$^{87}Sr/^{86}Sr$, ALKALI AND ALKALINE EARTH ELEMENT GEOCHEMISTRY OF CHICHINAUTZIN SIERRA, MEXICO

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RESUMEN

Se reportan los contenidos de elementos álcali (K, Rb y Cs) y tierras alcalinas (Ba y Sr) así como también las razones de $^{87}Sr/^{86}Sr$ para ocho muestras seleccionadas de basalto y andesita de la Sierra de Chichinautzin y una muestra de dacita más vieja que aflora en el área. Los datos de elementos trazas son compatibles con la cristalización fraccionada de hornblenda, plagioclasa, olivino y piroxenas (en el orden aproximado de mayor a menor importancia). Las razones iniciales de $^{87}Sr/^{86}Sr$ varían de 0.7034 a 0.7045. En vista de estas y otras evidencias presentadas se favorece un origen en el manto para los magmas de Chichinautzin, con sólo una pequeña contribución de la corteza oceánica alterada o de la siálica continental.

ABSTRACT

Contents of alkali (K, Rb and Cs) and alkaline earth (Ba and Sr) elements as well as $^{87}Sr/^{86}Sr$ ratios are reported for eight selected samples of basalt and andesite from Chichinautzin Sierra and one sample of older dacite from this area. Trace element data are compatible with fractional crystallization of hornblende, plagioclase, olivine and pyroxenes (in approximately decreasing importance). Initial $^{87}Sr/^{86}Sr$ ratios range from 0.7034 to 0.7045. In the light of this and other evidence a mantle origin with only a small contribution from altered oceanic crust or sialic continental crust is favored for the Chichinautzin magmas.

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INTRODUCTION

The study area is located in the Valley of Mexico towards southern Mexico City and lies in the central part of the Mexican Volcanic Belt (MVB, Fig. 1). There are several different hypotheses (summarized below) on the origin of volcanism in this area.
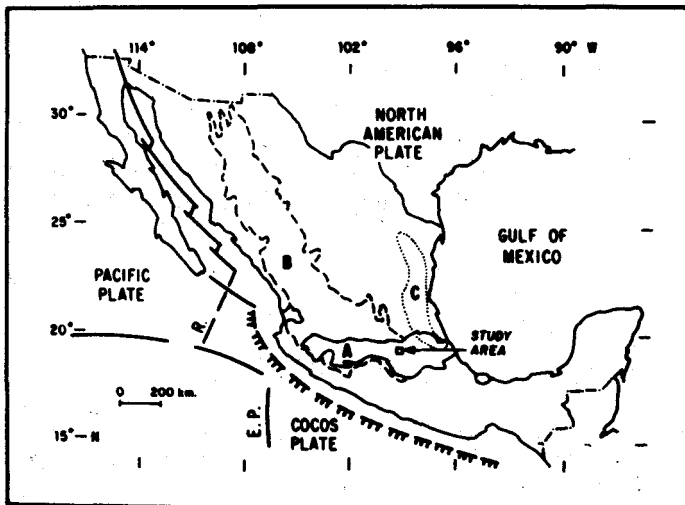

Fig. 1. Location of the study area (the map is simplified after López-Ramos and Sánchez-Mejorada, 1976 and Atwater, 1970). A = Mexican Volcanic Belt, B = Sierra Madre Occidental and C = Eastern Cordillera (all after Demant and Robin, 1975).

The Cocos plate is presently being subducted beneath the North American plate, along the Middle America trench (*e.g.*, Atwater, 1970; Karig *et al.*, 1978). We describe the results of a study of Sr isotopes and alkali and alkaline earth elements in eight selected samples of Quaternary to Recent basalts and andesites and one sample of older (perhaps Mio-Pliocene) dacite from the Chichinautzin Sierra.

