene volcanic rocks of Chimborazo volcano (Figs. 1, 2) with a small range in SiO_2 (54-58 wt %), and a marked increase of K_2O (1.2-2.7 wt %), Rb (20-45 ppm), La (19-83 ppm), Th (4-25 ppm), and Ba (472-2500 ppm), as well as an increase to the La/Yb ratios from 18 to 65. $\delta^{18}\text{O}$ values range from +6.1 to +8.9‰. The concentrations of Cr (289-124 ppm) and Ni (126-86 ppm) decrease with increasing alkalinity. The high-K end member of this trend has the highest $^{143}\text{Nd}/^{144}\text{Nd}$ ratio (-0.51292) of all investigated volcanic rocks (Fig. 9...p. 211). The concentrations of Ta (0.53-0.55 ppm), Cs (0.65-0.78 ppm), and the K/Rb ratios (505-550) show no significant variation. Miocene to Pliocene volcanic rocks show a similar chemical variation (Fig. 5).

Trend B represents Late Pliocene and Early Pleistocene volcanic products of the Chimborazo I and Carihuairazo volcanos (volcanic stage 3; Figs. 1, 2). It shows a large range in SiO_2 content (54-66 wt%) and a moderate increase in K_2O (1.2-1.64 wt%), Rb (20-49 ppm), La (19-20 ppm), Th (4.5-5.9 ppm), Ta (0.53-0.91 ppm), Ba (472-772 ppm), and Cs concentrations (0.65 to 2.1 ppm), La/Yb ratios (18-25), and $\delta^{18}\text{O}$ values (+6.1 to +7.7‰). The concentrations of Cr (289-53 ppm), Ni (126-15 ppm), and the K/Rb ratios (505-317) decrease with increasing SiO_2 content. Sr/Y, Ba/La, and Th/Ta ratios show no significant variations. This trend is similar to that of volcanic rocks from the Pliocene-Pleistocene Paschocha and Pichincha volcanos, except that the latter volcanos have more mafic end members. These are characterized by a low-K basaltic composition (Pa-1), and by relatively low $^{87}\text{Sr}/^{86}\text{Sr}$ (~0.7038) and high $^{143}\text{Nd}/^{144}\text{Nd}$ ratios (~0.51288; Kilian et al., 1994).

Trend C represents Late Pleistocene and Holocene volcanic products of Chimborazo II, III and Puñalica volcanos (Figs. 1, 2) ranging from basaltic andesite to rhyolite. For a given SiO_2 content, the volcanic products have higher concentrations of LIL and LRE elements and higher Ba/La, Th/Ta, and Sr/Y ratios than volcanic rocks of Trend B (Figs. 5-8). Trends B and C show a similar increase of the concentrations of the LIL and HFS elements and little variations of the K/Rb, Sr/Y, Ba/La, and Th/Ta ratios.

TABLE 1. SELECTED TRACE ELEMENT AND ISOTOPIC COMPOSITIONS OF MIOCENE TO HOLOCENE VOLCANIC ROCKS. COMPOSITIONS FOR A PRIMITIVE ANDEAN BASALT, A BASALTIC ANDESITE OF PASOCHOA VOLCANO.

