Isotopic Footprint of Mexican Geothermal Fluids: Constraining the Tectonic Settings

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ABSTRACT

The geothermal fluids (water and gases) of all four major reservoirs currently exploited in Mexico by the CFE – Cerro Prieto, Las Tres Vírgenes, Los Azufres, and Los Humeros – were the focus of an extensive isotopic investigation between 2014 and 2018. This project – led by CeMIEGeo (*Centro Mexicano de Innovación en Energía Geotérmica*) and CONACYT-SENER (*Fondo Sectorial Conacyt-Secretaría de Energía-Sustentabilidad Energética*) – led to the acquisition of a very large isotopic database of geothermal fluids. The database includes all stable noble gas contents (He, Ne, Ar, Kr, and Xe) and their isotopes, stable isotopes of water (δ^2H and $\delta^{18}O$), CO_2 ($\delta^{13}C$ and $\delta^{18}O$), S ($\delta^{34}S$), Cl, and Br ($\delta^{37}Cl$ and $\delta^{81}Br$), and radiogenic isotopes of Sr in water ($^{87}Sr/^{86}Sr$), together with the major and trace element chemistry of water. Here, we report the results of our He, C, and Sr investigation, emphasizing in particular the distinct isotopic signatures among these geothermal fields, a reflection of their specific tectonic settings.

1. INTRODUCTION: NOBLE GASES AS TRACERS OF GEOTHERMAL PROCESSES

The aim of this project, funded by the CONACYT-SENER, was to determine the sources of fluids residing in the exploited Cerro Prieto, Las Tres Vírgenes, Los Azufres, and Los Humeros geothermal field reservoirs (Fig. 1) in order to plan sustainable future exploitation. The study undertook the elemental and isotopic investigation of a variety of natural tracers and noble gases in particular, specifically helium (He), neon (Ne), argon (Ar), krypton (Kr), and xenon (Xe) in the reservoir fluids.

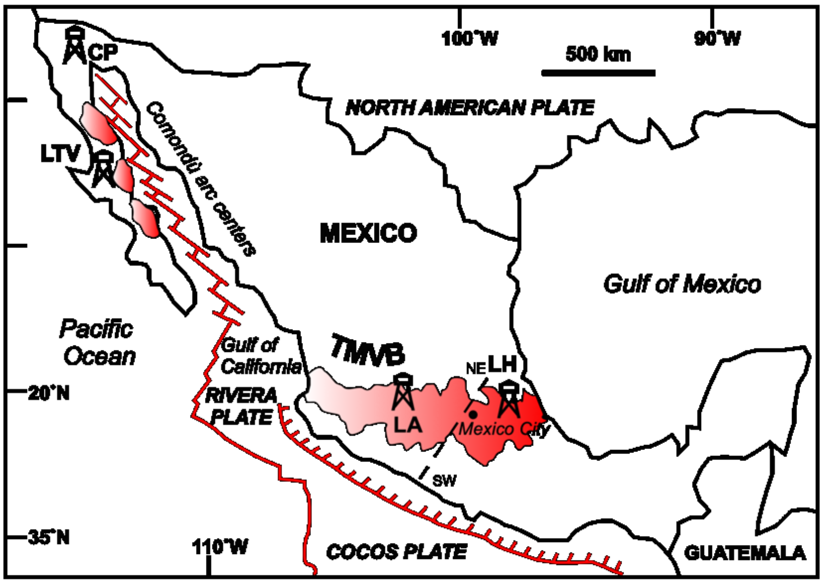

Figure 1: Locations of sampled geothermal fields. CP = Cerro Prieto (Baja California); LTV = Las Tres Vírgenes (Baja California Sur); LA = Los Azufres (Michoacán); LH = Los Humeros (Puebla). TMVB = Trans-Mexican Volcanic Belt; Comondú arc centers are possible Miocene arc centers formed by the paleo-subduction of the Farallon plate, according to Ferrari et al. (2012).

Noble gases display two important characteristics: 1) they are rare and 2) they are chemically inert (e.g., Porcelli et al., 2002; Ozima and Podosek, 2002). Because of their chemical inertness, the noble gas isotopic composition cannot be modified, so the sources of the fluids in which they are contained can be traced using them. Noble gases have two components: 1) primordial noble gases, added during Earth's accretion and contained in the atmosphere and its sourcing reservoir (i.e., the mantle (e.g., Marty, 2012)); and 2) radiogenic noble gases, produced in the crust by the decay of radioactive elements, such as U, Th (^{4}He), and K (^{40}Ar*) (e.g., Ballentine and Burnard, 2002).

Figure 2 schematically represents a convection-dominated geothermal reservoir (Moeck and Beardsmore, 2014) heated by a magmatic body at depth (Pinti et al., 2019c). Four types of fluids can be present, each one containing noble gases derived from different sources: 1) meteoric water; 2) magmatic water; 3) fossil meteoric water; and 4) reinjected brines (Fig. 2). For each fluid, the expected isotopic composition of He (^{3}He/^{4}He or R, which is often normalized to the ratio of the atmosphere, Ra = 1.384 x 10^{-6}), and Ar (^{40}Ar/^{36}Ar) is reported, in addition to the abundance of noble gases.

Meteoric waters, which are considered to be the dominant fluid phase, and 10 to 100 times more abundant by volume than fluids exsolved from magmas (e.g., Norton 1984), exclusively contain atmospheric noble gases (ANG). Their abundance corresponds to the amount dissolved at solubility equilibrium at recharge temperature and pressure conditions (Air-Saturated Water or ASW; Kennedy et al., 1999). Both ^{3}He/^{4}He and ^{40}Ar/^{36}Ar ratios are atmospheric (i.e. R/Ra =1 and 295.5, respectively (Ozima and Podosek, 2002)).

Magmatic water, whether an aqueous fluid exsolved during the crystallization of magmas (Goff and McMurtry, 2000) or a residual phase derived from the condensation of part of the ascending vapor (Hedenquist et al., 2018), contains deep-seated volatiles, such as H_2S, CO_2, and noble gases. Only the ^{3}He/^{4}He ratio and the ^{40}Ar/^{36}Ar ratio deviate from the atmospheric ratios. In particular, the mantle is enriched in ^{3}He compared to ^{4}He with respect to the atmosphere. Convective mantle sampled at Mid Ocean Ridges (MOR) has a R/Ra ratio of 8±1 (e.g., Allègre et al., 1995), while sub-continental lithospheric mantle (SCLM) is slightly lower; 6.1±1.9 Ra (Gautheron and Moreira, 2002). Finally, arc-magmatism shows R/Ra values even lower, of 5.4±1.9Ra, because of the possible addition of radiogenic ^{4}He from the subducting slab (e.g., Hilton et al., 2002).

