Geochemistry and tectonic controls of the effusive activity related with the ancestral Nevado del Ruiz volcano, Colombia

C. Borrero*, L. M. Toro, M. Alvarán and H. Castillo

Departamento de Ciencias Geológicas, Universidad de Caldas, Manizales, Colombia

Received: September 28, 2007; accepted: July 1, 2008

Resumen

Los aspectos geoquímicos y el marco tectónico de la actividad efusiva del período Ruiz Ancestral (2.0 a 1.0 Ma) del Volcán Nevado del Ruiz (VNR) son discutidos en este artículo. El VNR se localiza a 4° 50-55' N y 75° 14-20' W y se eleva a 5,390 msnm, en el sector más septentrional de la cadena volcánica andina en la Cordillera Central (Colombia).

Datos químicos de roca total en muestras de andesitas y riodacitas de los diferentes sitios de emisión reportados comparten características específicas: $SiO_2 = 56$ y 70.1% en peso, relativamente altos de MgO y medios de K₂O; proporciones bajas de FeO/MgO: < 1.9 patrones de contenidos elementos de tierras raras poco fraccionados, bajo contenido de Y y REE pesadas; Sr entre 500 y 1,000 ppm y Ba hasta 1,600 ppm. Las proporciones de K/Rb muestran correlación negativa con SiO₂ y con Rb, lo cual sugiere procesos de asimilación y cristalización fraccionada (ACF). Las proporciones de Rb/Sr, Ba/Sr y Rb/Ba muestran correlación positiva con SiO₂, típicas de tendencias calcoalcalinas, sólo las suites más ácidas presentan un marcado carácter adaquítico.

Durante el período Ruiz Ancestral, la falla de Villa María-Termales (N75°W) controló el emplazamiento de magmas al occidente del eje volcánico N-S, evidenciado por el alineamiento paralelo de pequeños volcanes monogenéticos con el sistema de fallas, los cuales fueron alimentados lateralmente por flujos de magma desde el sistema de almacenamiento intermedio localizado entre 5 y 10 km por debajo de la posición del actual Volcán Nevado del Ruiz.

Palabras clave: Magmatismo de K medio, firma adaquítica, lavas del Plioceno tardío-Pleistoceno temprano, falla de Villa María-Termales, volcán Nevado del Ruiz.

Abstract

In this paper, we discuss the geochemical aspects and the tectonic setting of the effusive activity between 2.0 to 1.0 Ma (the Ancestral Ruiz stage) of Nevado del Ruiz Volcano (NRV: 4° 50-55'N, 75° 14-20' W, 5,390 masl), this volcano rises at the northernmost end of the Andean volcanic chain in the Cordillera Central of Colombia.

Whole-rock geochemical data of andesitic to rhyodacitic samples from the different vents share specific characteristics: $SiO_2 = 56$ -70.1 wt. %, relatively high MgO (1.1 - 8.1 wt. %) and medium K₂O (1.06 - 4.36 wt. %) contents, low FeO/MgO ratios (typically less than 1,9), low fractioned rare earth element patterns with low Y and heavy rare earth elements contents, Sr commonly between 500 and 1,000 ppm and Ba up to 1,600 ppm.

K/Rb ratios always show a negative correlation with SiO_2 and Rb suggesting assimilation-fractional crystallization (AFC) mechanism. Rb/Sr, Ba/Sr and Rb/Ba ratios display a positive correlation with SiO_2 , typical of calcalkaline trends. The more acidic suites display the strongest adaktic character such as higher Sr, and lower HREE and Y contents.

The N75°W Villa Maria –Termales fault system was the controller of the magma displacement aside of the main N-S volcanic axis during the Ancestral Ruiz stage. This tectonic control is evidenced by the distribution of the small effusive eruptions in monogenetic vents aligned parallel to the fault system, which were fed by lateral magma flow from the intermediate storage system located 5-10 km below the position of the present Nevado del Ruiz Volcano.

Key words: Medium-K magmatism, adakitic signature, Late Pliocene –Early Pleistocene lavas, Villa María-Termales fault system, Nevado del Ruiz volcano.

Introduction

The subduction of the Nazca plate beneath the northwestern margin of South America is responsible for the Plio-Quaternary magmatic activity in the Northern Volcanic Zone province (NVZ, Bourdon *et al.*, 2003). The Nevado del Ruiz Volcano (NRV) is located in the northernmost part of the NVZ and is part of the former Ruiz – Tolima Volcanic Complex (Herd, 1982).

Research on the NRV has been focused on the recent activity and the paramount November 13, 1985 eruption products and its associated hazards. Some authors (Thouret *et al.*, 1990, Vatin-Perignon *et al.*, 1990 and Schaefer, 1995) have discussed a stratigraphic model for the NRV with different geomorphic, petrological and geochemical approaches. However, the activity of the NRV clearly can be defined by three main stages:

• the "Ancestral Ruiz" (stratovolcano construction and small caldera collapse, 1.8-1.0 Ma),

• "Older Ruiz" (stratovolcano construction and small caldera collapse, 0.8-0.2 Ma), and

• "Present Ruiz" (Composite lava domes, <0, 15 Ma). The recent NRV is composed of andesitic lava flows intercalated with pyroclastic deposits.

In this paper we consider the entire whole-rock chemical and geochronological data from andesitic to dacitic lavas as well as domes of the "Ancestral Ruiz" (Late Pliocene- Early Pleistocene constructive episode) located close to the "Present Ruiz" (Vatin-Perignon *et al.*, 1990 and Schaefer, 1995). We correlate this data with unpublished geochemical data from the monogenetic vents located to the southeast and northeast of Manizales (Ancochea *et al.*, 1991 and Gallego *et al.*, 2006). In addition to new data of domes and lavas also located to the southeast of Manizales (this work).

We reinterpret the former Ancestral Ruiz stage defined by Thouret *et al.* (1990) and present the hypothesis that the magmatism of the Ancestral Ruiz Volcano must be extended and include several monogenetic vents located around the "Present Ruiz". The distribution of the vents was controlled mainly by the Villa María-Termales fault zone located to the south-east of the city of Manizales (González and Jaramillo, 2002). We discuss the possibilities of the correlation of this magmatic activity with the geochemical data, and we suggest a model for the tectonic control during this stage.

Geological setting

The Northern Volcanic Zone (NVZ) of Colombia (Fig. 1) is defined by a narrow volcanic arc located above the

Benioff zone that clearly defines a steep subduction slab dipping ca. 45° (Ojeda and Havskov, 2001). The Nazca plate descends below the north Andes at a rate of 56 mm/yr (Trenkamp *et al*, 2002). Information on crustal thicknesses in the region surrounding NRV is limited; Bryant *et al*. (2006) displayed that the north Andean crust that underlies the currently active volcanoes varies systematically from 25 to 50 km in Ecuador. In Colombia, the gravity data indicate that the crust is 40 -50 km thick along the axis of the Andes. Nevertheless, Schaefer (1995) found a thin crust (< 35 Km) and/or an anomalous dense crust around the NRV.

Nevado del Ruiz Volcano

Nevado del Ruiz Volcano (NRV) is an ice-clad stratovolcano located in the middle Central Cordillera of the Colombian Andes (4° 50'-55'N, 75° 14'-20' W, 5390 masl). It is one of the northernmost active volcanoes in South America. The NRV is approximately 150 km above the Benioff zone (James and Murcia, 1984) and is one of the northernmost stratovolcanoes of the Ruiz-Tolima volcanic complex (Fig. 1). This complex is an arcuate line of nine volcanoes, which form the crest of the Central Cordillera. Hall and Wood (1985) locate this volcanoe rectonic segmentation of the NVZ.

The NRV is intersected by two fault systems: the N20°E right-lateral strike-slip Palestina fault system and the N75°W normal Villa María-Termales fault system (Londoño and Sudo, 2002). Thouret et al. (1990) performed detailed studies of the Quaternary eruptive history of NRV and proposed a general stratigraphy with three main stages: Ancestral, Older and Present Ruiz (Fig. 2). Most of the authors that have studied the volcano agree with the occurrence of a previous event associated with the Pre-Ruiz Lavas which correspond to a destructive phase attested by the volcaniclastic deposits surrounding the NRV area (e.g. the Casabianca Formation; Borrero and Naranjo, 1990). Also, Lescinsky (1990) and Young (1991) compiled and added new geochronological data especially of the recent activity. Schaefer (1995) established a main age for the Rio Claro Ignimbrite (ca. 100 ka) that defined the limit between the Older and Present Ruiz. In this paper we compare exclusively the geochemical data of the domes and lava flows of the constructive phase of the "Ancestral Ruiz" with ages between 1, 8 and 0, 97 Ma.

The composition of the effusive and explosive products of NRV varies from basaltic andesites to dacites that is characteristic of subduction-related calc-alkaline volcanoes, which are andesites and dacites most common rock types at NRV (Vatin-Perignon *et al.*, 1990).



Fig. 1. Location Map showing the northernmost volcanic chain and the Ruiz – Tolima Volcanic Complex in the Central Cordillera, Colombia, South America.

The NRV sits atop Paleozoic metamorphic rocks, Mesozoic sedimentary material, and Jurassic and Paleocene batholiths (Schaefer, 1995). As it was mentioned before, the NRV is located at the intersection of a major dextral strike-slip fault (Palestina fault) and a major transverse regional fault (Villa María-Termales fault, Fig. 3). Both faults have been active through the Quaternary (Herd, 1982; Thouret *et al.*, 1990). It is suggested that there is a close interaction between tectonics and volcanism in the NRV area, as evidenced not only by the active faults around the volcano, but also by the seismicity occurring at present (Zollweg, 1990 and Muñoz *et al.*, 1990).

Villa María – Termales Fault

The relationship between volcanism and tectonics has been on controversy for many years (Lara *et al.*,

2004). The early recognition of close spatial relationships between faults and volcanic centers has led to construction of models that try to explain the pattern of regional deformation as well as the distribution, evolution and morphostructure of the volcanic centers in different geodynamic settings. Some authors have shown direct links between the geometry of the faults that are used as pathways for magmatic ascent (Tibaldi, 1995), their displacements (Alaniz-Álvarez et al., 1998) and some morphologic characteristics of the volcanic centers. The distribution of volcanism in the Ancestral Ruiz stage is likely the product of two processes: the generation of magma due the Nazca Plate subduction and the formation of structures associated with tectonic activity. It is clear that regional faults have played a major role in channeling magma to the Nevado del Ruiz Volcano and its surroundings.



Fig. 2. Stratigraphic model of Nevado del Ruiz Volcano modified after Thouret *et al.* (1990), Lescinsky (1990), Young (1991) and Schaefer (1995).

Considering the physiographic expression to the south-east of Manizales, González and Jaramillo (2002) recognized a N75°W trending-structural system, the Villa María-Termales fault which presents volcanic vents along its trace, such as: Tesorito, El Bosque and Gualí volcanoes, the Sancancio, Gallinazo and El Plato Domes and the Lusitania Lavas. Its superficial expression is that of a normal fault system (Thouret *et al.*, 1990) segmented by N-S and NE-SW structural barriers (Fig. 3).

The Villa María-Termales fault was carefully mapped by González and Jaramillo (2002), based on the straight alignment of numerous geomorphic evidences such as: longitudinal valleys, lineal depressions, fault scarps, trenches, sag-ponds, linear and shutter ridges, saddles, offset features and tilted Quaternary deposits. These authors also divided the fault zone in seven segments based on physiographical expressions and the length of the fault traces limited by the structural barriers defined by N-S and NE-SW faults, which define blocks or wedges related with the high seismicity in the area.

