

## Slab melting and slab melt metasomatism in the Northern Andean Volcanic Zone : adakites and high-Mg andesites from Pichincha volcano (Ecuador)

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*Key words.* – Adakite, Slab melting, Subduction zone metasomatism, NVZ, Andes, Ecuador, Pichincha volcano, Geochemistry, Isotopes.

*Abstract.* – Situated in the fore-arc of the Northern Volcanic Zone (NVZ) of the Andes in Ecuador, Pichincha volcano is an active edifice where have been erupted unusual magmas as adakites and high-Mg andesites. The particular geodynamic setting of the ecuadorian margin (i.e. the flat subduction of the Carnegie Ridge) suggests that thermo-barometric conditions for the partial melting of the oceanic crust are accomplished beneath this volcano. Pichincha adakites possess all the geochemical and isotopic characteristics of slab melts described in various other arc settings. High-Mg andesites with geochemical characteristics close to those of adakites present strong enrichments in MgO that suggest that, once they were produced by ca. 10 % partial melting of the downgoing subducted slab, some adakites en route to the surface strongly interacted with the peridotitic mantle wedge. Adakitic magmas could then represent, as in many other arcs where slab melting occurs, the principal metasomatic agent of the mantle in the NVZ in Ecuador.

### Les adakites et les andésites riches en Mg du volcan Pichincha (Equateur) : témoins de la fusion de la croûte océanique et de la métasomatose adakitique sous la zone volcanique nord des Andes

*Mots clés.* – Adakite, Métasomatose, Fusion de zone de subduction, NVZ, Andes, Equateur, Pichincha, Géochimie, Isotopes.

*Résumé.* – Situé dans la zone volcanique nord des Andes en Equateur, le volcan Pichincha est un édifice actif entré récemment dans un nouveau cycle éruptif. La position exacte de la plaque plongeante sous l'Equateur est difficile à déterminer en raison de l'absence de sismicité intermédiaire dans la zone de subduction. Gutscher *et al.* [1999] ont cependant récemment proposé qu'il puisse exister sous la marge une portion de plaque horizontale portée par la ride de Carnegie de faible densité qui est actuellement en subduction. D'autre part, Gutscher *et al.* [2000] ont observé à l'échelle du globe une relation étroite entre les portions de plaque subductée horizontale et la production de magmas adakitiques. Cette association suggère que l'horizontalisation de la plaque subductante permet une modification importante de la structure thermique du coin de manteau et le maintien de la lithosphère subductante dans les conditions de pression et de température compatibles avec la fusion de la croûte océanique.

Un échantillonnage du volcan Pichincha a permis de mettre en évidence que les produits émis sont constitués d'andésites et de dacites moyennement potassiques possédant toutes les caractéristiques des adakites (c'est-à-dire des produits de fusion directe de la croûte océanique) telles que des enrichissements en Na<sub>2</sub>O, de fortes teneurs en Sr, mais de faibles concentrations en yttrium et en terres rares lourdes. Par ailleurs, on trouve parmi ces laves des andésites magnésiennes possédant à la fois les caractéristiques des adakites mais également des concentrations en magnésium élevées. Minéralogiquement, les laves du Pichincha contiennent essentiellement des cristaux de plagioclase, d'amphibole, d'orthopyroxène, de clinopyroxène et de magnétite. L'amphibole est généralement absente dans les andésites magnésiennes où le pyroxène devient le minéral dominant.

Une modélisation géochimique montre qu'il est parfaitement possible d'expliquer la formation des adakites du Pichincha par 10 % de fusion partielle d'un basalte issu de la dorsale des Galápagos métamorphisé dans le faciès amphibolite à grenat. Les données isotopiques en strontium, néodyme et plomb sur les laves du Pichincha confirment que la source de ces laves est vraisemblablement un MORB altéré présentant un rapport <sup>87</sup>Sr/<sup>86</sup>Sr proche de 0,7040 ainsi que des enrichissements en éléments mobiles comme le rubidium ou le potassium.

Les données isotopiques et géochimiques semblent écarter toute contribution significative de la croûte continentale ou des sédiments subductés lors de la formation des laves du Pichincha par quelque processus que ce soit.

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Cependant, la fusion de la croûte océanique ne peut expliquer seule toutes les caractéristiques des laves du Pichincha et notamment leurs concentrations en magnésium. L'enrichissement en Mg des adakites naturelles par rapport à leurs homologues expérimentaux issus des expériences de fusion de protolites basiques est une caractéristique bien connue qui suggère que les adakites naturelles lors de leur remontée vers la surface métasomatisent à des degrés divers le manteau péridotitique qu'elles traversent. Cette interaction semble être à l'origine de toute une gamme de laves allant des adakites "pures" jusqu'aux basaltes et andésites riches en Nb (supposés être des produits de fusion d'un manteau métasomatisé par des magmas adakitiques) en passant par les andésites plus ou moins magnésiennes. La présence d'andésites magnésiennes au volcan Pichincha associée à celle de laves aux caractéristiques adakitiques au volcan Antisana [Bourdon *et al.*, 1999; Bourdon *et al.*, 2002] situé en position arrière-arc par rapport au Pichincha suggère que les magmas adakitiques pourraient être l'agent de métasomatose principal sous la zone volcanique nord en Equateur.

## INTRODUCTION

The Quaternary volcanism along the South American continent western margin is classically separated into four distinct provinces namely, the Northern Volcanic Zone (NVZ, in Ecuador and Colombia), the Central Volcanic Zone (CVZ), the Southern Volcanic Zone (SVZ) and the Austral Volcanic Zone (AVZ) separated one from the other by volcanic gaps (fig. 1) [Thorpe *et al.*, 1982].

In the Ecuadorian NVZ, Pichincha volcano is an active volcano situated only 15 km away from Quito (fig. 1), inhabited by about 1.5 million people. Pichincha is a volcanic complex constituted by two edifices : the Rucu and Guagua Pichincha. The activity of the old Rucu Pichincha probably ceased 1 Ma ago [Barberi *et al.*, 1992] and the most recent edifice (Guagua Pichincha) is constructed on its western flank. The present activity takes place inside a large amphitheater widely opened towards the Pacific which was created by a major collapse that occurred ca. 50 ka ago [Barberi *et al.*, 1989]. The Guagua Pichincha erupted in the 16th and 17th centuries and experienced a new volcanic cycle from 1999 to 2001 (see GNV Bulletin).

The study of Pichincha lavas, the most trench-closed erupted magmas in the NVZ of Ecuador, is a keypoint to understand the complex process of recycling of oceanic crust that occurs in the NVZ subduction zone, as well as the composition and evolution of the mantle wedge. The aim of this paper is to show that all Pichincha lavas display the geochemical and isotopic characteristics of slab melts, a part of which could act as a metasomatic agent of the sub-arc mantle.

## PICHINCHA VOLCANO GEOTECTONIC SETTINGS

The Pichincha volcanic complex is located in the western Cordillera of Ecuador and lies above the youngest part of the Ecuadorian continental crust that was accreted to the South American paleo-margin during the early Paleogene [Feininger, 1986]. The crustal basement of the volcano is constituted by Cretaceous to Paleocene volcanic rocks of the Macuchi volcanic arc as well as by volcano-sedimentary rocks of the Sillante Formation [Feininger, 1986]. Slivers of basic to ultrabasic material belonging to the Piñon formation constitute relics of an oceanic suture that occurred along the north-western part of the South American margin at the end of the Cretaceous. The strong positive Bouguer anomaly (up to +162 mgal) affecting this part of the Ecuadorian Andes suggests that the entire crust is mainly mafic and less than 50 km thick [Feininger and Seguin, 1983].

As for the main part of Ecuador, the exact position of the subducting plate beneath Pichincha volcano is difficult to constrain because of the lack of seismicity in the subduction zone deeper than 60 km (fig. 2). Gutscher *et al.* [1999] proposed that a flat slab, supported by the buoyant aseismic Carnegie ridge presently subducting, could exist beneath the Ecuadorian margin. Following these authors, the plate could be at a depth of nearly 70-80 km beneath Pichincha volcano. More recently, Gutscher *et al.* [2000] have shown that flat subduction is often linked to adakite genesis. These authors point out that during flat subduction the lower plate travels several hundred kilometers at nearly the same depth, thus remaining in the pressure-temperature window allowing slab melting to occur.