Permeability heterogeneities in volcanic and sedimentary geothermal reservoirs should favor the preservation of connate waters, which could accumulate radiogenic ^{40}Ar*, as observed in Los Humeros (Pinti et al., 2017), and/or ^{4}He, as seen in Cerro Prieto (Pinti et al., 2019a), over time.

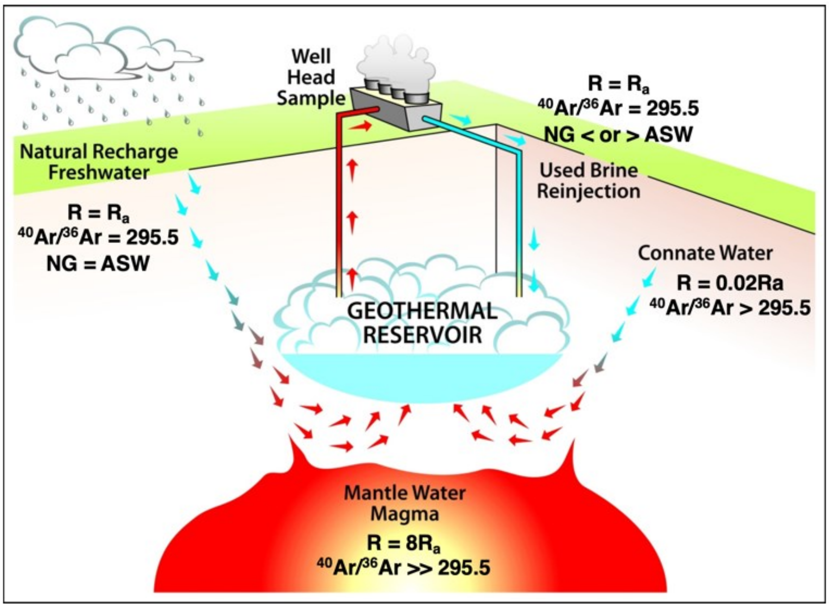

Figure 2: A schematic geothermal reservoir with expected fluid and isotopic signatures of He and Ar. NG = noble gas abundance; R = ^{3}He/^{4}He; Ra = (^{3}He/^{4}He)$_{Air}$ = 1.384 x 10^{-6}.

Finally, to increase production capacity and sustain geothermal system recharge, energy-depleted fluids are injected back into the reservoir. Because reinjected brines correspond to evaporated brines, the ANG contents are significantly lower than the ASW components, and elemental ratios, such as Ne/Ar and Xe/Ar, deviate slightly from the ASW values due to the different noble gas solubilities (e.g., Kennedy et al., 1999; Kennedy and Shuster, 2000).

2. GEOLOGICAL BACKGROUND

The Cerro Prieto Geothermal Field (CPGF) is located in Baja California (Fig. 1), 30 km south of the town of Mexicali. It is the largest high-enthalpy (> 280˚C) liquid-dominated geothermal system in Mexico, with more than 429 wells drilled at depths varying between 1,000 and 4,400 meters. 147 operating wells currently extract 34.6 million metric tons of steam per year (Gutiérrez-Negrín, 2015). The reservoir is located in a pull-apart basin formed by the active strike-slip Imperial Fault in the northeast and the Cerro Prieto Fault in the southwest of the field, both belonging to the San Andreas Fault System (Suárez-Vidal et al., 2008). The heat source is gabbros intruded as a stress response of the extensional crustal thinning (Elders et al., 1984). The basement is composed of Cretaceous granites, followed by a 2,400 m-thick sequence of Plio-Pleistocene deltaic sedimentary rocks (Colorado River sandstones interbedded with gray shales), which hosts the geothermal reservoir (Lira-Herrera, 2005). Brown shales and mudstones act as the caprock. The unconsolidated quaternary clastic sediments of the Colorado River lie at the top of the stratigraphic sequence (Lira-Herrera, 2005), in which connate waters likely constitute the natural recharge of the field (Pinti et al., 2019a). Reservoir temperature ranges from 250 to 310˚C. Water is of sodium chloride type, with neutral to alkaline pH (Gutiérrez-Negrín, 2015).

The Las Tres Vírgenes Geothermal Field (LTVGF) is located in Baja California Sur (Fig. 1), in a NW-SE-oriented Plio-Quaternary rift, called the Santa Rosalía Basin (López-Hernández et al., 1995). This basin constitutes the western limit of the deformation zone related to the Gulf of California opening, which created several young oceanic basins interconnected by transform faults (Fig. 1) (Arango-Galván et al., 2015). During the Miocene, this area was the subduction zone of the Farallon plate under the American plate (Comondú arc in Fig. 1; Ferrari et al., 2012). The LTVGF is located close to three volcanic eruptive centers: La Reforma caldera (3.5 to 0.8 Ma), Sierra de Aguajito (0.7-0.45 Ma), and Las Tres Vírgenes complex (0.44 Ma- 30 ka) (López-Hernández et al., 1995). The thermal activity is concentrated at the border of the Las Tres Vírgenes volcano. The reservoir is located in the basement and corresponds to low-permeability Upper Cretaceous granodiorites. The basement is overlain by 750 m of Upper Oligocene to Middle Miocene volcano-sedimentary sandstones and andesites (Santa Lucía Fm) of the Comondú Group, which may act as the caprock (López-Hernández et al., 1995). Overlying the Comondú Group is the Late Miocene Esperanza Fm, initially described as tholeiitic basalts, but now considered to be the product of subduction similar to adakites (Ferrari et al., 2012). These basalts are overlain by 300 m of sands, conglomerates, and pyroclastics, deposited in a shallow marine environment called the Santa Rosalía Basin. The shallow regional aquifer recharges the reservoir, which has temperatures ranging from 250 to 275˚C (Tello-López and Torres-Rodríguez, 2015). The water fraction is of sodium chloride to bicarbonate-sulfate type, with a neutral pH (Barragán et al., 2010).

