Geofísica Internacional (1993), Vol. 32, Num. 4, pp. 617-631

Sr-Nd-Pb isotope and trace element geochemistry of calc-alkaline andesites from Volcán Colima, Mexico

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Received: November 30, 1991; accepted: January 12, 1992.

RESUMEN

Se reportan los datos de elementos traza y las composiciones isotópicas de Sr, Nd y Pb en andesitas calco-alcalinas del Volcán Colima y se comparan con otros centros volcánicos del Cinturón Volcánico Mexicano. Los patrones de elementos de Tierras Raras normalizados con respecto a condritas demuestran un enriquecimiento en Tierras Raras ligeras y anomalías despreciables de Eu. Otros diagramas multi-elementos normalizados con respecto a MORB y manto "primitivo" demuestran anomalías negativas de Ta y Ti en las andesitas de Colima. Las relaciones isotópicas varían de 0.70355-0.70358 para $^{87}Sr/^{86}Sr$, 0.51295-0.51298 para $^{143}Nd/^{144}Nd$, y 18.57-18.59, 15.56-15.58 y 38.27-38.31 para $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$, y $^{208}Pb/^{204}Pb$ respectivamente. Las relaciones isotópicas de Sr y Pb son significativamente menores y $^{143}Nd/^{144}Nd$ mayor que para la mayoría de las andesitas del Cinturón Volcánico Mexicano.

PALABRAS CLAVES: Colima, Cinturón Volcánico Mexicano, calco-alcalino, México.

ABSTRACT

We report Sr, Nd and Pb isotopic compositions and trace element data on calc-alkaline andesites from Volcán Colima and compare them with other volcanic centers of the Mexican Volcanic Belt. The chondrite-normalized REE patterns of Colima andesites show LREE-enrichment with negligible Eu anomalies. MORB and primitive mantle normalized multi-element plots show negative Ta and Ti anomalies in Colima andesites. The isotope ratios range from 0.70355-0.70358 for $^{87}Sr/^{86}Sr$, 0.51295-0.51298 for $^{143}Nd/^{144}Nd$, and 18.57-18.59, 15.56-15.58 and 38.27-38.31 for $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$, and $^{208}Pb/^{204}Pb$ respectively. The Sr and Pb isotope ratios are considerably lower and $^{143}Nd/^{144}Nd$ higher than in most andesites from the Mexican Volcanic Belt.

KEY WORDS: Colima, Mexican Volcanic Belt, calc-alkaline, Mexico.

INTRODUCTION

The Mexican Volcanic Belt (MVB) is a 20-150 km-wide and ~1,000 km-long structure that extends approximately E-W from Veracruz to near Puerto Vallarta (Mooser, 1972; Demant and Robin, 1975; Demant, 1978, 1981; Pal *et al.*, 1978; Negendank *et al.*, 1981, 1985; Nixon, 1982; Robin, 1982a, b; Verma, 1987, 1991; Verma and Aguilar-Y-Vargas, 1988). The western end of the MVB is dominated by three large intersecting graben systems and associated volcanic centers related to active reorganization of the North American - Pacific plate boundary (Luhr *et al.*, 1985; Allan, 1986; Allan *et al.*, 1991). From the graben intersection area, the Colima Rift Zone runs southward into the Manzanillo Trough, which probably merges with the Cocos-Rivera Plate boundary (Bourgois *et al.*, 1987).

Volcán Colima is located in the Colima Rift Zone, close to the Middle America Trench (MAT, Figure 1). Petrological and geochronological studies of the products of this volcano and the Colima graben have been reported by Luhr and Carmichael (1980, 1981, 1982), Allan and Carmichael (1984), Robin *et al.* (1987, 1990, 1991), Luhr *et al.* (1989), Luhr and Carmichael (1990) and Luhr (1992). Radiogenic isotope data have been reported only in abstracts (Carmichael and DePaolo, 1980; Verma and Luhr, 1990) or in an unpublished thesis (Heatherington, 1988). We present here our combined Sr-Nd-Pb isotope and trace element data on calc-alkaline andesites from Volcán Colima.

VOLCAN COLIMA

A simplified geologic map of the area is given in Figure 1, which also includes sample locations. During the last 50,000 years or so (Robin *et al.*, 1987), ancestral Volcán Colima began to grow to an eventual height of 4,100 m or more, before collapsing southward during a Mount St. Helens style avalanche about 4,300 years ago, which left a horseshoe-shaped caldera 5 km in diameter open to the south (Luhr and Prestegaard, 1985). Included in the present study is an andesitic scoria fragment (S-8.1) from a fall layer that may have erupted during caldera formation (Luhr and Carmichael, 1982). This sample is from a thick sequence of ash- and scoria-fall deposits on the NE flank of ancestral Volcán Colima, downwind from the active vent. The area shown as debris avalanche deposit on Figure 1 actually includes material from two or more distinct deposits. Stoopes and Sheridan (1992) dated an ear-