Sample	Miocene				Late Pliocene and Early Pleistocene							Late Pleistocene to Holocene				
	MI-1 stage 1	MI-2	Hu-1	Pa-1 stage 2	Ch-1	Ch-2	Ca-1 stage 3	Ch-3	Ch-4	Pu-1	Pu-2	Ch-5 stage 6	Ch-6 stage 5	Ch-7	Ch-8 stage 4	Ch-9
SiO ₂	64.72	65.92	51.20	52.74	56.71	57.41	61.07	61.14	64.90	53.92	56.13	54.94	56.48	58.13	60.30	70.20
TiO ₂	0.51	0.45	0.82	0.86	0.77	0.79	0.73	0.78	0.55	0.81	0.75	0.97	0.92	0.87	0.80	0.95
Al ₂ O ₃	16.03	16.77	18.25	17.34	14.98	14.90	17.90	17.80	15.68	16.92	15.32	17.57	16.77	17.04	16.74	14.80
FeO	4.53	3.34	9.04	8.91	6.77	6.86	5.84	6.07	4.12	8.37	7.58	7.68	7.46	6.91	6.40	2.50
MnO	0.07	0.03	0.14	0.13	0.10	0.10	0.08	0.09	0.06	0.14	0.11	0.11	0.11	0.10	0.09	0.06
MgO	2.36	0.61	7.14	5.71	4.25	4.40	2.33	2.73	2.35	6.04	6.88	4.47	5.41	4.49	3.91	0.63
CaO	4.27	3.75	9.44	8.83	7.80	7.88	5.77	5.71	4.52	8.88	7.70	7.15	7.09	6.65	5.99	2.28
Na ₂ O	4.45	4.88	2.75	3.53	3.82	3.75	4.19	4.38	3.97	3.57	3.56	4.12	4.04	4.30	4.29	4.56
K ₂ O	1.69	1.61	0.46	0.65	2.74	2.71	1.41	1.36	1.87	1.20	1.22	1.24	1.27	1.29	1.60	2.69
P ₂ O ₅	0.17	0.13	0.18	0.17	0.43	0.47	0.24	0.22	0.10	0.24	0.20	0.27	0.24	0.24	0.21	0.22
H ₂ O	0.83	1.16	0.67	0.45	0.24	0.30	0.76	0.02	1.37	0.25	0.24	0.05	0.00	0.00	0.00	0.34
Sum	99.63	98.65	100.09	99.32	98.62	99.57	100.32	100.30	99.49	100.34	99.71	98.57	99.80	100.02	100.33	98.63
Cr	47	22	198	142	124	105	22	24	53	289		82	126	101	110	11
Ni	30	10	120	53	86	82		25		126		53	93	65	68	32
Sc	9	16	32	23	17	19	11	11	8	20	27	16	16	14	15	5
V	90	84	186	150	194	179		158		170	204	186	176	164	150	30
Zn	68	67	83	96	108	111	74	81	80	87	80	90	93	88	85	68
Rb	34	38	10	11	55	61	32	30	49	20	19	24	24	30	40	105
Cs	1.74	0.83	0.35	0.47	0.78	0.80	0.70	0.70	2.10	0.65	0.50	0.60	0.62	1.00	0.90	2.14
Ba	619	650	185	250	2,225	2,234	683	620	772	472	529	582	635	603	693	970
Sr	493	520	478	577	2,536	2,456	664	651	552	850	1,122	748	776	711	655	308
Ta	0.89	0.56	0.28	0.45	0.55	0.60	0.75	0.65	0.91	0.53	0.49	0.58	0.56	0.85	0.88	0.88
Hf	3.0	2.7	1.9	2.2	3.8	4.0	3.3	3.1	4.1	2.1	2.4	2.9	3.0	3.2	3.0	7.4
Zr	98	97	84	90	160	339	133	153	154	101	176	162	119	144	149	252
Y	10	7	20	18	13	13	13	17	18	17	17	16	18	20	18	24
Th	3.7	2.3	1.1	1.1	23.3	23.6	3.5	3.1	5.9	4.5	3.7	2.5	2.5	4.7	4.1	6.7
U	2.0	1.3	0.3	0.3	7.2	8.1				1.3			0.7			
La	12.9	10.1	9.1	9.8	81.8	85.5	15.1	14.8	18.8	19.0	20.8	14.7	16.3	16.9	15.1	0.2
Ce	26.6	17.3	19.1	20.1	139.3	142.3	32.1	30.5	38.1	36.0	41.4	31.7	32.2	33.9	31.5	29.1
Nd	13.7	10.6	12.6	12.3	71.3	73.4	15.7	15.0	20.0	20.0	21.5	18.5	18.5	17.9	17.6	52.3
Sm	2.8	2.4	3.3	3.5	11.4	12.2	3.7	3.5	3.4	3.9	4.5	4.0	3.9	3.7	3.8	5.9
Eu	0.7	0.6	1.0	1.1	2.8	2.9	1.1	1.1	0.9	1.1	1.3	1.2	1.1	1.1	1.1	1.3
Gd	2.1	1.5	2.5	2.5	11.0	0.0	0.0	0.0	0.0	3.2	0.0	0.0	0.0	0.0	0.0	0.0
Tb	0.30	0.22	0.48	0.52	0.85	0.76	0.00	0.42	0.57	0.49	0.00	0.46	0.54	0.51	0.61	0.80
Yb	0.82	0.46	1.67	1.55	1.02	1.05	1.31	1.15	1.2	1.25	1.20	1.45	1.41	1.35	1.56	1.7
Lu	0.12	0.13	0.31	0.22	0.19	0.22	0.18	0.15	0.12	0.20	0.22	0.25	0.27	0.31	0.28	0.28
δ ¹⁸ O(‰)	7.8	7.7		6.4	8.9					6.1				7.8		9.1
⁸⁷ Sr/ ⁸⁶ Sr	0.70407	0.70388		0.70416	0.70397					0.70377				0.70419		0.70415
¹⁴³ Nd/ ¹⁴⁴ Nd	0.51285	0.51288		0.51267	0.51292					0.51289				0.51289		0.51288
Mg #	49	25	59	53	53	53	42	45	50	56	62	51	56	54	52	31

