STRONTIUM ISOTOPE GEOCHEMISTRY OF BARITE MINERALIZATION AT LA MINITA, S.W. MEXICO

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ABSTRACT

The La Minita Fe-Ba-Zn-Pb-Ag deposits are located in the Michoacan Province of Mexico. Previous fluid inclusion and stable isotope studies showed that these deposits were generated around submarine hot-springs issuing in a Cretaceous island-arc environment.

A strontium isotope study was carried out to determine the source of Sr and Ba. The $^{87}Sr/^{86}Sr$ ratios in barites, mafic volcanics, felsic volcanics and carbonates range from 0.70492 to 0.70535, 0.70451 to 0.70557, 0.70660 to 0.75709 and 0.70571 to 0.70685 respectively. The data suggest that both the volcanics and limestones were the sources of Sr in the mineralizing fluids. On the other hand, trachytes and rhyolites seem to be the most viable sources of Ba, with possible minor contributions from andesite, basalt and limestone.

INTRODUCTION

The La Minita mining district (Lat. 18°52'06"N, Long. 103°17'06"W) is located in the Michoacan Province of Mexico (Fig.1) Although exploration for barite had been carried out in the 1950's, a quest for silver-lead zinc deposits by Peñoles Co. did not begin until 1976 (Gaytan et al., 1979). In 1979 an economic deposit of > $6x10^6$ tonnes, grading 4.0% Zn, 0.33% Pb, 48.0% BaSO$_4$ and 78 g/tonne Ag was outlined; however, the inventory of reserves as of October 1986 indicated that the ore consisted of over 2 x 10^6 tonnes, grading 4.48% Zn, 0.34% Pb, 34.9% BaSO$_4$, and 58 g/tonne Ag (Alonso and Jimenez, 1986).

Detailed fluid inclusion and stable iostopic studies on the mineralization of the distric revealed that the deposits formed from circulating seawater which caused replacement of the reefal limestones at low-rock ratios during the pre-ore stage/Fe-oxide mineralization and at higher water-rock ratios during sulfate-sulfide mineralization (Ortigoza-Cruz et al., 1990). The carbon isotope data suggested a marine origin for the carbon. The sulfur isotope suggested seawater sulfate and inorganically-reduced sulfur (and/or igneous sulfur) to be the main sources of sulfur in the system.

The importance of strontium isotopes as tracers for barium in ore deposits is well documented (Kessen et al., 1981; Lange et al., 1983; Kesler et al., 1988; Frimmel and Papesch, 1990). The present investigation on strontium isotopes of barites, carbonates and whole-rocks was undertaken to augment the existing geochemical data base on the deposits, and to shed additional information on the origin of these submarine exhalative deposits.

Regional geological setting

The Southern Sierra Madre of SW Mexico comprises an intricate series of belts whose stratigraphy and structure suggest allochthonous origins. These terranes were accreted to North-America during Late Cretaceous-Early Tertiary times. Mid Tertiary to Quaternary volcanic sequences blanket juxtaposed terranes, preventing interpretation of their boundaries and interrelationships (Campa and Coney, 1983).

Campa and Coney (1983) recognized five allochthonous terranes in the Southern Sierra Madre. The Guerrero terrane is an accreted ancient island arc, related to the Cretaceous subduction of the Pacific Plate, off the western coast of Mexico. The absence of a crystalline basement below this terrane is an indication of the generation of this terrane upon young continental, or oceanic crust. The Guerrero terrane has been further divided into three sub-terranes of similar stratigraphy but of contrasting structure, namely: the Zihuatanejo, the Huetamo, and the Teloloapan sub-terranes (Campa and Coney, 1983).

