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PRELIMINARY REPORT ON THE ANALYSIS OF SOME "IN-HOUSE" GEOCHEMICAL REFERENCE SAMPLES FROM MEXICO

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RESUMEN

Se colectaron 4 muestras de rocas ígneas de tamaño variable, 10 a 15 kg, en diferentes localidades de la República Mexicana, las cuales se trituraron y cuartearon con objeto de homogeneizarlas. Se analizaron por diversos métodos químicos y físicos, determinando su composición química tanto de elementos mayores como de varias trazas. Se ha establecido así un fondo de rocas estándares para uso interno del laboratorio, ya que estas muestras se han calibrado contra muestras de referencia geoquímica internacional. Se agrega una discusión de tipo petrológico y tectónico.

ABSTRACT

10 to 15 kg each of 4 samples of igneous rocks were collected from different places of Mexico, These were crushed and quartered in order to homogenize them and analyze their composition for major as well as several trace elements by chemical and physical methods. Thus a stock of standard rocks has been established for internal use of the laboratory because these samples have been calibrated against International geochemical reference samples. This report is complemented by a petrologic and tectonic discussion of these samples.

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INTRODUCTION

The need to prepare adequate reference materials for the standardization of instrumental analytical techniques and interlaboratory comparison has long been realized. Many organizations have prepared and 'certified' various international geochemical reference samples (Flanagan, 1969, 1973; Abbey, 1973, 1975, 1976; Abbey *et al.*, 1975; Russell *et al.*, 1968; Steale *et al.*, 1972; La Roche and Govindaraju, 1969, 1973, 1975; Roubault *et al.*, 1970; Ando *et al.*, 1971, 1974).

A complete list of reference samples for earth sciences is given by Flanagan (1974). Many of these reference samples have been analyzed in our laboratory and results sent to respective organizations. However, only very limited quantities (generally less than 100 g) of these samples are supplied to each laboratory. Therefore for routine work with instrumental techniques which are comparative and need standard samples for calibration, International reference samples cannot be employed for long. So there is a great need to prepare "in-house" standards and calibrate them against International standards for routine functioning of a laboratory.

This precisely constitutes a first step in our project "Muestras-tipo de la República Mexicana" ("Standard samples from de Mexican Republic" project).

This work reports collection, preparation and analysis of four "in-house" geochemical rock standards.

Samples

BCU-1 and BCU-2:	Olivine basalts from an outcrop behind underground paleomagnetic and nuclear geophysical laboratory, Ciudad Universitaria.
DCC-1:	Dacite from a road-cut near the 27 km marker on old Mexico-Cuernavaca road.
RSL-1:	Rhyolite from a road-cut on the Tepetate-San Luis Potosí road, about 16 km (NE) from Tepetate.

SAMPLE PROCESSING

The processing of the samples consists of the following steps: (1) examine rock specimens (~10-15 kg) for freshness; (2) break pieces with a sledge hammer and remove the outer weathered layer if present; (3) clean with deionized water; (4) pass through Chipmunk jaw crusher; (5) crush in ceramic disc grinder to about -80 mesh size; (6) mix manually; (7) quarter and store samples in several ~250 g portions in glass bottles. It should be mentioned that the ceramic plates used in the pulverizer-grinder cause very little contamination of the crushed sample.

EXPERIMENTAL DETAILS

Major elements

SiO_2 was determined gravimetrically (by weight) by direct evaporation with HF (Easton, 1972). For most other major elements a rock solution in first prepared by acid digestion with HF and $HClO_4$ (Volborth, 1969; Energlyn and Brealey, 1971; Obregón, 1973) and then Al, Ca, Mg, Mn and total Fe are determined by atomic absorption spectrometry; Na and K by flame photometry and P and Ti by colorimetry. Further details on the analytical methods used are given in López (1977).

Ferrous iron (FeO) is determined volumetrically by titrating an independent rock solution against potassium permanganate (Easton, 1972). H_2O^- (humidity) and H_2O^+ (combined water) are determined directly through weight loss at 105°C and 1000°C respectively. Finally CO_2 is determined by acid-base titration using a method slightly modified after that of Grimaldi *et al.* (1966).