Chemical and isotopic data for Pliocene to Holocene volcanic rocks from Chimborazo volcano (Ch-1 to Ch-9), Puñalica volcano (Pu-1 to Pu-2), underlying Miocene volcanic rocks (MI-1 to MI-2) and a basaltic andesite of Pasochoa volcano (Pa-1) in Ecuador are given. A primitive Andean basalt is shown for comparison (Hu-1, Kilian *et al.*, 1995). XRF data were produced at Tübingen University. Element concentrations were carried out by ICP-MS analysis at Memorial University of Saint John's Canada (*). The Sr, Nd, and O isotopes were measured at Tübingen University. For analytical details see Hegner *et al.*, in press.

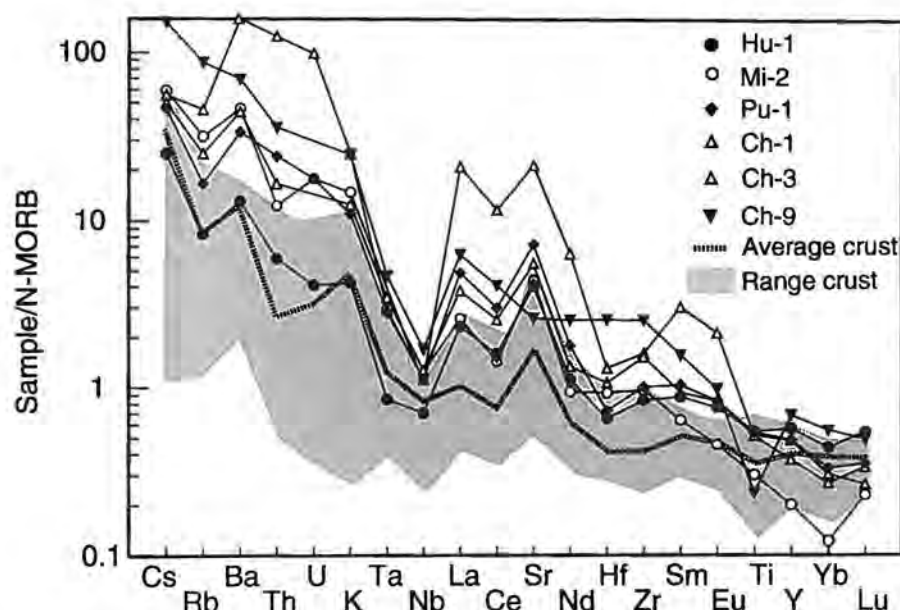


FIG. 8. Selected N-type MORB normalised trace element pattern of the investigated Quaternary volcanic rocks and the volcanic basement.

CHEMICAL AND ISOTOPIC CHARACTERISTICS OF THE BASEMENT

It has been shown that mantle-derived basalts assimilate crustal rocks and sometimes, induce melting of lower crust (Hildreth and Moorbath, 1988). Therefore, chemical and isotopic compositions of the crust are important to constrain this contribution to arc magmas. The basement in the Western Cordillera of Ecuador consists of basaltic and andesitic rocks of the Cretaceous accretionary Piñón, Macuchi, and Silante formations, and of Cenozoic plutonic rocks of mainly tonalitic and granodioritic composition (Fig. 1 inset and Fig. 2; Aly, 1980; Lebrat *et al.*, 1986; VanThoumout *et al.*, 1992; Wallrabe-Adams, 1991). Twenty two representative samples of these basement units (ranging from 48–68 wt% SiO₂) were investigated by Kilian *et al.* (1994) and Hegner *et al.* (1995). These rocks have low-K content in common and low concentrations of other incompatible elements (Fig. 9). An average trace element composition of the basement units is given in table 2 and was used as crustal component for modelling upper crustal AFC processes. Low Th/Ta ratios (0.7–3) of some basement rocks suggest an OIB or MORB origin, whereas other basement rocks have high Th/Ta ratios (6–12), suggesting formation in volcanic arcs. Although the Th/Ta ratios indicate an origin of the basement in different tectonic settings, its MORB-like ¹⁴³Nd/¹⁴⁴Nd ratios (–0.5130) indicate mantle sources containing little or no crustal component.