PREVIOUS STUDIES

Valle de México (Valley of Mexico) has been the subject of several investigations. Humboldt (1808) carried out the first geological study in the area and provided a scientific explanation for the alignment of volcanoes in the MVB. A listing of other geological studies in this Valley is given by Martin del Pozzo (1983) who also presented a geologic and structural description of the corresponding monogenetic volcanism. Previous petrographic and geochemical investigations include those by Gunn and

Mooser (1971), Negendank (1972a, b; 1973a, b; 1976), Bloomfield (1975), Richter and Negendank (1976), Pérez-R. *et al.* (1979) and Demant (1981).

Several different hypotheses have been proposed for the origin of volcanism in this area. Mooser (1969) believes that the volcanism in the Valley of Mexico is related to old fracture system existent in the area and that it has no direct connection with the Middle America trench. Gunn and Mooser (1971) hypothesize that the andesites in the Valley of Mexico were produced by partial melting of tholeiitic to pyrolitic material without significant subsequent fractional crystallization and contamination. Negendank (1973a, b; 1976) proposes the derivation of these magmas from the lower crust. Richter and Negendank (1976) favor this alternative. Mooser (1972) and Pal and Urrutia-Fucugauchi (1977) propose an origin related to the subduction of Cocos plate along the Middle America trench. Nixon (1979) observes that the chemistry of basalts in the Valley of Mexico is compatible with their derivation as primary mantle melts, but does not mention the origin of andesites in this area.

A more recent hypothesis (Verma, 1983a, 1984a) of a mantle origin for Quaternary magmas in Los Humeros caldera (located about 180 km east of Mexico) may have some bearing on the petrogenetic processes in the Valley of Mexico. Verma (1983b) uses a compilation of Sr and Nd isotopic ratios in the MVB to conclude that the source of these magmas, including those in the Valley of Mexico, lies in the upper mantle and that the component of continental crust or subducted oceanic plate may be quite restricted.

Lavas in the western part of the Chichinautzin Sierra have been dated by C-14 and are found to lie between 8 400 and 40 000 yr B.P. (Bloomfield, 1975). Still younger C-14 date of 2 400 yr has been obtained on Xitle flow (southern part of Mexico City) by Libby (cited in Mooser *et al.*, 1958). Only normal magnetic directions were observed in the paleomagnetic studies carried out on lavas from this Sierra (Mooser *et al.*, 1974; Herrero B. and Pal, 1978). This observation poses an upper limit of about 0.7 Ma (Brunhes epoch) on the age of Chichinautzin volcanism (Herrero B. and Pal, 1978).

ANALYTICAL METHODS

Seven rock-cores were selected from fifteen paleomagnetic sites described by Herrero B. and Pal (1978). One olivine basalt sample (BCU-1) from Ciudad Universitaria

(also from Chichinautzin) and one dacite (DCC-1; perhaps of Mio-Pliocene age) from a road-cut on Mexico-Cuernavaca federal road were also included in this study. Sampling locations are shown on a simplified geologic map (Fig. 2). Their petrographic descriptions can be found in Herrero B. and Pal (1978) and Pérez-R. *et al.* (1979).
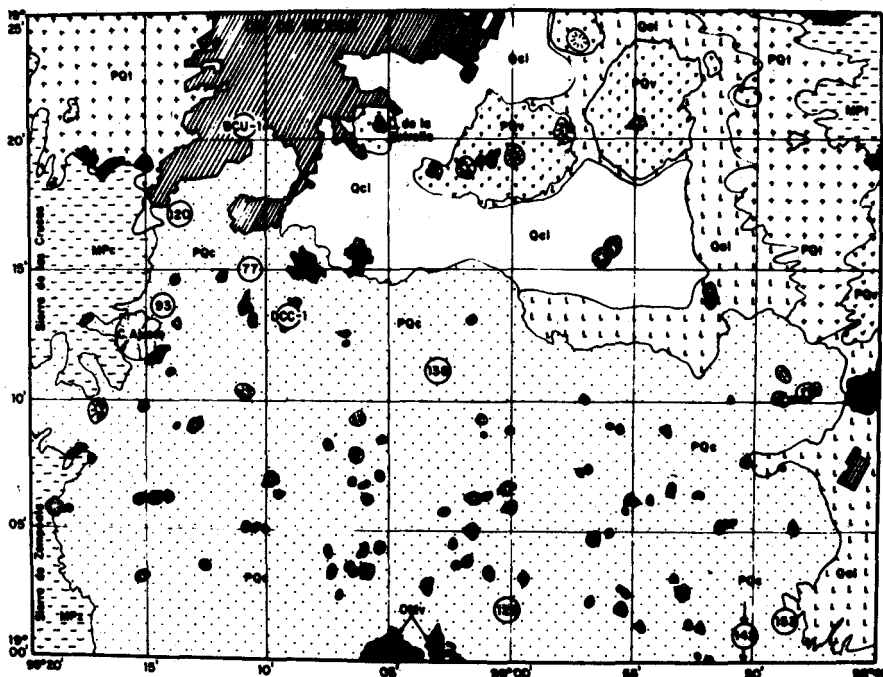

