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Helium and carbon isotopes in thermal waters of the Jalisco block, Mexico

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RESUMEN

El bloque de Jalisco es una parte compleja, tanto tectónica como geológicamente, del oeste de México. Se considera una unidad cortical distinta, que se une al continente por la sección sur-este de la trinchera mesoamericana, un contacto entre la placa de Rivera y el continente. Basados en análisis isotópicos de helio y carbono efectuados en 37 grupos de manantiales termales que se encuentran en el bloque de Jalisco, pueden distinguirse varios ambientes tectónicos mayores. La mayor relación R= $^3He/^4He$ con R/R_a cercana a los valores MORB (siendo Ra la relación atmosférica de $^3He/^4He$) se observó a lo largo del cinturón volcánico trans-mexicano (TMVB) y en el complejo volcánico de Colima. En manantiales situados en la parte interior del bloque y cerca de la costa del Pacífico, incluyendo los manantiales submarinos de Punta de Mita, los valores típicos fueron mucho menores, con R/Ra cercanos a 0.4. Se sugiere una correlación negativa entre $^3He/^4He$ y $\delta^{13}C$ of CO_2 como resultado de un acoplamiento entre He radiogénico y CO_2 formado por la oxidación de sedimentos ricos en materia orgánica. Las relaciones $C/^3He$ variaron entre ~10^9 para gases del TMVB, típico de los volátiles surgidos del manto, hasta > 10^{11} sugiriendo un aumento sustancial de carbono de la corteza.

PALABRAS CLAVE: Bloque de Jalisco, isótopos de helio y de carbono, geoquímica de agua y gas, tectónica.

ABSTRACT

The Jalisco block is a geologically and tectonically complex part of western Mexico. It is considered a distinct crustal unit bounded toward the mainland by rifting and toward the Pacific ocean by the SW section of the Mid-America trench, a contact between the subducting Rivera plate and the continent. On the basis of chemical, helium, and carbon isotopic analyses of 37 groups of thermal springs widely distributed over the Jalisco block, several major tectonic environments can be distinguished. The highest R= $^3He/^4He$ ratios with R/R_a (R_a being the atmospheric $^3He/^4He$ ratio) approaching MORB values were observed along the Trans-Mexican Volcanic Belt (TMVB) and within the Colima volcanic complex. For springs in the inner part of the block and close to the Pacific coast, including submarine springs at Punta de Mita, typical values were much lower, with R/Ra down to 0.4. A negative correlation between $^3He/^4He$ and $\delta^{13}C$ of CO_2 is suggested to be the result of coupling between radiogenic He and CO_2 formed by oxidation of organic-rich sediments. $C/^3He$ ratios vary from ~10^9 for TMVB, typical for volatiles released from the mantle, to > 10^{11} thus suggesting a substantial addition of carbon from the crust.

KEY WORDS: Jalisco Block, helium isotopes, carbon isotopes, water and gas geochemistry, tectonics.

INTRODUCTION

Geochemical indicators in thermal waters allow the determination of the sources of various dissolved components of water and gas or of other parameters such as temperature and/or pressure of the water-rock interaction (Ellis and Mahon, 1977; Giggenbach, 1988). According to many authors, the helium isotopic composition of local gases is one of the best indicators of the tectonic and geological environment. It can show the proportion of mantle-derived helium, and hence the presence of deep, permeable crustal structures or intrusive bodies; and in combination with the carbon gas content (CO_2 and CH_4), it may be used to estimate degree of mixing between mantle and crustal fluids (Marty and Jambon, 1987; O'Nions and Oxburgh, 1988; Giggenbach *et al.*, 1993). The Jalisco Block in western Mexico is a complex section of the convergent plate boundary involving subduction of the oceanic plate beneath the continental crust, rifting, batholith, intrusion, lower Cretaceous to Holocene volcanism, and sedimentary sequences. It thus provides a rare opportunity to apply geochemical indicator techniques for the determination of the origin of fluids.

The present work is a part of a comprehensive study of thermal water and gas discharges over the whole Jalisco Block. We report data on gas composition of 35 thermal springs and two volcanic fumaroles, together with helium and carbon isotopic composition. A preliminary discussion centers on the use of helium isotopic ratios to understand some unresolved problems of the tectonics of the Jalisco Block, and the role of carbon isotopes and carbon gases in the determination of the origin of fluids.

