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ISOTOPIC COMPOSITION AND CONCENTRATION OF INERT GASES IN MEXICAN HYDROTHERMAL SYSTEMS
(Genetic and applied aspects)

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RESUMEN

En este trabajo se estudian la composición isotópica y la concentración de gases inertes en muestras de fluidos hidrotérmicos de ocho áreas de descarga en la República Mexicana.

Se ha encontrado que Xe, Dr y una gran proporción de Ar y Ne son de composición isotópica atmosférica. Una pequeña fracción de Ar es de origen radiogénico. Todos los sistemas hi-

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drotérmicos mexicanos bajo estudio contienen helio del manto (de 4 a 44% del helio total). Los valores de la razón $^3He/^4He$ varían a lo largo y a través del Eje Volcánico Transmexicano, y son congruentes con el patrón geoestructural así como también con las características petroquímicas de los productos volcánicos del Plioceno tardío - Cuaternario.

La porción máxima del helio del manto es característica de los sistemas hidrotérmicos más calientes (Los Azufres y Cerro Prieto) y de los alrededores de la caldera de Los Humeros (manantiales de Quateloluco). Se observa un contenido anormalmente alto de Ne en las mismas áreas. Teniendo en mente las peculiaridades análogas de otros importantes sistemas hidrotérmicos del mundo, estas evidencias sugieren un alto potencial geotérmico para esas áreas.

ABSTRACT

Isotopic composition and concentration of inert gases in samples of hydrothermal fluids from eight discharge areas in Mexico are studied.

Xe, Dr, and a large proportion of Ar and Ne are found to be of atmospheric isotopic composition. A small fraction of Ar is of radiogenic origin. All of the Mexican hydrothermal systems under study contain mantle helium (from 4 to 44% of total He). Values of the $^3He/^4He$ ratio vary along and across the strike of the Transmexican volcanic belt, these values being consistent with the geostructural pattern as well as with the petrochemical features of the Late Pliocene - Quaternary volcanics.

The maximum portion of mantle helium is peculiar to the "hottest" hydrothermal systems (Los Azufres and Cerro Prieto) and to the vicinity of Los Humeros caldera (Quateloluço springs). Anomalous high content of Ne is observed in the same areas. Bearing in mind the analogous peculiarity of other powerful hydrothermal systems of the world, these evidences suggest a high geothermal potential for those areas.

INTRODUCTION

The hope of revealing a juvenile component in geothermal fluids has always stimulated their study. From this standpoint some features of the chemical composition of thermal fluids have been repeatedly analyzed, for instance, the composition of dissolved solids (common predominance of chlorides, frequently higher concentrations of boron, lithium, potassium, heavy metals) and gases (presence of CO_2, sulphur containing and especially halogenic gases and H_2). Yet, one can never exclude the possibility of the presence of these substances in thermal fluids as a result of the interaction of infiltrated and buried waters with the rocks of the Earth's crust.

The possibility of direct determination of genetically different components (atmospheric, crustal, mantle) in thermal fluids appeared only after study of the isotopic composition of the Ar and He contained in them. Argon of abyssal origin, as compared to atmospheric one ($^{40}Ar/^{36}Az = 295.5$) is enriched with the heavy isotope ^{40}Ar formed in the Earth due to the decay of radioactive ^{40}K. Such an enrichment is usually considered peculiar to crustal setting. However, recent data show that the argon from the mantle is also enriched with the radiogenic isotope thus the $^{40}Ar/^{36}Ar$ ratio in the mantle is about 500 (Tolstikhin, 1978).

Unequivocal evidences of the present-day supply of juvenile (mantle) material into the outer shells of the Earth (crust, hydrosphere and atmosphere) were obtained only after studying of the isotopic composition of the He contained in fluids of continental volcanic regions (Mamyrin *et al.*, 1969a), dissolved in oceanic waters (Clarke *et al.*, 1969) and occluded into other geologic materials (Krylov *et al.*, 1974; Kaneoka and Takaoka, 1978, 1980; Kaneoka *et al.*, 1977). The results of these studies have been recently summarized by Tolstikhin (1978, 1980). As a result of these studies, two types of He were recognized in nature: primordial helium which is present in meteorites and is characterized by a value of (1.5-3) x 10^{-4} for $^3He/^4He$ and radiogenic helium which is isotopically much heavier (in radioactive minerals these ratios approximate 10^{-10}). Primordial helium was captured by the Earth at accretion stage and then, during the subsequent geological evolution, was continuously diluted by radiogenic helium. Besides that, a constant withdrawal of He from the interiors took place. As a consequence of these two processes, the value of $^3He/^4He$ in the Earth decreased relative to the primary (cosmic) level. This diminution was especially appreciable in crustal layer which during its melting from the mantle was simultaneously growing enriched in radioactive elements and impoverished in helium with high isotopic ratio due to more complete degassing. As the newly-formed crust became older the generation of radiogenic helium (the loss of the remains of the primary one not being compensated) wiped off the initial mantle isotopic-helium mark. This mark has disappeared completely in continental Prebaikalian structures where only purely crustal radiogenic helium with ratio $^3He/^4He \approx (2 \pm 1) \times 10^{-8}$ is presently observed.

In the mantle this decrease must have proceeded more slowly. Indeed, in recent volcanic and hydrothermal gases and other geologically similar objects with apparently minimal contamination with crustal material and atmospheric gases, the $^3He/^4He$ ratio is higher by three orders of magnitude than that in the older crust, ranging (1-5) x 10^{-5}.

Precisely this helium with isotopic ratio of 1 x 10^{-5} was recognized for the first time in the Kurile-Kamchatka region; i.e. on the Kuriles, Eastern Kamchatka and in the regions of Central Kamchatka affected by Quaternary volcanism (Mamyrin *et al.*, 1969a; Tolstikhin *et al.*, 1982; Kamensky *et al.*, 1976). These are zones where the granite-metamorphic layer of the continental crust, enriched in radioactive elements was formed in the Miocene. In some places its formation is still in progress today (Tektonics of the Northern Eurasia, 1979). In the volcanically non-active regions of western and Central Kamchatka where the formation of this layer had been completed everywhere in Late Cretaceous, the $^3He/^4He$ ratio is at least one order of magnitude lower. This reflects the process of gradual substitution of mantle helium by the radiogenic helium; this process is most effective in the crust (Polak *et al.*, 1976, Fig. 2).

The $^3He/^4He$ ratio measured in thermal fluids of Iceland had still higher values than those on the Kuriles and Eastern Kamchatka (Kononov *et al.,* 1974). Here, the "mantle" value of this ratio characterized not only the present-day Median neovolcanic zone, but the remaining regions of the island as well. It evidences the absence of a granite-metamorphic layer (source of the radiogenic helium) throughout the whole territory of the island and thus testifies to the oceanic type of Iceland's crust.

Later it became evident that the high (mantle) value of the $^3He/^4He \approx 10^{-5}$ is a global peculiarity of the present-day geothermal activity. Such values are observed in fluids of all the studied volcanic regions: on the Hawaiian Islands (Craig and Lupton, 1976); in Japanese and Marian sectors of the pacific island arcs system (Craig, *et al.,* 1978a; Matsubayashi *et al.,* 1979; Nagao *et al.,* 1979, Wakita *et al.,* 1978), New Zealand (Craig and Lupton, 1978), Italy (Polak *et al.,* 1979a) in the Caucasus (Matveeva *et al.,* 1978), West of the USA (Craig *et al.,* 1978b, 1979; Welhan *et al.,* 1978a); as well as in the links of the global rift system: in Iceland (Kononov *et al.,* 1974), the Galapagos rift (Lupton *et al.,* 1977), Gulf of California (Welhan *et al.,* 1978a), Red Sea (Lupton *et al.,* 1977) and the African-Arabian (Craig and Lupton, 1978) and Baikalian (Lomonosov *et al.,* 1976) rifts.

Regional correlation of the isotopic composition of helium in fluids with the value of terrestrial heat flow (Polak *et al.,* 1976, 1979b), and with the isotopic composition of strontium in rocks (Polak *et al.,* 1979a) has shown that the mantle helium inside the earth's crust is not, in general, transported by an autonomous flow of volatiles, but by silicates from which this gas subsequently emanates and passes into composition of underground fluids.

Composition of other inert gases in various earth materials, including thermal fluids has been studied with the aim of searching for additional isotopic mantle "signatures" (Craig and Lupton, 1976; Phinney *et al.,* 1978; Matsubayashi *et al.,* 1979). The values of Ne, Kr and Xe isotopic ratios observed in fluids, as compared to those typical of the Earth's atmosphere, evidence the presence of an atmospheric constituent in these gases. Yet, the genetic sense of deviations of these values from the atmospheric ones is considerably less distinct than in case of argon and the more so in case of helium (Tolstikhin, 1980). Therefore, a complete study of the isotopic composition of all inert gases in geologically related materials appears necessary. From this standpoint fluids of volcanic areas seem to be most interesting: the study of helium has shown that it is just in such areas where the probability of revealing mantle marks (if there are any) in the isotopic composition of other inert gases is rather significant.

Mexico, abounding in manifestations of volcanic and hydrothermal activity offers exceptional interest for such studies owing to the following reasons. First, in fluids of the Mexican volcanic belt the isotopic composition of inert gases is not yet known; their study would provide new regional data for evaluation of the homogeneity of the mantle in this respect. Second, on the territory of Mexico the different types of geotectonic regime (island-arc and oceanic-rift) took place in Late Cenozoic. Studies in the Kurile-Kamchatka region (Kamensky *et al.*, 1976) and Iceland (Kononov *et al.*, 1974) showed that these types of regime result in appreciable differences in the characteristics of the distribution of the helium isotopes in underground fluids. Therefore, a corresponding investigation of the thermal manifestations in various regions of Mexico is of importance in the solution of the problems of its tectonics. Third, exploration and search for geothermal energy resources in Mexico are intensively developed at present and data on the composition of inert gases in hydrothermal systems, their genesis being related to magmatic (mantle) activity, can provide an indirect evidence of their heat potential.

With these aims in view, we analyzed the chemical composition of gases and the isotopic composition of He, Ne, Ar, Kr and Xe in fluids discharged in some geothermal regions of Mexico. The work was carried out within the framework of the Soviet-Mexican agreement of scientific-technical cooperation on the problem "Energetics: geothermal sources". Specimens were collected by the Soviet and Mexican co-authors in November-December of 1979 and analyzed in the USSR. This paper is a result of joint discussions and interpretation of the data obtained.

GEOLOGICAL SETTING OF THE SAMPLING REGIONS

The distribution of the sampled thermal fields is shown in Fig. 1. Seven of the eight sites are within the socalled Transmexican Volcanic Belt (TMVB) and its closest periphery. Existence of this belt was recognized as far back as 1867 by Humboldt who studied the position of its active volcanoes. Menard (1955) related the position of the belt to the oceanic Clarion fracture zone but the hypothesis is no longer accepted.