Fig. 2. A simplified geologic map of the area (modified after Schlaepfer, 1968), showing sampling locations. The encircled numbers and letters refer to sample identifications (see Table 1). Note that the sample 142 lies slightly below the place where it is marked (i.e., outside the map). Other symbols used are (in an approximate stratigraphic sequence from oldest to youngest rocks): OMv (midTertiary (?) volcanic rocks), MPc (Las Cruces FM; FM = Formation), MPz (Zempoala FM), MPt (Tlaloc FM), PQt (Tarango FM), PQv (Undifferentiated volcanic rocks), PQc (Chichinautzin FM; dotted area), Qal (Alluvium) and Qcl (Lake sediments).

The samples were washed with distilled millipore-filtered water and dried before crushing. Two samples (BCU-1 and DCC-1) were coarsely crushed and quartered. A representative fraction was pulverized in a ceramic disc-grinder to ~100 mesh. The rock-cores were broken into small pieces and ground in an automatic agate grinder.

K, Rb, Cs, Ba and Sr were measured by mass spectrometric isotope dilution (MSID). A V. G. Micromass 30 mass spectrometer at the University of Rhode Island (U. S.

A.) was employed for these as well as the isotopic analyses of $^{87}Sr/^{86}Sr$ ratios. The detailed experimental procedure is given by Verma (1981a).

RESULTS AND DISCUSSION

The rocks are classified as basalts, andesites and a dacite (Fig. 3) following the scheme of Peccerillo and Taylor (1976). All samples belong to the calc-alkaline series as is the case with most lavas in the western and central MVB (Pal *et al.*, 1978).
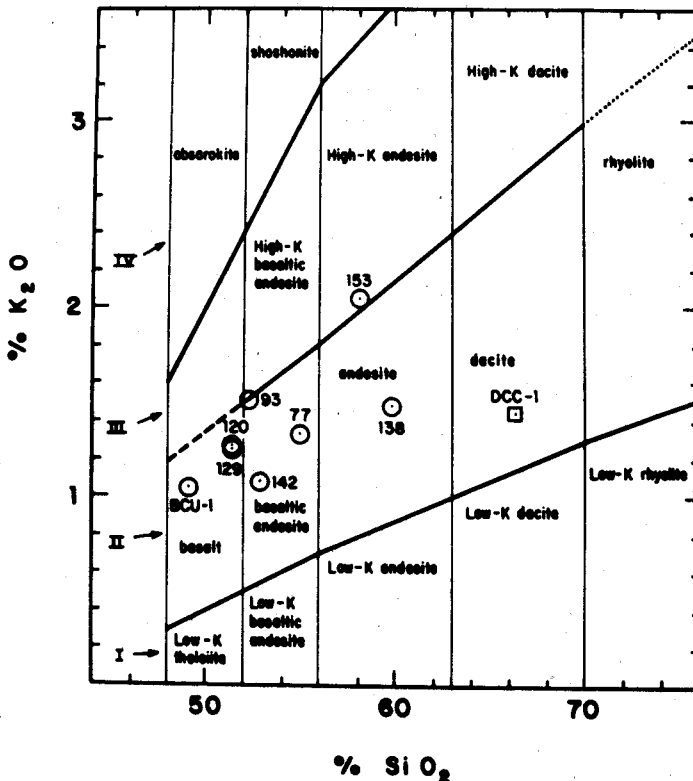

