

Origin and evolution of geothermal fluids from Las Tres Vírgenes and Cerro Prieto fields, Mexico – Co-genetic volcanic activity and paleoclimatic constraints



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ABSTRACT

Major and trace elements, noble gases, and stable (δD , $\delta^{18}O$) and cosmogenic (3H , ^{14}C) isotopes were measured from geothermal fluids in two adjacent geothermal areas in NW-Mexico, Las Tres Vírgenes (LTV) and Cerro Prieto (CP). The goal is to trace the origin of reservoir fluids and to place paleoclimate and structural–volcanic constraints in the region. Measured $^3He/^4He$ (R) ratios normalized to the atmospheric value ($R_a = 1.386 \times 10^{-6}$) vary between 2.73 and 4.77 and are compatible with mixing between a mantle component varying between 42 and 77% of mantle helium and a crustal, radiogenic He component with contributions varying between 23% and 58%. Apparent U–Th/ 4He ages for CP fluids (0.7–7 Ma) suggest the presence of a sustained 4He flux from a granitic basement or from mixing with connate brines, deposited during the Colorado River delta formation (1.5–3 Ma). Radiogenic *in situ* 4He production age modeling at LTV, combined with the presence of radiogenic carbon (1.89 ± 0.11 pmC – 35.61 ± 0.28 pmC) and the absence of tritium strongly suggest the Quaternary infiltration of meteoric water into the LTV geothermal reservoir, ranging between 4 and 31 ka BP. The present geochemical heterogeneity of LTV fluids can be reconstructed by mixing Late Pleistocene – Early Holocene meteoric water (58–75%) with a fossil seawater component (25–42%), as evidenced by Br/Cl and stable isotope trends. CP geothermal water is composed of infiltrated Colorado River water with a minor impact by halite dissolution, whereas a vapor-dominated sample is composed of Colorado River water and vapor from deeper levels. δD values for the LTV meteoric end-member, which are 20‰–44‰ depleted with respect to present-day precipitation, as well as calculated annual paleotemperatures 6.9–13.6 °C lower than present average temperatures in Baja California point to the presence of humid and cooler climatic conditions in the Baja California peninsula during the final stage of the Last Glacial Pluvial period. Quaternary recharge of the LTV geothermal reservoir is related to elevated precipitation rates during cooler-humid climate intervals in the Late Pleistocene and Early Holocene. The probable replacement of connate water or pore fluids by infiltrating surface water might have been triggered by enhanced fracture and fault permeability through contemporaneous tectonic–volcanic activity in the Las Tres Vírgenes region. Fast hydrothermal alteration processes caused a secondary, positive $\delta^{18}O$ -shift from 4‰ to 6‰ for LTV and from 2‰ to 4‰ for CP geothermal fluids since the Late Glacial infiltration.

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1. Introduction

The Las Tres Vírgenes geothermal field (LTV) is a liquid-dominated reservoir located in the central part of the Baja California peninsula, in northwestern Mexico (Fig. 1). Geothermal exploitation and electricity generation started in 1986 and 2001, respectively, with a current power capacity of 10 MWe from nine

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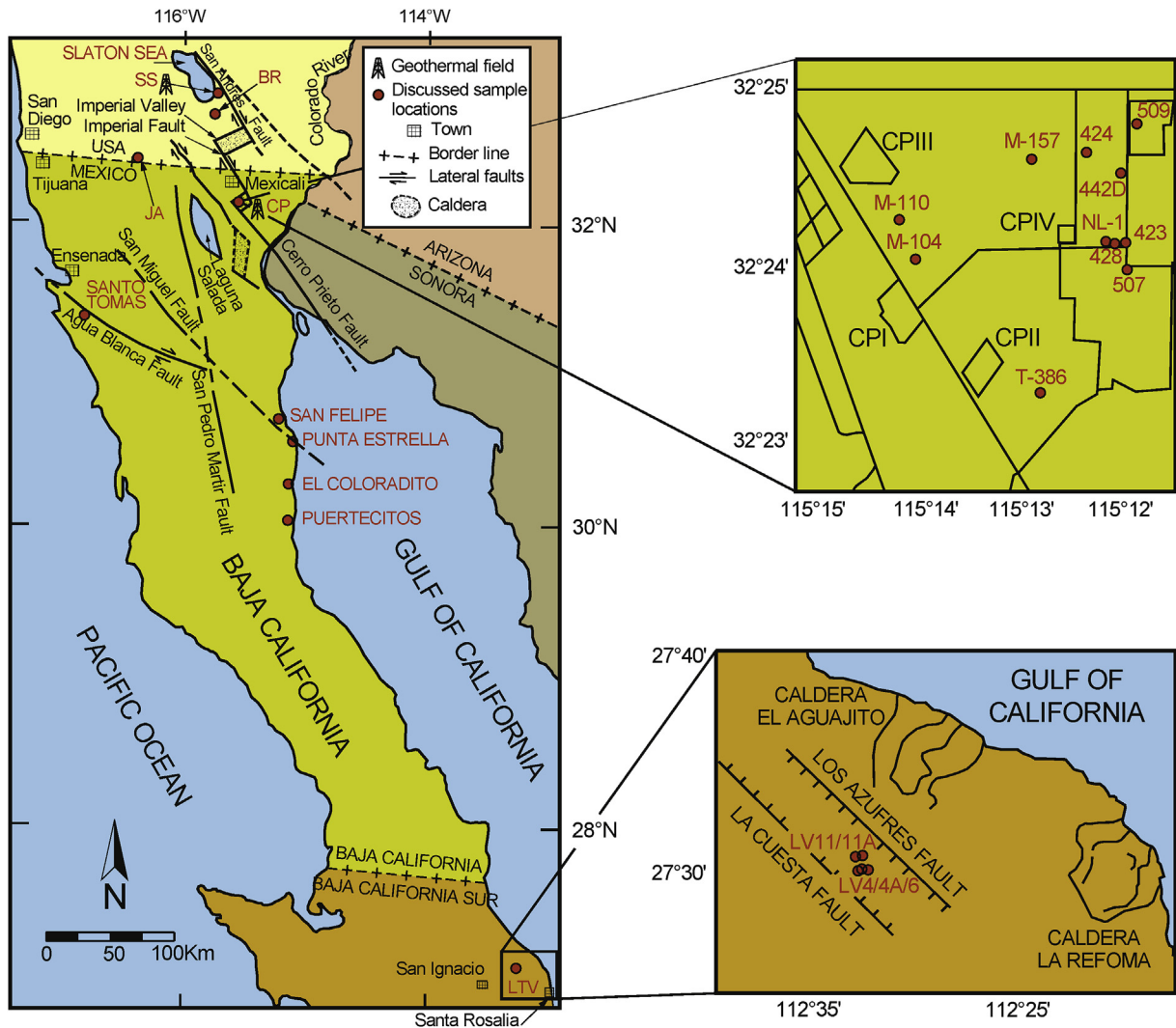


Fig. 1. Location of sampled and described wells from Las Tres Virgenes (Baja California Sur BCS, Mexico) and Cerro Prieto (Baja California, BC, Mexico) geothermal fields, Salton Sea (California, USA), thermal springs from Baja California (San Felipe, Punta Estrella, El Coloradito, Puertecitos), shallow groundwater wells (Santo Tomás, BC), and precipitation stations in southern California (Jacumba, Brawley).

geothermal wells. The extreme aridity in this region, with annual rainfall of 62.3 mm in the valleys and plains (Vargas, 1988; CFE, 1993), and maximum annual precipitation of 150 mm in the adjacent La Virgen and El Azufre volcanoes rises concerns about the long-term sustainability of electricity production and recharge conditions of the LTV geothermal reservoir. Indeed, the occurrence of modern recharge is unlikely due to present-day arid climatic conditions. Hydrochemical investigations on LTV geothermal waters are scarce. Based on chemical and stable isotope analyses, Portugal et al. (2000) concluded that LTV recharge by meteoric water during glacial periods and possible mixing with magmatic fluids took place. Based on measured Na/Cl ratios, Verma et al. (2006) suggested that significant recharge by seawater intrusion from the Gulf of California occurred, although no active recharge path of seawater to the geothermal system has been identified.

