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Chemical-Isotopic Evidences for the Origin and Evolution of Geothermal Fluids at the Las Tres Vírgenes Geothermal Field, B.C., NW-Mexico

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ABSTRACT

The Las Tres Vírgenes (LTV) geothermal reservoir is a liquid-dominated resource located in the Baja California Peninsula (NW-Mexico) with a currently installed power capacity of 10 MWe. The sustainability of future electricity production at the LTV geothermal field raises concerns about the origin and hydraulic dynamics of exploited geothermal fluids. As part of the present study, water samples were taken from the production wells LTV-4 and LTV-11 with a maximum bottom depth of 2,413 m and 1,974 m, respectively, to analyze a series of chemical (major and trace elements) and isotopic (^{2}H, ^{3}H, ^{11}B, ^{13}C, ^{14}C, ^{18}O, $^{87}Sr/^{86}Sr$) parameters. The chemical and isotopic composition of LTV geothermal fluids is compared with surface water types (precipitation, thermal springs, shallow groundwater, seawater) and host rocks from the Baja California region to define their primary provenance, as well as type and degree of hydrothermal alteration. Interpreted results are compared with data from the adjacent geothermal fields in Cerro Prieto (Baja California Norte, Mexico) and Salton Sea (California, USA).

Measured ^{14}C-concentrations from 19.8 to 35.6 pmC - combined with the absence of tritium - support evidence for a Late Pleistocene to Early Holocene recharge event (8,300 – 13,000 yr BP) of surface water into the geothermal reservoir. Elevated precipitation rates by humid climatic conditions in northwestern Mexico at the final stage of the Last Glacial period, combined with enhanced fracture and fault permeabilities through local volcanic eruptions (La Virgen Volcano: 6,515 yr BP) could have enabled and accelerated the meteoric recharge of the LTV geothermal reservoir. Cooler climatic conditions are reflected by depleted deuterium values ($\Delta\ \delta D$ = 19 to 30‰) of the meteoric component in comparison to present-day local precipitation. The intermediate composition of LTV geothermal fluid (^{2}H, ^{18}O, Na, Cl, Ca, Br) between meteoric water and seawater suggests a 60:40 contribution of both water types. In contrast to Salton Sea geothermal water, mineral dissolution to explain elevated fluid salinity (TDS: 10 – 12 g/L) can be excluded as Cl/Br- (245) and Na/Cl-ratios (0.57) are relatively close to seawater and Cerro Prieto geothermal fluid composition.

The assimilation and homogenization of strontium and boron isotopic signatures between LTV geothermal fluids and reservoir host rock, as well as fluid enrichment in K, Li and SiO_2 suggest a mature degree for hydrothermal alteration, mainly by de-sorption of exchangeable B in clays, albitization of K-feldspar, chloritization and interaction with siliciclastic rocks.

1. INTRODUCTION

The Las Tres Vírgenes geothermal field is located near the boundary between the States of Baja California Norte and Baja California Sur on the peninsula of Baja California, in the northwest portion of Mexico, about 35 km northwest of the town Santa Rosalía (Fig. 1). Geothermal exploitation and electricity generation initiated in 1986 and 2001, respectively, with a current installed electricity capacity of 10 MWe with a total of nine drilled geothermal wells. The extreme arid climatic conditions of the study zone, with reported annual rainfall of 62.3 mm in the valleys and plains (Vargas 1988; CFE 1993), and maximum precipitation values of 150 mm for the adjacent La Virgen and El Azufre volcanoes rises concerns about the long-term sustainability and current recharge conditions of the exploited geothermal reservoir. Recent recharge seems improbable due to arid climatic conditions in the study zone. In the past, little hydrochemical investigations were performed to characterize reservoir fluids. Based on chemical and stable isotope analysis, the geochemical study from Portugal et al. (2000) concluded recharge of the reservoir by meteoric water during glacial periods and possible mixing with magmatic fluids. Verma et al. (2006) suggest a significant amount of reservoir recharge by seawater intrusion from the Gulf of California, based exclusively on measured Na/Cl ratios.

Based upon concerns about the future of geothermal exploitation of the Las Tres Vírgenes (LTV) reservoir, this study addresses a broad range of chemical (major and trace elements) and isotope techniques (^{2}H, ^{3}H, ^{11}B, ^{13}C, ^{14}C, ^{18}O, $^{87}Sr/^{86}Sr$) to define (i) the origin and evolution of produced fluids, (ii) degree of water-rock interaction at depth, (iii) the impact and magnitude of hydrothermal alteration on fluid composition. The influence of possible primary sources (recent/fossil seawater, meteoric water, magmatic water) on reservoir feeding is discussed, calculating residence times and mixing models for reservoir fluids. Interpretations for the origin and evolution of deep fluids from adjacent geothermal fields of Cerro Prieto (Baja California Norte) and Salton Sea (South California) are compared with geological and hydrochemical information from the LTV reservoir. Based on ^{14}C-age dating, the postulated time period for reservoir recharge with surface water will be incorporated into a paleoclimatic environment and volcanic-structural context.

2. SAMPLING AND METHODS

In July 2006, two water samples were collected in weirboxes of the production wells LV-4 and LV-11 at maximal vertical depths of 2,413 m and 1,974 m, respectively, to analyze a series of chemical (major and trace elements) and isotopic (H-2, H-3, B-11, C-13, C-14, O-18, Sr-87) parameters. The analytical data was re-calculated to reservoir concentrations to eliminate the effect of steam removal during separation and sample collection.

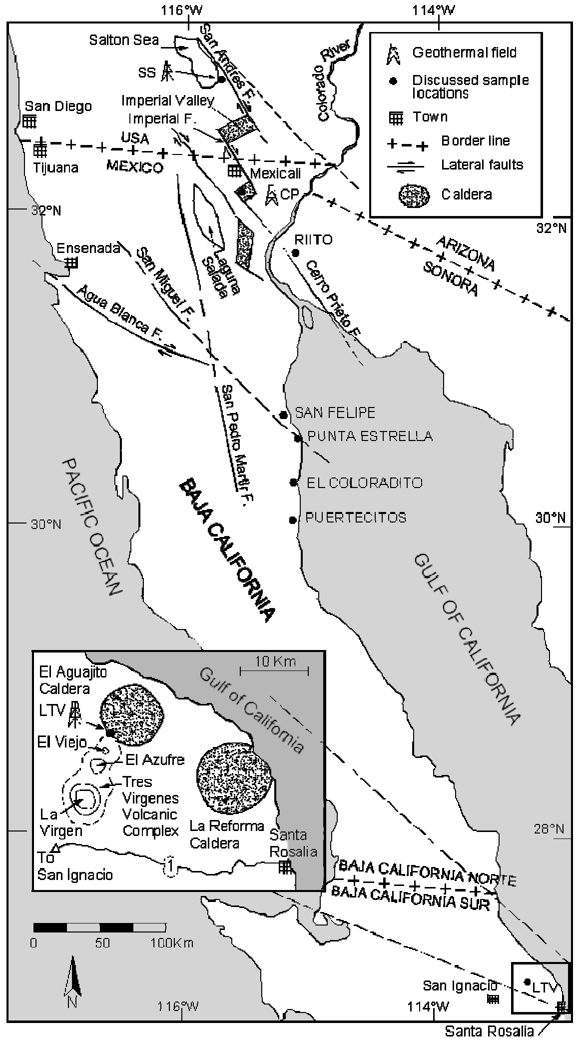

Figure 1: Location of the discussed geothermal fields of Las Tres Vírgenes (Baja California Sur BCS, Mexico), Cerro Prieto (Baja California Norte BCN, Mexico), Salton Sea (California, USA), thermal springs from BCN, and artesian and deep wells from the Riíto zone (Sonora State, Mexico).