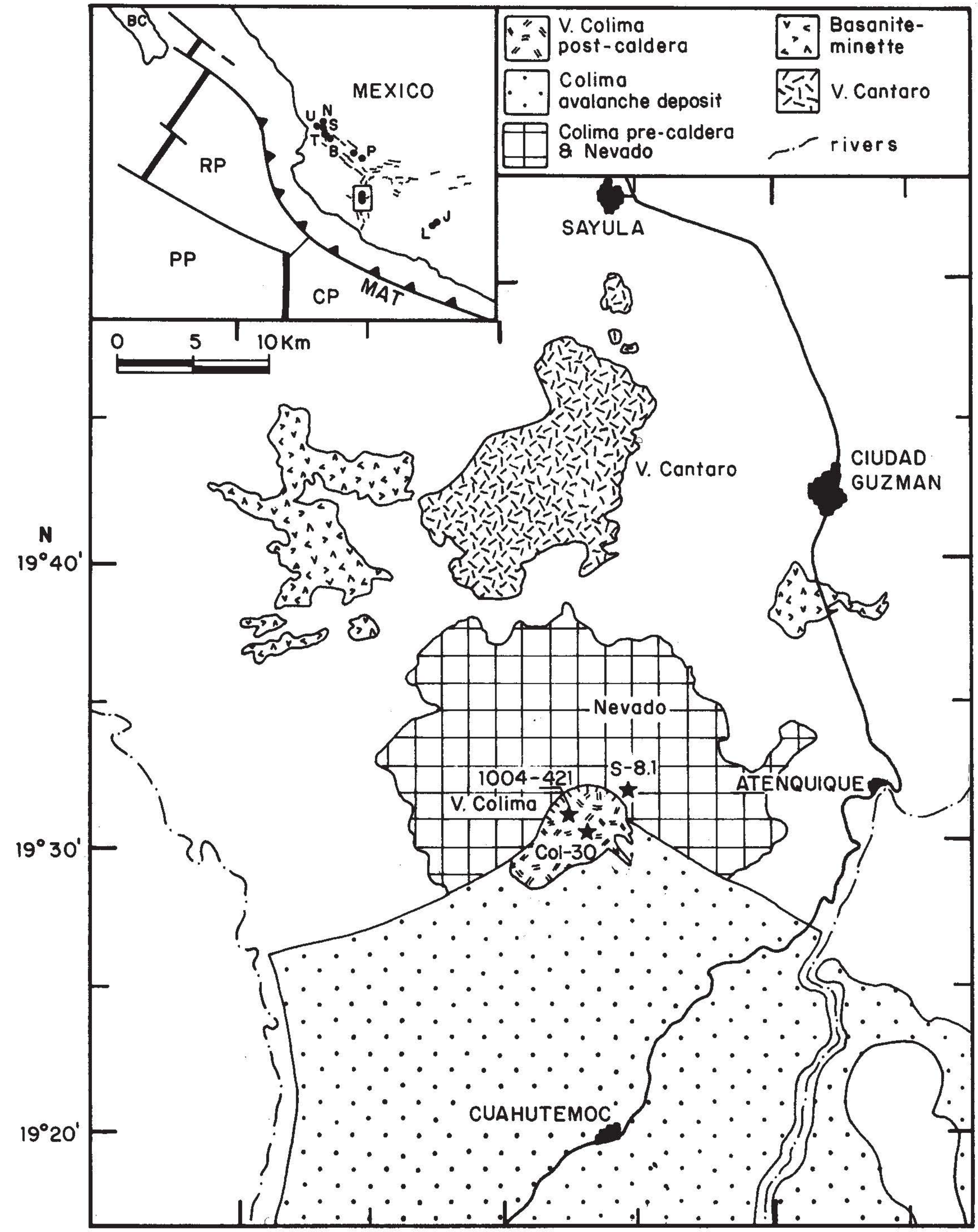

Fig. 1. Generalized location map of the area of study. Sample locations are shown by stars. Four towns along Hwy 54 are indicated. The map area is shown by a square on the inset map. Also on inset, other Quaternary volcanoes are shown by dots and labelled: U = San Juan, N = Las Navajas, S = Sanganguey, T = Tepetiltic, B = Ceboruco, P = Sierra La Primavera, J = Jorullo, L = La Pilita; important tectonic elements of the adjacent Pacific Ocean basin: RP = Rivera Plate, PP = Pacific Plate, CP=Cocos Plate, MAT = Middle America Trench.

lier collapse event at Nevado de Colima at 18,520 y.b.p. Robin *et al.* (1987, 1990) reported an age of 9,370 years for a debris avalanche from Volcán Colima. Multiple collapse events at Volcán Colima have also been proposed by Martin del Pozzo *et al.* (1990) and Siebe *et al.* (1992). Thus, some doubt now exists about the interpretation of Luhr and Prestegaard (1985) favoring a single collapse event at 4,300 years ago. Most of the missing volume of the ancestral cone has now been restored through repeated eruptions from Volcán Colima, which historically has been the most active volcano in Mexico and one of the most active in the Americas (Luhr and Carmichael, 1980). In this study we include, besides S-8.1, two historical andesites, Col-30 from the lava of 1982, and 1004-421 from the pyroclastic-flow deposit of 1913.

EXPERIMENTAL DETAILS

Major elements were determined by X-ray fluoresence (XRF) at Franklin and Marshall College on Li-tetraborate fused glasses. Accuracy (1σ) ranges from 1% to 5% for the major elements. FeO was determined by K-dichromate titration following the cold acid decomposition method of Wilson. Fe_2O_3 was then recalculated from the XRF value for total iron. LOI values are loss on ignition measurements at 1100°C for 50 minutes on powders dried for several hours at 110°C.

Trace element XRF analyses were carried out on pressed powder pellets by energy dispersive techniques at Univ. of California, Berkeley. Precisions are as follows: V=19%, Cu=8%, Zn=2%, Rb=3%, Sr=1%, Y=6%, Zr=2%, Ba=2%.

Other trace elements were determined by instrumental neutron activation analysis (INAA) at Washington University. Estimated counting errors (1σ) range from 1% to 5% for the INAA method.

The Sr, Nd and Pb isotopes were obtained using fully automated MAT 261 mass spectrometers. Sr was run on a double collector mass spectrometer using Ta-filaments. Nd and Pb were determined on a triple-collector system. More details are given in Verma *et al.* (1991a) and Verma (in preparation).

RESULTS AND DISCUSSION

Major elements

The major element data and corresponding CIPW norms are given in Table 1. All samples are q (quartz)-normative. Calc-alkaline volcanic rocks from the main edifice of Volcán Colima show only limited variations in silica content on the order of 2 wt.%, although other samples from this volcano range to lower values (Figure 2). As shown by Luhr and Carmichael (1980), major and trace element abundances among the Colima andesites are largely consistent with simple fractional crystallization from a mafic parent. A primitive basalt (SAE-22E) that is a likely parent to the calc-alkaline andesites of Volcán Colima was described by Luhr and Carmichael (1981) from a cinder cone on the eastern flank.

Trace elements

Table 2 gives the trace element data for these samples. The combination of chondrite, MORB and primitive mantle normalized multi-element plots is adopted following the recommendation of Rock (1987). Chondrite-normalized rare-earth (REE) concentrations are plotted in Figure 3. The chondritic values used are those of Nakamura (1974)

Table 1

Major element chemistry and CIPW norms of calc-alkaline rocks from Volcán Colima

	Col-30	1004-421	S-8.1
SiO_2	58.54	56.88	55.67
TiO_2	0.72	0.79	0.66
Al_2O_3	17.41	17.58	16.89
Fe_2O_3	2.32	3.00	2.52
FeO	3.72	3.42	3.99
MnO	0.12	0.11	0.11
MgO	4.42	4.11	5.70
CaO	6.50	6.92	6.96
Na_2O	4.54	4.45	3.97
K_2O	1.18	1.09	0.94
P_2O_5	0.19	0.19	0.16
LOI	0.22	0.97	1.89
Sum	99.88	99.51	99.46
Mg-V	60.11	57.08	64.34
q	7.45	7.08	5.91
or	7.00	6.54	5.69
ab	38.55	38.21	34.43
an	23.72	25.14	26.12
di-mg	4.52	5.47	5.17
di-fe	1.41	1.26	1.38
hy-mg	8.95	7.85	12.15
hy-fe	3.21	2.07	3.73
mt	3.38	4.41	3.74
il	1.37	1.52	1.28
ap	0.45	0.46	0.39
Salic	76.72	76.97	72.15
Femic	23.29	23.05	27.86
C.I.	39.74	42.44	45.79
D.I.	53.00	51.82	46.03
S.I.	27.32	25.58	33.29
A.R.	1.63	1.58	1.52

Col-30: andesitic lava erupted in 1982 (lat. 19°30.4' long. 103°37').

1004-421: hornblende andesite scoria from upper levels of intra-caldera 1913 pyroclastic-flow deposit (lat. 19°31' long. 103°37.4').