The focal mechanisms and the stress tensors defined by González and Jaramillo (2002) based on seismic data gathered from a discontinuous instrumental monitoring of the fault zone with support from OVSM (Observatorio Vulcanológico y Sismológico de Manizales), show that the deformation ellipses of the analyzed zones associated with the Villa María – Termales fault traces are consistent with a distensive regime. The continuity of this regime, especially in the easternmost sector of the fault, is evidenced by the higher ²²²Rn gas emission (González and Jaramillo, 2002) concomitant with the higher seismicity

(7, 5 km to the north-west of NRV).

Calculated stress tensors show a vertical maximum principal stress (σ 1) oriented with azimuths of ~231° and $\sim 312^\circ$, a horizontal minimum principal stress (σ 3) oriented with azimuths of ~82° and ~208°, and σ 2 lying on the horizontal plane, characteristic of normal faults (Fig. 3). This result is in agreement with Nakamura (1977 in Lara et al., 2004) who considered that the alignment of volcanic centers must be parallel to the maximum horizontal stress (σ_{hmax}). They assumes that the volcanic centers are the surface expression of near vertical feeder dikes, the σ 3 (minimum stress axis) should be horizontal (and perpendicular to the dikes) with $\sigma_{\!_{hmax}}$ corresponding to $\sigma 1$ or $\sigma 2$. If $\sigma_{_{hmax}}$ corresponds to $\sigma 2$, like in the data of the Villa María- Termales fault, the tectonic arc is extensional. Only, some of the focal mechanisms shown by González and Jaramillo (2002) have a slight dextral component.

Geochemistry

Spatial distribution

The lava flows and domes associated to the Ancestral Ruiz stage (Fig. 4, sample and map location numbers in Table 1) are scattered over a ca. 50 km2 in the present Nevado del Ruiz Volcano surroundings. Most of them are aligned along a NW-trending fracture parallel to the Villa María –Termales fault to the south-east of Manizales. Data from different authors and this work are shown in Table 1.



Fig. 3. Segmentation of the Villa María-Termales Fault zone, showing the associated seismicity and the deformation ellipses modified after González and Jaramillo (2002). DEM to 90 m from USGS data bank.



Fig. 4. Geological Map of the Nevado del Ruiz Volcano area, sample location and ages of the domes and lava flows. Map location number in Table 1. Ages from Thouret *et al.*, 1990. Geology modified from INGEOMINAS (1998a, 1998b).

Table 1

Whole rock chemical data from the ancestral Ruiz stage Hoyo Frio *(1)

SAMPLE	ACJ 8	ACJ 2.2	ACJ 2.21	ACJ 2.23	ACJ 2.25	ACJ 2.43	ACJ 3.11	ACJ 3.12	ACJ 3.20	ACJ 4.1	ACJ 6.4
Мар											
Location	1	2	3	4	5	6	7	8	9	10	11
SiO,	61,20	60,99	60,35	59,04	61,55	57,72	60,21	56,93	58,94	60,01	59,42
TiO,	0,71	0,67	0,68	0,91	0,71	1,05	0,79	0,79	0,81	0,79	0,69
Al ₂ O ₃	16,80	16,74	16,48	16,51	16,94	16,82	15,97	17,76	15,32	16,26	17,34
Fe ₂ O ₃	5,76	5,45	5,73	6,60	5,44	7,25	6,31	5,72	7,06	6,53	5,85
FeO											
MnO	0,08	0,09	0,10	0,08	0,09	0,11	0,08	0,04	0,09	0,10	0,08
MgO	2,53	2,72	3,43	3,43	2,38	3,88	3,78	1,67	4,70	3,75	2,69
CaO	5,00	5,28	5,43	5,71	4,99	6,48	5,66	4,35	5,33	5,05	5,77
Na ₂ O	3,50	3,93	3,94	3,23	3,89	2,98	3,73	2,91	3,43	3,69	4,15
K ₂ O	2,53	2,57	2,16	2,83	2,66	2,65	1,98	1,64	1,95	1,94	2,00
P_2O	0,27	0,29	0,25	0,36	0,34	0,39	0,25	0,17	0,26	0,24	0,27
$\operatorname{Cr}_2 \operatorname{O}_3$	0,006	0,004	0,016	0,013	0,005	0,005	0,016	0,01	0,028	0,019	0,003
LOI%	1,4	1	1,2	0,9	0,6	0,3	0,9	/,/	1,9	1,3	1,5
TOTAL D-	99,79	99,73	1208.8	99,61	99,59	1192.0	99,68	1006.2	99,82	99,68	99,76
Ба	1312,3	1383,9	1298,8	1448,8	1302,4	1185,2	981,0 52.2	1090,5	984,9 40.1	1090,5	1408,1
KD Th	/1,/	10	43,2	09,7	10.5	10.2	50	45,0	49,1 5.0	47,5	50,9
111 Nb	10,0	10 6.2	9,4 6.7	11,0	10,5	12,5	5,9	7,2	5,9	5,9	0,7 5.7
Sn Sn	661.5	852.8	706.8	5,0 662 5	787 1	712.8	600.5	504.2	565.0	603	1037.8
SI 7r	144.3	125.1	123.7	167.6	147.1	182.4	120.5	104.1	112.8	124.8	1037,8
V	24.9	17.2	15.9	44 7	24.7	25.5	18.2	16-,1	18.5	18.1	15.2
V	137	109	120	170	107	181	10,2	113	154	94	13,2
Ni	67	41	22.5	82	8.8	2.6	13	36	35	19	3
Co	11.4	12.1	15.4	13.7	10.4	12.3	15.1	16.2	20.4	17.3	15
Sc	15	11	15	19	11	21	17	15	19	17	14
Pb	3,2	1,3	1,8	2,5	1,7	2,1	1	7,3	1,8	1,6	1,3
Cu	14,7	7,9	9,8	15,5	9,2	5,4	17,9	11,7	21,7	7,9	7,9
Zn	53	27	31	36	48	27	41	53	29	29	21
Cs	3,2	3,1	1,1	2,7	1,8	2,2	1,1	3	1,5	1,1	2
Be	2	2	1	2	2	2	1	2	2	1	2
Ga	19,6	19,5	19,6	20,7	19,5	21,4	19,2	20,8	18,7	20,2	21,7
Мо	0,6	0,2	0,3	0,7	0,5	0,4	0,6	0,1	0,4	0,3	0,2
Sn	2	1	1	3	1	2	2	2	1	2	1
Tl	0,1	0,1	0,2	0,1	<0,1	<0,1	<0,1	0,1	<0,1	<0,1	<0,1
Та	0,5	0,4	0,5	0,7	0,6	0,8	0,5	0,6	0,5	0,4	0,3
Hf	4	3,5	3,8	5	3,8	5,3	3,6	4,2	3,4	3,4	3,2
U	3,6	3,6	2,9	3,5	3,5	2,9	2,5	2,7	2,3	1,8	2,5
La	34	28,2	23,3	61	46,1	35,3	21,4	20,8	22,4	19,5	26,1
Ce	61,/	56,4	52	84	65	/5,2	45,7	45,8	46,3	41,4	46
Pr	8,38	6,97	5,96	14,69	11,6	9,11	5,46	5,33	5,93	5,24	6,83
ING Com	51,4	20,0	25,9	39,4 0.5	44,7	51	22,9	21 4.1	23,8	21 4 1	27,3
SM Fu	0,1	4,8	4,2	9,5	1,4	0,/	4,4	4,1	4,4	4,1	5,1 1.26
Cd	1,47	3.74	3 50	2,4	5 75	5.6	3.65	3 75	3.83	3.51	3.82
Gu Th	4,00	0.6	0.53	9,02	0.01	0.03	0.6	0.54	0.6	0.58	0.56
Dv	4	2.97	28	6.72	4.68	4 53	2.86	3.03	3.25	3.18	2 77
Но	+ 0.71	0.57	0.52	1.25	0.83	0.83	2,00	0.54	0.62	0.58	0.48
Fr	2.23	1.65	1.51	3.85	2 37	2 37	17	1 59	1 79	1 74	1 36
Tm	0.33	0.25	0.21	0.54	0.36	0.37	0.24	0.24	0.27	0.28	0.19
Yh	2.09	1 74	1.52	3.48	2.32	2,39	1 57	1.66	17	1 72	1 29
Lu	0.31	0.24	0.2	0.47	0.33	0.33	0.23	0.22	0.26	0.26	0.17
							,				

Table 1
(continued)

	0	OLD RUIZ	LAVAS *(2)	DOMES AND LAVAS *(3)							
SAMPLE	83-267	83-278a	83-153	82-54	5150	5158	5151	5159	5160	5161	5157	
Map Location	12	13	14	15	16	17	18	19	20	21	22	
SiO,	60,56	59,26	57,94	56,66	58,86	59,57	62,8	63,55	61,88	61,59	63,23	
TiO	0,67	0,88	0,73	0,9	0,82	0,65	0,7	0,66	0,63	0,79	0,74	
Al,O,	15,07	16,87	17,81	17,36	17,15	16,21	15,62	15,87	16,4	16,19	15,58	
Fe ₂ O ₂	5,44	5,81	6,31	7,42	3,23	2,43	2,55	3,77	3	3,09	2,67	
FeO					3,73	3,43	2,27	1,5	1,89	2,41	2,32	
MnO	0,09	0,08	0,1	0,14	0,12	0,09	0,08	0,07	0,06	0,09	0,07	
MgO	6,15	3,66	3,89	4,78	4,19	5,04	2,82	2,55	2,96	3,46	2,95	
CaO	5,74	5,52	6,41	7,13	5,48	6,2	4,68	3,65	4,71	5,24	4,55	
Na,O	4,05	4,11	4,63	3,72	3,81	3,98	4,14	3,9	4,38	4,29	4	
K,Ô	1,45	1,94	1,1	1,54	1,05	1,36	2,47	2,89	2,35	2,26	2,72	
P,O.	0,17	0,3	0,24	0,24	0,2	0,2	0,24	0,22	0,3	0,3	0,24	
Cr,O,												
LOI%	0,11	0,7	1,31	0,57	1,48	1,01	0,98	0,84	0,99	0,47	1	
TOTAL	99,50	99,13	100,47	100,46	100,12	100,17	99,35	99,47	99,55	100,18	100,07	
Ba	937	1290	870	1346	937	1061	1361	1479	1396	1324	1319	
Rb	35	45	36	31	33	40	74	99	68	64	88	
Th	5,31	6,93	3,54	6,02	3	7	18	13	10	7	15	
Nb		2	6	3	10	8	8	8	10	7	11	
Sr	546	779	581	841	524	621	768	586	808	825	697	
Zr	118	129	101	86	94	100	166	210	153	164	186	
Y					22	18	17	18	18	18	16	
V												
Ni					22	106	47	44	39	30	38	
Со												
Sc	15,63	16,91	16,20	24,26								
Pb	,	,	· · · ·	,								
Cu												
Zn												
Cs	0,61	0,93	0,74	1,98								
Be												
Ga												
Мо												
Sn												
TI												
Та												
Hf	3,22	3,71	2,75	2,58								
U	2,71	2,37	1,60	2,16								
La	16,88	27,86	13,34	19,69	15	12,81	25	33	33	27	16	
Ce	31,59	47,87	25,95	35,82	44	31,56	47	64	53	49	61	
Pr												
Nd	18,72	28,61	15,15	21,94		14,61						
Sm	3,44	5,09	2,99	4,31		3,57						
Eu	1,09	1,52	0,96	1,37		0,96						
Gd												
Tb	0,44	0,71	0,39	0,59								
Dy						2,54						
Но												
Er						1,34						
Tm												
Yb	1,74	1,89	1,53	2,57	1,28							
Lu	0,16	0,27	0,27	0,29	0,24							