Thermal brines from the Cerro Prieto (CP) geothermal field in the northern part of the Baja California state (Fig. 1) were interpreted to originate from coastal lagoons similar to modern sabkhas by seawater evaporation, with salinities about six times that of seawater. Some of these brines migrated to the bottom of the

sediments in the southern part of the Salton Trough. The opening of the pull-apart basin caused their upward migration and mixing with Colorado River waters, leading to the saturation of overlying sediments (Truesdell et al., 1981). After 40 years of power production, declines of reservoir fluid pressure have resulted in the decommissioning of four turbines and the reduction of the installed capacity from 770 MWe to 570 MWe in 2011 (Miranda-Herrera, 2015).

Based on ^{14}C and ^3H data, Truesdell et al. (1979) reported local recharge ages varying between 50 and 10,000 years, adjacent to the western portion of the CP field. Nearly identical Cl/Br weight ratios (297 ± 5) for both seawater and CP geothermal brines support a seawater origin for the latter (Lippmann et al., 1999).

Formation of hypersaline Salton Sea (SS) brines in southern California (U.S.A.) is thought to result from a similar mechanism to that of CP brines except that SS brines originated from evaporated Colorado River water in closed basin lakes as opposed to that of seawater (White, 1981; Rex, 1985). The infiltrating water dissolved magnesium potassium salts that had been formed in the former seawater estuary area of the Salton depression. Subsequent

dolomitization converted most of the Mg content into Ca in the fluid phase. The 1420 Cl/Br measured ratio in the SS geothermal brines is similar to that of Colorado River waters downstream the Hoover Dam (1500–1900; Rex, 1972), suggesting a continental origin for the SS geothermal brines.

Here, we combine new data on Br/Cl ratios, stable (δD , $\delta^{18}O$) and cosmogenic (3H , ^{14}C) isotopes from geothermal waters with noble gas isotopic ratios and 4He , ^{20}Ne , ^{36}Ar , ^{84}Kr and ^{132}Xe gas abundances to identify the primary source of these geothermal fluids and to reconstruct their evolution. Calculated ^{14}C , U–Th/ 4He ages as well as a fluid-mixing model are also used to derive paleoclimatic information within a volcanic-structural context. New chemical and isotopic data from two sampling campaigns in 2006 (LTV, CP) and 2011 (LTV) is presented and compared with previously published analytical information from Las Tres Vírgenes (Portugal et al., 2000), Cerro Prieto (Truesdell et al., 1981), and from the adjacent Salton Sea geothermal system (Williams and McKibben, 1989). This study represents a novel approach to compare affinities of geothermal fluids from different reservoir types in northwestern Mexico and southern California, despite their distinct geological-tectonic settings. While the LTV system forms part of a hydrothermal regime developed in a post-subduction volcanic zone, the CP and SS reservoirs are part of a “pull-apart” extensional sedimentary basin with subsequent magmatic intrusions. The present work will also place new constraints on the sustainability of future geothermal exploitation and electricity production in the LTV and CP reservoirs.

2. Methodology

2.1. Well selection

The geothermal fields of Las Tres Vírgenes and Cerro Prieto produce currently from four and 147 production wells, respectively. The latter is a liquid-dominated system with more than 30.5 million produced tons of steam annually. Although representing an extensive aquifer, exploitation has caused significant changes in flow dynamics throughout the production area. Boiling processes, cold-water entry from surface sources, and mixing with evaporated brine previously re-injected, have been identified by Portugal et al. (2002), Truesdell et al. (1995), Lippmann et al. (1991) and Stallard et al. (1987). The most productive zone is located close to the identified thermal recharge zone (Lippman et al., 1991; Halfman et al., 1984). Taking into account potential alteration of sampled fluids by changes in flow dynamics, individual wells for the present study were selected from recent drilling projects from the deepest reservoir zones, where chemical and stable isotopic fingerprints suggest sampling of pristine, unaltered hydrothermal fluids under undisturbed conditions. In Cerro Prieto, sampled wells were selected close to the CP-IV zone (Fig. 1), an area which has been developed more recently with exploitation starting around mid-2000. Samples from CP-410, CP-423, CP-434, CP-445D wells are vapor-dominant, unaltered during time. Damages of surface infrastructure caused by low vapor pH (≤ 5.5 – 5.6) led to a change in exploiting from deeper to shallower production intervals. The area around well CP-507 is mainly fed by primary vapor, separated from a deep fluid source. Lippmann et al. (2000) and others related the observed fluid migration to the vicinity with Fault H, responsible for the upflow of deep recharge hot fluids and for the downflow of colder groundwaters from aquifers located above the producing formations. CP-507 fluids were sampled mainly for noble gases to define the vapor sources. In contrast, sampled fluids from well CP-509 are considered to be representative of formation water from a deep aquifer system.

2.2. Sampling and analytical procedures

In July 2006 water samples were collected in weir boxes from production wells LV-4 and LV-11, respectively, for analysis of major and trace elements as well as 3H , $\delta^{13}C$, ^{14}C (cf. Table 2), δD , $\delta^{18}O$ (cf. Table 1), and $^{87}Sr/^{86}Sr$. In September 2008, 15 water samples were collected from Cerro Prieto geothermal production wells and analyzed for major elements and oxygen and hydrogen stable isotopic composition ($\delta^{18}O$ and δD). From these, results of eight representative samples from wells with a homogeneous chemical record are included here (Table 1; M-104, M-110, M-157, N-L1, T-386, CP-423, CP-424-D, CP-428). In May 2011, five additional water samples were collected, three from LTV (LV-4A, LV-6, LV-11) and two from CP (CP-507, CP-509) production wells and analyzed for 3H , $\delta^{13}C$, ^{14}C (Table 2), δ^2H , and $\delta^{18}O$ (both in Table 1). Inhibitor fluid, used for stabilization of the production process, was chemically and isotopically fingerprinted (cf. Tables 1 and 2) for reference.

Water samples for chemical analysis were stored in HDPE bottles, pre-filtered with 0.45 μm Millipore filters, acidified with HNO₃-Suprapur, and analyzed by ACTLABS, Ontario, Canada, using ICP-MS, ICP-OES and IC-techniques. Measured data was recalculated to reservoir concentrations using the heat and mass balance equation from Henley et al. (1984) to correct for the effect of steam removal during separation and sample collection.

