GEOCHEMISTRY OF SOME METAMORPHIC AND SEDIMENTARY ROCKS FROM THE MINERAL DISTRICT OF ZACATECAS, ZAC., MEXICO

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RESUMEN

El área de estudio se caracteriza por una secuencia de flujos principalmente riolíticos que cubren rocas metamórficas de edades Mesozoicas y más antiguas y, un cuerpo grande andesítico porfirítico de edad Terciaria Temprana. Las rocas metamórficas tienen patrones de elementos tierras raras (REE) parecidos al compuesto de lutitas de Norteamérica (NASC), lo cual posiblemente nos permite asignarles una fuente Post-Arqueana. Una muestra de veta de mineral que consiste principalmente en cuarzo y calcita presenta contenidos y patrón de REE semejantes a los de las condritas. Sin embargo, algunos errores experimentales altos encontrados a bajas concentraciones requieren más investigación sobre muestras de este tipo.

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ABSTRACT

The area of study is caracterized by a thick succesion of mainly rhyolitic flows which cover Mesozoic and older metamorphic rocks and a large porphyritic andesite body of Early Tertiary age. Metamorphic rocks have rare earth element (REE) patterns similar to the North American Shale Composite (NASC) which possibly indicates a Post-Archean source. One mineral vein sample consisting mainly of quartz and calcite shows REE contents and pattern similar to those of chondrites. Considerable experimental errors at such low concentrations warrant further research on such samples.

INTRODUCTION

Geochemical studies in Mexico are rather scanty. There is a number of major element analyses on Mexican igneous and metamorphic rocks (Ca. 400 analyses) but trace element studies are sparse. This work is intended to describe a fairly detailed geochemical study on different rock types (except ignimbrites and rhyolites) from the Mineral District of Zacatecas, Zac., México.

GEOLOGY OF ZACATECAS ROCKS

The geology of the Mineral District of Zacatecas, Zac., has been described by Pérez M. *et al.* (1961). Igneous, sedimentary and metamorphic rocks are present in this area (Fig. 1). The oldest rocks are metamorphic and are considered to be of Mesozoic and Paleozoic (?) ages. These comprise strongly folded and faulted schists and phyllites of greenschist facies which are overlain by several bodies of sandstone and conglomerate of Late Triassic age. During the Cenozoic, this area was subjected to intense intrusive as well as extrusive igneous activity beginning with the intrusion of a large porphyritic body of andesitic composition (Early Tertiary). This rock ("roca verde" de Zacatecas) essentially constitutes the Zacatecas "sierra" and is highly altered (propylitized). This event was followed by extrusion of rhyolites and porphyritic rhyolites during the Oligocene. A continental red conglomerate (red-beds sequence) was deposited during Miocene times and was subsequently almost covered by rhyolitic tuffs and lavas of Miocene and Pliocene ages. It should be mentioned that no radiometric dates are yet available in this area and all ages are based on stratigraphy. Pb, Ag, Zn, Cu and Au mineralization is present in this area and is supposed to be of epithermal origin (Pérez M. *et al.*, 1961.)

ANALYTICAL METHODS

Major element chemistry was obtained by a combination of various techniques: gravimetry (SiO_2, H_2O^- and H_2O^+) atomic absorption spectrophotometry (Al_2O_3, total Fe, MnO, MgO and CaO), flame photometry (Na_2O and K_2O), colorimetry TiO_2, P_2O_5 and total Fe) and volumetry (FeO and CO_2). Trace element contents (REE. Cs, Th, U, Zr, Hf, Ta, Co, Cr, Sc and Sb) were determined by instrumental neutron activation analysis (INAA), whose details are similar to those given by Gordon *et al.* (1968), Pal (1972) and Terrell and Pal (1977). The accuracy (as judged from international geochemical reference samples) and precision (reproducibility) obtained for most major elements are better than 5%, while for trace elements these are about 5% (Cs, Ta, Co, Sc, Eu and Yb), 10% (Th, Cr, Hf, La, Ce, Sm, Tb, and Tm), 20% (U, Sb and Nd) and 30% (Zr, Gd and Lu).