GENERAL SETTING AND LOCATION OF SPRINGS

The Jalisco Block is located in the western part of Mexico. It consists mostly of Cretaceous granites and diorites, Cretaceous to Paleocene volcanics, and sedimentary rocks (Ferrari *et al.,* 2000). It is separated from the Mexican mainland by the Trans-Mexican Volcanic Belt (TMVB) to the north; by the Colima Rift to the east, and by the Pacific coast along the NW-SE boundary (Figure 1). There are still debates about the northern boundary of the Jalisco Block. Ferrari (1995) suggested a location of the boundary between the Jalisco Block and the Eocene-early Miocene Sierra Madre Occidental volcanic province, beneath the Mexican Volcanic Belt but not along the Tepic-Zacoalco rift axis to the south of TMVB. The major tectonic features of the Jalisco Block are: (1) two active rifting zones, Tepic-Zacoalco and Colima; (2) the triple junction between these two rifts

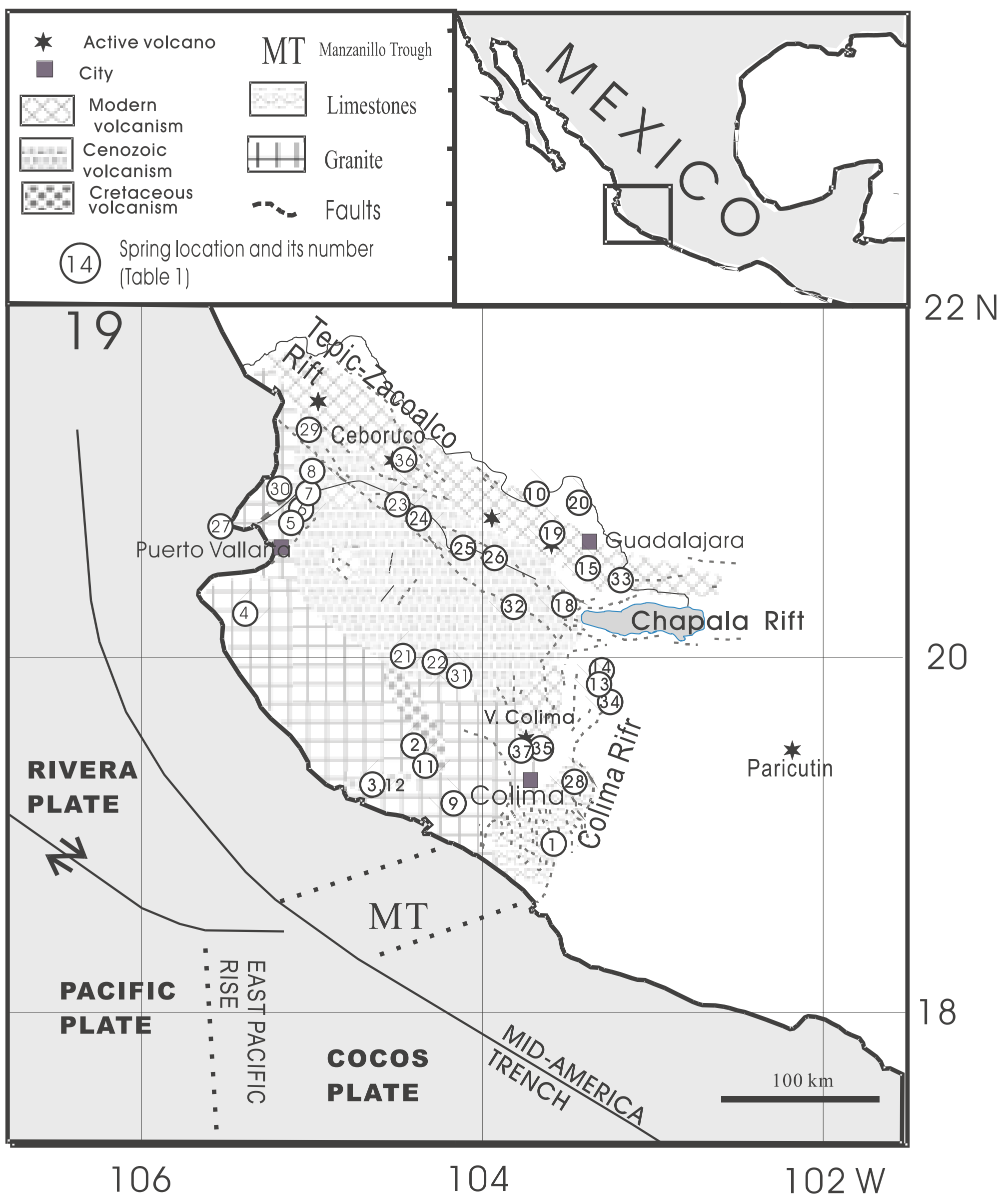

Fig. 1. A simplified geological sketch-map of the Jalisco Block (modified after Ferrari *et al.,* 2000) with main fault systems and location and numbers of thermal springs (See legend).

and the Chapala rift from the east; (3) western part of the TMVB and the Quaternary Colima volcanic complex located within the Colima graben, both with modern volcanic activity related to the subduction of the Rivera Plate; (4) the Puerto Vallarta graben, and Puerto Vallarta granitic batholith.

Four major regions of thermal manifestations are distinguished within the Jalisco block: (1) Western part of TMVB, with most of the presently active geothermal systems of the region including low-temperature fumaroles of Ceboruco volcano; (2) Colima graben (rift) with active fumaroles of Volcán de Colima and springs along the main fault systems of the SE boundary of the graben; (3) thermal springs along the Pacific coast; (4) springs of the inner part of the Jalisco Block. The latter group includes several springs related to the Puerto Vallarta graben. Figure 1 shows also the location of the springs with numbers corresponding to Table 1.

