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Paleogene and Neogene magmatism in the Valle del Cura region: New perspective on the evolution of the Pampean flat slab, San Juan province, Argentina

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Abstract

The Valle del Cura region is characterized by a thick volcanic and volcaniclastic sequence that records the Tertiary arc and backarc magmatic evolution of the Argentine Main Cordillera over the modern Pampean flatslab at 29.5–30°S. During the Eocene, a retroarc basin developed, represented by the Valle del Cura Formation synorogenic volcanosedimentary sequence, which includes rhyolites and dacitic tuffs. These silicic volcanic rocks have weak arc chemical signatures and high lithophile element concentrations and are isotopically enriched relative to the late Oligocene–early Miocene volcanic rocks that followed them. Their chemical characteristics fit with eruption through a thin crust. The Valle de Cura Formation was followed by the Oligocene–early Miocene Doña Ana Group volcanic sequence, which erupted at and near the arc front west of the border with Chile. The Doña Ana Group volcanic rocks have calc-alkaline chemical characteristics consistent with parental magmas forming in a mantle wedge and erupting through a normal thickness crust (35 km). Subsequent shallowing of the downgoing Nazca plate caused the volcanic front to migrate eastward. The volcanic sequences of the middle Miocene Cerro de las Tórtolas Formation erupted at this new arc front, essentially at the Argentine border. Two stages are recognized: an older one (16–14 Ma) in which magmas appear to have erupted through a normal thickness crust (30–35 km) and a younger one (13–10 Ma) in which the steeper REE pattern suggests the magmas last equilibrated with higher pressure residual mineral assemblages in a thicker crust. Isotopic ratios in the younger group are consistent with an increase in original crustal components and crust introduced into the mantle source by forearc subduction erosion. A peak in forearc subduction erosion near 12–10 Ma is consistent with when the main part of the Juan Fernandez Ridge began to subduct beneath the region. In addition to late Miocene Tambo Formation dacitic ignimbrites, the younger Cerro de las Tórtolas Formation volcanic rocks erupted at the height of contractional deformation in the Valle del Cura and to the east. The last important volcanic sequence to erupt in the Valle del Cura is the late Miocene Vacas Heladas Ignimbrite, the most isotopically enriched Tertiary magmas in the Valle del Cura that contain the highest proportion of crustal components. Subsequently volcanism ceased in the region in response to shallowing of the subduction zone.

Keywords: Valle del Cura; Volcanism; Paleogene; Neogene; Geochemistry

Resumen

El Valle del Cura está geológicamente caracterizado por una espesa secuencia volcánica y volcániclástica que registra la evolución del magmatismo terciario de arco y retroarco de la Cordillera Frontal de Argentina sobre la actual zona de subducción horizontal Pampeana entre los 29,5° a 30°S. Durante el Eoceno, se desarrollo una cuenca de retroarco donde se depositó una secuencia volcano-sedimentaria sinorogénica, la Formación Valle del Cura, la que incluye riolitas y tobas dacíticas. Estas rocas silíceas poseen débiles signaturas quím-

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icas de retroarco, alto contenido de elementos litófilos y un enriquecimiento isotópico en relación con el resto de la secuencia terciaria más joven; la signatura química es consistente con magmas desarrollados en condiciones de una corteza delgada. Le sucede el magmatismo de arco oligoceno-mioceno temprano del Grupo Doña Ana; arco localizado al oeste del límite con Chile. Las volcanitas de Doña Ana corresponden a una suite calcoalcalina producto de fusión en la cuña astenosférica bajo una corteza de espesor normal (30–35 km). Debido a la subhorizontalización de la placa de Nazca, se produce la migración del arco: la Formación Cerro de las Tórtolas, de edad miocena inferior a superior, representa este frente volcánico ubicado en el límite chileno-argentino. Dos etapas se reconocen: la más antigua (16–14 Ma) representa fundidos equilibrados en una corteza de espesor normal (30–35 km), mientras que la más joven (13-10 Ma) posee relaciones de tierras raras indicativas de magmas equilibrados con fases residuales de mayor presión, reflejo de una corteza engrosada (50 km). Las relaciones isotópicas de las lavas más jóvenes son consistentes con un incremento de los componentes corticales, incorporados durante su evolución ya sea en la corteza o introducidos al manto por subducción y erosión de sedimentos en el antearco. El comienzo de la subducción de la dorsal de Juan Fernández en la región, entre los 10 y 12 Ma, es consistente con un pico en los procesos de erosión y subducción en el antearco. Las lavas jóvenes de la Formación Cerro de las Tórtolas y las ignimbritas dacíticas del Mioceno Medio de la Formación Tambo se desarrollaron bajo las condiciones de máxima compresión. El último episodio volcánico significativo en la región corresponde a la Ignimbrita Vacas Heladas, del Mioceno Superior. Son las volcanitas isotópicamente mas enriquecidas, resultado de las altas proporciones de componentes corticales involucrados en su génesis. Luego de este volcanismo y como respuesta a la subhorizontalización de la placa subducida, cesó la actividad volcánica en el Valle del Cura.

Palabras clave: Valle del Cura; Volcanismo; Paleogeno; Neogeno; Geoquímica

1. Introduction

The Valle del Cura region, over the Pampean (Chilean) flatslab, represents the Argentinean continuity of the El Indio metallogenetic belt in Chile. The presence of world-class Au–Ag deposits has made the El Indio belt one of the best studied regions in the Andean Main Cordillera in recent years. The El Indio–Valle del Cura region, which runs along the Argentine–Chilean border in the Andean Main Cordillera, is characterized by a thick sequence of Tertiary volcanic and volcaniclastic arc sequences associated with both epithermal and porphyry Au–Ag–Cu-type mineral deposits (Maksaev et al., 1984; Nasi et al., 1990; Kay et al., 1987, 1988, 1991; Ramos et al., 1989). The origin of these ore deposits is linked to the evolution of the magmatic rocks, hydrothermal activity, host rock composition, and the tectonic regime in the region.

This article presents new mapping and major, trace element, and isotope data for Tertiary magmatic rocks in the Valle del Cura region in Argentina and uses these data to constrain the magmatic and tectonic evolution of the Andean Main Cordillera over the Pampean (Chilean) flatslab segment. Previous studies have emphasized the geochemical and tectonic evolution of the late Oligocene–latest Miocene magmatic rocks of the El Indio belt in the Main Cordillera on the Chilean side (e.g., Maksaev et al., 1984; Nasi et al., 1990; Kay et al., 1987, 1988, 1991, 1999; Kay and Abruzzi, 1996). Only reconnaissance studies have been presented on similarly aged rocks on the Argentine side (Ramos et al., 1989; Kay et al., 1991; Bissig et al., 2003). Essentially unstudied from a chemical point of view have been the Tertiary Valle del Cura magmatic rocks mapped in the Paleocene Río Frío Basalt and Eocene Valle del Cura Formation (Limarino et al., 1999; Bissig et al., 2001; Litvak and Page, 2002; Mpodozis and Kay, 2003). A principal focus therefore is to compare Eocene Valle de Cura Formation silicic rocks with the late Oligocene–Miocene units in deciphering the Tertiary crustal evolution of the Main Cordillera.

2. Geological setting

The Valle del Cura is located in the Andean Main Cordillera over the volcanically inactive Chilean (Pampean) flatslab segment of the southern central Andes (Fig. 1). Modern volcanic activity occurs to the north in the Central Volcanic Zone and to the south in the Southern Volcanic Zone. Miocene shallowing of the Nazca plate has been attributed to the collision of the Juan Fernández Ridge with the Nazca plate (Pilger, 1981, 1984; Yañez et al., 2001). As pointed out by Kay and Mpodozis (2002), the arrival of the East–West-trending segment of the ridge under the El Indio–Valle del Cura belt corresponds with the eruption of the middle Miocene (12–10 Ma) volcanic rocks. This perturbation resulted in pronounced shallowing of the subduction zone over the Pampean flatslab, resulting in changes in the magmatic and tectonic style of the region.

The Valle del Cura constitutes a mineralized hydrothermal system that, together with the El Indio belt in Chile, forms a North-trending block limited by high-angle reverse faults (Litvak et al., 2005a; Jones et al., 1996; Martin et al., 1997b). Geological column in the Valle del Cura includes a Permo-Triassic sedimentary, plutonic, and volcanic basement unconformably overlain by Tertiary sedimentary and volcanic rocks.

The studied area corresponds with the Argentine slope of the El Indio–Valle del Cura belt, shown in Fig. 2. Regionally, the Cenozoic magmatic and sedimentary history was first established (Maksaev et al., 1984; Nasi et al., 1990; Kay et al., 1987) and then refined (Martin et al., 1997a,b, 1999; Bissig et al., 2001) on the Chilean side. On the Argentine side, studies are more reconnaissance in nature (Groeber, 1951; Ramos et al., 1987, 1989; Nullo, 1988; Kay et al., 1991; Otamendi et al., 1994). A more pre-

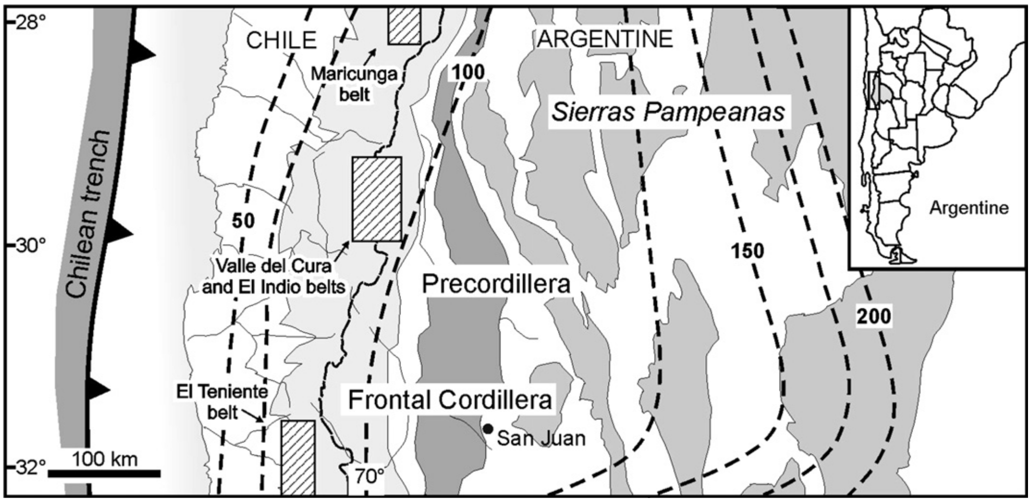

Fig. 1. Valle del Cura and the El Indio belt locations over the Chilean (Pampean) flatslab segment, southern central Andes. Dashed lines show subducted slab depth.

cise stratigraphy, along with new isotopic ages, recently was presented (Limarino et al., 1999; Litvak and Page, 2002; Litvak et al., 2004; Litvak and Poma, 2005). These studies show strong correlations in the units of the Valle del Cura and El Indio regions.

The Cenozoic stratigraphy of the Valle del Cura is characterized by a series of Paleocene–late Miocene magmatic and sedimentary sequences, as shown in Fig. 2. The oldest Tertiary magmatic rocks are thin lava flows of aphyric basalts that outcrop in the Río Frío Creek, where they are interbedded with red conglomerates. Litvak and Page (2002) report a K/Ar age of 55.9 ± 1.9 Ma for these flows and name them the Río Frío Basalt.

The Valle del Cura Formation records the main volcanic and sedimentary activity in the Eocene (Limarino et al., 1999; Litvak and Poma, 2005). This unit outcrops along the central part of the Valle del Cura, where it consists of more than 700 m of tuffs, conglomerates, volcanic arenites, and volcanic and volcaniclastic facies that include dacitic ignimbrites and rhyolite lava flows. Stratigraphic relationships and K/Ar ages (44 ± 2, 45 ± 2, 36 ± 1, 34 ± 1 Ma) reported by Limarino et al. (1999) show that these sequences range from middle Eocene to early Oligocene in age. Similar sequences occur in the Macho Muerto region to the north (Ploszkiewicz, 1997; Panteleyev and Cravero, 2000; Mpodozis and Kay, 2003). The Bocatoma Intrusive Unit, which outcrops at the northern latitude of Valle del Cura on the Chilean side, is also Eocene in age (Nasi et al., 1990; Martin et al., 1997a; Bissig et al., 2001). Martin et al. (1995) report K–Ar biotite and whole-rock dates ranging from 31 to 39.5 Ma for Bocatoma stocks, and Bissig et al. (2001) report three $^{40}Ar/^{39}Ar$ plateau ages of 35.9 ± 1.2, 35.5 ± 1.2, and 30.0 ± 1.9 Ma. The last indicate some Ar loss.