High ⁸⁷Sr/⁸⁶Sr ratios (0.7033–0.7052) are probably due to sea water alterations (Fig. 9). The samples of the mafic to intermediate basement rocks have highly variable $\delta^{18}\text{O}$ values of +6 to +12‰.

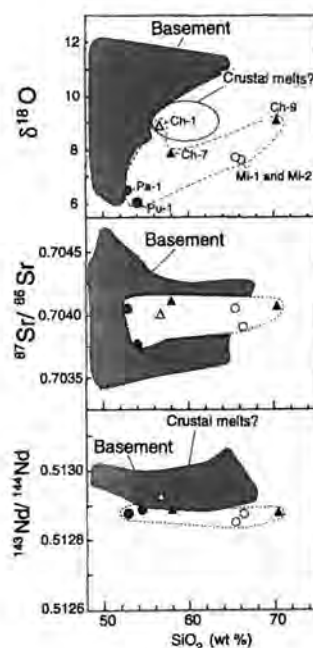


FIG. 9. SiO₂ versus ⁸⁷Sr/⁸⁶Sr, ¹⁴³Nd/¹⁴⁴Nd, and $\delta^{18}\text{O}$ for volcanic rocks of the Western Cordillera and Intra-Andean Valley of Ecuador ranging from basaltic andesites to rhyolites, and related basement (Hegner *et al.*, 1995).

MAGMA MIXING AND AFC MODELS

Simple two component mixtures and AFC models were used to calculate possible intra-crustal magmatic evolution (Table 2, Figs. 5-7):

- Mixing of melts derived from asthenosphere and crust: it can be supposed that a low-K and low Ce/Yb basalt (Hu-1) of the Southern Andes Volcanic Zone represents a primary composition produced in the mantle wedge (Kilian *et al.*, 1995). The crustal melt was assumed to have a similar composition as high-K andesites (Ch-1 and Ch-2) of the Chimborazo (Discussion, p. 214). The question arises, whether these high-K samples represent pure crustal melts or a mixture between a low-K basalt and a more alkaline as well as SiO₂-richer crustal melt. Melts produced by experiments in garnet-amphibolitic material with N-type MORB chemistry show andesitic and dacitic composition with medium-K to high-K content at melting degrees between 5 and 30% (Springer, 1992; Rapp and Watson, 1995). Therefore, such high-K andesitic melts principally can be produced in the lower crust of Western Ecuador. However, it can be expected that the primary crustal melt has higher SiO₂ contents. Disequilibrium melting may be able to produce still higher concentrations of incompatible elements than those observed in the samples Ch-1 and Ch-2 (Table 1). The calculated mixtures between proposed melts of the asthenosphere and lower crust can reproduce Trend A (Table 2, Figs. 5-7). The parental composition of Trend B (Pa-1) and Trend C (Pu-1) are on this mixing line. The parental composition (Pu-1) represents a mixture of 85% primitive basalt (Hu-1) derived mainly, from the asthenosphere with 15% high-K andesitic melt (Ch-1), probably derived from the lower crust.
- Crustal AFC processes were calculated after DePaolo (1981) for certain steps of the Trends A, B, and C (Fig. 5), and for the concentrations of K, Rb, Ba, La, Nb, Sr, Th, Y, Yb: (Table 2, Figs. 5-7). Sr, Nd and O isotopic composition was not included in the AFC calculations, because there is little contrast between the isotopic composition of the Cretaceous accretionary crust and an N-MORB-like mantle source. In addition, there is little or no isotopic evolution along these trends (Fig. 9). Petrographical observations suggest a significant change in the composition of the fractionated mineral assemblages during the development from basaltic andesitic to rhyolitic melt

composition (Fig. 3). This may affect the distribution of incompatible elements between phenocrysts and melt and was taken into account by calculating the AFC process stepwise with different fractionating mineral assemblages (AS-1 to AS-3, Fig. 3) and calculated distribution coefficients.