Analyses on dry-basis are recalculated without water and CO_2 in order to avoid possible secondary effects of weathering and Fe_2O_3 was adjusted to 1.5% in order to avoid artificial oversaturation of the norm (Coombs, 1963; Kay *et al.*, 1970).

Trace elements

Instrumental neutron activation analysis (INAA) was used to determine the trace elements. The method is similar to that of Gordon *et al.* (1968) and has been described by Pal (1972) and Terrell and Pal (1977).

Results of these measurements on the Mexican standard rocks are given in Tables 1 and 2.

PETROLOGY

Sample BCU-1 in hand-specimens is aphanitic, with dark gray color. In thin section it shows a pilotaxitic porphyritic texture, with phenocrysts of labradorite (Michel-Levy's method) having twinning of albite and occasionally zoned, and some phenocrysts of olivine (2V > 80°), essentially magnesian. The matrix consists of largely basic glass (n > 1.6) with numerous microcrysts of magnetite. Limonite can be seen in thin-section as a product of secondary alteration. Sample BCU-2 is very similar to BCU-1 except that its structure is vesicular and contains chlorite as product of alteration.

Both rocks are extrusives and belong to the flows that cover a vast area to the South of Mexico City (Mooser *et al.*, 1974).

C.I.P.W. norm (Table 1) suggests these rocks to belong to the alkaline series as they contain normative olivine and fall in the area of the alkaline series on the $Na_2O + K_2O$ Vs SiO_2 diagram (Macdonald and Katsura, 1964), Their solidification index (S.I.) is high (Table 1) implying a low degree of differentiation (Kuno *et al.*, 1957; Kuno, 1969).

Sample DCC-1 shows a light green color and a compact structure. Microscopically it shows a holocrystalline porphyritic texture with the largest phenocrysts of biotite with oxidation on the edges and with cleavage. Plagioclase phenocrysts with carlsbad-albite twinning are also present; their composition varies from oligoclase to andesine (Michel-Levy's method). The matrix is of microcrysts of plagioclase (oligoclase-andesine), quartz and trydymite. Hematite, limonite and chlorite are present as alteration minerals. This rock is volcanic in character and belongs to a succession of flows and tuffs denominated Chichinautzin Group (Fries, 1960).

Sample DCC-1 can be classified as a quartz tholeiite as it contains normative quartz and hypersthene (Yoder and Tilley, 1962); according to the Na_2O + K_2O Vs SiO_2 diagram (Kuno, 1969; Schwarzer *et al.*, 1974), it belongs to the high alumina basalt series.

RSL-1 is light brown with compact structure and phenocrysts of quarts. Microscopically it has a porphyritic hypocrystalline texture with phenocrysts of quartz in a glassy matrix of acidic composition. Numerous microcrysts of K-feldspar and a few of magnetite are also observed in this section. Hematite, limonite, sericite and chlorite are present as alteration minerals.

This is a volcanic rock belonging to a thick sequence of lava flows of rhyolitic composition of Miocene age (Carta Geológica de la República Mexicana, 1976).

Due to the presence of normative quartz in its C.I.P.W. norm, RSL-1 belongs to the tholeiitic series, while Na_2O + K_2O Vs SiO_2 diagram shows it to belong to the group of high alkaline basalts. Its low S.I. (Table 1) suggests that RSL-1 is a strongly differentiated rock.

The contents of several trace elements in these rocks have been given in Tables 2 and 3. Fig. 1 shows the REE patterns based on the REE data of Table 2.

The REE patterns of these rocks are quite interesting. BCU-1 and BCU-2 have practically identical patterns clearly implying similar origins. DCC-1 is quite similar in its REE pattern to the basalts BCU's though the former is considerably lower in REE content. Presence or absence of an Eu anomaly cannot be ascertained. If present, it should be very small (Fig. 1). Negendank (1973), based on geochemical studies on the rocks from the Valley of Mexico, has postulated an origin from partial fusion of the lower crust. Similar REE patterns of dacite and basalts imply that these rocks are derived from a similar source and by a similar mechanism. Much more REE data are needed, however, before Negendank's hypothesis can be tested.