Overlying the Valle del Cura Formation is the Doña Ana Group of late Oligocene–early Miocene age (Maksaev et al., 1984; Nasi et al., 1990; Martin et al., 1997a). The Doña Ana Group is divided into two formations: the Tilito, which is mainly composed of rhyolitic and dacitic lavas and ignimbrites, and the Escabroso, which is characterized by andesitic and basaltic lava flows. The Doña Ana Group is well exposed in Chile, where ages for the Tilito Formation range from 25.1 to 23.1 Ma and for the Escabroso from 21.9 to 17.6 Ma (Bissig et al., 2001). In exposures in Argentina, along the Chilean–Argentine border, some Tilito Formation outcrops are hydrothermally altered (Fig. 2). A biotite from a silicic breccia clast in the Valle del Cura yields an age of 25.8 ± 0.8 Ma (Litvak et al., 2005b), whereas one from a dacitic ignimbrite that crops out near the Zancarrón mining prospect yields a K/Ar age of 25.0 ± 0.7 Ma (Litvak, 2004). The Las Máquinas Basalt, dated by whole-rock K/Ar at 22.8 ± 1.1 Ma (Kay et al., 1991) and 22.0 ± 0.8 Ma (Litvak et al., 2005b), crops out at the southern extreme of the Valle del Cura near Máquinas Creek.

The middle–late Miocene Cerro de las Tórtolas Formation marks the peak of volcanic arc activity along the border and in the Valle del Cura (Maksaev et al., 1984; Kay et al., 1987, 1991). In Argentina, this unit was divided by Ramos et al. (1989) into an andesitic to basaltic andesitic lower section and a dacitic upper section. A compilation of K/Ar and $^{40}Ar/^{39}Ar$ ages indicates the lower section has an age of 16–14 Ma and the upper section and age of 13–10 Ma (Maksaev et al., 1984; Ramos et al., 1989; Kay et al., 1991; Bissig et al., 2001; Litvak, 2004). The Cerro de las Tórtolas Formation is broadly distributed in the Valle del Cura, but the upper section is restricted to the highest levels of the Vacas Heladas and Cerro de las Tórtolas volcanoes (Fig. 2). Two hornblende-bearing andesites from the Valle del Cura just north of Despoblados (Fig. 2) yield whole-rock K/Ar ages of 12.0 ± 0.4 and 8.1 ± 0.5 Ma (Litvak et al., 2005b).

Two levels of the Cerro de las Tórtolas Formation are recognized on the Chilean side by Martin et al. (1995),

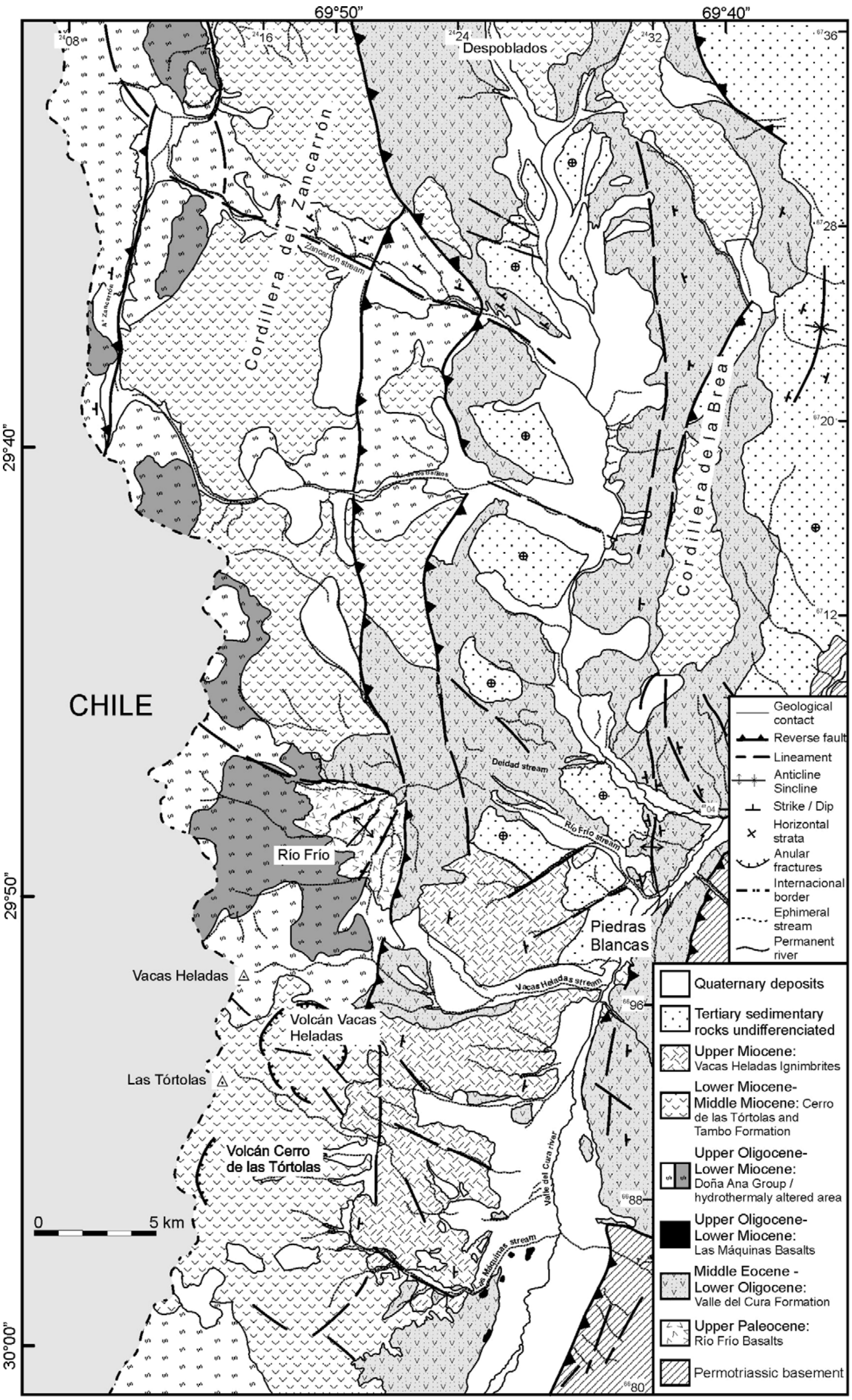

Fig. 2. Geological map of the central and southern area of the Valle del Cura region in the Frontal Cordillera, San Juan province, Argentina (Litvak, 2004).

who retains the name Cerro de las Tórtolas for the lower unit and calls the upper unit the Vacas Heladas Formation. Later, Martin et al. (1997a) renamed this unit the Tambo Formation to avoid confusion with the late Miocene Vacas Heladas Ignimbrites described on the Argentine side by Ramos et al. (1989). Kay et al. (1999) and Kay and Mpodozis (2002) refer to the two levels as Cerro de las Tórtolas I and Cerro de las Tórtolas II. Bissig et al. (2001) use the name Vacas Heladas Formation for a group of Miocene dacitic tuffs and block and ash deposits locally interbedded with fluvial deposits on the Chilean side. They report an age range of 11.0 ± 0.2 to 12.7 ± 0.9 Ma for these tuffs. On the Argentine side in the Valle del Cura, Litvak et al. (2004) report a K/Ar age of 12.0 ± 0.8 Ma for a dacitic tuff with amphibole and titanite phenocrysts. These tuffs occur along the Río Frío, Deidad Creek, and the Piedras Blancas area on the eastern margin of the Valle del Cura River. They appear in Fig. 2 as the Tambo Formation.

The late Miocene Vacas Heladas Ignimbrites, the youngest volcanic rocks in the region, are homogenous crystalline dacitic tuffs found in the region of the Vacas Heladas volcano, where they unconformably overlie Eocene–Miocene sequences. These tuffs yield ages that correlate with the Vallecito Formation on the Chilean side (Maksaev et al., 1984; Nasi et al., 1990; Ramos et al., 1989; Kay et al., 1987, 1991; Martin et al., 1997a; Bissig et al., 2001). Finally, Bissig et al. (2002) describe a small rhyolite dome dated at 2.0 ± 0.2 Ma as the Cerro de Vidrio Formation in the northern part of Valle del Cura.

3. Geochemistry of Paleogene and Neogene volcanic rocks

New major and trace elements plus isotope data are presented in Tables 1–3 for the Tertiary volcanic sequence of the Valle del Cura. Analyses are from fresh samples selected for their well-defined stratigraphic relationships and/or documented age. Sample locations and descriptions are in the tables. Details on the used methodology are described in Appendix A. Most samples are from the region in Fig. 2; a few come from the northern area of Valle del Cura in the Ortiga Cordillera and Despoblados area. Published data (Kay et al., 1991, 1999) complete the database.

The chemical data presented here are the first for the Eocene volcanic units of the Valle del Cura Formation (Tables 1, 2). Bissig et al. (2003) present data for the Eocene Bocatoma Intrusive Unit in Chile, which is considered to be the subvolcanic age equivalent of the Valle del Cura Formation further to the west. Together, their geochemical signatures reflect the Eocene tectonic and magmatic processes that influenced the evolution of the arc in this part of the central Andes. Other studies have presented and used geochemical data, from the younger magmatic suites of the Valle del Cura and El Indio belt, to explain the evolution and investigate the mineralized events of the region (Kay et al., 1991, 1999; Otamendi et al., 1994; Kay and Mpodozis, 2001, 2002; Bissig et al., 2003).

3.1. Major elements

Valle del Cura Eocene–Miocene mesosilicic to acid volcanic rocks have middle- to high-K calc-alkaline compositions that contrast with the alkaline compositions in the Paleocene Río Frío and early Miocene Maquinas basalts, erupted in the Valle de Cura (Fig. 3a). Harker diagrams in Fig. 3 show that the Valle del Cura Formation and early Miocene Tilito Formation volcanic rocks fall in the rhyolitic and dacitic field on the $Na_2O + K_2O$ vs. SiO_2 diagram (Fig. 3b) and that younger Miocene Escabroso Formation volcanic rocks are andesites and basaltic andesites. The younger Miocene Cerro de las Tórtolas Formation samples are andesites to dacites with 55–62% SiO_2. The Miocene Tambo Formation ignimbrites are dacites with higher silica content than those in the late Miocene Vacas Heladas Ignimbrites. Trends of major elements show that P_2O_5, TiO_2, CaO, FeO, MgO, and Al_2O_3 correlate negatively with SiO_2, whereas K_2O correlates positively in the entire suite (Fig. 3b). Overall, the chemical features of the Valle del Cura mesosilicic to silicic volcanic rocks overlap those of Neogene–Recent CVZ and northern SVZ volcanic rocks (e.g., Hildreth and Moorbath, 1988; Kay et al., 1999).

3.2. Trace element signatures: Arc signature

Trace element signatures indicate the sources, evolution, and geological setting of arc magmas. Generally, arc magmas are enriched in large ion lithophile elements (LILE) and rare earth elements (REE) are derived from fluids associated with the subducted slab and crustal sources. Ba/La ratios >20 are typical of frontal arc magmas (Kay, 1977; Gill, 1981). Arc magmas characteristically show depletion in high field strength elements (HFSE) relative to REE, which leads to the negative anomalies in Ta relative to La and Ba seen in extended trace element plots. Andean arc volcanic rocks characteristically have La/Ta ratios greater than 25 and Ba/Ta ratios greater than 450 (e.g., Hickey et al., 1986).

Neogene volcanic rocks in the Valle del Cura show typical arc-type trace element patterns on chondrite or mantle normalized trace element plots, as noted by previous authors (Kay et al., 1987, 1991, 1999; Ramos et al., 1989; Otamendi et al., 1994; Bissig et al., 2003). Middle Eocene–early Oligocene Valle del Cura Formation samples reveal the same type of pattern as shown on the plots in Fig. 4. All samples show enrichment of the LILE relative to HFSE and REE, moderate negative Eu anomalies, and light and middle REE enrichment relative to heavy REE. Negative anomalies of Ta and Hf with respect to La, Th, and Ce indicate their arc affinities.