The Zihuatanejo sub-terrane, within which the La Minita district occurs, consists of a thick sequence of andesitic volcanics intercalated with Albian-Cenomanian limesto-
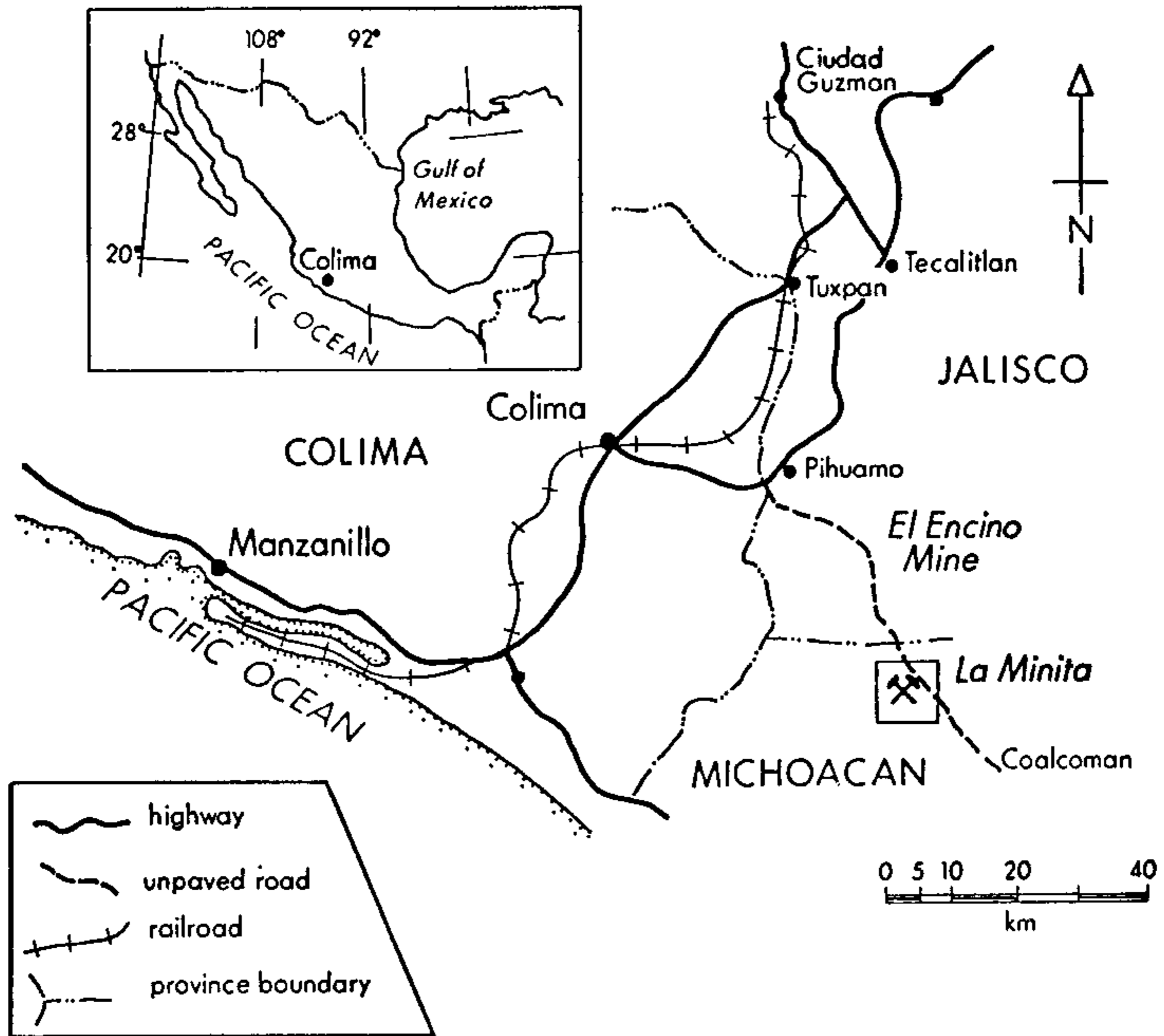
Figure 1. Location of the La Minita District, Mexico.

ne and some shale-sandstone interbeds (more than 3 000 m of this unit were recoverd from the Jalisco 1 drill-core (Lopez Ramos, 1981). The existence of evaporitic strata intercalated with these limestones has been described elsewhere (Lopez Ramos, 1981). The upper part of this sequence grades into a clastic unit. Folding and faulting have affected this subterrane, but no metamorphism has been detected.

The Huetamo sub-terrane consists of Upper Jurassic volcaniclastic sediments overlain by a Neocomian sandstone-shale sequence which grades into an Albian unit of limestone, tuff and redbeds. Late-Cretaceous redbeds and ignimbrites from the upper member of the unit. Tight,

upright folds and an absence of obvious metamorphism characterize this terrane.

The Teloloapan sub-terrane consists of a low-grade metamorphic, intensely deformed, andesitic volcanic-sedimentary sequence interbedded with shale, sandstone and limestone of Late-Jurassic to Early Cretaceous age (Campa, 1978; Campa and Coney, 1983).

In both the Zihuatanejo and Huetamo sub-terranes, the lithologic facies define a series of topographic highs with shallow to deep basins. The presence of patch reefs within volcanic-pyroclastic sequences, very common in the La Minita-Coalcoman area, suggests seamount-like environments with fringe reefs. Sediments deposited in
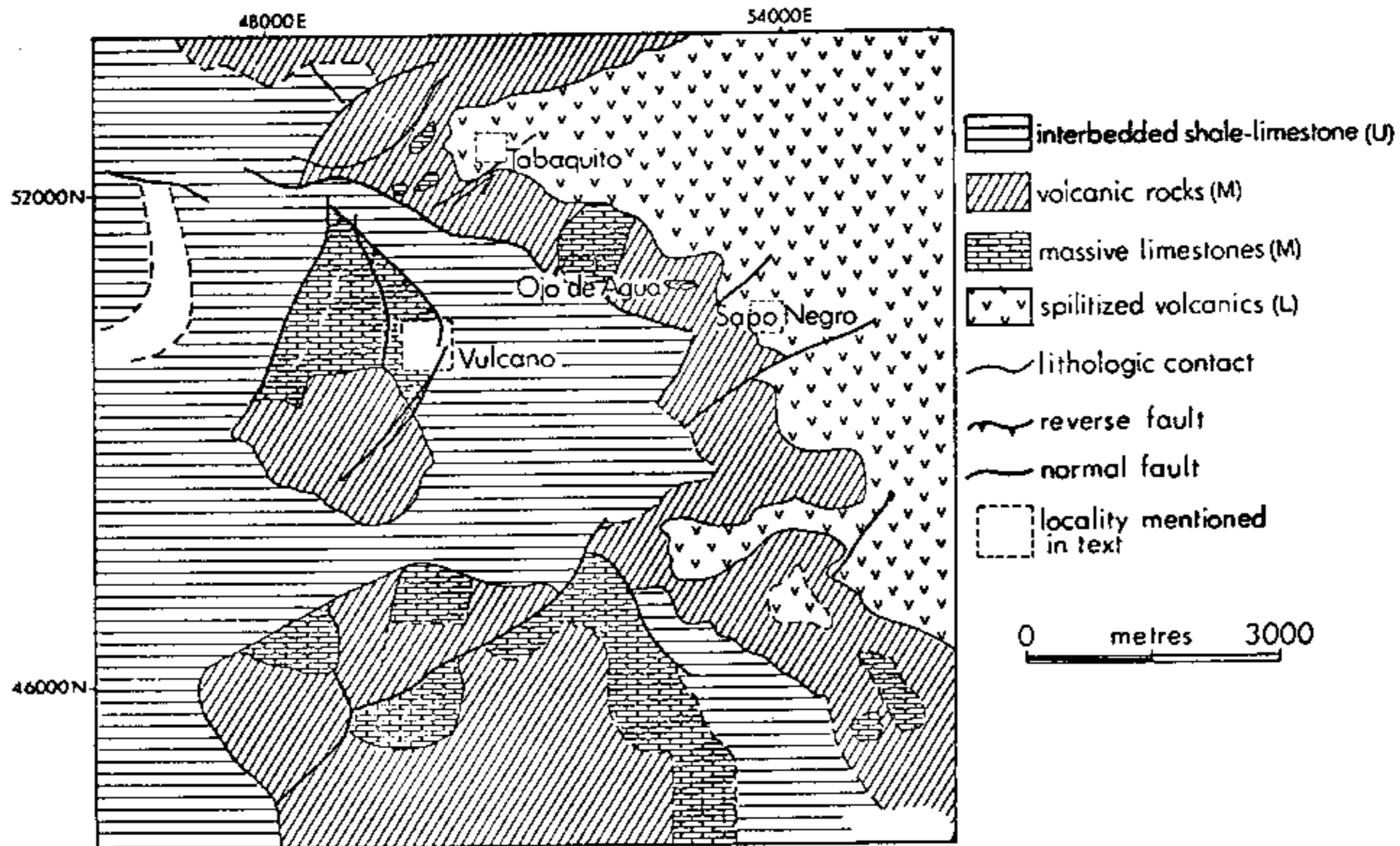
Figure 2. Geology of the La Minita District, Mexico.