PRE-RUIZ LAVAS*(d) MANIZALES SOUTHEAST *(5) SAMPLE 219 8910 320 PA-34.1 PA-34.2 PA-10.2 PA-15.2 PA-21.5 PA-31.4 PA-32.5 83 Location 23 24 25 26 27 28 29 30 31 32 33 34 Stop 62.1 56 64.7 64.29 63.86 63.77 67.88 62.46 60.92 67.91 62.74 63.53 FeO 51.6 15.4 16.70 16.45 15.91 14.84 14.8 16.20 16.83 FeO 51.6 2.187 16.1 138 12.5 138 2.45 103 CaO 3.6 3.4 3.8 3.16 3.51 4.64 3.71 3.04 3.67 3.65 4.80 0.77 NaO 3.6 3.4 3.8 3.16 3.51 4.64 3.71 3.04 3.67 3.68 9.7							(continu	ued)					
SAMPLP1P3-10P3-10P3-10P4-12P4-20P4-21-0P4-21-0P4-31.0P4-32.0P4-33.0 <t< th=""><th>]</th><th>PRE-RU</th><th>JIZ LAV</th><th>/AS*(4)</th><th></th><th></th><th>MA</th><th>NIZALES</th><th colspan="3">SOUTHEAST *(5)</th><th></th><th></th></t<>]	PRE-RU	JIZ LAV	/AS*(4)			MA	NIZALES	SOUTHEAST *(5)				
Instrume 23 24 25 26 27 28 29 30 31 32 33 34 SiO 62.1 56 64.7 64.29 63.86 63.77 67.88 62.46 60.92 67.91 0.274 63.51 0.55 0.46 0.45 0.41 0.57 0.38 0.64 0.54 0.55 0.56 1.88 1.58 16.34 14.18 16.20 16.85 FeO 5.18 6.23 4.63 5.00 5.09 3.56 4.38 4.56 2.85 5.02 4.56 FeO 5.38 7.32 82 1.19 1.76 1.99 2.61 3.54 3.37 2.56 4.67 1.55 No 3.6 3.31 4.54 3.31 3.54 4.54 3.37 2.56 4.67 1.25 3.31 5.43 3.37 2.56 4.57 1.55 No 2.20 1.17 1.33 3.78	SAMPLE Man	219	8910	320	PA-8A-1	PA-9-1	PA-10-2	PA-15g	PA-20-3	PA-21-5	PA-31A	PA-32-5	83
SiO_ 62.1 58. 64.7 64.29 63.86 63.77 67.88 62.46 60.92 67.71 62.74 63.33 TiO_ 0.64 1.19 0.63 0.57 0.55 0.46 0.45 0.41 0.57 0.58 0.63 0.41 0.57 0.58 0.64 0.58 0.53 0.63 4.18 0.56 0.53 0.53 0.53 0.53 0.53 0.53 0.53 0.53 0.53 0.53 0.53 0.53 0.53 0.53 0.53 0.53 0.53 0.45 0.53 0.55 0.57 0.55 0.50 0.55 0.57 0.55 0.50 0.50 0.50 0.50 0.51 0.23 0.24 0.50 0.50	Location	23	24	25	26	27	28	29	30	31	32	33	34
TO 0.64 1.19 0.63 0.67 0.57 0.46 0.45 0.41 0.57 0.38 0.64 0.54 ALO, 15.9 15.6 17.4 16.70 16.45 15.91 14.80 15.58 16.34 14.18 16.20 4.63 FeO 5.18 6.23 4.04 7.00 0.06 0.03 0.04 0.03 0.04 0.13 0.18 0.05 0.07 0.06 MoD 0.08 0.14 0.06 0.03 0.04 0.03 0.04 3.34 3.37 2.56 4.67 1.55 NaO 0.35 3.44 3.8 3.16 3.51 4.64 3.71 3.04 3.67 3.65 4.38 4.67 1.55 3.03 1.90 1.19 1.33 3.78 2.35 2.90 4.01 2.33 3.15 V_O 2.23 0.41 0.24 0.20 0.12 0.10 0.00 0.00 0.00 0.01 0.01 0.01 0.01 0.01 0.01 0.02 0.12 <t< td=""><td>SiO</td><td>62.1</td><td>56</td><td>64.7</td><td>64.29</td><td>63.86</td><td>63.77</td><td>67.88</td><td>62.46</td><td>60.92</td><td>67.91</td><td>62.74</td><td>63.53</td></t<>	SiO	62.1	56	64.7	64.29	63.86	63.77	67.88	62.46	60.92	67.91	62.74	63.53
	TiO.	0.64	1.19	0.63	0.57	0.55	0.46	0.45	0.41	0.57	0.38	0.64	0.54
PicO S.18 6.23 4.63 5.40 5.09 3.56 4.38 4.56 2.85 5.02 4.56 FeO S.18 6.23 4.04 0.05 0.04 0.03 0.04 0.13 0.18 0.05 0.07 0.06 MgO 3.9 8.1 2.2 1.18 1.61 1.38 1.25 1.19 1.35 1.38 2.45 1.03 CaO 5.39 7.32 8.2 1.19 1.33 3.78 2.56 4.67 1.55 NgO 2.49 1.55 3.03 1.90 1.19 1.33 3.78 2.35 2.90 4.01 0.23 3.15 PO 0.23 0.41 0.24 0.20 0.12 0.19 0.060 0.00 0.01 0.01 D174 99.51 99.51 99.72 10.145 10.27 10.146 99.24 10.239 10.49 99.49 99.19 10.249 Ba	ALO.	15.9	15.6	17.4	16.70	16.45	15.91	14.80	15.58	16.34	14.18	16.20	16.83
	Fe.O.	,-	,-	,-	4.63	5.40	5.09	3.56	4.38	4.56	2.85	5.02	4.56
Nm0 0.8 0.14 0.06 0.03 0.04 0.03 0.04 0.13 0.14 0.15 0.24 0.00 0.00 0.01	FeO	5,18	6,23	4,04		,	,		,	,	,	,	·
MgO 3.9 8.1 2.2 1.87 1.61 1.38 1.25 1.19 1.85 1.38 2.45 1.03 CaO 5.39 7.32 8.2 1.19 1.76 1.99 2.61 3.54 3.37 2.56 4.67 1.53 K,O 2.49 1.55 3.03 1.90 1.19 1.33 3.78 2.55 2.90 4.01 2.33 3.15 VEO 2.20 0.11 0.20 0.12 0.19 0.26 0.12 0.23 0.41 2.33 3.15 Cr_O	MnO	0,08	0,14	0,06	0,03	0,04	0.03	0,04	0,13	0,18	0,05	0,07	0,06
CaO5.397.328.21.191.761.992.613.543.372.564.671.55Na,O3.663.443.313.01 <td>MgO</td> <td>3,9</td> <td>8,1</td> <td>2,2</td> <td>1,87</td> <td>1,61</td> <td>1,38</td> <td>1,25</td> <td>1,19</td> <td>1,85</td> <td>1,38</td> <td>2,45</td> <td>1,03</td>	MgO	3,9	8,1	2,2	1,87	1,61	1,38	1,25	1,19	1,85	1,38	2,45	1,03
	CaO	5,39	7,32	82	1,19	1,76	1,99	2,61	3,54	3,37	2,56	4,67	1,55
	Na ₂ O	3,6	3,4	3,8	3,16	3,51	4,64	3,71	3,04	3,67	3,65	4,38	0,77
	K,Ô	2,49	1,55	3,03	1,90	1,19	1,33	3,78	2,35	2,90	4,01	2,33	3,15
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	P,O,	0,23	0,41	0,24	0,15	0,24	0,20	0,12	0,19	0,26	0,12	0,23	0,24
	Cr,O,							0,01	0,00	0,00	0,01	0,01	0,01
TOTAL 99,51 99,94 99,94 99,94 99,10 102,49 Ba 1279 895 1417 980,4 854,4 334 1273,5 945,9 1547,6 1133,9 1271,3 102,76 Ba 1319 4,5 15,7 8,4 4,7 6,13 131,7 82,3 74,7 149,3 64,5 89,9 Th 13,19 4,5 15,7 8,4 4,7 4,8 26,6 3,9 7,2 32,1 11,5 5 Nb 12 14 13,6 12 11,2 14,5 6,10 6,2 42,5 10,0 5,5 5,5 Ni 613 74 16,6 12,4 11,4 7,5 5,13 11,4 10,0 5,8 11,4 10,0 5,8 11,4 11,4 10,6 11,3 12,4 12,4 12,4 V 11,7 8,6 79 70 74 10,0 58	LÕI%				7,42	8,20	7,17	1,70	9,46	6,33	2,69	0,96	10,69
Ba 1279 895 1417 980,4 854,4 334 1273,5 945,9 1547,6 1133,9 1271,3 1027,5 Rb 71 25 98 72,1 45,7 61,7 131,7 82,3 74,7 149,3 64,5 89,9 Nb 12 15 10 6,3 5,8 5,8 9,6 5,3 6,5 10 6,9 5,5 Sr 613 745 526 448 438,1 351,5 437,5 367,2 472,5 425,1 739,4 94,4 Zr 140 141 167 116,8 119,7 114,9 145,6 10,16 124,8 150,8 125,6 103 Y 20 22 14 13,6 12 11,6 74 8,4 8,3 7 7,1 13,5 24 V 117 86 79 70 74 100 53 12,0 V<	TOTAL	99,51	99,94	99,92	101,45	102,27	101,46	99,54	102,29	100,49	99,49	99,19	102,49
	Ba	1279	895	1417	980,4	854,4	334	1273,5	945,9	1547,6	1133,9	1271,3	1027,5
Th 13,19 4,5 15,7 8,4 4,7 4,8 26,6 3,9 7,2 32,1 11,5 5 Nb 12 15 10 6,3 5,8 5,8 9,6 5,3 6,5 10 6,9 5,5 Sr 140 141 167 116,8 119,7 114,9 145,6 101,6 124,8 150,8 125,6 103 Y 20 22 14 13,6 12 12,6 13,1 16,7 14,3 12,4 27 Ni 66 44 41 7,5 5,8 8,7 11,4 5,6 6,8 8,2 14,2 20,2 Co 23,77 29,20 14,47 8,4 14,6 7,4 8,4 8,3 7 7,1 13,5 9,4 Sc 18,28 6,09 13,7 5,2 14,8 13,2 1,3 1,5 29,8 Cu 34 52 26 140,8 22,5,1 75 20,7 3,6 7,9 14,4	Rb	71	25	98	72,1	45,7	61,7	131,7	82,3	74,7	149,3	64,5	89,9
	Th	13,19	4,5	15,7	8,4	4,7	4,8	26,6	3,9	7,2	32,1	11,5	5
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	Nb	12	15	10	6,3	5,8	5,8	9,6	5,3	6,5	10	6,9	5,5
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	Sr	613	745	526	448	438,1	351,5	437,5	367,2	472,5	425,1	739,4	94,4
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	Zr	140	141	167	116,8	119,7	114,9	145,6	101,6	124,8	150,8	125,6	103
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	Y	20	22	14	13,6	12	11,2	12,6	13,1	16,7	14,3	12,4	27
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	V				117	86	79	70	74	100	58	115	95
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	Ni	66	44	41	7,5	5,8	8,7	11,4	5,6	6,8	8,2	14,2	20,2
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	Со	23,77	29,20	14,47	8,4	14,6	7,4	8,4	8,3	7	7,1	13,5	9,4
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	Sc	18,28	26,90	12,18	11	9	8	7	8	11	6	11	12,0
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	Pb				18,6	9,9	13,7	5,2	14,8	13,2	1,3	1,5	29,8
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	Cu	34	52	26	140,8	225,1	75	20,7	3,6	7,9	14,4	10	20,8
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Zn	83	78	60	2	62	83	47	39	72	17	43	764
Be111211211211Ga21,617,920,119,518,519,118,82117,5Mo5,32,20,51,60,710,51,70,5Sn331111212TI0,20,10,20,10,10,10,2Mf4,053,564,783,23,63,25,13,43,85,13,93U5,741,457,592,722,212,71,9214,34,42La23,7118,8022,6729,71718,923,514,520,826,720,818Ce46,2238,0043,9357,63638,243,530,341,549,140,434,8Pr7,114,624,705,253,845,235,945,164,43Nd20,4719,2018,9328,119,718,520,115,521,221,920,518,7Sm4,825,044,775,183,633,193,502,963,883,523,833,66Eu1,191,511,021,260,870,840,740,821,000,711,001,22Gd.2,822,321,872,27 <td>Cs</td> <td>2,47</td> <td>0,55</td> <td>2,99</td> <td>6,5</td> <td>11,3</td> <td>6,3</td> <td>3,7</td> <td>3</td> <td>3,5</td> <td>10,5</td> <td>2,1</td> <td>7,4</td>	Cs	2,47	0,55	2,99	6,5	11,3	6,3	3,7	3	3,5	10,5	2,1	7,4
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	Be				1	1	1	2	1	1	2	1	1
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	Ga				21,6	17,9	20,1	19,5	18,5	19,1	18,8	21	17,5
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	Mo				5,3	2,2	0,5	1,6	0,7	1	0,5	1,7	0,5
I1 $0,2$ $0,1$ $0,2$ $0,1$ $0,2$ $0,1$ $0,1$ $0,1$ $0,2$ Ta $0,54$ $0,72$ $0,69$ $0,4$ $0,4$ $0,4$ $0,9$ $0,3$ $0,4$ $1,1$ $0,5$ $0,4$ Hf $4,05$ $3,56$ $4,78$ $3,2$ $3,6$ $3,2$ $5,1$ $3,4$ $3,8$ $5,1$ $3,9$ 3 U $5,74$ $1,45$ $7,59$ $2,7$ 2 $2,2$ $12,7$ $1,9$ 2 $14,3$ $4,4$ 2 La $23,71$ $18,80$ $22,67$ $29,7$ 17 $18,9$ $23,5$ $14,5$ $20,8$ $26,7$ $20,8$ 18 Ce $46,22$ $38,00$ $43,93$ $57,6$ 36 $38,2$ $43,5$ $30,3$ $41,5$ $49,1$ $40,4$ $34,8$ Pr $7,11$ $4,62$ $4,70$ $5,25$ $3,84$ $5,23$ $5,94$ $5,16$ $4,43$ Nd $20,47$ $19,20$ $18,93$ $28,1$ $19,7$ $18,5$ $20,11$ $15,5$ $21,2$ $21,9$ $20,5$ $18,7$ Sm $4,82$ $5,04$ $4,77$ $5,18$ $3,63$ $3,19$ $3,50$ $2,96$ $3,88$ $3,52$ $3,83$ $3,66$ Eu $1,19$ $1,51$ $1,02$ $1,26$ $0,87$ $0,44$ $0,43$ $0,43$ $0,55$ $0,46$ $0,48$ $0,62$ Dy $2,82$ $2,32$ $1,87$ $2,27$ $2,44$ $2,87$ $2,26$ $2,34$ $3,55$ Ho<	Sn				3	3	1	1	1	1	2	1	2