As ebullition causes an enthalpy excess in the reservoir, the vapor fraction has to be numerically recalculated under separator and reservoir conditions, this for both chemical composition and stable isotopes. The balance equation to calculate compounds for both all-liquid and excess steam reservoir fluids is as follows (Truesdell et al., 1998):

$$X_{RW} = X_{SW} \cdot (1 - V_{SEP}) / (1 - IVF_{RES}) \quad (1)$$

$$IVF = (H_{TF} - H_{WIL}) / (H_{WIV} - H_{WIL}) \quad (2)$$

$$V_{SEP} = (H_{TF} - H_{WSEP}) / (H_{VSEP} - H_{WSEP}) \quad (3)$$

where X_{RW} and X_{SW} are the compounds in the reservoir water and separated water, respectively. The steam mass fraction (IVF) depends on the correlation between the enthalpies of the total fluid (production enthalpy H_{TF}), the liquid at the well inlet (H_{WIL}), and the vapor at the well inlet (H_{WIV}). IVF is a measure of vapor saturation or the amount of ebullition in the reservoir liquid which causes enthalpy excess in the surface discharge. The fraction of separated vapor (V_{SEP}) is correlated to the enthalpy for vapor (H_{VSEP}) and liquid (H_{WSEP}). Reservoir temperature are normally derived from cationic geothermometer (Na–K–Ca; Fournier and Truesdell, 1973), and used to calculate the reservoir enthalpy (H_{WIL}).

Reported ^{18}O and 2H isotopic data from separated vapor at the surface was recalculated to reservoir conditions, with isotopic fractionation coefficients published by Horita and Wesolowski (1994) as follows (Hoefs, 1980).

$$\delta_m = y\delta_v + (1 - y)\delta_l, \quad (4)$$

$$10^3 \ln \alpha_{l-v} \cong \delta_l - \delta_v \quad (5)$$

For carbon isotope analysis, all samples were condensed by a double coil and cooled down to 4 °C. The condensate was directed into a cylindrical container, which is isolated from the atmosphere through a valve, while a second valve allows for sample collection into a vacuum borosilicate bottle. ^{13}C and ^{14}C contents of water and gas samples were measured through AMS at the NSF-Arizona AMS Laboratory, University of Arizona, Tucson, U.S.A., with % modern as

Table 1
Stable isotope composition of reservoir fluids from the Las Tres Virgenes, Cerro Prieto and Salton Sea geothermal reservoirs.

Well sample	Sampling date [dd/mm/yyyy]	$\delta^{18}\text{O}$ [‰]	$\delta^2\text{H}$ [‰]	References	Well sample	Sampling date [dd/mm/yyyy]	$\delta^{18}\text{O}$ [‰]	$\delta^2\text{H}$ [‰]	References
Las Tres Virgenes:					Cerro Prieto:				
LV-1	13/06/1997	-2.3	-52.0	Portugal et al. (2000)	M-35	*	-8.9 ^b	-95.2 ^b	Truesdell et al. (1981)
LV-4	13/06/1997	-3.3	-53.0	Portugal et al. (2000)	M-42	*	-8.8 ^b	-94.8 ^b	Truesdell et al. (1981)
LV-4	28/07/2006	-3.9	-57.1	This paper	M-104	15/09/2008	-9.2 ^a	-95.6 ^a	This paper
LV-4A	30/05/2011	-2.9	-53.1	This paper	M-110	15/09/2008	-8.0 ^a	-88.1 ^a	This paper
LV-5	28/02/1998	-3.7	-59.0	Portugal et al. (2000)	M-157	15/09/2008	-8.6 ^a	-97.5 ^a	This paper
LV-6	30/05/2011	-2.8	-53.2	This paper	N-L1	15/09/2008	-9.9 ^a	-97.5 ^a	This paper
LV-11	28/07/2006	-4.0	-59.2	This paper	T-386	16/09/2008	-8.7 ^a	-94.6 ^a	This paper
LV-11	30/05/2011	-2.6	-52.4	This paper	CP-423	30/09/2008	-8.8 ^a	-94.5 ^a	This paper
Inhibitor	30/05/2011	-8.7	-62.5	This paper	CP-424-D	10-01-2008	-9.2 ^a	-97.4 ^a	This paper
Cerro Prieto:					Salton Sea:				
M-5	*	-8.3 ^b	-95.5 ^b	Truesdell et al. (1981)	SSSDP well 2-14	1988	2.0 (2.6)	-70 (-72)	Williams and McKibben (1989)
M-8	*	-9.4 ^b	-96.6 ^b	Truesdell et al. (1981)	Commercial well#11b	1989 (?)	1.6	-70.0	Williams and McKibben (1989)
M-11	*	-8.3 ^b	-93.9 ^b	Truesdell et al. (1981)	Commercial well#10	1989 (?)	1.1	-70.0	Williams and McKibben (1989)
M-14	*	-9.2 ^b	-96.9 ^b	Truesdell et al. (1981)	Commercial well #B1	1989 (?)	-0.6	-81.0	Williams and McKibben (1989)
M-19A	*	-8.3 ^b	-94.5 ^b	Truesdell et al. (1981)	Dear.#2	1989 (?)	-3.7	-88.5	Williams and McKibben (1989)
M-20	*	-9.5 ^b	-97.0 ^b	Truesdell et al. (1981)	Land.#3	1989 (?)	-1.5	-86.0	Williams and McKibben (1989)
M-21A	*	-8.4 ^b	-96.1 ^b	Truesdell et al. (1981)	Kalin#1	1989 (?)	-3.6	-81.5	Williams and McKibben (1989)
M-25	*	-8.3 ^b	-95.1 ^b	Truesdell et al. (1981)	Land.#2	1989 (?)	2.2	-83.0	Williams and McKibben (1989)
M-26	*	-10.9 ^b	-98.5 ^b	Truesdell et al. (1981)	Land.#1	1989 (?)	3.4	-85.5	Williams and McKibben (1989)
M-27	*	-9.7 ^b	-97.6 ^b	Truesdell et al. (1981)	CW# 112	1989 (?)	1.9	-57.5	Williams and McKibben (1989)
M-29	*	-9.1 ^b	-96.3 ^b	Truesdell et al. (1981)					
M-30	*	-8.7 ^b	-95.3 ^b	Truesdell et al. (1981)					
M-31	*	-9.4 ^b	-97.9 ^b	Truesdell et al. (1981)					

^aTotal discharge.

^bReservoir conditions.

*Samples taken from 1976 to 1977.

Table 2
Concentration of cosmogenic (^3H , ^{14}C) and stable isotopes ($\delta^{13}\text{C}$), with calculated Conventional Radiocarbon Ages (CRA) for the multi-component mixture of geothermal water* maximum depth; n.a. not analyzed.