shallow-water and transitional environments also suggest a typical island-arc archipelago environment (Campa, 1978).

The presence of the metamorphosed Teloloapan sub-terrane in between the apparently unmetamorphosed Zi-huatanejo and Huetamo sub-terranes, all three being of similar age, has constituted an enigma. Campa (1978) suggested that these sub-terranes were tectonically jux-taposed and that the outcrops of the Teloloapan terrane represent the upper block of a nappe, for in some instances they have been found overlying unmetamorphosed se-quences. The presence of these metamorphosed and un-metamorphosed terranes of similar age, could be ascribed to stacking of thrust-sheets into a melange during the process of accretion.

Local geology

Lithologic Setting

The mineral deposits (Vulcano, Tabaquito, Sapo Negro and Ojo de Agua) of the La Minita District are hosted by a Middle Cretaceous volcano-sedimentary sequence, the majority of the mineralized zones being located within or near reefal carbonate horizons.

Three lithologic units can be recognized (Fig.2), namely:

(i) A lower unit, predominantly of mafic, submarine-volcanic origin, occurring in the NNE sector of the district. This unit consists of hydrothermally-altered, submarine andesitic volcanics and pyroclastics with autoclastic-hy-aloclastic textures. No pillow structures have been ob-served. The rocks carry propylitized assemblages con-sisting of albite + chlorite + epidote + calcite + hematite + quartz. Iron-manganese rich-beds within spilitized basalts are present at the Sapo Negro locality.

(ii) A middle unit which hosts all of the mineralized bodies and occurs in the north and central sectors, is composed of hydrothermally-altered mafic to intermediate volcanics (pyroclastics and lavas), reef limestones and thinly-stratified carbonates. This unit consists of volcanic and sedimentary rocks deposited within a shallow marine, sub-tropical environment. The volcanic components are trachyandesitic to trachytic pyroclastics and lavas. Vitric and lithic tuffs predominate, volcanic breccias also being common. At places biohermal patches of fossiliferous limestone are intercalated with volcanic sequences. At Vulcano there is clear evidence of coeval reef growth and sulfate-sulfide/oxide mineralization.

(iii) An upper unit consisting of turbiditic shale-lime-

stone interbeds which blanket the middle unit in many areas and do not exhibit any hydrothermal alteration. The youngest unit consists of basinal shale-limestone interbeds. Its base consists of coarse to fine-grained turbiditic strata unconformable upon a kaolinized-chloritized tuff which in turn lies on the reef limestone (at Vulcano). No basal conglomerate exists at the unconformity, however the lack of alteration and of volcanic material on the shale-limestone unit suggests a sharp change in the tectonic/volcanic regime of the region. The upper part of the sequence is composed of a black shale-limestone with frequent thin pyritic layers. This unit seems to have been deposited within small graben-like basins of variable depth (Gaytan *et al.*, 1979). This observation is reinforced by the intensely sheared nature of the middle unit in the center of Vulcano pit and the relatively mild deformation of this upper unit, at least south of the pit.

Mineralization

Mineralization in the La Minita district is dominated by iron oxides with occasional associated barite and Zn-Pb-sulfide mineralization. The mineralization is of two principal varieties, namely:

(i) Epigenetic, stratabound mineralization carrying iron oxides, barite and Zn-Pb sulfides and replacing carbonate horizons (at Vulcano, Tabaquito and probably Ojo de Agua).

(ii) Syngenetic, stratiform mineralization in the form of massive bedded pyritites (at Vulcano) and iron formations (at Vulcano, Tabaquito and Sapo Negro).