- Lower crustal AFC was calculated with two different rates of assimilation relative to crystallization (r) of $r=2$ and $r=0.2$. The average composition of the samples Ch-1 and Ch-2 was assumed to represent a crustal melt with an assimilated component from the lower crust. The first steps of Trends A and B (Figs. 5-7, Table 2) were calculated with fractionation of mineral assemblages As-1. The step from Hu-1 to Pa-1 composition (Trend B) was calculated with a low r -value of 0.2. The steps from Hu-1 to Pu-1 composition (Trend A) require a high r -value of 2 to reproduce the strong increase of Sr/Y, Th/Ta, Ta/Yb, and La/Yb ratios, the little variation of K/Rb and Ba/La ratios, and the little decrease of Mg and Cr contents. Results from calculations with such high r -values (2) are similar to the simple mixing model discussed before. Lower crustal AFC processes with variable r -values between 0.2 and 2 can explain the chemical variations observed in low-K to high-K andesites.
- Upper crustal AFC was calculated with a r -value of 0.5. An average composition of the Cretaceous accretionary basement (Kilian *et al.*, 1994; Hegner *et al.*, 1995) was taken as assimilated crustal component which is characterized by relatively low concentrations of incompatible elements, low La/Yb, intermediate Ba/La, and relatively high K/Rb ratios (Fig. 8, Tables 1 and 2). These characteristics differ little from the average compositions of Quaternary basaltic andesites of the investigated area, but differ significantly from felsic cratonic components which have been involved in AFC processes in the Central and Southern Andes (López-Escobar *et al.*, 1993). The Early Pleistocene Trend B was calculated for the steps from samples Pa-1 to Ch-5 (As-2; Fig. 3) and Ch-5 to Ch-7 (with As-3). The Late Pleistocene Trend C was calculated for the steps from samples Ch-3 to Ch-4 (with As-2) and Ch-7 to Ch-9. Calculated AFC products show little or no variations of Sr/Y, K/Rb, La/Yb, and Th/Ta ratios and cannot be distinguished from fractional crystallization trends in a closed system (r -value=0).

TABLE 2. STEP-WISE CALCULATION OF LOWER (LC) AND UPPER (UC) CRUSTAL AFC PROCESSES (DEPAOLO, 1991) FOR THE CHEMICAL DEVELOPMENT OF THE TRENDS A, B, AND C PRESENTED IN FIGURES 5, 6, 7).

	TREND B								Bulk D's		
	LC-AFC		UC-AFC		UC-AFC		UC-AFC		Fractionated mineral assemblage/liquid:		
	As-1, r=0.2		As-2, r=0.5		As-3, r=0.5		As-3, r=0.5		basaltic	andesitic	dacitic
	Hu-1	Ma 2%	Pa-1	Ma 20%	Ch-3	Ma 10%	Ch-4		As-1	As-2	As-3
Rb	10	11	11	25	30	43	49		0.03	0.06	0.08
Ba	250	275	345	594	520	776	772		0.04	0.19	0.35
Th	1.1	1.2	1.1	2.2	3.1	4.5	5.9		0.02	0.04	0.03
K	5,023	5,560	5,144	11,657	11,290	16,323	15,521		0.03	0.04	0.07
Ta	0.28	0.35	0.55	0.98	0.65	0.94	0.91		0.04	0.15	0.08
La	9.1	10.0	9.8	15.4	14.8	19.6	18.8		0.05	0.28	0.24
Ce	19.1	20.9	20.1	28.4	30.5	39.8	38.1		0.06	0.42	0.28
Nd	12.6	13.7	12.3	21.0	15.0	20.7	20.0		0.16	0.27	0.21
Sr	478	514	677	577	651	436	552		0.22	0.87	1.72
Zr	84	92	90	167	153	200	154		0.08	0.14	0.27
Y	20.0	21.4	18.0	30.3	17.0	23.6	18.0		0.32	0.41	0.31
Yb	1.67	1.81	1.55	2.79	1.25	1.80	1.20		0.29	0.42	0.33