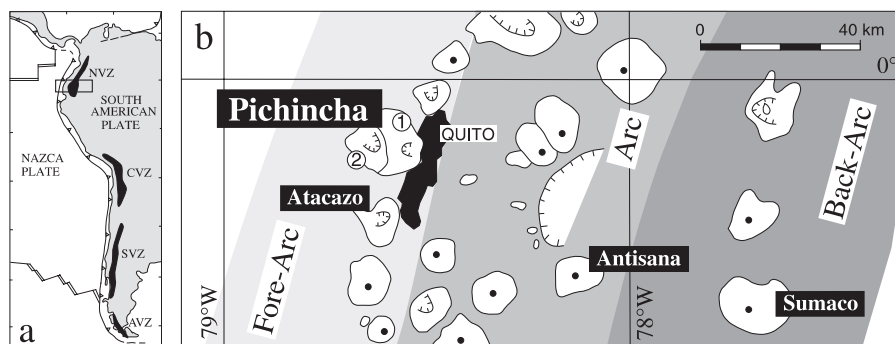


FIG. 1. – a) Location of the NVZ on the South American continent ; b) Location of the Pichincha volcano in the Northern Volcanic Zone in Ecuador [(1) Rucu Pichincha, (2) Guagua Pichincha].  
 FIG. 1. – a) Localisation de la NVZ sur le continent sud-américain ; b) Localisation du volcan Pichincha dans la zone volcanique nord en Equateur [(1) Rucu Pichincha, (2) Guagua Pichincha].

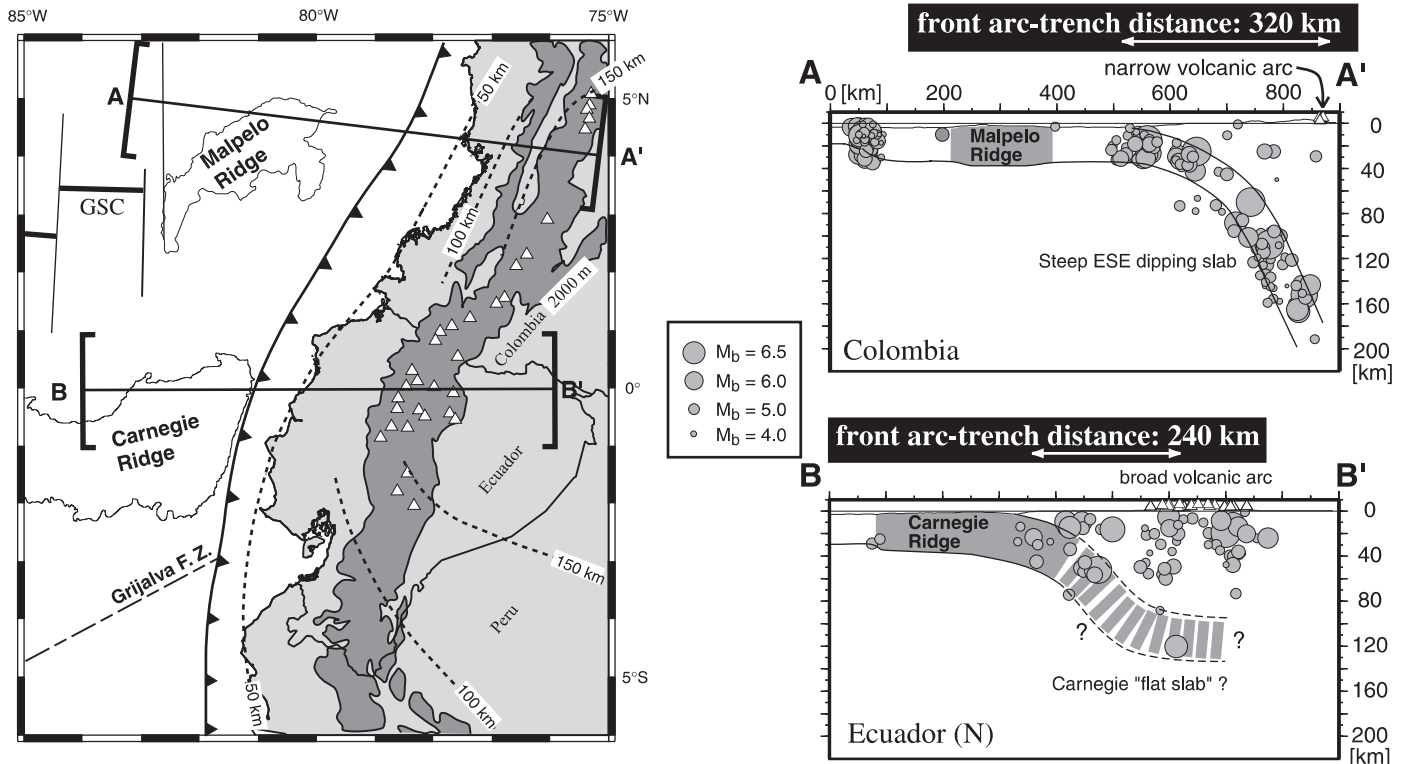


FIG. 2. – Schematic map of the northwestern part of South America and associated seismicity along profile AA' (Colombia) and BB' (Ecuador). Active volcanoes are designated by white triangles. Note the subduction of the Carnegie Ridge. Modified from Gutscher *et al.* [1999]. GSC : Galápagos Spreading Center. Mb = earthquakes magnitude

FIG. 2. – Carte schématique du Nord-Ouest de l'Amérique du Sud et sismicité associée le long des profils AA' (Colombie) et BB' (Equateur). Les volcans actifs sont marqués par des triangles blancs. Noter l'entrée en subduction de la ride de Carnegie. Modifié d'après Gutscher *et al.* [1999]. GSC : dorsale des Galápagos. Mb = magnitude des séismes.

In Ecuador, the estimated depth of the subducting plate (ca. 70 km) beneath Pichincha volcano is compatible with the “adakitic window” that predicts the partial melting of the oceanic crust between 1 to 2 GPa and 700 to 800°C [Rapp *et al.*, 1991; Maury *et al.*, 1996]. These thermobarometric conditions imply that adakites should be erupted in a fore-arc position relatively to “normal” calc-alkaline magmatism [Defant and Drummond, 1990].

Within the Northern Volcanic Zone, Ecuador's western volcanic chain is situated in a fore-arc setting, with a trench-arc gap of only 250 km compared to 300 km in Colombia. It is also important to note that Barberi *et al.* [1988] estimated that active magmatism shifted westwards into the western Cordillera ca. 2 Ma ago, approximately at the same time as the Carnegie ridge was entering the subduction zone and thus corresponding to the beginning of flat subduction. The fore-arc setting of Pichincha volcano as well as the flat subduction that seems to occur beneath Ecuador both suggest that slab melting conditions could exist beneath Pichincha volcano.

## PETROLOGY AND MINERALOGY

Pichincha lavas are characterized by a limited range in SiO<sub>2</sub> content (57 to 65 %) and plot in the medium potassic acid andesite to dacite domains of the Peccerillo and Taylor [1976] diagram (fig. 3). Five andesites display high MgO contents (6.02-3.2 %) and high Mg# (61.5-57.5) and can be considered as high-magnesian andesites (table I). They also

display the highest TiO<sub>2</sub> concentrations although these values are typical for subduction-related lavas (fig. 4). The other Pichincha lavas present lower MgO content (3.7-2 %) and Mg# (54-45). All Pichincha lavas (except one) have Al<sub>2</sub>O<sub>3</sub> contents greater than 16 % and relatively high Na<sub>2</sub>O concentrations (up to 4.4 %). The sodic character of these lavas is reinforced by their Na<sub>2</sub>O/K<sub>2</sub>O ratios as high as 3.6. These geochemical characteristics are typical of adakites (table II) [Defant and Drummond, 1990].

Pichincha rocks contain phenocrysts of (in order of decreasing abundance) plagioclase and amphibole, orthopyroxene, clinopyroxene and magnetite (of which representative chemical analyses are given in table III). Although orthopyroxene crystals (mostly hypersthene) are present in all the lavas, they are generally more abundant in the andesites than in the dacites and can even be the dominant phase in magnesian andesites (where amphibole is rare). Diopside is mostly found in the magnesian andesites. Pyroxene in the magnesian andesites can be Cr-rich (up to 1 %) while Cr<sub>2</sub>O<sub>3</sub> contents of pyroxenes in other andesites is always less than 0.4 %. In the same way, Mg# of pyroxenes in magnesian andesites are systematically higher and ranges between 90 to 70. Fe-Ti oxides occurs in all the lavas and are constituted by magnetite and titanomagnetite.