The equation applied for this processes is the heat and mass balance equation as described by Henley et al. (1984):

$$C_{RES} = (1-y)\,C_L + yC_V$$

where C is the concentration of any compound, including heat and isotopes, C_{RES} represents the concentration in the reservoir, and C_L and C_V refer to the concentration in produced liquid and vapor phases, respectively.

The water samples for chemical analysis were stored in HDPE bottles, pre-filtered with 0.45 µm Millipore filters, acidified with HNO_3-Suprapur, and analyzed by *ACTLABS*, Ontario, Canada, using ICP-MS, ICP-OES and IC-techniques. The AMS-technique was applied to measure the ^{13}C and ^{14}C content at the NSF-Arizona AMS Laboratory of the University of Arizona, Tucson, U.S., with % modern as defined by Stuiver and Polach (1977). Sigma % modern comprises statistical errors, combined in quadrature with a system error component. Low standard deviation values between 0.17 and 0.28 percentage of modern carbon (pmC) for the analyzed water samples reflect the negligible analytical error of the ^{14}C technique. The Dissolved and Noble Gas Laboratory at the University of Utah (Salt Lake City, US), conducted tritium measurements using the in ^{3}He growth method with detection limit for tritium generally on the order of 0.1 TU. The $\delta^{18}O$ and $\delta^{2}H$ measurements were performed by the Environmental Isotope Laboratory at the University of Arizona (Tucson, US) and δ values are reported relative to V-SMOW with an analytical precision of 0.08‰ and 0.9‰, respectively. Thermal Ionization Mass Spectrometry (TIMS) was applied at the Saskatchewan Isotope Laboratory, Dept. of Geological Sciences at the University of Saskatchewan, Canada to measure $^{87}Sr/^{86}Sr$ ratios. Sr isotope ratios are quoted relative to a value of 0.710250 for the NIST SRM 987 standard, and with a 1σ analytical uncertainty for the samples of 0.005%. Chemical and isotopic analytical results are shown in Table 1 and 2, respectively.

3. RESULTS

3.1 Primary Origin of Geothermal Fluids

3.1.1 Groundwater Dating

Due to its short half-life of 12.43 years (Unterweger et al., 1980), tritium (^{3}H) can be used to identify the presence of modern recharge, whereas ^{14}C is the leading tool in estimating the age of paleo- and fossil groundwater due to its longer half-life of 5,730 years. Measured tritium values of 0.04 ± 0.10 T.U. and 0.15 ± 0.10 T.U. for geothermal fluids from the Las Tres Vírgenes wells LTV-4 and LTV-11, respectively, suggest the absence of modern recharge (< 100 years BP) for the geothermal reservoir. The measured ^{14}C-ratios of standards and samples were corrected to values corresponding to $\delta^{13}C = -25‰$, as described in Donahue et al. (1990). Measured ^{14}C concentrations of 19.80 ± 0.17 pmC (LTV-4) and 35.61 ± 0.28 pmC (LTV-11) resulted in ^{14}C ages of 8,294 ± 62 years BP (well LTV-11) to 13,011 ± 68 years BP (well LTV-4), indicating a Late Pleistocene to Early Holocene time period for recharge of the geothermal reservoir by atmospheric-derived water. The detection of ^{14}C in geothermal fluids is very uncommon, either by dilution of the fluid with ^{14}C-free magmatic CO2, or by major magmatic contributions, lowering the initial ^{14}C activity. Less than 0.5 pmC have been reported for geothermal fluids from the Geysers, Steamboat Springs and Salton Sea, USA (Craig 1963), and 0.2 pmC for deep well fluids from Wairakei, New Zealand (Fergusson and Knox 1959).

Magmatic or andesitic water, as initially proposed from Giggenbach (1992), is a frequently mentioned component of reservoirs fluids, such as postulated for the Larderello (Italy) and the Geysers geothermal fields (California) (D'Amore and Bolognesi 1994). In the LTV case, assuming hypothetical ^{14}C- and ^{3}H-concentrations of 100 pmC and 2.0 T.U. for the current atmospheric input (e.g. 1.8 T.U. for precipitation in SE-Mexico in June 2001, Birkle et al. 2006), mixed with a ^{14}C- and ^{3}H-free magmatic component, a magmatic contribution between 64 and 80% would fit with measured ^{14}C-values of the geothermal fluids (19.8 – 35.6 pmC), but the atmospheric contribution of 20 to 36% would result in unrealistic elevated ^{3}H-concentrations between 0.40 and 0.72 T.U. for the hypothetical mixture composition. The only option to reconstruct the existence of a magmatic end-member would be a slighter younger time period for the infiltration of surface water, as mixing of late Holocene surface water (e.g. ^{14}C ~50 pmC) with ^{14}C-free magmatic water could also produce the present radioactive isotopic composition of geothermal fluids. It can be postulated, that Las Tres Vírgenes (LTV) geothermal fluids do not require a magmatic component to explain their current isotopic composition.

Table 1: Chemical composition of geothermal fluids from the wells LTV-4 and LTV-11 (units in mg/L, except pH)

Well	pH	TDS	Li	Na	K	Mg	Ca	Sr	Cl	Br	B	SO_4	SiO_2	HCO_3
LTV-4	7.42	9855	21.0	3113	691	0.0	107	4.0	5498	22.0	110	29.0	284	49.0
LTV-11	7.35	11978	30.0	3990	921	0.13	158	6.0	7020	28.6	125	32.0	445	33.0

Table 2: Isotopic composition of geothermal fluids from the wells LTV-4 and LTV-11.

Well	$\delta^{18}O$	$\delta^{2}H$	$^{11}B/^{10}B$	$\delta^{11}B$	d^{13}C	$^{87}Sr/^{86}Sr$	^{14}C	2σ ^{14}C	^{3}H	2σ ^{3}H
Units	[‰]	[‰]		[‰]	[‰]		[pmC]	[pmC]	[T.U.]	[T.U.]
LTV-4	-3.9	-57.1	4.0539216	3.7	-7.3	0.704335	19.80	0.17	0.04	0.10
LTV-11	-4.0	-59.2	4.0539989	3.8	-9.4	0.704328	35.61	0.28	0.15	0.10

3.1.2 Chemical Evidence

Figure 2 shows the log Br–log Cl trend of the seawater evaporation trajectory (SET) in comparison to the composition of LTV, Salton Sea (SS) and Cerro Prieto (CP) geothermal water. During the evaporation of seawater into and beyond halite facies Br- is concentrated progressively as an incompatible element in the residual brine (Carpenter, 1978). Evaporation of seawater causes a linear enrichment trend for the residual fluid in Br- and Cl- until reaching halite saturation at Cl- ~162,000 mg/L. LTV fluidal composition lies within the more heterogeneous range of CP fluids, and are more diluted in respect to present seawater composition. Halite dissolution with fluidal enrichments in Cl and stable Br conditions is not observed for LTV fluids types.

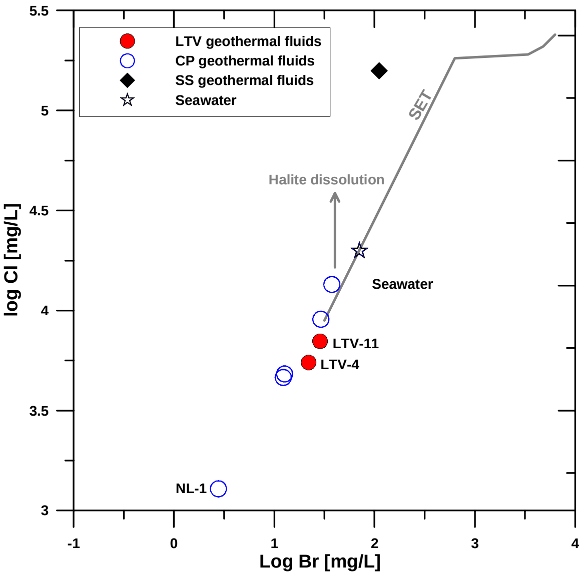

Figure 2: Log Br–log Cl ratio of Las Tres Vírgenes (LTV), Cerro Prieto (CP, Portugal et al. 2005) and Salton Sea (SS) geothermal fluids from well SSSDP 2-14 (Lippmann et al. 1999), compared with the evaporation trajectory of seawater (SET).