The ratios of light to heavy REE are expressed as ΣLREE/ΣHREE where ΣLREE is the sum of the abundances of La, Ce, Nd and Sm, and ΣHREE is the sum of the abundances of Gd, Tb, Tm, Yb and Lu. This method is adopted from Nance and Taylor (1976) instead of using simple La/Yb ratios, to provide a somewhat more precise index of light to heavy REE fractionation.

RESULTS AND DISCUSSION

The results of chemical analyses are given in Table 1, while trace element data are reported in Table 2. Masuda-Coryell plots of these samples are given in Figs. 2-4. Chondrite data used in this work for normalization are those given for Leedey chondrite by Masuda *et al.* (1973) and Masuda (1975). The normalization of the REE data against chondrite values is a rather conventional approach. Alternatively data on North American Shale composite (NASC) has been used for normalization by many authors.

The metamorphic samples (ZMI – 5) have only been subjected to low grade metamorphic effects (greenschists facies) so their REE abundances and patterns (Fig. 2) might still be the same as those of the original rocks (Hermann, 1970, Cullers *et al.*, 1974; Condie, 1976a). Based on their petrography (Appendix I), these samples are probably derived from a shale except for ZM4 whose source rock seems to be a sandstone. The behaviour of the REE during erosion, transport and deposition has been studied by Balashov and Khitrov (1967), Ronov *et al.* (1967) and Piper (1974). Deposition under arid conditions is shown to cause a little change in REE ratios whereas deposition under humid conditions may lead to relative fractionation of light and heavy REE. The absence or near absence of cerium anomalies in these samples might be taken as an indication of a lack of equilibrium with sea water during deposition of their source rocks (shales or sandstones).

Schists and phyllites show a LREE-enriched pattern with an average of Σ LREE/Σ HREE = 9.0 ± 2.3 and a negative Eu anomaly with Eu/Eu* = 0.6-0.8. This characteristic is very similar to Post-Archean shales and greywackes from Australia obtained by Nance and Taylor (1976). Furthermore since Precambrian sedimentary rocks have been shown (Wildeman and Haskin, 1973; Wildeman and Condie, 1973; Jakes and Taylor, 1974; Nance and Taylor, 1976, 1977) to have a positive Eu anomaly with respect to North American Shale Composite (NASC) and these rocks from Zacatecas do not show any marked positive anomaly w.r.t. NASC, they may be derived from a Post-Archean or even a Post-Cambrian source in agreement with the age assigned to them by Pérez-M. *et al.* (1961).

Another point to be noted in the REE characteristics of these rocks is that stress effects on the mylonite (ZM5) sample have apparently not appreciably modified its REE abundance. One epidote hornfelds ZM6 studied here has a Σ REE = 37.6, a value similar to the one given by Balashov and Tugarinov (1976) for such rocks.

One sedimentary rock studied in this work is a protoquartzite (ZS7). Its REE pattern and contents (Fig. 3) are surprisingly similar to Permian Orthoquartzite from Canning basin (Fig. 3), Western Australia (Nance and Taylor, 1976). Further no significant Eu anomaly is shown relative to NASC. ZS7 has a similar REE pattern when compared to a Mungari K-granite (Nance and Taylor, 1977) but the Σ REE is considerably less in ZS7 than in the K-granite. The similitude of REE patterns of ZS7 and K-granite may possible be taken as an indication that this rock (ZS7) was derived from a granitic source. This interpretation is further supported by the presence of fragments with micrographic texture in ZS7. Its lower Σ REE can be readily explained by very high quartz content. This is further evidenced by the examination of a vein sample (ZH25) which also shows very low contents of trace elements including REE. As ZH25 contains in addition to quartz, calcite and hematite, neither of these minerals incorporates appreciable amounts of trace elements. It should also be pointed out that although this sample (ZH25) apparently has its REE pattern similar to that of chondrites, the analytical errors in INAA at such low concentrations can be as high as 50% or more. However it should be interesting to undertake more precise determinations of trace elements in this sample.

It should be mentioned that the dating of the rocks, or the characterization of the source material by means of comparison with NASC or a single K-granite, or with the Eu anomaly in Precambrian sediments are not satisfactory unless accompanied by other independent approaches.