Table 1

Isotopic composition of helium, He/Ne ratios, CO_2 and CH_4 contents, $\delta^{13}C$ of CO_2 and log C/^{3}He, spring names and type of discharge (B – bubbling gas; D – dissolved gas; F- fumarole). *) Data from Prasolov *et al.,* 1999. nd- not detected

No	Name of spring	type	(°C)	R/R_a	He/Ne	He ppm	CO_2 vol%	CH_4 vol%	$\delta^{13}C$ CO_2	logC/^{3}He
1	La Tuna	B	46	2.4	660	516	0.08	0.03	-18	7.1
2	Cuautitlán	B	36	0.86	18	143	0.10	0.26	-16.6	9.7
3	Purificación	B	77	0.66	454	211	0.15	48.7	-22.5	9.4
4	El Tuito	D	34	2.01	0.43	12.2	0.3	nd	-19.6	11.1
5	Desembocada	B	44	4.5	57	289	0.01	0.61	-17.8	8.2
6	Las Palmas	B	53	0.99	9.3	138	0.01	1.22	-14.7	9.9
7	Los Sauses	B	52	1.91	27	162	0.02	1.88	-12.9	9.1
8	Nuevo Ixtlán	D	50	0.86	0.6	57	1.3	0.25	-10.1	11.4
9	Puente de Agua*	B	32	0.75	3.7	7.3	20.4	0.001	-	10.9
10	R.Higueras	D	60	4.7	8	118	26.7	0.05	-4.6	9.9
11	La Concha	D	35	0.72	1.0	15	12.9	nd	-11.3	11
12	Purificación1	B	46	0.62	122	214	0.12	41.3	-12.8	9.4
13	Las Jaras	B	58	1.95	153	448	52	0.3	-7.7	9.5
14	La Plomosa	D	37	1.4	0.8	29	-	-	-19	10.5
18	San Marcos	B	83	3.0	176	392	-	-	-	9.1
19	La Primavera	W	260	6.2	176	16	85	0.5	-3.9	9.8
20	La Soledad	B	100	1.5	0.49	5.8	59	0.002	-2.3	11.9
21	Juichitlán	B	39	1.1	88	1575	2.3	0.04	-4.8	8.8
22	Guamuchil	B	37	0.68	48	957	1.2	0.002	-12.1	9.0
23	Jamurca	B	47	2.6	63	880	2.1	9.2	-6.2	9.7
24	San Juan de Arriba	B	80	2.2	24	335	0.05	1.9	-	8.7
25	Los Mezquitos	D	79	1.23	1.22	-	-	-	-	8.6
26	Amatlán de Canas	D	72	1.1	2.4	-	-	-	-8.2	7.4
27	Punta de Mita	B	89	0.40	38	196	0.56	6.40	-22.0	10.3
28	AC de Colima	B	32	4.0	27	102	0.4	0.45	-4.9	9.3
29	El Molote	B	90	3.2	25	282	0.1	0.02	-	9.8
30	Tecomate*	B	53	4.5	0.89	187	-	-	-	-
31	Tacotán*	B	48	0.66	51	644	-	-	-	-
32	Ervores *	B	90	1.3	112	107	-	-	-	-
33	Barreno*	B	32	5.1	2.1	6.2	-	-	-	-
34	Chilatán*	B	62	1.5	85	395	-	-	-	-
35	Volcán de Colima	F	840	6.2	44	21	43	0.000	-5.2	9.5
36	Ceboruco	F	83	7.5	0.6	7.3	20.4	0.001	-4.1	9.4
37	Santa Cruz	D	34	4.2	10	32	65	1.2	-5.4	9.2