Comparisons of the Ba/Ta, Ba/La, and La/Ta ratios of the Eocene Valle del Cura Formation samples with those from the younger Valle del Cura volcanic sequences and the SVZ are useful. As shown in Fig. 5, the Ba/Ta and La/Ta ratios for Valle del Cura Eocene to Miocene mesosilicic volcanic sequence are mostly arc like in that their Ba/Ta

Table 1
Major element data for the Tertiary volcanic rocks of the Valle del Cura

Unit	Valle del Cura Formation					Doña Ana Group									
						Tilito Formation					Escabroso Formation				
Sample	Z27	RF168	MQ143	DI044	RF130	I62*	I63*	HC101*	ZN137	I131*	NBT10*	I100*	I64*	I61*	ZN159
SiO_2	67.03	67.85	72.63	72.26	78.46	73.63	73.99	74.78	71.53	77.31	53.34	54.25	57.87	58.15	59.14
TiO_2	0.78	0.56	0.42	0.40	0.19	0.29	0.33	0.31	0.45	0.17	1.06	1.47	1.07	0.91	0.77
Al_2O_3	16.17	15.96	13.11	13.88	10.20	14.51	14.11	13.65	12.85	12.44	19.47	18.35	18.60	18.87	16.79
FeO	4.66	2.58	2.63	2.06	1.58	1.42	1.78	1.21	2.52	1.11	7.86	9.03	5.96	6.03	5.36
MnO	0.05	0.06	0.06	0.03	0.01	0.03	0.03	0.02	0.04	0.02	0.12	0.13	0.10	0.1	0.09
MgO	0.46	0.63	0.41	0.44	0.38	0.34	0.37	0.29	0.29	0.14	4.80	3.80	3.07	2.67	4.17
CaO	3.19	1.85	1.29	0.69	1.51	1.64	1.57	1.41	0.92	0.59	9.80	8.08	6.34	6.4	6.04
Na_2O	3.26	5.64	4.21	4.16	5.02	4.12	3.9	3.48	3.56	3.21	3.19	3.98	5.04	4.72	4.54
K_2O	3.95	4.85	5.16	6.00	2.63	3.91	3.79	4.81	6.03	5.00	0.59	0.67	1.65	1.8	2.81
P_2O_5	0.43	0.02	0.09	0.09	0.03	0.10	0.11	0.04	1.81	0.11	0.17	0.23	0.29	0.33	0.30
Total	99.99	100.00	100.00	100.00	100.00	99.99	99.98	100	100	100.1	100.40	99.99	99.99	99.98	100.00
Location	29°36′50″ 69°46′34″	29°49′27″ 69°50′09″	29°58′57″ 69°46′51″	29°59′13″ 69°49′01	29°47′40″ 69°46′52″	29°47′ 70°08′	29°47′ 70°08′	30°10′ 69°51′	29°36′33″ 69°46′36″	29°49′ 69°55′	29°36′ 70°08′	29°38′ 70°02′	29°48′ 70°08′	29°48′ 70°07′	29°33′57″ 69°51′23″
Type	Dacitic ignimbrite	Dacitic ignimbrite	Rhyolite	Rhyolite	Dacitic ignimbrite	Dacitic tuff	Dacitic tuff	Dacitic tuff	Vitric tuff	Rhyolite	Basaltic andesites	Basaltic andesites	Andesites	Andesites	Amph-, biotite bearing Andesite

Unit	Cerro de las Tórtolas Formation								Tambo Fm.	Vacas Heladas Ignimbrites	
Sample	DI039	DI040	MQ28	ZN162	DI082	SP29C	DI073	SP79C	RF125	DI093	DI095
SiO_2	60.19	61.12	62.04	55.77	56.79	55.81	58.60	62.77	65.58	70.74	70.84
TiO_2	0.76	0.75	0.75	1.04	0.96	0.99	1.05	0.77	0.72	0.23	0.17
Al_2O_3	17.63	17.41	17.56	16.91	17.57	17.56	17.21	16.73	15.60	15.73	15.67
FeO	5.51	5.69	4.59	7.30	6.59	6.80	6.12	5.54	4.35	1.64	1.46
MnO	0.15	0.14	0.10	0.22	0.15	0.15	0.12	0.13	0.09	0.04	0.00
MgO	2.24	2.27	2.33	4.10	3.63	3.06	3.23	2.60	1.73	0.47	0.46
CaO	5.65	5.75	5.12	8.14	7.75	8.58	6.96	5.35	4.78	2.50	2.48
Na_2O	3.54	3.62	4.63	3.69	3.52	4.22	4.10	3.05	3.84	4.79	5.04
K_2O	3.06	3.10	2.46	2.51	2.70	2.37	2.30	3.00	3.07	3.76	3.84
P_2O_5	1.28	0.13	0.42	0.33	0.35	0.46	0.31	0.04	0.23	0.10	0.03
Total	100.1	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Location	29°58′24″ 69°49′42″	29°57′48″ 69°50′05″	29°56′36″ 69°51′22″	29°36′49″ 69°46′60″	29°37′05″ 69°46′01″	29°30′57″ 69°45′57″	29°24′30″ 69°45′35″	29°43′45″ 69°41′53″	29°48′00″ 69°45′16″	29°57′16″ 69°50′04″	29°59′20″ 69°49′05″
Type	Opx-, clpx-bearing andesite	Opx-, clpx-, amph-bearing andesite	Amph-bearing andesite	Opx-, clpx-bearing andesite	Opx-, clpx-bearing andesite	Amph-bearing andesite	Opx-, clpx-, amph-bearing andesite	Opx-, clpx-bearing andesite	Crystalline dacitic tuff	Dacitic ignimbrite	Dacitic ignimbrite

* These samples correspond to Kay et al. (1987).

Table 2
Trace element data for the Tertiary volcanic rocks of the Valle del Cura

Unit	Valle del Cura Formation										Tilito Formation – Doña Ana Group				
Sample	RF130B	LB25	Z27	RF168	MQ143	DI044	MQ37	DI094	XDI094	RF130a	ZN140C	ZN121	ZN133	ZN107	ZN137
La	31.2	21.7	26.8	56.0	42.9	63.5	57.1	57.9	47.1	54.7	27.8	21.4	27.1	64.0	47.3
Ce	60.9	47.9	59.1	116.9	85.9	140.6	121.5	126.4	103.0	108.2	61.7	46.4	57.5	143.8	102.2
Nd	20.4	22.4	29.2	57.1	27.7	50.0	48.9	45.5	46.4	43.5	23.4	17.2	20.9	63.9	38.5
Sm	4.1	5.0	5.8	10.3	5.8	11.6	9.7	10.5	8.6	8.3	23.6	4.0	4.7	11.2	7.7
Eu	0.94	1.12	1.29	2.08	0.87	1.95	1.66	1.85	1.44	1.06	0.66	0.88	0.80	1.62	1.07
Tb	0.38	1.72	0.80	1.51	0.58	1.45	1.09	1.22	0.99	0.87	0.63	0.45	0.37	1.39	0.98
Yb	1.92	2.17	2.83	6.01	2.68	4.92	4.15	4.44	3.85	3.48	2.76	1.50	2.27	6.56	4.28
Lu	0.261	0.273	0.395	0.821	0.347	0.633	0.528	0.575	0.442	0.407	0.366	0.180	0.328	0.955	0.577
Sr	456	413	252	196	103	117	125	89	76.6	190	118	275	90	234	276
Ba	427	376	601	913	659	1651	1201	1557	1500	488	601	581	441	1483	423
Cs	44.1	7.2	7.9	4.2	10.4	14.5	9.6	39.6	27.2	13.0	6.3	3.1	2.1	4.6	12.5
U	2.5	4.0	2.5	4.9	4.7	7.4	6.6	6.8	5.2	9.2	3.1	4.9	3.5	7.3	2.3
Th	6.2	12.9	9.6	16.5	20.0	28.7	24.3	26.6	24.0	15.2	11.8	9.2	13.1	29.4	15.9
Hf	4.6	4.4	6.7	11.3	5.9	9.4	8.1	8.9	8.1	3.6	4.5	4.3	5.3	12.9	7.5
Ta	0.81	0.71	0.91	2.58	1.25	1.83	1.50	1.75	1.36	0.87	1.01	0.67	1.21	2.48	2.36
Sc	10.0	20.5	11.0	9.1	7.9	7.9	6.9	7.4	8.0	5.1	3.7	9.6	4.8	7.5	5.4
Cr	15	33	6				0		140	0		22	0	0	0
Ni	3	11	3	4			0		24	0	1	7	1	2	1
Co	12	20	9	3	0	0	1	0	1	1	1	10	3	6	1
Ba/La	13.7	17.3	22.4	16.3	15.4	26.0	21.0	26.9	31.8	8.9	21.7	27.2	16.3	23.2	9.0
La/Sm	7.6	4.3	4.6	5.4	7.4	5.5	5.9	5.5	5.5	6.6	1.2	5.3	5.8	5.7	6.2
La/Yb	16.3	10.0	9.5	9.3	16.0	12.9	13.8	13.0	12.2	15.7	10.1	14.2	12.0	9.8	11.0
Sm/Yb	2.1	2.3	2.0	1.7	2.2	2.4	2.3	2.4	2.2	2.4	8.5	2.7	2.1	1.7	1.8
Ba/Ta	530	531	663	355	526	900	801	888	1103	558	597	864	364	597	179
La/Ta	38.7	30.6	29.5	21.7	34.2	34.6	38.1	33.1	34.6	62.7	27.6	31.8	22.4	25.8	20.0
Tipo	Vitric tuff	Andesite	Crystalline tuff	Crystalline tuff	Rhyolite	Rhyolite	Rhyolite	Rhyolite	Rhyolite	Crystalline tuff	Vitric tuff	Vitric tuff	Dacitic tuff	Vitric tuff	Dacitic tuff
Creek	Río Frío	Bañitos	Zancarrón	Deidad	Máquinas	Máquinas	Máquinas	Máquinas	Máquinas	Río Frío	Zancarrón	Zancarrón	Zancarrón	Zancarrón	Zancarrón
Coordenates	29°47′40″ 69°46′52″	29°41′15″ 69°46′17″	29°36′50″ 69°46′34″	29°49′27″ 69°50′09″	29°58′58″ 69°46′51″	29°59′13″ 69°49′01″	29°59′13″ 69°49′01″	29°59′20″ 69°49′07″	29°59′20″ 69°49′07″	29°47′40″ 69°46′52″	29°36′43″ 69°46′21″	29°34′24″ 69°55′28″	29°36′33″ 69°46′50″	29°35′37″ 69°53′22″	29°36′33″ 69°46′36″

Unit	Tilito Formation –Doña Ana Gropu (cont.)					Escabroso Formation – Doña Ana Group							
Sample	ZN111	ZN137C	XDI046	DI077b	ZN115	ZN158	ZN154	ZN114	ZN147	MQ153	ZN159	XDI081	ZN157F
La	31.2	47.3	40.8	28.4	25.3	16.5	12.2	35.6	27.6	20.5	26.7	19.3	32.6
Ce	66.1	109.3	82.6	59.5	53.4	36.5	26.1	71.7	56.3	41.8	57.0	42.3	71.3
Nd	30.1	44.0	34.1	23.0	15.0	15.1	14.1	39.4	33.7	18.1	21.6	24.6	28.0
Sm	5.7	8.2	7.9	4.4	3.4	3.8	3.6	6.2	6.5	4.0	4.7	5.0	6.0
Eu	0.86	1.21	1.69	0.61	0.65	1.16	1.11	1.56	1.84	0.97	0.96	1.62	0.85
Tb	0.59	2.61	1.02	0.26	0.42	0.82	0.55	0.69	0.96	0.56	0.47	0.67	0.73
Yb	3.17	3.69	3.60	2.26	1.71	1.78	1.74	2.53	2.63	1.78	1.37	1.93	2.95
Lu	0.402	0.506	0.567	0.315	0.232	0.224	0.248	0.341	0.383	0.241	0.155	0.262	0.393
Sr	98	602	126	197	359	432	486	783	412	416	445	608	97
Ba	654	738	910	602	397	283	293	1049	219	347	599	500	649
Cs	2.0	20.3	23.2	3.4	2.3	2.1	1.3	2.6	1.5	12.9	6.9	2.0	9.3
U	3.2	2.3	2.4	4.3	2.2	1.1	0.3	2.9	0.6	3.1	5.7	0.5	3.6
Th	14.4	17.4	15.6	18.0	9.2	4.0	1.1	8.8	2.4	9.3	15.2	2.1	12.3
Hf	6.8	7.9	10.5	4.6	4.6	3.3	2.4	5.2	5.4	3.5	4.1	4.1	5.1
Ta	1.23	2.57	1.98	1.48	1.30	0.40	0.38	0.72	0.56	1.07	0.91	0.42	1.02
Sc	3.8	4.1	4.0	2.3	2.7	23.0	23.0	11.24	20.0	16.9	8.9	9.0	4.7
Cr	0	0	130	0	0	10	7	4	3	30	11	82	0
Ni	2	0	0	1	2	8	6	4	3	11	8	19	1
Co	2	1	2	2	1	25	27	15	16	16	12	11	2