TREND A				TREND C					Assimilated component		
Mixture		LC-AFC		UC-AFC		UC-AFC			Lower crust: partial melt (Ch-1)	Upper crust: accretionary bulk crust	
Hu-1: Ch-1		As-2, r=2		As-2, r=0.5		As-3, r=0.25					
Hu-1	15:85	As 15%	Pu-1	CH-5	Ma 10%	Ch-7	Ma 16%	Ch-9			
Rb	10	18	18	20	24	32	30	57	105	60	12
Ba	250	543	538	472	582	716	582	877	970	2200	198
Th	1.1	4.4	4.3	4.5	2.5	3.2	4.7	9.0	6.7	23.3	0.63
K	5,023	7,675	7,828	9,960	10,294	13,934	10,709	20,902	22,327	22,700	5,314
Ta	0.28	3.40	0.35	0.53	0.58	0.82	0.85	1.61	0.88	0.55	0.31
La	9.1	19.7	19.6	19.0	14.7	17.5	16.9	27.9	29.1	80	5.4
Ce	19.1	37.2	37.2	36.0	31.7	35.7	33.9	54.4	52.3	140	12.4
Nd	12.6	21.2	21.3	20.0	18.5	22.7	17.9	31.4	28.4	70	9.5
Sr	478	781	784	850	748	689	711	344	308	2500	261
Zr	84	95	100	101	162	205	144	235	252	60	59
Y	20.0	19.0	20.0	12.7	15.0	20.1	18.0	31.7	24.0	13	20
Yb	1.67	1.57	1.66	1.25	1.20	1.72	1.40	2.56	1.70	1.02	2.08

Bulk phenocryst/melt element partition coefficients (D) depend on the composition and proportions of the fractionated mineral assemblage and the SiO_2 content of the melt in equilibrium with the phenocryst assemblage. The authors used three different mineral assemblages (As-1 to As-3, representing typical modal phenocryst composition of figure 3) in the range of basaltic, andesitic and dacitic liquids. Bulk D 's between As-1 and a basaltic liquid, between As-2 and an andesitic liquid, and between As-3 and a dacitic liquid were calculated after Green (1994), Rapp and Watson (1995), Klein (1995) and references therein. Significant increase between the three different D 's is indicated with arrows. Bulk D 's of Sr become >1 in the dacitic system, so that Sr content decreases in the AFC product. Lower crustal AFC processes (LC-AFC: Trend A) was calculated with assimilation of a most likely crustal melt (Discussion, p. 214) which was assumed to be similar to the high-K andesite (Ch-1 of table 1). Upper crustal AFC processes (UC-AFC: Trend B, C) were calculated by assimilation of an average Cretaceous accretionary basement (Kilian *et al.*, 1994). The rate between assimilation and crystallization (r) and the assimilated mass (Ma), and crystallized mass (Mc) compared to the initial mass of 100% are calculated for each AFC product.

DISCUSSION

The primary source of calc-alkaline basalts is the mantle wedge which in many cases is contaminated by sediments (Morris *et al.*, 1990; Hawkesworth *et*

al., 1991). In some tectonic settings the subducted slab may be hot enough to produce 'adakitic' melts (Kay *et al.*, 1993; Stern and Kilian, in press). Other

sources of arc magmas may be located within the lithospheric mantle and the lower continental crust. The lithosphere is often assimilated by melts raising up from the asthenosphere. In the following, the genesis of the investigated volcanic rocks is discussed in the context of multiple sources.

Low Ce/Yb and low-K basalts are assumed to reflect the composition of primary melts from the asthenosphere (Hawkesworth *et al.*, 1991). Some volcanos of the Western Cordillera and Intra-Andean Valley of Ecuador like Pichincha and Paschoa volcanos have produced basaltic andesites with low Ce/Yb ratios and low K contents (sample Pa-1 in Figs. 5-7, Table 1). The calculated AFC process (Table 2) indicates that a low-K basaltic andesite (Pa-1) of the Western Cordillera of Ecuador may be derived from a primitive Andean low-K basalt (Hu-1) by about 10% mass fractionation of a typical basaltic phenocryst assemblage (AS-1; Fig. 3) and by only 2% mass contribution by melts produced in a garnet-amphibolite of the lower crust (r -value = 0.2). This suggests that the parental magma of the investigated volcanos in Ecuador is derived mainly, in the asthenosphere, similar to a primitive basalt (Hu-1) of the Southern South Andean Volcanic Zone, and characterized by low La/Yb (~10) and low Sr/Y ratios (~20), intermediate Th/Ta ratios (6-8), high K/Rb (>500) and Ba/La ratios (30-40), and by intermediate concentrations of Y (18-22 ppm) and the Heavy Rare Earth (HRE) elements (e.g., Yb = 1.5-2.2 ppm).