The Vulcano orebody

At Vulcano the main replacement body occurs at the center of the mine and extends radially outwards in a domal structure (Gaytan *et al.*, 1979). It consists of irregular hematite-magnetite-pyrite zones, principally in the lower part of the body. Most of the orebody contains radial intergrowths of fine-grained barite with disseminated sphalerite, pyrite, galena and tetrahedrite. The top of the body is rich in jasper which occurs mixed with brecciated limestone; this zone grades upwards into recrystallized limestone and finally into fresh limestone. The whole body is transected by quartz-pyrite-calcite veins. Sporadic occurrences of limestone remnants and of replaced fossils within the ore zone support an epigenetic origin for this body. At depth, there are two limestone-magnetite beds, only detected in the deepest drill-holes, whose thickness reaches up to 20 m thick. These strata are enclosed by a dominantly pyroclastic sequence of highly-chloritized, sil-

icified trachyte underlying the main ore body. Fine-grained magnetite, hematite, and jasper are ubiquitously present with minor associated sulfides (sphalerite, pyrite and chalcopyrite). Recrystallized calcite is generally associated with the oxide-rich zones. Veins and irregular replacement of limestone are common.

At the southwestern sector of the pit there is a reefal limestone, largely silicified and replaced by magnetite. Here almost all of the fossils, mainly caprinulid rudists, are replaced by quartz and magnetite. Irregular magnetite-quartz veinlets transect the rock, however no appreciable recrystallization of the limestone occurs. This seems to suggest that the alteration of the limestone occurred shortly after its deposition, perhaps, during the diagenetic stage.

The second variety of mineralization at Vulcano consists of massive and internally-bedded syngenetic pyrite which occurs in the northeast sector of the pit. This ~15x10 m body occurs at a fault zone and is intensely sheared. Graded bedding, pseudo-layering and framboidal textures are present and confirm the exhalative-sedimentary nature of this body. It consists of fine-grained pyrite with minor sphalerite-barite and traces of galena. Laterally this body grades into a zone of pyrite-marcasite-barite-calcite with minor sphalerite. The whole body is overlain by marine limestone and seems to be a lateral equivalent of the replacement body. It would appear that the aforesaid fault zone existed prior to the mineralizing event, and probably constituted a vent for the ore-solutions (Gaytan *et al.*, 1979) which generated the proximal pyritic body. Further reactivation of the fault disrupted the pyritic ore.

The third variety of mineralizations consists of stratiform iron mineralization which occurs at the southeastern sector of the mine. It consists of at least two strata of jasper-hematite, enclosed within pyroclastic rocks. The unsorted, massive structure of the underlying pyroclastic member, which may constitute an ignimbritic unit, points to the existence of a shallow environment of deposition. Chloritization and baritization of the enclosing tuffs is extensive. Fossils replaced by barite are found in the tuffs underneath the ferriferous layers. Additionally, olistostromes of limestone within the tuffs are, as well, highly-altered to jasper and barite, and late barite-sphalerite associations.

It is thus apparent that syngenetic and epigenetic ores were coeval at Vulcano. The former resulted from replacement of reef limestone by sulfate-sulfide-iron oxide mineralization, whilst the latter formed by precipitation onto the seafloor of proximal pyrite and "more distal" jasper hematite beds.

The Tabaquito Deposit

On the whole, the mineralized zone at Tabaquito is stratabound within the volcano-sedimentary sequence. The limestone component is much less than in Volcano. However, the mineralization is again clearly spatially associated with this rock-type. The main ore zone is massive and consists of barite-quartz and minor sulfides (including sphalerite, chalcopyrite, galena and proustite). Although the continuity of the body has been disrupted by a series of normal faults, it seems that its lateral equivalent is a massive reefal limestone which is almost totally replaced by magnetite and carrying silicified-baritized fossils. In the distal sectors, the magnetite content decreases and the limestone shows extensive replacement by barite laths; this peripheral zone then grades into an unaltered limestone. Covering the main replacement body, there is an irregular mass of subtly-layered jasper a few meters in diameter, which is extensively transected by barite veinlets.

The main body is generally fine-grained. It consists of radial aggregates of barite and euhedral, often doubly-terminated quartz. Occasionally, irregular zones of coarse barite are present. In a few cases remnants of highly sericitized K-feldspar are recognizable in the upper pav of the body. Occasional, circular structures within this zone could be interpreted as totally replaced fossils. The sulfide content of this body is very low. Sphalerite and galena are generally associated with the most silicified zones and are often replaced by quartz. Coarse-barite veins and hematite-quartz veins frequently transect the body.

The mineralized bodies are underlain by chloritized-silicified-baritized andesitic to trachytic volcanics. The bodies are overlain by a less-altered volcanic-volcaniclastic sequence. Laterally the volcanics are kaolinized and transected by black veins of pyrolusitebraunite which, in a general sense, rim the main mineralized zone.

In short, as it is the case with Vulcano, Tabaquito presents evidence of a paragenetic development of initial iron mineralization followed by barite-sulfide mineralization. The stratabound nature of the body and some relict textures again point to a selective replacement of reefal limestones and of associated volcanic rocks. Further introduction of barite-quartz and hematite through veins affected not only the main body, but the base of the overlying lithologies as well. In contrast, the jasper body seems to have been deposited as a siliceous sinter, prior to the last mineralizing event.

The Sapo Negro Deposit

At this locality a series of Mn-Fe-rich strata (iron-formation) is enclosed by a volcanic unit which grades upwards into a layered sequence of carbonates. These strata extend over an area ~200x100 m and are 10 cm to ~1.0 m thick. The Mn and Fe contents of the richest stratum are 27% and 14% respectively (Castillo-Madrid, 1986). Two sequences may be distinguished, separated by an horizon of kaolinized tuff. The upper member consists of two strata of layered jasper, hematite and Mn-bearing brownish zones, separated by a thin layer of brownish (montmorillonitic) tuff. The lower member consists of four shale horizons, rich in Mn oxides and hematite, with almost negligible jasper. Internal folding due to seismically-induced (?) gravitational slides are common in this lower member.