Fig. 3. A plot of K_2O versus SiO_2 for volcanic rocks from Chichinautzin (K_2O based on MSID K-values of Table 1). The boundaries and nomenclature shown are from Peccerillo and Taylor (1976). The sequences I through IV are: arc tholeiitic series (I), calc-alkaline series (II), high-K calc-alkaline series (III) and shoshonite series (IV). Note that a different symbol (square) is used for the older dacite sample.

The results of the mass spectrometric measurements of alkali and alkaline earth elements as well as $^{87}Sr/^{86}Sr$ ratios are given in Table 1.

Table 1   Analytical results on igneous rocks from the Chichinautzin Sierra, Mexico

Sample I.D.	Rock-type	SiO₂ *1	$^{87}Sr/^{86}Sr$ *2	Sr	K	Rb	Ca	Ba	Rb/Sr	$^{87}Rb/^{86}Sr$
BCU-1+	Basalt	49.1	0.70352 ± 5	532 ± 1.5	10530 ± 60	18.3 ±0.1	0.55 +0.01	295 ± 2	0.0344 ± 2	0.0985 6
77	Basaltic-andesite	55.0	0.70445 ± 5	460 ± 1.9	12250 ± 70	29.6 ±0.2	0.92 +0.02	441 ± 5	0.0643 ± 5	0.1842 15
93	Basaltic-andesite	52.2	0.70385 ± 4	513 ± 1.5	11030 ± 60	22.8 ±0.1	0.73 +0.01	369 ± 2	0.044 ± 2	0.1272 7
120	Basalt	51.4	0.70338 ± 4	518 ± 1.5	0990 ± 40	16.9 ±0.1	0.48 +0.01	272 ± 2	0.0326 ± 2	0.0934 6
129	Basalt	51.4	0.70366 ± 6	512 ± 1.7	8690 ± 40	13.6 ±0.1	0.41 +0.01	315 ± 2	0.0265 ± 2	0.0759 5
138	Andesite	59.8	0.70385 ± 7	506 ± 1.4	11950 ± 60	36.3 ±0.3	1.85 +0.02	370 ± 2	0.0717 ± 6	0.2054 18
142	Basaltic-andesite	52.9	0.70413 ± 5	398 ± 1	10330 ± 50	26.2 ±0.2	1.07 +0.01	323 ± 2	0.0658 ± 5	0.1894 15
153	Andesite	58.1	0.70418 ± 5	442 ± 1.2	12470 ± 70	35.0 ±0.2	1.61 +0.01	387 ± 3	0.0792 ± 5	0.2267 15
DCC-1	Dacite	66.3	0.70395 ± 3	501 ± 1.5	16990 ± 90	50.1 ±0.6	1.30 +0.01	483 ± 3	0.1000 ± 10	0.2860 40

*1 SiO₂ measured by gravimetry, following the method of López M. (1977).

*2 The measured $^{87}Sr/^{86}Sr$ ratios are normalized to $^{86}Sr/^{88}Sr = 0.11940$ and adjusted to SRM 987 $^{87}Sr/^{86}Sr$ ratio of 0.71021. The measured ratio for the SRM 987 standard is 0.710280 ± 40 (2σ, n = 18) during the period of measurements of about one year. In this period, E & A SrCO₃ standard gave a value of 0.708071 ± 34 (2σ, n = 9). The errors reported on individual $^{87}Sr/^{86}Sr$ ratios are two times the standard error of the mean multiplied by 10⁵. The initial $^{87}Sr/^{86}Sr$ ratios are practically the same as the measured ones for all samples including the older dacite (DCC-1). The error on Rb/Sr and $^{87}Rb/^{86}Sr$ is one standard deviation multiplied by 10⁴.