Miocene (volcanic stage 1) and Pleistocene (volcanic stage 3) andesites display large variations of the LIL, HFS and HRE elements for a restricted SiO₂ range (53-58 wt%). Pleistocene variations form Trend A and may include two end members (Figs. 5-7): a- a low-K/low Ce/Yb basalt of assumed asthenospheric origin, and b- a high-K andesite (samples Ch-1 and Ch-2) characterized by very high Sr/Y (~350), La/Yb (~65), Sr/Nd ratios (~35) and very low Rb/Sr ratios (0.001) as well as relatively low Y (<18 ppm) and Yb (~1.2 ppm) concentrations (Figs. 5-7; Tables 1, 2). The latter chemical characteristics cannot be derived from a low-K basaltic parent (e.g., Hu-1; Table 2) by an AFC process involving assimilation of the mafic basement of Western Ecuador. Instead, the chemical data of the high-K andesitic end member suggest an origin from a garnet-amphibolite representing either subducted oceanic crust or basaltic lower continental crust (Drummond and Defant, 1990; Kay *et al.*, 1993; Peacock *et al.*, 1994;

Stern and Kilian, in press). Partial melting of subducted oceanic crust at depths of 80-100 km requires temperatures of 850-900°C. These temperatures may be reached in the slab, if the age of subducted oceanic crust is young (<10 Ma), the convergence rate is low (2-3 cm), and the subduction angle is greater than 25° (Peacock, 1993). Below the Ecuadorian Andes, the Nazca Plate is subducted with a velocity of 9 cm/yr and is aged 15-20 Ma at the trench. Under these circumstances the geothermal gradients may not be high enough to produce melting of the subducted slab (Peacock *et al.*, 1994).

This conclusion suggests that the lower crust of Western Ecuador is a likely source for the high-K and low-Y andesites. The lower crust consists probably of Cretaceous altered oceanic MORB (Fig. 1 inset; Hegner *et al.*, 1995) converted to amphibolites or eclogites. Underplating basalts could trigger partial melting of such a lower crust. Low degrees of melts (<10%) produced by experiments of similar systems have dacitic compositions with medium-K to high-K content (1.5-3.5 wt % K₂O; Rapp and Watson, 1995; Springer, 1992). However, the amphibolitic source must be located in the stability field of garnet (>35 km depth) to explain the low Y (12-13 ppm) and Yb (<1.1 ppm) concentrations of the high-K andesites. Experimentally produced partial melts of amphibolites at lower crustal pressures (8-15 Kbar) show negative Eu and Sr anomalies and significantly lower Ti (HFS) concentrations than partial melts at 24 Kbar (Beard and Lofgren, 1991; Rapp *et al.*, 1991; Rushmer, 1991, 1993). The high-K andesites (Ch-3) have a slightly negative Eu-anomaly, but high Sr concentrations limiting the amount of residual plagioclase and they have high Th/Ta ratios, suggesting the existence of a residual Ti-bearing mineral phases, like rutile (Ayers and Watson, 1991, 1993). The high-K andesites have the highest ¹⁴³Nd/¹⁴⁴Nd (0.51292) of all Ecuadorian volcanic rocks and relatively high $\delta^{18}\text{O}$ values (+9‰) similar to the composition of the accretionary crust (Kilian *et al.*, 1994; Figs. 6, 7).

In summary, Trend A shows increase of alkalinity, increasing fractionation of HFS and HRE elements, and increase in the ¹⁴³Nd/¹⁴⁴Nd ratios and $\delta^{18}\text{O}$ values. These chemical and isotopic variations can be modelled by mixtures of asthenospheric-derived basalts and andesitic to dacitic melts from a garnet-amphibolitic lower crust.