The metamorphic and sedimentary rocks show normal abundances of antimony (Onishi, 1970). Not much information is available for Cs in low-grade metamorphic rocks (Heier and Adams, 1964; Heier and Billings, 1970). Information in literature on other trace elements analyzed in this work is also quite limited.

Only one andesitic sample (ZI9) was studied in this work. It also shows a negative Eu anomaly (Fig. 4) which suggests magmatic differentiation at relatively shallow depths, unless such an anomaly can be shown to result from the strong hydrothermal alteration suffered by this rock (Condie, 1976a, b).

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APPENDIX I
A PETROGRAPHIC DESCRIPTION OF THE SAMPLES

The phyllites (ZM1, ZM2, ZM3) have a slaty texture and contain quartz fragments (clay-size), chlorite, sericite, and minor quantites (~ 3%) of hematite and limonite. These rocks were possibly derived from shale.

The sample ZM4, having a schistose texture is classified as a schist and contains ~ 60% quartz (grain size ~ 1 mm), ~ 15% recrystallized calcite, ~ 17% chlorite and minor proportions of hematite, magnetite, limonite and pyrite. The subrounded nature of quartz grains in this rock possibly suggests sandstone as its parent material. The phyllites as well as the schists are low grade greenschist facies metamorphic rocks.

Many faults are present in the area. They were probably caused by the intrusion of andesitic porphyry, transforming the phyllites, under cataclastic metamorphism, into mylonites (ZM5), in which a clear fracturing and sliding can be seen microscopically.

ZM6 is an epidote hornfels with granuloblastic texture which was collected near the andesitic body and a porphyritic rhyolite. It is composed of ~ 70% epidote, ~ 10% quartz, ~ 8% chlorite and smaller proportions of calcite, hematite and limonite.

The sample ZS7 has an epiclastic psammitic texture and is classified as a protoquartzite (Pettijohn, 1963). It is composed of almost 80% quartz, ~ 10% rock fragments posssibly granitic (as they have micrographic texture) and minor amounts of sericite, hematite, limonite and sphene. The other sedimentary sample studied in this work (ZS8) is a continental red conglomerate with an epiclastic psephitic texture containing numerous fragments of tuff, andesite, schist and phyllite.

ZI9 is a dark green andesitic rock having a compact structure and trachytic texture. Petrographic study reveals the presence of oriented andesine microliths, augite, epidote, chlorite, limonite, pyrite and a few quartz veins (an alteration which can be termed as propylitization).

Table 1. Major element chemistry of metamorphic and sedimentary rocks from Zacatecas

	ZM1	ZM2	ZM3	ZM4	ZM5	ZM6	ZS7	ZI9	ZH25
SiO_2	75.08	71.53	66.60	60.63	72.75	52.10	91.09	51.12	54.80
Al_2O_3	12.07	14.88	19.61	7.47	11.99	17.63	5.03	13.11	0.83
TiO_2	0.36	0.54	0.90	0.37	0.44	1.60	0.11	0.46	0.01
CaO	0.12	0.08	0.35	11.87	0.21	2.47	0.06	9.84	25.80
MgO	0.66	0.71	0.91	0.80	0.62	0.82	0.20	0.27	0.22
Na_2O	0.20	0.26	0.18	2.32	5.39	3.26	0.06	1.48	0.09
K_2O	2.52	5.30	4.12	1.05	0.88	2.40	1.26	2.12	0.38
Fe_2O_3	5.08	3.38	1.11	3.09	4.96	8.29	0.78	7.10	0.08
FeO	0.36	0.65	0.71	1.33	0.08	6.25	0.16	1.25	0.14
MnO	0.01	0.03	0.05	0.12	0.03	0.33	0.002	0.14	0.16
P_2O_5	0.10	0.10	0.13	0.14	0.04	0.20	0.01	0.09	0.004
H_2O^+	2.42	1.89	3.06	2.67	1.21	2.46	0.87	4.41	1.26
H_2O^-	1.04	0.61	1.15	0.50	0.96	0.81	0.20	4.02	0.16
CO_2	0.22	0.39	0.40	7.85	0.42	0.70	0.08	4.19	15.74
Total	100.24	100.35	99.28	100.21	99.98	99.32	99.91	99.59	99.67
$Fe_2O_3^T$	5.46	4.10	1.90	4.57	5.05	15.64	0.93	8.49	0.27

Table 2. Rare earths and other trace elements in metamorphic and sedimentary rocks from Zacatecas.