The Los Azufres Geothermal Field (LAGF) is located in the Trans-Mexican Volcanic Belt (TMVB; Fig. 1), 80 km east of Morelia in the central Michoacán State. It is the second largest geothermal field in Mexico in terms of energy production after Cerro Prieto (Gutiérrez-Negrín et al., 2015). Most of its geothermal activity is concentrated in the southern portion of a volcanic complex, which erupted Miocene andesites and Quaternary dacites, rhyolites, and basalts. The southern portion is divided geographically into two zones; the Northern Production Zone (NPZ), where reservoir conditions are in the compressed liquid region, and the Southern Production Zone (SPZ), which has different systems depending on the depth, varying from vapor-dominated, to liquid-dominated, and to compressed-liquid regions at shallower depths (Torres-Rodríguez et al., 2005). The geothermal reservoir is hosted in 2,700 m-thick fractured Upper Miocene to Pliocene basaltic andesite to dacite, called the Mil Cumbres unit (Pérez et al., 2010). The reservoir is overlain by Quaternary andesitic lavas and basaltic andesites of the Zinapecuaro unit that act as a caprock, followed by a silicic sequence of rhyodacites, rhyolites, and dacites, with ages between 1.6 Ma and 15 Ka (Pérez et al., 2010). The field heat source is likely MORB-like parental magmas, as suggested by helium and strontium isotopic data (Wen et al., 2018). The reservoir has a temperature range of 240 to 320˚C, and is recharged by the shallow regional aquifer and local precipitation (Torres-Rodríguez et al., 2005). Geothermal brines are of sodium chloride type, with pH of between 5.8 and 7.2 (Birkle et al., 2001).

The Los Humeros Geothermal Field (LHGF) is located in the north-eastern portion of the Plio-Pleistocene TMVB (Fig. 1), near the border with the Sierra Madre Oriental Cordillera. The LHGF is located inside a twofold nested caldera complex produced by a caldera-forming phase 1, a Plinian phase, and caldera-forming phase 2, with volcanic activity starting in the Pleistocene and lasting until 7.3 ka ago, with eruption of rhyolitic and basaltic lavas (Carrasco, et al., 2018). The external Los Humeros Caldera is the oldest (460 ka) and largest, with a diameter of 15-20 km. The internal Los Potreros Caldera is the youngest (100 ka), has a diameter of 8-10 km (e.g., Norini et al., 2015), and is the location of the LHGF, with a 17 km^2 surface area. The heat source of the LHGF is a magmatic chamber at the terminal hydrothermal stage (Gutiérrez-Negrín et al., 2010). The LH geothermal reservoir consists of a sequence of blocks delimited by faults arranged as graben and horst formed during the collapse of the external Los Humeros Caldera. The LHGF stratigraphy is composed of four geological units. The deepest, Unit (4), is the basement, with granites and schists of Paleozoic age covered by a thick series of Jurassic and Cretaceous limestones, metamorphosed during the Laramide orogeny and by Oligocene magmatic intrusions (De la Cruz, 1983). This is overlain by Unit (3), Mio-Pliocene (10-1.9 Ma) pre-caldera volcanic deposits represented by the Teziutlán and Alseseca andesites intercalated with tuff horizons, and then Unit (2), composed of Quaternary caldera volcanic products (164 ka – 70 ka), namely the Xaltipan and Zaragoza ignimbrites (Carrasco, et al., 2018). The shallowest, Unit 1, consists of post-caldera Quaternary rocks (<70 ka) related to the collapse of the internal Los Potreros Caldera. Recharge might occur locally through fault and fracture systems (Cedillo Rodríguez, 2000) bordering the Los Potreros escarpment (Pinti et al., 2017). The reservoir has a temperature range of 210 to 380 ˚C (Gutiérrez-Negrín, 2015) and contains fluids of sodium chloride to bicarbonate-sulfate type with a neutral pH (Arellano et al., 2003). However, very acidic fluids (pH < 4-5) were found in the center of the field, related to condensation of superheated steam containing HCl.

3. SAMPLING

Surveys were carried out in November 2014 (LAGF), January 2015 and 2018 (LHGF), November 2016 (CPGF and LTVGF), and June 2018 (LTVGF). Gases (CO_2 and noble gases) were collected at the Webre separator of the wells and from local hot and cold springs and fumaroles. Gas samples were collected directly into standard refrigeration-grade 3/8″ copper tubes (~14 cm^3), sealed by stainless steel pinch off clamps. In wells not equipped with a Webre steam/water separator, gas samples were collected directly at the wellhead, using a mini-separator and a cooling coil. In wells equipped with a Webre separator, the copper tube was fixed to a small stool aligned with one of the output valves of the steam conduit. A single copper tube was extended from the sampler to the NPT-type male connector screwed onto the steam conduit valve. The clamps were closed using an electric 12V battery drill, which reduced air contamination to nearly zero (e.g., Pinti et al., 2017; 2019b). Water was also collected at the well weirboxes using Nalgene bottles for analyses of major elements and Sr, halogens, as well as water stable and radiogenic isotopes. Analytical techniques used for determining dissolved ions, gases, and isotopes can be found in Pinti et al. (2019a; 2019b).

4. SOURCES OF HELIUM, CARBON, AND STRONTIUM, AND THEIR RELATION TO TECTONICS

In geothermal systems, helium isotopes are the best tracer of the heat source, both in magma-hosted systems and crustal-radiogenic ones. Indeed, the primordial ^3He isotope is more abundant than ^4He in the mantle compared to the other terrestrial reservoirs, so the presence of magmatic bodies at depth, and their original source, can be traced using $^3He/^4He$ ratios (e.g., Wen et al., 2018). In crustal regimes, where water is heated by circulation in deep-rooted faults (e.g., Kennedy and Van Soest, 2006) or heating is furnished by U-rich bodies, such as granitic intrusions (e.g., Sun et al., 2015), the production of ^{4}He is dominant (e.g., O'Nions and Oxburgh, 1988).

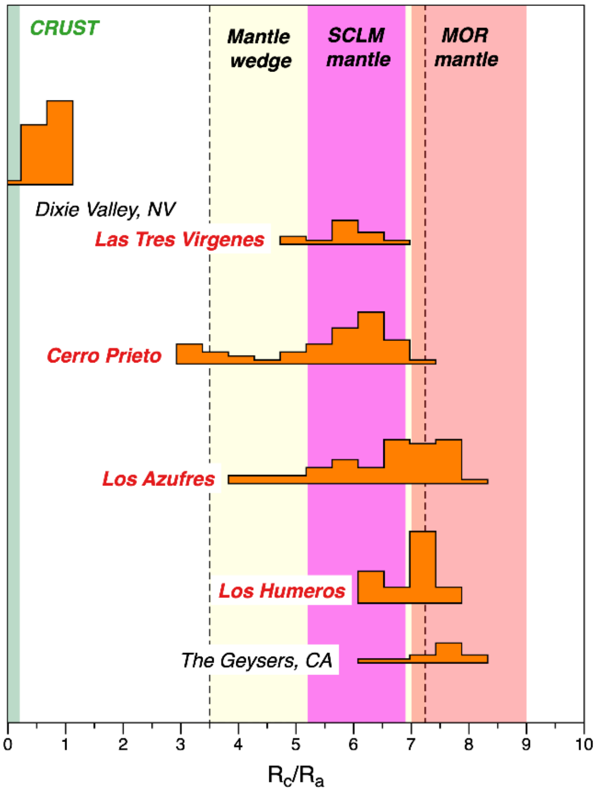

Figure 3: The ^{3}He/^{4}He ratio corrected of the air component (Rc) and normalized to that of the atmosphere (Ra = 1.384 x 10^{-6}) measured in wells and springs of deep convective hydrothermal systems in Mexico, and compared with those of the Geyser (California) and Dixie Valley (Nevada). Data sources are: the Geysers: Kennedy and Truesdell, 1996; Los Humeros: Pinti et al., 2017 and unpublished data; Los Azufres: Pinti et al. (2013) and Wen et al. (2018); Cerro Prieto: Pinti et al., 2019a; Las Tres Vírgenes: Pinti et al., 2019b; Dixie Valley: Kennedy and Van Soest, 2006. The three colored bands show R/Ra values for the mantle as sampled at MOR, beneath continents (SCLM), and beneath subduction zones respectively.