Sample	Depth [m]	TDS [mg/L]	Date [dd/mm/yy]	pH	^3H [T.U.]	^3H [yr BP]	$\delta^{13}\text{C}$	^{14}C – total fluid [pmC]	^{14}C – total fluid [CRA] [yr BP]
LV-4	2413*	9550	28/07/06	7.4	0.04 ± 0.10	>60	-7.3	19.8 ± 0.17	13,009 ± 69
LV-4A	1332–2101	11,700	30/05/11	7.4	0.18 ± 0.06	>60	-8.0	1.86 ± 0.11	32,008 ± 462
LV-6	1247–2500	14,700	30/05/11	7.3	0.21 ± 0.05	>60	-7.6	13.40 ± 0.48	16,146 ± 283
LV-11	1974*	12,200	28/07/06	7.4	0.15 ± 0.10	>60	-9.4	35.61 ± 0.28	8294 ± 63
LV-11	1974*	15,300	30/05/11	7.4	0.16 ± 0.05	>60	-8.9	18.80 ± 0.13	13,426 ± 55
Inhibitor	Surface	18,700	30/05/11	n.a.	0.81 ± 0.06	<20	n.a.	n.a.	n.a.
CP-507	2400–2750	355	22/05/11	6.1	0.03 ± 0.05	>60	-8.5	30.93 ± 0.63	9426 ± 162
CP-509	2395–2650	25,700	23/05/11	7.0	0.06 ± 0.05	>60	-0.7	19.04 ± 0.33	13,324 ± 138

defined by Stuiver and Polach (1977). Low standard deviations between 0.17 and 0.28% of modern carbon (pmC) for the analyzed water samples reflect the negligible analytical error of the ^{14}C technique. Measured ^{14}C -ratios of standards and samples were corrected to values corresponding to $\delta^{13}\text{C} = -25\text{‰}$, as described in Donahue et al. (1990).

The Dissolved and Noble Gas Laboratory at the University of Utah (Salt Lake City, USA) conducted tritium measurements using the in-growth of ^3He method with a detection limit of 0.1 TU. The $\delta^{18}\text{O}$ and δD 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.

Noble gas concentrations (He, Ne, Ar, Kr, Xe) and isotopic ratios were measured in 5 gas samples collected from geothermal wells in May 2011, three from Las Tres Virgenes (LV-4A, LV6 and LV-11, the latter in duplicate) and three from Cerro Prieto (CP-507, CP-509, CP-442D) during the May 2011 campaign. Gas samples were collected directly from the geothermal wells in standard refrigeration grade 3/8" Cu tubes (14 mL) sealed with stainless steel pinch-off clamps after gas flowed through for several minutes (Pinti et al., 2013). Noble gases were measured at the Noble Gas Laboratory at the University of Michigan using a MAP-215 mass spectrometer.

Isotopic abundances for each sample were normalized to a calibrated amount of air standard after blank correction. Elemental abundances of ^4He , ^{22}Ne , ^{36}Ar , ^{84}Kr , and ^{132}Xe have typical uncertainties of 1.5%, 1.3%, 1.3%, 1.5%, and 2.2%, respectively, with uncertainties reported at $\pm 1\sigma$ level. Details on analytical procedures are given elsewhere (Ma et al., 2009; Pinti et al., 2013).

2.3. Uncertainty and validation of analytical methods

Air-free water samples were collected from weir boxes, which is a standard sampling procedure for ^3H and ^{14}C analysis of brines, as described in Lico et al. (1982), Watson (1978), and Ellis et al. (1968). Atmospheric contamination through weir boxes is minimal, as the large fluid discharge allows filling up of HDPE sample bottles within several seconds without leaving air bubbles in the bottleneck. Prior to the weirbox, overpressure conditions of rising vapor and fluids do not allow the inflow of any atmospheric components into the separator system. For the most part, due to extreme temperature and pressure conditions in geothermal reservoirs, weir box sampling at the well-head is the only feasible and standard sampling method for geothermal fluids. Due to the common installation of extended, uncased well sections in geothermal reservoir pay-zones (i.e., well LTV-4A from a depth of 1332 m to 2101, and well LTV-6

from 1247 m to 2500 m), the provenance of produced fluids cannot be assigned to a specific lithological unit, as water can be derived from multiple horizons.

Due to the use of chemical reagents during drilling and production, sampled fluids from petroleum and geothermal wells are often contaminated. Small volumes (few liters) of inhibitor are injected daily in LTV wells during production to prevent scaling. Despite injection of inhibitor in these wells, chemical and isotopic evidence points to negligible contamination of our geothermal fluid samples. In particular:

- Lack of evidence for the recovery of any fraction of injected Na–NO₃–SO₄–K water type, the common inhibitor fluid type used;
- Elevated NO₃ concentrations from inhibitor fluid (4450 mg/L) contrast to measured concentrations in our sampled geothermal water, which is below the detection limit of 1 mg/L.
- Tritium concentrations of geothermal fluids range between 0.16 ± 0.05 to 0.21 ± 0.05 T.U., while surface water, used for the preparation of inhibitor fluid, displays an atmospheric value of 0.81 ± 0.06 T.U. (Table 2);
- Inhibitor fluids, which were used for injection purposes, are isotopically (δD , $\delta^{18}O$) close to the Global Meteoric Water Line (GMWL), in contrast to ¹⁸O-enriched values for geothermal fluids (Fig. 3);
- Inhibitor fluids are considerably enriched in ⁸⁷Sr/⁸⁶Sr ratios (0.70670) with respect to LTV geothermal fluids (0.70432–0.70434);

3. Results

3.1. Chemical evidence for fluid provenance

Fig. 2 shows the Br–Cl trend of the seawater evaporation trajectory (SET) together with the Br–Cl composition of LTV, Salton Sea (SS) and Cerro Prieto (CP) geothermal waters. During seawater evaporation, Br concentrates progressively as an incompatible element in the residual brine (Carpenter, 1978). Seawater evaporation leads to a Br and Cl linear enrichment trend until halite saturation is reached, for Cl ~162,000 mg/L. LTV geothermal water samples are diluted with respect to modern seawater and their alignment with the depleted SET suggests mixing between seawater and a meteoric component.

A similar trend can be observed for Cerro Prieto fluids, but the compositional range of the latter is very heterogeneous from low saline (CP-507: TDS = 355 mg/L) toward close to seawater composition (CP-509: TDS = 25,700 mg/L). A minor degree of halite dissolution, reflected by the aqueous enrichment in Cl with stable Br conditions, is observed for most saline geothermal fluids from the CP reservoir. Elevated Cl concentrations with respect to Br suggest a significant impact on groundwater mineralization by halite dissolution for various sections of the SS reservoir column. Both, hypersaline ($25.6 \leq \text{TDS} \leq 26.5$ wt%) geothermal fluids from the Salton Sea Scientific Drilling Project (SSSDP) well State 2–14 from depths between 1830 and 3220 m (Lippmann et al., 1999; Williams and McKibben, 1989), hypersaline wells (#10, #11B; $20.0 \leq \text{TDS} \leq 21.4$ wt%) and less saline wells (#B1, #3, #113; $1.3 \leq \text{TDS} \leq 6.2$ wt%) from shallower production fluids at depths ranging between 410 and 1070 m (Williams and McKibben, 1989; Muffler and White, 1968) seem to be dominated by saline dissolution processes.