A slight deviation of CP geothermal fluids towards the left side of SET suggests slight dissolution processes. Elevated Cl-concentrations in comparison to Br reflect a significant impact on groundwater mineralization by halite dissolution of geothermal fluids, taken from the Salton Sea Scientific Drilling Project (SSSDP) well 2-14 (Lippmann et al. 1999).

Na/Cl and Cl/Br ratios of ~245 and 0.57 for LTV geothermal waters are very similar to CP geothermal fluids and seawater composition, which suggest a marine origin for conservative elements in LTV fluids. In contrast, Cl/Br-ratio of high salinity fluids from SS is similar to Colorado river composition (~1600, Coplen and Kolesar 1974) and is explained by the dissolution of evaporites, which were formed from Colorado River water (White 1968). On the other hand, global Cl/Br ratios of 50 to 150 for atmospheric precipitation and 100 to 200 for shallow groundwater (Davis et al. 2005) are not too distinct from LTV thermal fluids.

3.1.3 Stable Isotope Evidence

Comparing stable isotope values (^{18}O and ^{2}H), most of the thermal spring from Baja California Norte, and thermal and deep wells from Riíto in Sonora, plot along a line which is the path between the GMWL and evaporating water from the lower Colorado River (Lake Mead) (Fig. 3). The isotopic composition of local precipitation lies to the left of this evaporation path. This strongly suggests that most of the subsurface water in the Imperial Valley was derived from the Colorado River (Coplen and Kolesar, 1974). Artesian wells form the Riíto zone with reservoir temperatures between 109 and 118°C are typical surface or shallow groundwater from the Mexicali Valley, whereas deep fluids from the Riíto zone ($Temp_{res}$ = 126 - 192°C) were originated by the evaporation of infiltrated waters with similar characteristics to those located in the Mexicali Valley. Puertecitos coastal springs from Baja California Norte (BCN) were interpreted as mixing of high portion of seawater (> 80 wt%) with local waters. San Felipe is additionally affected by secondary leaching of evaporates (Barragán et al. 2001), with similar formation processes and isotopic composition as Salton Sea brines. Other thermal springs from BCN are isotopically close to present-day precipitation (El Coloradito, CO), to volcanic steam-heated water (Valle Chico, VC) or a mixture of meteoric water with seawater (Punta Estrella (PE) (Barragán et al. 2001).

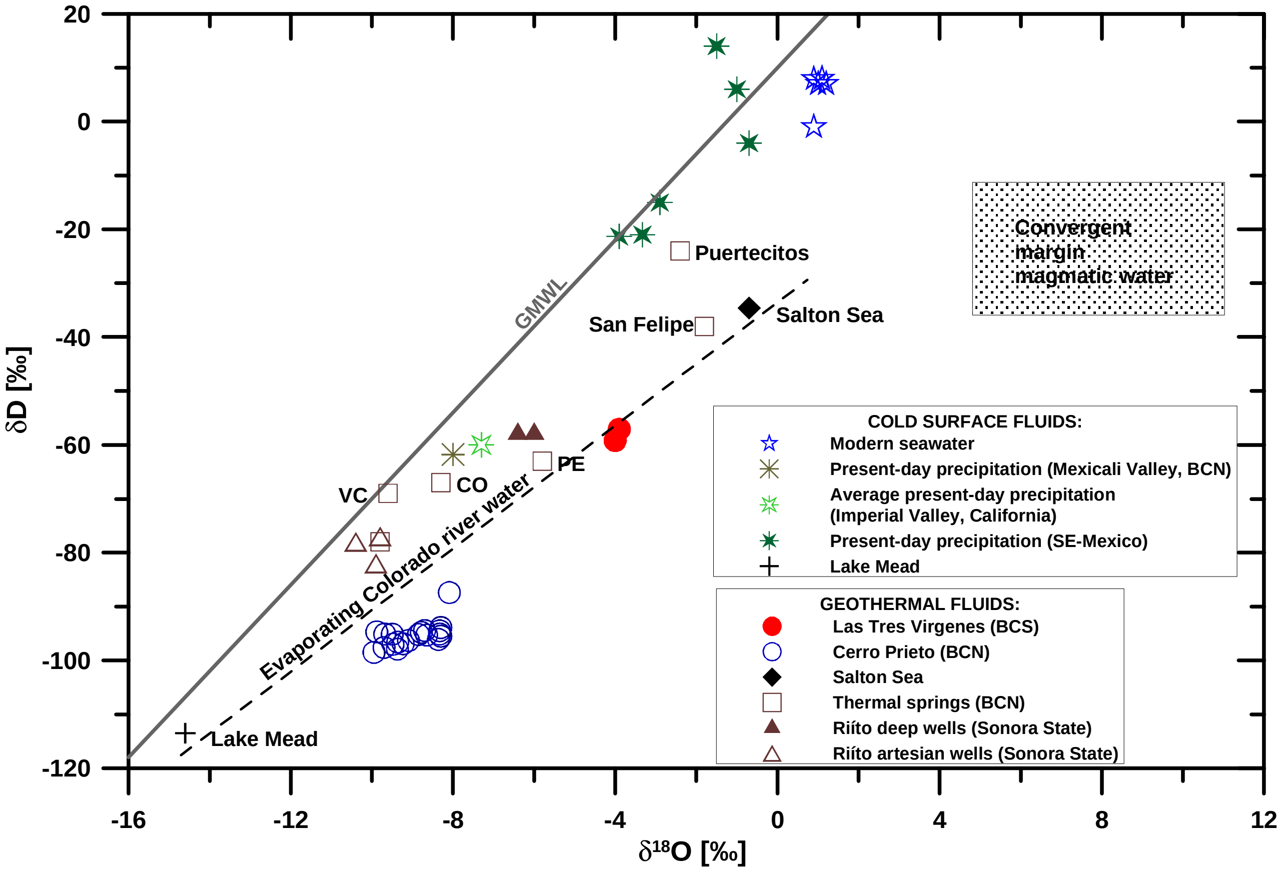

Figure 3: δ^{18}O and δD composition of LTV geothermal fluids, compared with reservoir fluids from the Cerro Prieto (State of Baja California Norte, Truesdell et al. 1981) and Salton Sea geothermal fields (S-California, Coplen and Kolesar 1974), thermal springs from Baja California Norte (Barragán et al. 2001), artesian and deep wells from the Riíto zone (Sonora State, Barragán et al. 2001), present-day precipitation water from Mexicali Valley (BCN, Barragán et al. 2001), Imperial Valley (S-California, Coplen & Kolesar 1974), and SE-Mexico (Birkle et al. 2006, 2002), as well as modern seawater from the Gulf of Mexico (Birkle et al. 2006, 2002) and Lake Mead water (Coplen and Kolesar 1974). Dashed line shows evaporating trend for water from the lower Colorado River (Lake Mead, Coplen and Kolesar 1974). Shaded box shows range "convergent margin magmatic waters" (D´Amore and Bolognesi 1994).

The Salton Sea brine is derived from local precipitation followed by the leaching of sediments by surface water circulating downward to a geothermal reservoir (Craig 1966). The high salinities of the Salton Sea geothermal brines are derived in part from the in-situ hydrothermal metamorphism and dissolution of halites and $CaSO_4$ from relatively deeply-buried lacustrine evaporates, with a further modification of their Na-Ca-K-Fe-Mn-Cl composition by on-going sediment metamorphism and water-rock interaction (McKibben et al. 1988).