	ZM1	ZM2	ZM3	ZM4	ZM5	ZM6	ZS7	ZI9	ZH25
Cs	14	7.1	22	1.6	1.4	7.2	2.3	18	2.0
Th	7.8	10	9.1	1.0	12	1.5	2.4	5.5	<0.5
U	3.9	2.7	1.9	1.1	1.7	0.7	0.9	1.2	0.1
Zr	204	226	259	192	221	84	142	173	24
Hf	6.1	6.2	6.6	3.7	6.5	2.0	3.2	2.9	0.1
Ta	0.9	1.3	1.0	0.3	0.9	0.2	0.3	0.5	<0.1
Co	2.8	10	4.5	9.5	4.7	33	0.53	23	1.2
Cr	140	130	14	20	67	70	24	155	13
Sc	12	17	13	13	14	35	2.7	23	1.0
Sb	12	2.3	3.1	2.3	1.2	4.4	1.6	0.4	16
La	16	24	30	9.2	34	3.9	7.1	12	0.37
Ce	33	50	61	20	52	13	13	28	-
Nd	18	30	34	14	30	9.0	4.9	19	-
Sm	3.3	7.6	6.3	3.3	8.2	3.0	0.74	3.6	0.17
Eu	0.93	1.42	1.02	0.84	1.9	1.2	0.15	0.67	0.08
Gd	3.5	5.5	5.0	3.4	7.5	3.5	1.0	3.0	-
Tb	0.65	0.95	0.70	0.58	1.3	0.53	0.16	0.55	0.05
Tm	0.45	0.42	0.41	0.40	0.56	0.40	0.09	0.41	-
Yb	3.3	4.0	3.5	2.4	4.5	2.9	0.52	2.4	0.22
Lu	0.80	0.81	0.82	0.61	0.90	0.26	0.18	0.57	-

Table 2. (Cont/d)

	ZM1	ZM2	ZM3	ZM4	ZM5	ZM6	ZS7	ZI9	ZH25
ΣREE	79.93	124.70	142.75	54.73	140.86	37.69	27.84	70.20	0.89
(Eu/Eu^{*})	0.84	0.68	0.57	0.78	0.77	1.19	0.54	0.62	-
ΣLREE/ΣHREE	8.1	9.6	12.6	6.3	8.4	3.8	13.2	9.0	-
$(K/Cs)x10^{-3}$	1.5	6.2	1.6	5.4	5.2	2.8	4.5	1.0	1.6
Th/U	2.0	3.7	4.8	0.9	7.1	2.1	2.7	4.6	< 5
Zr/Hf	33	37	39	52	34	42	44	60	240
Hf/Ta	6.8	4.8	6.6	12.3	7.2	10.0	10.7	5.8	>1
$(Fe/Co)x10^{-3}$	13.6	2.9	3.0	3.4	7.5	3.3	12.3	2.6	1.6
$(Fe/Sc)x10^{-3}$	3.2	1.7	1.0	2.5	2.5	3.1	2.4	2.6	1.9