S-8.1: hornblende andesite scoria from upper levels of scoria-fall layer probably related to caldera formation (4,300 ybp) (lat.19°31.8' long. 103°35.25').

The CIPW norms are calculated using a computer package (RIGD) developed at IIE (Verma *et al.*, 1991b). Salic=sum of salic normative minerals; Femic=sum of femic normative minerals; C.I.=crystallization index; D.I.=differentiation index; S.I.=solidification index; A.R.=alkalinity ratio.

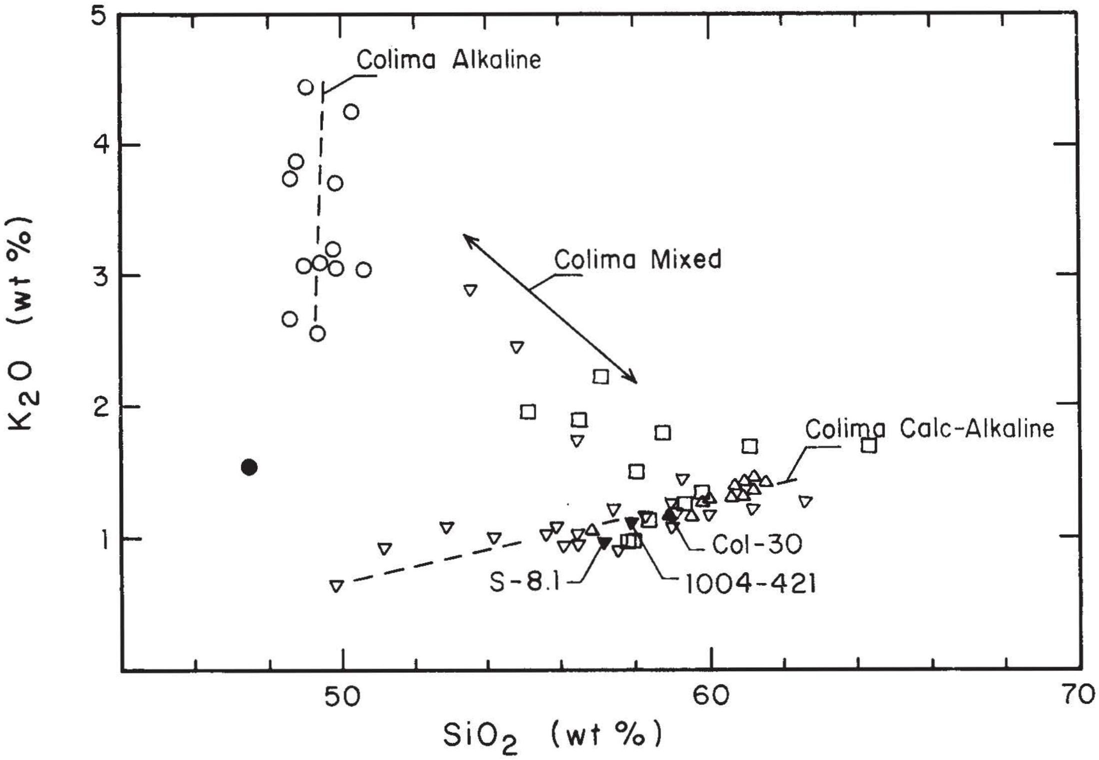

Fig. 2. Whole-rock concentrations of K_2O and SiO_2 (normalized to 100% volatile free with all Fe as FeO) for the samples discussed in this paper (solid triangles for Col-30, 1000-421 and S-8.1) and other samples from the same suites (open triangles). Triangles and inverted triangles indicate lavas and scoriae, respectively, from Volcán Colima (Luhr and Carmichael, 1980). Circles represent the basanites and minettes of the Colima alkaline suite (Luhr and Carmichael, 1981). The filled circle is basanite ash A38 from the Colima pyroclastic series (Luhr and Carmichael, 1982). Squares are clasts from the Colima avalanche deposit, including mixed calc-alkaline/alkaline sample M82-4 (unpublished data).

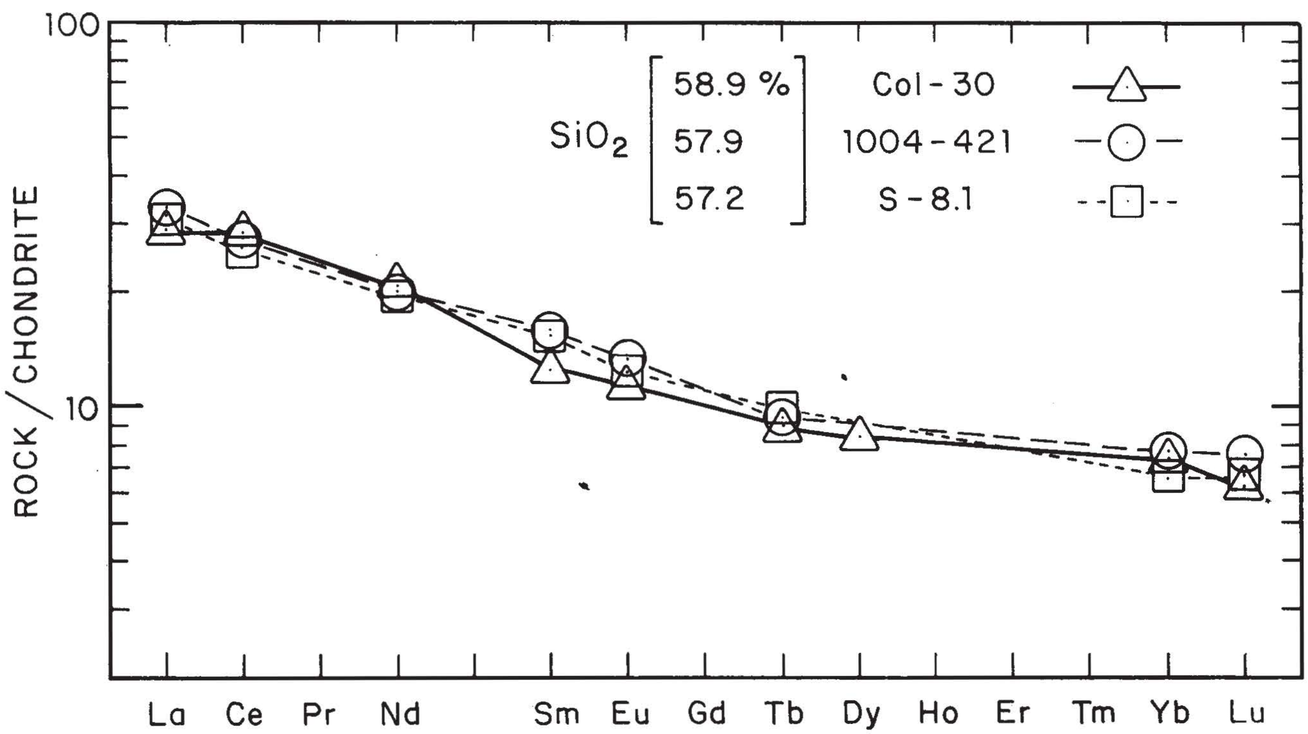

Fig. 3. Chondrite-normalized rare-earth element plots for calc-alkaline andesites from Volcán Colima. The symbols used are [illegible]iangles for Col-30, circles for 1000-421 and squares for S-8.1. The chondritic values for normalization are from Nakamura (197[illegible]) [illegible] Haskin *et al.* (1968).