Several authors consider its origin as related to the subduction zone between the Cocos and the American Plate (Molnar and Sykes, 1969; Mooser, 1972; Urrutia, 1975; Pal and Urrutia, 1977) or to the tectonics of the Gulf of Mexico (Robin, 1975). Its genesis nevertheless remains still unclear.

The structural-tectonic analysis of the distribution of volcanic rocks over the Territory of Mexico, their petrochemical study and radiometric dating (Cantagrel and Robin, 1979; Demant and Robin, 1975; Gunn and Mooser, 1970; Pal *et al.*, 1978) show that the history of Cenozoic volcanism in this region is rather compli-

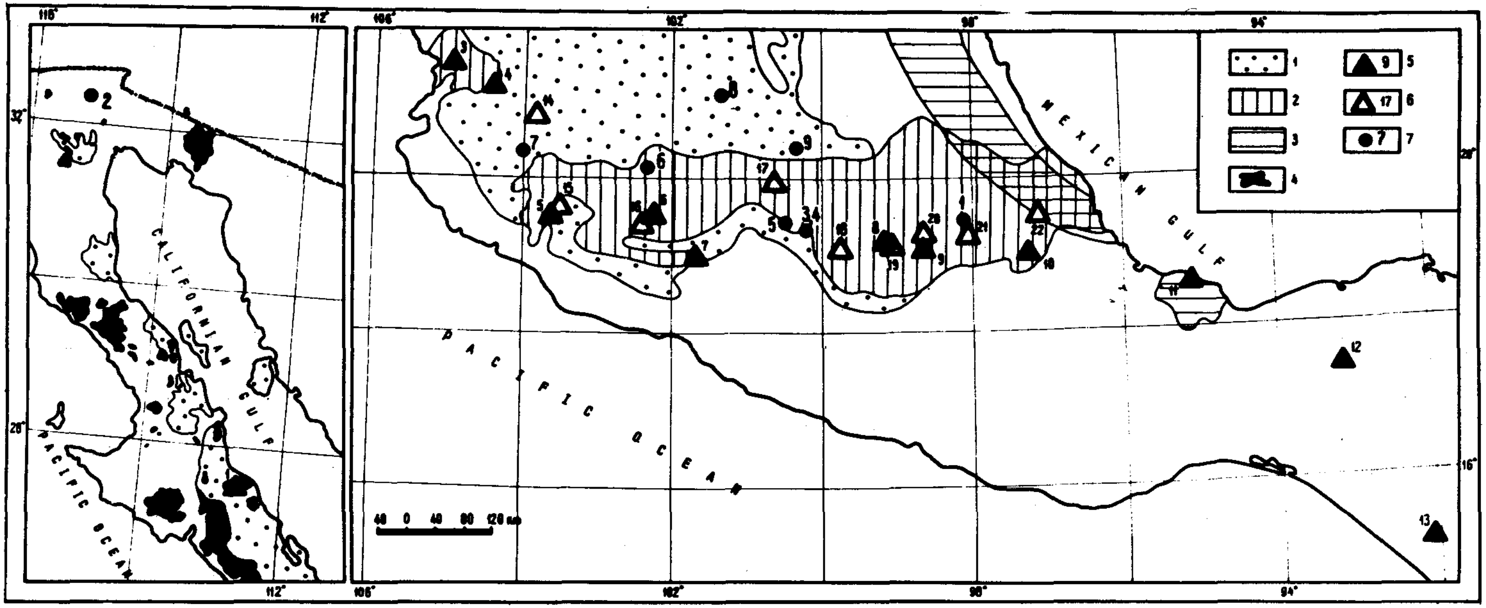

Fig. 1. Distribution of tested thermomanifestations over the territory of Mexico.
1-3 - zones of occurrence (from Demant a. Robin, 1975) of: Ca-alkaline andesite series in the West Sierra Madre and California Peninsula (1), Alkaline-basaltic series in the Eastern province (2), Late pliocene/Quaternary basalts in the area of California Gulf (4); 5 - tested thermomanifestations (1 - Los Azufres de Quatélolulco, 2 - Cerro Prieto, 3 - Los Azufres, Agua Fría area, 4 - Los Azufres, Tejamaniles, 5 - Araró, 6 - Ixtlán de los Hervores, 7 - Hervores de la Vega, 8 - Comanjilla, 9 - San Bartolo), 6 - active volcanoes (10 - Las Tres Vírgenes, 12 - San Juan, 13 - Ceboruco, 14 - Colima, 15 - Paricutín, 16 - Jorullo, 17 - Xitli, 18 - Popocatépetl, 19 - Orizaba, 20 - Tuxtla - San Martín, 21 - El Chichón, 22 - Tacaná), 7 - Extinct volcanoes (23 - Tequila, 24 - Nevado de Colima, 25 - Tanzítaro, 26 - San Andrés, 27 - Nevado de Toluca, 28 - Ajusco, 29 - Iztaccíhuatl, 30 - Malinche, 31 - Cofre de Perote).

cated. In the west of Mexico a thick calc-alkaline andesitic series, considered as a product of the island-arc geodynamic condition, has been accumulating. In the east of Mexico quite different petrochemically volcanic rocks, alkaline basalts of the "trap type", usually connected to extension conditions have been produced. Displacement of calc-alkaline volcanic manifestations eastwards, and that of alkaline basalts southeastwards resulted at the end of the Miocene in their interference in the Pachuca-Veracruz region (Cantagrel and Robin, 1979) (Fig. 4). West of this region the volcanic activity had weakened, or ceased by the middle Pliocene. At the end of the Pliocene it recommenced again in a narrower sublatitudinal zone forming the present-day Transmexican volcanic belt (TMVB). The secondary nature of the TMVB is emphasized by its other frequently used name: "neovolcanic axis" (eje neovolcánico).

Appreciable differences were observed in the petrochemistry of TMVB Pliocene-Quaternary volcanics. In the western part of the belt their composition abounds in basalts and andesite-basalts, whereas in the eastern part it is rather andesitic and dacitic. Large poligenic stratovolcanoes produced mostly andesites inheriting petrochemical habitus of Pre-Pliocene volcanic activity over the territory of the TMVB. Most of its volcanoes are present in the eastern part of the belt gravitating towards its southern margin. Gunn and Mooser (1970) concluded that the contents of K, Al, Ti and ratios K/Rv, K/SiO_2 in the Quaternary volcanics increase along the TMVB strike from east to west, whereas the Mg/SiO_2 ratio decreases. These tendencies are considered as an evidence of increasing pressure in a zone of magma generation, i.e. a westward subsidence of the top of the magma formation zone. The more recent and detailed work of Pal *et al.* (1978) did not confirm the conclusion of Gunn and Mooser. On the contrary, this work found out the opposite trend of the contents of K and Ti in volcanics along the strike of TMVB. Such a trend is in a better accordance with an island-arc geodynamic environment commonly considered to be responsible for the volcanic activity in this part of Mexico.

The eight thermal manifestation studied by us was the hydrothermal system Cerro Prieto located in the extreme northwest of the country. The Pre-Pliocene volcanic activity in this region was of the same *island-arc* character that along the entire Pacific coast manifest itself in an accumulation of calc-alkaline andesitic series. In the Pliocene-Quaternary time the volcanic activity consisted of the eruptions of alcaline basalts. In some places there are even basalts of "tholeiitic tendency" (Hawkins, 1970; cited by Demant and Robin, 1975) which are usually generated in the zones of oceanic rifts. Such a change of petrochemical composition of volcanics reflects cardinal reconstruction of the geodynamic conditions in northwest Mexico caused by active rifting in the California Gulf zone during the last 4-6 M.y. (Atwater, 1970).

Considering the results of the studies of thermal fluids in other regions of the world, such geological history of the sampled regions is of interest in regard to the possible geotectonic interpretation of the peculiarities of the inert gas composition in Mexican hydrothermal systems.

ANALYTICAL METHODS

The specimens under study represent gases spontaneously emanating from springs or included in a steam-gaseous mixture. Specimens were collected by the routine replacing method used in similar investigations by other authors (Mazor and Wasserburg, 1965; Kamensky *et al.,* 1976). Single-neck 200 ml glass bottles were used as collector vessels. In most of the cases these bottles were filled up with water from the sampled springs (i.e., water saturated by the sampled gas) in order to minimize the possibility of contamination of specimens by air gases. The only exception is specimen No.4 representing gas from underground fluids captured in a drill hole; in this case water from the nearest spring was used after saturation by the sampled gas.

Inert gases were extracted from the measured volume of a specimen by means of absorption of active gases with two titanium getters in a vacuum installation. Volumes of fractions of the light inert gases (He + Ne) and the heavy ones (Ar+Kr+Xe) were measured with McLeod gauges after separating these fractions on activated charcoal at a temperature of − 196°C. Both fractions were analyzed by mass spectrometry. In doing so isotopic compositions of He, Ne, Ar, Kr and Xe and ratios He/Ne, Ar/Kr, Ar/Xe were determined. ^{3}He/^{4}He ratios were measured with magnetic-resonance MI 9301 mass-spectrometry (Mamyrin *et al.,* 1969b), other isotopic ratios were measured with MI-1201 and MS 10 mass-spectrometers. Content of all inert gases was estimated through results of volumetric and mass spectrometric measurements.

In the determination of the isotopic composition and concentrations of the inert gases, artificial mixtures and atmospheric air that had undergone the same analytical procedures as the specimens studied, were taken as standards. The resolution of the MI 1201 mass spectrometer provided complete separation of the ion currents of the inert gases from those of background organic radicals as well as separation of the $^{40}Ar^{++}$and $^{20}Ne^{+}$lines. The accuracy of the measurements is summarized in the tables.

RESULTS

The total chemical composition of the analyzed gases is presented in Table 1.

Table 1

General chemical composition of gases

No. of specimens*	$t_{surf.}$, °C ($t_{at\ depth}$)	Concentration of component, 10^4 ppm							
		O_2	Ne_2	CO_2+CO+ H_2S+SO_2	H_2	CH_4	C_2H_6	C_3H_8	C_4H_{10}
1	2	3	4	5	6	7	8	9	10
1.	19	0.0	1.3	98.5	0.0	0.16	0.061	0.001	0.001
2.	84(347)	0.0	8.9	77.9	6.25	6.91	0.021	0.016	0.002
3.	82(320)	0.0	not. det.**	100.0	not det**	0.001	0.001	0.001	0.001
4.	(320)	0.0	4.2	94.6	0.12	1.0	0.02	0.01	0.002
5.	70	2.8	22.0	74.7	0.00	0.47	0.002	0.001	0.001
6.	93	3.6	33.1	59.8	0.0	3.4	0.023	0.015	0.008
7.	90	0.0	7.2	83.7	0.04	8.8	0.17	0.07	0.013
8.	90	0.0	25.2	70.7	0.14	4.2	0.001	0.001	0.001
9.	70	2.8	62.0	22.5	0.02	12.7	0.015	0.001	0.001

* Sampling areas: 1 - Los Azufres de Quatelolulco, 2 - Cerro Prieto, 3 - Los Azufres, Agua Fría (spring), 4 - Los Azufres, Tejamaniles (hole A-6), 5 - Araró, 6 - Ixtlán de Los Hervores, 7 - Hervores de la Vega, 8 - Comanjilla, 9 - San Bartolo.