Figure 3 reports the ^{3}He/^{4}He ratio variability measured in the four investigated geothermal fields of Mexico through frequency histograms. The ^{3}He/^{4}He ratios are corrected for the air component (Rc) and reported as Rc/Ra where Ra is the atmospheric ratio of 1.384 x 10^{-6}. The helium isotopic signature represented by the Rc/Ra ratio derived from two sources, the mantle and the crust.

Our data are compared to those measured in two geothermal fields from the western US: the Geysers, California (Kennedy and Truesdell, 1996) and Dixie Valley, Nevada (Kennedy and van Soest, 2006). The first represents a magma-hosted field with active magmatic degassing from a source representing a MOR convective mantle (Kennedy and Truesdell, 1996). The second represents a field where there is no recent volcanic activity and mantle He is transported through deep-rooted regional faults by fluids enriched locally in radiogenic ^{4}He (Kennedy and van Soest, 2006). We also report the expected range of ^{3}He/^{4}He ratios for the convective mantle as sampled at MOR (8±1Ra; Allègre et al., 1995), the SCLM (6.1±0.9Ra; Gautheron and Moreira, 2005), and the mantle wedge at subduction zones (5.37±1.87Ra; Hilton et al., 2002). The highest radiogenic ^{3}He/^{4}He ratio of the SCLM may be related to the nature of the SCLM. The SCLM is considered to be a mantle reservoir isolated from the convective mantle, where He is sourced by the asthenosphere and by *in situ* production from U decay during its residence time in the SCLM, which is estimated to be 100 Myrs (Gautheron and Moreira, 2005). The mantle wedge could be more radiogenic at the subduction zones through the addition of crustal material – and associated radiogenic ^{4}He – from the subducting plate. However, several arc segments do not show a clear difference in the helium composition from that of MOR mantle (Hilton et al., 2002), suggesting minimal contribution of volatiles from the subducting plate (Poreda and Craig, 1989; Hilton and Craig, 1989).

The helium isotopic signature of Mexican geothermal fluids (Fig. 3) clearly indicates that they are active magmatic-hosted systems, releasing volatiles of almost pure mantle signatures. The source is certainly related to melts emplaced either into the crust or at the crust-mantle boundaries. It is interesting to note that the highest ^{3}He/^{4}He ratios measured at Los Azufres (7.93±0.09Ra; Wen et al., 2018) and Los Humeros (7.49±0.05Ra; Pinti et al., 2017 and unpublished 2018 data) are compatible with a pure mantle end-member, as sampled at the MOR, while Las Tres Vírgenes shows slightly lower values, compatible with a SCLM source. The majority of Cerro Prieto Rc/Ra values are compatible with a SCLM source, except for one value, measured at 7.32±0.07Ra (Pinti et al., 2019a).

The ^{3}He/^{4}He ratio alone cannot univocally constrain the mantle source beneath each of these fields, due to the large variability of some sources. For example, LHGF and LAGF helium isotopic compositions could be related to either MOR-type mantle or to the mantle wedge (Fig. 3). Indeed, in the arc segments of Sumatra (Gasparon et al., 1994), Bali (Hilton and Craig, 1989), and Lesser Antilles (Pedroni et al., 1999; Jean-Baptiste et al., 2014), MOR-type mantle $^3He/^4He$ ratios have been measured.

The presence of nearly pure MOR-type helium in LAGF and LHGF can be explained by the particular geometry of the slab under central Mexico. Under the TMVB (Fig. 1), which is the surface expression of the Cocos Plate subduction under the North American plate (e.g., Ferrari et al., 2012), the plate plunges almost vertically into the mantle (Pérez-Campos et al., 2008; Fig. 4), rendering the direct ascent of lithospheric mantle material into the LA- and LHGF possible (Richard et al., 2019).

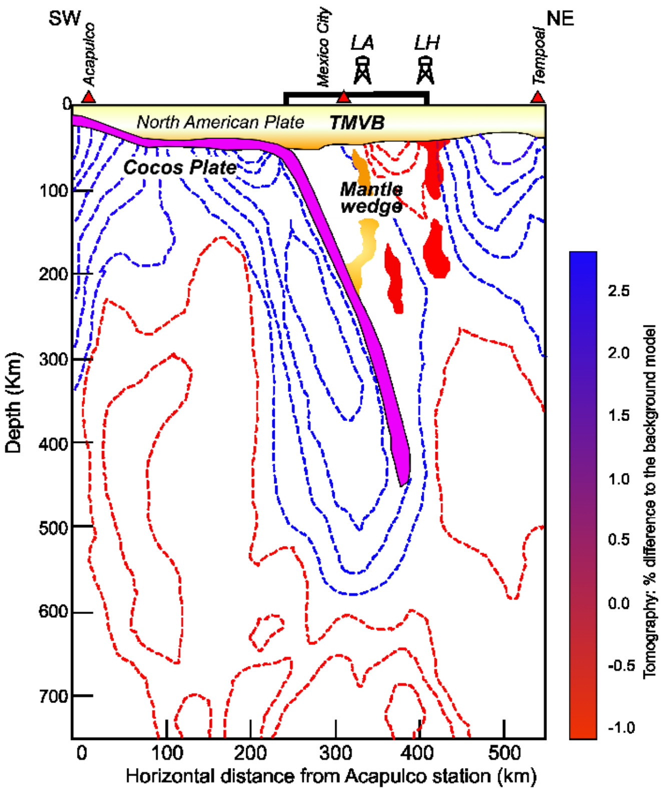

Figure 4: Cross-section of the Coco plate subduction zone (adapted from Peréz-Campo et al., 2008), with the relative locations of the Trans-Mexican Volcanic Belt (TMVB) and the Los Azufres (LA) and Los Humeros (LH) geothermal fields. Blobs of mantle material of different natures (fertilized mantle = orange and lithospheric mantle = red) are drawn as possible He sources in the two fields (modified from Richard et al., 2019).