The rhyolite RSL-1 is characterized by a large negative Eu anomaly which could be interpreted as caused by plagioclase removal at shallow depths. Considerably large size of the Eu anomaly might however need a source with a negative Eu anomaly itself. The presence of Quaternary volcanism suggests the possibility of encountering magma chambers at relatively shallow depths in this area.

FUTURE WORK

This is the first step in a long-term project on Mexican Reference Samples for Geochemistry for which National and International collaboration would be sought. Naturally it will be necessary to handle sample quantities of the order of 100 Kg requiring special facilities not presently available to us: adequate means to assess sampling and subsampling errors by processing synthetic samples (e.g., Russell *et al.*, 1968) and by employing proper sampling constants (Ingamells and Switzer, 1973; Ingamells, 1974 a, b). The results of analyses by different laboratories will be compiled and treated statistically in order to finally "certify" the samples.

TABLE 1

CHEMICAL COMPOSITION AND C.I.P.W. NORMS[†] OF MEXICAN STANDARD ROCKS

	BCU-1		BCU-2		DCC-1		RSL-1	
	Actual Analysis	Dry-basis	Actual Analysis	Dry-basis	Actual Analysis	Dry-basis	Actual Analysis	Dry-basis
SiO_2	49.25	50.02	48.48	49.20	66.90	67.28	76.59	77.21
TiO_2	1.67	1.70	1.76	1.79	0.50	0.50	0.09	0.09
Cr_2O_3	0.41	0.42	0.43	0.44	0.05	0.05		
Al_2O_3	14.44	14.66	16.78	17.03	17.08	17.18	12.99	13.09
Fe_2O_3	2.73	1.50	1.25	1.27	3.21	3.50	1.15	1.16
FeO	5.84	7.08	6.98	7.08	0.62	2.18	0.20	0.20
MnO	0.15	0.15	0.15	0.15	0.07	0.07	0.02	0.02
MgO	9.14	9.28	8.95	9.08	1.17	1.08	0.05	0.05
CaO	9.98	10.14	8.25	8.37	3.59	3.61	0.08	0.08
Na_2O	2.90	2.95	3.58	3.63	4.21	4.23	1.72	1.73
K_2O	1.46	1.48	1.42	1.44	2.00	2.01	6.28	6.23
P_2O_5	0.50	0.51	0.51	0.52	0.13	0.13	0.03	0.03
CO_2	1.02		1.08		0.17		0.15	
H_2O^+	0.04				0.30		0.49	
H_2O^-			0.01		0.61		0.22	
TOTAL:	99.53		99.63		100.61		100.06	
QZ	-	-	-	-	25.83	25.08	42.38	42.73
CB	-	-	-	-	1.77	1.78	3.29	3.32
OR	8.63	8.76	8.39	8.52	11.82	11.89	37.11	37.41
AB	24.54	24.92	27.45	27.86	35.62	35.83	14.55	14.67
AN	22.07	22.42	25.52	25.90	16.96	17.06	0.20	0.20
NE	-	-	1.54	1.56	-	-	-	-
DI	19.23	19.72	9.70	9.85	-	-	-	-
HY	4.94	2.56	-	-	2.66	4.66	0.12	0.13
OL	9.97	14.12	18.76	19.04	-	-	-	-
MT	3.96	2.17	1.81	1.84	0.63	2.17	0.45	0.45
HM	-	-	-	-	-	-	0.84	0.85
IL	3.17	3.22	3.34	3.39	0.95	0.96	0.17	0.17
CR	0.84	0.85	0.88	0.89	0.10	0.10	-	-
AP	1.17	1.18	1.19	1.21	0.30	0.30	0.07	0.07
C.I.	48.69		46.76		18.94		0.29	
*S.I.	41.65		40.35		9.78		0.53	
D.I.	33.68		37.94		72.29		94.81	

[†] Washington (1917)

*C.I. Crystallization Index. S.I. Solidification Index. D.I. Differentiation Index.
(Thorton and Tuttle, 1960; Poldervaart and Parker, 1964).