** Not determined.

Table 2

Isotopic composition of He, Ne and Argon (in brackets – number of measurements)

No. No. of specimens*	$(^3He/^4He) \times 10^{-6}$		$\frac{^{21}Ne}{^{22}Ne}$	$\frac{^{20}Ne}{^{22}Ne}$	$\frac{^{40}Ar}{^{36}Ar}$	$\frac{^{36}Ar}{^{38}Ar}$	$\delta^{40}Ar$ per cent	$\delta^{38}Ar$ per cent
	measured	corrected for air admixture						
1	2	3	4	5	6	7	8	9
1.	8.5(3)	8.8	2.88(2)	9.86(2)	300(3)	5.27 ± 0.08 (3)	1.5	1.5
2.	7.0(2)	7.1	2.92(1)	10.11(1)	303(1)	5.27 ± 0.03 (3)	1.5	1.5
3.	7.7(3)		2.89(1)	9.85(1)	306(1)	5.25 ± 0.08 (3)	3.4	1.9
4.	8.3(2)		2.81(2)	10.10(2)	312(3)	5.27 ± 0.04 (3)	5.3	1.5
5.	6.2(2)	6.3	2.91(2)	9.85(2)	298(2)	5.34 ± 0.07 (3)	0.8	0.2
6.	5.6(2)		2.93(1)	10.15(1)	301(2)	5.35 ± 0.06 (3)	1.8	0.0
7.	1.85(2)		2.87(1)	9.86(1)	309(1)	5.34 ± 0.04 (3)	4.4	0.2
8.	0.85(2)		2.90(1)	9.85(1)	297(1)	5.53 ± 0.15 (3)	0.5	-3.4
9.	2.3(2)		2.89(1)	9.85(1)	295(1)	5.45 ± 0.10 (3)	1.2	-1.9
$\sigma x/X$, %	4-8	4-8	0.5	0.3	0.5		0.5	1.4
$\sigma\bar{x}/\bar{X}$	2.5-6	2.5-6	0.3-0.5	0.2-0.3	0.3-0.5		0.3-0.5	0.8
atmosphere****	1.40		2.89	9.85	295.5	5.35	0.0	0.0

* See note "x" to Table 1.

** Relative mean-square error of one measurement.

*** Relative mean-square error of mean value.

**** For He see Mamyrin *et al.*, 1970; Ne see Schukoljukov *et al.*, 1973; Ar see Nier, 1950.

The $^3He/^4He$ ratio in the specimen studied varies within 0.85 - 8.5 x 10^{-6} (table 2). Following the method described by Kamenskiy *et al.* (1976), the influence of atmospheric helium admixture on the isotopic composition of He in the specimens was determined. In most of the samples it is negligible. Only in three cases the values $^3He/^4He$ corrected for this factor differ slightly from the measured ones.

Maximum values of this ratio were observed in gases on Los Azufres and Cerro Prieto fields, which are the "hottest" and most productive hydrothermal systems.

In the vicinity of Cerro Prieto the isotopic composition of He was previously studied by other researchers (Welhan *et al.*, 1978b). It was analyzed in gases of holes and seven natural thermal manifestations. In one of them - mud pot No.31 - a value of $^3He/^4He = 7.1 \times 10^{-6}$ was determined.

This value is the minimum on this thermal field whereas in other specimens it was within the range of (8.1 - 8.7) x 10^{-6}. We found a value of $^3He/^4He = 7.0 \times 10^{-6}$ in the spontaneous gas of a nameless spring situated at 30 m from the mud pot No. 31 (sp. No. 2). Considering the analytical precision such a coincidence confirms a local minimum indicating a high reliability of the data on He isotopic composition in thermal fluids and its stability in time.

The values of the $^{40}Ar/^{36}Ar$ ratio in all the samples exceeds the atmospheric one (Table 2), showing the presence of excess (radiogenic) argon. However, deviations do not exceed 5.3%; thus, the largest portion of argon (95-99%) is of atmospheric origin. Precise estimation of the contents of radiogenic argon and its ratio to radiogenic helium in such materials requires control of the effects of mass-fractionation by measuring the $^{38}Ar/^{36}Ar$ ratio as well. Unfortunately, we failed to provide the required accuracy of the small deviations of the $^{38}Ar/^{36}Ar$ value. Therefore, the $^4He/^{40}Ar$ values in the specimens were estimated only roughly (approximately 0.7 - 3.5).

The isotopic composition of Ne (Table 2) in six specimens does not differ from the atmospheric composition. The deviations of the $^{21}Ne/^{22}Ne$ and $^{20}Ne/^{22}Ne$ ratios from the atmospheric values are observed in three specimens only (No. 2, 4, 6). These deviations are similar to those previously obtained in some volcanic gases and rocks, where enrichment by ^{20}Ne was found; possible causes will be considered below (see: Discussion of results).

Ratios of Kr and Xe isotopes in all specimens do not differ significantly from the values of these ratios in the atmosphere (Tables 3 and 4).

Table 3

Isotopic composition of Kr

No. No. of specimens x)	number of measurements	$\frac{^{82}\mathrm{Kr}}{^{86}\mathrm{Kr}}$	$\frac{^{83}\mathrm{Kr}}{^{86}\mathrm{Kr}}$	$\frac{^{84}\mathrm{Kr}}{^{86}\mathrm{Kr}}$
1	2	3	4	5
1	2	0.663	0.658	3.280
2	1	0.660	0.658	3.278
3	1	0.660	0.660	3.276
4	2	0.659	0.659	3.281
5	3	0.661	0.661	3.276
6	1	0.664	0.669	3.267
7	1	0.660	0.658	3.280
8	1	0.664	0.663	3.278
9	1	0.667	0.667	3.270
$\sigma x/X$, % xx)		0.5	0.5	0.2
$\sigma\bar{x}/\bar{X}$, % xxx)		0.3-0.5	0.3-0.5	0.1-0.2
atmosphere*		0.662	0.660	3.276

See footnotes to Tables 1 and 2

*See Nief, 1960.

Isotopic composition of Xe

Table 4

No. No. of specimens$^{x)}$	number of measurements	$\frac{^{128}Xe}{^{136}Xe}$	$\frac{^{129}Xe}{^{136}Xe}$	$\frac{^{130}Xe}{^{136}Xe}$	$\frac{^{131}Xe}{^{136}Xe}$	$\frac{^{132}Xe}{^{136}Xe}$	$\frac{^{134}Xe}{^{136}Xe}$
1	2	3	4	5	6	7	8
1.	2	0.216	2.993	0.465	2.406	3.041	1.182
2.	1	0.215	2.980	0.460	2.396	3.030	1.175
3.	1	0.217	2.963	0.460	2.390	3.037	1.180
4.	2	0.215	2.968	0.459	2.383	3.024	1.178
5.	1	0.216	2.971	0.459	2.396	3.042	1.184
6.	1.	0.216	2.964	0.456	2.385	3.027	1.176
7.	1	0.215	2.970	0.456	2.383	3.023	1.173
8.	1	0.216	2.975	0.457	2.390	3.027	1.174
9.	1	0.217	2.989	0.460	2.393	3.040	1.179
$\sigma x/X$, %^{XX}		1	0.3	0.7	0.3	0.3	0.4
$\sigma\bar{x}/\bar{X}$, %^{XXX}		0.7-1.0	0.2-0.3	0.5-0.7	0.2-0.3	0.2-0.3	0.3-0.4
Atmosphere*		0.216	2.981	0.458	2.394	3.0312	1.1764

See footnotes to Tables 1 and 2

*See Podosek et al., 1971.

Concentrations of all the inert gases in the samples analysed are presented in Table 5. The fifth column of this table shows atmospheric argon content estimated from data on the isotopic composition of this gas in a given specimen. Inspection of Tables 5 and 1 shows that the fluids under study differ appreciably in concentra-

Table 5

Concentration of inert gases, ppm
(in brackets - a number of measurements)

No. No. of specimens	He	Ne	Ar	Ar atm.	Kr	Xe
1	2	3	4	5	6	7
1	1.9 (3)	0.27 (2)	145 (3)	143	0.037 (2)	0.0078 (2)
2	17.8 (1)	0,85 (1)	874 (3)	852	0.18 (1)	0.022 (1)
3	16.9 (1)	0.18 (1)	135 (1)	130	0.032 (1)	0.0061 (1)
4	12.0 (3)	0.056 (2)	51.7 (3)	49	0.011 (2)	0.0019 (2)
5	103 (2)	4.9 (2)	3710 (2)	3680	0.71 (2)	0.070 (2)
6	262 (1)	2.2 (1)	4410 (1)	4330	0.93 (1)	0.14 (1)
7	107 (1)	1.2 (1)	3530 (1)	3370	1.1 (1)	0.19 (1)
8	251 (1)	1.3 (1)	8570 (1)	8530	2.0 (1)	0.30 (1)
9	1110 (2)	6.9 (1)	9970 (2)	9850	1.9 (1)	0.22 (1)
σ_x/x, %[xx]	1-5	10-15	1-5	1-5	5	5
$\sigma_{\bar{x}}/\bar{x}$, %[***]	0.6-5.0	7-15	0.6-5.0	0.6-5.0	3.5-5.0	3.5-5.0
atmosphere	5.24	18.2	9340	9340	1.14	0.086

See footnotes to Tables 1 and 2.

tion of components. For instance, He content varies from 1.8 to 1100 ppm (a factor over 600), whereas the concentrations of other inert gases vary by factors of 100 to 200.