Plagioclase phenocrysts from the magnesian andesites show almost systematically a reverse zoning with cores less calcic (An<sub>38-44</sub>) than rims (An<sub>39-59</sub>). In the non-magnesian

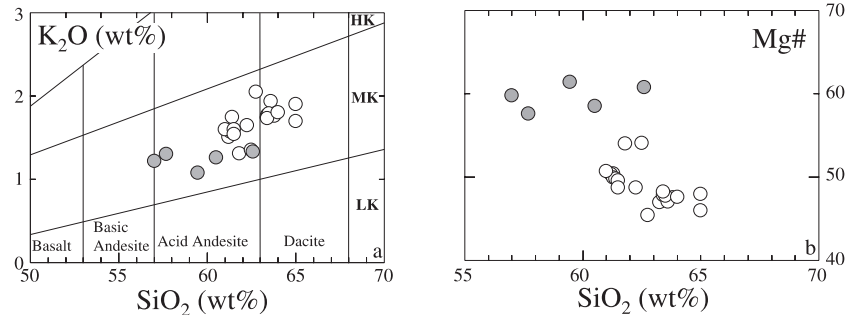


FIG. 3. – a)  $K_2O$  vs.  $SiO_2$  classification diagram [modified from Peccerillo and Taylor [1976] for the Pichincha lavas. LK : low-K; MK : medium-K; HK : high-K. (White circles are adakites ; grey circles are magnesian andesites). b)  $Mg\#$  vs.  $SiO_2$  diagram.  $Mg\# = Mg / (Mg + Fe_T)$  with  $Fe_T =$  total iron. FIG. 3. – a) *Diagramme de classification  $K_2O$  vs.  $SiO_2$  [modifié d'après Peccerillo et Taylor 1976], pour les laves du Pichincha. LK : faiblement potassique; MK : moyennement potassique; HK : fortement potassique (Les ronds blancs représentent les adakites et les ronds gris, les andésites magnésiennes). b) Diagramme  $Mg\#$  vs.  $SiO_2$ .  $Mg\# = Mg / (Mg + Fe_T)$  avec  $Fe_T =$  fer total.*

TABLE I. – Geochemical and isotopic data of representative lavas from Pichincha volcano. Amg : magnesian andesite; A : normal andesite; D : dacite. TABL. I. – *Données isotopiques et géochimiques de laves représentatives du volcan Pichincha. Amg : andésite magnésienne; A : andésite normale; D : dacite.*

Type Sample	Amg Pich32K	Amg Pich 4C	A Pich 8E	A Pich 9C	D Pich 10	D Pich 4A
$SiO_2$	57	57.7	61.4	61.5	65	63.8
$TiO_2$	0.52	0.56	0.51	0.48	0.45	0.41
$Al_2O_3$	15.6	16	16.5	16.6	16.2	16.7
$Fe_2O_3$	8.02	7.45	6.12	6.05	5.2	5.5
MnO	0.13	0.11	0.09	0.09	0.07	0.09
MgO	6.02	5.1	3.06	2.9	2.42	2.54
CaO	7.3	6.6	5.57	5.6	4.7	5
$Na_2O$	3.17	3.61	4	3.97	4.2	4.18
$K_2O$	1.22	1.3	1.75	1.54	1.7	1.76
$P_2O_5$	0.09	0.15	0.15	0.14	0.13	0.13
LOI	0.45	1.15	0.9	1.45	0.48	0.45
Total	99.52	99.73	100.05	100.32	100.55	100.56
Rb	45	29	41.5	35.5	38.5	42.5
Sr	415	505	513	490	505	518
Ba	565	550	680	640	740	800
Sc	23	18	12	12.5	10.6	11.5
V	195	177	140	135	115	120
Cr	265	165	71	55	80	48
Co	28	33	19	29	15	20
Ni	82	81	38	26	27	25
Y	12.5	10.8	7.8	8.5	6	9.5
Zr	77	81	73	86	88	74
Nb	2.4	3	3	2.9	3.1	2.8
La	9.8	12.1	15	11.5	10.8	12
Ce	18	25	27	23	22	22.5
Nd	9.7	13	13.5	11.8	10.5	11
Sm	2.2	2.6	2.7	2.6	2.3	2.15
Eu	0.7	0.77	0.81	0.72	0.7	0.6
Gd	2.3	2.4	2.6	2.6	2.5	2
Dy	2.1	2	1.65	1.45	1.3	1.75
Er	1.25	1.1	0.8	0.85	0.6	0.85
Yb	1.23	0.99	0.78	0.87	0.64	0.84
Th	2.8	2.65	4.1	2.85	2.8	3.3
$^{206}Pb/^{204}Pb$	-	19.006	-	18.992	18.996	-
$^{207}Pb/^{204}Pb$	-	15.589	-	15.585	15.579	-
$^{208}Pb/^{204}Pb$	-	38.721	-	38.698	38.692	-
$^{87}Sr/^{86}Sr$	-	0.704043	-	0.704065	0.704055	-
$^{143}Nd/^{144}Nd$	-	0.512880	-	0.512882	0.512894	-

Major element (in wt%) and trace element analyses (in p.p.m.) have been performed in Brest by ICP-AES following the method given in Cotten *et al.* [1995]. Relative standard deviations are equal to, or less than 2% and 5% for major and trace elements respectively. Elements separations and isotopes ratios determinations have been performed at the Laboratoire de Géochimie Isotopique de l'UMR 6538 "Domaines Océaniques" in Brest following the method given in Dosso *et al.* [1991].  $^{87}Sr/^{86}Sr$  is corrected for mass fractionation by normalizing to  $^{86}Sr/^{88}Sr = 0.1194$  and given relative to a NBS SRM987 standard value of 0.710267 (n=7).  $^{143}Nd/^{144}Nd$  is corrected for mass fractionation by normalizing to  $^{146}Nd/^{144}Nd = 0.7219$  and given relative to a AMES standard value of 0.511961 (n=7). Pb isotopic data were corrected for instrumental mass fractionation by applying a discrimination factor determined by multiple analysis of NBS SRM981 for lead using the value of Todt *et al.* [1984]. Two standard errors of the mean are < 0,003% for Sr, < 0,004% for Nd and < 0,1% for Pb.

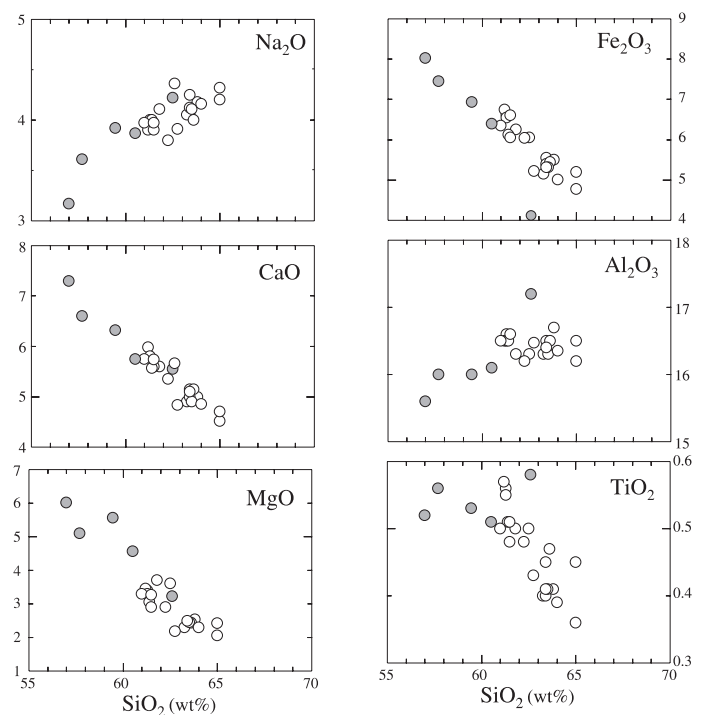


FIG. 4. – Harker diagrams for the Pichincha lavas (same symbols as in figure 3). FIG. 4. – *Diagrammes de Harker pour les laves du Pichincha (mêmes symboles que dans la figure 3).*

lavas, anorthite contents of the plagioclase are almost the same ( $An_{34-65}$ ) but zoning is generally normal.

Amphibole phenocrysts frequently display destabilization rims formed by opaque minerals, due to a variation in pressure-temperature conditions during eruption. Amphibole, with plagioclase, is the most abundant phase in the non-magnesian lavas. These amphiboles are calcic and have a constant  $Mg\#$  (ca. 85) ranging in composition from magnesio-hornblende to tschermakite, following the classification of Leake [1978]. Lastly, abundant chrome-spinels are present as inclusions in pyroxenes of the magnesian andesites.