ISOTOPIC AND CHEMICAL DATA

Isotopic compositions of He in the Jalisco Block thermal discharges are given in Table 1 in terms of R/R_a, where R is measured and R_a is atmospheric value of $^3He/^4He$. Also tabulated are temperatures, He/Ne ratios, CO_2 and CH_4 concentrations in dry gas, $\delta^{13}C$ of CO_2 or the total dissolved carbon, and estimates of the $C/^3He$ ratio in the total discharge, where C is the total dissolved + free-gas carbon. Some $^3He/^4He$ and He/Ne data are added to the Table 1 for several sampling points from Prasolov *et al.,* (1999).

EVALUATION OF DATA

The plot R/R_a vs $^4He/^{20}Ne$ (Figure 2) is a common way to estimate proportions of the mantle He, radiogenic He and atmospheric He in a gas (e.g. Sano and Wakita, 1988). The "magmatic" helium signature in the Jalisco Block thermal discharges is represented by two analyses of fumarolic gases from Ceboruco volcano and Volcán de Colima. The Ceboruco fumaroles are weak low-temperature (83°C) steam vents mixed with a large proportion of air; however, their corrected R/R_a value is very high (7.5), close to the highest values for subduction type volcanic gases (Poreda and Craig, 1989). Colima volcanic gas is from a fumarole with a "magmatic" temperature (~850°C), with low air contamination (Ne/He = 41); nevertheless, this gas is lower in mantle He (R/R_a =6.2) than the Ceboruco gas. This difference most probably reflects different positions of these two volcanoes in respect to the subducting Rivera plate, as discussed by Luhr (1993).

Thermal springs of the TMVB which extends to the Jalisco Block are mainly surface manifestations of high-temperature hydrothermal systems. They are CO_2-rich and have high He isotopic ratio. Most of the springs within the block are N_2-rich with a low to very low CO_2 content, but, in general, the gases still contain a significant proportion of the mantle He (Figure 2). The four springs closest to the Pacific coast: Tecomate (30), Punta de Mita (27), Purificación (3) and Puente de Agua (9), despite different water and gas compositions, have the lowest R/R_a values (between 0.4 and 1.0). All thermal waters discharging within areas of deep fault systems, like the Puerto Vallarta graben, Colima Rift, Tepic-