The concentrations of various inert gases are interrelated in most of the cases, and are also consistent with the N_2 content (Table 6). Such a relationship is known

Table 6

Correlation between concentrations of N_2, He, Ne, Ar, Kr and Xe

Gases	No. No. of specimens* included in sample	Coefficients of linear correlation, r					
		minimal significant value at 0.05 confidence level in a sample of a given size	He	Ne	Ar	Kr	Xe
N_2	1.2,4-6	0.878	+0.962	$\|r\| < r_{min}$	+0.979	+0.988	+0.982
	1.2,4-9	0.707	+0.938	+0.862	+0.864	+0.752	$\|r\| < r_{min}$
Xe	1-6	0.811	+0.888	$\|r\| < r_{min}$	+0.953	+0.917	
	1-9	0.666	$\|r\| < r_{min}$	$\|r\| < r_{min}$	+0.914	+0.975	
Kr	1-6	0.811	+0.933	$\|r\| < r_{min}$	+0.998		
	1-9	0.666	+0.726	$\|r\| < r_{min}$	+0.980		
Ar	1-6	0.811	+0.911	+0.835			
	1-9	0.666	+0.822	+0.719			
Ne	1-6	0.811	$\|r\| < r_{min}$				
	1-9	0.666	+0.820				

* See Footnotes to Table 1.

to be typical of underground fluids. There is, however, a certain difference between fluids discharged inside and outside of the neovolcanic zones (TMVB and Cerro Prieto area). In the "volcanic" samples consisting of specimens No.1 to 6 the concentrations of all inert gases (excluding Ne) are correlated at the 95% probability level. The content of Ne correlated only with that of Ar. Furthermore, in the whole set of samples, the concentration of Ne is correlated with those of Ar, He, and N_2 but there are no correlations between Xe content and N_2 contents.

DISCUSSION OF RESULTS

a) *Isotopic composition of helium*

The values of the $^3He/^4He$ ratios found in all specimens clearly indicate the presence of He of present-day mantle. The somewhat smaller values of this ratio in the fluids studied as compared to the mantle level (see Introduction) are due to a certain admixture of crustal radiogenic helium.

Given the values of $^3He/^4He$ in the crust and mantle, ii) its value in the studied specimens and iii) the negligible content of atmospheric helium, one can estimate the relative portion of mantle helium "M" contained in them. This portion is deduced from the expression:

$$M = \frac{C_{m}^{He}}{C_{sp}^{He}} = \frac{(^3He/^4He)_{sp} - (^3He/^4He)_{cr}}{(^3He/^4He)_{m} - (^3He/^4He)_{cr}}$$

where C^{He} and C^{He} are the concentration of mantle helium and total He content in the specimen respectively. Assuming that the values of $^3He/^4He$ in the crust and mantle denoted by symbols "cr" and "m" are 2.18^{-8} and 2.10^{-5} respectively*, we find that in the fluids under study M = (4 - 44)% of the total He content in the specimen.

The data on He isotopic composition (Table 7, Fig. 2), as well as on the concentration of the inert gases show that the hydrogeochemical environment in the zone of Late Pliocene-Quaternary volcanics somewhat differs from that outside this zone. In fluids of the TMVB and the Cerro Prieto system (sp. Nos. 1-6) the portion of mantle helium M is inversely proporcional to the total content of active gases (CO_2, CO, CH_4, H_2, H_2S, SO_2), carbon dioxide always prevailing. Such relationships do not contradict the common concept on the composition of magmatic (mantle) emanations, though do not exclude the possibility of supplying of one or another portion of the active gases from shallower sources into the thermal fluids. There is no correlation between M values in these fluids and concentrations of H_2 and CH_4. Yet, a relatively high content of these two gases in fluids of the Cerro Prieto system in association with their presence in underwater manifestations of hydrothermal activity on the bottom of the Gulf of California (Welhan and Craig,

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* The use of other values of the same order will not significantly alter our conclusions.

1979) indicates the possible presence of these gases in mantle emanations discharged in the oceanic rifts.

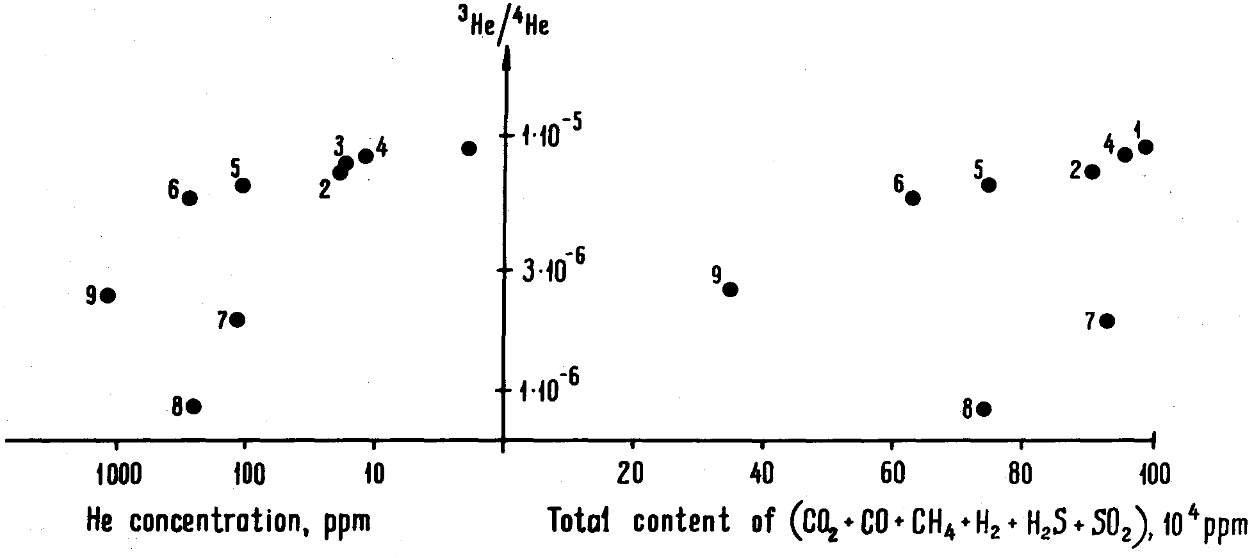

Fig. 2. Relationship between the value of $^3He/^4He$ in the tested thermo-manifestations and concentrations of helium and active gases. Numbers of sites correspond to fig. 1 and the first column of Tables 1-5.

Table 7

Correlation of a mantle helium portion, M, with concentrations of different gases

Gases	Coefficient of linear correlation, r^*, with M	
	in a sample of TMVB (specimens No.No. 1-6**)	in a total sample (specimens No.No.1-9**)
He	-0.863	$\|r\| < r_{min}$
Ne	$\|r\| < r_{min}$	$\|r\| < r_{min}$
Ar	-0.929	-0.861
Kr	-0.926	-0.939
Xe	-0.897	-0.969
N_2***)	-0.958	$\|r\| < r_{min}$
$CO_2+CO+CH_4+$ $+H_2+H_2S+SO_2$	+0.921	$\|r\| < r_{min}$
CH_4	$\|r\| < r_{min}$	+0.691

* Minimal significant values r_{min}, at 0.05 confidence level in Samples of size are given in the column 3 of Table 6.

** See note "*" to Table 1.

*** Data on sp. No. 3, in which concentration of N_2 is not determined are not taken into consideration.

Addition of the data on three thermal manifestations lying outside the contour of the newest TMVB volcanics (sp. Nos. 7-9) abruptly deteriorates correlation between M values and concentrations both of He, Ne and all active gases; i.e. the correlation becomes statistically insignificant (Table 7). Concentration of CH_4 in all specimens proves to be in inverse dependence with the portion of mantle helium. Such relationship may result from increasing mixing with nonmagmatogenic, i.e. crustal (metamorphogenic, biogenic and radiogenic) gases with distance of the sampling area from the TMVB. This fact, along with the position of data in Fig. 2 shows that fluids of the San Bartolo system, are more similar to fluids of the TMVB than the fluids in sp. No. 7 and 8. Such conclusion is supported by the similarity of the total composition of gases, as well as the high deep temperatures estimated from geochemical thermometers in the vicinity of San Bartolo (Templos, 1980, a, b; Templos and Palomares, 1980) and the hydrothermal TMVB systems (Los Azufres, La Primavera, and others).

Thus, certain irregularities in the spatial distribution of the values of $^3He/^4He$ or M in deep-seated gases over Mexican territory can be outlined. The maximum values of these parameters are fixed in fluids of the high-temperature hydrothermal systems of Cerro Prieto (associated with oceanic rifts) and Los Azufres, as well as in gases of Quatelolulco field situated not far from Los Humeros caldera, this last considered as one of the largest manifestations of hydrothermal activity in the TMVB. West of Los Azufres region along the TMVB the $^3He/^4He$ values somewhat decreases, especially when the Hervores de la Vega thermal field is included into the TMVB (sp. No. 7). This tendency if it really exists, can be explained by an increase of the depth of the magmatic source i.e., the sources of fluids carrying mantle helium. As these fluids migrate up to the surface they should be more contaminated by crustal gases than fluids emanated from shallower foci. It is also possible that the mechanism of contamination of mantle matter by crustal gases is of another type. For example a similar trend in the change of the $^3He/^4He$ values was observed in thermal fluids discharged along the Apennine peninsula and is consistent with the distribution of the $^{87}Sr/^{86}Sr$ values in recent volcanics and is explained by participation in the volcanic process both of mantle matter and crustal one in proportion changing regularly along the strike of the volcanic zone (Polak *et al.*, 1979).

In addition to the decrease of the $^3He/^4He$ values in the latitudinal direction there is also a decrease with distance from the belt (TMVB) northward, for instance in fluids of the San Bartolo region, as compared to Los Azufres and Araro hydrothermae discharging within the TMVB. The minimum value of $^3He/^4He$ was recorded in the Comanhilla thermae, Guanajuato (sp. No. 8). When judged by studies of fluids in Kamchatka, decrease of the values $^3He/^4He$ in the back of island-arc volcanic belts is a peculiar feature of such structures. Manifestation of the same tendency in Central Mexico can be considered as evidence of certain analogy in the geotectonic structures of both regions. More reliable conclusions of regional peculiarities of the He isotopic composition in thermal fluids of Mexico, especially along the strike of TMVB, require the study of a greater number of geothermal areas.

b) *Concentration of inert gases*

The isotopic studies showed that in the specimens studied He is entirely or largely of non-atmospheric origin, whereas on the contrary, argon is almost completely atmospheric. The other inert gases (except, perhaps, a certain part of Ne in sp. No.4) are of atmospheric origin as well. However, the concentration ratios of these gases in the specimens concerned do not correspond to those observed in the atmosphere (see Table 5). Differences can be related to peculiarities of the interaction on the inert gases with water. These, in general terms are:

Atmospheric gases, including inert gases, penetrate into the interior of the Earth mostly due to the infiltration of meteoric and surface waters and burial of sediments. These are saturated with air components in quantities corresponding to the partial pressure of these components in the atmosphere and their solubility at a given temperature. Due to the differences in the solubility coefficients of the various gases the composition of water dissolved air differs from the atmospheric one. During subsequent degassing of waters caused by the appearance of non-atmospheric gases (CH_4, CO_2, etc.) and/or rise of temperature, air components will separate as a gas phase in ratios different from those existing in the liquid phase owing to the same variations of the solubility coefficients. The solubility varies with temperature but with different coefficients for each gas (Fastovsky *et al.*, 1972; Potter and Clynne, 1978). If water is degassed uncompletely, the composition of the free gaseous phase should be determined as well as the differences in solubility by the degree of degassing. Repeated degassing (this phenomenon appears to be frequent under natural conditions) will make the real picture still more complicated.