Table 2

Trace element data on calc-alkaline rocks from Volcán Colima

	Col-30	1004-421	S-8.1
Sc	15.12	17.78	18.92
V	128	138	199
Cr	74	60	193
Co	17.50	19.60	23.60
Ni	30	<33	77
Cu	24	14	35
Zn	62	65	59
Rb	20	19	12
Sr	558	583	597
Y	17	16	18
Zr	120	125	121
Cs	0.56	0.47	0.38
Ba	421	416	382
La	9.4	10.8	10.6
Ce	24.4	24.1	23.0
Nd	13.1	12.9	12.9
Sm	2.56	3.27	3.15
Eu	0.88	1.02	0.93
Tb	0.42	0.44	0.44
Dy	2.89		
Yb	1.61	1.64	1.46
Lu	0.210	0.255	0.232
Hf	2.88	3.14	2.79
Ta	0.192	0.204	0.167
Th	1.38	1.38	1.27
U	0.54	0.61	0.52

by isotope dilution for all elements, except Tm from Haskin *et al.* (1968) by INAA. All samples are light-REE enriched with negligible Eu-anomalies. Their La/Yb and La/Sm ratios range from 5.8 to 7.3 and 3.3 to 3.7 respectively. For comparison, the chondritic La/Yb and La/Sm ratios are about 1.5 and 1.6 respectively. The absence of negative Eu anomalies in the REE patterns of these andesites may indicate that plagioclase fractionation did not dominate the differentiation of the parental magmas.

We present in Figure 4 multi-element MORB-normalized plots for our andesite samples because no basalts were analyzed in this study (Pearce, 1982). The patterns show large negative Ta and small negative Ti anomalies in all three samples. Negative Nb, Ta and Ti anomalies are considered characteristic of the subduction-related magmas (e.g., Saunders *et al.*, 1980; Green, 1981; Pearce, 1982; Morris and Hart, 1983; Ryerson and Watson, 1987). A Thompson (1982)-type multi-element diagram is given in Figure 5 (using the normalizing values of the primitive mantle from Sun and McDounough, 1989). The Ta and Ti anomalies are similar to those in the earlier diagram (Figure 4).

Radiogenic isotopes

Table 3 presents the data on Sr and Nd radiogenic isotopes for Volcán Colima. The Pb isotopic data are given in Table 4 and compared with other volcanoes and mineral deposits from the MVB. The measured isotope ratios can be taken as the initial ratios, because "in-situ" radiogenic growth correction is extremely small, given the very young age of the andesites from Volcán Colima.

Table 3

Sr and Nd isotope data on calc-alkaline rocks from Volcán Colima

	Col-30	1004-421	S-8.1
$^{87}Sr/^{86}Sr$	0.703573±27	0.703554±23	0.703577±34
$^{143}Nd/^{144}Nd$	0.512984±23	0.512943±23 0.512959±19	0.512941±16
ϵ_{Nd}	6.7±0.4	5.9±0.4 6.3±0.3	5.9±0.3

The $^{87}Sr/^{86}Sr$ ratios are normalized to $^{86}Sr/^{88}Sr$=0.11940 and adjusted to NBS-987 $^{87}Sr/^{86}Sr$ ratio of 0.710230. The measured $^{87}Sr/^{86}Sr$ ratio for the NBS-987 standard was 0.710202±22 (1σ; n=15), using Ta filaments during September-December, 1986. The $^{143}Nd/^{144}Nd$ ratios are normalized to $^{146}Nd/^{144}Nd$=0.72190 and adjusted to La Jolla $^{143}Nd/^{144}Nd$ ratio of 0.511860. The measured $^{143}Nd/^{144}Nd$ ratio for the La Jolla standard was 0.511833±12 (1σ; n=82) during the period of measurement of about one year (September, 1986 - August, 1987).

$\epsilon Nd = [((^{143}Nd/^{144}Nd)_m/(^{143}Nd/^{144}Nd)_{CHUR})-1]10^4$ (DePaolo and Wasserburg, 1976), using $(^{143}Nd/^{144}Nd)_{CHUR}$= 0.512638.

The analytical uncertainties quoted for Sr and Nd isotopic ratios are two times the standard error of the mean ($2\sigma_E$) multiplied by 10^6.

The Sr isotopic data for Volcán Colima are compared in Figure 6 with other andesites from the MVB. Within the uncertainties of the analyses, the three calc-alkaline andesites from Volcán Colima are isotopically identical in Sr, showing no systematic variations with SiO_2 content (Figure 6). They also have very low $^{87}Sr/^{86}Sr$ ratios (0.70355-0.70358) as compared to most other andesites. The exceptions are two Miocene basaltic andesites from Arandas-Atotonilco area (Verma *et al.*, 1985), which have slightly lower values (0.70331 and 0.70344; Figure 6). The only other sample with a low Sr isotopic ratio (0.70344; Verma