+ $^{143}Nd/^{144}Nd$ ratio has also been measured on this sample. A normalized and adjusted $^{143}Nd/^{144}Nd$ value of 0.51291 ± 3 is obtained (details on the technique can be found in Verma, 1983a; 1984b).

1. Trace elements.

Some trace element ratios in Chichinautzin rocks (excluding DCC-1) are K/Rb (range 329 - 640, average = 466); K/Cs (6 500 - 21 200, ave = 11 700); K/Ba (27.6 - 35.7, ave = 31), Rb/Sr (0.0265 - 0.0792, ave = 0.052), Ba/Rb (10.2 - 23.2, ave = 15), and 1 000 Cs/Rb (28.4 - 51, ave = 36). Most of these ratios for DCC-1 lie within or close to the range observed for the Chichinautzin group.
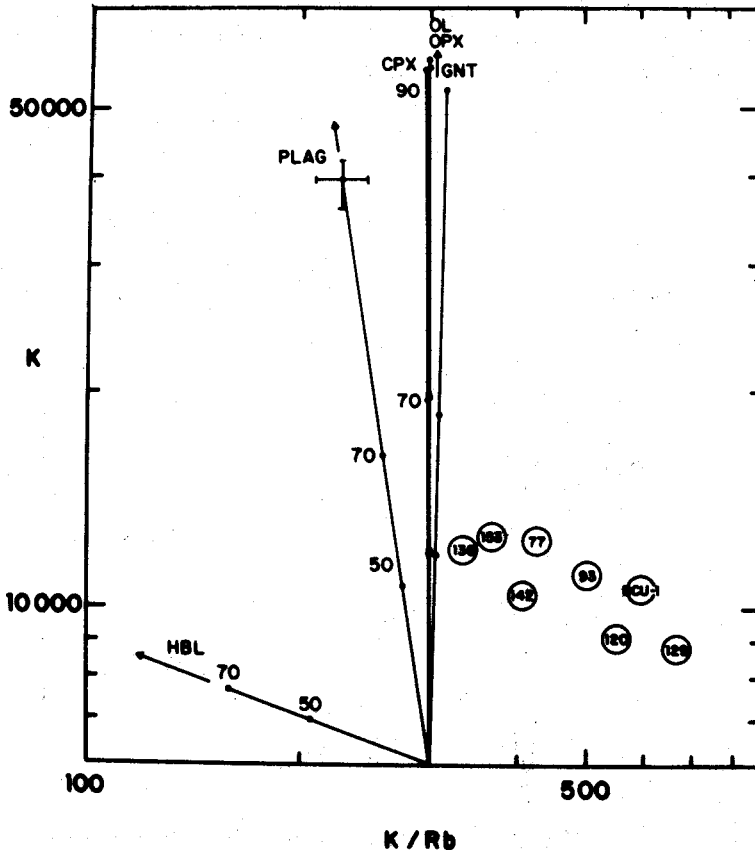

Fig. 4. A log-log plot of K versus K/Rb ratio for Chichinautzin rocks. The theoretical effects of fractional crystallization are shown by solid lines where HBL = Hornblende, PLAG = Plagioclase, CPX = Clinopyroxene, OPX = Orthopyroxene, OL = Olivine and GNT = Garnet. "Mafic" solid-liquid partition coefficients are used to construct these curves. The numbers on them are the % of minerals separated and the arrows give the possible direction of continued mineral separation. It should be pointed out that the theoretical curves in this as well as in Fig. 5 can be moved anywhere on the plot without changing their shape or size.