TABLE 2

INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS OF SOME TRACE ELEMENTS OF MEXICAN STANDARD ROCKS

	BCU-1	BCU-2	DDC-1	RSL-1
Rb	43 ± 3	55 ± 5	60 ± 5	460 ± 20
Cs	0.5 ± 0.1	0.5 ± 0.1	0.9 ± 0.3	5.7 ± 0.2
Th	1.7 ± 0.3	2.3 ± 0.3	4.3 ± 0.3	43 ± 3
U	0.9 ± 0.3	1.4 ± 0.5	1.6 ± 0.5	7.6 ± 0.9
Hf	5.4 ± 0.5	5.5 ± 0.6	4.5 ± 0.5	6.9 ± 0.3
Ta	1.6 ± 0.3	1.5 ± 0.2	0.5 ± 0.2	3.3 ± 0.3
Co	44 ± 5	42 ± 5	12 ± 1	0.2 ± 0.1
Sc	26 ± 2	25 ± 3	10.6 ± 0.2	11.4 ± 0.3
Sb	1.5 ± 0.6	1.9 ± 0.7	2.0 ± 0.8	1.5 ± 0.6
Fe(%)	7.4 ± 0.7	7.5 ± 0.9	3.5 ± 0.1	1.2 ± 0.2
La	22 ± 2	21 ± 3	16 ± 2	74 ± 2
Ce	52 ± 2	53 ± 2	31 ± 2	125 ± 4
Nd	34 ± 2	40 ± 6	16 ± 1	83 ± 3
Sm	8.2 ± 0.6	7.8 ± 0.8	4.4 ± 0.2	20.3 ± 0.9
Eu	2.2 ± 0.3	2.1 ± 0.2	1.13 ± 0.09	0.25 ± 0.07
Cd	8 ± 1.5	8 ± 1.5	3 ± 1	9 ± 2
Tb	1.4 ± 0.2	1.4 ± 0.1	0.60 ± 0.05	1.4 ± 0.1
Dy	4.9 ± 0.8	5.1 ± 0.8	1.6 ± 0.6	13 ± 2
Tm	0.43 ± 0.08	0.32 ± 0.07	0.13 ± 0.04	0.64 ± 0.08
Yb	2.7 ± 0.4	2.7 ± 0.2	1.2 ± 0.1	5.3 ± 0.6
Lu	0.6 ± 0.2	0.45 ± 0.08	0.25 ± 0.06	0.9 ± 0.2
Σ REE	136.4	139.8	75.3	332.8

TABLE 3

SPARK SOURCE MASS SPECTROGRAPHIC ANALYSES OF SOME MEXICAN STANDARDS
Preliminary Results
(carried out in Department of Geology, Manchester University,
Manchester, England).

	BCU-1	BCU-2	RSL-1
Ni	69.8	193	4.5
Cu	7.6	7.6	0.3
Zn	80	152	55
Ga	9.3	15.4	3.4
Ge	0.19	0.21	0.08
Br	0.17	0.16	
Rb	7	40	29
Sr	304	1013	26
Y	0.89		0.94
Zr	274	96	38
Nb	23.1	7.24	6.14
Cs	0.81	1.05	7.2
Ba	89	80	43.5
La	8.6	12.4	13.5
Ce	10.6	22.8	12.4
Pr	6.1	5.0	8.2
Nd	24.4	19.7	41
Sm	8.4	10.5	11.0
Eu	2.3	3.0	0.42
Gd	7.2	10.4	8.9
Tb	0.8	1.52	1.95
Dy	14	18	24
Ho	2.1	1.3	0.9
Er	3.1	6.9	3.2
Tm		0.5	0.2
Pb	17.2	43.8	55.4
U			2.5