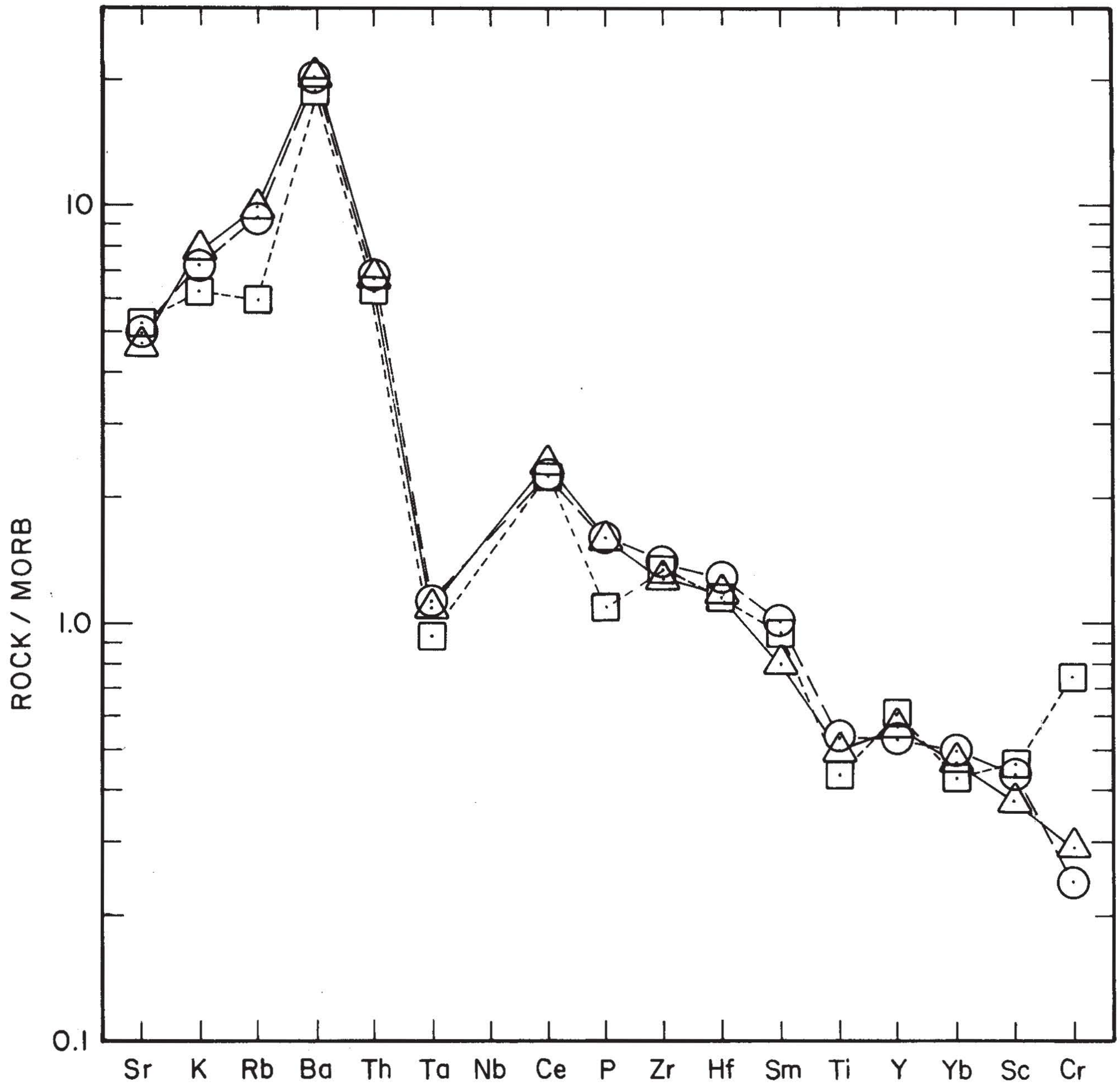

Fig. 4. Multi-element MORB-normalized plots for calc-alkaline andesites from Volcán Colima. For symbols, see explanations of Fig. 3. MORB values for normalization are from Pearce (1982).

and Dobson, 1987) is a basaltic andesite from a locality close to the Los Azufres geothermal field. Earlier Sr isotopic data for andesites from Volcán Colima by Moorbath *et al.* (1978) are only slightly higher than our results (0.7037-0.7038; excluding the two basaltic andesites, which may in fact be alkaline basanites or minettes and not calc-alkaline rocks).

The combined Sr and Nd isotopic data for Colima andesites are plotted in Figure 7 and compared with other data from the MVB. All samples fall within the broad "mantle array". The Colima andesites have lower $^{87}Sr/^{86}Sr$ and higher $^{143}Nd/^{144}Nd$ than the andesites from Sanganguey and Tepetiltic areas (northwestern part of the MVB; Verma and Nelson, 1989a), Amealco caldera (central part of the MVB; Verma *et al.*, 1991a) and Los Humeros caldera (eastern part of the MVB; Verma, 1983).

Pb isotopic ratios from Table 4 are plotted in Figure 8. The andesites from Volcán Colima have the lowest Pb isotopic ratios of any andesites (Heatherington, 1988) or mineral deposits (Cumming *et al.*, 1979) from the MVB. Our results are also lower than the range of values recently reported by Mango *et al.* (1990) for volcanic rocks from

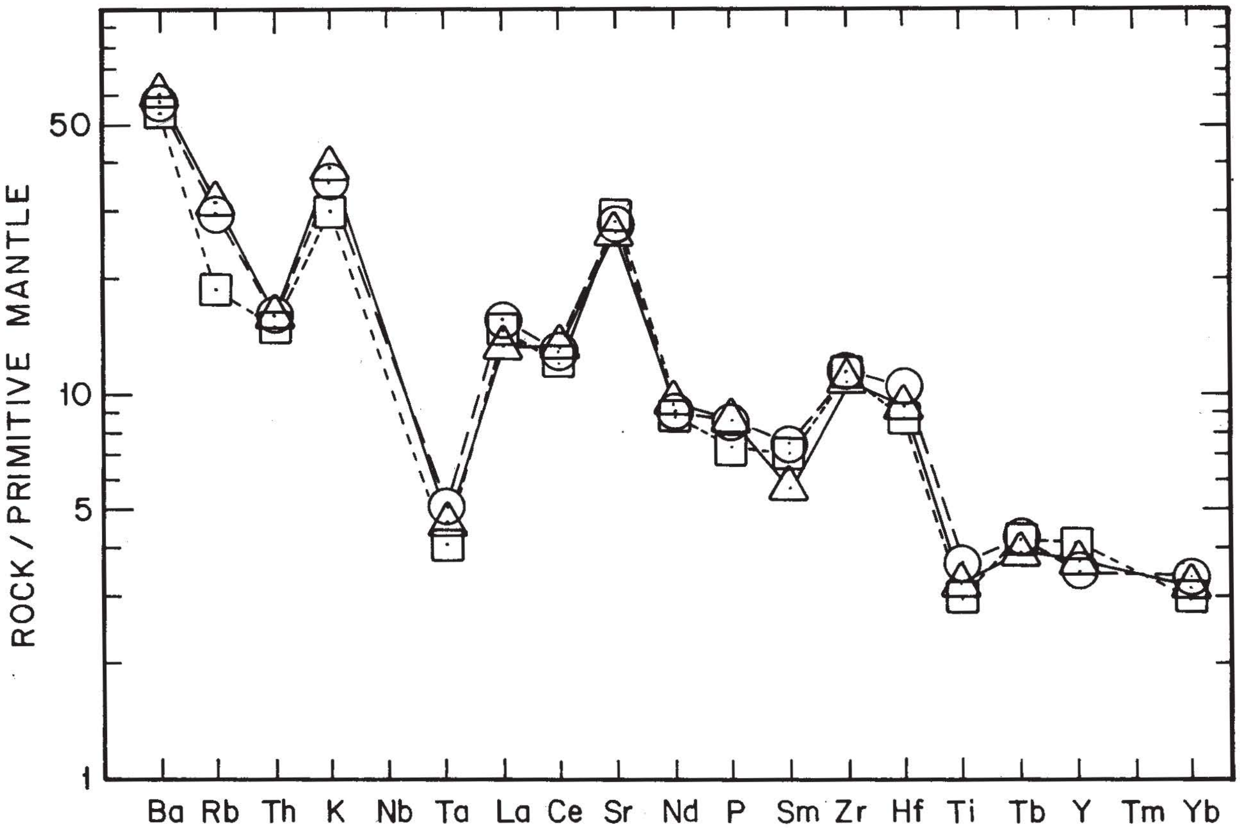

Fig. 5. Multi-element primitive mantle-normalized plots for calc-alkaline andesites from Volcán Colima. For symbols used, see explanation of Fig. 3. Primitive mantle values for normalization are from Sun and McDounough (1989).