Both mineralogies from adakites and magnesian andesites are typical from those found in other arcs where such rocks are erupted.



TABLE II. – Comparison between typical adakites [data from Drummond and Defant, 1990; Maury *et al.*, 1996] and Pichincha lavas.  
 TABL. II. – Comparaison des caractéristiques géochimiques des adakites typiques (données de Drummond et Defant, 1990; Maury et al, 1996) avec celles des laves du Pichincha.

	Adakites	Pichincha lavas
SiO <sub>2</sub>	≥57%	57-65%
Al <sub>2</sub> O <sub>3</sub>	≥15%	15.6-17.2%
Sr	>400 ppm	415-570 ppm
Y	<18 ppm	6-12.5 ppm
Yb	<1.8 ppm	0.64-1.23 ppm
La/Yb	≥20	8-24
Sr/Y	≥40	33-84

TABLE III. – Representative chemical analyses of hornblende, pyroxene and plagioclase.  
 TABL. III. – Analyses chimiques représentatives de hornblendes, pyroxènes et plagioclases.

	PICH 9B	PICH 8E	PICH 8E	PICH 12A	PICH 12A	PICH 12A	PICH 12A	PICH 8E
	A-Hb	A-Hb	A-Px	Amg-Px	Amg-Px	Amg-Pl-R	Amg-Pl-C	A-Pl
SiO <sub>2</sub>	44.39	45.77	53.75	52.80	55.80	54.26	58.94	57.79
TiO <sub>2</sub>	1.89	1.84	0.11	0.21	0.05	0.03	0.00	0.00
Al <sub>2</sub> O <sub>3</sub>	9.33	8.52	0.35	1.36	1.90	27.27	24.91	26.56
Fe <sub>2</sub> O <sub>3</sub>	9.19	7.63	1.59	1.77	1.85	1.24	0.30	0.25
Cr <sub>2</sub> O <sub>3</sub>	0.01	0.00	0.04	0.00	0.69	-	-	-
FeO	6.16	6.60	18.83	7.35	6.41	-	-	-
MnO	0.22	0.20	0.80	0.20	0.14	-	-	-
NiO	-	-	0.02	0.03	0.15	-	-	-
MgO	13.60	14.23	24.32	14.52	32.66	0.06	0.04	0.01
CaO	11.20	11.29	0.97	21.70	1.22	11.13	7.90	9.09
Na <sub>2</sub> O	1.71	1.64	0.00	0.44	0.06	4.98	6.77	6.09
K <sub>2</sub> O	0.56	0.66	0.01	0.00	0.00	0.25	0.35	0.39
H <sub>2</sub> O	2.09	2.11	-	-	-	-	-	-
Total	100.33	100.49	100.79	100.36	100.94	99.21	99.20	100.19
Si	6.46	6.62	1.97	1.96	1.93	2.48	2.66	2.59
Al	1.60	1.45	0.02	0.06	0.08	1.47	1.32	1.40
Ti	0.21	0.20	0.00	0.01	0.00	0.00	0.00	0.00
Fe <sup>2+</sup>	0.99	0.82	0.04	0.05	0.05	0.04	0.01	0.01
Cr	0.00	0.00	0.00	0.00	0.02	-	-	-
Mg	2.95	3.07	1.33	0.80	1.68	0.00	0.00	0.00
Ni	-	-	0.00	0.00	0.00	-	-	-
Fe <sup>2+</sup>	0.77	0.81	0.58	0.23	0.19	-	-	-
Mn	0.03	0.02	0.03	0.01	0.00	-	-	-
Ca	1.75	1.75	0.04	0.86	0.05	0.55	0.38	0.44
Na	0.48	0.46	0.00	0.03	0.00	0.44	0.59	0.53
K	0.10	0.12	0.00	0.00	0.00	0.01	0.02	0.02
OH	2.00	2.00	-	-	-	-	-	-
Total	17.33	17.33	4.00	4.00	4.00	4.99	4.98	4.98

A, Andesite; Amg, Magnesian andesite; Hb, Hornblende; Px, Pyroxene; Pl, Plagioclase; R, Rim; C, Core

**TRACE ELEMENTS AND ISOTOPIC CHARACTERISTICS**

Regarding the trace elements, felsic rocks from Pichincha volcano display typical geochemical characteristics of slab melts [Defant and Drummond, 1990] (table II), including low concentrations of heavy rare earth elements (HREE) and Y (ex : Yb < 1 ppm, except for one sample at 1.23 ppm). Pichincha lavas also display high concentrations in Sr (415-570 ppm) which are typical of adakites and have been attributed to the total removal of plagioclase in the residual amphibolitic source during partial melting. In the Sr/Y vs. Y diagram (fig. 5), Pichincha lavas plot in the adakitic field in contrast with the "normal" calc-alkaline rocks characterized by higher Y concentrations and lower Sr/Y ratios.

On the primitive mantle-normalized multi-element diagram (fig. 6), Pichincha lavas display HFSE negative anomalies, typical of orogenic magmas. These very strong Nb anomalies are associated with high La<sub>N</sub>/Nb<sub>N</sub> ratios ranging from 3.5 to 5.3. Nb concentrations are very low (between 2

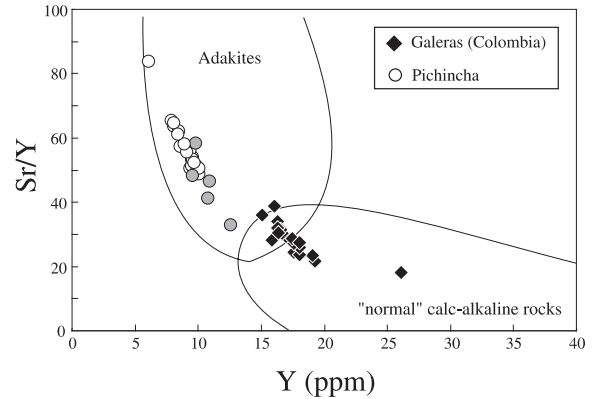


FIG. 5. – Sr/Y vs. Y discrimination diagram between adakites and "normal" calc-alkaline rocks [after Drummond and Defant, 1990]. Galeras volcano unpublished data from C. Robin. (Same symbols as in figure 3)  
 FIG. 5. – Diagramme de discrimination Sr/Y vs. Y entre les adakites et les laves calco-alkalines "normales" [d'après Drummond et Defant, 1990]. Données non-publiées sur le volcan Galeras d'après C. Robin. (Mêmes symboles que dans la figure 3).

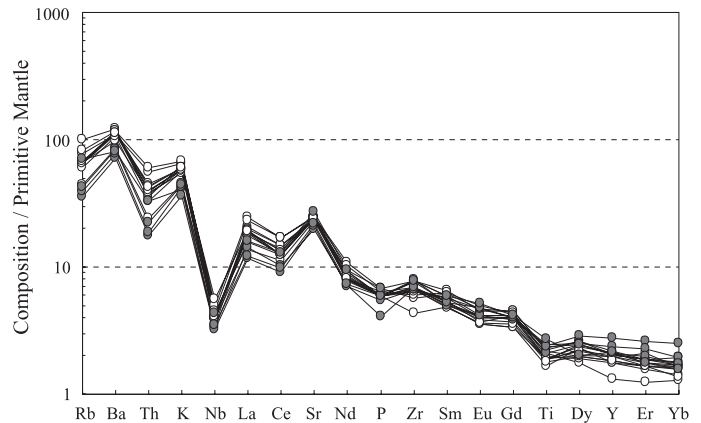


FIG. 6. – Extended trace elements diagrams of representative lavas of Pichincha volcano. Open circles : magnesian andesites ; closed circles : normal andesites and dacites. Normalization to primitive mantle of Sun and McDonough [1989].  
 FIG. 6. – Diagrammes multiélémentaires élargis de laves représentatives du volcan Pichincha. Cercles blancs : andésites magnésiennes ; cercles noirs : andésites et dacite normales. Normalisation au manteau primitif de Sun et McDonough [1989].

and 4 ppm, but generally less than 3 ppm), close to those usually found in MORBs [2.33 ppm; Sun and McDonough, 1989]. Pichincha lavas spidergrams also show strong Sr positive anomalies and clear enrichments in LILE and Th, with incompatible element ratios (for example Ba/La ranging from 40 to 70) typical of arc magmas. Lastly, the strong slope of chondrite-normalized rare earth elements patterns (not shown as a figure) characterizes the important LREE/HREE fractionation. All Pichincha lavas, except two, display a Eu negative anomaly, while typical adakites show a positive anomaly (or none) ; that is the only difference between Pichincha adakites and common adakites.