The higher temperatures at the Cerro Prieto reservoir promote oxygen exchange between water and silicates, causing a positive isotopic shift of fluidal δ^{18}O-values. The isotopic composition of present-day precipitation in the Imperial and Mexicali Valley reflects arid climatic conditions of southern California and northern Baja California State, whereas precipitation in SE-Mexico is extremely enriched in ^{18}O and ^{2}H by humid, sub-tropical conditions.

The LTV geothermal fluids are positioned beyond the evaporation trend of Colorado River water towards the SS geothermal fluid composition, which could indicate the evaporation of river water to explain current isotopic composition (Fig. 3). On the other hand, fluctuating climatic conditions in northwestern Mexico and southwestern U.S. with temporary cooler and more humid conditions during Late Pleistocene and Early Holocene (Li et al. 2008, Roy et al. 2007, Metcalfe et al. 2000, Ortega et al. 1998) could have propitiated the enhanced recharge of meteoric water into the geothermal reservoir. This case is supported by lower δ^{18}O and δD-ratios for glacial precipitation water, as shown for Late Pleistocene groundwater from the Ojo Alamo and Nacimiento aquifers in the central San Juan Basin, New Mexico with a stable isotope content about 25‰ lighter in D and 3‰ lighter in ^{18}O than modern precipitation and groundwater (Phillips et al. 1986). The correlation between δD and chlorine values for LTV geothermal fluids (vapor + liquid) supports the hypothesis of a Late Pleistocene meteoric recharge under cooler climatic conditions than present-day (Fig. 4). While the origin of CP fluids can be reconstructed by mixing of evaporated seawater with Colorado River water (Truesdell et al. 1981), the LTV fluidal composition is derived by mixing of meteoric water and a non-evaporated seawater component. With a range from -81‰ to -92‰ (see hatched area in Fig. 4), the δD-value of the reconstructed meteoric end-member seems to be 19‰ to 30‰ lower as present precipitation values (-61.8‰ for the Mexicali Valley), which is in agreement with glacial precipitation water from the central San Juan Basin. In the central San Juan Basin, the isotopic depletion is attributed to colder mean annual temperature with a temperature decrease of 5° to 7°C during the late Wisconsin and perhaps to increased winter precipitation (Phillips et al. 1986).

In contrast, the elevated mineralization of Salton Sea geothermal fluids is explained by the dissolution of evaporates with meteoric water and a hypothetical initial deuterium ratio of ~70‰, which represents an intermediate value between present-day recharge (~-62‰) and fossil recharge (~-81 to -92‰) or Colorado river water (~-110‰).

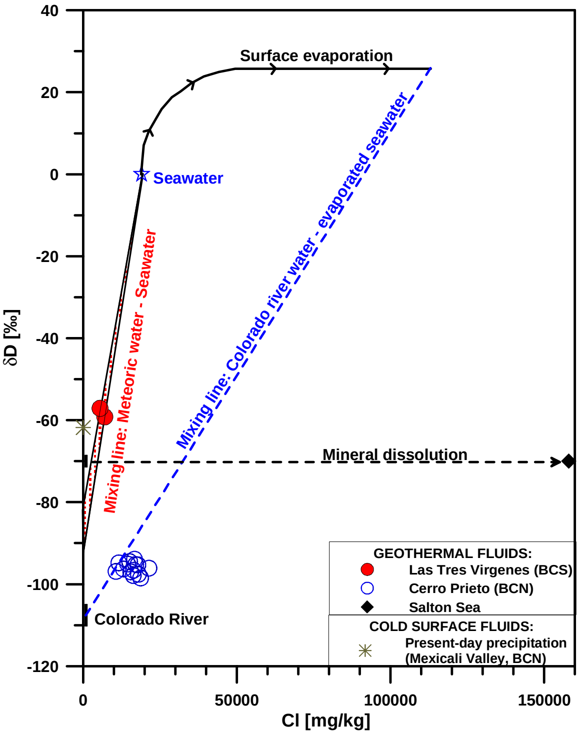

Figure 4: Models for mixing, a) Colorado River water with evaporated seawater to produce the Cerro Prieto aquifer (samples from early 1977, Truesdell et al. 1981), b) glacial meteoric water with seawater to produce the LTV geothermal fluid, and, c) evaporite dissolution by meteoric water to form Salton Sea geothermal fluid (Coplen and Kolesar 1974).

3.2 Impact of Potential Water-Rock Interaction

3.2.1 Hydrochemical tracers

The degree of hydrothermal alteration of primary fluid and host rock composition by thermal-induced reactions should be reflected in variations of the primary chemical composition of non-conservative elements, whereas highly soluble elements (e.g Na, Cl, Br) should maintain their initial composition. The application of a mixing model with meteoric water and non-evaporated seawater as end-members (as suggested by isotopic indications in Section 3.1.3) and concentrations of conservative elements (Na, Cl, Br, Ca) in LTV fluids, present-day meteoric water (MW) and seawater (SW) and results in a homogeneous mixing proportion from 37 to 44 % for the seawater component, and 56 to 63% for the meteoric component (Table 3).

In contrast, K (Fig. 5), Li and SiO_2 are enriched in LTV fluids (in comparison to SW and MW), indicating the impact of additional dissolution processes by hydrothermal alteration. Derived from the K/Cl vs. Cl/Br correlation, the fluid enrichment in K can probably be related to dissolution of K feldspar and albitization. The depletion of Mg in LTV fluids (in comparison to SW and MW), suggests the precipitation of Mg-minerals as secondary process. Whereas Na, Cl, Br and Ca concentrations reflect a stable mixing proportion between SW and SW end-members, SO_4 is strongly depleted in LTV fluids, probably by bacterial reduction processes, therefore calculated mixing proportions are not valid for the mentioned anion.

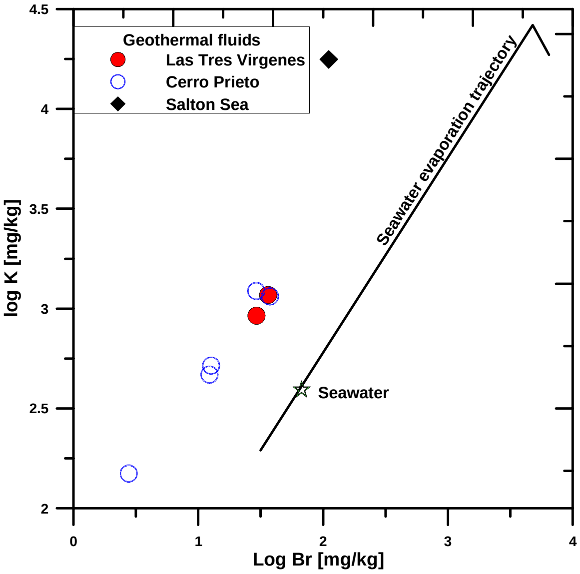

Figure 5: log Br vs. log K concentrations for LTV, CP (Portugal et al. 2005) and SS geothermal fluids (Lippmann et al. 1999) in comparison to present-day seawater and the seawater evaporated trajectory (SET).