Mexico. Plots of Pb isotopic ratios versus SiO_2 for the MVB andesites are given in Figure 9. Once again, the Colima andesites are characterized by low and uniform Pb isotopic ratios.

Low Sr and Pb and high Nd isotope ratios of the calc-alkaline andesites from Volcán Colima are probably consistent with their derivation from a source region less enriched in radiogenic isotopes and large-ion lithophile elements than elsewhere in the MVB. On the other hand, during their evolution from a mafic parent these andesites could also have assimilated a much smaller radiogenic crustal component than magmas in other areas of the MVB. The crust is likely to be more radiogenic than these andesites (e.g., Verma, 1984; Ruiz *et al.*, 1988a, b; Pier *et al.*, 1991) and its assimilation will therefore increase the Sr and Pb and decrease the Nd isotopic ratios.

CONCLUSIONS

Calc-alkaline andesites from Volcán Colima have LREE-enriched chondrite-normalized patterns with negligible Eu anomalies. Other multi-element plots show negative Ta and Ti anomalies with respect to MORB and primitive mantle. The Colima andesites are characterized by low Sr and Pb and high Nd isotopic ratios compared to most andesites from elsewhere in the MVB, suggesting their derivation from a less radiogenic source, or lower levels of crustal contamination.

ACKNOWLEDGEMENTS

Surendra Pal Verma is grateful to Al Hofmann for use of experimental facilities at MPI. His stay in Germany was funded by the Alexander von Humboldt Foundation. A. Patiño professionally drafted the figures for this paper.

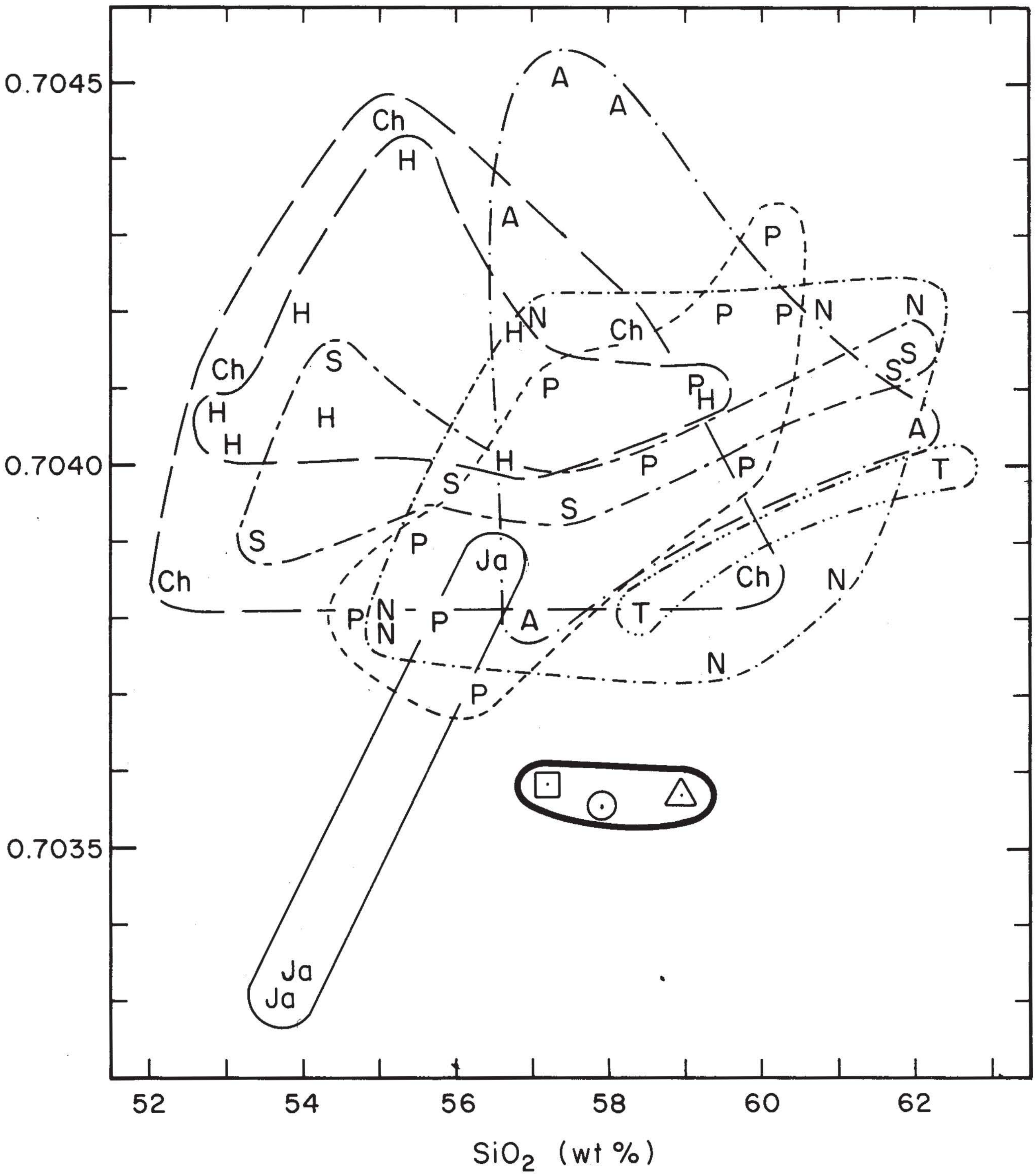

Fig. 6. Plot of Sr isotope ratios versus SiO_2 contents of calc-alkaline andesites from Volcán Colima and other centers of the MVB. The symbols for Colima samples are same as in Fig. 3. Other samples are shown by letters: S=Sanganguey area, T=Tepetiltic area (Verma and Nelson, 1989a, b); Ja=Arandas-Atotonilco area, NE Jalisco (Verma *et al.*, 1985); P=Paricutín (McBirney *et al.*, 1987); A=Amealco caldera (Verma *et al.*, 1991a); N=Nevado de Toluca area (Whitford and Bloomfield, 1976); Ch=Sierra de Chichinautzin (Verma and Armienta-H., 1985); H=Los Humeros caldera (Verma, 1983).