Ia $0,54$ $0,72$ $0,69$ $0,4$ $0,4$ $0,4$ $0,9$ $0,3$ $0,4$ $1,1$ $0,5$ $0,4$ Hf $4,05$ $3,56$ $4,78$ $3,2$ $3,6$ $3,2$ $5,1$ $3,4$ $3,8$ $5,1$ $3,9$ 3 U $5,74$ $1,45$ $7,59$ $2,7$ 2 $2,2$ $12,7$ $1,9$ 2 $14,3$ $4,4$ 2 La $23,71$ $18,80$ $22,67$ $29,7$ 17 $18,9$ $23,5$ $14,5$ $20,8$ $26,7$ $20,8$ 18 Ce $46,22$ $38,00$ $43,93$ $57,6$ 36 $38,2$ $43,5$ $30,3$ $41,5$ $49,1$ $40,4$ $34,8$ Pr $7,11$ $4,62$ $4,70$ $5,25$ $3,84$ $5,23$ $5,94$ $5,16$ $4,43$ Nd $20,47$ $19,20$ $18,93$ $28,1$ $19,7$ $18,5$ $20,1$ $15,5$ $21,2$ $21,9$ $20,5$ $18,7$ Sm $4,82$ $5,04$ $4,77$ $5,18$ $3,63$ $3,19$ $3,50$ $2,96$ $3,88$ $3,52$ $3,83$ $3,66$ Eu $1,19$ $1,51$ $1,02$ $1,26$ $0,87$ $0,84$ $0,74$ $0,82$ $1,00$ $0,71$ $1,00$ $1,22$ Gd $5,94$ $2,77$ $2,3$ $2,39$ $2,43$ $3,05$ $2,74$ $2,90$ $3,43$ Tb $0,87$ $0,61$ $0,33$ $0,59$ $0,45$ $0,4$ $0,43$ $0,43$ $0,55$ $0,46$	TI	0.54	0.50	0.60	0,2	0,1	0,2	0,1	0,2	0,1	0,1	0,1	0,2
Hr4,053,564,783,23,63,25,13,43,85,13,93U5,741,457,592,722,212,71,9214,34,42La23,7118,8022,6729,71718,923,514,520,826,720,818Ce46,2238,0043,9357,63638,243,530,341,549,140,434,8Pr7,114,624,705,253,845,235,945,164,43Nd20,4719,2018,9328,119,718,520,115,521,221,920,518,7Sm4,825,044,775,183,633,193,502,963,883,523,833,66Eu1,191,511,021,260,870,840,740,821,000,711,001,22Gd3,492,72,32,392,433,052,742,903,43Tb0,870,610,330,590,450,40,430,430,550,460,480,62Dy2,822,321,872,272,442,872,262,343,55Ho0,610,330,590,450,40,400,460,520,420,73Er1,291,231	Ta	0,54	0,72	0,69	0,4	0,4	0,4	0,9	0,3	0,4	1,1	0,5	0,4
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Hf	4,05	3,56	4,78	3,2	3,6	3,2	5,1	3,4	3,8	5,1	3,9	3
La $23,71$ $18,80$ $22,67$ $29,7$ 17 $18,9$ $23,5$ $14,5$ $20,8$ $26,7$ $20,8$ 18 Ce $46,22$ $38,00$ $43,93$ $57,6$ 36 $38,2$ $43,5$ $30,3$ $41,5$ $49,1$ $40,4$ $34,8$ Pr $7,11$ $4,62$ $4,70$ $5,25$ $3,84$ $5,23$ $5,94$ $5,16$ $4,43$ Nd $20,47$ $19,20$ $18,93$ $28,1$ $19,7$ $18,5$ $20,1$ $15,5$ $21,2$ $21,9$ $20,5$ $18,7$ Sm $4,82$ $5,04$ $4,77$ $5,18$ $3,63$ $3,19$ $3,50$ $2,96$ $3,88$ $3,52$ $3,83$ $3,66$ Eu $1,19$ $1,51$ $1,02$ $1,26$ $0,87$ $0,84$ $0,74$ $0,82$ $1,00$ $0,71$ $1,00$ $1,22$ Gd $3,49$ $2,7$ $2,3$ $2,39$ $2,43$ $3,05$ $2,74$ $2,90$ $3,43$ Tb $0,87$ $0,61$ $0,33$ $0,59$ $0,45$ $0,4$ $0,43$ $0,43$ $0,55$ $0,46$ $0,48$ $0,62$ Dy $2,82$ $2,32$ $1,87$ $2,27$ $2,44$ $2,87$ $2,26$ $2,34$ $3,55$ Ho $0,48$ $0,4$ $0,34$ $0,40$ $0,46$ $0,52$ $0,42$ $0,42$ $0,73$ Er $1,29$ $1,23$ $1,00$ $1,16$ $1,21$ $1,47$ $1,22$ $1,03$ $2,11$ Tm $0,22$ $0,19$ $0,17$ <th< td=""><td>U</td><td>5,74</td><td>1,45</td><td>7,59</td><td>2,7</td><td>2</td><td>2,2</td><td>12,7</td><td>1,9</td><td>2</td><td>14,3</td><td>4,4</td><td>2</td></th<>	U	5,74	1,45	7,59	2,7	2	2,2	12,7	1,9	2	14,3	4,4	2
Ce46,2238,0043,9557,63638,243,530,341,549,140,434,8Pr7,114,624,705,253,845,235,945,164,43Nd20,4719,2018,9328,119,718,520,115,521,221,920,518,7Sm4,825,044,775,183,633,193,502,963,883,523,833,66Eu1,191,511,021,260,870,840,740,821,000,711,001,22Gd3,492,72,32,392,433,052,742,903,43Tb0,870,610,330,590,450,40,430,430,550,460,480,62Dy2,822,321,872,272,442,872,262,343,55Ho.0,480,40,340,400,460,520,420,420,73Er.1,291,231,001,161,211,471,221,032,11Tm0,220,190,170,190,190,240,190,190,33Yb1,771,691,281,371,150,941,21,161,511,341,080,93	La	23,71	18,80	22,67	29,7	1/	18,9	23,5	14,5	20,8	26,7	20,8	18
Fr7,114,624,703,255,645,255,945,164,45Nd20,4719,2018,9328,119,718,520,115,521,221,920,518,7Sm4,825,044,775,183,633,193,502,963,883,523,833,66Eu1,191,511,021,260,870,840,740,821,000,711,001,22Gd3,492,72,32,392,433,052,742,903,43Tb0,870,610,330,590,450,40,430,430,550,460,480,62Dy2,822,321,872,272,442,872,262,343,55Ho.0,480,40,340,400,460,520,420,420,73Er.1,291,231,001,161,211,471,221,032,11Tm0,220,190,170,190,190,240,190,190,33Yb1,771,691,281,371,150,941,21,161,511,341,080,93Vb0,270,260,230,230,240,240,240,240,240,240,24O0,270,260,230,260,240,240,240,240,240,24 <td>Ce D-</td> <td>40,22</td> <td>38,00</td> <td>43,93</td> <td>J/,0 7 11</td> <td>30</td> <td>38,2</td> <td>43,5</td> <td>2.04</td> <td>41,5</td> <td>49,1</td> <td>40,4</td> <td>34,8</td>	Ce D-	40,22	38,00	43,93	J/,0 7 11	30	38,2	43,5	2.04	41,5	49,1	40,4	34,8
Nd $20,47$ $19,20$ $18,95$ $28,1$ $19,7$ $18,5$ $20,1$ $13,5$ $21,2$ $21,9$ $20,5$ $18,7$ Sm $4,82$ $5,04$ $4,77$ $5,18$ $3,63$ $3,19$ $3,50$ $2,96$ $3,88$ $3,52$ $3,83$ $3,66$ Eu $1,19$ $1,51$ $1,02$ $1,26$ $0,87$ $0,84$ $0,74$ $0,82$ $1,00$ $0,71$ $1,00$ $1,22$ Gd $3,49$ $2,7$ $2,3$ $2,39$ $2,43$ $3,05$ $2,74$ $2,90$ $3,43$ Tb $0,87$ $0,61$ $0,33$ $0,59$ $0,45$ $0,4$ $0,43$ $0,43$ $0,55$ $0,46$ $0,48$ $0,62$ Dy $2,82$ $2,32$ $1,87$ $2,27$ $2,44$ $2,87$ $2,26$ $2,34$ $3,55$ Ho $0,48$ $0,4$ $0,34$ $0,40$ $0,46$ $0,52$ $0,42$ $0,42$ $0,73$ Er $1,29$ $1,23$ $1,00$ $1,16$ $1,21$ $1,47$ $1,22$ $1,03$ $2,11$ Tm $0,22$ $0,19$ $0,17$ $0,19$ $0,19$ $0,24$ $0,19$ $0,19$ $0,33$ Yb $1,77$ $1,69$ $1,28$ $1,37$ $1,15$ $0,94$ $1,2$ $1,16$ $1,51$ $1,34$ $1,08$ $0,93$	PT NJ	20.47	10.20	10.02	7,11	4,02	4,70	3,23	5,04	3,25	3,94	3,10	4,45
Sin 4,82 5,04 4,77 5,18 5,05 5,19 5,30 2,96 5,68 5,22 5,63 5,00 Eu 1,19 1,51 1,02 1,26 0,87 0,84 0,74 0,82 1,00 0,71 1,00 1,22 Gd 3,49 2,7 2,3 2,39 2,43 3,05 2,74 2,90 3,43 Tb 0,87 0,61 0,33 0,59 0,45 0,4 0,43 0,43 0,55 0,46 0,48 0,62 Dy 2,82 2,32 1,87 2,27 2,44 2,87 2,26 2,34 3,55 Ho 0,48 0,4 0,34 0,40 0,46 0,52 0,42 0,42 0,73 Er 1,29 1,23 1,00 1,16 1,21 1,47 1,22 1,03 2,11 Tm 0,22 0,19 0,17 0,19 0,19 0,24 0,19 0,19 0,33 Yb 1,77 1,69 1,28 1,37 1,15	INU Sm	20,47	19,20	10,95	20,1	19,7	2 10	20,1	2.06	21,2	21,9	20,5	10,7
Ed 1,19 1,31 1,02 1,20 0,87 0,84 0,74 0,02 1,00 0,71 1,00 1,22 Gd 3,49 2,7 2,3 2,39 2,43 3,05 2,74 2,90 3,43 Tb 0,87 0,61 0,33 0,59 0,45 0,4 0,43 0,43 0,55 0,46 0,48 0,62 Dy 2,82 2,32 1,87 2,27 2,44 2,87 2,26 2,34 3,55 Ho 0,48 0,4 0,34 0,40 0,46 0,52 0,42 0,42 0,73 Er 1,29 1,23 1,00 1,16 1,21 1,47 1,22 1,03 2,11 Tm 0,22 0,19 0,17 0,19 0,19 0,24 0,19 0,19 0,33 Yb 1,77 1,69 1,28 1,37 1,15 0,94 1,2 1,16 1,51 1,34 1,08 1,931	SIII En	4,62	3,04	4,77	5,10	5,05	5,19	5,50	2,90	3,00	5,52	3,03	5,00
Gu 5,49 2,7 2,3 2,59 2,45 5,05 2,74 2,90 5,45 Tb 0,87 0,61 0,33 0,59 0,45 0,4 0,43 0,43 0,55 0,46 0,48 0,62 Dy 2,82 2,32 1,87 2,27 2,44 2,87 2,26 2,34 3,55 Ho 0,48 0,4 0,34 0,40 0,46 0,52 0,42 0,42 0,73 Er 1,29 1,23 1,00 1,16 1,21 1,47 1,22 1,03 2,11 Tm 0,22 0,19 0,17 0,19 0,19 0,24 0,19 0,19 0,33 Yb 1,77 1,69 1,28 1,37 1,15 0,94 1,2 1,16 1,51 1,34 1,08 1,93	Cd	1,19	1,51	1,02	3.40	0,07	2 2	2 20	2 /2	3.05	2.74	2 00	3 /2
Dy 2,82 2,32 1,87 2,27 2,44 2,87 2,26 2,34 3,55 Ho 0,48 0,4 0,34 0,40 0,46 0,52 0,42 0,42 0,73 Er 1,29 1,23 1,00 1,16 1,21 1,47 1,22 1,03 2,11 Tm 0,22 0,19 0,17 0,19 0,19 0,24 0,19 0,19 0,33 Yb 1,77 1,69 1,28 1,37 1,15 0,94 1,2 1,16 1,51 1,34 1,08 1,93	Th	0.87	0.61	0.33	0.50	0.45	2,5	0.43	0.43	0.55	2,74	0.48	0.62
L_y L_{32} L_{32} L_{32} L_{33} L_{24} L_{34} L_{20} L_{34} S_{35} Ho $0,48$ $0,4$ $0,34$ $0,40$ $0,46$ $0,52$ $0,42$ $0,42$ $0,73$ Er $1,29$ $1,23$ $1,00$ $1,16$ $1,21$ $1,47$ $1,22$ $1,03$ $2,11$ Tm $0,22$ $0,19$ $0,17$ $0,19$ $0,19$ $0,24$ $0,19$ $0,19$ $0,33$ Yb $1,77$ $1,69$ $1,28$ $1,37$ $1,15$ $0,94$ $1,2$ $1,16$ $1,51$ $1,34$ $1,08$ $1,93$	Dv	0,07	0,01	0,35	2.82	2 22	1.87	2 27	2 11	2.87	2.26	2 3/	3 55
Er 1,29 1,23 1,00 1,16 1,21 1,47 1,22 1,03 2,11 Tm 0,22 0,19 0,17 0,19 0,19 0,24 0,19 0,19 0,33 Yb 1,77 1,69 1,28 1,37 1,15 0,94 1,2 1,16 1,51 1,34 1,08 1,93	Но				0.48	0.4	0.34	0.40	0.46	0.52	0.42	0.42	0.73
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	Er				1 29	1.23	1.00	1 16	1 21	1 47	1 22	1.03	2 11
Yb $1,77$ $1,69$ $1,28$ $1,15$ $0,94$ $1,2$ $1,16$ $1,51$ $1,34$ $1,08$ $1,93$	Tm				0.22	0.19	0.17	0.19	0.19	0.24	0.19	0.19	0.33
$\mathbf{X} = \{1, 1, 1, 5, 7, 1, 25, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1,$	Vh	1 77	1 69	1.28	1 37	1 15	0.94	12	1 16	1 51	1 34	1.08	1.93
Lu = 0.27 = 0.26 = 0.3 = 0.23 = 0.2 = 0.16 = 0.21 = 0.2 = 0.24 = 0.23 = 0.16 = 0.31	Lu	0.27	0.26	0.3	0.23	0.2	0.16	0.21	0.2	0.24	0.23	0.16	0.31

