# 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  ${}^3He/{}^3C$  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  ${}^{\sim}10^9$  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  $\sim 10^9$  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<sub>2</sub> and CH<sub>4</sub>), 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

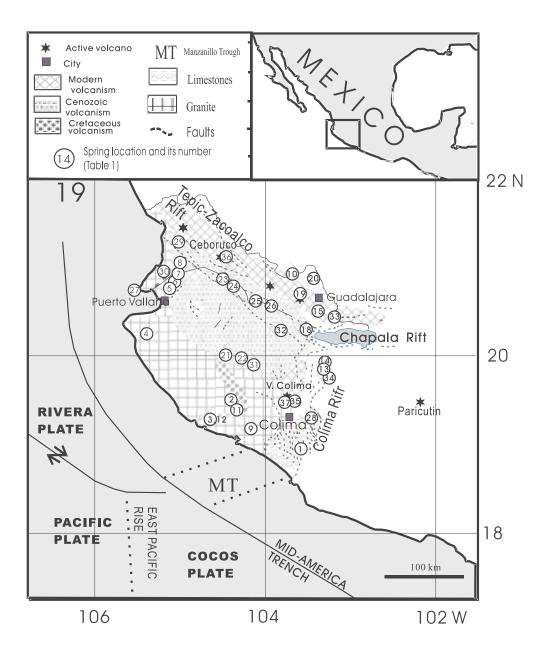


Fig. 1. A simplified geological sketch-map of the Jalisco Block (modified after Ferrari *et al.*, 2000) with main fault systems and location and numbers of thermal springs (See legend).

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<sub>2</sub> and CH<sub>4</sub> contents, δ<sup>13</sup>C of CO<sub>2</sub> and log C/<sup>3</sup>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 <sub>a</sub>	He/Ne	He ppm	CO <sub>2</sub> vol%	CH <sub>4</sub> vol%	δ <sup>13</sup> C CO <sub>2</sub>	logC/³He
1	La Tuna	В	46	2.4	660	516	0.08	0.03	-18	7.1
2	Cuautitlán	В	36	0.86	18	143	0.10	0.26	-16.6	9.7
3	Purificación	В	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	В	44	4.5	57	289	0.01	0.61	-17.8	8.2
6	Las Palmas	В	53	0.99	9.3	138	0.01	1.22	-14.7	9.9
7	Los Sauses	В	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*	В	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	В	46	0.62	122	214	0.12	41.3	-12.8	9.4
13	Las Jaras	В	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	В	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	В	100	1.5	0.49	5.8	59	0.002	-2.3	11.9
21	Juichitlán	В	39	1.1	88	1575	2.3	0.04	-4.8	8.8
22	Guamuchil	В	37	0.68	48	957	1.2	0.002	-12.1	9.0
23	Jamurca	В	47	2.6	63	880	2.1	9.2	-6.2	9.7
24	San Juan de Arriba	В	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	В	89	0.40	38	196	0.56	6.40	-22.0	10.3
28	AC de Colima	В	32	4.0	27	102	0.4	0.45	-4.9	9.3
29	El Molote	В	90	3.2	25	282	0.1	0.02	-	9.8
30	Tecomate*	В	53	4.5	0.89	187	-	-	-	-
31	Tacotán*	В	48	0.66	51	644	-	-	-	-
32	Ervores *	В	90	1.3	112	107	-	-	-	-
33	Barreno*	В	32	5.1	2.1	6.2	-	-	-	-
34	Chilatán*	В	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<sub>a</sub>, where R is measured and R<sub>a</sub> is atmospheric value of  $^3$ He/ $^4$ He. Also tabulated are temperatures, He/Ne ratios, CO<sub>2</sub> and CH<sub>4</sub> concentrations in dry gas,  $\delta^{13}$ C of CO<sub>2</sub> or the total dissolved carbon, and estimates of the C/ $^3$ He ratio in the total discharge, where C is the total dissolved + free-gas carbon. Some  $^3$ He/ $^4$ He 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<sub>a</sub> vs <sup>4</sup>He/<sup>20</sup>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<sub>a</sub> 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 ( $\sim$ 850°C), with low air contamination (Ne/He = 41); nevertheless, this gas is lower in mantle He (R/R<sub>a</sub> =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<sub>2</sub>-rich and have high He isotopic ratio. Most of the springs within the block are N<sub>2</sub>-rich with a low to very low CO<sub>2</sub> 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<sub>a</sub> 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-

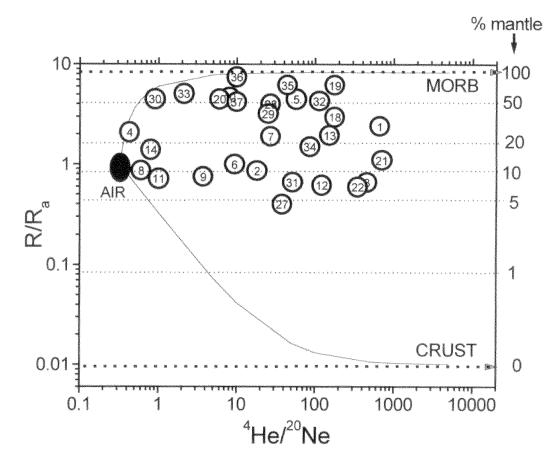


Fig. 2. Helium isotopic composition (in terms of R/R<sub>a</sub>, where R is a measured <sup>3</sup>Ne/<sup>4</sup>He and R<sub>a</sub> is its atmospheric value of 1.39x10<sup>-6</sup>) vs <sup>4</sup>He/<sup>20</sup>Ne ratio. For the mantle and radiogenic R/R<sub>a</sub> the values of 8.3 and 0.01 respectively 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<sub>a</sub> (right axis).