(*continued on next page*)

Table 2 (*continued*)

Unit	Tilito Formation –Doña Ana Gropu (cont.)					Escabroso Formtaion – Doña Ana Group							
Sample	ZN111	ZN137C	XDI046	DI077b	ZN115	ZN158	ZN154	ZN114	ZN147	MQ153	ZN159	XDI081	ZN157F
Ba/La	20.9	15.6	22.3	21.2	15.7	17.1	24.0	29.5	7.9	16.9	22.4	25.9	19.9
La/Sm	5.5	5.8	5.1	6.5	7.5	4.3	3.4	5.7	4.3	5.1	5.6	3.9	5.4
La/Yb	9.9	12.8	11.3	12.5	14.7	9.3	7.0	14.1	10.5	11.5	19.4	10.0	11.1
Sm/Yb	1.8	2.2	2.2	1.9	2.0	2.10	2.10	2.5	2.50	2.3	3.5	2.6	2.0
Ba/Ta	530	287	460	406	304	700	760	1450	388	325	660	1190	634
La/Ta	25.3	18.4	20.6	19.1	19.4	40.9	31.7	49.2	48.9	19.2	29.4	46.0	31.9
Type	Vitric tuff	Dacitic tuff	Dacitic tuff	Rhyolite	Dacitic tuff	Basandesite	Basandesite	Basandesite	Andesite	Andesite	Andesite	Dacite	Vitric tuff
Creek	Zancarrón	Zancarrón	Zancarrón	Zancarrón	Zancarrón	Zancarrón	Zancarrón	Bañitos	Zancarrón	V. Heladas	Zancarrón	Zancarrón	Zancarrón
Coordenates	29°35′39″ 69°53′28″	29°36′33″ 69°46′36″	29°50′06″ 69°53′05″	29°36′32″ 69°56′15″	29°34′26″ 69°55′44″	29°33′57″ 69°51′23″	29° 34′38″ 69° 51′32″	29°37′46″ 69°55′42″	29°34′22″ 69°54′41″	29°51′10″ 69°51′46″	29°33′07″ 69°51′23″	29°35′15″ 69°51′31″	29°33′57″ 69°51′23″

Unit	Cerro de las Tórtolas Formation												
Sample	DI039	XDI039	DI040	XDI04I	MQ28	MQ30	ZN162	DI082	SP79C	DI073	XDI073	SP29C	SP28
La	32.6	29.3	29.1	26.4	27.1	29.3	28.9	26.4	25.1	26.4	19.3	27.1	24.6
Ce	67.4	60.2	58.9	55.4	57.9	62.8	65.1	61.8	55.8	57.4	41.6	60.5	51.3
Nd	28.5	25.2	25.5	22.2	22.5	31.4	32.9	29.5	25.2	28.7	21.8	27.9	21.7
Sm	5.4	5.4	5.1	3.9	4.7	5.0	6.4	6.1	5.3	5.4	4.2	5.3	4.8
Eu	1.40	1.63	1.32	1.25	1.13	1.41	1.35	1.23	1.13	1.42	1.06	1.43	1.12
Tb	1.35	0.65	0.60	0.30	0.42	0.41	0.94	0.82	0.70	0.61	0.43	0.61	0.58
Yb	2.19	2.15	2.32	0.76	0.99	0.70	3.07	2.64	2.30	1.45	1.04	1.70	1.87
Lu	0.313	0.348	0.312	0.144	0.121	0.088	0.415	0.352	0.318	0.194	0.154	0.239	0.256
Sr	549	494	447	565	675	794	388	354	395	602	597	560	472
Ba	776	774	618	983	782	885	447	353	512	597	742	475	462
Cs	1.3	1.3	2.2	6.8	1.9	2.1	2.6	2.3	5.3	2.9	2.4	2.6	2.1
U	2.4	2.8	2.2	2.1	2.5	1.3	3.2	2.9	3.4	2.2	2.0	1.3	1.4
Th	8.4	7.7	7.7	8.9	7.3	4.6	10.1	9.2	12.2	6.7	6.2	6.1	5.5
Hf	5.0	6.4	4.8	6.5	4.2	4.7	6.1	5.5	5.2	5.1	4.1	4.8	4.3
Ta	1.12	1.30	0.96	1.09	0.69	0.48	0.85	0.76	0.78	0.93	0.59	0.71	0.65
Sc	7.1	8.0	10.5	0.0	8.9	8.2	24.1	21.3	16.2	9.8	10.0	8.7	10.3
Cr	1	51	0	163	14	30	21	15	14	12	201	3	5
Ni	2	0	3	0	10	15	11	9	7	14	32	4	3
Co	8	12	11	3	13	14	22	21	17	17	16	3	12
Ba/La	23.8	26.4	21.2	37.2	28.9	30.2	15.5	13.3	20.8	22.6	38.4	17.5	18.8
La/Sm	6.1	5.4	5.7	6.7	5.9	5.9	4.5	4.3	4.7	4.9	4.6	5.1	5.1
La/Yb	14.9	13.6	12.6	34.7	27.4	41.8	9.4	10.0	10.9	18.3	18.6	16.0	13.1
Sm/Yb	2.5	2.5	2.2	5.2	4.7	7.1	2.1	2.3	2.3	3.7	4.1	3.1	2.6
Ba/Ta	696	595	644	902	1139	1826	528	465	658	645	1258	669	710
La/Ta	29.2	22.5	30.4	24.2	39.5	60.4	34.2	34.9	32.3	28.6	32.7	38.2	37.8
Type	Andesite	Andesite	Andesite	Andesite	Andesite	Andesite	Andesite	Andesite	Andesite	Andesite	Andesite	Andesite	Andesite
Location	Cerro de las Tórtolas	Cerro de las Tórtolas	Cerro de las Tórtolas	Cerro de las Tórtolas	Cerro de las Tórtolas	Cerro de las Tórtolas	Zancarrón Creek	Zancarrón Creek	Brea Cordillera	Ortiga Cordillera	Ortiga Cordillera	Despoblados area	Despoblados area
Coordenates	29°58′24″ 69°49′42″	29°58′24″ 69°49′42″	29°57′48″ 69°50′05″	29°57′48″ 69°50′05″	29°56′36″ 69°51′22″	29°56′09″ 69°50′60″	29°36′49″ 69°46′60″	29°37′06″ 69°46′02″	29°43′45″ 69°41′53″	29°24′30″ 69°45′35″	29°24′30″ 69°45′35″	29°36′49″ 69°46′60″	29°37′06″ 69°46′02″

Unit	Tambo Formation			Vacas Heladas Ignimbrite				
Sample	DI091	RF125	RF170	XDI042	DI093	XDI093	DI095	XDI093
La	50.4	23.2	21.9	29.9	22.0	20.2	24.5	19.8
Ce	74.3	49.8	46.4	60.2	45.9	41.8	50.9	41.3
Nd	28.6	17.8	19.3	26.6	19.0	19.2	24.0	19.2
Sm	4.8	3.6	4.1	5.2	3.4	3.1	3.9	3.1
Eu	0.92	0.90	0.84	1.76	0.66	0.61	0.73	0.63
Tb	0.19	0.37	0.20	0.77	0.21	0.24	0.24	0.24
Yb	1.05	1.20	1.18	2.75	0.82	0.76	0.88	0.80
Lu	0.123	0.141	0.155	0.393	0.070	0.120	0.077	0.108
Sr	487	609	391	440	507	590	604	594
Ba	536	536	840	746	756	928	994	946
Cs	56.8	77.1	28.3	2.4	5.8	8.5	6.1	4.9
U	6.1	5.00	5.8	4.6	4.0	3.7	4.7	4.0
Th	17.2	13.0	13.9	7.9	6.9	7.5	7.8	7.4
Hf	3.7	4.6	4.1	7.9	3.5	3.7	3.9	3.8
Ta	0.86	0.91	0.88	1.28	0.72	0.66	0.83	0.71
Sc	4.6	5.9	4.9	9.0	2.1	0.0	2.2	0.0
Cr	4	6	5	129	1	174	1	148
Ni	0	0	1		1	24	0	0
Co	6	8	5	12	2	2	2	2
Ba/La	10.6	23.1	38.4	24.9	34.4	45.9	40.6	47.8
La/Sm	10.5	6.4	5.3	5.8	6.5	6.6	6.3	6.4
La/Yb	47.8	19.4	18.6	10.9	26.7	26.6	27.9	24.8
Sm/Yb	4.6	3.0	3.5	1.9	4.1	4.1	4.4	3.9
Ba/Ta	620	591	955	583	1055	1406	1197	1332
La/Ta	58.3	25.5	24.9	23.4	30.7	30.6	29.5	27.9
Type	Crystalline dacitic tuff	Crystalline dacitic tuff	Crystalline dacitic tuff	Crystalline dacitic tuff	Crystalline dacitic tuff	Crystalline dacitic tuff	Crystalline dacitic tuff	Crystalline dacitic tuff
Location	Piedras Blancas	Río Frío Creek	La Deidad Creek	Ignimbritic plateau located eastern Vacas Heladas volcano				
Coordenates	29°48′00″ 69°45′16″	29°48′00″ 69°45′16″	29°46′50″ 69°44′26″	29°58′30″ 69°49′24″	29°57′17″ 69°50′05″	29°57′17″ 69°50′05″	29°59′20″ 69°49′06″	29°59′20″ 69°49′06″

Table 3
Isotopic data for a dacitic ignimbrite from the middle Eocene–early Oligocene Valle del Cura Formation, and for an andesite from the early to middle Miocene Cerro de las Tórtolas Formation

	$^{87}Sr/^{86}Sr$	Error	$^{143}Nd/^{144}Nd$	Error	εNd
Valle del Cura Formation					
Sample Z27	0.7053359	0.0008	0.5126172	0.0012	−0.4
Cerro de las Tórtolas Formation					
Sample SP79C	0.7054166	0.0008	0.5126107	0.0009	−0.5

Notes: εNd calculated with a CHUR value of 0.512638; errors are expressed in 2 sigma.

ratios exceed 450 and La/Ta ratios exceed 25. In contrast, Valle del Cura Paleocene and early Miocene alkaline basalts have ratios similar to those in MORB and OIB rocks. The Valle del Cura Formation dacites and rhyolites have higher La/Ta and similar Ba/Ta ratios relative to the silicic Tilito samples and similar La/Ta ratios (>25) and lower Ba/Ta ratios relative to the late Miocene Vacas Heladas. Tambo Formation dacites are most similar to Vacas Heladas Ignimbrite samples.

Fractionation of sanidine in silicic magmas can dramatically decrease Ba contents and lower Ba/La ratios. An argument that sanidine fractionation is not the primary explanation for lower Ba/La ratios in the Tilito Formation emerges from the association of low Ba/La ratios with low La/Ta ratios, which cannot be explained by sanidine fractionation. Instead, low Ba/La and Ta/La ratios seem to be a primary feature that reflects the magma source region. The scatter in Ba/Ta and Ba/La ratios compared with La/Ta ratios may reflect mobility of Ba due to hydrothermal alteration.

A distinguishing feature of the middle Eocene–lower Oligocene volcanism is high U and Th concentrations (Fig. 6). The Valle del Cura Formation volcanic rocks are enriched in these trace elements relative to the Tilito Formation rocks, which have similar silica content. Very high concentrations of U and Th are present in the early Miocene Infiernillo andesitic intrusives in the El Indio belt (Kay et al., 1987) that postdate the Doña Ana Formation. Hildreth and Moorbath (1988) and Kay et al. (1987, 1991) argue that high concentrations such as these relate to crustal contamination that affects the magmas during their passage through the crust from a deep source.

3.3. Rare earth patterns

The REEs offer useful indicators of the residual mineral assemblages in equilibrium with magmas at their source. Temperature and pressure conditions of magma generation can be evaluated by considering these residual assemblages. Kay et al. (1987, 1991, 1999) use REE in El Indio and Valle del Cura samples as petrogenetic indicators and discuss their significance as a guide to mineral behavior.

The REE diagrams in Fig. 4 and the La/Sm versus Sm/Yb plot in Fig. 7 show the behavior of the light versus heavy REEs. The light REE enrichment shown by the late Eocene–early Oligocene Valle del Cura Formation is similar to that described by Bissig et al. (2003) for subvolcanic rocks from the Bocatoma Intrusive Unit in Chile. However, the Bocatoma rocks lack an Eu anomaly, though it is present in the Valle del Cura Formation.