Na/Cl and Cl/Br ratios ranging from 0.51 to 0.57 and from 247 to 343, respectively, for LTV geothermal waters are relatively close to CP geothermal fluid values (Na/Cl = 0.46–0.57, Cl/Br = 302–463) as well as those of seawater composition (Na/Cl = 0.56, Cl/

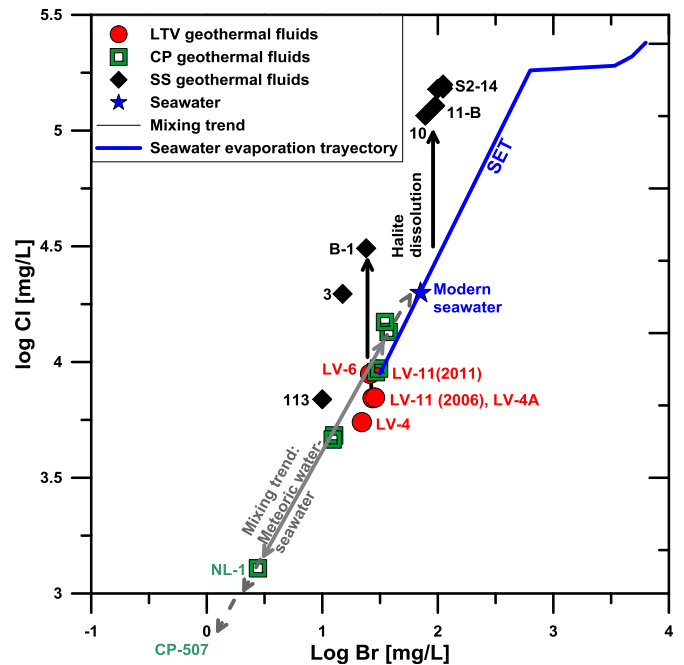


Fig. 2. Log Br–log Cl ratio of geothermal water from the 2006 (LV-4, LV-11) and 2011 sampling campaign in Las Tres Virgenes (LV-4A, LV-6, LV-11), from Cerro Prieto (well M-5 from Truesdell et al., 1981; M-104, M-110, M-157, NL-1, and T-386 from present study) and Salton Sea (SS) geothermal fluids from the well State 2–14 (Williams and McKibben, 1989) and shallower wells B1, 3, 10, B-11, 113 (Williams and McKibben, 1989; Muffler and White, 1968), compared with the evaporation trajectory of seawater (SET).

Br = 288–292; McCaffrey et al., 1987), and suggest a marine origin for the conservative elements in both reservoir fluids. On the other hand, Cl/Br ratios from 50 to 150 for global precipitation and 100 to 200 for shallow groundwater (Davis et al., 1998) are low and relatively close to LTV thermal fluids. Elevated Cl/Br-ratios varying between 1347 and 1525 for high salinity SS fluids are close to those of Colorado River waters (~1600, Coplen and Kolesar, 1974; 1500–1900, Rex, 1972). The latter has been explained by re-dissolution of evaporites in closed basin lakes (White, 1968). Less saline SS fluids with lower Cl/Br ratios (690 for “C.W. #113”) are close to the meteoric water composition. Low saline water from CP-507 with a TDS value of 355 mg/L and a Cl/Br ratio of 2311, close to that of Colorado River water, might be representative of the river water end-member.

3.2. Hydrogen and oxygen isotope trends

3.2.1. Las Tres Virgenes

Stable isotope ratios from LTV (Portugal et al., 2000; this study) geothermal fluids are compared with published isotope data from local cold springs and wells around the LTV site (Portugal et al., 2000), regional groundwater within a latitude range of 27°N to 28°N in BCS (Wassenaar et al., 2009), shallow groundwater from Santo Tomás and Todos Santos in the northwestern part of Baja California (BC) and most southern part of Baja California Sur (BCS), respectively (Eastoe et al., 2015) and thermal springs (San Felipe, Punta Estrella, El Coloradito, Puertecitos) from the eastern part of BC (Barragan et al., 2001) (Table 1, Figs. 1 and 3).

Meteoric water from shallow groundwater and springs from BC and BCS are generally aligned along the Global Meteoric Water Line (GMWL). A latitude-related isotope trend is indicated for Baja California groundwater, from isotopically depleted groundwater in the

southern part of BCS (Todos Santos, Eastoe et al., 2015) toward enriched groundwater in the northwestern part of BC (“Santo Tomás, Eastoe et al., 2015) (Fig. 3).

Depleted isotope ratios in southern Baja California are related to the tropical cyclonic weather system with most precipitation occurring during the hurricane season and a rapid response of groundwater to different precipitation events, such as shown for the Todos Santos watershed (Eastoe et al., 2015). The southward transition from predominant winter + spring to predominant summer + fall precipitation along Baja California is therefore accompanied by a decrease in the $\delta^{18}\text{O}$ and δD values of groundwater and not by typical latitude variations (Eastoe et al., 2015). Shallow groundwater from and close to the LTV area (Portugal et al., 2000; Wassenaar et al., 2009), located between BC and BCS (along the BC-BCS border) displays an intermediate isotopic position between BC and BCS samples.

Exceptions from the general GMWL alignment are Puertecitos spring waters from the coast of the Gulf of California (“PC” in Fig. 3) with enriched $\delta^{18}\text{O}$ and δD values as being primarily composed of seawater (>80 wt%). San Felipe (“SF” in Fig. 3) is additionally affected by secondary leaching of evaporites (Barragán et al., 2001), with similar formation processes and isotopic composition as Salton Sea brines. Strongly depleted isotopic ratios for Valle Chico samples (“VC” in Fig. 3) are related to volcanic steam-heated water. Punta Estrella samples (“PE” in Fig. 3) are described as a mixture of meteoric water with seawater (Barragán et al., 2001), although evaporation of meteoric water best fit the observed deviation from the LMWL. Evaporation is also the likely cause for the slight deviation of Santa Lucía groundwater in the LTV area (“SL” in Fig. 3) from the GMWL.

δD values between -52.0‰ and -59.2‰ for geothermal fluids from the LTV reservoir are within the upper cold groundwater value range in the LTV area, but strongly depleted in comparison to present seawater from the Gulf of California (2.8‰ , Dettman et al., 2004). Enriched $\delta^{18}\text{O}$ ratios with maximum values of -2.3‰ must be related to secondary alteration processes. Below (sections 4.1 and 4.2), we document the evaporation-independent evolution of LTV geothermal fluids by mixing of

two end-member fluids with subsequent hydrothermal alteration. Sample contamination by flowback of injected inhibitors can be excluded, as inhibitor fluids are isotopically depleted ($\delta^{18}\text{O} = -8.7\text{‰}$, $\delta\text{D} = -62.5\text{‰}$) in comparison to LTV geothermal fluids, with an affinity to local meteoric water (Fig. 3, Table 1). The recovery of representative and uncontaminated reservoir fluids is also suggested by the homogeneous isotopic fingerprint for the described water samples during 14 years of continuous production (1997–2011).