Above this iron formation is a unit of spilitized, pillowed basalt which grades into layered carbonates. The spilitic rocks carry an aphanitic association of plagioclase (oligoclase), chlorite, calcite and minor tremolite, vesuvianite (melilite?), and zeolites. There are two spilitized flows, the thickest apparently lying directly upon the iron formation. The other is intercalated with layered carbonates which contain japser at the bottom of the sequence. The limestone is micritic and contains poorly-preserved microfossils, probably Calcispherulae.

The Ojo de Agua Mineral Ocurrence

At this locality, barite and Fe-Mn oxides replace a biohermal mound of massive limestone. Barite laths occur disseminated and less frequently, concentrated within irregular zones. In some cases, fossils are replaced by barite and by sparry calcite. Hematite occurs in irregular veinlets containing ankerite-siderite and calcite. Mn oxides alter the rock along irregular zones within the micritic matrix.

In contrast to the other areas, the alteration of the limestone is mild at Ojo de Agua. Although there are zones where hematite-silica veinlets are abundant, no major occurrence of mineralization has been yet found. However, recent geophysical data indicate the presence of a magnetic body at depth.

Experimental Techniques

Barite and whole rocks from several localities in the La Minita District were analyzed. Barite was dissolved by the sodium carbonate method. 100 mg of the mineral was fused with 1 g of sodium carbonate (the Sr content of the carbonte was determined by spiking) in a platium vessel. The resulting "cake" was dissolved in distilled water; the insoluble residue centrifuged, and the solution discarded. The residue was dissolved in HNO_3, and the Sr and Ba

TABLE 1 Sr-Rb DATA FOR BARITE AND WHOLE ROCK

SAMPLE	MINERAL/ROCK	87Sr/86Sr*		Sr ppm**	Rb ppm***	87Rb/86Sr	87Sr/86Sro
111 (T)	BARITE	0.704926±16	a	- - -	- - -	- - -	- - -
18B (T)	" "	0.70507±17	b	- - -	- - - -	- - -	- - -
DD 33-5 (V)	" "	0.70524±8	a	3211	- - -	- - -	- - -
DD 33-7 (V)	" "	0.70491±2	b	- - -	- - -	- - -	- - -
DD 31-6 (V)	" "	0.70525±2	b	- - -	- - -	- - -	- - -
46 (O)	" "	0.705408±45	b	- - -	- - -	- - -	- - -
68A (V)	" "	0.705223±21	b	- - -	- - -	- - -	- - -
68A (V)	" "	0.705223±28	a	- - -	- -	- - -	- - -
75B (V)	" "	0.70528±10	b	- - -	- - -	- - -	- - -
82 (V)	" "	0.705350±26	b	- - -	- - -	- - -	- - -
16C (T)	TRACHYTIC TUFF	0.75709±2	b	18	221.2	35.8616	0.70578
16D (T)	TRACHYTIC TUFF	0.75522±3	b	25	313.3	35.8745	0.70389
25 (T)	ANDESITIC SPILITE	0.70546±10	a	186	36.4	0.3256	0.70499
26A (T)	ANDESITIC SPILITE	0.70503±7	a	113	6.2	0.1574	0.70481
31-7 (V)	ALTERED LIMESTONE	0.70607±6	a	60	1	0.0674	0.705974
38 (V)	LIMESTONE	0.70685±7	b	755	5.6	0.0214	0.706819
65 (V)	SILICIFIED TUFF	0.706608±36	a	525	185.3	1.0292	0.70514
68A (V)	TRACHYTIC TUFF	0.721434±30	b	95	454.5	13.85	0.70162
78' (V)	RECRYSTALLIZED LIMESTONE	0.70571±3	b	386	0.45	0.0033	0.705705
78' (V)	" "	0.70573±6	a	*	*	*	0.705725
91 (S)	BASALTIC SPILITE	0.704517±26	a	792	18.6	0.06805	0.70442
94 (S)	BASALTIC SPILITE	0.70557±2	b	741	19.1	0.0735	0.70546

Notes:

Measuring error, as determined with succesive runs of the NBS SRM 987 standard is 0.1% for $^{86}Sr/^{87}Sr$ and 0.5% for $^{87}Rb/^{86}Sr$

(T) Tabaquito, (V) Vulcano, (O) Ojo de Agua, (S) Sapo Negro

* error is 2σ

a- measured in MM30 mass-spectrometer; b- mesured in VG 354 mass-spectrometer

** Sr spike utilized; 4.865 ppm; $^{84}Sr/^{86}Sr$=185.6; $^{87}Sr/^{86}Sr$=0.417; $^{88}Sr/^{86}Sr$=3.072

*** Rb spike utilized: 10.819 ppm; ^{85}Rb=2%(atomic); ^{87}Rb=98%

87Sr/86Sro calculated at 100 M.a. using λ=1.42x10^{-11}y^{-1} (Steiger and Jäger, 1977)

precipitated as nitrates with an excess HNO₃, the solution being discarded and the precipitate dried. The nitrates were then dissolved in 2N HCl and the solution evaporated to dryness. Next the Sr was extracted by ion-exchange chromatography.