As Fig. 7 shows, the Eocene Valle del Cura Formation volcanic rocks resemble those of the Oligocene–early Miocene Doña Ana Group, in their low and constant HREE slope (Sm/Yb ∼2.2), along with higher concentrations of light and intermediate REEs with variable LREE slopes (La/Sm ∼5–8). The Miocene Cerro de las Tórtolas samples show an increase in the Sm/Yb ratio from the lower to the upper section, which reflects the fractionation of a residual mineral phase that retains the HREE (Fig. 7). The late Miocene Tambo Formation and Vacas Heladas Ignimbrite have higher Sm/Yb ratios (>3) than the older Valle del Cura and Doña Ana Group Tilito suites.

Eu anomalies are useful for evaluating pressure conditions, because small Eu anomalies and high Sr concentrations in silicic rocks reflect a lack of plagioclase fractionation, inhibited at higher pressures. Fig. 8 shows the relation between Sr and LREE contents as expressed by the La/Sr ratio, the steepness of the REE pattern as expressed by chondrite-normalized La/Yb ratios, and the Eu anomaly (Eu/Eu*). Kay et al. (1991) mention that the coexistence of high La/Yb ratios, low La/Sr ratios, and low Eu anomalies corroborate less plagioclase fractionation, which means a high pressure condition for that particular assemblage. Fig. 8 compares rocks with similar silica content. Dacitic ignimbrites and rhyolites of the Valle del Cura Formation have high La/Sr ratios and the highest Eu anomalies, along with low La/Yb ratios. This behavior reflects plagioclase fractionation. The younger, more intermediate composition sequences show evidence of lesser degrees of feldspar fractionation, according to their moderate to high Eu/Eu* ratios. The main change in the chemical trend, signaled by a decrease in plagioclase fractionation, occurs in the upper section of the Cerro de las Tórtolas Formation, which shows the highest La/Yb ratios with small Eu anomalies (Kay et al., 1991).

The break in geochemical behavior divides the Tertiary sequence into two trends. The first trend, from the middle Eocene to the early Miocene, includes the Valle del Cura Formation and Doña Ana Group. These magmas may have variably equilibrated with low to medium pressure residual assemblages, including plagioclase, pyroxene, biotite, and, in some cases, amphibole. The second trend, from the middle to late Miocene, includes the upper section of the Cerro de las Tórtolas Formation, the Tambo Forma-

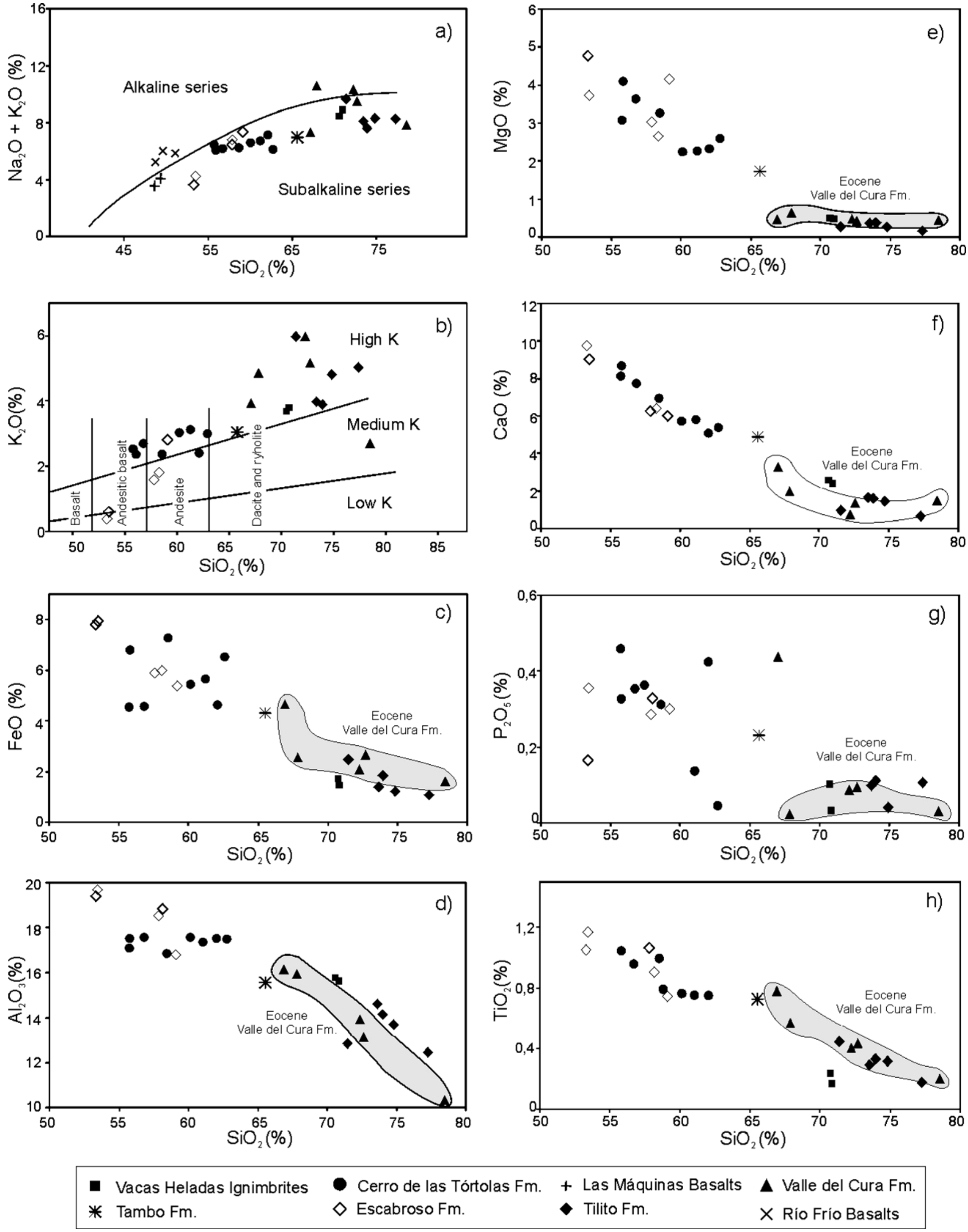

Fig. 3. Harker-type variation diagrams versus SiO_2 for major elements of the Tertiary magmatic units of the Valle del Cura: (a) $Na_2O + K_2O$, alkaline/subalkaline fields are those from Irvine and Baragar (1971); (b) K_2O discrimination fields are those from Le Maitre et al., 1989); (c) FeO; (d) Al_2O_3; (e) MgO; (f) CaO; (g) P_2O_5; (h) TiO_2. Shadowed area includes Eocene Valle del Cura Formation samples. Río Frío and Las Máquinas basalts are plotted in (a).

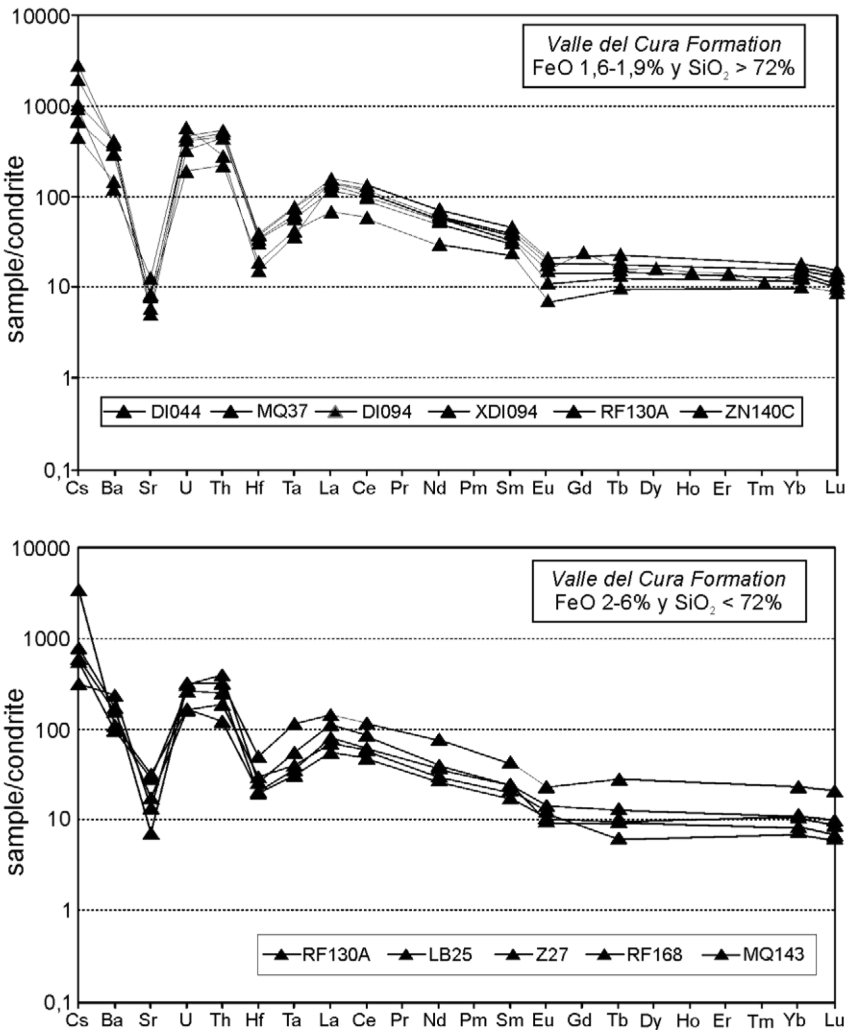

Fig. 4. Chrondrite-normalized multielement diagram for the middle Eocene–early Oligocene Valle del Cura Formation rocks. Chrondrite values are from Leedy (Rollinson, 1993).

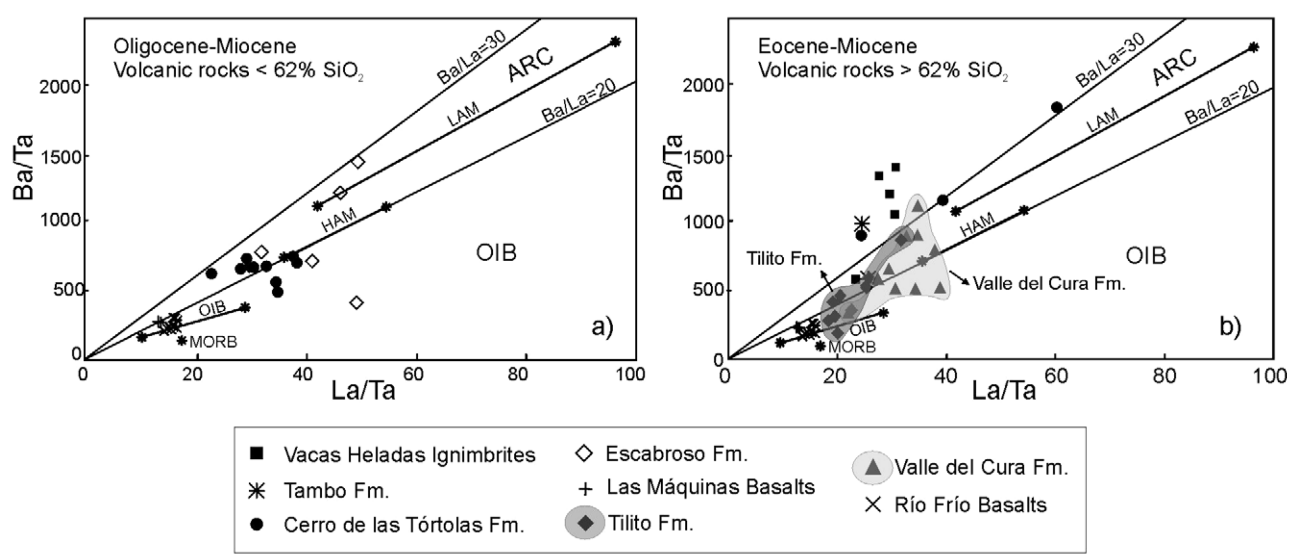

Fig. 5. Ba/Ta vs. La/Ta ratios for the Eocene to Miocene volcanic sequences of the Valle del Cura. (a) Rocks <62% SiO_2 and (b) rocks >62% SiO_2. MORB, OIB, and LAM/HAM volcanic rocks for the SVZ defined by Hickey et al. (1986) are also included. Solid lines define constant Ba/La ratios of 20 and 30.