For interpretation of the experimental data it will be more convenient to present the concentration of each inert gas in the specimen under study as a relative value $R_i^G = (C_i^{sp} : C_{Ar}^{sp}) : (C_i^a : C_{Ar}^a)$, where C_i^{sp} and C_i^a , are the concentrations of the i-th inert gas in a specimen and atmospheric air respectively, C_{Ar}^{sp} and C_{Ar}^a are respectively the concentrations of argon with atmospheric isotopic composition in the specimen and in air.

The values R_i^G in the gaseous phase estimated for various theoretical models of degassing of water and degassing history (Prasolov *et al.*, 1981) are presented graphically in Fig. 3. These values were obtained taking into account the effects of temperature. The horizontal A-A line in all diagrams corresponds to atmospheric air, the solid inclined B-B line shows air dissolved in water at 20°C (close to the climatic conditions of Mexico).

In Fig. 3a the area of possible values R_i^G in the gaseous phase being in equilibrium with water at 20°C and different degree of single stage degassing is shaded; the I-I line corresponds to a degree of water degassing (after a normalizing component - argon) equal to $\eta = 0.5$. Two other lines in the same figure express the values R_i^G corresponding to the two stage (II-II) and three stage (III-III) degassing at the same temperature 20°C and a degree of degassing $\eta = 0.5$ in each event (stage).

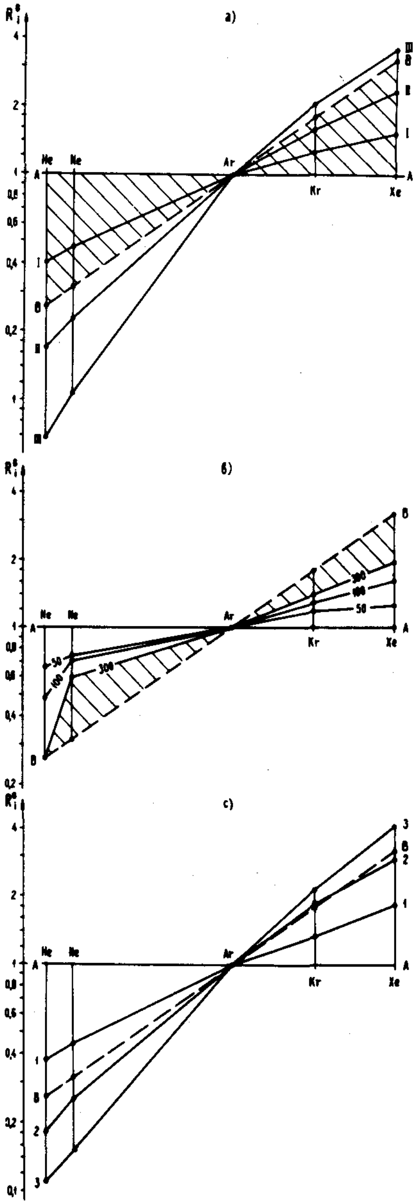

Fig. 3. Theoretical (calculated) ratios of inert gases in gas phase (Ri_I^G) for different models of degassing of water, saturated with air under 20°C (explanations in the text).

Fig. 3b shows the estimated values R_i^G in a case of complete ($\eta = 1.0$) one stage degassing of water saturated with air at 20°C (the B-B line) when the degassing temperature is 50°, 100° and 300°C.

Fig. 3c gives the change of R_i^G ratios under conditions of partial degassing of infiltrated water and simultaneous rise of temperature and number of degassing stages (degree of degassing in each stage $\eta = 0.5$). Line I-I in this Figure corresponds to one stage degassing at $t_1 = 50°$, line 2-2-to two stage degassing at $t_1 = 50°$ in the first stage and $t_2 = 100°$ in the second stage; line 3-3 - three stage at $t_1 = 50°$, $t_2 = 100°$ and $t_3 = 150°$.

Data displayed in Fig. 3 shows that the value R_i^G depends on temperature, number of degassing stages and degree of degassing in each stage. In addition, mixing of gases separated during the various stages of degassing is likely to take place in nature. This facts will result in appreciable differences of the real situation versus the models considered. Nevertheless, the results of theoretical estimations limit a set of possible values R_i^G and give a general idea of the mutual behaviour of inert gases in the system "gas-water". They enable judgement on the degree of conformity between the results of the measurements and any of the models and to establish, in some cases, the presence of excessive (non-atmospheric) gases.

Proceeding from these models, we analyzed relative concentrations of inert gases (R_i^G values) in the sampled hydrothermal systems of Mexico. Fig. 4 shows that in all fluids under study the He content is hundreds and thousands times higher than possible in any model of degassing of waters saturated with air. Such a fact has already been established in many hydrothermal systems (Mazor and Wasserburg, 1965; Kamensky *et al.*, 1976; Mazor, 1979) and is, in general, typical of underground fluids. It indicates the non-atmospheric origin of the largest portion of helium in these fluids, this in complete agreement with data on its isotopic composition.

Relative concentration of other inert gases (combination of R_i^G values) in the analyzed specimens are diverse. In four specimens (Nos. 6-9) these combinations correspond to the concept of an atmospheric origin for all these gases and to models of equilibrium degassing of meteoric waters. In Sp. No.6 and 9 these combinations may be approximated by a model in which almost complete one stage degassing of waters saturated with air is considered. Repeated degassing of such waters can be

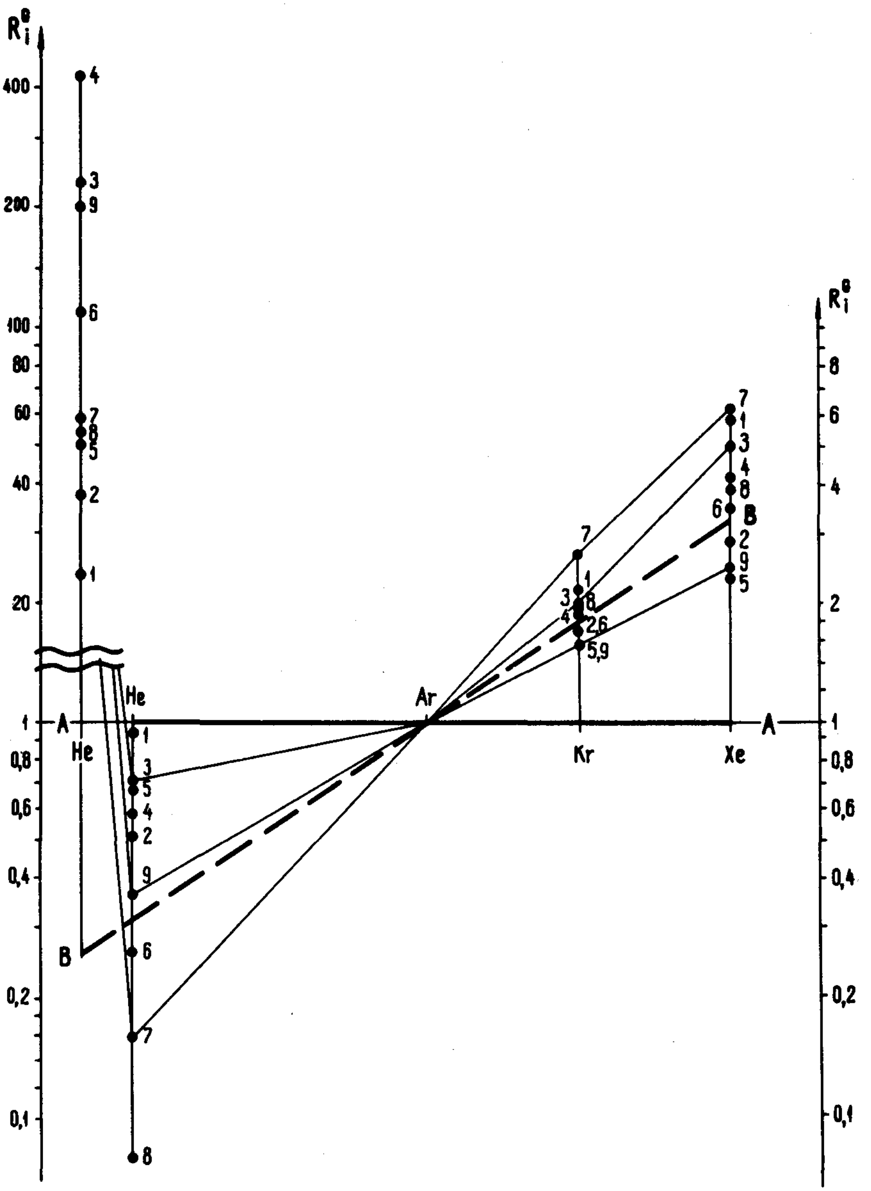

Fig. 4. Measured ratios of inert gases in gas phase of thermal fluids in Mexico (R_i^G, standardized by concentration of atmospheric Ar).
Lines A-A and B-B- are the same as in fig. 3, numbers of sites correspond to fig. 1 and the first column of Tables 1-5. "Typical" sites NN3, 7 and 9 are connected by lines.

assumed in the systems characterized by Sp. No. 7 and 8. In the remaining specimens (No. 1 to 5) the combinations of R_i^G values do not correspond to the models under consideration. If R_{kr}^G and R_{Xe}^G values in these specimens agree with the models of repeated degassing of waters saturated with air, the R_{Ne}^G values are too high for these models. Such an excess of Ne* cannot be explained by different alteration of solubility coefficients of various gases depending on temperature. That is