Several element versus element-ratio log-log plots are used to check whether these rocks could be related by fractional crystallization processes. One such plot of K versus K/Rb is given in Fig. 4. Theoretical curves are drawn using "mafic" solid-liquid partition coefficients (compiled by Verma, 1984a) and the well-known Doerner-Hoskins or Raleigh law for trace element distribution. The numbers on these curves represent the effect of a given percentage of fractional crystallization of the corresponding minerals. The error-bars on the plagioclase curve depict the possible effects on the predicted K concentration and the K/Rb ratio of the liquid remaining at 90% crystallization of plagioclase as the corresponding partition coefficients differ from the mean by ± 1 σ (one standard deviation).
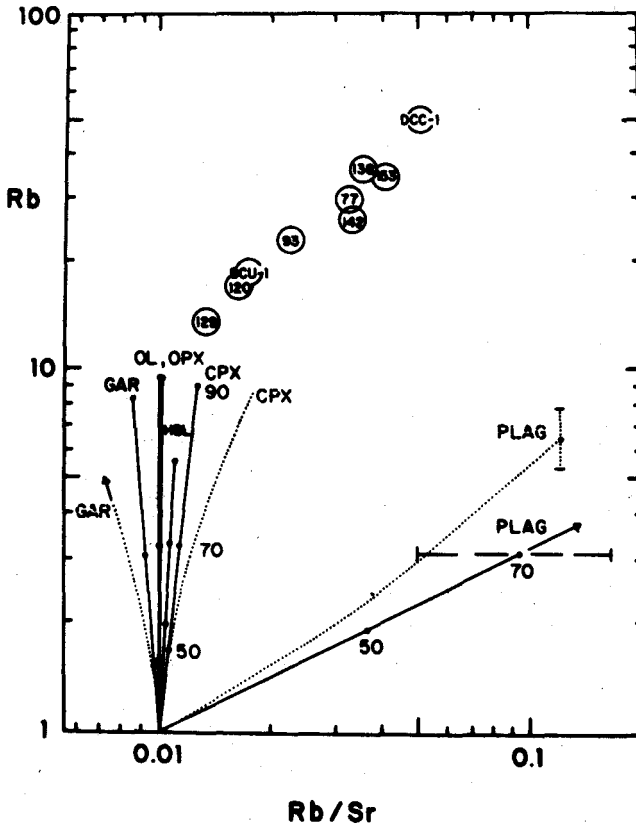

Fig. 5. A log-log plot of Rb versus Rb/Sr for Chichinautzin rocks and the theoretical fractional crystallization curves. The solid lines refer to logarithmic law (R = 0) whereas the dotted ones are for homogeneous law (R = 1). See explanation of Fig. 4 for more details.

Rb versus Rb/Sr plot is shown in Fig. 5. For the sake of illustration, two different (extreme) cases (R = 0: logarithmic law and R = 1: homogeneous law) are included in this figure. The plots given in Figs. 4 and 5 strongly suggest the role of hornblende and plagioclase (with some olivine and pyroxenes) in the fractional crystallization of these magmas. The involvement of garnet is ruled out by the REE data presented earlier (Pal and Urrutia-Fucugauchi, 1977).

Cs/Rb ratios in Chichinautzin magmas (ave = 36) are higher than those observed in most of the fresh basalts compiled by Hofmann and White (1983). Low-temperature seawater alteration can, however, enhance this ratio in oceanic basalts to values as high as 80 (Verma, 1981b). It is difficult to test the Cs/Rb data in terms of partial melting and fractional crystallization models as the corresponding partition coefficients for Cs are not readily available (Verma, 1984a).

In the absence of any microprobe mineral-composition data on the volcanic rocks from Chichinautzin Sierra, the fractional crystallization model can not be tested precisely using the available major-element whole rock data (Gunn and Mooser, 1971; Negendank, 1973a, b).