For whole rock analysis, 200 to 300 mg of finely ground sample was dissolved in three steps. The samples were placed in teflon beakers and moistened with distilled water. A mixture of 2/3 HF+1/3 HNO₃ was added, and the beaker was covered with a lid, and left overnight at approximately 80° C. HNO3 was added to the dried fluoride salts, and left overnight on a hot plate. Next the nitrates were converted to chloride by adding 4N HCI.

Prior to spiking, the dissolved sample was split into two amounts, one for Sr and the other for Rb analyses. The aliquots were weighed and a specific amount of spike was added. Samples which had an insoluble residue were centrifuged to get rid of the solid material. The solution was

evaporated, then transferred in 2 ml 1.25N HCl to the Sr columns. Rb was extracted in the same columns.

$^{87}Sr/^{86}Sr$ ratios were measured on MM30 and VG354 solid source mass spectrometers. Rb measurements were made on a home-built 12" 90° magnet sector solid source mass spectrometer.

Results and discussion

The $^{87}Sr/^{86}Sr$ ratios in barites range from 0.70492 to 0.70535. The analytical results are presented in Table 1. The $^{87}Sr/^{86}Sr$ ratios in mafic volcanics range from 0.70451 to 0.70557, whilst in felsic volcanics the values range from 0.70660 to 0.75709. The carbonate samples have a $^{87}Sr/^{86}Sr$ range from 0.70571 to 0.70685. The magnitude of the $^{87}Sr/^{86}Sr$ ratio of the volcanics correlates with the amount of Rb in the sample; the more radiogenic Sr occurring in the more Rb-enriched samples.
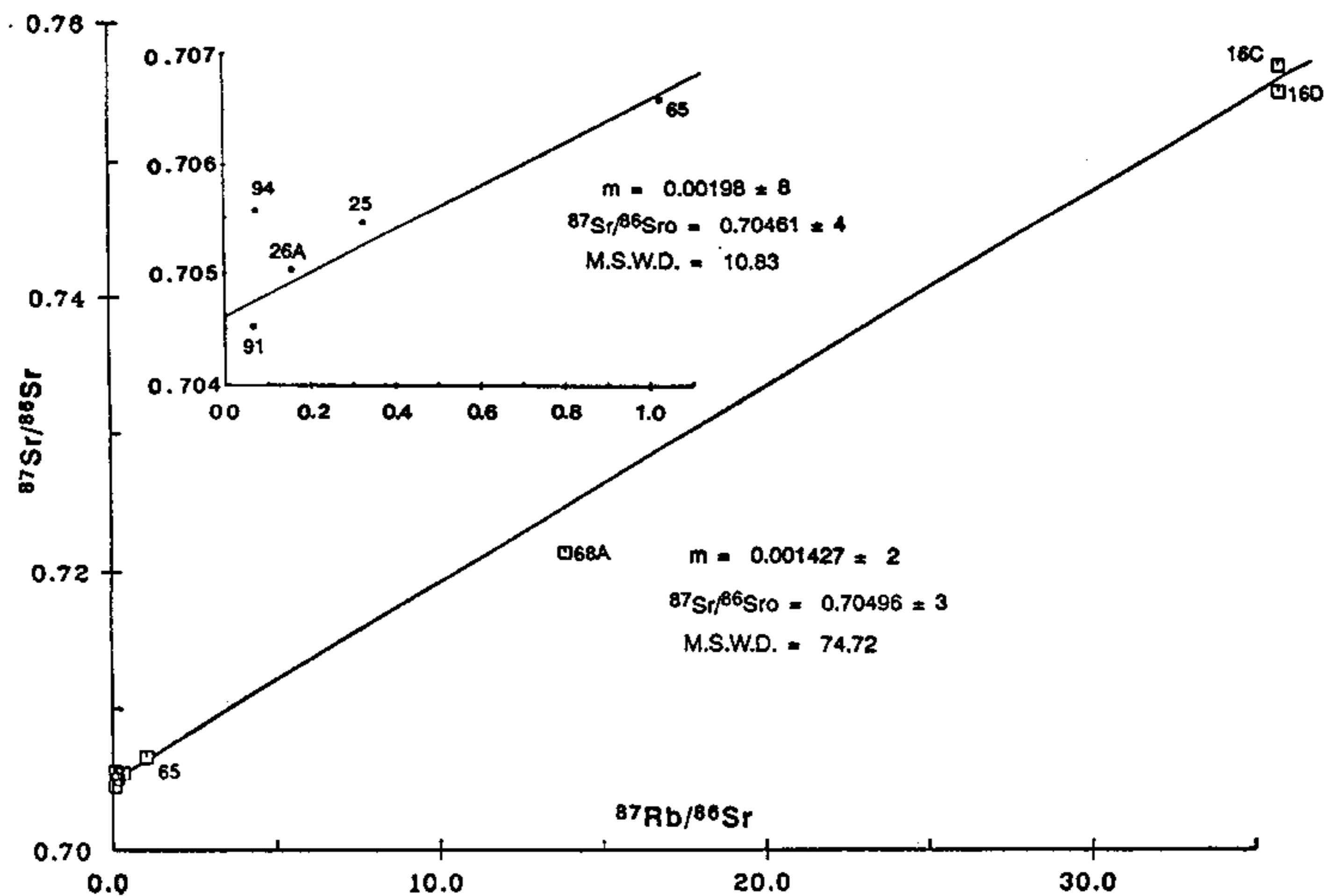
Figure 3. Rb-Sr plot of volcanic rocks from La Minita, Michoacan.