All the compatible elements display the same decreasing concentrations correlated with SiO<sub>2</sub> enrichment (fig. 7). Magnesian andesites always contrast with their higher concentrations in compatible elements (especially Ni and Cr). The evolution among incompatible elements is less clear.

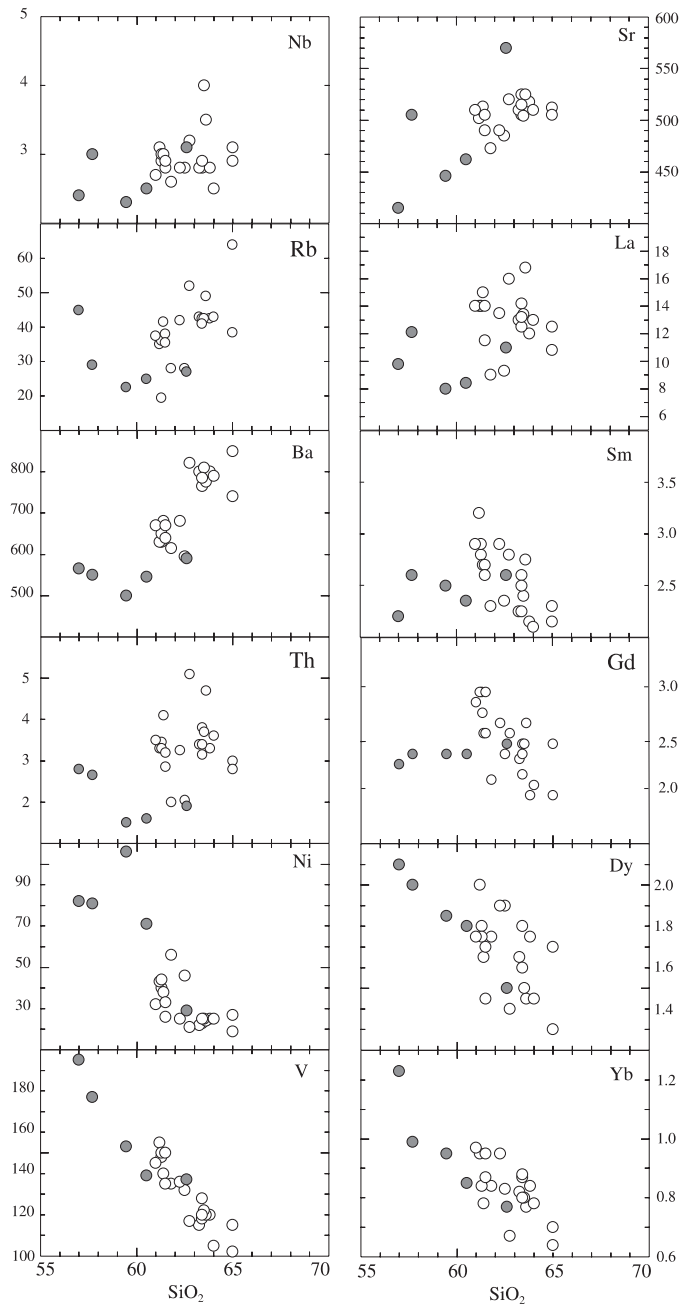


FIG. 7. – “Harker-like” diagrams showing the trace element variations of Pichincha lavas. (Same symbols as in figure 3).

FIG. 7. – Pseudo-diagrammes de Harker montrant les variations en éléments en traces dans les laves du Pichincha. (Même symboles que dans la figure 3).

For example, Ba concentrations increase with SiO<sub>2</sub> enrichment while Th and La have more complex evolutions. MREE (ex : Sm) do not show clear variations as magnesian andesites display lower concentrations than “normal” andesites, close to those of dacites. Nb shows increasing concentrations with SiO<sub>2</sub> enrichment but this is less obvious if the richest sample (only 4 ppm) is omitted. Sr also displays increasing concentrations correlated to SiO<sub>2</sub> enrichment suggesting that plagioclase fractionation is not a dominant process in the evolution of the series. HREE, present in low concentrations, display a clear impoverishment correlated to SiO<sub>2</sub> increase. HREE fractionation is re-

sponsible for high La/Yb ratios ranging from 8 to 24 (typically higher than 14).

Pichincha lavas present the lowest <sup>87</sup>Sr/<sup>86</sup>Sr ratios among the Ecuadorian recent lavas (< 0.70407) (fig. 8). Only two samples from Puñalica volcano (in the southern arc) have lower radiogenic ratios (<sup>87</sup>Sr/<sup>86</sup>Sr < 0.70390) [Harmon *et al.*, 1984]. The western Cordillera of Ecuador is characterized by low Sr isotope ratios and also by high Nd isotope ratios (> 0.512860) systematically higher than those from the eastern Cordillera. Isotopic data from the western Cordillera are close to or overlap those from oceanic arc lavas [low <sup>87</sup>Sr/<sup>86</sup>Sr, high <sup>143</sup>Nd/<sup>144</sup>Nd; Hawkesworth *et al.*, 1993] and are clearly distinct from the other Andean data (specially from the CVZ rocks) displaying a strong isotopic imprint of crustal contamination [Hawkesworth *et al.*, 1979; Harmon *et al.*, 1984]. Pichincha lavas also differ from other Ecuadorian rocks by lower <sup>207</sup>Pb/<sup>204</sup>Pb ratios at a given <sup>206</sup>Pb/<sup>204</sup>Pb ratio (fig. 9). These values fall in the domain of Galápagos Islands rocks and even correspond to the extremity of the Galápagos spreading center domain. Among the Quaternary rocks from the Andes, only rocks from the Austral Volcanic Zone display lower Pb isotope ratios closer to those of typical MORBs.

It is important to point out that Sr isotope ratios of Pichincha lavas are exactly the same than those estimated for a typical altered MORB [= 0.7039-0.7041; Spooner, 1976; Tatsumi and Kogiso, 1997]. Adakites from various arcs also display isotopic characteristics close to those of MORB [ex : Drummond *et al.*, 1996], suggesting that the principal source of these magmas is the partial melting of altered subducted oceanic crust, without significant contribution of subducted sediments.

## DISCUSSION ON THE ORIGIN OF PICHINCHA LAVAS

### Slab melting

Pichincha adakites have all the geochemical characteristics displayed by melts considered to be generated by partial melting of the oceanic crust. Mineralogically, they can be distinguished from typical adakites by abundant clinopyroxene and orthopyroxene crystals that should be absent in adakites *s.s.* [e.g. Maury *et al.*, 1996]. Pichincha adakites also display La/Yb ratios ranging from 8 to 24, although it is usually admitted that typical adakites show La/Yb ratios higher than 20 [Drummond and Defant, 1990]. Nevertheless, adakites from Zamboanga (Philippines) also display contrasted La/Yb ratios ranging from 8.8 to 24 [Sajona *et al.*, 1996], and abundant crystals of pyroxene are described in adakites from the Aleutians [Kay, 1978; Yogodzinski and Kelemen, 1998]. In addition, Hörmann and Pichler [1982] have already suggested, on the basis of geochemical data, that part of the magmas from the NVZ could be produced by partial melting of the subducted oceanic crust metamorphosed in the amphibolite facies.