3.2.2 Boron isotopes

In general, B concentration and B isotopic signature can be altered by following mechanism: (i) alteration of volcanic products (Palmer and Swihart 1996); (ii) carbonate precipitation with a preferential uptake of tetrahedral borate, $^{10}B(OH)_4^-$; (iii) ^{10}B uptake in B-bearing-minerals (tourmaline, borosilicate) (Palmer and Swihart 1996); (iv) illitization of smectite with advanced levels at ~120-150°C (Weaver 1989; Williams et al. 2001); (v) de-sorption of exchangeable B in clays (You et al. 1993a, b); (vi) mixing of fluids with different sources (Deyhle et al. 2004); (vii) Opal-C to Opal-CT transition (Brumsack and Zuleger 1992); and (viii) involvement of deep generated fluids. The processes (i) to (iv) decrease B concentrations and elevate $\delta^{11}B$ in fluids, whereas (v) increase B concentrations and lower $\delta^{11}B$ in fluids. Rather variable compositions can be achieved by the mechanisms of (vi) and (vii). Liebscher et al. (2005) suggest liquid-vapor separation as one of the most important processes that control the composition in hydrothermal systems associated with calc-alkaline magmatism.

Table 3. Chemistry of meteoric water (MW, Cd. del Carmen, unpub.), global present-day seawater and geothermal fluid from the well LTV-11, with the calculated percentage contribution of MW and SW to calculate the mixing composition of LTV fluids. Concentrations in mg/L, n.c.: not calculated as $Conc_{LTV} > Conc_{SW} > Conc_{MW}$ for K, Li, and SiO_2); and as $Conc_{LTV} < Conc_{MW} < Conc_{SW}$ for Mg.

Water type/Element	Na	Ca	Cl	Br	SO_4	K	Li	SiO_2	Mg
MW	32.1	6.0	42.7	0.08	8.4	1.7	0.01	< 4.3	2.06
SW	10500	400	19000	65.0	265	380	0.17	6.0	1350
LTV-11	3990	158	7020	28.6	32.0	921	30.0	445	0.13
Contr. MW [%]	62.2	61.4	63.2	56.1	(90.8)	n.c.	n.c.	n.c.	n.c.
Contr. SW [%]	37.8	38.6	36.8	43.9	(9.2)	n.c.	n.c.	n.c.	n.c.

In the case of the LTV fluids, boron concentration values of 110 mg/L (LV-4) to 125 mg/L (LV-11) are elevated in comparison to common meteoric water (< 1.0 mg/L) and seawater (4.5 mg/L), while the δ^{11}B value range from 3.7‰ (LV-4) to 3.8‰ (LV-11) seems strongly depleted in comparison to dissolved boron in present-day seawater with a constant world-wide δ^{11}B value of + 39.5 ‰ (Barth 1993) and meteoric water. Therefore, most probable mechanism that affect B and B isotope signature in LTV fluids could be, a) de-sorption of exchangeable B in clays, resulting in elevated B with low ^{11}B (in fluids), and/or, b) a potential involvement of deep generated fluids. The second option can be excluded, as elevated ^{14}C-concentrations of the LTV reservoir fluids exclude major contributions of deep, ^{14}C-free magmatic fluids. As B partitions preferentially into vapor and $\Delta^{11}B_{\text{vapor-liquid}}$ values are small for geothermal systems ranging from ~3‰ to 1‰ at ~140 to 300°C (Leeman et al. 1992), effects by liquid-vapor separation are negligible for LTV fluids.

A hydrothermal alteration rate between 20% and 69%, as reported for andesites and sandstones of the Comondú Group in well LV-11 (depth: 654 - 804 m), as well as a common abundance of secondary clay minerals (montmorillonite, smectite, illite) (Viggiano et al. 2009) suggest the de-sorption of exchangeable B in clays as principal mechanism to alter the primary boron isotopic composition of reservoir fluids.

Desorption as principal mechanism as documented for interstitial water from the ODP Site 1202, Okinawa Trough (Huang et al. 2005), is also indicated by the negative trend from seawater towards LTV-fluidal composition (Fig. 6). In this specific case, intensive water-rock interaction reached probably a complete isotopic homogenization between host rock and formation fluids, camouflaging the original ^{11}B/^{10}B-ratio of both phases. No data is available on the boron isotopic composition of local host rock to reconstruct the quantitative degree of homogenization, but similarities in boron isotopic composition between LTV geothermal fluids and degassed rhyolithic glasses from Long Valley caldera, California (Schmitt and Simon 2004) support the hypothesis of a complete isotopic exchange between both phases. On the other hand, the low δ^{11}B-values of LTV fluids could also be related to a meteoric water source, as shown for meteoric-water dominated geothermal fluids in Iceland (-6.7‰ to +3.1‰) in contrast to seawater-dominated fluids with elevated δ^{11}B -ratios (+29.6‰ to +30.7‰) (Aggarwal et al. 1992). The boron isotopic composition of LTV-fluids lies within the value range of Cerro Prieto fluids (Portugal et al. 2005), although the larger lateral and vertical size of the CP reservoir explains the wider spread of δ^{11}B-values and boron concentrations (Fig. 6).

3.2.3 Strontium isotopes

La Virgen and El Mezquital scoria, pumice and juvenile clast deposits from the La Virgen volcano have Sr-concentration between 341 and 530 ppm (Capra et al. 1998). Dacitic lava (12 m.y.) and glass (< 0.7 m.y.) from the La Virgen volcano have ^{87}Sr/^{86}Sr-ratios of 0.70427 to 0.70438 and from 0.70381 to 0.70384, respectively (Cameron and Cameron 1985). Conly et al. (2006) presented a ^{87}Sr/^{86}Sr-range from 0.070370 to 0.70453 for plutonic and volcanic rocks from the Baja California basement (Fig. 7).

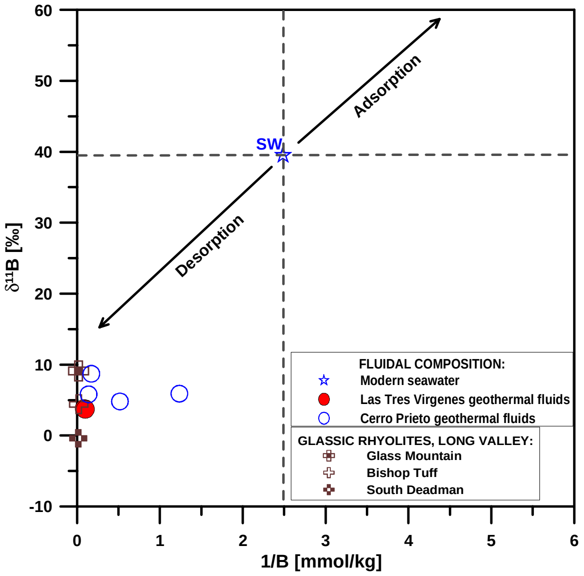

Figure 6: Correlation plot of 1/B vs. δ^{11}B to compare Las Tres Vírgenes geothermal fluidal composition with geothermal water from the Cerro Prieto Reservoir (Baja California Norte, Portugal et al. 2005), present seawater and rhyolitic glasses from Glass Mountain Dome (shown is sample with maximum δ^{11}B value), Bishop Tuff and South Deadman (latter ones with average δ^{11}B values), Long Valley caldera, California (Schmitt and Simon 2004).