Absolute age of mineralization

The presence of rudists (caprinuloidea) in the limestone constrains the age of the deposit being Albian-Cenomanian. The boundary between these epochs has been placed at 97.5 Ma (Harland *et al.*, 1982). In order to calculate the absolute age of the deposit, the $^{87}Sr/^{86}Sr$ vs $^{87}Sr/^{86}Sr$ ratios of the coeval volcanics are plotted in Figure 3. The inset is an enlargement of the points which lie close to the vertical axis. Calculation of the best fit line by the method of Cumming, *et al.* (1972), gives a slope (m) of 0.001427 ± 2 and initial $^{87}Sr/^{86}Sr$ ratio of 0.704963 ± 3, with MSWD of 74.72. The age calculated with such a slope is 100.4 Ma. If the data in the inset are only used, a slope of 0.001986 ± 8, with an initial ratio of 0.704618 ± 4 and age of 139.7 Ma are obtained. Although an isochron is not defined, 100 Ma and 0.704963 might be close to the actual age and initial $^{87}Sr/^{86}Sr$ ratio, since such an age is in approximate agreement with the paleontologic age.

The range of initial $^{87}Sr/^{86}Sr$ ratios of the volcanics is rather wide. One plausible explanation may be due to alteration of the rock which modified the original concentration of Sr and Rb.

Source of Sr

Since the Rb content of the barites is negligible, they must retain the Sr isotope composition of the fluid at the time of deposition. At La Minita, the possible sources of Sr were the volcanics, the limestone, and the seawater (the last two having similar $^{87}Sr/^{86}Sr$ ratios). Taking 0.7049 as the best estimate of the initial ratio of the volcanics, it becomes apparent that they and the barites had a similar $^{87}Sr/^{86}Sr$ ratio, although that of barites being somewhat higher. On the other hand, the limestone has a considerably higher $^{87}Sr/^{86}Sr$ ratio which, on the whole, is lower than the average value for Albian-Cenomanian limestones [(~0.7072 (Burke *et al.*, 1982)]. Even more the recrystallized limestone shows both lower Sr isotope ratio and lower Sr contents than fresh limestone. All this strongly suggests a very large influence of the volcanics in controlling the Sr ratio of not only the hydrothermal fluid, but perhaps, of the local seawater environment as well. Localized, short term fluctuation of the sea has previously been reported by Faure *et al.* (1978).

A clearer picture of the mixing of components from various sources in the ore fluid at La Minita is better shown

in a $^{87}Sr/^{86}Sr$ vs $\delta^{18}O$ plot (Figure 4). The range of $\delta^{18}O$ values of the barites are from Ortigoza-Cruz *et al.* (1990). Since the oxygen isotopic composition of the La Minita volcanics is not known, the average composition of fresh volcanic rocks summarized by Taylor (1974) has been used. The influence of seawater can be discarded due to the opposite trend defined by the barite and the altered limestone.

It is evident from the diagram that the volcanics controlled the Sr ratio of the hydrothermal system. Although they might not have supplied the large amounts of Sr required to explain the contents of this element in the barites. Probably a large Sr-contribution came from the limestone. Such an Sr suffered some exchange with the volcanic rocks, which thus lowered the $^{87}Sr/^{86}Sr$ ratio of the fluid. However, if large volumes of volcanic rock were involved, the limestone contribution is not required. The variability in the $^{87}Sr/^{86}Sr$ ratios of the barite may have resulted from temperature fluctuations and variations in the water/rock ratio of the hydrothermal system.

Source of barium

Direct application of the previous conclusions may explain the origin of barium at La Minita. This would be a logical procedure, due to the geochemical similarities between Sr and Ba. However, it would be unlikely that all the different types of volcanic rocks contributed Ba in similar proportions. Farrel and Holland (1983) concluded that the Sr ratio of barites of the Kuroko deposits do not provide a categorical conclusion with regard to the source of barium. They rather combined such ratios with barium contents to identify the possible sources.