3.2.2. Cerro Prieto

$\delta^{18}\text{O}$ and δD data of geothermal water from the Cerro Prieto reservoir are compared with isotopic fingerprints from regional precipitation in the Imperial (Coplen and Kolesar, 1974) and local average rain from the Mexicali Valley (Coplen, 1972), together with precipitation from Jacumba station close to the US-Mexican border (“JA” in Figs. 1 and 4) and Brawley station in the Imperial Valley (“BR” in Figs. 1 and 4) (Friedmann et al., 1992). Samples from present-day precipitation are mostly aligned along the GMWL, but systematically elevated in δD in comparison to CP fluids due to the current arid climatic conditions in southeastern California (Fig. 4). JA and BR summer isotopic signatures are generally enriched in both isotopes with respect to winter signatures, approaching those of Colorado River water undergoing evaporation (see dashed trend in Fig. 4). In addition to seasonal variations, rainfall at lower elevations (i.e., BR at -40 m) appears to be slightly enriched in $\delta^{18}\text{O}$ with respect to higher altitude areas in southern California (i.e., JA with 1280 m). CP fluids are slightly displaced to the right side of the evaporating Colorado river water trend (dashed line in Fig. 4), shown from the lower Colorado River (Lake Mead) toward Salton Sea (Coplen and Kolesar, 1974). With $\delta^{18}\text{O}$ values from -8.0‰ to -10.9‰ , CP fluids are 2‰ – 4‰ enriched in $\delta^{18}\text{O}$ in comparison to average Colorado River water (-12.0‰ ; Dettman et al., 2004) and to river water in the Mexicali Valley (-12.0‰ to -12.3‰ ; Payne et al., 1979).

The alignment of shallow groundwater from the Imperial Valley (Smith et al., 1992) with the evaporating trend suggests that Colorado River water is a major recharge source for shallow aquifer

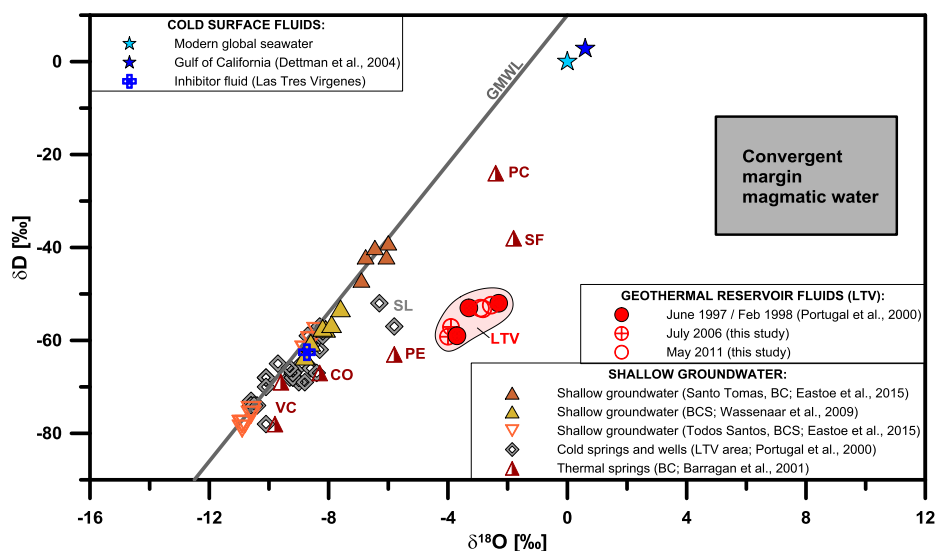


Fig. 3. $\delta^{18}\text{O}$ and δD composition of LTV geothermal fluids from 1997 to 2011 (Portugal et al., 2000; this study) is compared with published isotope data from local cold springs and wells around the LTV site (Portugal et al., 2000), regional groundwater within a latitude range of 27°N to 28°N in BCS (Wassenaar et al., 2009), shallow groundwater from Santo Tomás and Todos Santos in the northwestern part of Baja California (BC) and most southern part of Baja California Sur (BCS), respectively (Eastoe et al., 2015), thermal springs (San Felipe, Punta Estrella, El Coloradito, Puertecitos) from the eastern part of BC (Barragán et al., 2001), as well as global seawater and seawater from the Gulf of California (Dettman et al., 2004). Shaded box shows range of “convergent margin magmatic waters” (D’Amore and Bolognesi, 1994).

systems in the Imperial Valley. The isotopic similarity of CP geothermal fluids with Colorado River water (Dettman et al., 2004; Payne et al., 1979) and shallow groundwaters from the Imperial Valley (Smith et al., 1992) suggests direct infiltration of Colorado River water into the CP reservoir. Distinct isotopic fingerprints for CP fluids in comparison to the GMWL and to seawater from the Gulf of California (Dettman et al., 2004) suggest that infiltration of local meteoric water or seawater is not significant.

High temperatures in the Cerro Prieto reservoir (>325 °C) promote oxygen exchange between water and silicates, leading to a positive isotopic shift of $\delta^{18}\text{O}$ -values in the fluid phase. The narrow and homogeneous range of $\delta^{18}\text{O}$ values (–8.0‰ to –10.9‰) for CP brine samples collected in 1976–1977 (Truesdell et al., 1981), September 2008 and May 2011 (this study) point to a negligible influence of the geothermal extraction and reinjection process on the fluid composition. As observed for the Larderello geothermal field, evaporation of re-injected water would cause large isotopic fractionation at depth (D'Amore et al., 1987).

3.2.3. Salton Sea

The Salton Sea brine is derived from local precipitation followed by leaching of sediments by surface water circulating downward to a geothermal reservoir (Craig, 1966). Salton Sea geothermal brines with hypersaline compositions (TDS = 14.7–26.5 wt%) are derived in part from *in situ* hydrothermal metamorphism and dissolution of halite and CaSO_4 from relatively deeply-buried lacustrine evaporites, with 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 uniform isotopic composition of hypersaline brines, in particular in comparison to low saline Salton Sea fluids, suggests a single, relatively homogeneous source and a uniform alteration process for the waters which

evolved into the saline reservoir brines (Fig. 4). In contrast, the isotopic variety of low-TDS water (1.0–14.0 wt. %) points to evolution of separate water sources (Williams and McKibben, 1989). Alternatively, its heterogeneous positive ^{18}O shift could also be explained by site-specific variations in the level of water-rock interactions, assuming that Colorado River water was the primary water source responsible for the filling of the Salton Sea basin in the past.

Below, we show that the impact of cooler climatic conditions preceding and during the Last Glacial Maximum (LGM), more specifically, between 26,500 and 19,000–20,000 yr BP as well as during the Early Holocene pluvial phases on reservoir recharge are capable of explaining the stable isotopic composition of LTV and CP fluids.

3.3. ^{14}C and ^3H reservoir fluid ages

Due to the tritium short half-life of 12.32 ± 0.02 yrs (Lucas and Unterwieser, 2000) and the release of large amounts of ^3H in the environment during nuclear weapon tests in the 60s', post-bomb tritium (^3H) can be used to identify the presence of modern recharge. On the other hand, ^{14}C is a better chronometer to estimate the age of paleo- and fossil groundwater up to ~40,000 years, due to its longer half-life of 5730 years.

Measured tritium values ranging from 0.04 ± 0.10 T.U. to 0.21 ± 0.05 T.U. and from 0.03 ± 0.05 T.U. to 0.06 ± 0.05 T.U. in the Las Tres Vírgenes (LV-4, LV-4A, LV-6, LV-11) and Cerro Prieto reservoir fluids (CP-507, CP-509), respectively, clearly indicate the absence of post-bomb tritiated water ($^3\text{H} > 0.8$ TU; Clark and Fritz, 1997) (Table 2). Thus, modern recharge (<60 years BP) is excluded for both geothermal reservoirs.