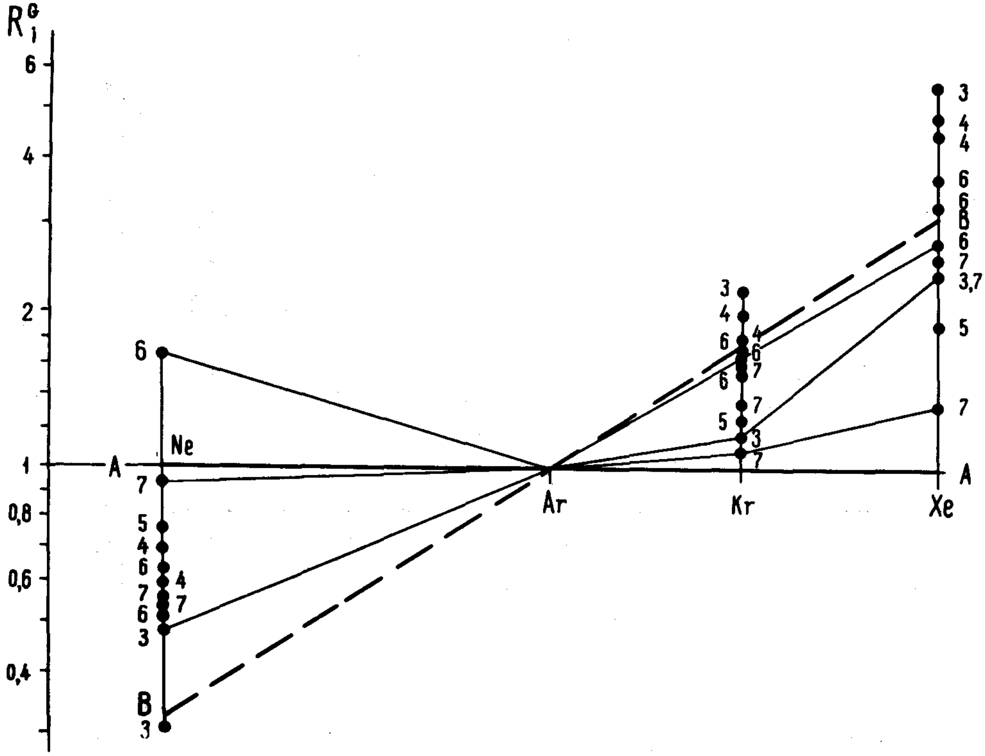

Fig. 5. Measured ratios of Ne, Ar, Kr and Xe in gas phase for the fluids of the Yellowstone and Lassen parks, USA and hydrotherms of Larderello, Italy (data by Mazor a. Wasserburg, 1965 Mazor 1979).

Lines A-A and B-B correspond to fig. 3, 3-4- fluids of Larderello with "normal" (3) and excessive" (4) concentration of Ne, 4-6 -fluids of the Yellowstone park with "normal" and "excessive" (5) concentration of Ne, 7- fluids of the Lassen park (with "normal" concentration of N).

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* The idea of excess of Ne (compared to the model) is certainly relative. In these cases one can assume that the content of Ne is "normal", and Kr and Xe are excessive. Besides, these gases, contrary to Ne, are characterized by purely atmospheric isotopic composition (see tables 3 and 4) and can hardly have other noticeable sources.

probably why there is no correlation between concentrations of Ne and heavy inert gases (Table 6). These specimens contain the highest content of mantle helium (though no appreciable correlation between the Ne content and values "M" is observed, Table 7).

Relative enrichment of thermal fluids with Ne has been recognized in other regions of the globe as well. This can be evidenced, for instance, by results obtained through studying geothermal regions of Yellowstone Park, USA (Mazor and Wasserburg, 1965) and Larderello, Italy (Mazor, 1979). These values are displayed as the value R_i^G in Fig. 5. A similar picture is also observed in the region of Matushiro, Japan (Nagao *et al.*, 1980), where in 1966 an earthquake, supposedly associated with magma intrusion into the uppermost horizons of the crust, took place. Interesting enough is the fact that a high value of $^3He/^4He = (0.2 - 2.0) \times 10^{-5}$ (Craig *et al.*, 1978b; Polak *et al.*, 1979a; Wakita *et al.*, 1978) was recognized in gases of all three regions. Thus, the excess of Ne in thermal fluids of Mexico is not unique.This can be due to: i) the existence of a non-atmospheric source of Ne, isotopically similar to air; ii) the inadequacy of theoretical models to describe the real situation (for instance, in the case of the absence of equilibrium in the system "gas-water".

Regardless of the reasons for the anomalies in the Ne content, it is worth noticing that the hydrothermal systems with excess Ne both in Mexico (Cerro Prieto and Los Azufres) and outside (Yellowstone and Larderello) are characterized by very high underground temperatures and extensive geothermal resources. Therefore, presence of excess Ne in the thermal fluids seems an indication of especially high geothermal potential of such areas. This peculiarity of fluids is worth using as a tentative indicator of the most favourable areas for prospection and exploitation of geothermal energy.

The high $^3He/^4He$ ratio in such fluids underlines their close relationship to present-day degassing of the mantle. Therefore the isotopic composition of Ne in these materials is of interest, more so because in three of the thermal manifestations studied, as mentioned above, the ratios of Ne isotopes differ from those in the atmosphere.

c) *Isotopic composition of Ne*

The isotopic composition of Ne in present-day mantle remains obscure. Study of the isotopic composition of Ne in thermal fluids containing, as it is known, mantle He started with the work by Mazor and Wasserburg (1965) in Yellowstone Park, USA, where this composition was found to be similar to the atmospheric one (accuracy up to 2%). Further studies in the same geothermal area (Mazor and Fournier, 1973) as well as the study of hydrothermae of Larderello, Italy (Mazor, 1979) provided similar results. However, hydrothermae of the Kuril-Kamchatka region (Anufriev *et al.*, 1976) and of Japan (Nagao *et al.*, 1979), as well as gases of the Kilauea volcano on the Hawaiian Islands (Craig and Lupton, 1976) revealed an enrichment of ^{20}Ne as compared to air. Appreciable enrichment of ^{20}Ne was observed in the CO_2 gas of a well in Harding County, New Mexico, USA. This gas contains an excess of ^{129}Xe assumed to be of mantle origin (Buttler *et al.*, 1963; Phinney *et al.*, 1978).

Data on the isotopic composition of Ne in rocks and minerals (tentatively of a mantle origin) are also conflicting. Though all the samples studied contain mantle He and some of them have abnormally high concentrations of inert gases, the Ne isotopic composition in most of these materials do not differ from the atmospheric one (Hennecke and Manuel, 1975; Kaneoka *et al.*, 1977; Kaneoka and Takaoka, 1978, 1980; Saito *et al.*, 1978). The exception are some oceanic basalts (Anufriev *et al.*, 1976; Craig and Lupton, 1976) in which an excess of ^{20}Ne is sometimes observed.

Thus, the Ne isotopic composition frequently is "normal" (atmospheric) in such materials where the probability of its anomalies (judged, in particular by the He isotopic composition) would seem maximum. In addition, samples with an excess of ^{20}Ne are characterized by strong variations of the ^{3}He/^{20}Ne ratio, by four orders of magnitude, even when a hypothetical juvenile neon with the ^{20}Ne/^{22}Ne ratio observed in the solar wind (Tolstikhin, 1980) is considered. In rocks these variations could have appeared in the process of capture of inert gases or their subsequent losses. It is known, however, that during the degassing of the Earth's crust no separation of He and Ne took place, and it is also possible that such separation did not occur during the degassing of the mantle either. Therefore, it would be more correct to use, in the genetic interpretation, the data on materials in which the ratio ^{4}He/^{21}Ne $\approx (1 - 3) \times 10^7$, this corresponding to the rates of generation of these radiogenic isotopes in rocks (Verkhovsky *et al.*, 1976, 1977, 1980).

If the mantle is homogeneous in the ^{3}He/^{20}Ne value (this is the most reasonable assumption on the basis of the general considerations; therefore the opposite assumption is not considered in this paper), and if no separation of He and Ne occurs during its degassing, the following expression will be true for gases in which ^{3}He is of mantle origin and ^{20}Ne consists of mantle and atmospheric ^{20}Ne:

$$\left(\frac{^{22}\mathrm{Ne}}{^{20}\mathrm{Ne}}\right)_{sp} = \left(\frac{^{3}\mathrm{He}}{^{20}\mathrm{Ne}}\right)_{sp} \frac{\left(\frac{^{22}\mathrm{Ne}}{^{20}\mathrm{Ne}}\right)_m - \left(\frac{^{22}\mathrm{Ne}}{^{20}\mathrm{Ne}}\right)_a + \left(\frac{^{22}\mathrm{Ne}}{^{20}\mathrm{Ne}}\right)_a}{\left(\frac{^{3}\mathrm{He}}{^{20}\mathrm{Ne}}\right)_m}$$

The indices "sp", "m" and "a" in this expression designate the gas under study, gas of the mantle, and atmospheric air respectively. This expression is the equation of a straight line in co-ordinates ($^{22}Ne/^{20}Ne$) and ($^{3}He/^{20}Ne$).

If the excess of ^{20}Ne is purely of mantle origin, the points on the diagram should be arranged along one and the same straight line. However, data on hydrothermal systems of Mexico and other thermal manifestations show that such a universal trend is not observed (Table 8, column 5). Scattering of experimental data is a serious argument against the assumption of an identical (mantle) origin of excess ^{20}Ne in the specimens studied. In addition, the idea of a higher $^{20}Ne/^{22}Ne$ ratio in the mantle as against its value in the atmosphere causes serious difficulties in explaining the isotopic composition of atmospheric neon (Craig and Lupton, 1976).

In the light of the available data, anomalous ^{20}Ne content in underground gases by mass-fractionation of atmospheric Ne in its redistribution in the system 'melt-rock fluid-atmosphere' (Nagao *et al.*, 1979; Kaneoka, 1980) seems a better explanation. The data obtained in Mexico (Fig. 6) correspond to this model. Two of the three specimens, in which isotopic composition of Ne differs from the atmospheric one, lie exactly on the mass fractionation line (sp. No. 2 and 6). Deviations of the third specimen (No. 4) from this line can be related to an exaggerated concentration of ^{22}Ne because of superposition of $^{22}Ne^{+}$ and CO_2^{++} lines in the mass-spectrometer, as just in this sample the ratio of CO_2/Ne concentrations is maximum (2×10^7 in comparison with 6×10^6 to 4×10^4 in other cases).

The above mentioned presence of abnormally high Ne concentrations in some specimens is accompanied by the isotopic effect in two cases only. This effect is observed in one of the specimens (No.6) where the Ne content corresponds to the model of degassing of water saturated with air. This means that the total excess of neon and that of ^{20}Ne is of a different origin. Assuming a juvenile nature of the entire excessive Ne leads to a conclusion of identical isotopic composition in mantle and atmosphere and does not explain the causes of broad variations of the $^{3}He/^{20}Ne$ ratio in rocks. Thus, the question of presence of juvenile, mantle Ne in thermal fluids remains a problem and requires further study.