The lower $^3He/^4He$ ratios of the two fields located in Baja California – CPGF and LTVGF – are more difficult to explain. It is expected that melts that drive heat into these magma-hosting systems are derived from the spreading center of the Gulf of Baja California (Fig. 1; Pinti et al., 2019b; Batista Cruz et al., 2019), which continues into the Cerro Prieto and Salton Sea Through (Pérez-Flores et al., 2015). Based on the C isotopic systematics of Las Tres Vírgenes ($\delta^{13}C$ of -11-12‰ vs PDB), Richard et al. (2019) suggested that organic-C sediments from the ancient subducting Farrallon Plate have contaminated the local mantle with C-rich and ^4He-rich fluids (Pinti et al., 2019b). It is worth noting that in central Baja California, a fragment of the Farallon Plate is possibly stacked into the local mantle and other fragments are possibly present north of LTVGF, in the Cerro Prieto-Salton Sea Through area (Barak et al. 2015).

The nature of the crustal contamination that affects magmatic volatiles in these fields can be further investigated by comparing the helium isotopic signature with those of C and Sr. In Figure 5, we reported the $CO_2/^3He$ vs. $\delta^{13}C$ measured in the four geothermal fields. Four sources of C are also reported: the MORB-like mantle (red box: $\delta^{13}C$ = -9 to -4‰; Sano and Marty, 1995; $CO_2/^3He$ = 2±0.5 x 10^9; Marty and Jambon, 1987); limestone (blue box: $\delta^{13}C$ = -2 to +2‰; $CO_2/^3He$ = 1 x 10^{13}; Sano and Marty, 1995); and organic sediments (orange box: $\delta^{13}C$ = -30±10‰; $CO_2/^3He$ = 1 x 10^{13}; Sano and Marty, 1995). Finally, the purple box represents the C and He signature of arc-related geothermal fluids ($\delta^{13}C$ = -6.5 to -2‰; $CO_2/^3He$ = 4.5 x 10^9 to 3 x 10^{10}; Sano and Marty, 1995).

It is interesting to note in Figure 5 that the LAGF carbon source seems to be MOR-like, as for helium (Fig. 3), while both LHGF and CPGF seem to lie within the arc-related geothermal fluid sources. In this plot, it is clear that the dominant crustal source, able to dilute both mantle He and C, is limestone rather than sediment (which are organic-C-rich) (Fig. 5). For each sample, it is possible to determine the percentage of each source, following mass balance equations (e.g., Sano and Marty, 1995):

$$(\delta^{13}C)_{sample} = M(\delta^{13}C)_{mantle} + L(\delta^{13}C)_{limestone} + S(\delta^{13}C)_{sediments} \quad (1)$$

$$1/\left(\frac{CO_2}{^3He}\right)_{sample} = M/\left(\frac{CO_2}{^3He}\right)_{mantle} + L/\left(\frac{CO_2}{^3He}\right)_{limestone} + S/\left(\frac{CO_2}{^3He}\right)_{sediments} \quad (2)$$

$$M + L + S = 1 \quad (3)$$

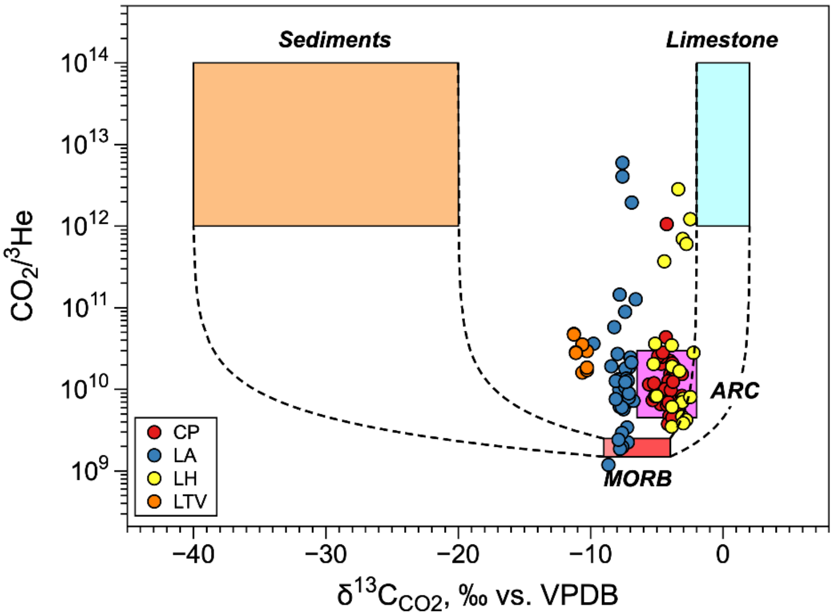

Figure 5: Carbon isotopic composition of the studied geothermal fluids vs. the $CO_2/^3He$ ratio.

The minimum and maximum contributions of the mantle, limestone, and sediment He and C sources for the four investigated geothermal fields are reported in Table 1. The dominance of limestone as a crustal contribution is not surprising. A literature review of He and C isotopic compositions of volcanic gases in arc settings has shown that the major C source is carbonate (Mason et al., 2017). Sano and Williams (1996) arrived at the same conclusion, estimating that subducted marine limestone and slab carbonate supply the 70-80% of the non-mantle carbon, the remaining ~10-15% is contributed from subducted organic (sedimentary) carbon.

Geothermal field	Mantle %	Limestone %	Sediments %
Cerro Prieto	0.2-32.55	58.62-85.59	8.80-14.23
Las Tres Vírgenes	4.26-11.96	56.17-59.02	31.87-36.77
Los Azufres	0.01-96.61	1.27-74.65	4.6-25.33
Los Humeros	0.15-60.60	38.59-91.68	0.81-8.16

Table 1: Minimum and maximum relative % contributions of the mantle, limestone, and sediments in geothermal fluids from the four sampled Mexican geothermal fields. Relative % contributions are calculated using average values for end-members as follows: Mantle $\delta^{13}C$ and $CO_2/^3He$ of -6.5‰ and 2 x 10^9; Sediments $\delta^{13}C$ and $CO_2/^3He$ of -30‰ and 1 x10^{13}; Limestone $\delta^{13}C$ and $CO_2/^3He$ of 0‰ and 1 x10^{13}.