Detection of ^{14}C in geothermal fluids is relatively uncommon,

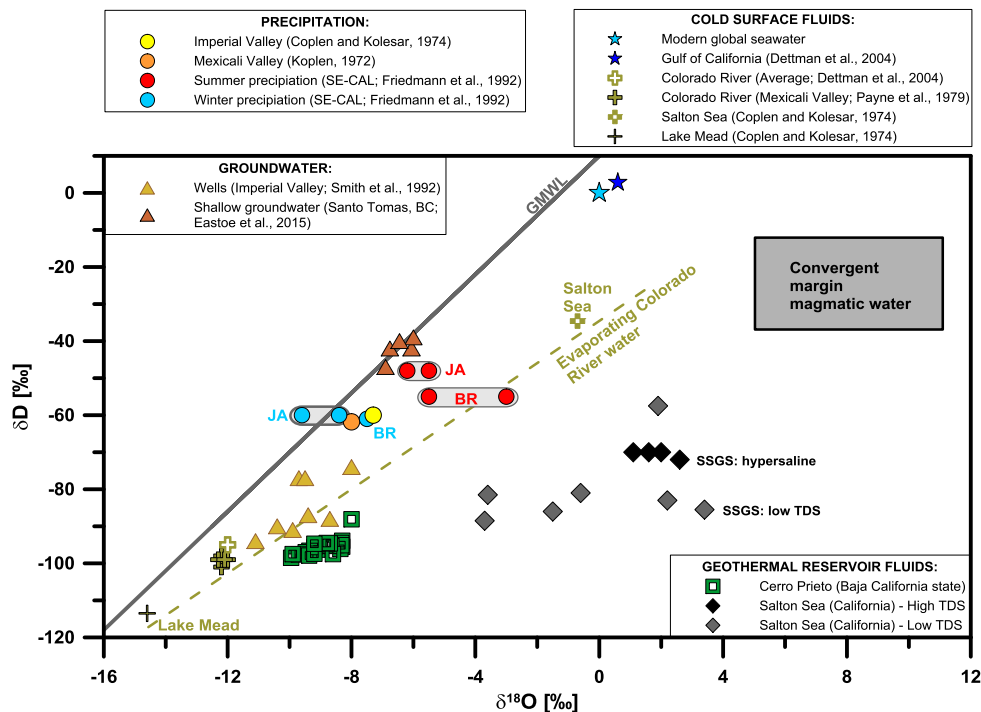


Fig. 4. $\delta^{18}\text{O}$ and δD composition of geothermal fluids from the Cerro Prieto (State of Baja California, September 2008 and May 2011) and Salton Sea geothermal fields (S-California; Williams and McKibben, 1989), compared with present-day precipitation water from the Mexicali Valley (BC; Copen, 1972), Imperial Valley (S-California; Copen and Kolesar, 1974), summer and winter precipitation from Jacumba (JC) and Brawley (BR) stations in Southern California (Friedmann et al., 1992), modern global seawater and seawater from the Gulf of California (Dettman et al., 2004), Lake Mead and Salton Sea water (Copen and Kolesar, 1974), Colorado River water as an average (Dettman et al., 2004) and in the Mexicali Valley (Payne et al., 1979), and shallow groundwater from the Imperial Valley (Smith et al., 1992) and from Santo Tomás in Baja California (Eastoe et al., 2015). Dashed line shows evaporating trend for water from the lower Colorado River (Lake Mead) toward Salton Sea (Copen and Kolesar, 1974). Shaded box shows range "convergent margin magmatic waters" (D'Amore and Bolognesi, 1994).

due to mixing of DOC with ^{14}C -free magmatic or metamorphic CO_2 , which decreases 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), 0.2 pmC for deep well fluids from Wairakei, New Zealand (Fergusson and Knox, 1959), and maximum ^{14}C activities of 1.7 ± 0.6 pmC for fluids from the Los Azufres geothermal field (Birkle et al., 2001). Marques et al. (2003) determined an apparent ^{14}C groundwater age of 15.66 ± 2.86 ka BP for deep thermal groundwater at the Caldas do Moledo geothermal site in northern Portugal, with a measured ^{14}C content of 13.97 ± 1.33 pmC and a maximum depth circulation of 1.8 ± 0.4 km. The combined presence of ^3H and ^{14}C in CO_2 -rich mineral waters in the Vialrelo da Raia-Pedras Salgadas region (N-Portugal) indicates that the total C in the recharge waters is being masked by considerable quantities of ^{14}C -free CO_2 from upper mantle sources (Carreira et al., 2008), which could result in overestimated groundwater ages. Geothermal fluids that currently discharge in the Great Basin are of Pleistocene origin, recharged from alluvial fans and ^{14}C concentrations between <0.5 pmC and 8.7 pmC (Flynn and Buchanan, 1990).

Because the water samples for radiocarbon dating were taken using weir boxes at the steam separator, we could suspect an atmospheric CO_2 uptake that increased artificially the ^{14}C content (Aggarwal et al., 2014). However, studies related to groundwater flow in travertines (i.e., in hyper-alkaline environments) (Clark et al., 1992) and recent laboratory experiments of CO_2 uptake (Aggarwal et al., 2014) showed that this process is rapid and important for hyper-alkaline waters with pH of 12 or higher, while sampled geothermal fluids are neutral or slightly acidic (pH from 7.4 to 6.1; Table 2). CO_2 uptake also cause depletion of ^{13}C by kinetic fractionation of atmospheric CO_2 (Clark et al., 1992) while in our samples, except for an elevated $\delta^{13}\text{C}$ value of -0.7‰ (CP-509), all $\delta^{13}\text{C}$ are relatively constant with an average value of $-8.3 \pm 0.8\text{‰}$ (Table 2). If atmospheric CO_2 uptake can be reasonably excluded, then it is possible to correct the measured ^{14}C activities for the dead carbon component (magmatic and metamorphic CO_2) and to calculate fluid residence times in the reservoir. At Cerro Prieto and Salton Sea, the decarbonation of authigenic calcite to form new framework minerals could produce considerable flux of CO_2 (Elders et al., 1981).

Except for one sample showing relatively low ^{14}C activity (LV-4A; 1.86 ± 0.11 pmC) all other samples show high ^{14}C activities for geothermal fluids, ranging from 13.40 ± 0.48 pmC (LV-6) to 35.61 ± 0.28 pmC (LV-11), which can be converted into a Conventional Radiocarbon Age (CRA) between $32,008 \pm 462$ yr BP and 8294 ± 63 years BP (Table 2). These ^{14}C concentrations point to a Late Pleistocene to Early Holocene time period for the LTV geothermal reservoir recharge by surface-derived water. The apparent ^{14}C ages for groundwaters in the Ojo Alamo Sandstone and Nacimiento formation, New Mexico, appeared to be remarkably insensitive to the individual correction procedures (Stute et al., 1995; Phillips et al., 1989). In case of LTV fluids, the mixing of different fluid types, as evidenced by chemical and stable isotope trends, is the dominant process to correct apparent ^{14}C ages (c.f. Section 4.2.). Enhanced correction methods of apparent ^{14}C ages for LTV fluids are very speculative due the uncertainties of host rock and basement characteristics with respect to $\delta^{13}\text{C}$ of rock carbonate or deep-derived CO_2 .