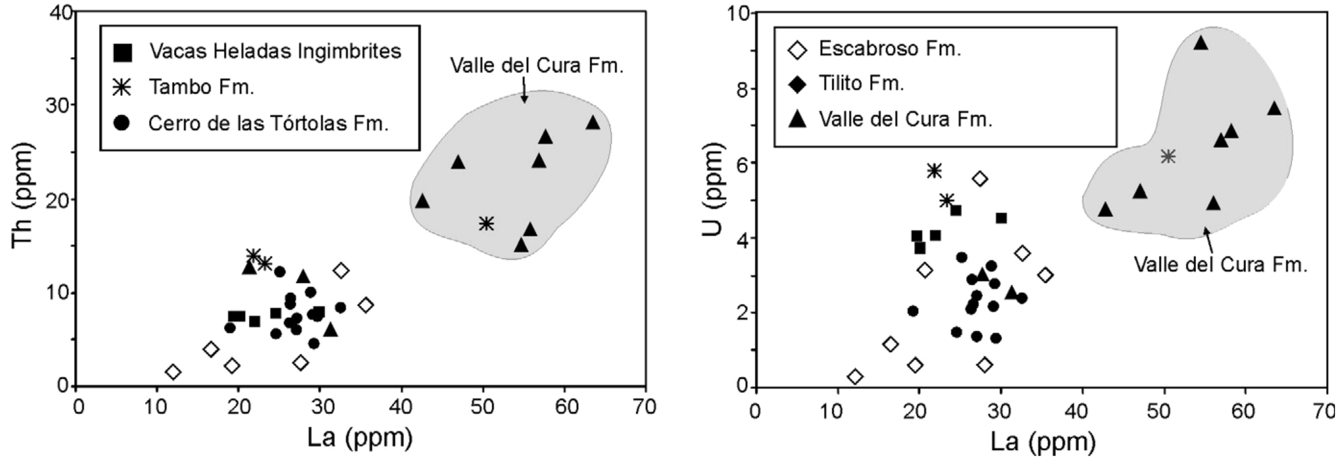

Fig. 6. U and Th content for the Tertiary volcanic units. Note the high U and Th concentrations of the middle Eocene to late Oligocene Valle del Cura Formation rocks (shadowed area) at similar silica contents to the Oligocene Doña Ana Group.

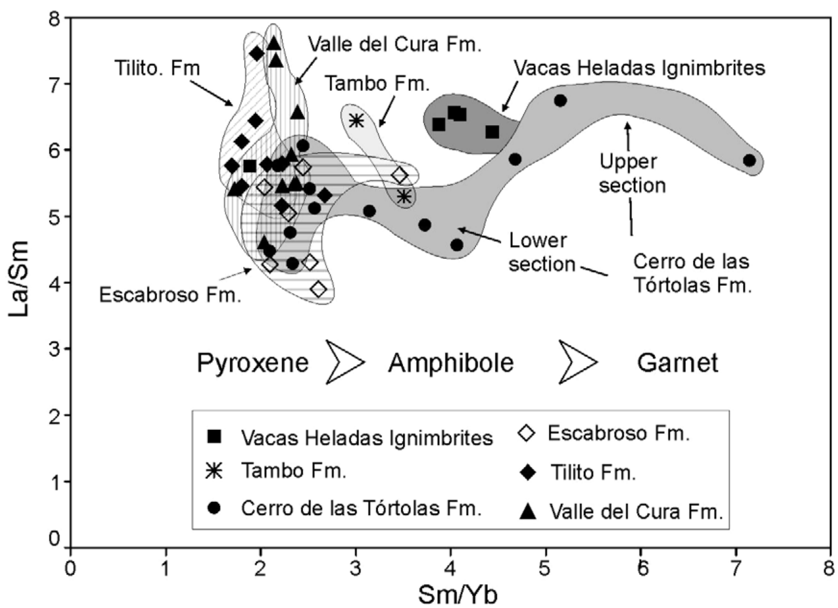

Fig. 7. REE chemical evolution for the Tertiary volcanic rocks of Valle del Cura, reflected in their La/Sm and Sm/Yb ratios. The trend shows a gradual increase toward fractionation of high-pressure mineral residual phases; the upper section of the Cerro de las Tórtolas Formation (middle Miocene) requires a grantiferous residual phase.

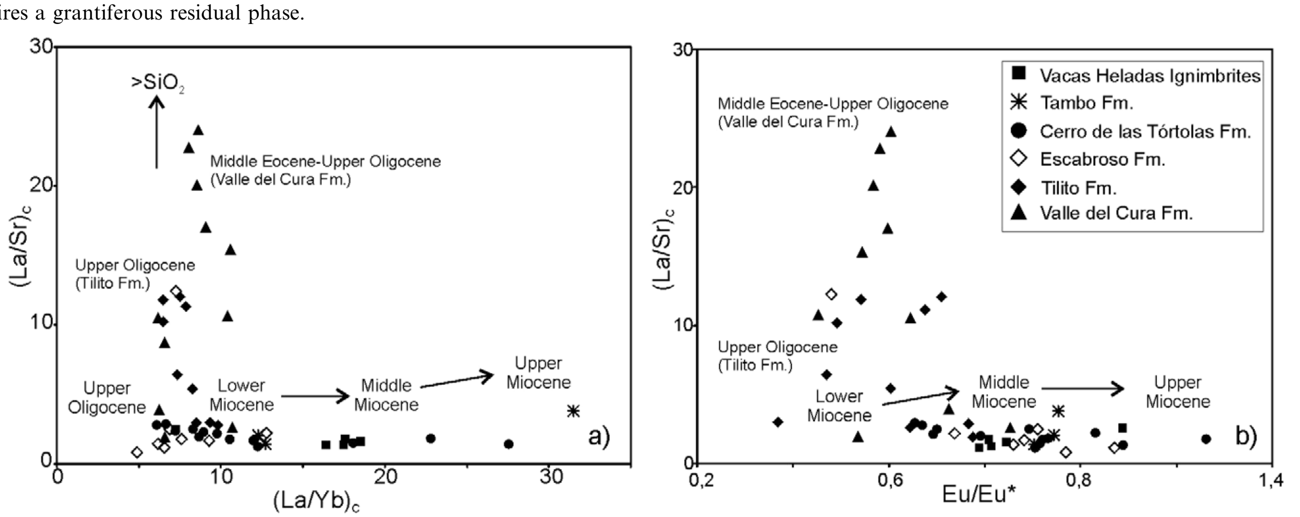

Fig. 8. (a) (La/Sr)c vs. (La/Yb) ratios; (b) (La/Sr)c vs. Eu/Eu* ratios for the Tertiary volcanic rocks of Valle del Cura. As described by Kay et al. (1991), the coexistence of high La/Yb ratios, low La/Sr ratios, and low Eu anomalies corroborate less plagioclase fractionation.

tion, and the Vacas Heladas Ignimbrite. These magmas appear to have variably equilibrated with higher pressure assemblages, including amphibole, garnet, and lesser amounts of plagioclase. The Miocene volcanic rocks of the lower section of the Cerro de las Tórtolas Formation show transitional behavior between both trends. The described evolution extends the low to high pressure scheme of Kay et al. (1987, 1991, 1999) and Bissig et al. (2003) for the El Indio belt to the middle Eocene–early Oligocene volcanism of the Valle del Cura Formation. The trends reflect an increase in pressure conditions related to a deeper site of magma equilibration. This increase in depth may relate to an increase in crustal thickness, as proposed for the temporal evolution of the El Indio belt by Kay et al. (1987, 1988, 1991) and the spatial variation along the SVZ arc by Hildreth and Moorbath (1988).

3.4. Isotopic data

New isotopic data for Valle del Cura and Cerro de las Tórtolas Formations samples are shown in Table 3. The andesite analyzed from the Cerro de las Tórtolas Formation comes from a lava flow in the upper part of the La Brea Cordillera (Fig. 2) dated by K/Ar at 14.5 ± 0.9 Ma (Litvak, 2004). The $^{87}Sr/^{86}Sr$ ratio is 0.70541 and the εNd is -0.5. The dacitic ignimbrite analyzed from the Valle del Cura Formation crops out in the Zancarrón Creek in the sequence dated by Limarino et al. (1999) at 34 ± 1 Ma (K/Ar). It has a $^{87}Sr/^{86}Sr$ ratio = 0.70533 and $\varepsilon Nd = -0.4$. The isotopic ratios for the Cerro de las Tórtolas andesite fall in the range of Miocene andesites from the Valle del Cura and El Indio belts (Kay et al., 1991, 1999; Kay and Abruzzi, 1996; Bissig et al., 2003). The $^{87}Sr/^{86}Sr$ and εNd values from the Valle del Cura Formation rocks are within the range reported by Bissig et al. (2003) for the Eocene Bocatoma Intrusive samples.

To appraise the isotopic evolution of the Eocene–Miocene volcanic sequence, Fig. 9 plots Sr and Nd isotopic data from the literature (Kay et al., 1991; Kay and Abruzzi, 1996), along with the ratios in Table 3. The plot shows that the $^{87}Sr/^{86}Sr$ ratios for the Tertiary volcanic sequence range from 0.70367 to 0.70552 and the εNd values range from -4 to 2. Paleocene and early Miocene basalts show an isotopically depleted nature, whereas the more silicic magmas contain a crustal component (Fig. 9). The gradual increase in $^{87}Sr/^{86}Sr$ ratios and decrease in εNd values from the Oligocene to late Miocene, as noted by Kay et al. (1991) and Kay and Abruzzi (1996), indicates an increase in the importance of a radiogenic crustal component with time. This crustal component increases in prominence in the Cerro de las Tórtolas Formation lavas and Vacas Heladas Ignimbrite and parallels changes in the inferred residual mineralogy in equilibrium with these magmas (Fig. 10). The late Eocene–early Oligocene Valle del Cura Formation lavas do not fit this trend. Their isotopic ratios are similar to those of the lower sector of the Cerro de las Tórtolas Formation lavas, whereas their inferred residual mineral assemblage is low pressure. These features of the Valle del Cura Formation magmas indicate an important role for crustal-derived material in the evolution of the middle Eocene–early Oligocene magmas. The process was independent from the one that led to increased participation of crustal components in the post-late Oligocene trend.

The increasing $^{87}Sr/^{86}Sr$ ratio and decreasing εNd value trends in the late Oligocene–late Miocene volcanic sequences in the Valle del Cura belt also appear in Miocene–Quaternary volcanic suites from the El Teniente region at the northern end of the SVZ (Stern and Skewes, 1995; Kurtz et al., 1997; Kay et al., 1999, 2005). The various authors agree that the geochemical behavior shown by these volcanic suites reflects an increase in crustal-derived

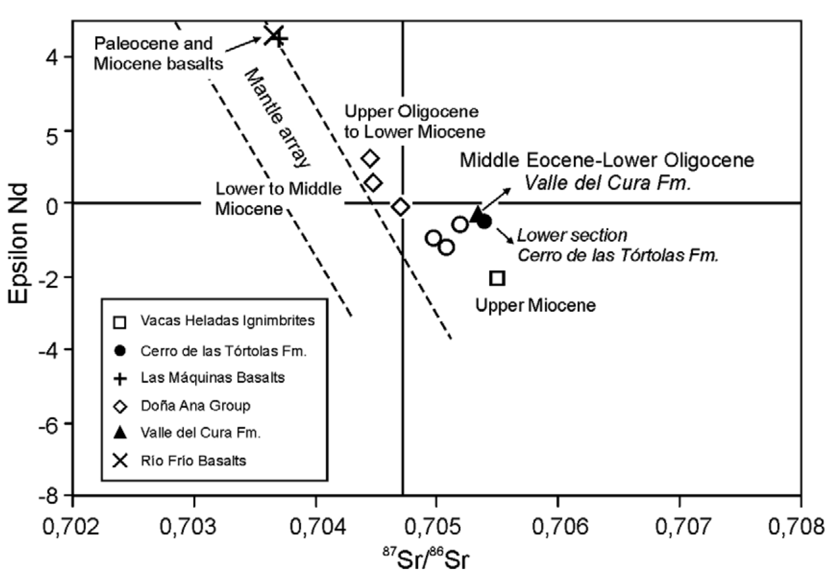

Fig. 9. Isotopic values for the middle Eocene–late Miocene volcanic sequence. The Valle del Cura Formation sample shows a distinct isotopic behavior relative to the rest of the Tertiary sequence. Unfilled samples correspond to values from Kay et al. (1991).