Table 8

Isotopic composition of He and Ne in some gases containing an excess of ^{20}Ne

Sampling area	$\frac{^{3}He}{^{4}He} \times 10^{5}$	$\frac{^{3}He}{^{20}Ne} \times 10^{5}$	$\frac{^{20}Ne}{^{22}Ne}$	$^{*}t_{g}$	References
1	2	3	4	5	
Tungor area, Sakhalin Isl., USSR	0.7	6000	9.8	-0.018	Verkhovsky et al., 1976.
Harding County, New Mexico, USA	0.44	20000	11.6	-0.075	Phinney et al., 1978.
Kilauea volcano, Hawaii Isl., USA	2.1	3800	10.3	-0.12	Craig and Lupton, 1976.
Nigorikawa area, Hokkaido Isl., Japan	1.0	280	9.95	-0.36	Nagao et al., 1978.
Ixtlán, México (Sp. No. 6)	0.56	73	10.15	-4.1	Table 2
Los Azufres, México (Sp. No. 4)	0.83	200	10.9	-5	"
Cerro Prieto, México (Sp. No. 2)	0.71	16	10.1	-15	"
Solar wind	30(-10?)	24500	13.6		Geiss, 1973
Atmosphere	0.14	$0.45.10^{-11}$	9.85		

$$* \ tg = \frac{(^{22}Ne/^{20}Ne)M-(^{22}Ne/^{20}Ne)a}{(^{3}He\ /^{20}\ Ne)_{m}}$$

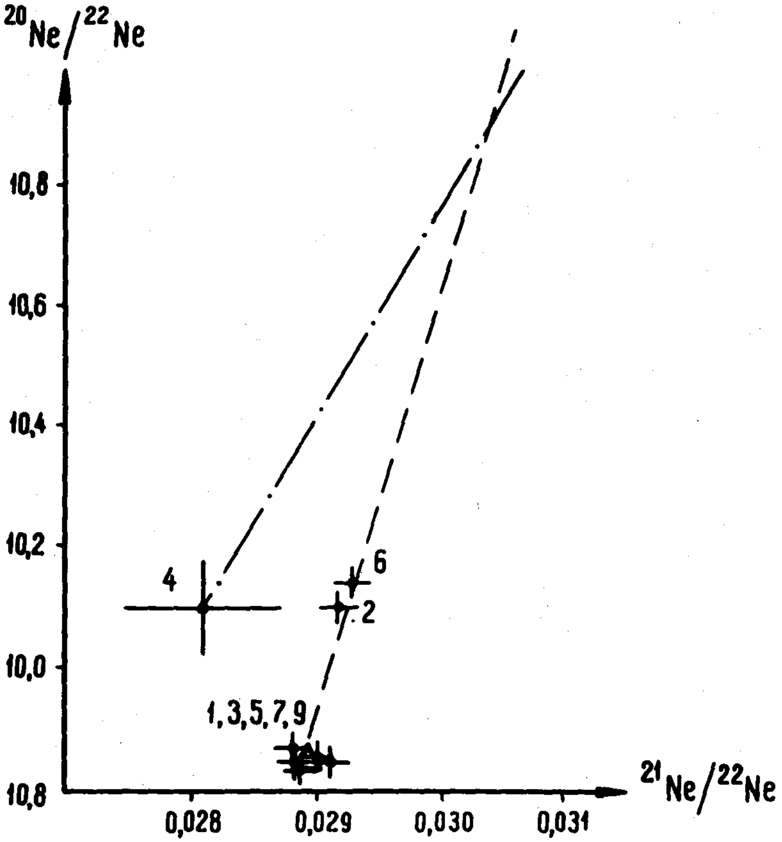

Fig. 6. Isotopic composition of Ne in the studied fluids of Mexico. Numbers of sites correspond to fig. 1 and the first column of Tables 1-5, atmospheric value is shown by a triangle, fine lines show the 95% probability limits (±2), dotted line shows the trend in mass-fractionation, dashed-dotted line expresses an influence of CO_2^{++} contribution in sp. No. 4 on isotopic composition of Ne.

CONCLUSIONS

The investigation carried out is the first experience of studying the isotopic composition of all inert gases in hydrothermal fluids of Mexico. Such an analysis enables us to draw important conclusions on the origin of these gases and opens up the possibility of interpretation of the data obtained for solution of problems in tectonics and magmatism, as well as the use of these data for the tentative evaluation of geothermal resources.

In the light of the data obtained, Xe, Kr and the large part of Ar and Ne do not differ in isotope composition from those in the atmosphere. The rest of Ar is radiogenic. The He isotopic composition indicates the presence of about 4 to 44% of mantle He in which the $^3He/^4He$ ratio is $(2\pm1) \times 10^{-5}$. The admixture of air He in the analyzed specimens is negligible. The spectrum of values $^3He/^4He = (0.85 - 8.5) \times 10^{-6}$ is explained by a different admixture of crustal radiogenic helium. The portion of mantle helium is maximum in the eastern part of TMVB (in the vicinity of Los Humeros caldera, in the hydrothermal system of Los Azufres, etc.), as well as in the rift zone of the Gulf of California (Cerro Prieto).

In the western part of the TMVB (in Hervores de la Vega thermal springs) the proportion of the mantle helium is less. These agrees well with petrochemical data of greater depth magmatic foci in this part of the TMVB, but is badly conformed with previous ideas on the morphology of the zone of magma generation in the interior of the TMVB resulting from typical "island-arc" models. The portion of mantle helium in fluids decreases as the distance of sampling area from the TMVB increases northwards (thermal fluids of Comanjilla and San Bartolo). Such a decrease is usually observed on the periphery of other volcanic belts as well and is explained mostly by obliteration of a mantle isotopic-helium mark by means of generation of radiogenic helium within the crust.

The largest values of $^3He/^4He$ are observed in thermo-manifestations, where an excess of Ne was recognized as compared with the model of degassing of infiltration waters saturated with air. These manifestations are the highest-temperature hydrothermal systems of Cerro Prieto and Los Azufres, as well as fluids of Quatelolulco. An excess of Ne and high values of the $^3He/^4He$ ratio are peculiar to some other powerful hydrothermal systems of the world (Larderello and Yellowstone). Therefore, the combination of these features appears to be an indicator of the existence of appreciable hydrothermal resources in the interiors of such regions.

BIBLIOGRAPHY

* ANUFRIEV, G. S., I. L. KAMENSKY and V. P. PAVLOV, 1976. Anomalous isotopic composition of Ne in hydrothermal springs of the recent volcanic zones. *Doklady of the USSR Acad. Sci. 231,* 6, 1454-1457.

ATWATER, T., 1970. Implications of plate tectonics for the Cenozoic tectonic evolution of Western North America. *Soc. of Am. Bull., 81,* 12, 3513-3536.

BUTTLER, W. A., P. M. JEFFRERY, J. H. REYNOLDS and G. J. WASSERBURG, 1963. Isotopic variation in terrestrial xenon. *J. Geophys. Res. 68,* 10, 3283-3291.

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* Asterisks note works published in Russian.

CANTAGREL, J. M. and C. ROBIN, 1979. K-Ar dating on Eastern Mexican volcanic rocks - relations between the andesitic and the alkaline provinces. *J. of Volcanic and Geothermal Res.*, 5, 99-114.

CLARKE, W. B., M. A. BEG and H. CRAIG, 1969. Excess ^{3}He in the sea: evidence for terrestrial primordial helium. *Earth and Planet. Sci. Lett., 6,* 3, 213-220.

COOK, G. A. (editor), 1961. Argon, Helium and Rare Gases. Interscience Publishers, N. Y. - London.

CRAIG, H. and J. E. LUPTON, 1976. Primordial neon, helium and hydrogen in oceanic basalts. *Earth and Planet. Sci. Lett., 31,* 3, 369-385.

CRAIG, H. and J. E. LUPTON, 1978. Helium isotope variations: Evidence for mantle plumes at Yellowstone, Kilauea and Ethioppian rift valley. *Amer. Geophys. Un. Transactions, 59,* 12, p. 1194.

CRAIG, H., J. E. LUPTON and HORIBE, 1978a. A mantle helium component in Circum-Pacific volcanic gases: Hakone, the Marians and Mt. Lassen. In: terrestrial Rare Gases (Japan Sci. Soc. Press, Tokyo), pp.3-16.

CRAIG, H., J. E. LUPTON, J. A. WELHAN and R. POREDA, 1978b. Helium isotope ratios in Yellowstone and Lassen Park volcanic gases. *Geophys. Res. Lett., 5,* 11, 869-900.

CRAIG, H., J. A. WELHAN, R. POREDA and J. E. LUPTON, 1979. Helium isotope variations in the Yellowstone Snake River Plain Region and the Western U. S. *Amer. Geophys. Un. Transactions (EOS), 60,* 46, p. 945.

DEMANT, A. and C. ROBIN, 1975. Las fases del volcanismo en México, una síntesis en relación con la evolución geodinámica desde el Cretácico. *Bol. Rev. Inst. Geol. UNAM, 75,* 1, 70-82.

* FASTOVSKY, V. G., A. E. ROVINSKY and YU. V. PETROVSKY, 1972. The inert gases. Moscow, *Atmozdat,* p. 352.

GUNN, B. M. and F. MOOSER, 1970. Geochemistry of the volcanics of Central Mexico. *Bull. Volcanol., 34,* f.2, 577-616.

HENNECKE, E. M. and O. K. MANUEL, 1975. Noble gases in lava rock from Mount Capulin, New Mexico. *Nature, 256,* 5515, 284-287.

HUMBOLDT, A., von, 1867. *Kosmos, Vol. IV,* Paris.

* KAMENSKY, I. L., V. A. LOBKOV, E. M. PRASLOV, N. S. BESKROVNY, B. I. KUDRAYAVTSEVA, G. S. ANUFRIEV and V. P. PAVLOV, 1976. The upper mantle components in gases of Kamchatka (according to isotopes of He, Ne, Ar, C). *Geokhimiya, 5,* 682-695.

KANEOKA, I., 1980. Rare gas isotopes and mass-fractionation: indicator of gas transport into or from a magma. *Earth and Planet. Sci. Lett., 48,* 2, 284-292.

KANEOKA, J. and N. TAKAOKA, 1978. Excess ^{129}Xe and high ^{3}He/^{4}He ratios in olivine phenocrysts of Kapulo lava and xenolithic dunites Hawaii. *Earth and Planet. Sci. Lett., 39,* 3, 382-386.

KANEOKA, I. and N. TAKAOKA, 1980. Rare gas isotopes in Hawaiian ultramafic nodules and volcanic rocks: genetic relationships. *Science, 208,* 4450, 1366-1368.

KANEOKA, I., N. TAKAOKA and K. AOKI, 1977. Rare gases in a phlogopite nodule and a phlogopite-bearing peridotite in South African kimberlites. *Earth and Planet. Sci. Lett., 36,* 1, 181-186.

*KONONOV, V. L., B. A. MAMYRIN, B. G. POLAK and L. V. KHABARIN, 1974. The helium isotopes in gases of Icelandic hydrotherms. *Doklady of the USSR Acad. Sci., 217,* 1, 172-175.

* KRYLOV, A. YA., B. A. MAMYRIN, L. V. KHABARIN, T. I. MAZINA and YU. A. SILIN, 1974. Helium isotopes in bedrock of the Ocean floor. *Geokhimiya,* 8.