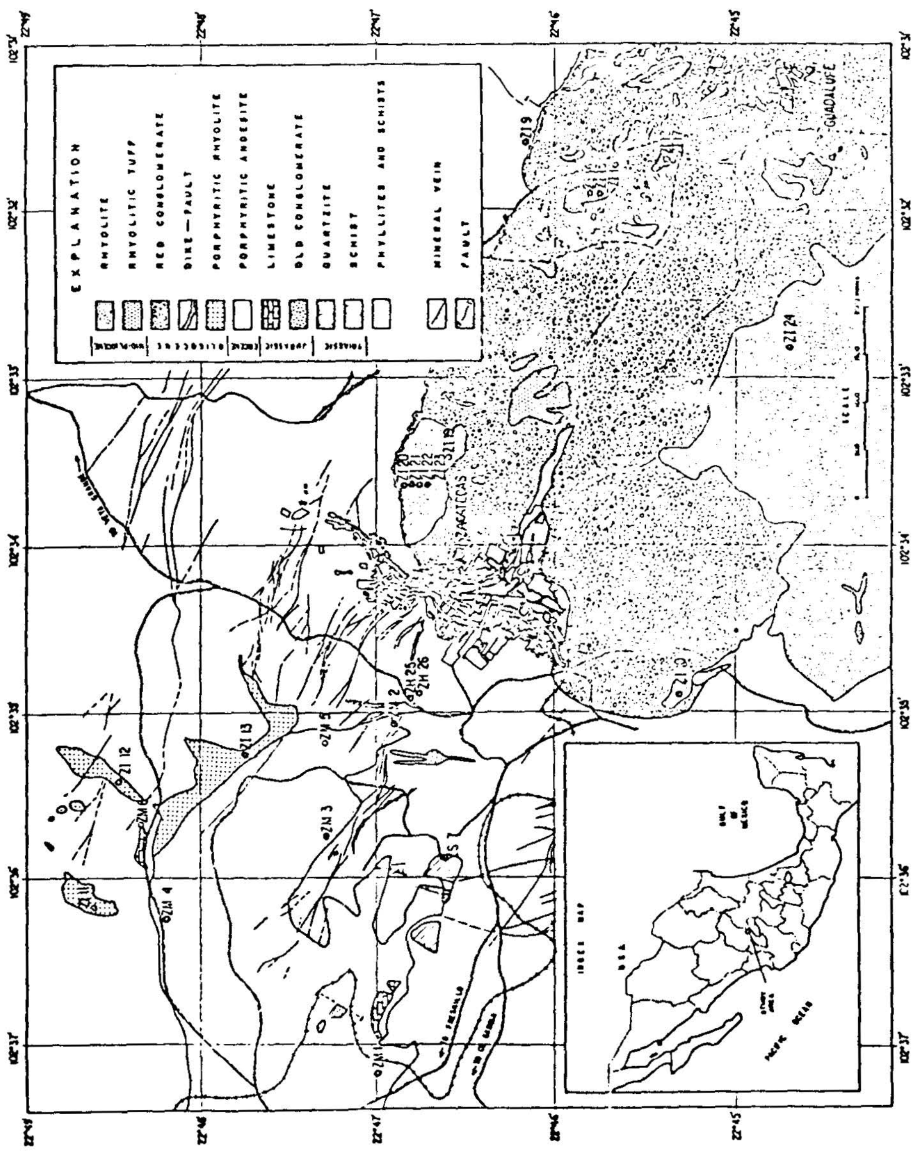

Fig 1. A SIMPLIFIED GEOLOGIC MAP (after Pérez-M. et al, 1961) OF THE ZACATECAS REGION INDICATING SAMPLE LOCATIONS.