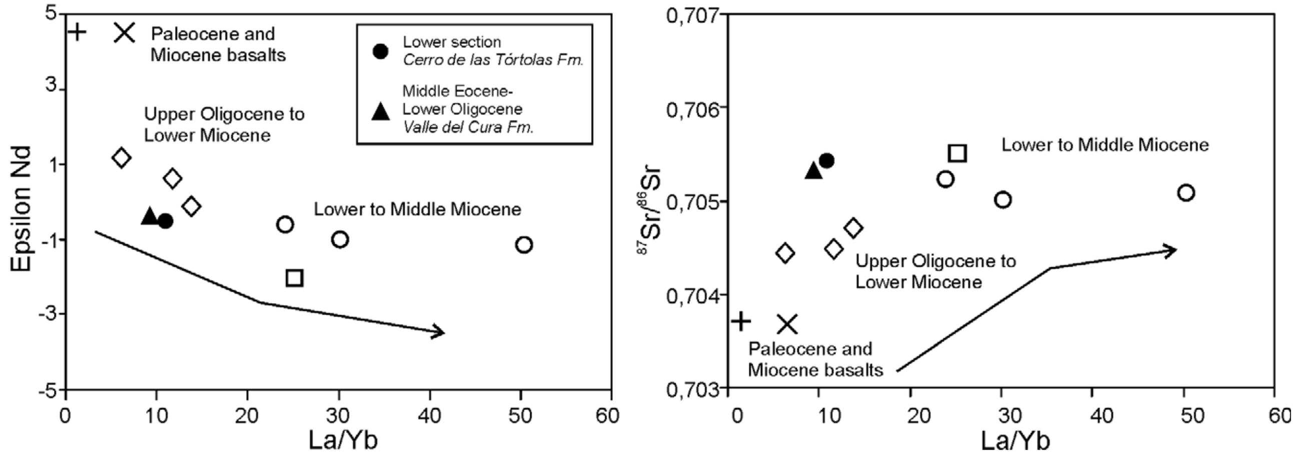

Fig. 10. Relationship between La/Yb ratios and isotopic signatures of the Tertiary magmatic suites. The arrows indicate the trend toward an increase in isotopic enrichment (higher $^{87}Sr/^{86}Sr$ and lower εNd) as the La/Yb ratios increase. Symbols are as in Fig. 9.

components during magma evolution, but they differ in terms of the processes responsible for crustal contamination.

4. Petrogenetic implications and geochemical evolution

4.1. Late Eocene–early Oligocene magmatism

Late Eocene–early Oligocene volcanism in the Valle del Cura is represented by the acid volcanic rocks and ignimbrites of the Valle del Cura Formation. Their low La/Yb and Sm/Yb ratios, along with their negative Eu anomalies, provide evidence that they last equilibrated with a low-pressure residual mineral assemblage. Evidence of the strong influence of a crustal component in their genesis comes from their enriched isotopic signatures relative to the Paleogene Río Frío and early Miocene Máquinas basalts. Influence of slab components is evidenced by the Ba/Ta and La/Ta ratios of Valle del Cura Formation rocks, which contrast with those of the primitive basalts. The Paleocene Río Frío Basalts are alkaline, intraplate-type magmas with no influence of a subducted component (Litvak and Page, 2002; Litvak, 2004).

The contrast between the higher arc-like La/Ta ratios in the Eocene Valle del Cura Formation silicic volcanic rocks and the more OIB/MORB-like in both the older Río Frío and younger Máquinas backarc basalts suggests that the arc-like character of the Valle del Cura silicic rocks could reflect a crustal origin. The Eocene Valle del Cura silicic rocks may contain a large fraction of a melt from an arc-like crust, consistent with their high $^{87}Sr/^{86}Sr$ and low εNd ratios compared with those of the basalts, as well as eruption in a backarc setting. Alternatively, the Valle del Cura Formation could reflect a broad volcanic arc that extended from the Bocatama stocks in Chile into the backarc of the Valle del Cura in the Eocene.

Overall, the major, trace element, and isotopic characteristics of the Valle del Cura volcanic rocks, as well as their location east of the Bocatoma stocks in Chile, is consistent with their origin in a retroarc foreland basin east of the volcanic arc front in Chile. The Eocene mafic magmas responsible for providing the heat that generated the Valle del Cura Formation silicic melts were generated in a retroarc, whereas the silicic melts originated under low- to moderate-pressure conditions in a thin crust.

4.2. Late Oligocene–late Miocene volcanic suite

The subsequent late Oligocene to late Miocene volcanic suite includes the Doña Ana Group, Cerro de las Tórtolas and Tambo Formations, and Vacas Heladas Ignimbrite. Magmas responsible for the late Oligocene–early Miocene Doña Ana Group volcanism are the consequence of melts from the mantle wedge interacting with the crust as pointed out Kay et al. (1987, 1991). Amphibole and pyroxene are the principal mafic residual mineral phases that indicate magma equilibration in low- to intermediate-pressure conditions. Nd and Sr isotopic ratios show that these volcanic rocks were influenced by less radiogenic crustal components than the younger Miocene volcanic sequence. Their relatively low La/Ta and Ba/La ratios and nonradiogenic isotopes in the Tilito volcanic rocks are consistent with the participation of crustal melts derived from older magmatic rocks. The mantle melts that generate crustal melts probably were arc-like, as are the Coya Machali basalts to the south in the Teniente region near 34 S (e.g., Kay et al., 1999, 2005; Charrier et al., 2002). The more arc-like, higher La/Ta ratios of the mafic early Miocene Escabroso Formation andesites and dacites show that typical arc magmas were generated in the mantle wedge at 20 Ma.

The early to middle Miocene Cerro de las Tórtolas Formation has calc-alkaline mesosilicic arc-like signatures. Geochemically, two groups are recognized. In the older one, trace element–inferred residual assemblages are dominated by amphibole and pyroxene, whereas in the younger, garnet reflects higher pressures for magma equilibration. Isotopic data also follow this trend; the upper section is isotopically more enriched than the lower, as a result of the higher degree of crustal-derived contributions. The younger group is contemporaneous with the Tambo Formation ignimbrites, which show similar geochemical behavior. These units mark an inflection in the geochemical history of the late Oligocene–late Miocene volcanic sequence that continues with the Vacas Heladas Ignimbrite, which are the least voluminous in the sequence. The Vacas Heladas Ignimbrite shows evidence of a more radiogenic crustal contribution, because it has the most enriched isotopic signature among the Tertiary volcanic units in the Valle del Cura.

4.3. Crustal contributions and adakitic signal

A major question pertains to the origin of the crustal contaminants that influenced the trace elements and isotopic behavior of the late Oligocene–late Miocene magmatic sequence. Different models have been proposed for similar geochemical trends in central Andean volcanic rocks.

Hildreth and Moorbath (1988) explain the chemical variation along the SVZ arc as a result of *MASH* processes that occur in the transitional zone between the mantle and the crust during the upward evolution of melts generated at a certain depth. The depth of the MASH zone influences the character of the magmas. Similarly, Kay et al. (1987, 1988, 1991) and Kay and Abruzzi (1996) correlated chemical changes in the El Indio belt with an increase in crustal thickness, as evidenced by the mineral residual assemblages that equilibrate at depth with the magmas. The increase in crustal thickness is linked to backarc crustal shortening that led to crustal thickening under the main arc as the Nazca plate shallowed to produce the flatslab region (Kay and Abruzzi, 1996).

Stern and Skewes (1995, 2003) and Skewes et al. (2002) propose an alternative to explain the chemical variations in the Miocene–Pliocene volcanic suite of the El Teniente region at the northern end of the SVZ. They suggest that subducted sediment, along with crust that entered the mantle asthenospheric wedge as a result of forearc subduction erosion, was responsible for the changing isotopic signatures and steepening REE patterns in the central Andes. They argue isotopic and trace element variations may be independent of crustal thickness. Kay and Mpodozis (2002) also argue for some role of forearc subduction erosion in the evolution of the El Teniente and El Indio Belt magmatic rocks. Kay et al. (2005) present evidence that both forearc erosion and crustal thickening are responsible for the chemistry in the Oligocene–Holocene sequence of volcanic rocks at the latitude of the El Teniente deposit and the northern SVZ.

The chemical evolution described for the late Oligocene–late Miocene Valle del Cura volcanic sequence indicates changes in the residual mineral assemblages and variations in isotopic signatures, consistent with a gradual increase of crustal thickness. The trace element signatures were influenced by the fractionation of higher pressure residual mineral phases, and the isotopic ratios of the magma generated at depth were modified as a result of crustal contamination processes during ascent through a thickened crust. The data presented herein are consistent with this explanation for most of the Valle del Cura sequence, with the exceptions of the Cerro de Tórtolas andesite with its extreme La/Yb ratios of >50 (Ramos et al., 1989; Kay et al., 1991), which erupted near the time the Juan Fernandez Ridge began to subduct on the Nazca plate below this region. As argued by Kay et al. (2005) for the south central Andes, the crustal contributions in the Valle del Cura volcanic rocks could be related to both episodes of crustal thickening and peaks of forearc subduction erosion (see also Kay and Mpodozis, 2002). The extremely steep REE pattern in the upper section of Cerro de las Tórtolas and Tambo formations at 12 Ma could reflect an episode of accelerated forearc subduction erosion as the Chile Ridge arrived, coincident with periods of arc migration and maximum compressional regimens by the middle Miocene.

Another question pertains to the origin of the strong adakitic signatures in some Cerro de las Tórtolas Formation rocks. Rocks with adakitic characteristics also occur in the Maricunga and Teniente belts (Kay et al., 1991, 1999). Adakites, as defined by Drummond and Defant (1990), are dacitic to andesitic subduction-related rocks with $SiO_2 > 56\%$, $Al_2O_3 > 15\%$, and $Sr > 400$ ppm; low values of Y (<18 ppm); and high La/Yb ratios (>20). The chemical signatures of some adakites have been attributed to melting of the downgoing oceanic eclogitic facies, followed by interaction of those melts with the asthenospheric wedge (Kay, 1978; Drummond and Defant, 1990). Gutscher et al. (2000) proposed that melting of the downgoing slab produced magmas with adakitic signatures in the retroarc of the Pampean flatslab. As pointed out by many authors for the Chilean (Pampean) flatslab (Kay and Mpodozis, 2002; Richards, 2002; Bissig et al., 2003), the chemical definition of adakites requires that dacitic to andesitic magmas equilibrate with a grantiferous residual phase not that they reflect melting of a downgoing slab. Asthenospheric wedge-derived magmas that interact with thickened crust, such as that in the Main Cordillera of the flatslab region, can generate adakitic chemical signatures. This mechanism, along with forearc subduction erosion, is a much more logical way to explain the adakitic signatures of the Miocene volcanic rocks in the Valle del Cura and El Indio belt. Furthermore, slab melting is inconsistent with a cooling mantle wedge over a shallowing subduction zone (Kay and Mpodozis, 2002). The only convincing slab melt adakites in the Andes occur in Patagonia, in the region of the Chilean triple junction (Kay et al., 1993; Ramos et al., 2004).

5. Geodynamical model and tectonic evolution

The geochemical history of the Tertiary magmatic sequence of Valle del Cura provides new evidence to refine the Paleogene–Neogene tectonic evolution of the Chilean (Pampean) flatslab segment in a transect at 29–30° latitude. Fig. 11 shows the proposed geodynamical scheme.

An Eocene–early Oligocene magmatic arc is poorly developed along the central Andean margin due to the oblique convergence direction and low subduction rate (Pardo Casas and Molnar, 1987). At the latitude of Valle del Cura, Nasi et al. (1990) describe small subvolcanic bodies of the Bocatoma Intrusive Unit, assigned to the Eocene–early Oligocene on the basis of K/Ar, U/Pb, and Ar/Ar ages (Mpodozis and Cornejo, 1988; Martin et al., 1995, 1997a; Bissig et al., 2001). Similarly aged intrusive bodies occur in the Copiapó region, related to porphyry copper mineralization (Mpodozis and Kay, 2003). These bodies represent the location of the Eocene–early Oligocene magmatic arc for these latitudes. The present position of the Bocatoma unit is closer to the trench than expected for a volcanic arc. The location of the Bocatoma arc could reflect subsequent removal of the continental margin by forearc subduction erosion.