Table 4

Pb isotope data on calc-alkaline andesites from Volcán Colima and their comparison with Pb data from volcanoes and mineral deposits in the Mexican Volcanic Belt

	$^{206}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{208}Pb/^{204}Pb$	SiO_2(%)	Ref.
		VOLCANOES			
Colima:					
Col-30	18.568 ± 2 18.565 ± 2	15.564 ± 2 15.560 ± 2	38.261 ± 7 38.270 ± 6	58.88	t
Col-11	18.59	15.58	38.31	56.78	a
Col-2	18.58	15.55	38.29	61.16	a
Ceboruco:					
983-47	18.69	15.59	38.44	58.87	a
V. San Juan:					
1004-22	18.72	15.60	38.50	61.08	a
Jorullo volcano:					
Jor-11	18.65	15.62	38.38	54.80	a
Mascota:					
Mas-21	18.69	15.62	38.45	53.60	a
		MINERAL DEPOSITS			
Cuale (Jalisco):					
CL-CA	18.653	15.665	38.621		b
CL-CS	18.648	15.631	38.594		b
Etzatlan (Jalisco):					
76-ETZ-CAL	18.773	15.637	38.667		b
Angangueo (Michoacan):					
ANG	18.751	15.630	38.640		b

The Pb isotopic ratios measured in this work are corrected for fractionation estimated by running simultaneously the NBS-982 standard and are relative to values of $^{206}Pb/^{204}Pb$=36.73845, $^{207}Pb/^{204}Pb$=17.15946, $^{208}Pb/^{204}Pb$=36.74432, and $^{207}Pb/^{206}Pb$=0.46707 for this standard. The analytical uncertainties are the combined uncertainties in within-run statistics and in the estimation of fractionation correction, and are multiplied by 10^3.

Ref.: t = this work; a = Heatherington (1988); b = Cumming *et al.* (1979).

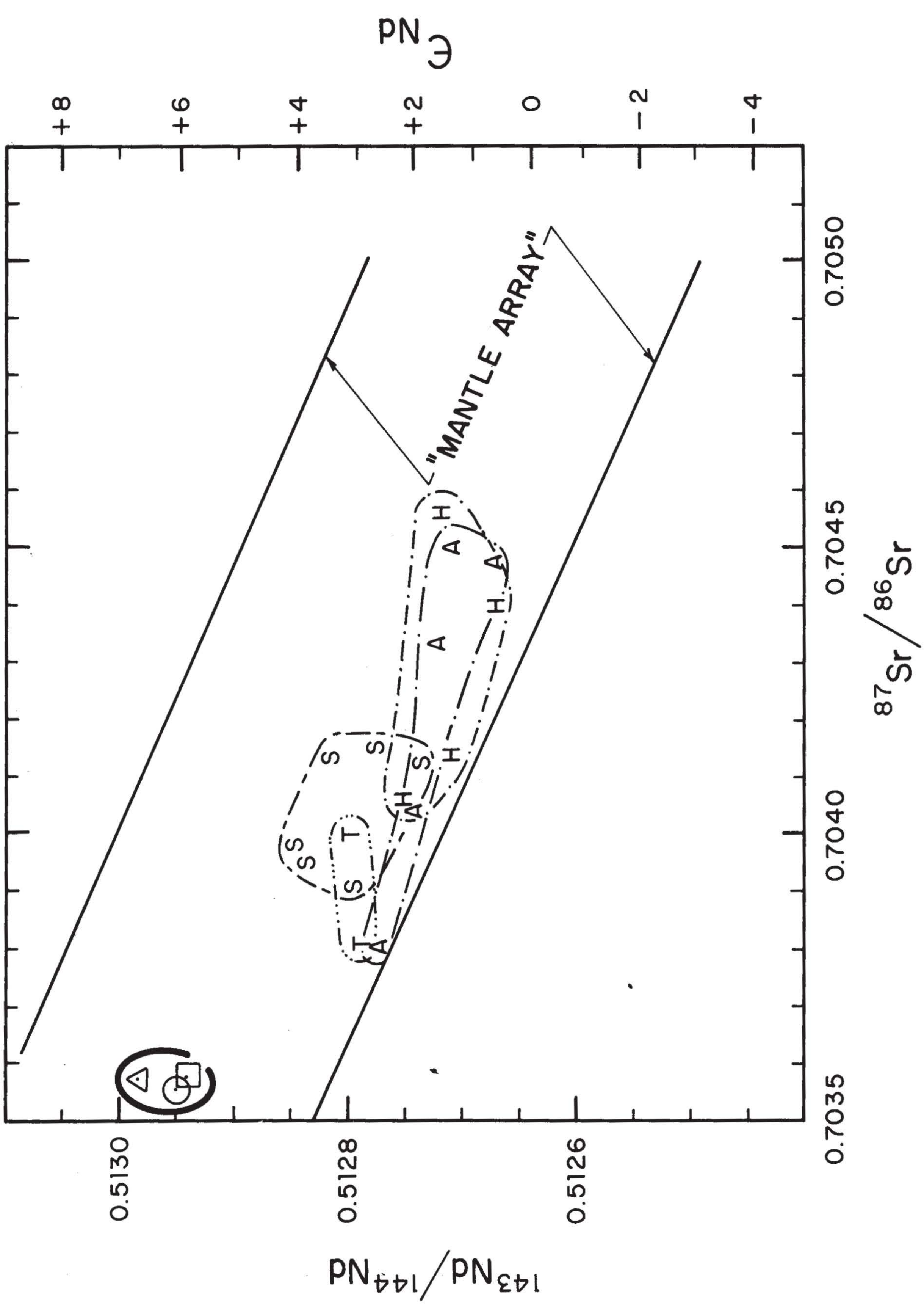

Fig. 7. Sr and Nd isotopic compositions for calc-alkaline andesites from Volcán Colima and other areas of the MVB. For symbols and letters used, see explanations of Figs. 3 and 6. The trace of the "mantle array" is shown for reference.