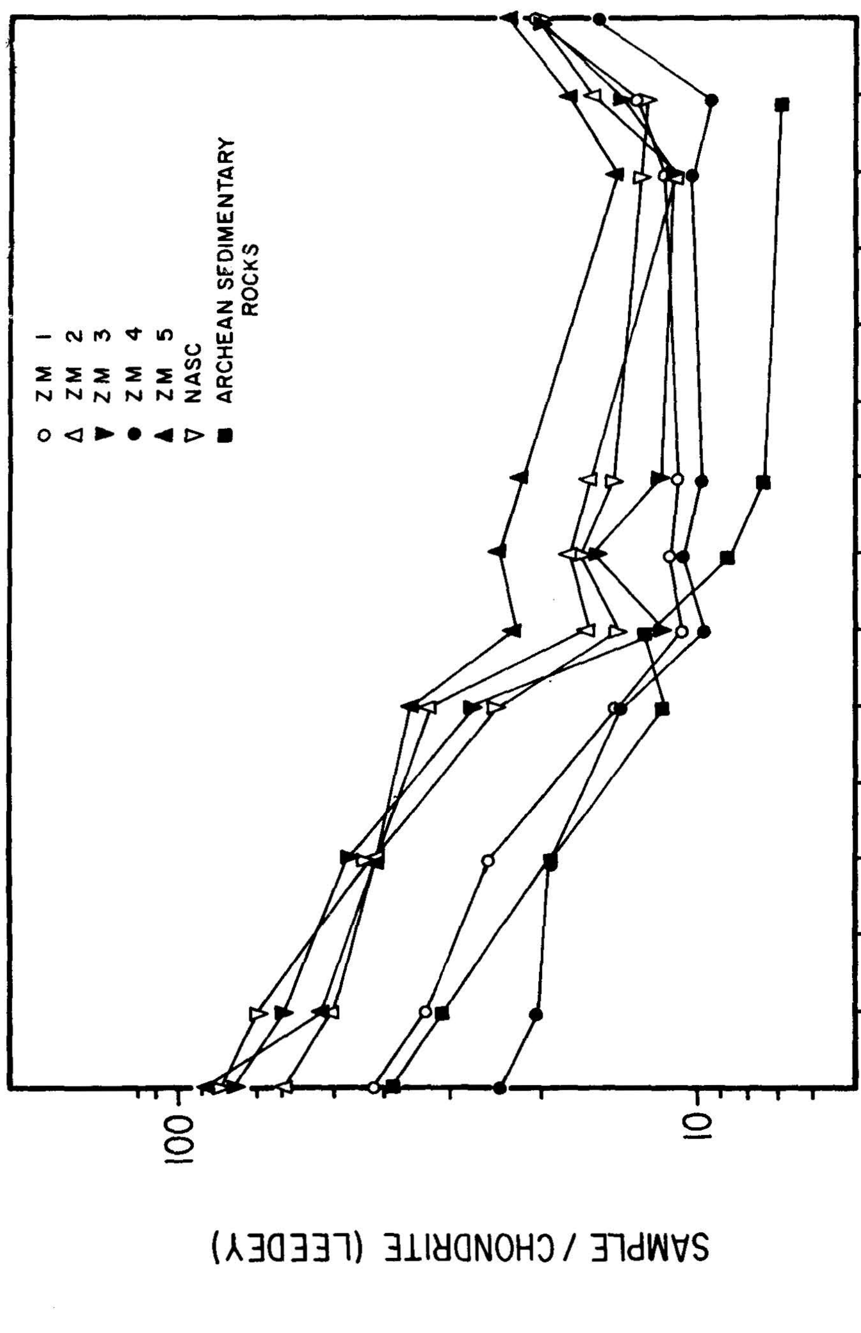

FIG. 2 THE REE PATTERNS OF LOW-GRADE METAMORPHIC ROCKS FROM ZACATECAS.