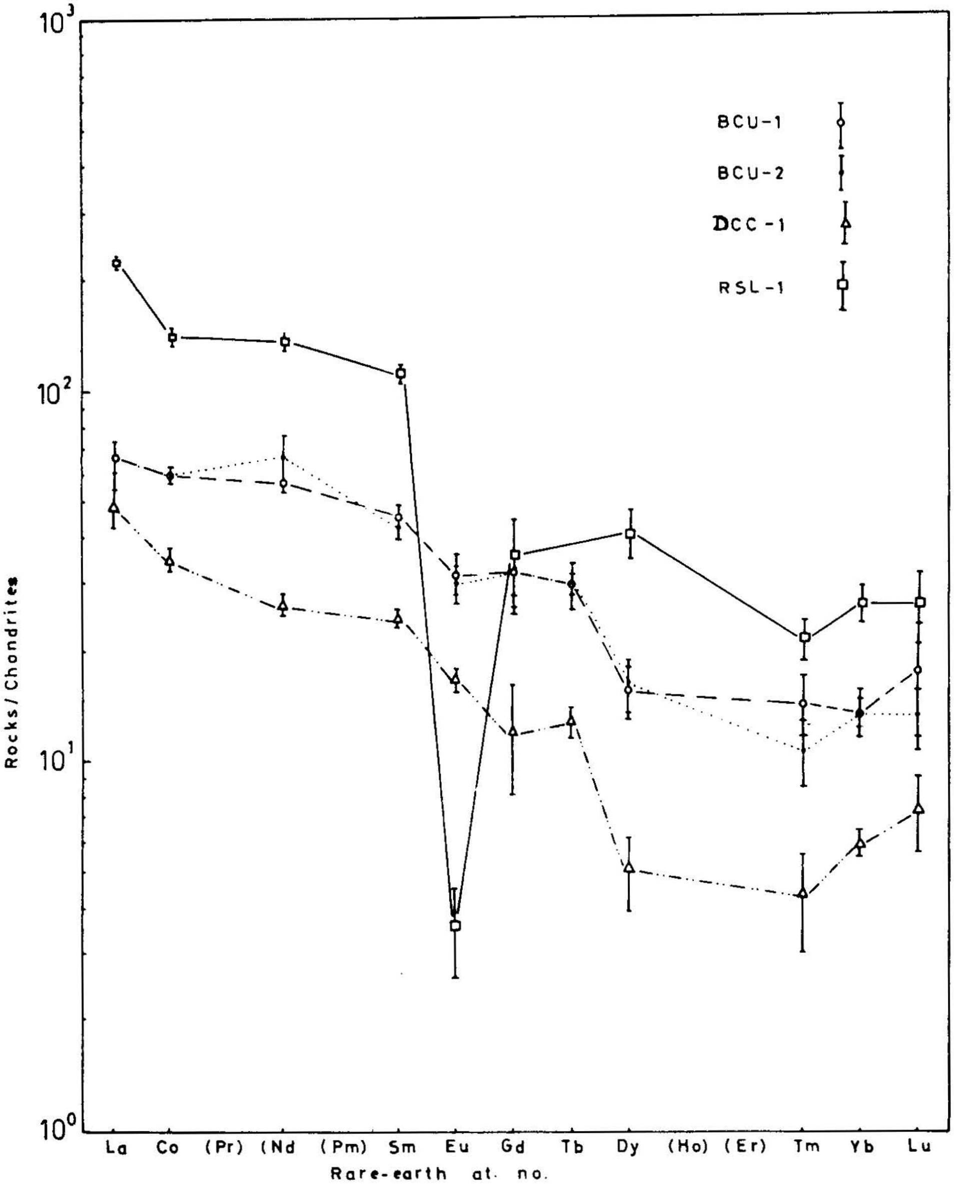

Fig. 1. Comparison plots for some Mexican rocks.
(taken from Pal and Urrutia, 1977.)

BIBLIOGRAPHY

ABBEY, S., 1973. Studies in "Standard samples" of silicate rocks and minerals. Part 3: 1973 Extension and revision of "usable" values. *Geol. Sur. Can. Paper, 73-36*: 25 p.

ABBEY, S., 1975. Studies in "Standard samples" of silicate rocks and minerals. Part 4: Edition of "usable" values. *Geol. Sur. Can. Paper, 74-41*: 23 p.

ABBEY, S., 1976. SY-2, SY-3 and MRG-1 report on the collaborative analysis of three Canadian rock samples for use as certified reference materials – Supplement I. *CANMET Report, 76-36*: 27 p.