The crustal contamination could derive from the subducting slab or could be local, within the crust. This could be the case for LHGF, where higher $\delta^{13}C$ has been associated with the occurrence of meta-carbonates in the basement underlying the reservoir (González-Partida et al., 1993; Peiffer et al., 2018; Richard et al., 2019). Local crustal contamination could be also associated with the CPGF, as suggested for radiogenic ^4He (Pinti et al., 2019a). Alternatively, it could be related to contamination by crustal fluids from the ancient Farallon Plate, as suggested by the He and C signatures measured in the hydrothermal systems of the entire Baja California Peninsula (Batista Cruz et al., 2019). Recent work by Garciá-Sánchez et al. (2017) showed that Cerro Prieto volcanics contain chemical anomalies typical of subduction zones, which suggests that all Cerro Prieto magmas could have been generated by the partial melting of the remains of the subducted Farallon plate.

To discern which scenarios and sources are responsible for the observed geochemical patterns, the Rc/Ra were plotted against the $^{87}Sr/^{86}Sr$ ratios measured in the geothermal fluids (Fig. 6). This plot suggests that there is a unique mantle source for the volatiles, with a clear MOR-like footprint, in all sampled geothermal fields; those located within subduction zones (LH and LA; Figs. 1 and 4) and those in spreading centers (LTV and CP; Fig. 1) alike. The second source has an estimated Rc/Ra value of 0.05 (Lowenstern et al., 2014) and a minimum $^{87}Sr/^{86}Sr$ of 0.712, which represents the crust. This crustal end-member could represent either local sources (e.g., the carbonate-shale sediments constituting the Cerro Prieto reservoir; Lira Herrera, 2005) or regional sources related to subducting sediments. The estimated $^{87}Sr/^{86}Sr$ end-member value of 0.712 is higher than marine carbonates (0.708-0.709; e.g., Veizer et al., 1999), but could result from the mixing of subducting marine carbonates with the addition of, for example, 30% of local Precambrian crust (0.720; Hilton and Craig, 1989).

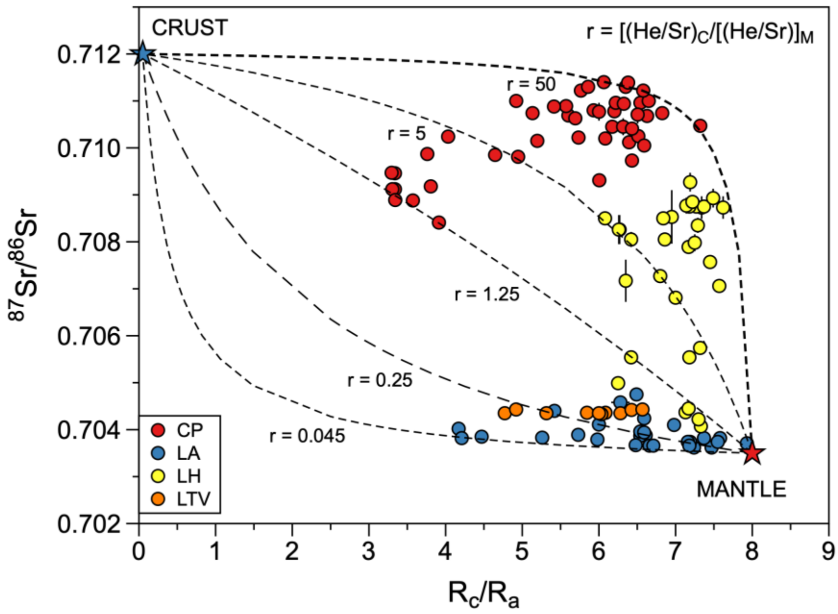

Figure 6: Rc/Ra vs. $^{87}Sr/^{86}Sr$ measured in the geothermal fluids of the four sampled Mexican geothermal fields. Several mixing hyperbolas have been drawn. "r" represents the hyperbola curvature factor, which is equal to $[He/Sr]_{crust}/[He/Sr]_{mantle}$.

4. CONCLUSIONS

The He, C, and Sr isotopic footprints of the Mexican geothermal systems suggests that a unique mantle source, parented to that sampled at Mid Ocean Ridges, is responsible for the generation of the major hydrothermal systems in Mexico. Crustal contamination by carbonate-dominated sediments, either locally within the crust or from present (Cocos Plate in central Mexico) or paleo-subducting (Farallon Plate in northern Mexico) plates modifies the original He, C, and Sr isotopic footprint. The presence of almost pure MOR-mantle He signatures within the TMVB at Los Azufres indicates that fresh melts can reach crustal levels and generate heat, which may support the occurrence of other potential geothermal sites that could be explored and exploited in the future in the region.

REFERENCES

Allègre, C.J., Moreira, M., and Staudacher, T.: $^{4}He/^{3}He$ dispersion and mantle convection. *Geophys. Res. Lett.* **22**, (1995), 2325-2328.

Arango-Galván, C., Prol-Ledesma, R.M., and Torres-Vera, M.A.: Geothermal prospects in the Baja California Peninsula. *Geothermics* **55**, (2015), 39-57.

Arellano, V., García, A., Barragán, R., Izquierdo, G., Aragón, A., Nieva, D.: An updated conceptual model of the Los Humeros geothermal reservoir (Mexico). *J. Volcanol. Geotherm. Res.* **124**, (2003), 67-88.

Ballentine, C.J., and Burnard, P.G.: Production, release and transport of noble gases in the continental crust. *Rev. Mineral. Geochem.* **47**, (2002), 481-538.

Barragán, R.M., Iglesias, E.R., Arellano, V.M., Torres, R.J., Tapia, R., Hernández, P., and Ramírez, M.: Chemical modeling of fluids from the Las Tres Vírgenes BCS (México) geothermal field, *Proceedings*, World Geothermal Congress, Bali, Indonesia, (2010).

Batista Cruz, R.Y., Rizzo, A.L., Grassa, F., Bernard Romero, R., González Fernández, A., Kretzschmar, T.G., and Gómez-Arias, E.: Mantle Degassing Through Continental Crust Triggered by Active Faults: The Case of the Baja California Peninsula, Mexico. *Geochem. Geophys. Geosyst.* **20**, (2019), 1912-1936.

Birkle, P., Merkel, B., Portugal, E., and Torres-Alvarado, I.S.: The origin of reservoir fluids in the geothermal field of Los Azufres, Mexico—isotopical and hydrological indications. *Appl. Geochem.* **16**, (2001), 1595-1610.

Carrasco Núñez, G., Bernal, J.P., Dávila, P., Jicha, B., Giordano, G., Hernández, J.: Reappraisal of Los Humeros volcanic complex by new U/Th zircon and $^{40}Ar/^{39}Ar$ dating: Implications for greater geothermal potential. *Geochem., Geophys., Geosyst.* **19**, (2018), 132–149.

Cedillo Rodríguez, F.: Hydrogeologic model of the geothermal reservoirs from Los Humeros, Puebla, Mexico, *Proceedings*, World Geothermal Congress, Kyushu - Tohoku, Japan, (2000).