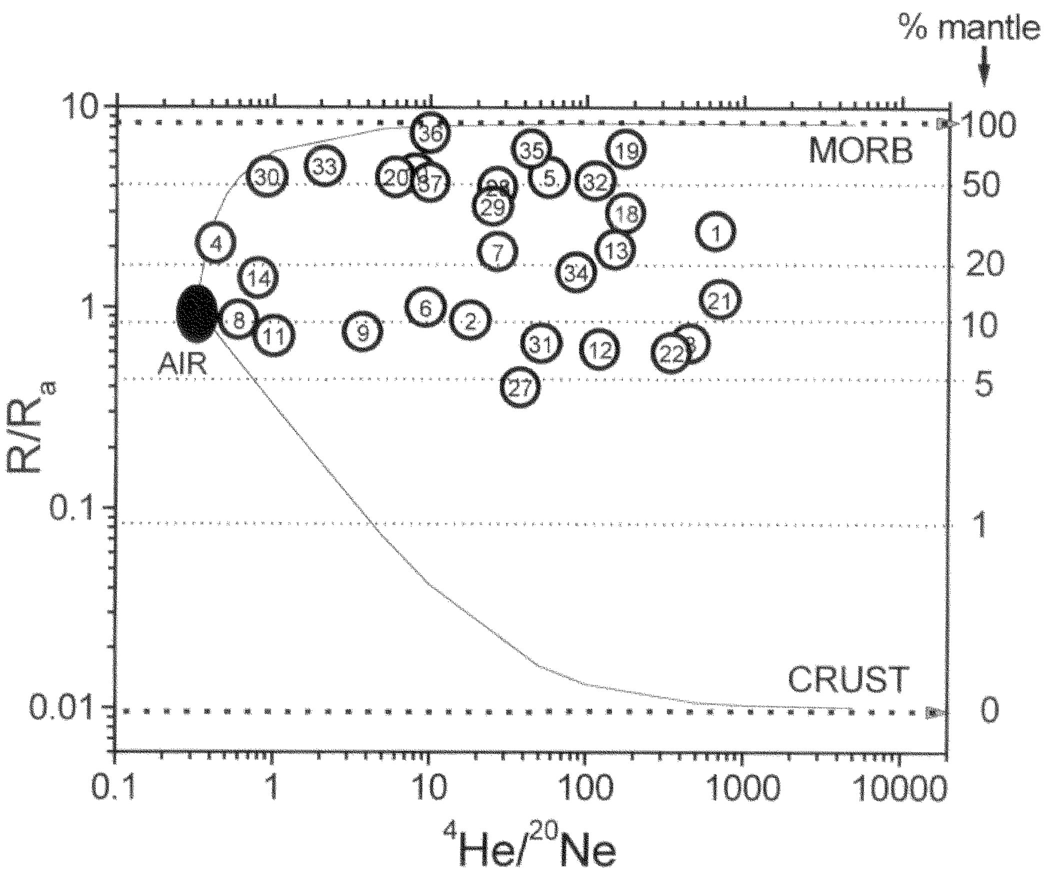

Fig. 2. Helium isotopic composition (in terms of R/R_a, where R is a measured $^3Ne/^4He$ and R_a is its atmospheric value of $1.39x10^{-6}$) vs $^4He/^{20}Ne$ ratio. For the mantle and radiogenic R/R_a the values of 8.3 and 0.01 respectively are assumed. Also shown are mixing lines between the atmospheric helium and helium from mantle and crust, and a fraction of the mantle-derived helium for a given R/R_a (right axis).