Table 1

Major elements (wt.%) compositions are reported on an anhydrous basis and normalized to 100% LOI= loss on Ignition Data taken from :*(1) Gallego *et al.* 2007; *(2) Vatin-Perignon *et al.* 1990; *(3) Ancochea *et al.* 1991; *(4) Schaefer (1995); *(5) This work

The Hoyo Frio sector located to the Northeast of Manizales (in Fig. 4, located as a single point) is a small area covered by a dome and associated pyroclastic deposits in the Rio Guacaica watershed, which extended ~ 5 km to the west. This sector is located north of the main trace of the Villa María –Termales fault, but the major N-S trending- structural system, the Romeral fault (Fig. 3) that is crossed by the Villa María –Termales fault may be the pathway of magmas from the Ancestral Ruiz stage to this sector.

The chemical data of this sector correspond to unpublished research work of Gallego *et al.* (2006). In the Hoyo Frio sector, the pyroclastic deposits are dominated by block and ash flows over the block-pumice and ash flows (Gallego *et al.*, 2006). Chemical analyses from juvenile samples (Table 1, Map location 1-10, samples: ACJ 8; ACJ 2.2; ACJ 2.21; ACJ2.23; ACJ 2.25; ACJ 2.43; ACJ 3.11; ACJ 3.12; ACJ 3.20 and ACJ 4.1), as well as the dome related to the pyroclastic deposits (Table 1, Map location 11, sample: ACJ 6.4) suggest an affinity with the products of Ruiz Ancestral (Vatin-Perignon *et al.*, 1990).

The Old-Ruiz lavas of Vatin-Perignon *et al.* (1990) include the first episode of activity of the basal unit of the Ruiz volcano deposited at 1.8-0.6 Ma. Voluminous andesitic lava and pyroclastic flows were erupted. The samples named Old Lavas Ruiz (OLR) in Table 1 (map location: 12-15) (Vatin-Perignon *et al.*, 1990 Fig. 2) are as follows: sample 83-267, an andesitic lava from Fonda El Placer, sample 83-278a, a lithic of amphibole-bearing andesitic lava in a pyroclastic flow from Fresno (1.8-0.6 Ma), sample 83-153, a basaltic andesite lava from Alto de la Cruz, Manizales and sample 82-54, 2: a pyroxenebearing andesitic lava from Peña Margarita (1.05 \pm 0.8 Ma from Thouret *et al.*, 1990).

The data of Ancochea *et al.*(1991) listed as Domes an Lavas in Table 1 (map location: 16-22) are related to the monogenetic vents with crypto-domes and lava flows that crop out along the pathway of Villa María –Termales fault (Fig.4). They correspond to: sample 5150, the La Enea lava flow, sample 5158, San Cancio or Alto de La Cruz Dome with an age of 1, 2 ± 0 , 08 Ma (Thouret *et al.*, 1990), sample 5151, Tesorito or Tesoro volcano dated at 1, $2 \pm 0,2$ Ma (Thouret *et al.*, 1990), sample 5160 and 5161, Piedrablanca Domes and sample 5157, the Termales lava flow.

The Pre-Ruiz lavas of Schaefer (1995) named PRL in Table 1 (map location 23-25), form an eroded apron upon which the present Nevado del Ruiz Volcano was edified. The lavas in the Pre-Ruiz stage have been dated at 1.8 ± 0.1 to 0.97 ± 0.05 Ma (Schaefer, 1995, Thouret *et al.*, 1990). Lava flow samples (Table 1, Map location: 23-25, samples: 219, 8910 and 320) were approximately

localized in the Fig. 4 from the description given by Schaefer (1995).

Our data, named Manizales Southeast correspond to domes and lava flows located 4 km to the west of city of Manizales, included the small hills of Gallinazo, Amazonas y La Negra (in Fig. 4 located as a single point). Refer to Table 1 (map location 26-34), samples: PA-8A-1; PA-9-1; PA-10-2; PA-15g; PA-20-3; PA-21-5; PA-31A PA-32-5 and 83.

The Chemical analyses of our samples were made at ACTLABS (Activation Laboratories Ltd. Ontario, Canada) using Inductively Coupled Plasma (ICP) techniques for the major elements, Ba, Sr, Y and Zr, and, Instrumental Neutron Activation Analysis (INAA) for trace and REE elements.