The model calculations show that upper crustal AFC trends (Trends B and C, Figs. 5-7, Table 2) start

from different mixtures (Trend A) between parental magma (Hu-1), and derived from the asthenosphere and melts similar in composition to the high-K andesites (CH-1) probably produced by fusion of the lower crust. The basaltic andesite sample Pa-1, a parent for the Early Pleistocene Trend B, shows little contribution of crustal melts. AFC calculations which include assimilation of bulk Cretaceous accretionary crust and simultaneous fractionation of typical phenocryst assemblages (As-1 to As-3) are able to reproduce the trace element compositions of the medium-K andesites and dacites of the Early Pleistocene Trend B (Figs. 5-7, Table 2). Table 2 and figure 7 show that this AFC process does not fractionate significantly the element ratios of K/Rb, Th/Ta, Ba/La.

The sample Pu-1 representing the starting composition of the Late Pleistocene Trend C is also a member of Trend A which involves more contribution of lower crustal melts (about 15%; Figs. 5-7, Table 2). The upper crustal development of Trend C is represented by Late Pleistocene and Holocene volcanic rocks of the Chimborazo II, III and Puñalica

volcanos, showing a similar development at overall higher alkali element content than the Early Pleistocene Trend B.

Miocene to Holocene volcanic rocks of the Chimborazo volcano and associated volcanos representing the compositional range of Trends B and C have higher $^{87}\text{Sr}/^{86}\text{Sr}$ and lower $^{143}\text{Nd}/^{144}\text{Nd}$ ratios than N-MORB mantle (Fig. 9), suggesting a contamination of the mantle source by subducted sediment (Morris *et al.*, 1990; Stern 1991a, b; Stern *et al.*, 1990), or a contamination of primary melts by enriched components of the lithospheric mantle or continental crust (e.g., Ellam, 1992; Hildreth and Moorbath, 1988). Since the volcanic basement has N-MORB-like $^{143}\text{Nd}/^{144}\text{Nd}$ (Hegner *et al.*, in press), the higher Sr and lower Nd isotopic ratios cannot be produced by contamination with basement rocks, leaving subducted sediments as a likely contaminant. However, the $\delta^{18}\text{O}$ values (+6.2 to +9.0‰) are variable and overlap the range of the basement (Kilian *et al.*, 1994). This suggests a melt interaction with basement rocks which leaves the Sr and Nd isotopic compositions unchanged.

CONCLUSIONS

The composition of low-K basaltic andesites at Pichincha and Paschoa volcanos of Ecuador can be inherited from basalts of the mantle wedge which were little evolved by intra-crustal AFC processes. The asthenospheric source of the primary basalt must have been contaminated by slab-derived fluids to produce the observed high Th/Ta ratios and the more enriched isotopic compositions of the volcanic rocks when compared to upper mantle-like Cretaceous accretionary basement.

Miocene and Pleistocene volcanic rocks display a trend ranging from low-K basaltic andesites to high-K andesites. Trace element and isotopic compositions suggest that the high-K end member is derived from a garnet-amphibolitic lower crust. Mixing between asthenospheric melts and partial melts of the lower crust explains the strong variations of Th/Ta, Sr/Y and Ba/La ratios.

Two calc-alkaline trends ranging in composition

from andesite to rhyolite can be distinguished. The Early Pleistocene trend has low alkali contents and may be derived from a low-K andesitic parent with little contribution from the lower crust (<2% mass contribution). The Late Pleistocene trend may have originated from a medium-K andesitic parent which was contaminated by partial melts from the lower crust (15% mass contribution). Both trends are characterized by a moderate increase in the K_2O content (0.5 wt% K_2O per 5 wt% increase in the SiO_2), and little variations of Th/Ta, K/Rb, Ba/La and Sr/Y ratios. The chemical development can be explained by an upper crustal AFC process involving assimilation of Cretaceous accretionary basement. The complex chemical clusters of the Miocene-Pliocene volcanic rocks do not permit to identify single trends due to missing local geographic and stratigraphic information.

ACKNOWLEDGEMENTS

The German Research Foundation (DFG) is acknowledged for its support to R. Kilian (Ki-345-1 and Ki-456/2-1). The authors are grateful to A. Grun-der (Oregon State University, U.S.A.), B. Déruelle (Université de Pierre et Marie Curie) and W. Hildreth

(U.S. Geological Survey) for their careful revisions of the manuscript, thus contributing to the improvement of the text. This is a contribution to IGCP Project 345 'Andean Lithospheric Evolution'.

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