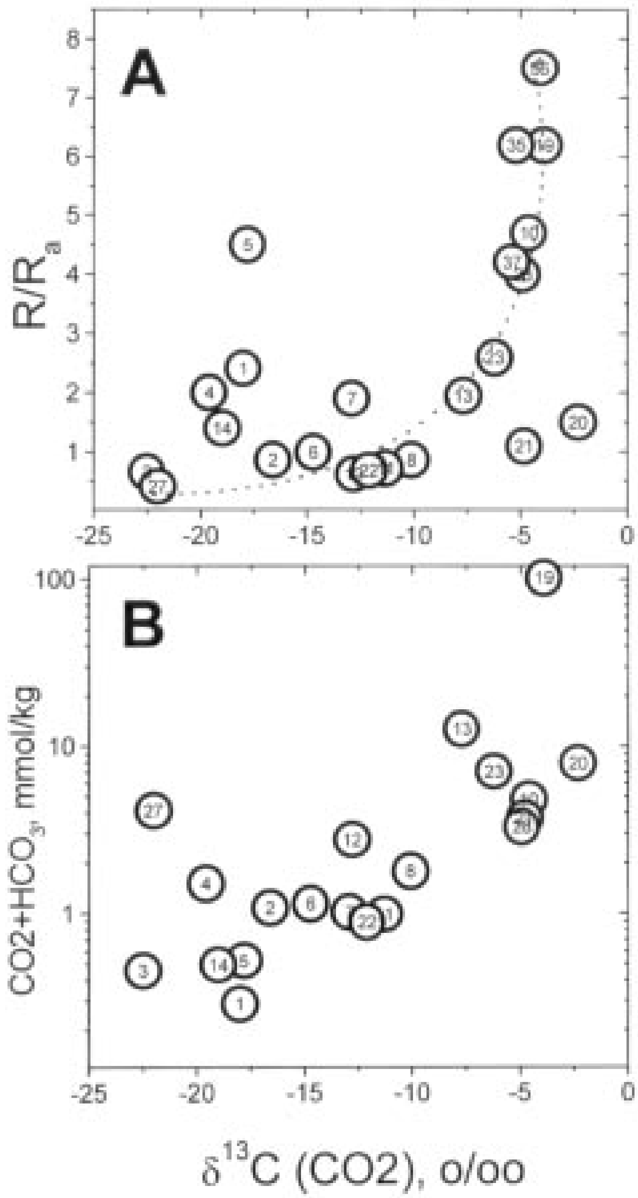

Fig. 3. **A**. Correlation between $\delta^{13}C$ and R/R_a for the Jalisco Block thermal springs. **B.** Correlation between the total inorganic carbon (CO_2+HCO_3) and d^{13}C of CO_2.

Zacoalco rift, have elevated R/R_a values, implying relatively high proportion of deep, mantle-derived He. The triple point (Chapala, Tepic-Zacoalco and Colima rifts intersection) is represented by one hot spring located near Lake Chapala (San Marcos, 18) with R/R_a =3.0.

There are two main trends in the behavior of the carbon in the Jalisco Block springs:

1) a positive correlation between $\delta^{13}C$ and R/R_a (Figure 3A and 2). The isotopic composition of carbon from CO_2 depends mainly on the CO_2 concentration in the gas phase or total dissolved inorganic carbon (TDC) (Figure 3 B). Higher-CO_2 gases are characterized by higher $\delta^{13}C$ values, close to typical "magmatic" or "mantle" CO_2 at –5 to –4 ‰ (Taylor, 1986), whereas CO_2-poor, N_2-rich waters are depleted in ^{13}C. This may be caused by the loss of CO_2 at depth and isotopic fractionation of C between CO_2-gas, dissolved CO_2 and carbonate species or by a high proportion of CO_2 formed by the oxidation of organic-rich sediments.

It is interesting, that within the Jalisco Block, despite the presence of relatively large limestone provinces, there are no so-called soda-springs – CO_2-rich cold or warm waters with CO_2 derived by processes of metamorphism. All CO_2-rich waters are of typical hydrothermal origin.

DISCUSSION

Spatial distribution of helium isotopic ratios

Figure 4 shows the distribution of R/R_a ratios over the Jalisco Block with the larger circles corresponding to the higher R/R_a ratios. The western part of the Mexican Volcanic Belt lies along a complicated system of grabens and semigrabens created by the Tepic-Zacoalco rift. With this data set it remains impossible to distinguish the origin of He in fluids discharging along this part of TMVB: whether it originates from deep active faults or from relatively shallow levels, from magmatic chambers and intrusive bodies related to the subduction-type magmatism of the TMVB. The southern boundary of the Tepic-Zacoalco rift, along the Sierra Guamuchil, Miocene-Pliocene volcanic ridge, is characterized by a substantial low-temperature hydrothermal activity with elevated R/R_a in the range 1-2.6 (springs 23-26).

On the basis of He isotopic data presented in this paper, we can contribute to recent debates concerning the SE and W boundaries of the Jalisco Block. Garduño *et al.* (1998), based on a microtectonic study, suggested that the Tamazula Fault is the main controlling factor of the geometry of the Colima rift, and that the southern boundary of the Jalisco Block, starting from the Colima volcanic complex, is limited by the Tamazula fault, which has a NE-SW direction and a length of more than 160 km. Therefore, the accepted earlier (Bandy *et al.,* 1998) SE boundary of the Colima rift might not exist. Nevertheless, many thermal springs discharge along this part of the Colima rift, and moreover, He from these springs (La Tuna (1), Agua Caliente de Colima (27), Chilatan (34)) is characterized by a significant fraction of mantle-derived He (R/R_a = 2.5 - 4.0), which suggests active deep faulting. Conversely, the only warm spring is located exactly at the SW extreme of the "Tamazula fault" at Puente del Agua; it contains a much lower fraction of mantle-derived He (R/R_a=0.75), similar to that of other thermal springs close to the