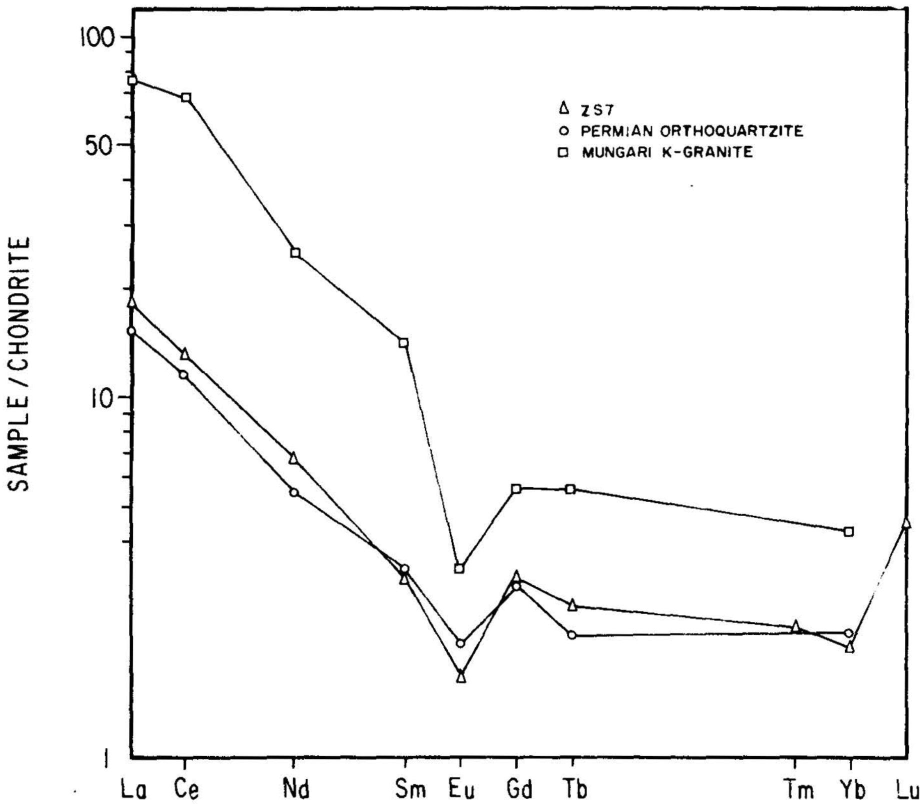

FIG. 3 THE REE PATTERN OF A SEDIMENTARY ROCK FROM ZACATECAS.

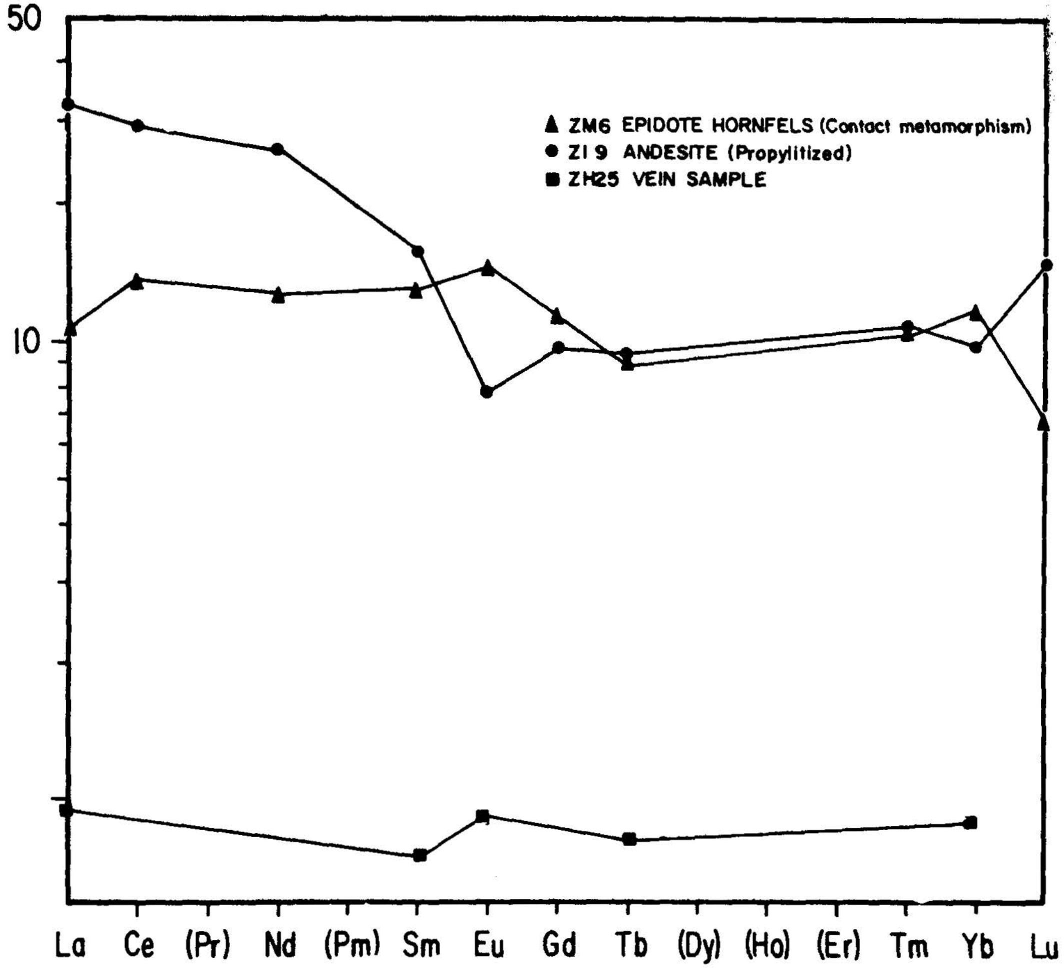

FIG. 4 THE REE PATTERNS OF OTHER ROCKS INCLUDED IN TABLE 2.

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