De la Cruz, M.P.: Estudio geológico a detalles de la zona geotérmica de Los Humeros, Pue. CFE, Internal Report, (1983).

Elders, W., Bird, D., Williams, A., and Schiffman, P.: Hydrothermal flow regime and magmatic heat source of the Cerro Prieto geothermal system, Baja California, Mexico. *Geothermics* **13**, (1984), 27-47.

Ferrari, L., Orozco-Esquivel, T., Manea, V., and Manea, M.: The dynamic history of the Trans-Mexican Volcanic Belt and the Mexico subduction zone. *Tectonophysics* **522-523**, (2012), 122-149.

García-Sánchez, L., Macías, J.L., Sosa-Ceballos, G., Arce, J.L., Garduño-Monroy, V.H., Saucedo, R., Avellán, D.R., Rangel, E., Layer, P.W., López-Loera, H., Rocha, V.S., Cisneros, G., Reyes-Agustín, G., Jiménez, A., and Benowitz, J.A.: Genesis and evolution of the Cerro Prieto Volcanic Complex, Baja California, Mexico. *Bull. Volcanol.* **79**, (2017), 44.

Gasparon, M., Hilton, D.R., and Varne, R.: Crustal contamination processes traced by helium isotopes: Examples from the Sunda arc, Indonesia. *Earth Planet. Sci. Lett.* **126**, (1994), 15-22.

Gautheron, C., and Moreira, M.: Helium signature of the subcontinental lithospheric mantle. *Earth Planet. Sci. Lett.* **199**, (2002), 39-47.

Goff, F., and McMurtry, G.M.: Tritium and stable isotopes of magmatic waters. *J. Volcanol. Geotherm. Res.* **97**, (2000), 347-396.

González-Partida, E., Barragán, R., and Nieva, D.: Análisis geoquímico-isotópico de las especies carbónicas del fluido geotérmico de Los Humeros, Puebla, México. *Geof. Intern.* **32**, (1993), 299-309.

Gutiérrez-Negrín, L.C.: Mexican geothermal plays. *Proceedings,* World Geothermal Congress, Melbourne, Australia, (2015).

Gutiérrez-Negrín, L.C., Izquierdo-Montalvo, G., and Aragón-Aguilar, A.: Review and update of the main features of the Los Humeros geothermal field, Mexico, *Proceedings*, World Geothermal Congress, Bali, Indonesia, (2010).

Hedenquist, J.W., Taguchi, S., and Shinohara, H.: Features of large magmatic–hydrothermal systems in Japan: characteristics similar to the tops of porphyry copper deposits. *Resour. Geol.* **68**, (2018), 164-180.

Hilton, D.R., and Craig, H.: A helium isotope transect along the Indonesian archipelago. *Nature* **342**, (1989), 906-908.

Hilton, D.R., Fischer, T.P., and Marty, B.: Noble gases and volatile recycling at subduction zones. *Rev. Mineral. Geochem.* **47**, (2002), 319-370.

Jean-Baptiste, P., Allard, P., Fourré, E., Parello, F., and Aiuppa, A.: Helium isotope systematics of volcanic gases and thermal waters of Guadeloupe Island, Lesser Antilles. *J. Volcanol. Geother. Res.* **283**, (2014), 66-72.

Kennedy, B.M., and Truesdell, A.H.: The northwest geysers high-temperature reservoir: evidence for active magmatic degassing and implications for the origin of the Geysers geothermal field. *Geothermics* **25**, (1996), 365-387.

Kennedy, B.M., and Shuster, D.L.: Noble gases: sensitive natural tracers for detection and monitoring injectate returns to geothermal reservoirs. *Geother. Resour. Counc. Trans*. **24**, (2000), 24-27.

Kennedy, B.M., and van Soest, M.C.: A helium isotope perspective on the Dixie Valley, Nevada, hydrothermal system. *Geothermics* **35**, (2006), 26-43.

Kennedy, B.M., Janik, C., Benoit, D., and Shuster, D.L.: Natural geochemical tracers for injectate fluids at Dixie Valley, *Proceedings*, 24th Workshop on Geothermal Reservoir Engineering, Stanford University, Stanford, CA (1999).

Lira Herrera, H.: Actualización del modelo geológico conceptual del yacimiento geotérmico de Cerro Prieto, BC. *Géotermia* **18**, (2005), 37-46.

López-Hernández, A., Garcia-Estrada, G.H., and Arellano Guadarrama, J.F.: Geothermal exploration at Las Tres Vírgenes, B.C.S. Mexico, *Proceedings*, World Geothermal Congress, Florence, Italy, (1995).

Lowenstern, J.B., Evans, W.C., Bergfeld, D., and Hunt, A.G.: Prodigious degassing of a billion years of accumulated radiogenic helium at Yellowstone. *Nature* **506**, (2014), 355-358.

Marty, B.: The origins and concentrations of water, carbon, nitrogen and noble gases on Earth. *Earth Planet. Sci. Lett.* **313–314**, (2012), 56-66.

Marty, B., and Jambon, A.: $C/^3He$ in volatile fluxes from the solid earth: implications for carbon geodynamics. *Earth Planet. Sci. Lett.* **83**, (1987), 16-26.

Mason, E., Edmonds, M., and Turchyn, A.V.: Remobilization of crustal carbon may dominate volcanic arc emissions. *Science* **357**, (2017), 290-294.

Moeck, I., and Beardsmore, G: A new 'geothermal play type' catalog: Streamlining exploration decision making, *Proceedings*, 39th Workshop on Geothermal Reservoir Engineering, Stanford University, Stanford, CA (2014).

Norini, G., Groppelli, G., Sulpizio, R., Carrasco-Núñez, G., Dávila-Harris, P., Pellicioli, C., Zucca, F., and De Franco, R.: Structural analysis and thermal remote sensing of the Los Humeros Volcanic Complex: Implications for volcano structure and geothermal exploration. *J. Volcanol. Geother. Res*. **301**, (2015), 221-237.

Norton, D.L.: Theory of hydrothermal systems. *Annu. Rev. Earth Planet. Sci.* **12**, (1984), 155–177.

O'Nions, R.K., and Oxburgh, E.R.: Helium, volatile fluxes and the development of continental crust. *Earth Planet. Sci. Lett.* **90**, (1988), 331-347.

Ozima, M., and Podosek, F.A.: Noble Gas Geochemistry. 2nd edition. Cambridge University Press, Cambridge, (2002).

Pedroni, A., Hammerschmidt, K., and Friedrichsen, H.: He, Ne, Ar, and C isotope systematics of geothermal emanations in the Lesser Antilles Islands Arc. *Geochim. Cosmochim. Acta* **63**, (1999), 515-532.