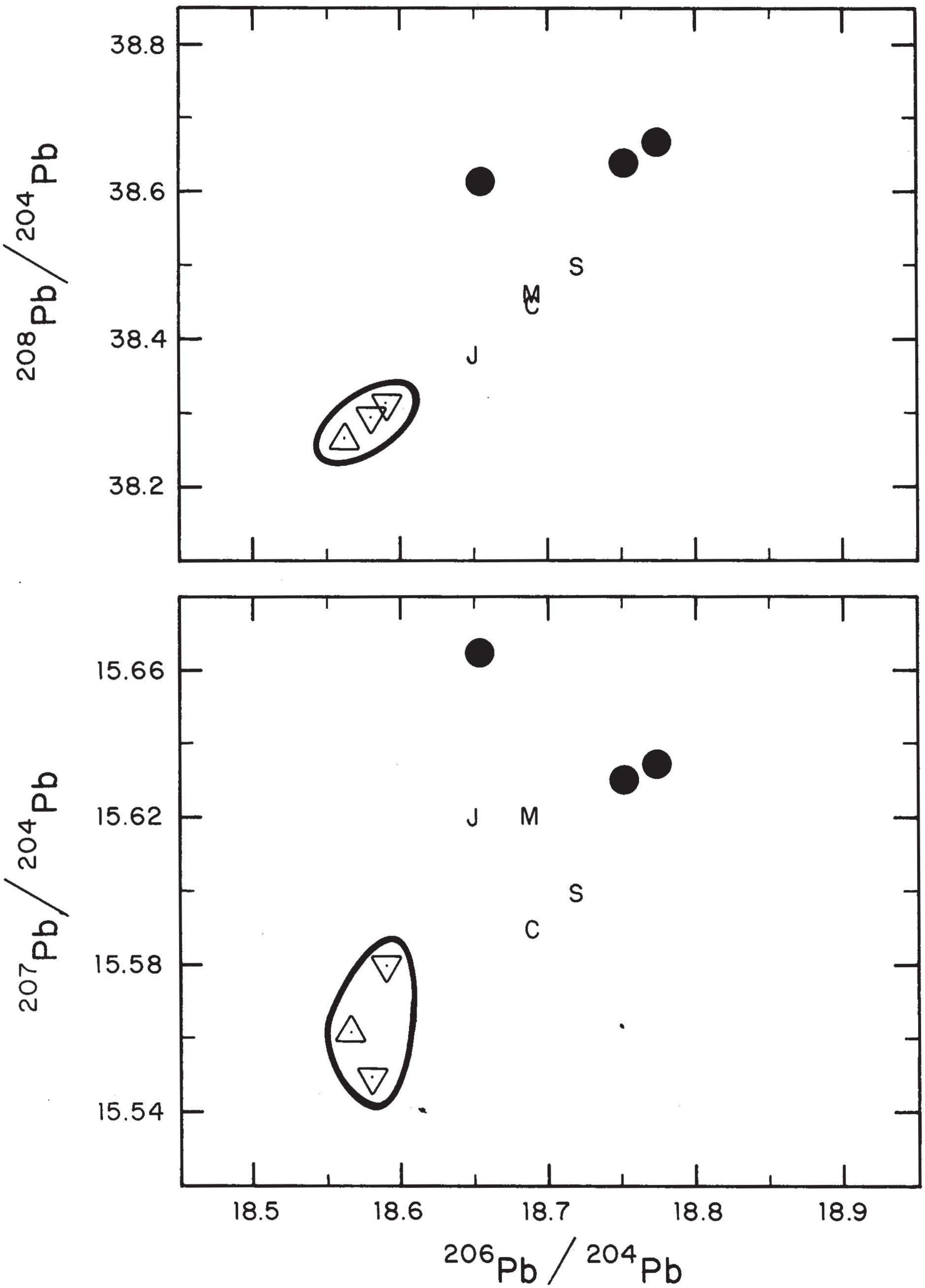

Fig. 8. Isotopic compositions of calc-alkaline andesites from Volcán Colima (open symbols) and elsewhere in the MVB (letters). The symbols are: triangles for Col-30; inverted triangles for Col-11 and Col-2. The letters are: C=Ceboruco; S=Volcán San Juan; J=Jorullo volcano; M=Mascota. For comparison, mineral deposits in the western and central MVB are shown by solid circles (see Table 4).

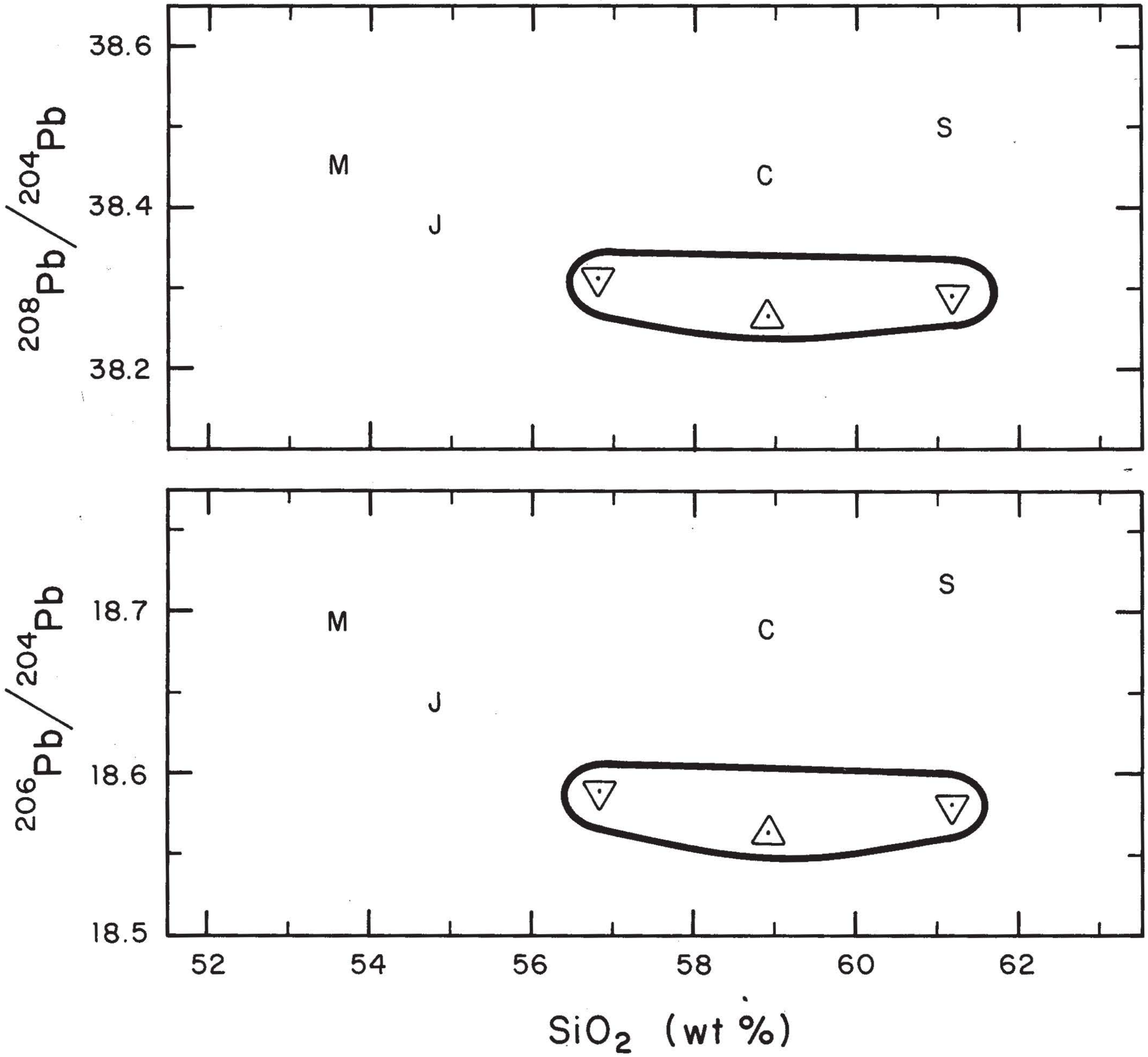

Fig. 9. $^{206}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$ versus SiO_2 contents, using symbols as in Fig. 8.

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