Major elements

All samples collected from the different units show a similar chemical composition for major elements (Fig 5. Total alkali-silica diagram). All the samples are in the sub-alkaline field, the SiO₂ contents vary between 56 and 70.1 wt. %. Most of the samples are andesites and dacites and in minor amounts basaltic andesites and rhyolites. The andesites show porphyritic texture with groundmass of vitrophyric-microlitic texture and contain plagioclase + orthopyroxene + clinopyroxene + magnetite + hornblende \pm biotite. The dacites show porphyritic and microlitic textures with glassy groundmass and contain phenocrysts of plagioclase + hornblende + biotite. The rhyolites show porphyritic textures with perlitic cracks in the groundmass and contain phenocrysts of plagioclase + biotite + hornblende \pm k-feldspar (Toro *et al.*, in press).

The samples in the K₂O versus SiO₂ diagram (Fig.6) typically lie in the medium-K field and only few in the high-K field showing good correlation of the different magmatic suites. Most of the samples are andesites and dacites, and only three samples of the Manizales Southeast data are rhyodacites. These results support the statement of Schaefer (1995): "The high-K suite has been volumetrically dominant throughout the history of the volcano, and comprises more than 98% of the exposed eruptive products". For this author, the high-K suite of Nevado del Ruiz Volcano is included in the medium-K field of Gill (1981). While in the Ancestral Ruiz stage the medium-K suite dominates.

Most of the samples including basaltic andesites, andesites, dacites and rhyodacites have high Al_2O_3 contents (> 15.3 wt. %), $SiO_2 > 55.66$ wt. %, MgO < 6.15 wt. % and CaO>1.2 wt. %. Nevertheless, the most primitive sample corresponds to a basaltic andesite.



Fig. 5. Location of samples in the Total alkali-silica diagram (Le Bas *et al.*, 1986). The Irvine and Baragar (1971) line (bold line) is also reported. Data are from Table 1. Anhydrous basis for all the samples



Fig. 6. K₂O versus SiO₂ diagram, fields modified after Peccerillo and Taylor (1976). Data are from Table 1. Anhydrous basis for all the samples

Geofis. Int. 48 (1), 2009

MgO, CaO and TiO₂ versus silica contents plots (Fig.7) show well-correlated trends from the more mafic compositions to the more felsic ones. These well defined evolution trends are consistent with the fact that the more abundant phenocrysts in the basaltic, andesitic and dacitic samples are Plagioclase + Clinopyroxene + Hornblende. All of these imply that the fractionating of these minerals in the magmatic series could have controlled at most the differentiation of the major elements of the Ancestral Ruiz Volcano stage. However, all the other major-element abundances (MnO, Na₂O, P₂O₅, K₂O and FeO) show a poor correlation with silica content. Although we observe a compositional gap from 65 to 67 wt. % silica between intermediate to felsic rocks, no significant total differences exist between the magmatic suites.

Trace elements

The main processes that control the evolution and diversification of magmas are: fractional crystallization and contamination by assimilation and magma mixing (co-genetics). Trace elements are commonly used to determine geochemical evolution, assimilation of crustal materials, and/or emplacements in low/medium levels of the crust (Hildreth and Moorbath, 1988). Nevertheless, in the Ancestral Ruiz stage there is not a clear tendency in the trace-element patterns (Fig.8) which show a similar random distribution for Ce, and La (light rare earth elements); Yb (heavy rare earth element); Nb and Zr (high field strength elements), and Ba and Sr (compatible elements).

Conversely, the "Hoyo Frio" suite (Table 1) show the highest values of the trace-elements in almost all the diagrams, although, in general, there is no big difference in the random trends with the other suites. This suggests that these magmas suffered little fractionation, which is consistent with crystallization of a parental magma suffering little crustal contamination in the Northern Andes (Thorpe *et al.*, 1984).

Comparison between elements

Sr decreases with SiO₂ but does not vary significantly with differentiation, which is typical of the medium and high-K calc-alkaline trend (Gill, 1981). It is anticipated that the decreasing Sr content with increasing silica implies plagioclase fractionation. CaO/Al₂O₃ ratios versus SiO₂ (Fig. 9A) for the Pre-Ruiz Lavas, Old-Ruiz Lavas and Domes and Lavas suites present the lowest values and this probably indicates that, the plagioclase was not a significant residual phase but also may reflect the influence of the different basement for each magmatic suite (Fig. 4).

The K/Rb ratios of most of the samples show a negative correlation with SiO_2 and Rb (Figs. 8 and 9B). K/Rb declines steeply for the lowest Rb values during the first stage of differentiation that corresponds to Pre-Ruiz Lavas and Old-Ruiz Lavas suites, but remains constant for the most silicic rocks (the Manizales Southeast suite). The K/Rb decreases from 514 to 256 between 25 to 99 ppm Rb. The slope displayed by the K/Rb ratio versus Rb suggest assimilation- fractional crystallization (AFC) trend of the model of Davidson *et al.* (1988) similar to the results of Droux and Delaloye (1996) for three southwestern Colombian volcanoes. Vatin-Perignon *et al.* (1990) also discussed that in the NRV, the Pre-Ruiz lavas series (Fig. 2) may feasibly be produced by a closed-system fractional crystallization model of a basaltic parental magma.

The best way of visualizing the relative variations of the trace-elements in the different magmatic suites is the normalized multi-element diagrams (Fig.10), our data represent typical comagmatic suites enriched in large-ion lithophile elements (LILE), Rb, Ba, Th and K and the light REE, and the negative anomalies of high field strength elements (HFSE), Ta-Nb and Zr-Hf are notables. These trace-element patterns are typical of rocks associated to magmatic-arc related to subduction zones especially in the Andean magmatism (Hildreth and Moorbath, 1988). Ba and Sr abundances of the most of the andesitic and dacitic samples (Fig.10) ascertain the effects of both fractional crystallization and phenocryst accumulation with similar tendencies with the data of the different stages of the NRV (Vatin-Perignon *et al.*, 1990).

REE elements

The magmatic suites discussed in this paper and as well as the entire Ruiz suites, including the historical series (Vatin-Perignon et al., 1990; Schaefer, 1995) have a LREE-enrichment pattern (Fig. 11), typical of the continental-margin/arc setting (Vatin-Perignon et al., 1990); this fact is further supported by the La/Yb ratios. The Hoyo Frio suite, which is atop the thicker Cretaceous basement (Fig. 4) shows the more evolved tendency, and may correspond to volcanic activity stemming from longer pathways from the original magmatic source. Despite the lack of data completion from some magmatic suites (Old-Ruiz lavas, Pre-Ruiz Lavas and Domes and Lavas), the low HREE values displayed are typical of calc-alkaline suites. The lack of Eu anomaly is noticeable, which implies that there was not plagioclase fractionation or the magmas were in equilibrium with a mantle source that already contained plagioclase.



Fig. 7. Variation diagrams for K_2O , MgO, MnO, TiO₂, Na₂O, P₂O₅, CaO, FeOt and Al₂O₃ versus SiO₂. FeOt = FeO(wt.%) + Fe₂O₃ (wt.%)* 0.8998 when the samples have Fe₂O₃ and FeO (All data are from Table 1).

Adakites

Drummond and Defant (1990) proposed that adakites are the result of partial melting of subducting oceanic crust at the amphibole-eclogite transition, before its dehydration. The more acidic samples of Domes and Lavas, Manizales Southeast and Hoyo Frio suites (Table 1, Fig. 12) display the strongest adakitic characters such as higher Sr contents, lower HREE and Y and higher Sr/Y ratios. In addition, the Al₂O₃ contents (>15% at 70% SiO₂) is the expected for slab melts, but the K₂O contents are much higher (1.5 -2.4) than in typical adakites (usually <1.5%) resulting in low Na₂O/K₂O ratios (<2.7) -untypical of slab melts (Drummond and Defant, 1990, Bourdon *et al.*, 2002).



Fig. 8. Variation diagrams for Ce, La, Ba, Rb, Sr, Nb, Zr and Yb versus SiO,. Data are from Table 1.

Although these rocks have been recognized in the Ecuadorian volcanic arc of the NVZ since the last decade, modern adakitic magmatism is apparently restricted to where a young and relatively hot oceanic crust or an active spreading center is subducted (Hidalgo *et al.*, 2007). The combination of adakites with calc-alkaline suites is frequent. Mixing between these suites may occur along magma pathways or in subcrustal/crustal magma chambers, e.g. Iliniza Volcanic Complex (Hidalgo *et al.*, 2007). This is the first report of the presence of adakite-like rocks within young volcanic sequences in Colombia, but it is necessary to obtain additional data to establish the geodynamics of this adakitic signature.

Discussion

Most of the stratovolcanoes in the Northern Volcanic Zone (NVZ) have a similar history of construction and destruction of stacked edifices. A good example is the Pichincha Volcanic Complex located at the Cordillera Occidental of the Ecuadorian Andes, which consists of an extinct older volcano (Rucu Pichincha) and a younger and still-active edifice (Guagua Pichincha) which has been constructed upon the western remnants of the older edifice (García-Aristizabal *et al.*, 2007). The Nevado del Ruiz Volcano (NRV) has a similar history with three main constructive stages (Fig. 2), the Ancestral Ruiz, Older



Fig. 9. A. CaO/Al₂O₃ versus SiO₂ diagram B. K/Rb versus Rb diagram showing the tendency of assimilation and fractional crystallization (AFC) modelling.

Ruiz and Present Ruiz, all of them constructed over the Pre-Ruiz Lavas (Thouret *et al.*, 1990).

The most significant difference (between the Pichincha Volcanic Complex and Nevado del Ruiz Volcano) is that the distribution of magmatism in the Nevado del Ruiz Volcano, during the Late Pliocene –Early Pleistocene Ancestral Ruiz stage, was developed along the N75°W trending-structural system, the Villa María-Termales fault. Whereas the results of the calculated stress tensors for this fault (González and Jaramillo, 2002), show normal faulting with a slight dextral component (Fig. 3).

The NRV is an andesitic-dacitic stratovolcano, whose products have been erupted through the same crustal material, and from the same position along the volcanic front, with similar tectonic factors and subduction zone geometry. Andesites and dacites in the range of 59-70 wt. % SiO₂ are the most common rocks; the same range shown in Fig. 5 for the lavas and domes of the Ruiz Ancestral stage. Besides, their mineral compositions are similar to those observed from other Andean volcanoes (Vatin-Perignon *et al.*, 1990). Previous works have proposed fractional crystallization from common parental magmas to produce the NRV rocks (Vatin-Perignon *et al.*, 1995).

In the NRV, Schaefer (1995) reported on whole rock and melt inclusion chemistry two distinct suites: low-K and medium-K, which have been operated concurrently but located independently. The preservation of these distinct suites has been allowed during transit through and storage in the crust. This author explained the petrogenesis of the two distinct suites as caused by a varying degree of melting within the astenosphere mantle. He further proposed the NRV as a "controlled experiment" with physical subduction zone parameters held as constants, for assessing the cause and extent of variation in arc magma compositions. Our results show that in the Ancestral Ruiz stage the dominance corresponds to the medium-K suite (Fig. 6).

In the current discussion we use the scheme defined by Scandone *et al.* (2007) for volcanic systems. They define four different regions, namely: the supply system, the intermediate storage system, the transport system and the eruptive system. For these authors it is of the utmost importance the existence of a fracture network for the ascent of magma from the intermediate storage system through the transport system to the eruptive system.