2. Sr isotope ratios.

Initial $^{87}Sr/^{86}Sr$ ratios in Chichinautzin rocks range from 0.70338 ± 4 to 0.70445 ± 5, averaging at 0.70388 ± 36 ($1\sigma \times 10^5$; n = 8). These ratios, though somewhat variable, are quite low and similar to other areas of the MVB and to circum-Pacific regions, including Central America (Verma, 1981c, 1984a).

These observations are compatible with the derivation of the MVB magmas (including those in the Chichinautzin) principally from the underlying mantle. Further support for a mantle origin of Chichinautzin magmas comes from one $^{143}Nd/^{144}Nd$ measurement (see footnotes Table 1) on a basalt sample (BCU-1) from Ciudad Universitaria. In $^{143}Nd/^{144}Nd$ versus $^{87}Sr/^{86}Sr$ diagram, this sample plots on the "mantle array" (DePaolo and Wasserburg, 1976; O'Nions et al., 1977; Cohen et al., 1980; Ito et al., 1981; also see Verma, 1983a). However, interpretations of Nd and Sr isotopic data by some authors (e.g., White and Hofmann, 1982; White and Patchett, 1984) favor a continental component in all island arc magmas, in addition probably to mantle and oceanic crust contributions, even for the arcs with the isotopic ratios

close to those of MORB (mid-ocean ridge basalts). Nevertheless, the component of an altered oceanic crust, subducted sediments or old sialic continental crust should be small in the magmas from the Chichinautzin Sierra.

An independent line of evidence comes from a study of [10]Be in one sample of Xitle lava flow (Chichinautzin group) from Tlalpan (Cuicuilco piramides, a few km south of Ciudad Universitaria). The results of this study (Louis Brown, Carnegie Institution of Washington, U. S. A., written communication, 1984) do not seem to support a component of subducted sediment in this magma. However, this single data can not be taken as a conclusive evidence because the uppermost sediment layers carrying most of the [10]Be may be scraped off in the subduction process (W. M. White, Max Plank Institut für Chemie, written communication, 1984).

Another plausible explanation for the small variations observed in the initial $^{87}Sr/$ ^{86}Sr ratios (0.7034 - 0.7045) could be the assimilation of the underlying continental crust by the mantle derived magmas (e.g., Briqueu and Lancelot, 1977). This mixing hypothesis was tested by plotting $^{87}Sr/^{86}Sr$ against 1/Sr, Ba/K, K/Rb and other ratios (plots not shown). Owing to rather large dispersion in most of these plots, no strong case could be made in favor of a simple assimilation-mixing hypothesis. However, with the data at hand it is not possible to rule out that the variability in trace elements and Sr-isotopes may partly be due to variation in contaminant composition (Myers et al., 1984).

The Benioff zone beneath the Chichinautzin Sierra is not very well defined and in fact, the area under study may be located more than 50 km beyond the "terminus" of the inclined seismic zone (Nixon, 1982). We may, therefore, suggest that the source of magmas in the study area lies in the mantle itself.

Other isotopic data, for example, $^{143}Nd/^{144}Nd$, $^{176}Hf/^{177}Hf$, $^{207}Pb/^{204}Pb$ and $^{206}Pb/$ ^{204}Pb, would certainly help in testing the various possibilities for the petrogenesis of these magmas (e.g., White and Patchett, 1984; White et al., 1984; Patchett et al., 1984; Verma, 1983a, 1984b). Furthermore, similar data on samples from the Cocos plate should be helpful not only for a better understanding of the petrogenesis in this area but also of the entire Mexican Volcanic Belt.

CONCLUSIONS

The following conclusions can be drawn from this study:

1 The rocks from the Valley of Mexico (Chichinautzin Sierra) belong to the calc-alkaline series.

2 Fractional crystallization of hornblende, plagioclase, olivine and pyroxenes (in approximately decreasing importance) is compatible with the trace element data presented.

3 The magmas most likely originated in the upper mantle, with only a small contribution from the altered oceanic crust, subducted sediments or sialic continental crust.

ACKNOWLEDGMENTS

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