Peiffer, L., Carrasco-Núñez, G., Mazot, A., Villanueva-Estrada, R.E., Inguaggiato, C., Romero, R.B., Miller, R.R., and Rojas, J.H.: Soil degassing at the Los Humeros geothermal field (Mexico). *J. Volcanol. Geother. Res.* **356**, (2018), 163-174.

Pérez, H., J.L., M., Garduño V.H., Arce Saldaña, J.L., García Tenorio, F., Castro Goeva, R., Layer, P., Saucedo Gíron, R., Martínez, C., Jimenéz Haro, A., Valdéz, G., Meriggi, L., and Hérnandez, R.: Estudio vulcanológico y structural de la secuencia estratigráfica Mil Cumbres y del campo geotérmico de Los Azufres, Mich. *Géotermia* **23**, (2010), 51-63.

Pérez-Campos, X., Kim, Y., Husker, A., Davis Paul, M., Clayton Robert, W., Iglesias, A., Pacheco Javier, F., Singh Shri, K., Manea Vlad, C., and Gurnis, M.: Horizontal subduction and truncation of the Cocos Plate beneath central Mexico. *Geophys. Res. Lett.* **35**, (2008), L18303.

Pérez-Flores, M.A., Herrera-Barrientos, F., Gómez-Trevino, E. Salomé-Charre, A, Romo-Jones, J.M., Gallardo-Delgado, A., Brassea-Ochoa, J., Esparza, F.J., and Flores-Luna, C.: Resistivity image of the San Andreas Fault System around the Cerro Prieto geothermal area (México), *Proceedings*, World Geothermal Congress, Melbourne, Australia, (2015).

Pinti, D., Castro, M., Shouakar-Stash, O., Tremblay, A., Garduño, V., Hall, C., Hélie, J.-F., and Ghaleb, B.: Evolution of the geothermal fluids at Los Azufres, Mexico, as traced by noble gas isotopes, $\delta^{18}O$, δD, $\delta^{13}C$ and $^{87}Sr/^{86}Sr$. *J. Volcanol. Geother. Res.* **249**, (2013), 1-11.

Pinti, D.L., Castro, M.C., Lopez-Hernandez, A., Han, G., Shouakar-Stash, O., Hall, C.M., and Ramírez-Montes, M.: Fluid circulation and reservoir conditions of the Los Humeros Geothermal Field (LHGF), Mexico, as revealed by a noble gas survey. *J. Volcanol. Geother. Res.* **333**, (2017), 104-115.

Pinti, D.L., Castro, M.C., López-Hernández, A., Hernández Hernández, M.A., Richard, L., Hall, C.M., Shouakar-Stash, O., Flores-Armenta, M., and Rodríguez-Rodríguez, M.H.: Cerro Prieto Geothermal Field (Baja California, Mexico) – A fossil system? Insights from a noble gas study. *J. Volcanol. Geother. Res.* **371**, (2019a), 32-45.

Pinti, D.L., Castro, M.C., López-Hernández, A., Hernández Hernández, M.A., Shouakar-Stash, O., Richard, L., Nuñez-Hernández, S., Hall, C.M., and Ramírez-Montes, M.: Signature of ongoing brine reinjection on noble gas isotopes and fluid chemistry at Las Tres Vírgenes geothermal field, Mexico. *J. Volcanol. Geoth. Res.* **377**, (2019b), 33–42.

Pinti, D.L., Castro, M.C., Hall, C.M., López-Hernández, A., and Shouakar-Stash, O.: Noble gas isotopes applied to geothermal resources. Eglington B, Fayek M, Kyser K (eds) Applied Isotope Geochemistry. Mineralogical Association of Canada, Topics in Mineral Science **48**, Vancouver, BC, (2019c) 139-154.

Porcelli, D.P., Ballentine, C.J., and Wieler, R.: Noble Gases in Geochemistry and Cosmochemistry, *Rev. Mineral. Geochem.* **47**, (2002), p. 845.

Poreda, R., and Craig, H.: Helium isotope ratios in circum-Pacific volcanic arcs. *Nature* **338**, (1989), 473-478.

Richard, L., Pinti, D.L., Hélie, J.F., López Hernández, A., Shibata, T., Castro, M.C., Sano, Y., and Sandoval-Medina, F.: Variability of deep carbon sources in Mexican geothermal fluids. *J. Volcanol. Geother. Res.*, **370**, (2019), 1-12.

Sano, Y., and Marty, B.: Origin of carbon in fumarolic gas from island arcs. *Chem. Geol.* **119**, (1995), 265-274.

Sano, Y., and Williams, S. N.: Fluxes of mantle and subducted carbon along convergent plate boundaries. *Geophys. Res. Lett.* **23**, (1996), 2749-2752.

Suárez-Vidal, F., Mendoza-Borunda, R., Navarrete-Zamarripa, L.M., Rámirez, J., and Glowacka, E.: Shape and dimensions of the Cerro Prieto pull-apart basin, Mexicali, Baja California, Mexico, based on the regional seismic record and surface structures. *Intern. Geol. Rev.* **50**, (2008), 636-649.

Sun, Z., Wang, A., Liu, J., Hu, B., Chen, G.: Radiogenic heat production of granites and potential for hot dry rock geothermal resource in Guangdong Province, Southern China, *Proceedings*, World Geothermal Congress, Melbourne, Australia, (2015).

Tello-López, M., and Torres-Rodríguez, M.: Behavior of the production characteristics of the wells in the Las Tres Vírgenes, BCS, Geothermal Field, México, *Proceedings*, World Geothermal Congress, Melbourne, Australia, (2015).

Torres-Rodríguez, M.A., Mendoza-Covarrubias, A., and Medina-Martínez, M.: An update of the Los Azufres geothermal field, after 21 years of exploitation, *Proceedings*, World Geothermal Congress, Antalya, Turkey (2005).

Veizer, J., Ala, D., Azmy, K., Bruckschen, P., Buhl, D., Bruhn, F., Carden, G.A.F., Diener, A., Ebneth, S., Godderis, Y., Jasper, T., Korte, C., Pawellek, F., Podlaha, O.G., and Strauss, H.: $^{87}Sr/^{86}Sr$, $\delta^{13}C$ and $\delta^{18}O$ evolution of Phanerozoic seawater. *Chem. Geol.* **161**, (1999), 59-88.

Wen, T., Pinti, D.L., Castro, M.C., López-Hernández, A., Hall, C.M., Shouakar-Stash, O., and Sandoval-Medina, F.: A noble gas and $^{87}Sr/^{86}Sr$ study in fluids of the Los Azufres geothermal field, Mexico – Assessing impact of exploitation and constraining heat sources. *Chem. Geol.* **483**, (2018), 426-441.