The supply system in the different stages of the NRV may be a "primitive basic magma", which may feasibly be the source of the evolved magmas of the Ancestral Ruiz stage. During its ascent to shallower depths through the heterogeneous continental crust the basaltic parental magma was subject to a closed-system of fractional crystallization (Fig. 9.B) similar to the volcanism in southern Colombia (Droux and Delaloye, 1996) and central Chile (Hildreth and Moorbath, 1998).

The volcanic activity in the NRV probably begun ca. 2 Ma ago and it was located at the intersection of a major N20°E dextral strike-slip fault (Palestina fault) and a major N75°W transverse regional fault (Villa María-Termales fault; Herd, 1982; Thouret *et al.*, 1990 and González and Jaramillo, 2002). The crossing of these faults permitted the formation of an initial fracturing, once a fracture network was created, buoyant magma could enter into the system following the fracture pathways. Shortly after, the connectivity between fractures increased easing upward magma movement. This situation corresponds probably

to the initial NRV intermediate storage system, currently existing evidenced by the distribution of the volcanic products around the 2 Ma old source (Fig. 4).

In order to locate the magma chamber, the intermediate storage system during the Ancestral Ruiz stage, we follow the results of the seismic tomographic study performed by Londoño and Sudo (2002). They suggested a model for the seismic activity of the NRV in combination with seismicity, geochemistry, geology, and gravimetry data and defined three low-Vs zones, which showed the location of the heat sources. The intermediate zone, at mid-to-shallow crustal depths of 5-10 km corresponds to the main magma chamber, located at the intersection of the main faults. This proposal agreed with the volcanic-magmatic-hydrothermal system from the NRV model of Giggembach *et al.* (1990) based on their geochemical findings.

This situation is similar for other volcanoes in the NVZ like the Guagua Pichincha Volcano (Ecuador) (García-Aristizabal *et al.*, 2007), based on their petrologic analyses of 1999 eruptive products, the authors defined a magma storage region beneath Guagua Pichincha with a vertical extent of 7-8 km with the upper boundary at about sea level. De Natale *et al.* (2006) in the Somma-Vesuvius also defined a main zone of magma accumulation at shallow depth (about 5 km), this was observed at Vesuvius, and they observed it to be common to many other volcanoes.

The transport system connects the storage system with the eruptive system. It is located at the upper part of the volcanic edifice at the shallowest low-Vs zone in the NRV, 2-4 km, found by Londoño and Sudo (2002). The transport system at the NRV was developed once a fracture network was created and buoyant magma entered into the system. When the ascent rate prevailed over the supply rate, the magma ascended as an individual magma batch. This transport system in the Late Pliocene- Early Pleistocene epoch probably was enlarged to the west of NRV by the activity of the Villa María-Termales fault and its associated fracture network (Fig 13). Schaefer (1995) described a set of domes located to the northern of the present NRV, in a line that may represent a preexisting crustal structure related to the Palestina fault, but there is no geochemical data of these domes available for comparison against our results.

It is anticipated that the volcanic eruptions in the Ancestral Ruiz stage were probably primarily controlled by the interplay between magma buoyancy and the local stress field. The volcanic products of this stage are scattered in the present NRV surroundings (Old-Ruiz Lavas and Pre-Ruiz Lavas, Table 1) and a set of small effusive eruptions in monogenetic vents aligned with the Villa María-Termales fault (Domes and Lavas and Manizales Southeast samples, Table 1, Fig. 4). The fracture zone associated to this fault located to the northwest of the Present NRV permitted the ascent of a series of magma batches detached from this source, which explains the pulsatory character of some eruptions in this zone. These eruptions were fed by lateral magma flow from the intermediate storage system located bellow the position of the present NRV (Fig. 13).

It is also clear, that the ascent of isolated and discrete magma batches escaped from the intermediate storage system through the enlarged transport system was sporadic. The magma supply for each one of these vents distributed along the Villa María-Termales fault favour longer residence times (centuries to millenniums?) of the isolated magma batches in the crust (cf. Schaefer, 1995). Therefore, this type of magmatic supply controlled tectonically increased the possibility of cooling and differentiation of the evolved magma. This is evidenced by most of the studied andesites from the Ancestral Ruiz stage that show porphyritic texture and are composed by plagioclase + orthopyroxene + clinopyroxene + magnetite + hornblende \pm biotite, similar to the mineral assemblage described by Schaefer (1995) for the medium-K suites. The presence of equilibrium phenocryst assemblages in the Ancestral Ruiz lavas suggests that magma rose slowly from depth, with long-time ponding in a shallow-seated crustal transport system. Notwithstanding, the magmatic transport has a shorter time-scale with respect to the larger time-scale of the residence times in the magma chamber (Costa et al., 2007).

In the Ancestral Ruiz stage, the fracture network associated to the Villa María-Termales fault (Fig. 13) allowed the ascent of individual magma batches by opening and then closing after their passage, apparently sealing the transport system associated with the fault system and disconnecting it from the intermediate storage. This total disconnection is evidenced by the location of the post-Ancestral Ruiz stage magmatic activity, the Older and Present Ruiz stages (Fig. 2), which occur exclusively in the "present edifice" of NRV and surroundings.

The Eruptive system is the shallow region from which magma is erupted. In general, an eruption is effusive if the magma loses most of its volatiles during ascent through the transport system, otherwise it is explosive. Wallace (2001) proposed several parameters in order to explain the gas amount in the magma bodies and discuss how the extent of pre-eruptive gas loss during transport of magma from deep to shallow reservoirs, and the influence of reservoir, vent, and conduit geometry on magma withdrawal processes and transport dynamics. Most of the eruptions in the vents along the Villa María-Termales fault were relatively short-time extrusions of lava domes and lava flows when the magma batches probably lost most of their volatiles during ascent through this transport system. The loss of the gas of the small magma batches was strongly controlled by the time spent in the upper part of the transport system. Longer span times permit efficient pre-eruptive degassing by both two phase flow or gas loss through a permeable network and microlite growth in response to that degassing (Toro *et al.*, in press). Similar arguments have been given by Scandone *et al.* (2007) and references therein.

The geochemistry of the effusive products of Ancestral Ruiz stage of NRV presented in this paper (Figs. 10 and 11) is typical of calc-alkaline magmatism within an active subduction zone, most of the samples including basaltic andesites, andesites, dacites and rhyodacites have $SiO_2 > 56.28 \text{ wt.}\%$, $Al_2O_3 > 15.3$, MgO < 6.15, and CaO > 1.2 wt.% (Figures 5 and 7). Well-correlated trends were defined on plots of MgO, CaO and TiO₂ versus silica contents, although there is a poor correlation between silica contents and the other major-elements: MnO, Na₂O, P₂O₅, K₂O and FeO (Fig.7).

In the Ancestral Ruiz stage there is not a clear tendency of the trace-element patterns (Fig.8), showing a similar random distribution of the LREE, HREE, HFSE, and compatible elements, which is consistent with crystallization of a parental magma suffering little crustal contamination in the Northern Andes (Thorpe *et al.*, 1984). The magmatic suites of this paper have a LREE-enrichment (Fig. 11), typical of continental-margin/arc context (Vatin-Perignon *et al.*, 1990).

The main factor controlling the evolution of the magma was a simple fractional crystallization in the Ancestral Ruiz Stage. Crystal fractionation is the mechanism by which the medium-K suite can be produced in the Ancestral Ruiz stage (Fig. 9-B). Schaefer (1995) proposed that this suite came from a sub-volcanic reservoir system that is long-lived, large and with injection of new magma batches. Similar of pumice samples of the 13 November 1985 eruption Schaefer (1995) applied internal ²³⁸U systematic to indicate that there have been recent injections (~6-7 ka) of new magma into the high-K magmatic system.

The more acidic samples of Domes and Lavas, Manizales Southeast and Hoyo Frio suites (Table 1) display the strongest adakitic character such as higher Sr contents, and lower HREE and Y, as well as higher Sr/Y ratios (Fig. 12). Drummond and Defant (1990) proposed that adakites are the result of partial melting of subducting oceanic crust at the amphibole-eclogite transition, before its dehydration. The discussion of the adakitic origin of these samples is beyond the scope of this paper.



Fig. 10. Average extended trace-elements plots for lavas and domes (Normalized to MORB after Hofmann, 1988).



Fig. 11. Average chondrite normalized rare earth element (REE) diagram for the samples from each magmatic suite.



Fig. 12. Sr/Y vs. Y discrimination diagram between adakites and "normal" calc-alkaline rocks (fields after Drummond and Defant, 1990).

Lack of a complete set of geochemical data from other volcanoes and of their different stages of constructiondestruction in Colombia inhibits a more ample discussion on the crustal interaction with the magmas in the northernmost volcanoes of the Northern Volcanic Zone (NVZ). On the contrary, in Ecuador, the complete data of some volcanoes have been published elsewhere (Bryant et al., 2006). Nevertheless, lavas from the NVZ have uniform ⁸⁷Sr/⁸⁶Sr ratios (~0,704) that are consistent with derivation by fractional crystallization of basaltic parent magmas formed by partial melting of the asthenospheric mantle wedge containing components from subducted oceanic lithosphere (Thorpe et al., 1984). The results of James and Murcia (1984) based on isotopes of oxygen and strontium indicates that the andesitic magmas of Ruiz Volcano may have assimilated up to 10-20% of crustal material. However, the model does not constrain the source of the crustal components incorporated. They could be added during the melt generation process in the mantle by fluid or melts from the subducted continental sedimentary material. Also, these crustal components could be aggregated by oceanic crust, which is indicated by the adakitic signature of our data (Fig. 12). Furthermore, addition of crustal components were probably result or by crustal anatexis when the transport system connects the storage system with the eruptive system. Vatin-Perignon et al. (1990) used Ce/Yb ratios of ~6 as indicators of little or no crustal assimilation, but the samples are only related to the Paleozoic metamorphic basement.

Conclusions

Recent studies have emphasized the control of strikeslip structures in the rise of magmas in the extensional regimes in modern volcanic arcs: Andes, NE Japan, and Mexico (Murphy, 2006). However this research shows how normal faulting also controls magma displacement aside of a volcanic axis, in this case, the Villa Maria –Termales fault during the Ancestral Ruiz stage of the Nevado del Ruiz Volcano (Colombia).

Monogenetic effusive eruptions correlated by their geochemical signatures and distinguished by morphological characteristics and their emplacement aligned with the Villa María-Termales fault, indicate that they were fed by lateral magma flow from the larger reservoir located at 5-10 km depth below the position of the present NRV (Fig. 13). The ascent of isolated magma batches that escaped from the main magma chamber into the fracture network associated to the Villa María-Termales fault enlarged the transport system in the Ancestral Ruiz stage. This phenomenon allowed the ascent of individual magma batches by opening part of this transport system associated with the fault. But, at the end of the Ancestral Ruiz stage (Early Pleistocene), this transport system was disconnected from its intermediate storage system. Finally, the post-Ancestral Ruiz stage magmatic activity only occurred in the present NRV and surroundings.



Fig. 13. Cartoon showing the magma ascent pathways from the intermediate storage system (magma chamber) to the transport system enlarged by the fracture network associated to the Villa María -Termales Fault during the Late Pliocene – Early Pleistocene Ancestral Ruiz stage.

The presence of equilibrium phenocryst assemblages, plagioclase + orthopyroxene + clinopyroxene + magnetite + hornblende \pm biotite in the Late Pliocene – Early Pleistocene Ancestral Ruiz lavas suggests that magma rose slowly from depth, with long-time ponding in a shallow-seated crustal magma chamber.