Studies on the origin of adakites by partial melting of subducted oceanic crust often focused on the evaluation of the degree of partial melting using the more incompatible elements and considering their partition coefficient relative to melt residues close to zero [e.g. Mahlburg Kay *et al.*, 1993]. Nevertheless, the use of the more incompatible elements (Cs, K, Ba and Rb) does not seem appropriate con-

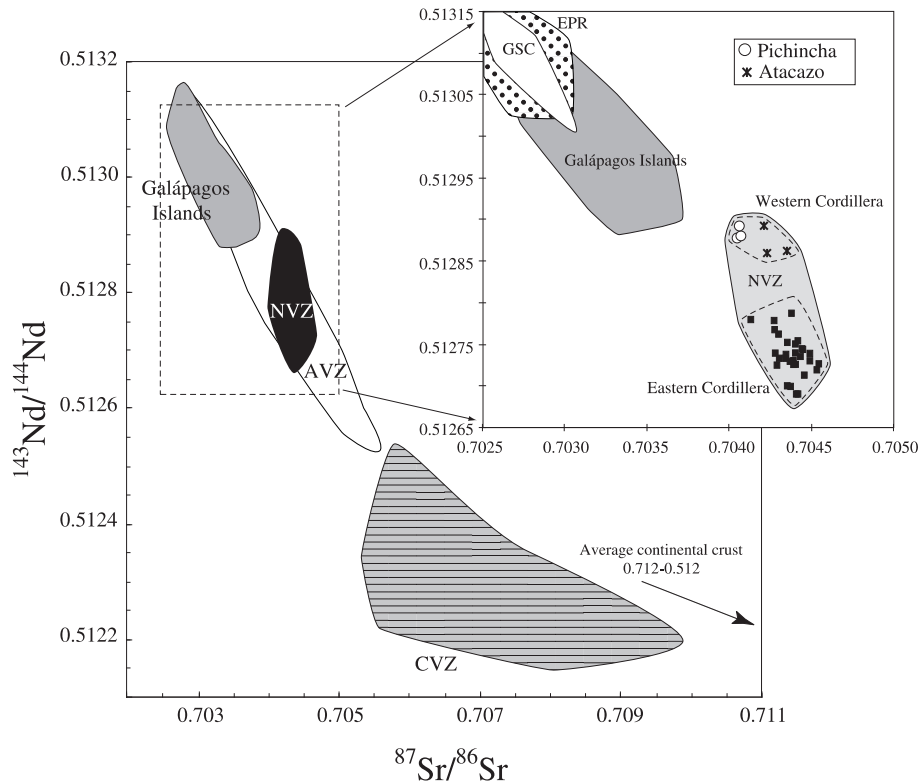


FIG. 8. –  $^{143}\text{Nd}/^{144}\text{Nd}$  vs.  $^{87}\text{Sr}/^{86}\text{Sr}$  diagram. Comparison of Pichincha (open circles) and Atacazo rocks (crosses) data with those of the eastern Cordillera of Ecuador (black squares) [Bourdon *et al.*, 2002 and unpublished data]. Fields of isotopic data from Galápagos Islands, Galápagos spreading center (GSC) and the East Pacific Rise (EPR) [White *et al.*, 1993 and references therein], from the Austral Volcanic Zone [Stern *et al.*, 1984; Stern and Killian, 1996] and the Central Volcanic Zone [James, 1982; Hawkesworth *et al.*, 1982; Harmon *et al.*, 1984; Davidson *et al.*, 1990] are also shown.

FIG. 8. – Diagramme  $^{143}\text{Nd}/^{144}\text{Nd}$  vs.  $^{87}\text{Sr}/^{86}\text{Sr}$ . Comparaison des données des roches du Pichincha (cercles vides) et de l'Atacazo (croix) avec celles de la Cordillère orientale d'Equateur (carrés noirs); [Bourdon *et al.*, 2002; et données inédites]. Les champs des données isotopiques des îles Galápagos, de la dorsale des Galápagos et de la ride Est-Pacifique [White *et al.*, 1993 et références incluses], ainsi que de la zone volcanique australe [Stern *et al.*, 1984; Stern et Killian, 1996] et de la zone volcanique centrale [James, 1982; Hawkesworth *et al.*, 1982; Harmon *et al.*, 1984; Davidson *et al.*, 1990] sont également reportés.

sidering their behavior and their high mobility during oceanic crust alteration prior to subduction. For example, Sun and McDonough [1989] recommend a mean value of 0.56 ppm for Rb concentration in typical fresh MORB, while Tatsumi and Kogiso [1997] estimate a value of 12 ppm for a typical altered MORB. Uncertainties on highly incompatible elements concentrations in altered oceanic crust prevent their use in any calculation that aims to evaluate degrees of partial melting. The use of rare earth elements, whose concentrations are supposed to be less affected by seawater alteration, seems to be more appropriate.

Rare earth elements distribution in Pichincha lavas, and particularly the important fractionation of LREE over HREE, suggest that the source of these lavas is a basalt metamorphosed in the amphibolite or eclogite facies (i.e. containing garnet with, or without, amphibole) [Defant and Drummond, 1990]. Figure 10 presents the theoretical evolution of the La/Yb ratio as a function of La or Yb, obtained by using the equilibrium partial melting equation of Shaw [1970] for a "mean" MORB from the Galápagos Spreading Center [Clague *et al.*, 1981] and using mineral-liquid partition coefficients of Martin [1987]. Various source melting residues are also considered. It appears that the distribution of rare earth elements in Pichincha lavas is best explained by 5 to 20 % partial melting of a GSC basalt transformed

into garnet amphibolite and leaving a melting residue quite rich in amphibole.

The degrees of partial melting as well as the percentage of garnet and amphibole considered in our model are close to those evaluated by Martin [1987] in his genetic modelisation of TTG in Finland (which are the Archean analogues of modern adakites) [Martin, 1999]. In figure 11, a 10 % melt model is applied to a larger spectrum of trace elements. When compared with Pichincha adakites patterns, the model can fully explain the typical Nb anomaly of adakites, due to the presence of a great amount of amphibole in the source (having a high partition coefficient respect to Nb). Nevertheless, the high LILE concentrations are not reproduced. This suggests that either the partial melting degree considered is too high or concentrations of these elements in the source (oceanic crust) are higher. Considering the unavoidable process of alteration experienced by oceanic crust prior to its subduction, affecting especially LILE, the latter hypothesis seems more appropriate. A calculation shows that, in order to obtain the high LILE concentrations of Pichincha lavas, considering their global partition coefficients close to zero ( $= 0.01$ ) and a mean degree of partial melting of 10 %, concentrations of Rb, Ba and K in the oceanic crust should be as high as 6 ppm, 80 ppm and 0.2 %, respectively. These are typical values for altered MORB [Tatsumi and Kogiso, 1997]. On the other