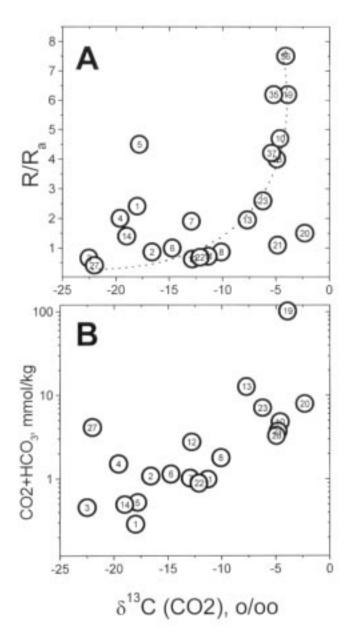


Fig. 3. **A.** Correlation between  $\delta^{13}$ C and R/R<sub>a</sub> for the Jalisco Block thermal springs. **B.** Correlation between the total inorganic carbon (CO<sub>2</sub>+HCO<sub>3</sub>) and d<sup>13</sup>C of CO<sub>2</sub>.

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 (Figure 3A and 2). The isotopic composition of carbon from CO  $_2$ 

depends mainly on the  $\rm CO_2$  concentration in the gas phase or total dissolved inorganic carbon (TDC) (Figure 3 B). Higher- $\rm CO_2$  gases are characterized by higher  $\delta^{13}\rm C$  values, close to typical "magmatic" or "mantle"  $\rm CO_2$  at –5 to –4 ‰ (Taylor, 1986), whereas  $\rm CO_2$ -poor,  $\rm N_2$ -rich waters are depleted in  $\rm ^{13}\rm C$ . This may be caused by the loss of  $\rm CO_2$  at depth and isotopic fractionation of C between  $\rm CO_2$ -gas, dissolved  $\rm CO_2$  and carbonate species or by a high proportion of  $\rm CO_2$  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 –  $\mathrm{CO}_2$ -rich cold or warm waters with  $\mathrm{CO}_2$  derived by processes of metamorphism. All  $\mathrm{CO}_2$ -rich waters are of typical hydrothermal origin.

#### DISCUSSION

Spatial distribution of helium isotopic ratios

Figure 4 shows the distribution of R/R<sub>a</sub> ratios over the Jalisco Block with the larger circles corresponding to the higher R/R<sub>a</sub> 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<sub>a</sub> 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 mantlederived 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

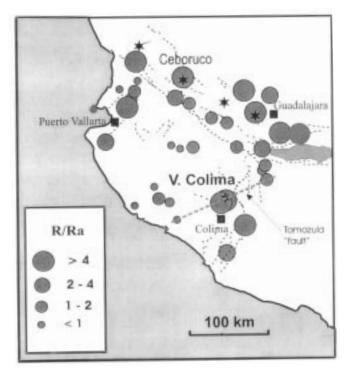


Fig. 4. A map of the Jalisco block showing a relative proportions of the mantle-derived He in gases of thermal springs.

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 <sup>3</sup>He/<sup>4</sup>He ratios, up to R/R<sub>a</sub> =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<sub>a</sub>=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<sub>a</sub> 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<sub>2</sub>+HCO<sub>3</sub>+CH<sub>4</sub> in the total discharge. The gas content in the total discharge was estimated by

$$X_g \text{ (mmol/kg H}_2\text{O)=10/X}_{Ne}\text{(ppm)},$$

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<sub>a</sub> =8.3 and  $CO_2$ / $^3$ He=2x10 $^9$  (Marty and Jambon, 1987). "Crustal" gases have R=0.01Ra and log C/ $^3$ He 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/ $^3$ He 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, and CH, at depth. The main process of CO<sub>2</sub> 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<sub>2</sub>) and degassing of hydrocarbons from organic-rich sediments (CH<sub>4</sub>). 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<sub>2</sub>-content, La Tuna and Desembocada (1, 5) are "depleted" in C. It should be noted that the río Purificación (3, 12) CH<sub>4</sub>-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 <sup>3</sup>He/ <sup>4</sup>He ratio (0.66R<sub>a</sub>), essentially "thermogenic" δ<sup>13</sup>C of CH<sub>a</sub> (-45%) and low  $\delta^{13}$ C of CO<sub>2</sub> (-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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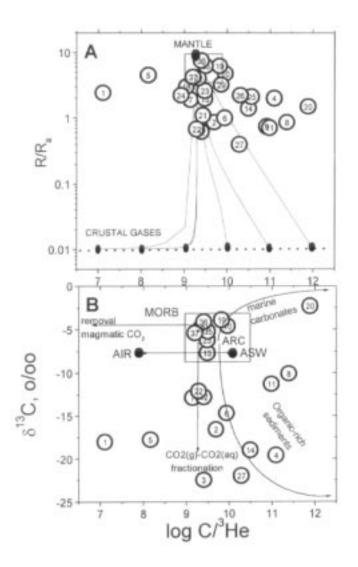


Fig. 5. **A**: The log (R/R<sub>a</sub>) vs log (C/³He) plot for the Jalisco Block thermal discharges. Mixing lines are drawn between the R/R<sub>a</sub>=8.3 and R/R<sub>a</sub>=0.01 endmembers for different C/³He ratios of the "crustal" endmember. **B**: The  $\delta^{13}$ C of CO<sub>2</sub> vs log (C/³He) plot for the Jalisco Block gases (see text for discussion)

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