* LOMONOSOV, I. S., B. A. MAMYRIN, E. M. PRASOLOV and I. N. TOLSTIKHIN, 1976. Isotopic composition of He and Ar in some hydrotherms of the Baikal rift zone. *Geokhimiya,* 11, 1743-1746.

LUPTON, J. E., R. F. WEISS and H. CRAIG, 1977. Mantle helium in hydrothermal plumes in the Galapagos Rift. *Nature,* 267, 603-604.

MAMYRIN, B. A., G. S. ANUFRIEV, I. L. KAMENSKY, L. N. TOLSTIKHIN, 1970. Determination of isotopic composition of atmospheric helium. *Geochim. Int. 7,* 498-505.

* MAMYRIN, B. A., I. N. TOLSTIKHIN, G. S. ANUFRIEV and I. L. KAMENSKY, 1969a. Anomalous isotopic composition of helium in volcanic gases. *Doklady of the USSR Acad. Sci., 184,* 5, 1197.

* MAMYRIN, B. A., I. N. TOLSTIKHIN, G. S. ANUFRIEV and I. L. KAMENSKY, 1969b. Application of magnetic-resonance mass-spectrometer for isotopic analysis of natural helium. *Geokhimiya, 5,* 595.

MATSUBAYASHI, O., K. NAGAO and N. TAKAOKA, 1979. Magmatic isotopic anomaly of He found in natural gases along the Japanese Islands. *Bull. of Volc. Soc. of Japan, 24,* 1, 21-22.

* MATVEEVA, E., I. N. TOLSTIKHIN and V. P. YAKUTSENI, 1978. The "isotopic-helium" criterion of the gases origin and reveal of the neotectogenesis zones (on the example of the Caucasus). *Geokhimiya, 3,* 307-317.

MAZOR, E., 1979. Noble gases in section across the vapor dominated geothermal field of Larderello, Italy. *Pageoph.,* 117, 262-275.

MAZOR, E. and R. O. FOURNIER, 1973. More on noble gases in Yellowstone National Park hot waters. *Geochim. Cosmochim. Acta, 37,* 3, 515-525.

MAZOR, E. and G. J. WASSERBURG, 1965. Helium, neon, argon, krypton and xenon in gas emanations from Yellowstone and Lassen volcanic National Parks. *Geochim. Cosmochim. Acta, 29,* 5, 443-454.

MENARD, H. W., 1955. Deformation of the Northeastern Pacific Basin and the West coast of North America. *Amer. Geol. Soc. Bull., 66,* 9, 1149-1198.

MOLNAR, P. and L. R. SYKES, 1969. Tectonics of the Caribbean and Middle America Region from Focal Mechanism and Seismicity. *Geol. Soc. America Bull., 80,* 1639-1684.

MOOSER, F., 1968. The Mexican Volcanic Belt structure and development formation of structures by differential crustal heating. Panamerican Symposium on the Upper Mantle, Mexico, D. F., March 18-21, 1968.

MOOSER, F., 1972. The Mexican Volcanic Belt: structure and tectonics. *Geof. Intern., 12,* 2, 55-70.

NAGAO, K., N. TAKAOKA and O. MATSUBAYASHI, 1979. Isotopic anomalies of rare gases, Nigorikawa geothermal area, Hokkaido, Japan. *Earth Planet. Sci. Lett., 44,* 1, 83-90.

NAGAO, K., N. TAKAOKA, H. WAKITA, S. MATSUO and N. FUJII, 1980. Isotopic composition of rare gases in the Matsushiro earthquake Saito region. *Geochemical Jour., 14,* 2.

* Natural gases of sedimentary cover. Leningrad, Nedra, 1976, p. 344.

NIEF, G., 1960. Isotopic abundance ratios reported for reference sample stocked by the National Bureau of Standards. NBS Technical Note, 51 (ed. F. Mohler).

NIER, A. O., 1950. A redetermination of the relative abundances of the isotopes of neon, kripton, rubidium, xenon and mercury. *Phys. Rev. 79,* pp. 450-454.

PAL, S. and J. URRUTIA F., 1977. Paleomagnetism, Geochronology and Geochemistry of some igneous rocks from Mexico and their tectonic implications Proceed. IV Intern. Gondwana Symp., Calcutta, India, pp. 814-831.

PAL, S., M. LOPEZ, J. PEREZ R., and D. J. TERRELL, 1978. Magma characterization of the Mexican Volcanic Belt (Mexico) *Bull. Vulcanol., 41-4,* pp.379-389.

PHYNNEY, D., J. TENNYSON and U. FRICK, 1978. Xenon in CO_2 well gas revisited. *Journ. Geophys. Res., B5,* 2313-2319.

PODOSEK, F. A., J. C. HUNECKE, D. S. BURNETT, and C. Y. WASSERBURG, 1971. Isotopic composition of xenon in the lunar soil and in the solar wind. *Earth and Planet. Sci. Lett., 10,* pp. 199-216.

POLAK, B. G., V. I. KNONOV, I. N. TOLSTIKHIN, B. A. MAMYRIN and L. V. KHABARIN, 1976. The helium isotopes in thermal fluids. In: "Thermal and chemical problems of thermal waters" (edit. by A. J. Johnson), *Intern. Assoc. of Hydrological Sci.,* Publ. 119.

* POLAK, B. G., E. M. PRASOLOV, G. I. BUACHIDZE, V. L. KONONOV, B. A. MAMYRIN, L. N. SUROVTSEVA, L. V. KHABARIN and V. S. YUDENICH, 1979a. Isotopic composition of He and Ar in fluids of Alps-Apennines region and its relation to volcanicity. *Doklady of the USSR Acad. Sci., 247,* 5, 1220-1225

* POLAK, B. G., I. N. TOLSTIKHIN and V. P. YAKUTSENI, 1979b. The isotopic composition of helium and heat flow: geochemical and geophysical aspects of tectogenesis. *Geotectonica, 5,* 3-23.

POTTER, R. W. and M. A. CLYNE, 1978. The solubility of the noble gases He, Ne, Ar, Kr and Xe in water up to the critical point. *Journ. of Solution Chim. 7,* 11, 837-844.

* PRASOLOV, E. M., A. B. VERKHOVSKIY and B. G. POLAK, 1981. Noble gas-

es of atmospheric origin in recent hydrothermae (theoretical calculations and experimental data). *Geokhimiya* (in press).

SAITO, K., A. R. BASU and E. C. ALEXANDER, 1978. Planetary-type rare gases in an upper mantle derived amphibole. *Earth and Planet. Sci. Lett., 39,* 2, 274-280.

* SCHUKOLJUKOV, JU. A., V. B. SCHARIF-ZADE and G. S. ASCHKINADZE, 1973. Neon isotopes in natural gases. *Geochemistry, 4,* 475-483.

* Tectonics of the Northern Eurasia (explanatory notes for Tectonic map of the Northern Eurasia, scale 1:5,000,000). *GUGK SSSR,* 1979, pp. 222.

TOLSTIKHIN, I. N., 1980. The nature and history of volatiles of the terrestrial planets (in the light of recent isotopic data). Geol. Inst. of the Xola Depart. of the USSR. Acad. Sci., *Apatity,* 1-54.

TEMPLOS, L. A., 1980a. Geoquímica preliminar del campo geotérmico de La Primavera, Jalisco, México. Memoria de geotérmica (Tomo I), Tercera Reunión Nacional de Geotecnia y Geotermia, 8-10 sept. de 1980, C. F. E., Mexico, D. F., pp. 107-132.

TEMPLOS, L. A., 1980b. Geoquímica preliminar de la zona geotérmica de San Bartolomé de Los Baños - El Salitre. Memoria de geotermia (Tomo II) Tercera Reunión Nacional de Geotecnia y Geotermia, 8-10 sept. de 1980, C. F. E., México, D. F., pp. 409-432.

TEMPLOS, L. A. y F. L. PALOMARES, 1980. Geoquímica de los gases incondensables del grupo geotérmico de Los Azufres, Michoacán, México. Memoria de geotermia (Tomo I), Tercera Reunión Nacional de Geotecnia y Geotermia, 8-10 sept. de 1980, C. F. E., México, D. F., pp. 25-56.

TOLSTIKHIN, I. N., 1978. Review: Some recent advances in isotope geochemistry of light rare gases. In: "Terrestrial Rare Gases" (Japan Sc: Soc. Press, Tokyo), pp. 33-59.

* TOLSTIKHIN, I. N., B. A. MAMYRIN, E. A. BASKOV, I. L. KAMENSKY, G. S. ANUFRIEV and S. N. SURIKOV, 1972. The helium isotopes in gases of thermal springs of the Kuril-Kamchatka volcanic region. In: "Ocherki sovremennoy geokhimii i analiticheskoy Khimii", Moscow, *Nauka,* pp. 405-414.

URRUTIA F., J., 1975. Estudio tectonofísico sobre la Placa de Cocos, B. Sc. (engineering Geophysics) Thesis, UNAM, p. 93.

* VERKHOVSKY, A. B., YU. A. SHUKOLYUKOV and G. SH. ASHKINADZE, 1977. The radiogenic He, Ne and Ar in gases studied. In: "Problemy dokembriyskikh obrazovaniy", Leningrad, *Nauka,* pp. 152-170.

* VERKHOVSKY, A. B. and YU. A. SHUKOLYUKOV, 1976. Isotopic composition of Ne in rocks of the Earth crust and origin of ^{21}Ne rad in natural gases. *Geokhymiya, 5,* pp. 778-781.

* VERKHOVSKY, A. B., Yu. A. SHUKOLYUKOV, R. I. MATUKOV, T. I. KIRKOZOVA and A. V. SUMIN, 1980. The Xe isotopes in berills. VIII Vsesoyuzn. simpz. po stabilnym izotopam v geokhimii (abstr. of papers), Moscow, p. 83.

WAKITA, H., N. FUJII, S. MATSUO, K. NAGAO and N. TAKAOKA, 1978. Helium spots: caused by a diapiric magma from the upper mantle. *Science, 200,* 4340, 430-432.

WELHAN, J. A. and H. CRAIG, 1979. Methan and hydrogen in the East Pacific Rise hydrothermal fluids. *Geophys. Res. Lett., 6,* 11, 829-831.

WELHAN, J. A., J. E. LUPTON and H. CRAIG, 1978a. Helium isotope ratio in Southern California fault zones. *Geophys. Un. Trans. 59,* 12, p. 1197.

WELHAN, J. A., R. POREDA and J. E. LUPTON, 1980b. Gas chemistry and helium isotopes at Cerro Prieto. Proceed. I. Symp. on the Cerro Prieto geothermal field, Baja California, Mexico, 1978, pp. 11-118.