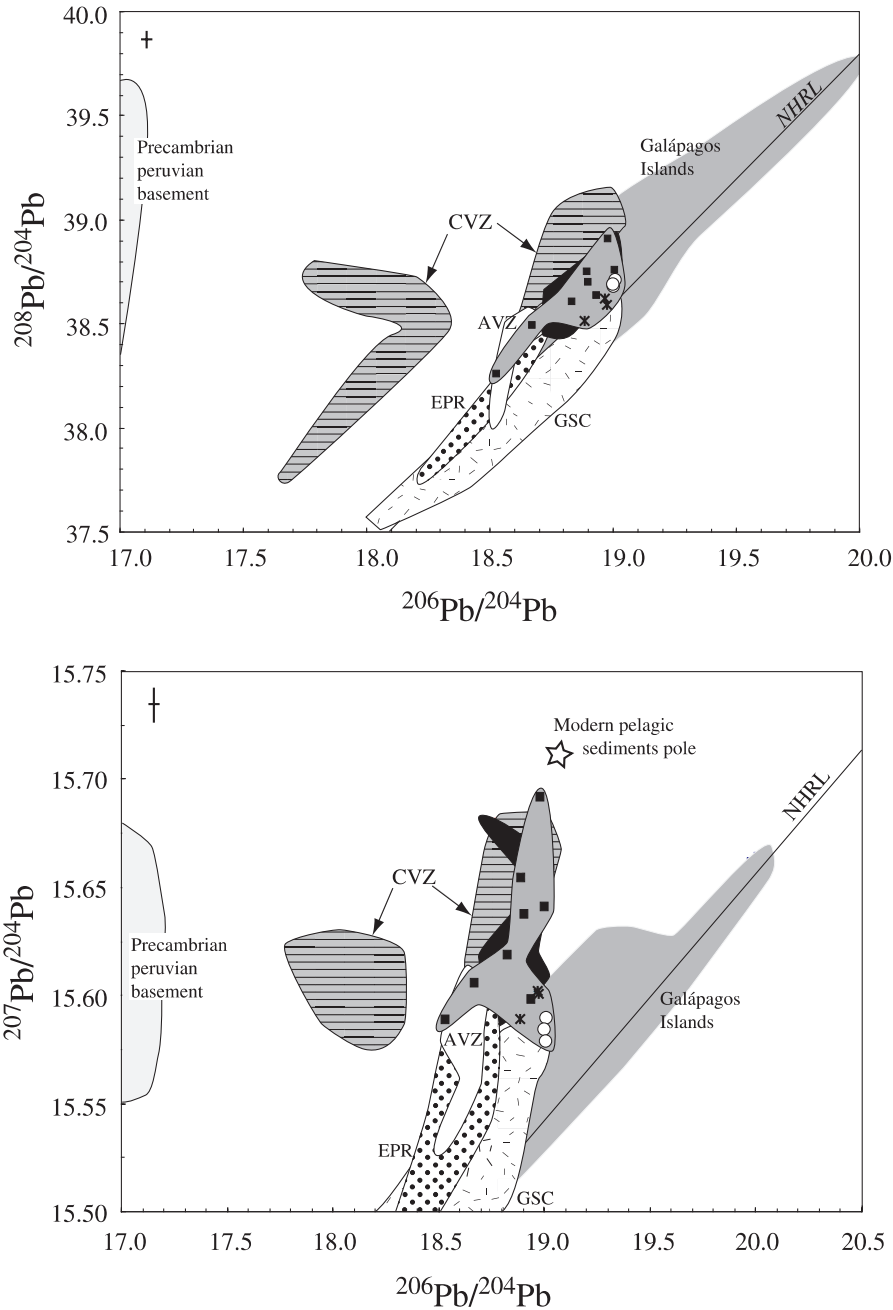


FIG. 9. –  $^{207}\text{Pb}/^{204}\text{Pb}$  vs.  $^{206}\text{Pb}/^{204}\text{Pb}$  and  $^{208}\text{Pb}/^{204}\text{Pb}$  vs.  $^{206}\text{Pb}/^{204}\text{Pb}$  diagrams. See figure 8 for references. Same symbols as in figure 8. Black field corresponds to data from Harmon *et al.* [1984] on recent volcanic rocks from Ecuador. Modern pelagic sediments pole from Sun [1980]. Data from the Peruvian basement from Tilton and Barreiro [1980]. Uncertainties bars are given in the upper-left corner of the diagrams.

FIG. 9. – Diagrammes  $^{207}\text{Pb}/^{204}\text{Pb}$  vs.  $^{206}\text{Pb}/^{204}\text{Pb}$  et  $^{208}\text{Pb}/^{204}\text{Pb}$  vs.  $^{206}\text{Pb}/^{204}\text{Pb}$ . Voir la figure 8 pour les références et les symboles. Le champ noir contient les données de Harmon *et al.* [1984] sur les roches volcaniques récentes d'Equateur. Le pôle des sédiments pélagiques modernes est celui donné par Sun [1980]. Les données du socle péruvien sont de Tilton et Barreiro [1980]. Les barres d'incertitudes sont données dans le coin supérieur-gauche des diagrammes.

hand, the hypothesis of derivation of Pichincha adakites from the subducted altered oceanic crust is reinforced by their Sr isotopic signature close to 0.7040 and also typical of altered MORB [Spooner, 1976; Tatsumi and Kogiso, 1997].

A contribution of the subducted sediments to the source of Pichincha lavas could alternatively explain the enrichments in the more incompatible elements and particularly in Ba. In figure 9, some NVZ lavas display, like those from the CVZ, a relative enrichment in  $^{207}\text{Pb}$  towards the modern

pelagic sediments pole ( $^{207}\text{Pb}/^{204}\text{Pb} = 15.7$ ;  $^{206}\text{Pb}/^{204}\text{Pb} = 19$ ; Sun [1980]). However, the very low  $^{206}\text{Pb}/^{204}\text{Pb}$  ratios of lavas from Pichincha and Atacazo volcanoes are close to those of lavas from the GSC, which suggest that there was no important contribution of the subducted sediments to their genesis. The conjunction of Sr isotopic ratios slightly higher than MORBs but typical of altered basalts, and low Pb isotopic ratios typical of MORBs strongly supports the idea that the principal source of Pichincha lavas is the subducted altered oceanic crust.



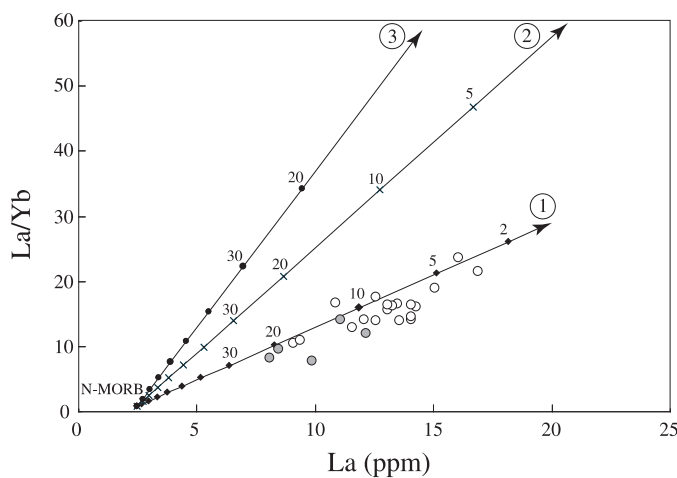
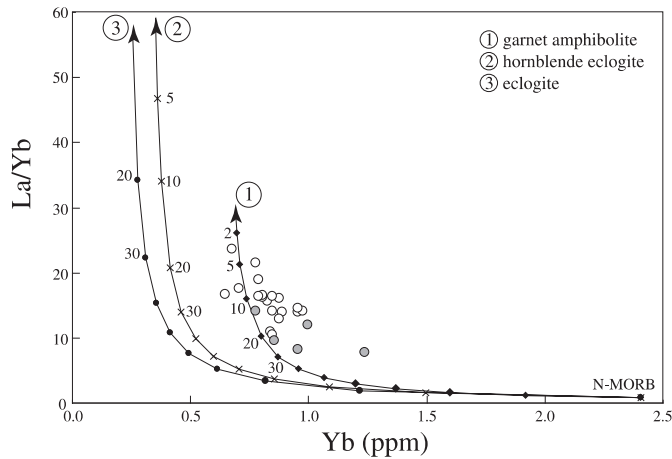


FIG. 10. – Evolution of La/Yb ratio vs. Yb (a) and La (b) obtained by a model of partial melting of a MORB from the GSC considering three different melting residues: (3) an eclogite (50 % grt, 50 % cpx), (2) a hornblende eclogite (35 % grt, 35 % cpx, 30 % hbl) and (1) a garnet amphibolite (44 % hbl, 44 % cpx, 12 % grt). Ticks on the curves are percentages of partial melting. (grt : garnet; hbl : hornblende; cpx : clinopyroxène)

FIG. 10. – Evolutions du rapport La/Yb en fonction de Yb (a) et La (b) obtenues par un modèle de fusion partielle d'un MORB issu de la dorsale des Galápagos, en considérant trois résidus de fusion différents : (3) une éclogite (50 % grt, 50 % cpx), (2) une éclogite à hornblende (35 % grt, 35 % cpx, 30 % hbl) et (1) une amphibolite à grenat (44 % hbl, 44 % cpx, 12 % grt). Les marques sur les courbes correspondent aux taux de fusion partielle. (grt : grenat; hbl : hornblende; cpx : clinopyroxène)

### Interaction with the lower continental crust ?

As an alternative to the partial melting of oceanic crust, Atherton and Petford [1993] suggested that adakitic magmas could be produced by the partial melting of accreted mafic crust beneath thick (> 50 km) orogenic belts. They showed that HREE depletion in plutonic rocks from the Cordillera Blanca batholith could be explained by the partial melting of the lower overthickened crust of Peru in the pressure stability domain of garnet. The contribution of lower crust partial melts has also often been invoked in the genesis of lavas from numerous volcanoes from the CVZ [e.g. Hildreth and Moorbath, 1988]. Rocks from the CVZ and from Cordillera Blanca display high Sr isotopic ratios [Atherton and Petford, 1993] suggesting an important con-

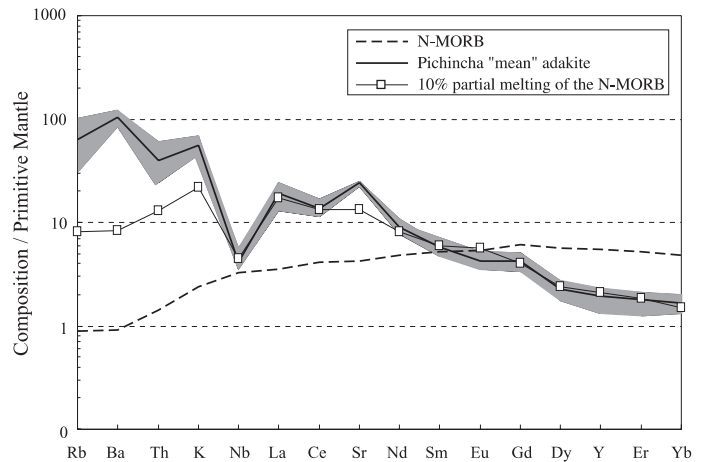


FIG. 11. – Theoretical spidergram obtained by a model of 10 % partial melting of a " mean " MORB of the GSC, using the garnet amphibolite residue. The stipple field corresponds to the trace element variations of Pichincha adakites, enclosing a calculated mean of all Pichincha adakites (n=21). Normalization to primitive mantle of Sun and McDonough (1989). FIG. 11. – Spectre théorique obtenu par un modèle de 10 % de fusion partielle d'un MORB de la dorsale de Galápagos, en utilisant comme résidu l'amphibolite à grenat. Le champs grisé correspond aux variations des éléments dans les adakites du Pichincha et entoure une adakite de Pichincha "moyenne" calculée (n=21). Normalisation au manteau primitif de Sun et McDonough [1989].

tribution of the radiogenic continental crust [Hawkesworth *et al.*, 1979; Thorpe *et al.*, 1982]. On the contrary, lavas from the western Cordillera (and in particular Pichincha lavas) have  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios lower than 0.7044, considered to be typical of mantle source [Hawkesworth *et al.*, 1979]. Moreover, lavas from the western Cordillera do not show  $^{207}\text{Pb}$  enrichments, suggesting that the contribution from the upper continental crust was limited or even non-existent [Zartman and Haines, 1988].