In this context, the volcanic and sedimentary rocks of the Valle del Cura Formation can be interpreted as being emplaced in a retroarc setting (Fig. 11a). The presence of silicic volcanic rocks with a subduction zone signature could signal a shallowly subducting plate that would allow arc-like magmas to erupt behind the frontal arc. These melts intruded into a thin crust and were strongly contaminated by crustal material during ascent. Eocene–early Oligocene Valle del Cura Formation retroarc volcanic and volcaniclastic activity developed regionally, as shown by similar sequences in the Macho Muerto area, Cordon de la Brea, and along the Valle del Cura belt (Limarino et al., 1999; Panteleyev and Cravero, 2000; Mpodozis and Kay, 2003; Litvak and Poma, 2005). The arc characteristics of the Valle del Cura silicic magmas could alternatively reflect arc-like crust, melted by underplated backarc intraplate alkaline magmas related to the Río Frío basalts (Litvak, 2004).

During the late Oligocene (∼24 Ma), the tectonic configuration of the Andean margin changed due to the the break up of the Farellon plate into the Nazca and Cocos, which resulted in changes to the orthogonal convergence direction at increased subduction rates (e.g., Pardo Casas and Molnar, 1987). Under these conditions, an Andean type arc developed, as represented by the Doña Ana Group volcanics (Fig. 11b). One of the principal eruptive centers was at Cerro Escabroso in the Doña Ana Cordillera in Chile (Maksaev et al., 1984). Another possible center, according to aeromagnetic studies, is in the Zancarrón Cordillera (Fig. 2; Litvak et al., 2005a). The Doña Ana volcanics are calc-alkaline rocks whose parental magmas formed in the asthenospheric wedge and erupted through a crust of normal thickness (30–35 km). This volcanic activity developed in a subduction-related setting influenced by an extensional tectonic regimen, as evidenced by the eruption of the Máquinas basalt (Ramos et al., 1989; Kay et al., 1991). This extensional regime is well developed in the El Teniente

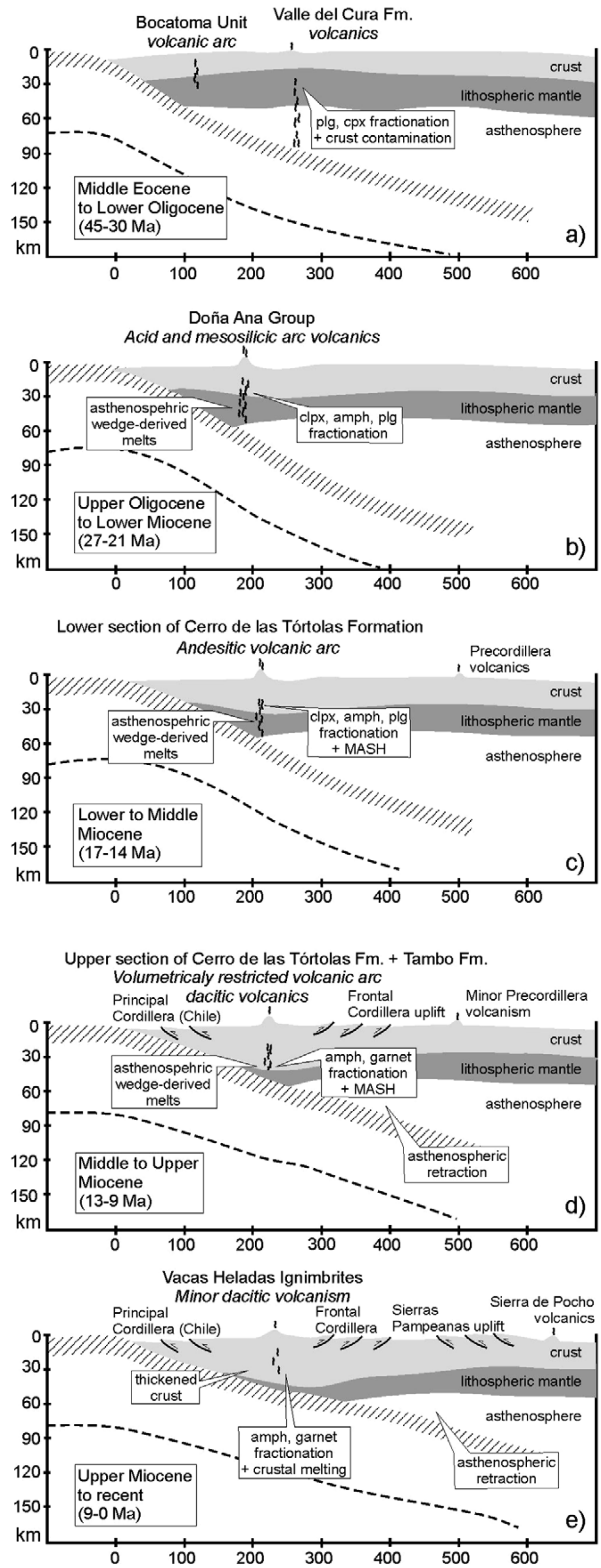

Fig. 11. (a)–(e) Consecutives stages of the geodynamical evolution model proposed for the Tertiary magmatic history of the Valle del Cura over the Pampean flatslab segment at approximately 29–30°S.

region, where normal fault-related depositional basins described by Charrier et al. (2002) inverted in the latest early Miocene (Kurtz et al., 1997; Godoy et al., 1999).

By the end of the early Miocene, the tectonic regimen in the El Indio/Valle del Cura region had become compressional (Kay et al., 1987). The cause of this change could be related to the subduction of the Juan Fernandez Ridge, which arrived at the northern extreme of the flatslab segment at 18 Ma (Yañez et al., 2001). During this time (18–16 Ma), the volcanic activity decreased and is represented only by the younger andesitic lavas of the Escabroso Formation. This period ended with the migration of the volcanic front to the east (Maksaev et al., 1984) as a result of the flattening of the subducted slab (Kay et al., 1987, 1991; Kay and Abruzzi, 1996).

Cerro de las Tórtolas volcanism represents the mid- to early late Miocene peak of andesitic and dacitic magmatism, which characterizes this part of the Andes (see Kay et al., 1991; Kay and Mpodozis, 2002). The volcanic front was located on the western margin of the Valle del Cura. These volcanics formed from asthenospheric wedge-derived melts, but two contrasting stages are recognized (Fig. 11c and d). In the first stage, melts (lower Cerro de las Tórtolas Formation, 16–14 Ma) last equilibrated at crustal depths, where pyroxene and amphibole are residual phases (30–35 km). These melts evolved in a compressive tectonic regimen across the crust in intermediate magmatic chambers, where they were differentiated through MASH processes (Kay et al., 1987; Hildreth and Moorbath, 1988). As the Juan Fernández Ridge begins to subduct, subduction erosion processes also affected the evolution of the magmas.

As a consequence of the gradual flattening of the subduction angle and the increase of the compression regimen, the volume of the asthenospheric wedge was reduced below the main arc (Kay and Abruzzi, 1996), leading to a decrease in magmatic activity (Fig. 11d). The newly generated melts produced the younger Cerro de las Tórtolas Formation magmas (13–10 Ma), which require a garnet-bearing residual mineral assemblage and indicate higher pressure conditions in the melt generation site. This high-pressure condition is consistent with tectonic shortening and crustal thickness in a contractional setting. The smaller volume Tambo Formation also erupted at this time. The presence of titanite (Litvak and Poma, 2004) indicates very oxidizing conditions during the genesis of the Tambo magmas in accord with shallowing of the downgoing slab.

As the volcanic front gradually migrated to the East during the late Miocene, andesitic volcanism ended in the Valle del Cura as well as across the flatslab segment (Kay et al., 1988; Kay and Mpodozis, 2002). The final stage of volcanism in the Valle del Cura corresponds to the dacitic Vacas Heladas Ignimbrite. The remaining fluids and heat derived from the volcanic arc favored melting of the crust and contributed to the genesis of these rocks (Fig. 11e). The continuous broadening of the volcanic arc to the east, since the beginning of flat subduction by 18 Ma, is evidenced by a migration of volcanic activity to the foreland. Miocene volcanic sequences (16–6 Ma) are registered in the Precordillera (Limarino et al., 2002; Vergés et al., 2001) and as far from the trench as the Pocho volcanic field in the Sierra de Cordoba in the Sierras Pampeanas (Kay et al., 1988; Kay and Gordillo, 1994; Kay and Mpodozis, 2002).

6. Conclusions

The new chemical analyses of the middle Eocene–early Oligocene and Miocene volcanic rocks provide new constraints on the Tertiary magmatic history and evolution of the Valle del Cura belt in Argentina. These magmatic rocks record the Tertiary arc and near backarc magmatic evolution and tectonic setting of the Chilean (Pampean) flatslab region and the El Indio mineral belt. The first stage of volcanic activity in the middle Eocene–early Oligocene produced dacitic and rhyolitic lavas and ignimbrites in the Valle del Cura Formation. Their subdued arc trace elements and enriched isotopic signatures indicate that crustal components played a major role in the genesis of these retroarc magmas. Petrogenesis and the chemical signature of the Eocene magmatic unit are unique and independent from the younger upper Oligocene–late Miocene volcanic suite, which follow a difference trend. The chemistry of the subsequent upper Oligocene–early Miocene volcanic sequences show a more arc-like chemical signature consistent with their evolution in a mildly extensional retroarc basin. The chemistry of the middle Miocene magmatic rocks indicates more deep-seated magma equilibration in the crust and an increase in crustally derived components. This behavior fits with a combination of crustal thickening and forearc subduction erosion associated with a compressional regime linked to the shallowing of the downgoing slab and tectonic shortening.

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Appendix A

Major and most trace elements analyses were done at Cornell University. All samples were sawed into slabs, and fresh interior sections were chosen for whole-rock analysis. Slabs were broken into 0.25–0.5 cm size in a steel mortar; these pieces were pulverized in an aluminum oxide ceramic shatterbox. Major elements analyses were per-formed on a JEOL-733 Superprobe electron microprobe on glasses made from rock powders; $Li_2B_4O_7$ was used as flux in silicic glasses. Analyses correspond to averages of 4–6 spots in WDS mode with a 15 kV accelerating voltage, 15 nA beam current, 40 s count time, and 30 mm beam. Data were reduced using the Bence-Albee program. Typical 2σ precision is ±1–5% at >1 wt%. Trace elements analyses were carried out by Instrumental Neutron Activation Analysis (INAA) at Cornell University and provided results for La, Ce, Nd, Sm, Eu, Tb, Yb, Lu, Sr, Ba, Cs, U, Th, Hf, Ta, Sc, Cr, Ni, and Co. These analyses were done on approximately 0.5 g of sample powder packed in ultrapure Suprasil® quartz tubing. The INAA runs consisted of 11 samples and three internal standards (PAL, WBD, and SIT) irradiated in the TRIGA reactor at Ward Laboratory (Cornell University) at a power level of approximately 400 kW for 3–4 h. Samples and standards were counted for 4–10 h on an Ortec GeLi detector after 6 and approximately 40 days following irradiation. The INAA precision (2s) based on replicate analysis of basalt PAL is ±2–7% for most elements and between ±8–16% for U, Sr, Nd, and Ni. The detail of used techniques and standards can be found in Kay et al. (1987). Some trace element analyses were done in Xral Laboratory (Canadá) by inductively coupled plasma mass spectroscopic (ICP-MS), according the standards and procedures of the laboratory. In these cases, Rb, Nb, Y, and Zr elements were also measured for the analyzed rocks.

Sr and Nd isotopes were analyzed at Cornell University on a multicollector VG Sector 54 thermal ionization mass spectrometer. For lavas, approximately 250 mg of hand-picked sample chips (<50 mg per chip) were leached in hot 6 N HCl for 30 min and then dissolved in sealed 15 ml Savillex capsules with HF and HNO_3 acids. Sr and REE were separated using cation exchange columns with AG50W-x12 resin and 2.5 N and 6 N HCl as eluants. Nd was eluted using organically coated PFTE cation exchange resin and 0.16 N HCl. All ratios were measured by thermal ionization mass spectrometry. Sr and Nd ratios were corrected for mass fractionation assuming $^{86}Sr/^{88}Sr = 0.1194$ and $^{146}Nd/^{144}Nd = 0.7219$. The average measured value for the NBS987 Sr standard was $^{87}Sr/^{86}Sr = 0.710235 \pm 34$ (2σ), based on 67 analyses. The La Jolla Nd standard was $^{143}Nd/^{144}Nd = 0.511864 \pm 14$ (2σ) from July 1993 to August 1997, based on 10 analyses, and 0.511817 ± 12 (2σ) from August to November 1990, based on 15 analyses. The Ames Nd standard was $^{143}Nd/^{144}Nd = 0.512138 \pm 20$ (2σ), based on 10 analyses. The εNd values calculated assume $\varepsilon Nd = -15.15$ for the La Jolla standard.

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