ABBEY, S., A. H. GILLIESON and G. PERRAULT, 1975. SY-2, SY-3 and MRG-1. A report on the collaborative analysis of three Canadian rock samples for use as certified reference materials. *Energy, Mines and Resources Canada MRP/MSL.* 75-132: 56 p.

ANDO, A., H. KURASAWA, T. OHMORI and E. TAKEDA, 1971. 1971 Compilation of data on rock standards JG-1 and JB-1 issued from the Geological Survey of Japan. *Geochem. J., 5*: 151-164.

ANDO, A., H. KURASAWA, T. OHMORI and E. TAKEDA, 1974. 1974 Compilation of data on the GSJ geochemical reference samples JG-1 granodiorite and JB-1 basalt. *Geochem. J., 8*: 175-192.

CARTA GEOLÓGICA DE LA REPÚBLICA MEXICANA, 1976. Univ. Nal. Autón. México. *Inst. Geología.*

CETENAL, 1973. Hoja Tepetate F-14-A-83, S.L.P.

COOMBS, D. S., 1963. Trends and affinities of basaltic magmas and pyroxene as illustrated on the diopside-olivine-silica diagram. *Miner. Soc. Am. Sp. Paper, 1*: 227-250.

EASTON, A. J., 1972. Chemical analysis of silicate rocks. Series 6 of Methods in Geochemistry and Geophysics, *Elsevier Publ. Co.*, 258 p.

ENERGLYN, T. L. and L. BREALEY, 1971. Analytical Geochemistry Series 5 of Methods in Geochemistry and Geophysics. *Elsevier Publ. Co.*, 426 p.

FLANAGAN, F. J., 1969, U. S. Geological Survey standards-II. First compilation of data for the new U.S.G.S. rocks. *Geochim. Cosmochim. Acta, 33*: 81-120.

FLANAGAN, F. J., 1973. 1972 values for international geochemical reference samples. *Geochim. Cosmochim. Acta, 37*; 1189-1200.

FLANAGAN, F. J., 1974. Reference samples for the earth sciences. *Geochim. Cosmochim. Acta, 38*: 1731-1744.

FRIES, C.,Jr., 1960. Geología del Estado de Morelos y de partes adyacentes de México y Guerrero, región Central-Meridional de México. Univ. Nal. Autón. Mexico. *Inst. Geología. Bol. 60*, 236 p.

GRIMALDI, F. S., L. SHAPIRO and M. SCHNEPFE, 1966. Determination of carbon dioxide in limestone and dolomite by acid-base titration. *U.S. Geol. Surv. Prof. paper, 550-B*:B186-B188.

GORDON, G. E., K. RANDLE, G. G. GOLES, J. B. CORLISS, M. H. BEESON and S. S. OXLEY, 1968. Instrumental activation analysis of standard rocks with high resolution gamma-ray detectors. *Geochim. Cosmochim. Acta, 32*: 369-396.

INGAMELLS, C. O., 1974a. New approaches to geochemical analysis and sampling. *Talanta, 21*: 141-155.

INGAMELLS, C. O., 1974b. Control of geochemical error through sampling and subsampling diagrams. *Geochim. Cosmochim. Acta, 38*: 1225-1237.

INGAMELLS, C. O. and P. SWITZER, 1973. A proposed sampling constant for use in geochemical analysis. *Talanta, 20*: 547-568.

KAY, R., N. J. HUBBARD and P. W. GAST, 1970. Chemical characteristics and origin of oceanic ridge volcanic rocks. *J. Geophys. Res., 75*: 1585-1613.

KUNO, M., K. YAMASAKI, C. IIDA and K. NAGASHIMA, 1977. Differentiation of Hawaiian magmas. *Japanese Geol. and Geogr. Jour., 28*, 179-218.

KUNO, M., 1969. Differentiation of basalt magma *in* H. H. Hess and A. Poldervaart (Ed.) *Basalts, 2*: 623-688.

LA ROCHE, H. (de) and K. GOVINDARAJU, 1969. Rapport sur deux roches, diorite DR-N et serpentine UB-N, proposées comme étalons analytiques par un groupe de laboratoires français. *Bull. Soc. Fr. Cér., 85*: 35-50.