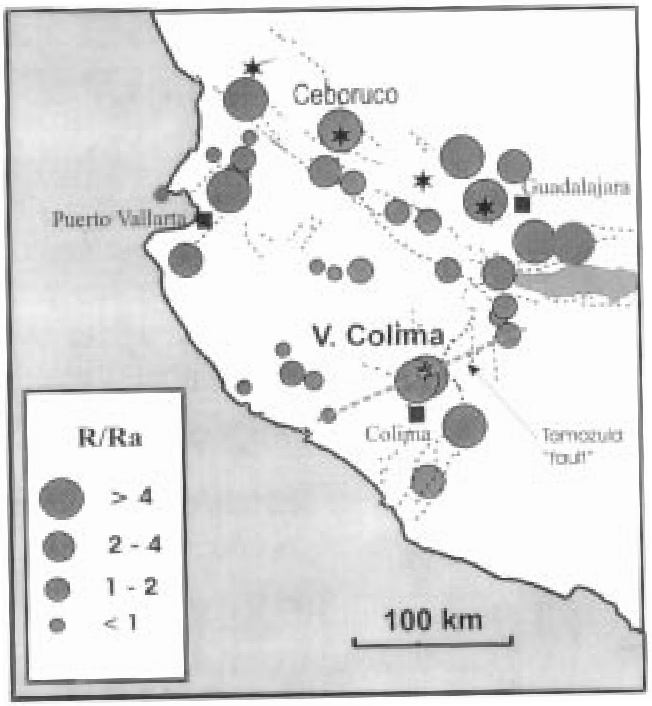

Fig. 4. A map of the Jalisco block showing a relative proportions of the mantle-derived He in gases of thermal springs.

Pacific coast of the Jalisco Block to the NW. No hydrothermal activity exists along the "Tamazula Fault" south of Volcán de Colima, which is further evidence that if this fault does exist, it is not as deep as was inferred, and at least not a "basement structure that has governed the geometry of the Jalisco Block." (Garduño *et al.,* 1998).

The Puerto Vallarta graben and surrounding structures is another tectonically complex area (Ferrari *et al.,* 1994; Bandy *et al.,* 1995). The NW boundary of the Puerto Vallarta graben is characterized by a high hydrothermal activity (Desembocada, Las Palmas, Los Sauces hot springs), whereas its SE limit is less active. However, there is a group of very diluted springs near El Tuito, discharging warm water through fractures in Cretaceous granites of the Puerto Vallarta batholith. Free and dissolved gases of these springs from both sides of the graben contain He with higher than atmospheric $^3He/^4He$ ratios, up to R/R_a =4.5 in Desembocada spring. There is no evidence of any younger volcanism than Oligocene in this area, so this mantle signature in gases is the evidence of deep and active faulting. The younger volcanism, Miocene to Pliocene occurred ~ 30 km to the NW of Puerto Vallarta, close to the recently discovered Punta de Mita submarine springs (Núñez-Cornú *et al.,* 2000; Taran *et al*., 2002), which discharge hot (89°C) gas-rich water at 11 m depth, ~ 400 m off the shore line. Gas from the Punta de Mita spring contains He with the lowest fraction of mantle-derived He of all Jalisco thermal manifestations (R/R_a=0.4). These springs are not related to the extensional tectonics of Puerto Vallarta graben. Rather they are derived from an over-pressured aquifer with some kind of connate waters in oceanic sediments underlying the granites of the Puerto Vallarta batholith, as discussed elsewhere (Taran *et al.*, 2002).

Carbon isotopes, C/³He ratio and origin of fluids

A commonly used technique to evaluate correlations among carbon species and He isotopic ratio consists of plots of R/R_a vs $C/^3He$ or $\delta^{13}C$ vs $C/^3He$ (Sano and Marty, 1995; Giggenbach *et al.,* 1993). Figure 5 is based on $C=CO_2+HCO_3+CH_4$ in the total discharge. The gas content in the total discharge was estimated by

$$X_g \text{ (mmol/kg } H_2O)=10/X_{Ne}\text{(ppm)},$$

where X_{Ne} is the measured analytical concentration of Ne in a gas sample (Taran, 1988; Taran *et al.,* 1998). The composition of the deep mantle component corresponds to volatiles of MORB with R/R_a =8.3 and $CO_2/^3He=2x10^9$ (Marty and Jambon, 1987). "Crustal" gases have R=0.01Ra and log $C/^3He$ has a wide range of values from 6 to 14 (O'Nion and Oxburgh, 1988). Gases of the Jalisco Block scatter within the log $C/^3He$ range of 7 to 12.