Average barium concentrations of such lithologies as are present at La Minita, as obtained from the literature, are: trachyte 1177 ppm; rhyolite 1127 ppm; andesite 703 ppm; basalt 300-600 ppm; and limestone 92 ppm (Puchelet, 1978). The reason that trachytes and rhyolite contain large amounts of barium is the presence of K-feldspar, principally sanidine. This mineral exhibits barium contents averaging 3370 to 6850 ppm (Carmichael, 1965). On the other hand, the low barium content of basalts-andesites is due to the fact that plagioclase (andesine-oligoclase) usually has lower barium contents of up to 3480 ppm (Anderson, 1966). The larger barium content of the sanidine is due to the similar ionic radii of barium and potassium, which enable more complete diadochy. During initial differentiation of basaltic magmas, barium is preferentially concentrated in the melt. With further crystallization, the melt becomes depleted in barium due to crystallization of sanidine and micas. Consequently, both the initial and final
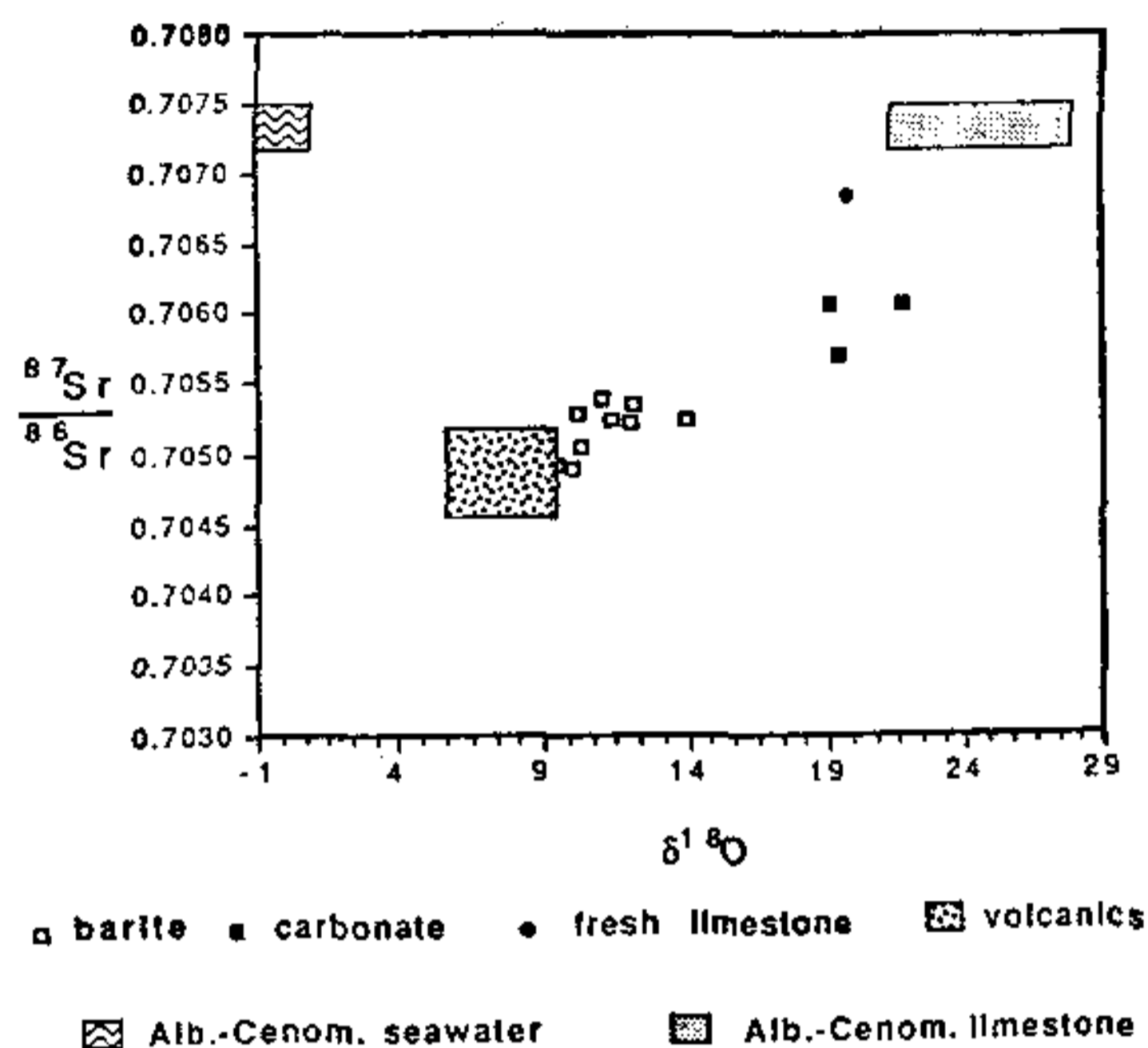
Figure 4. Comparison of the Sr-and O-isotope composition of La Minita's barites with that of carbonates and volcanic rocks of the district, and with that of marine limestone and seawater. The Sr composition of the volcanics is the average and variation obtained in this study, whilst the O-isotope composition was adopted from the summary of Taylor (1974). The Sr composition of Albian Cenomanian Limestone is from Burke *et al.* (1982). The O-isotope composition of limestone is from Keith and Weber (1964).

stages of crystallization may produce phases with comparatively low barium contents (Puchelet, 1978).

This discussion leads to a more definitive identification of the source of barium. It is apparent from the Sr isotope information and from the average barium contents of the rocks, that trachytes and rhyolites are the most viable sources of barium. Contribution by andesite, basalt, and limestone must have been minor, its relative importance following the indicated order. Therefore, it is concluded that the $^{87}Sr/^{86}Sr$ isotope ratio cannot alone distinguish the source of barium, due to the complex numerous steps that intervene in the hydrothermal leaching and isotopic exchange.

CONCLUSIONS

Based on the above discussion the following scenario is proposed for the La Minita exhalative deposits:

A series of events were involved during the evolution of the $^{87}Sr/^{86}Sr$ isotope ratio of the ore fluid. The process started with percolation of seawater into the substratum, through the volcanic pile. The Sr content of this fluid was low and its $^{87}Sr/^{86}Sr$ ratio comparatively high. As

the temperature increased a larger rock-water exchange took place which decreased the Sr ratio of the fluid and probably increased, slightly, its Sr content. Interaction of the fluid was not only with the volcanics, but with the limestones as well. Leaching of Sr from the limestone considerably increased the Sr content of the fluid. However this would have to suffer some exchange with the volcanics (or mixing with fluid already affected by such rocks) in order to lower the $^{87}Sr/^{86}Sr$ ratio of the hydrothermal fluid. The process of isotopic exchange caused the Sr ratio of the volcanics to increase in variable proportions. Mafic volcanics were probably more affected due to the formation of alteration minerals which consumed some of the Sr in the solution.

On the other hand the explanation of the barium seems to be more straightforward. Since the barium concentration in the trachytes and rhyolites overwhelmed that of the other rocks, there was just one possible direction of movement of this element. That is, as soon as the solution leached it from the sanidine, the final destination of this element would be the barite. Probably the concentration of this elment in the ore solution was augmented by minor contributions from the basalts and from the limestone.

ACKNOWLEDGEMENTS

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