LA ROCHE, H. (de) and K. GOVINDARAJU, 1973. Étude coopérative sur un verre synthétique VS-N proposé comme étalon analytique pour le dosage des éléments en traces dans les silicates. *Analysis, 2*: 59-72.

LA ROCHE, H. (de) and K. GOVINDARAJU, 1975. Rapport preliminaire (1974) sur deux nouveaux standards géochimiques de L.A.N.R.T.: Granite GS-N et Feldspath FK-N. *Association National de la Recherche Technique, Circulaire Nº 9699*, 48 p.

LOPEZ M., M., 1977. Una comparación de algunos métodos de análisis geoquímico de rocas: resultados preliminares. *Anales del Inst. de Geof.*, 22/23: 57-66.

MACDONALD, G. A. and T. KATSURA, 1964. Chemical composition of Hawaiian lava *J. Petrol., 5*: 82-133.

MOOSER, F., A. E. M. NAIRN and J. F. W. NEGENDANK, 1974. Paleomagnetic investigations of the Tertiary and Quaternary igneous rocks: VIII A paleomagnetic and petrologic study of Volcanics of the Valley of Mexico. *Sond. Geol. Rundschau, 63*: 451-483.

NEGENDANK, J. F. W., 1973, Geochemical aspects of the Valley of Mexico. *Geofísica Internacionl, 13*: 267-278.

OBREGÓN A., P., 1973. Método de análisis químico de rocas y materiales similares. *Instituto de Geología*, UNAM., 52 p.

PAL, S., 1972. Reconnaissance geochemistry of some rocks of the Guanajuato

Mineral District, Mexico, *Geofísica Internacional, 12*: 163-199.

PAL, S. and J. URRUTIA F., 1977. Paleomagnetism, geochronology and geochemistry of some igneous rocks from Mexico and their tectonic implications. *Proc. IV Int. Gondwana Symp., Calcutta*, vol. II, pp. 814-831.

POLDERVAART, A. and A. B. PARKER,1964. The crystalization index as a parameter of igneous differentiation in binary variation diagrams. *Amer. J. Sci., 262*: 281-289.

ROUBAULT, M., H. (de) LA ROCHE and K. GOVINDARAJU, 1970. Etat actuel (1970) des études coopératives sur les standards géochimiques du Centre de Recherches Petrographiques et Géochimiques. *Sci. de la Terre, 15*: 351-393.

RUSSELL, B. G., J. LEVIN, G. DOMEL, P. K. FAURE, H. STOCH and T. W. STEELE, 1968. Collection and preparation of standard rock samples. *National Institute for Metallurgy Report*, 332: 18 p.

SCHWARZER, R. R. and J. J. W. ROGERS, 1974. A worldwide comparison of alkali olivine basalts. *Earth Planet. Sci. Lett 23*: 286-296.

STEELE, T. W., B. G. RUSSELL, R. G. GOUDVIS, G. DOMEL and J. LEVIN, 1972. Preliminary report on the analysis of the six NIMROC geochemical standard samples. *National Institute for Metallurgy Report, 1351*: 76 p.

TERRELL, D. J. and S. PAL, 1977. Procedimientos generales del análisis instrumental por activación con neutrones aplicado a rocas y minerales. *Anales del Inst. de Geof.*, 22/23: 9-23.

THORTON, C. P. and O. F. TUTTLE, 1960. Chemistry of igneous rocks I. Differentiation Index. *Amer. J. Sci. 268*: 664-684.

VOLBORTH, A., 1969. Elemental analysis in geochemistry. A. major elements. Series 8 of Methods in Geochemistry and Geophysics. *Elsevier Publ. Co.*, 373 p.

WASHINGTON, H. S., 1917. Chemical analyses of igneous rocks. *U. S. Geol. Surv., 99*: 1157-1164.

YODER, H. S. and C. E. TILLEY, 1962. Origin of basaltic magmas – an experimental study of natural and synthetic rock systems. *J. Petrol., 3*: 342-532.