On the other hand, contamination by young immature crust (and thus unradiogenic) could be responsible for the enrichment in incompatible elements in the more acid lavas. This hypothesis also is not satisfactory considering that most of the basement from the western Cordillera is composed of MOR basalts of the Piñon Formation, and calc-alkaline rocks of the Macuchi Formation [Van Thournout *et al.*, 1992]. Both types of rocks are characterized by high concentrations in HREE and Yttrium (ex : Y > 28 ppm). A simple calculation shows that enrichment in incompatible elements should be accompanied by enrichment in HREE and Y, whereas the opposite is observed (fig. 7). Contribution from the (upper or lower) continental crust by any process (melting, mixing or even AFC) to the genesis of Pichincha lavas seems then very limited or even unlikely.

### MgO enrichment : the mantle component

Slab melting cannot alone explain all the geochemical characteristics of Pichincha lavas, especially the magnesian characteristics of some andesites, that could be the signature of some interaction with the mantle. The magnesium enrichment of natural adakites, compared to their experimental analogues obtained by partial melting of a basaltic

protolith, is a well-known feature [Kay, 1978; Mahlburg Kay *et al.*, 1993; Sen and Dunn, 1994].

Among Pichincha lavas, five andesites are distinguished by their important concentrations in MgO suggesting that they could be primitive lavas or close to their primitive parents. In the different elements vs. SiO<sub>2</sub> diagrams including compatible elements (e.g. Ni and V; fig. 7), magnesian andesites seem to define a clear trend with other Pichincha lavas, suggesting that they could be their magnesian parent magmas. But calculating derivation of non-magnesian andesite from magnesian andesites by fractional crystallization gave unsatisfactory results. Major elements modelization shows, for example, that dacite Pich 4A could be derived from andesite Pich 12A by removing 40 % of a cumulate composed of 1 % clinopyroxene, 25 % orthopyroxene, 27 % amphibole and 47 % plagioclase. A least squares calculation gave a satisfactory sum of the squares of residuals lower than 0.06. But the trace elements variation could not be described by this model, and particularly the decreasing HREE concentrations. This model could explain the HREE fractionation (due to the presence of amphibole in the cumulate) but in no way their depletion. Furthermore, the Sr enrichment described from andesites to dacites is not reproduced either. Last, the lack of clear correlation between SiO<sub>2</sub> and highly incompatible elements (ex : Th, Rb or even La; fig. 7) suggests that fractional crystallization is not the main process affecting the evolution of Pichincha lavas.

If magnesian andesites are unlikely to be the magmatic parents of normal andesites and dacites, they could be, a contrario, derived from the latter by a process of interaction with a peridotitic component during their ascent through the mantle wedge.

Interaction of adakitic magmas with peridotitic material of the mantle wedge has often been invoked to explain the MgO enrichment of natural adakites compared to their experimental analogues produced by dehydration-melting of basalts [Kay, 1978; Sen and Dunn, 1994; Drummond *et al.*, 1996]. It was shown experimentally that during this kind of interaction, hydrous minerals (pargasitic amphibole and phlogopite) crystallize in the mantle, while olivine and clinopyroxene are consumed [Sen and Dunn, 1995; Rapp *et al.*, 1999; Prouteau *et al.*, 2001]. As a result, the ensuing interacting magma is notably enriched in MgO and depleted in SiO<sub>2</sub>. This kind of metasomatism was also observed in natural xenoliths found in lavas from the Kamchatka volcanic field [Kepezhinskias *et al.*, 1996]. Last, Rapp *et al.* [1999], have experimentally shown that magnesium-rich liquids with geochemical characteristics close to those of HMA could be the result of close interaction between slab melts and peridotitic material from the mantle wedge.

Such an interaction between adakitic magmas and the mantle wedge provides an explanation for much of the unusual geochemical and mineralogical characteristics of Pichincha lavas. Pichincha dacites can be seen as the closest representatives of pristine adakites (slab melts "uninteracted" with mantle): richest in silica, weakly magnesian, lowest concentrations in HREE and Y, highest concentrations in Sr and highest Na<sub>2</sub>O/K<sub>2</sub>O ratios. Interaction between dacites and the peridotitic mantle wedge could yield the magnesian andesites, poorer in silica and much richer in MgO. It could also explain the systematic

reverse zoning presented by plagioclase crystals in the magnesian andesites: Interaction between pristine adakite and peridotite could induce enrichment in Ca of the resulting magma, due to the consumption of mantle clinopyroxene, and thus enrichment in anorthite of plagioclase crystals. These latter previously had a core richer in Na<sub>2</sub>O; a character inherited from the parental sodic magma produced by partial melting of the amphibolitic oceanic crust [Barker and Arth, 1976]. This would suppose the early crystallization of plagioclase in the sodic magma. Among all the andesites from Pichincha volcano, magnesian andesites show the lowest MREE concentrations (fig. 7) which could result from the crystallization within the mantle of pargasitic amphibole (presenting high Kd's for MREE). Lastly, crystallization of hydrous metasomatic phases (pargasite and phlogopite) could also explain the erratic distribution of highly incompatible elements (like Th and Rb) that are alternatively compatible with phlogopite and incompatible with pargasitic amphibole [Halliday *et al.*, 1995].

Interaction between slab melts and the peridotitic mantle wedge suggests that adakitic magmas are likely to constitute the principal metasomatic agent beneath the NVZ in Ecuador. Recent works on modern [Sajona *et al.*, 1996; Kepezhinskias *et al.*, 1996; Maury *et al.*, 1998] or Archean [Wyman *et al.*, 2000] subduction-related lava fields and experimental petrology [Rapp *et al.*, 1999] have shown that metasomatism of the mantle wedge by adakitic magmas might produce various "exotic" rocks ranging from Nb-enriched basalts to high-Mg andesites or andesites with geochemical signatures close to adakites. If it is admitted that the mantle metasomatized beneath Pichincha volcano is dragged down by mantle convection beneath the Eastern Cordillera, the occurrence of adakite-like rocks at Antisana volcano [Bourdon *et al.*, 1999; 2002] argues strongly for considering slab melts as the principal metasomatic agent beneath the NVZ in Ecuador.

## CONCLUSIONS

The study of andesites and dacites from Pichincha volcano shows that their genesis is dominated by a partial melting process of subducted altered oceanic crust. Compared to the Colombian volcanic arc, Ecuadorian volcanoes of the western Cordillera are in a fore-arc position, in a geotectonic setting compatible with the genesis of adakitic magmas. Moreover, the presently occurring process of "slab flattening" seems to have largely modified the thermal structure of the subduction zone beneath Ecuador and apparently favors the partial melting of oceanic crust.

Pichincha adakites display all the geochemical characteristics of slab melts and more particularly: high Sr/Y and La/Yb ratios, very low HREE and Y concentrations, high contents in Sr and also Pb and Sr isotopic ratios typical of altered oceanic crust. Occurrence of magnesian andesites suggests that adakitic magmas en route to the surface have metasomatized and enriched the depleted peridotitic mantle wedge (modally and chemically). It is important to note that if the slab melt-metasomatized mantle is dragged down beneath the eastern Cordillera (and particularly Antisana volcano), its specific composition is likely to generate original magmas with geochemical characteristics close to adakites [Bourdon *et al.*, 1999; 2002]. It appears that in many

arcs worldwide, including now the NVZ in Ecuador, adakitic magmas may act as important metasomatic agents. This is an alternative to the hypothesis of mantle wedge enrichment by hydrous fluxes released from the downgoing slab.

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