Saunders et al. (1987) published a series of ^{87}Sr/^{86}Sr-values from 0.70320 to 0.70629 and Sr-concentration from 506 to

3,728 ppm for late Cenozoic volcanic rock in Baja California Norte (BCN), similar in their signature and origin as Las Tres Vírgenes host formations. Specific values for the San Borja (SB), Jaraguay (J) and San Quintín (SQ) volcanic fields in BCN are compared with the composition of LTV geothermal fluids, the global composition of present to Late Pleistocene seawater ($^{87}Sr/^{86}Sr$ = 0.7092, McArthur et al. 2001), Colorado River water ($^{87}Sr/^{86}Sr$ = 0.70971-0.7103, Gross et al. 2001) and a representative meteoric water sample ($^{87}Sr/^{86}Sr_{MW}$ = 0.7090) from Cd. del Carmen, SE-Mexico (Birkle, unpub.). Both, the extreme isotopic depletion of LTV geothermal fluids ($^{87}Sr/^{86}Sr_{LTV\text{-}4}$ = 704335; $^{87}Sr/^{86}Sr_{LTV\text{-}11}$ = 0.704328) in comparison to present-day to Late Pleistocene seawater, Colorado river water, and to present-day meteoric water, as well as isotopic similarities with dacitic host rock ($^{87}Sr/^{86}Sr_{La\ Virgen}$= 0.70381 - 0.70438) and the plutonic and volcanic basement from Baja California ($^{87}Sr/^{86}Sr_{Cenozic\ volcanic\ rock}$ = 0.70320 – 0.70629) suggest intensive hydrothermal alteration to explain the isotopic homogenization of reservoir host rock and geothermal fluids. A rock-derived source for the strontium isotopic composition has also been reported for Salton Sea geothermal brines, concluding that 80-100 percent of the strontium and 50-100 percent of the lead in these brines were acquired from associated sediments rather than from rhyolite (Doe et al. 1966).

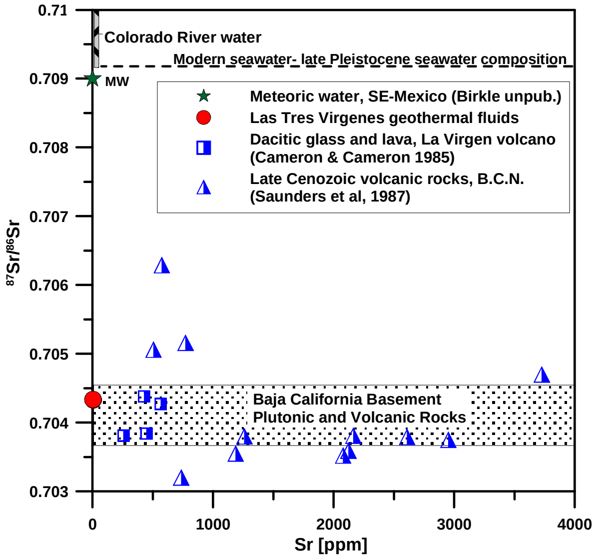

Figure 7. Strontium concentrations and $^{87}Sr/^{86}Sr$-values of Las Tres Virgenes geothermal fluids (LTV-4, LTV-11), dacitic lava and glass from La Virgen volcano (Cameron and Cameron 1985), late Cenozoic volcanic rock from San Borja, Jaraguay and San Quintín volcanic fields in Baja California Norte (Saunders et al 1987), plutonic and volcanic basement rocks from Baja California (Conly et al. 2006), the global composition of present to Late Pleistocene seawater (McArthur et al. 2001), Colorado river water (Gross et al. 2001) and meteoric water from Cd. del Carmen, SE-Mexico (Birkle, unpub.).

4. DISCUSSION

4.1 Paleoclimatic Evidences for Late Pleistocene Recharge

A Late Pleistocene to Early Holocene ^{14}C-age of the studied LTV-geothermal fluids could be related to recharge events during major periods of increased humidity. Ortega et al. (1998) observed two major periods of increase humidity by lake-level variations of the Laguna Babícora, near the Chihuahuan Desert in NW-Mexico, during the Late Wisconsinan and Early Holocene, related to jet stream migration to southerly latitudes and the influence of the mobile polar high. The dated record for Late Wisconsinan (16,342 ± 210 yr BP) and Younger Dyan (10,976 ± 115 yr BP; 9,614 ± 130 yr BP) sediments is characterized by a temperature decrease and cold paleoclimate conditions. Roy et al. (2007) determined high inflow rates and high lake stands from cores studies from the Laguna San Felipe, Sonoran Desert, NW-Mexico, during 14,000-13,000 yr BP, 12,000-8,500 yr BP and 6,000-3,000 yr BP by ^{14}C age determinations, intercalated by drier periods (27,000-14,500 yr BP, 13,000-12,000 yr BP, 7,000 yr BP) with higher evaporation in the basin and increased aeolian activity. A regional-scale for the recharge of deep aquifers (> 1000 mbsl) at the end of the Last Glacial period is evidenced by abundant ^{14}C-concentrations between 1 pmC and 35 pmC for formation water in several on- and off-shore oil reservoirs in SE-Mexico (Birkle et al. 2002, 2006, 2009). The variations in $\delta^{18}O$ and $\delta^{13}C$ values of lake tufa deposits in the Salton Basin, S-California, ranging from − 8.52‰ to − 2.50‰ (PDB) and from 0.8‰ to 3.76‰, respectively, reflect changes in the relative humidity in Salton Basin and variations in the Colorado River inflow and hence climatic conditions in the Colorado River drainage basin (Li et al. 2008). The tufa record exhibits (1) relatively dry paleoclimate between 20 and 18 kyr BP of Salton Basin, (2) a wet climate between 18 and 17 kyr BP, (3) decreasing effective moisture from 17 to 16 kyr BP, (4) increased effective moisture at ca.15.5 kyr BP during the Trans-US Wet Period, (5) wet/warm Early Holocene corresponding to the Maximum Effective Moisture Period perhaps brought about by the strengthening of North American monsoon, and (6) especially around 6.2 and 2.5 kyr BP, the climate became dryer, apparently resulting from weakening of the monsoons.

4.2 Correlation between Late Pleistocene Volcanism and Reservoir Recharge

Besides the presented indications of enhanced recharge rates by the periodical occurrence of cooler and humid climatic conditions in northwestern Mexico during Late Pleistocene and Early Holocene period, volcanic activity in the LTV region seems to have triggered additional hydrologic processes: Early Holocene tectonic-volcanic activities in the Las Tres Vírgenes region, reflected by the last eruptive phase of La Virgen volcano at 6,515 yr BP with the deposition of a sequence of fall and hydromagmatic surge horizons from the El Mezquital formation (Capra et al. 1998) represent a co-genetic process to the postulated meteoric recharge of the adjacent LTV geothermal reservoir. Therefore, elevated precipitation rates by humid climatic condition in NW-Mexico at the end of the Last Glacial period, in combination with increased fracture permeabilities by tectonic extensional processes during volcanic eruptions could have enabled and accelerated the glacial-period recharge of the present geothermal reservoir with surface-derived fluids. As hydromagmatic activities are of minor impact (Capra et al. 1998), the possibility of a water-induced volcanic eruption, caused by the contact of infiltrating cold surface water with a shallow located magma chamber, can be excluded. Similar as for the La Virgen eruptive event, a young eruptive, intermittently cycle from 110,000 to 10,000 yr BP has been reported for the Cerro Prieto volcano, based on paleomagnetic data (de Boer 1980). Also, Kasameyer et al. (1984) suggest a young age for the Salton Sea geothermal field from 3,000 to 20,000 years, which indicates a common young age for the initiation of hydrothermal fluid migration in deep reservoirs of southern California and northwestern Mexico.

4.3 Recommendations for future exploitation

The commercial lifespan of any geothermal field depends on the presence of recharge sources to feed the reservoir. In the case of the LTV reservoir, isotopic analysis indicate the existence of infiltration processes during Late Glacial periods during Late Pleistocene and Early Holocene, whereas no proves were found for present-day recharge. Therefore, unknown hydrological parameters for this glacial aquifer, especially the available fluid volume, require an extreme careful management for the future exploitation process. In order to protect the non-renewable energy source of the LTV reservoir and to extend the lifespan of geothermal exploitation, a continuous and complete reinjection of residual fluids is suggested to maintain a closed-production cycle. The production history of each production well should continuously be monitored, combined with permanent chemical and isotopic fluid analysis in order to detect any anthropogenic-caused hydraulic alterations at the geothermal reservoir.