Ten sample points fall in the space representing gases associated with arc volcanism: two fumarolic gases, and several springs from the TMVB, at the southern boundary of the Tepic-Zacoalco rift, and springs located near Volcán de Colima (Figure 5A). Giggenbach *et al.* (1993) have discussed in detail the causes of the loss or gain of CO_2 and CH_4 at depth. The main process of CO_2 loss is precipitation of calcite and, for high-temperature hydrothermal systems, chemical fractionation at boiling. The main processes responsible for excess carbon are metamorphism (CO_2) and degassing of hydrocarbons from organic-rich sediments (CH_4). The combination of the two plots (Figure 5 A and B) for the Jalisco Block gases shows that low CO_2 and low $\delta^{13}C$ gases are generally enriched in carbon with respect to the MORB-value. Only two springs with extremely low CO_2-content, La Tuna and Desembocada (1, 5) are "depleted" in C. It should be noted that the río Purificación (3, 12) CH_4-rich, high salinity (12,000 mg/l of Cl), Na-Ca-Cl spring has $C/^3He$ ratios very close to the MORB value. However, it has a quite low $^3He/^4He$ ratio ($0.66R_a$), essentially "thermogenic" $\delta^{13}C$ of CH_4 (-45‰) and low $\delta^{13}C$ of CO_2 (-22.5‰) (Figure 5B), which are evidence for a crustal source of carbon, and this coincidence is likely to be accidental.

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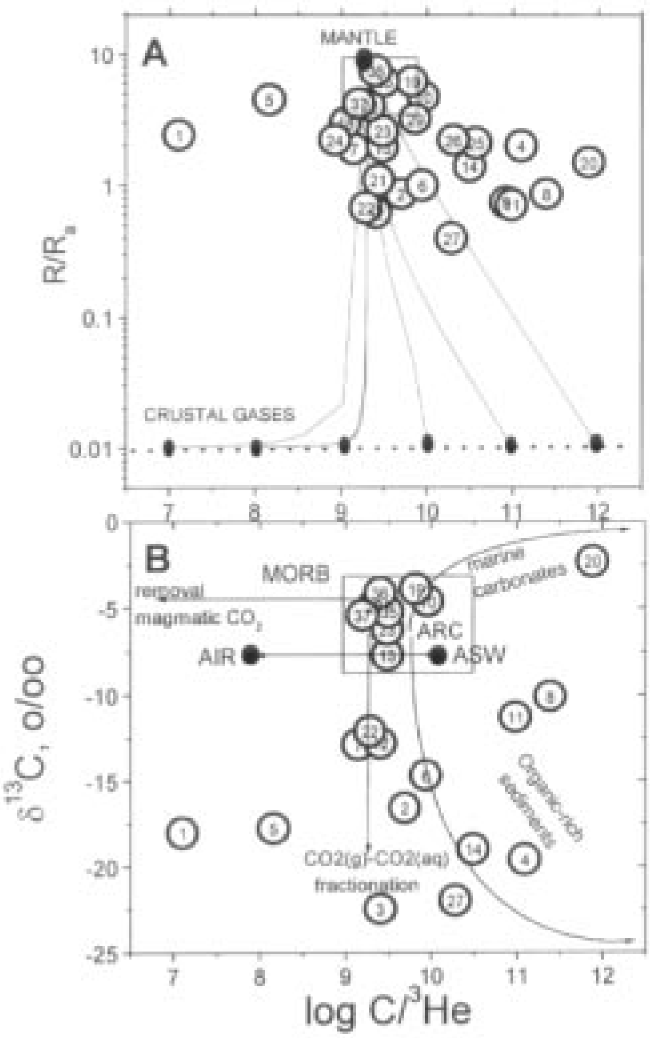

Fig. 5. **A**: The log (R/R_a) vs log ($C/^3He$) plot for the Jalisco Block thermal discharges. Mixing lines are drawn between the R/R_a=8.3 and R/R_a=0.01 endmembers for different $C/^3He$ ratios of the "crustal" endmember. **B**: The $\delta^{13}C$ of CO_2 vs log ($C/^3He$) plot for the Jalisco Block gases (see text for discussion)

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