The geochemistry of major, trace and REE elements presented in this paper is typical of calc-alkaline magmatism within an active subduction zone, and for the Ancestral Ruiz Stage demonstrates that the main factor controlling the evolution of the magma was a simple fractional crystallization with little or null crustal assimilation (Thorpe *et al.*, 1984). Some of the samples have adakite-like signature, believed to be the result of partial melting of subducting oceanic crust.

Acknowledgements

The authors would like to thank Marcelo Jaramillo for allowing access to his geophysical data and preliminary maps. We gratefully acknowledge Juan Manuel Espindola and José Luis Macías (UNAM, Mexico City) for their editorial support. Careful review by Richard and Sandra Hanner and by our colleagues: Vicky Mejía, Miriam Ríos and Juan Sebastián Herrera improved the English style of the final manuscript. Two official reviewers, Dr. José Luis Arce (UNAM, Mexico City) and an anonymous reviewer made important suggestions that improved considerably the final manuscript. Financial support was provided by the Vicerrectoría de Investigaciones de la Universidad de Caldas (Manizales, Colombia) to Luz Mary Toro and Mauricio Alvarán.

Bibliography

- Alaniz-Álvarez, S., A. Nieto-Samaniego and L. Ferrari, 1998. Effect of strain rate in the distribution of monogenetic and poly-genetic volcanism in the Transmexican volcanic belt. *Geology* 26, 591-594.
- Ancochea, E., J. L. Naranjo, J. M. Fuster, C. and Borrero, 1991. Geoquímica de las lavas antiguas del Volcán del Ruiz (Colombia), Sector Noroccidental. Simposio sobre Magmatismo Andino y su Marco Tectónico, Manizales, Colombia. Memorias Tomo I: 65-79.
- Borrero, C. A. and J. L. Naranjo, 1990. Casabianca Formation: a Colombian example of volcanisminduced aggradation in a fluvial basin. J. Volcanol. Geotherm. Res. 41, 253-267.
- Bourdon, E., J. P. Eissen, M. Monzier, C. Robin, H. Martin, J. Cotton and M. Hall, 2002. Adakite-like Lavas from Antisana Volcano (Ecuador): Evidence for Slab Melt

Metasomatism beneath the Andean Northern Volcanic Zone. J. of Petrol. 43, 2, 199-217.

- Bourdon, E.,J. P. Eissen, M. A. Gutscher, M. Monzier, M. Hall and J. Cotton, 2003. Magmatic response to early aseismic ridge subduction: the Ecuadorian margin case (South America), Earth and Plan. *Sci. Lett.* 205, 123-138.
- Bryant, J. A., G. M. Yogodzinsky, M. L. Hall, J. L. Lewicki and D. G. Bailey, 2006. Geochemical Constraints on the Origin of Volcanic Rocks from the Andean Northern Volcanic Zone, Ecuador. J. of Petrol. 47, 1147-1175; doi: 10.1093/petrology/egl006
- Costa, A., O. Melnik and R. S. J. Sparks, 2007. Controls of conduit geometry and wallrock elasticity on lava dome eruptions. *Earth and Plan. Sci Lett.* 260, 137-151.
- Davidson, J. P., K. M. Fergurson, T. Colucci and M. A. Dungan, 1988. The Origin and evolution of magmas from San Pedro-Pellado Volcanic Complex, S. Chile, multicomponent sources and open system evolution. *Contrib. Mineral. Petrol.* 100, 429-445.
- De Natale, G., C. Troise, F. Pingue, G. Mastrolorenzo and L. Pappalardo, 2006. The Somma-Vesuvius volcano (Southern Italy): Structure, dynamics and hazard evaluation. *Earth Sci. Rev.* 74, 73-111.
- Droux, A. and M. Delaloye, 1996. Petrography and Geochemistry of Plio-Quaternary Calc-Alkaline volcanoes of Southwestern Colombia, *J. of South Am. Earth Sci. 1-2*, 27-41
- Drummond, M. S. and M. J. Defant, 1990. A model fpr trondhjemite-tonalite-dacite genesis and crustal growth via slab melting: Archean to modern comparisons. J. Geophys. Res. 95, 21503-21521
- Gallego, C. A., A. Tabares and L. J. Valencia, 2006. Cartografía Geológica 1:25.000 de los Depósitos Volcánicos ubicados en el Sector de Hoyo Frio al NE de la ciudad de Manizales. Bachelor Thesis. Universidad de Caldas, Manizales, Caldas, Colombia. 109 pp.
- García–Aristizabal, A., H. Kumagai, P. Samaniego, P. Mothes, H. Yepes and M. Monzier, 2007. Seismic, petrologic, and geodetic analyses of the 1999 domeforming eruption of Guagua Pichincha volcano, Ecuador. J. Volcanol. Geotherm. Res. 161, 333-351.
- Giggembach, W. F., P. N. García, C. A. Londoño, V. L. Rodríguez, G. N. Rojas and M. L. Calvache, 1990.

The chemistry of fumarolic vapor and thermal spring discharges from the Nevado del Ruiz volcanic magmatic hydrothermal system, Colombia. *J. Volcanol. Geotherm. Res.* 42, 13-39.

- Gill, J., 1981. Orogenic andesites and plate tectonics: Springer-Verlag, Berlin, 390 pp.
- González, L. and C. M. Jaramillo, 2002. Estudio Neotectónico multi-disciplinario aplicado a la Falla Villa María- Termales. Bachelor Thesis. Universidad de Caldas, Manizales, Caldas, Colombia. 298 pp.
- Hall, M. L. and C. A. Wood, 1985. Volcano-tectonic segmentation of the northern Andes. *Geology* 13, 3, 203-207.
- Herd, D. G., 1982. Glacial and volcanic Geology of the Ruiz-Tolima complex, Cordillera Central, Colombia. Publicaciones Especiales 8, INGEOMINAS, Bogotá, 48 pp.
- Hidalgo, S., M. Monzier, H. Martin, G. Chazot, J. P. Eissen and J. Cotton, 2007. Adakitic magmas in the Ecuadorian Volcanic Front: Petrogenesis of the Illiniza Volcanic Complex (Ecuador). J. Volcanol. Geotherm. Res. 159, 366-392.
- Hildreth, W. and S. Moorbath, 1988. Crustal contributions to arc magmatism in the Andes of Central Chile. Contrib. *Mineral. Petrol.* 98, 455-489.
- Hofmann, A. W., 1988. Chemical differentiation of the earth. The relationship between mantle, continental crust and oceanic crust. *Earth and Plan. Sci. Lett.* 90, 297-314.
- INGEOMINAS, 1998a. Geología de la Plancha 206 Manizales, escala 1:100,000.
- INGEOMINAS, 1998b. Geología de la Plancha 225 Nevado del Ruiz, escala 1:100,000.
- Irvine, T. N. and W. R. A. Baragar, 1971. A guide to the chemical classification of the common volcanic rocks. Canad. *J. of Earth Sci.* 8, 523-548.
- James, D. E. and L. A. Murcia, 1984. Crustal contamination in northern Andean volcanics. J. of the Geolol. Soc. of London 141, 823-830.
- Lara, L. E., J. A. Naranjo and H. Moreno, 2004. Rhyodacitic fissure eruption in Southern Andes (Cordón Caulle; 40.5°S) after the 1960 (Mw: 9.5) Chilean earthquake: a structural interpretation. J. Volcanol. Geotherm. Res. 138, 127-138.

- Le Bas, M., R. Le Maitre, A. Streckeisen and B. Zanettin, 1986. A chemical classification of volcanic rock son the total alkali-silica diagram: *J. of Petrol.* 27, 3, 745-750
- Lescinsky, D. T., 1990. Geology, volcanology and petrology of Cerro Bravo, a young dacitic stratovolcano in west-central Colombia. MSc Thesis. Lousiana State University, 244 pp.
- Londoño, J. M. Y. and Sudo, 2002. Velocity structure and a seismic model for Nevado del Ruiz Volcano (Colombia). J. Volcanol. Geotherm. Res. 119, 61-87.
- Muñoz, F., A. Nieto and H. Meyer, 1990. Analysis of swarms of high-frecuency seismic events at Nevado del Ruiz Volcano, Colombia January 1986-August 1987: Development of a procedure. J. Volcanol. Geotherm. Res. 41, 327-354.
- Murphy, J. B., 2006. Fault-controlled emplacement of arcrelated magmas along the Neoproterozoic northern Gondwanan margin: An example from the Antigosnish Highlands, Nova Scotia. *Precambrian Research 147*, 305-319.
- Nakamura, K., 1977. Volcanoes as possible indicators of tectonic stress orientation: principle and proposal. J. Volcanol. Geotherm. Res. 2, 1-16
- Ojeda, A. and J. Havskov, 2001. Crustal structure and local seismicity in Colombia. *J. of Seismology* 5, 575-593.
- Peccerillo, A. and S. R. Taylor, 1976. Geochemistry of Eocene calc-alkaline volcanic rocks from the Kastamony area, northern Turkey. *Contrib. Mineral. Petrol.* 58, 63-81.
- Scandone, R., K. V. Cashman and S. Malone, S. (2007). Magma supply, magma ascent and style of volcanic eruptions. *Earth and Plan. Sci. Lett.* 253, 513-529
- Schaefer, S. J., 1995. Nevado del Ruiz Volcano, Colombia: Magmatic System and Evolution, PhD. Thesis, Arizona State University. 147 pp.
- Thorpe, R. S., P. W. Francis and L. O'Callaghan, 1984. Relative roles of source composition, fractional crystallization and crustal contamination in the petrogenesis of Andean volcanic rocks. *Philos. Trans. R. Soc. London Ser. A*, 310, 675-692.
- Thouret, J. C., J. M. Cantagrel, R. Salinas and A. Murcia, 1990. Quaternary eruptive history of Nevado del Ruiz (Colombia). J. Volcanol. Geotherm. Res. 41, 225-251.

- Tibaldi, A., 1995. Morphology of pyroclastic cones and tectonics. J. Geophys. Res. 100, 24521-24535.
- Trenkamp, R., J. N. Kellog, J. T. Freymueller and H. Mora, 2002. Wide plate margin deformation, southern Central America and northwestern South America, CASA GPS observations, J. of South Am. Earth Sci. 15, 157-171.
- Vatin-Perignon, N., P. Goemans, R. Oliver and E. Parra-Palacio, 1990. Evaluation of magmatic processes for the products of the Nevado del Ruiz Volcano, Colombia from geochemical and petrological data. *J. Volcanol. Geotherm. Res.* 41, 153-176.
- Wallace, P. J., 2001. Volcanic SO₂ emissions and the abundance and distribution of exsolved gas in magma bodies. *J. Volcanol. Geotherm. Res. 108*, 85-106.
- Young, R. H., 1991. Eruption dynamics and petrology of the most recent eruptions of Nevado del Ruiz Colombia, South America, MSc. Thesis, Louisiana State University, 121 pp.
- Zollweg, J. E., 1990. Seismicity following the 1985 eruption of Nevado del Ruiz, Colombia. *J. Volcanol. Geotherm. Res.* 41, 355-367.

C. Borrero^{*}, L. M. Toro, M. Alvarán and H. Castillo Depto. Ciencias Geológicas Universidad de Caldas, Manizales, Colombia E-mail: mtoro21@yahoo.com mauricio_alvaran@ucaldas.edu.co hcastillo@hotmail.com *Corresponding author: borrero_c@yahoo.com