5. CONCLUSIONS

The study of the Las Tres Virgenes geothermal reservoir represents a unique global case, where the recharge event of a geothermal reservoir can genetically be linked to tectonic-volcanic activities, as radiometric methods (^{14}C) confirm a homogeneous age for final volcanic eruptions from the La Virgen volcano (6,515 yr BP), located adjacent to the LTV geothermal field, and for the infiltration period of surface water into the geothermal reservoir (8,300 - 13,000 yr BP). Na/Cl- and Br/Cl-ratios as well as mixing calculation with conservative elements (Na, Ca, Cl, Br) from LTV fluids suggest an approximate 60:40 contribution between meteoric water and seawater components within the LTV reservoir. The δD-value of the reconstructed meteoric end-member seems to be 19‰ to 30‰ lower as present precipitation values (-61.8‰ for the Mexicali Valley), supporting evidence for cooler and more humid climatic conditions in NW-Mexico during Late Pleistocene and Early Holocene. As demonstrated analogously for the central San Juan Basin in New Mexico, USA, isotopic depletion is attributed to colder mean annual temperature with a temperature decrease of 5° to 7°C during the late Wisconsin and perhaps increased winter precipitation (Phillips et al. 1986).

Subsequently to infiltration (< ~8,000 yr BP), enhanced hydrothermal alteration at about 300°C resulted in Mg and SO_4 depletion by chloritization, whereas increased Li, K, and SiO_2 concentrations of geothermal fluids are related to interaction with siliciclastic rocks and albitization of K-feldspar. The assimilation of strontium and boron isotopic signatures between LTV geothermal fluids and reservoir host rock suggest de-sorption of exchangeable B in clays - supported by the common abundance of secondary clay minerals (montmorillonite, smectite, illite) - as principal hydrothermal mechanism.

REFERENCES

Aggarwal, J.K., Palmer, M.R., and Ragnarsdottir, K.V.: Boron isotopic composition of Icelandic hydrothermal systems, *Proceedings,* 7th International Symposium on Water-Rock Interaction (eds. Y. K. Kharaka and A. S. Maest) WRI-7, Balkema, Rotterdam (1992), 893-895.

Barragán, R.M., Birkle, P., Portugal, E., Arellano, V.M., and Alvarez, J.R.: Geochemical survey of medium temperature geothermal resources from the Baja California Pensinsula and Sonora, Mexico, *J. Volcanol. Geotherm. Res.*, **110**, (2001), 101-119.

Barth, S.: Boron isotope variations in nature: a synthesis, *Geol.Rundsch.,* **82**, (1993), 640–651.

Birkle, P., Martínez, B.G., Milland, C.P., and Eglington, B.: Origin and evolution of formation water at the Jujo-Tecominoacán oil reservoir, Gulf of Mexico. Part 2: Isotopic and field-production evidence for fluid connectivity, *Appl. Geochem.,* **24**, (2009), 555-573.

Birkle, P., Angulo, M., and Lima, S.: Hydrochemical-isotopic tendencies to define hydraulic mobility of formation water at the Samaria-Sitio-Grande oil field, Mexico, *J. Hydrol.,* **317**, (2006), 202-220.

Birkle, P., Rosillo, J.J., Portugal, E., and Fong, J.L.: Evolution and origin of deep reservoir water at the Activo Luna oil field, Gulf of Mexico, Mexico, *AAPG Bulletin,* **86**, (2002), 457-484.

Brumsack, H. J., and Zuleger, E.: Boron and boron isotopes in pore waters from ODP Leg 127, Sea of Japan, *Earth Planet. Sci. Lett.,* **113**, (1992), 427-433.

Cameron, K.L., and Cameron, M.: Rare earth elements, 87Sr/86Sr, and 143Nd/144Nd compositions of Cenozoic orogenic dacites from Baja California, northwestern Mexico, and adjacent west Texas: evidence for the predominance of a subcrustal component, Contrib. Mineral. Petrol., 91, (1985), 1-11.

Capra, L., Macías, J.L., Espíndola, J.M., and Siebe, C.: Holocene plinian eruption of La Virgen volcano, Baja California, Mexico, J. Volcanol. Geotherm. Res., 80, (1998), 239-266.

Carpenter, A.B.: Origin and chemical evolution of brines in sedimentary basins, *Oklah. Geol. Surv. Circ.*, **79**, (1978), 60-77.

CFE: Informe final del sistema hidrogeológico regional de la zona geotérmica de Las Tres Vírgenes, B.C.S., Comisión Federal de Electricidad, Gerencia de Proyectos Geotermoeléctricos, Morelia, Internal report OGL/TV/001/93, (1993) 82 pp.

Conly, A.G., Beaudoin, G., and Scott, S.D.: Isotopic constraints on fluid evolution and precipitation mechanisms for the Boléo Cu-Co-Zn district, Mexico, *Miner. Deposita,* **41**, (2006), 127-151.

Coplen, T.B., Kolesar, P.: Part A: Geochemistry, *Proceedings* Conference on Research for the Development of Geothermal Energy Resources, Sept. 23 - 25, Pasadena, California, (1974), 46-60.

Craig, H.: Isotopic Composition and Origin of the Red Sea and Salton Sea Geothermal Brines, *Science*, **154**, (1966), 1544-1548.

Craig, H.: The isotopic geochemistry of water and carbon in geothermal area, Tongiorgi E. (Ed.) Nuclear Geology on Geothermal Areas. Spoleto, Consiglio Nazionale delle Ricerche, Laboratorio di Geologia Nucleare, Pisa (1963), 17-53.

D'Amore, F., and Bolognesi, L.: Isotopic evidence for a magmatic contribution to fluids of the geothermal systems of Larderello, Italy, and The Geysers, California, *Geothermics*, **23**, (1994), 21-32.

Davis, S.N., Whittemore, D.O., and Fabryka-Martin, J.: Uses of Chloride/Bromide Ratios in Studies of Potable Water, *Ground Water*, **36,** (2005), 338 – 350.

de Boer, J.: Paleomagnetism of the Quaternary Cerro Prieto, Crater Elegante, and Salton Buttes volcanic domes in the northern part of the Gulf of California rhombochasm, *Proceedings*, 2^{nd} Symp. Cerro Prieto Geothermal Field, Baja California, Mexico (1980), 91-102.

Deyhle, A., Kopf, A., Frape, S., and Hesse, R.: Evidence for fluid flow in the Japan Trench forearc using isotope geochemistry (Cl, Sr, B): Results from ODP Site 1150, *Island Arc*, **13**, (2004), 258-270.

Doe, B.R., Hedge, C.E., and White, D.E.: Preliminary investigation of the source of lead and strontium in deep geothermal brines underlying the Salton Sea geothermal area, *Economic Geology*, **61**, (1966), 462-483.

Donahue, D. J., Linick, T.W., and Jull, A. J. T.: Isotope ratio and background corrections for accelerator mass spectrometry radio carbon measurements, *Radiocarbon*, **32**, (1990), 135-142.

Fergusson, G.J, and Knox, F.B.: The possibilities of natural radiocarbon as a ground water tracer in thermal areas, *N.Z. J. Sci*., **2**, (1959), 431-441.

Giggenbach, W.: Isotopic shifts in water from geothermal and volcanic systems along convergent plate boundaries and their origin, *Earth Planet. Sci. Lett*., **113**, (1992), 495-510.

Gross, E.L., Patchett, P.J., Dallegge, T.A., and Spencer, J.E.: The Colorado river system and Neogene sedimentary formations along its course: Apparent Sr isotopic connections, *The Journal of Geology*, **109**, (2001), 449-461.

Henley, R.W., Truesdell, A.H., Barton, P.B., and Whitney, J.A.: Fluids-mineral equilibria in hydrothermal systems, Reviews in Economic Geology, Vol 1. Society of Economic Geologists, (1984), 267 pp.

Huang, K. F., You, C.F., Shen, M.L., and Lin, H.L.: Geochemistry of major constituents, boron and boron isotopes in pore waters from ODP Site 1202, Okinawa Trough, Terr. *Atmos. Ocean. Sci*., **16**, (2005), 75-93.

Kasameyer, P. W., Younker, L. W. and Hanson, J.M.: Development and application of a hydrothermal model for the Salton Sea geothermal field, California, *GSA Bull*., **95**, (1984), 1242-1252.

Leeman, W. P., Vocke, R. D., and McKibben, M. A.: Boron isotopic fractionation between coexisting vapor and liquid in natural geothermal systems, *Proceedings,* 7th International Symposium on Water-Rock Interaction (eds. Y. K. Kharaka and A. S. Maest) WRI-7, Balkema, Rotterdam (1992), 1007–1010.

Li, H.-C., Lu, X.-M., Ku, T.-L., You, C.-F., Buchheim, H.P., and Peters, R.: Isotopic and geochemical evidence of palaeoclimate changes in Salton Basin, California, during the past 20 kyr: 1.δ^{18}O and δ^{13}C records in lake tufa deposits, *Palaeogeography, Palaeoclimatology, Palaeoecology,* **259**, (2008): 182-197.

Liebscher, A., Meixner, A., Romer, R.L., and Heinrich, W.: Liquid-vapor fractionation of boron and boron isotopes: Experimental calibration at 400°C/23 MPa to 450°C/42 MPa, *Geochim. Cosmochim. Acta*, **69**, (2005): 5693–5704.

Lippmann, M., Truesdell, A., and Frye, G., 1999. The Cerro Prieto and Salton Sea geothermal fluids – are they really alike? *Proceedings,* 24th Workshop on Geothermal Reservoir Engineering, Stanford University, Stanford, CA (1999).

McArthur, J.M., Howarth, R.J., and Bailey, T.R.: Strontium isotope stratigraphy: LOWESS version 3: Best fit to the marine Sr-isotope curve for 0-509 Ma and accompanying look-up table for deriving numerical age, *The Journal of Geology*, **109**, (2001), 155-70.

McKibben, M.A., Williams, A.E., and Okubo, S.: Metamorphosed Plio-Pleistocene evaporites and the origins of hypersaline brines in the Salton Sea geothermal system, California: Fluid inclusion evidence, *Geochim. Cosmochim. Acta*, **52**, (1988), 1047-1056.

Metcalfe, S.E., O’Hara, S.L., Caballero, M., and Davies, S.J.: Records of Late Pleistocene–Holocene climate change in México – a review, *Quat. Sci. Rev.,* **19**, (2000), 699–721.

Ortega-Ramírez, J.R., Valiente-Banuet, A., Urrutia-Fucugauchi, J., Mortera-Gutiérrez, C.A., and Alvarado-Valdez, G.: Paleoclimatic changes during the late Pleistocene–Holocene in Laguna Babícora, near the Chihuahuan Desert, Mexico, *Can. J. Earth Sci*., **35**, (1998), 1168–1179.

Palmer, M. R., and Swihart, G.H.: Boron isotope geochemistry: An overview, In: Grew, E. S. and L. M. Anovitz, (eds). Boron. Mineralogy, Petrology, and Geochemistry. *Mineral. Soc. Am., Rev. Mineral.*, **33**, (1996), 709-744.

Phillips, F.M., Peeters, L.A., Tansey, M.K., and Davis, S.N.: Paleoclimatic inferences from an isotopic investigation of groundwater in the central San Juan Basin, New Mexico, *Quaternary Research*, **26**, (1986), 179-193.

Portugal, E., Izquierdo, G., Barragán, R.M., and de León, J.V.: Reservoir processes inferred by geochemical, stable isotopes and gas equilibria data in Cerro Prieto, BC. México, *Proceedings,* World Geothermal Congress, Antalya, Turkey (2005).

Portugal, E., Birkle, P., Barragán, R.M., Arellano, V.M., Tello, E., and Tello, M.: Hydrochemical-isotopical and hydrogeological conceptual model of the Las Tres Vírgenes geothermal field, Baja California, Mexico, J. Volcanol. Geotherm. Res., 101, (2000), 223-244.

Roy, P. D., Ortega, B., Caballero, M., Lozano, R., and Pi, T.: Paleoclimatic changes between ca.2 and 27 ka cal BP derived from lacustrine sediments of Laguna San Felipe, Sonoran Desert, NW Mexico, AGU Meeting, Acapulco, Mexico, Abstract - Paleoceanography and Paleoclimatology Session (2007).

Saunders, A.D., Rogers, G., Marriner, G.F., Terrell, D.J., and Verma, S.P.: Geochemistry of Cenozoic volcanic rocks, Baja California, Mexico: Implications for the petrogenesis of post-subduction magmas, J. Volcanol. Geotherm. Res., 32, (1987), 223-245.

Schmitt, A.K., and Simon, J.I.: Boron isotopic variations in hydrous rhyolitic melts: A case study from Long Valley, California, *Contrib. Mineral. Petrol*., **146**, (2004), 590-605.

Stuiver, M., and Polach, H.A. Discussion: Reporting of 14C Data, *Radiocarbon,* **19** (1977), 355-363.

Truesdell, A.H., Thompson, J.M., Coplen, T.B., Nehring, N.L., and Janik, C.J.: The origin of the Cerro Prieto geothermal brine, *Geothermics*, **10**,(1981), 225-238.

Unterweger, M.P., Coursey, B.M., Shima, F.J., and Mann, W.B.: Preparation and calibration of the 1978 National Bureau of Standards tritiated water standards, *International Journal of Applied Radiation and Isotopes*, **31**, (1980), 611-614.

Vargas, L.H.: Estudio geohidrológico de Las Tres Vírgenes, B.C.S. Comisión Federal de Eléctricidad, Gerencia de Proyectos Geotermoeléctricos, Morelia, Internal report 14/88, (1988), 62 pp.

Verma, S.P., Pandarinath, K., Santoyo, E., González-Partida E., Torres-Alvarado I.S., Tello-Hinojosa E.: Fluid chemistry and temperatures prior to exploitation at the Las Tres Vírgenes geothermal field, Mexico, *Geothermics*, **35** (2006), 156-180.

Viggiano-Guerra, J.C., Sandoval-Medina, F., Flores-Armenta, M.C., Pérez, R.J., and González-Partida E., Aplicación del SPCALC en la especiación química y termodinámica de fluidos: ejemplo del caso de los pozos LV-4A, LV-11 y LV-13, de Las Tres Vírgenes, BCS, *Geotermia*, **22**, (2009), 12-27.

Weaver, C. E.: Clays, Muds, and Shales. Development in Sedimentol. 44, Elsevier (1989).

White, D. E.: Environments of generation of some basemetal ore deposits, *Econ. Geol*., **63**, (1968), 301-335.

Williams, L. B., Hervig, R.L., Holloway, J.R., and Hutcheon, I.: Boron isotope geochemistry during diagenesis. Part I. Experimental determination of fractionation during illization of smectite, *Geochim. Cosmochim. Acta*, **65**, (2001), 1769-1782.

You, C. F., Spivack, A.J., Smith, J.H., and Gieskes, J.M.: Mobilization of boron at convergent margins: Inplication for boron geochemical cycles, *Geology*, **21**, (1993a), 207-210.

You, C. F., Gieskes, J.M., Chen, R.F., Spivack, A.J., and Gamo, T.: Iodide, bromide, manganese, boron, and dissolved organic carbon in interstitial of organic carbon-rich marine sediments: Observations in Nankai accretionary prism, *Proceedings, ODP, Init. Reports*, **131**, (1993b), 165-174.