Cerro Prieto fluids from wells CP-507 and CP-509 display a smaller range of calculated residence times of 9426 ± 162 yr BP for produced vapor from CP-507 and $13,324 \pm 138$ yr BP for formation water from CP-509 (with an assumed Early Holocene atmospheric activity A_{50} of 110 pmC; Clark and Fritz, 1997), as evidenced by ^{14}C concentrations of 30.93 ± 0.63 pmC and 19.04 ± 0.33 pmC, respectively. The occurrence of metamorphic CO_2 and the exchange with old carbonate host rocks might have led to dilution of the

original ^{14}C concentrations by “dead carbon” with an even younger apparent age for the analyzed CP fluids. No ^{14}C data is available for the Salton Sea reservoir.

In subsequent sections, we present chemical and stable isotope evidence including Br/Cl trends, mixing calculations with conservative elements and paleoclimatic conditions that differentiate water types and to strengthen the postulated hypothesis of infiltrating surface water into the LTV and CP geothermal reservoirs during the Late Glacial period.

3.4. CO_2 radiometric dating

One gas sample was taken from each of the LTV (LV-4A, LV-6, LV-11) and CP (CP-442D, CP-507 and CP-509) wells and analyzed for gas chemistry, $\delta^{13}\text{C}$ ratios and ^{14}C abundances (no isotope analysis of CP-442D samples was done). Sampled gases are mainly composed of CO_2 (1665–15,492 mg/kg of vapor), CH_4 (0.60–360.7 mg/kg), H_2 (1.80–117.5 mg/kg) and NH_3 (1.40–27.1 mg/kg) with an overall enrichment of several orders of magnitude in CP samples with respect to LTV gases (Table 3).

^{14}C concentrations range from <0.28 pmC (below detection limit) to maximum values of 0.58 ± 0.10 pmC, which can be recalculated to a minimum ^{14}C residence time of $41,400 \pm 1400$ yr BP. The hypothetical fraction of radiocarbon input by atmospheric recharge seems to be diluted by ascending metamorphic and/or magmatic gases.

3.5. Noble gases

Noble gas abundances are reported in Table 4. Measured water volume inside the copper tubes was far smaller ($<2\text{--}7$ cc) than the volume of the tube itself (14 cc) and thus the samples were treated as “gas samples”. Consequently, ^4He , ^{20}Ne , ^{36}Ar , ^{84}Kr and ^{132}Xe abundances are reported as volume fraction ($\text{cm}^3\text{STP}/\text{cm}^3_{\text{steam}}$; Table 4) using the F-notation. In F-notation, measured abundances are normalized to the air abundance with ^{36}Ar as the reference isotope, i.e. $F(i) = (i/^{36}\text{Ar})_{\text{sample}} / (i/^{36}\text{Ar})_{\text{air}}$ where i represents one of the five analyzed noble gases. F-values are fractionation factors that provide a measure of enrichment or depletion relative to the atmospheric composition and thus they are very useful fingerprints of occurrence of boiling and/or gas depletion in the reservoir (e.g., Mazor and Truesdell, 1984; Pinti et al., 2013).

Figs. 5 and 6 show $F(^{20}\text{Ne})$ vs. (^{132}Xe) and $F(^{84}\text{Kr})$ vs. (^{132}Xe) , respectively, for both LTV and CP. The pattern of the F-values in Las Tres Vírgenes wells shows some degree of atmospheric contamination which has likely occurred during sampling (ASGW or Air Saturated Geothermal Water).

Noble gas elemental composition of the Cerro Prieto geothermal fluids departs from an initial ASGW composition (Air Saturated Geothermal Water) and it can be explained by boiling and subsequent steam separation at depth (Mazor and Truesdell, 1984). During this process, the residual liquid phase will retain the more soluble, heavier noble gases (Kr and Xe compared to Ar) than the less soluble lighter noble gases (Ne compared to Ar).

The departure from ASGW composition by boiling phenomena is modeled as a Rayleigh distillation process, assuming that the vapor phase is being continuously removed from the system. In the residual liquid, this process is governed by the equation (e.g., Pinti et al., 2013):

$$F(i)_{rl} = F(i)_{ASGW} \cdot f^{\left(\frac{K_i}{K_{Ar}} - 1\right)} \quad (6)$$

where $F(i)_{rl}$ is the final fractionation factor between the “ i ” gas isotope and ^{36}Ar in the residual liquid; f is the fraction of remaining

Table 3
Chemical and isotope composition of the gas phase from LTV (LV-4A, LV-6, LV-11) and CP (CP-507, CP-509, CP-442D) wells. P_{S1} is the fluid separation pressure used to reconstruct the primary reservoir composition.

Well	Date [dd/mm/yy]	P_{S1} [psig]	base humidity [ppm] – vapor [mg/kg]									$\delta^{13}\text{C}$ [‰]	^{14}C [pmC]	^{14}C age [yr BP]
			He	H ₂	Ar	N ₂	CH ₄	CO ₂	H ₂ S	NH ₃				
LV-4A	30/05/11	54	nd	1.80	2.08	97.61	4.3	2757	63	2.5	–10.1	0.16 ± 0.1	>49,800	
LV-6	30/05/11	54	nd	2.13	3.67	207.92	0.6	1665	48	1.4	–10.1	0.58 ± 0.1	41,400 ± 1400	
LV-11	30/05/11	56	nd	1.86	4.54	260.71	2.1	2251	55	1.6	–10.1	<0.20	>47,200	
CP-507	22/05/11	190	nd	112.1	0.48	20.08	122.96	7900	381	17.3	–5.2	0.21 ± 0.11	49,600 ± 3900	
CP-509	23/05/11	190	nd	44.7	1.56	273.89	360.67	9641	498	24.7	–2.2	<0.28	>47,200	
CP-442D	23/05/11	190	nd	117.5	nd	25.90	181.98	15,492	656	27.1	na	na	na	

gas in the liquid; K is the gas constant for the two gases (atm^{-1}). The observed decrease in $F(^{20}\text{Ne})$ (Fig. 5) and contemporary increase of $F(^{84}\text{Kr})$ and $F(^{132}\text{Xe})$ (Fig. 6) in wells CP-507 and CP-509 can be explained by boiling and steam separation of an ASGW component from an initial ASGW composition at 309–322 °C and steam separation at 110–185 °C.

3.6. $^3\text{He}/^4\text{He}$ and $\text{U}\text{--}\text{Th}/^4\text{He}$ reservoir fluid dating

Table 5 reports measured $^3\text{He}/^4\text{He}$ ratios (R) normalized to that of present-day atmospheric values ($R_a = 1.386 \times 10^{-6}$; Ozima and Podosek, 1983) together with Ne and Ar isotopic ratios. $^3\text{He}/^4\text{He}$ ratios and associated uncertainties are corrected for air contamination using relevant equations from Sano et al. (2006). Uncertainties are propagated errors at 1σ level (e.g., Pinti et al., 2013). These corrections are particularly significant in the Las Tres Virgenes wells where air contamination is pronounced (Fig. 7). Kr and Xe isotopic ratios were atmospheric and they are not reported here.

Measured $R/R_{a,c}$ of 2.73–4.77 (Table 5) are lower than those expected for a pure mantle component ($R/R_a = 8 \pm 1$; Ozima and Podosek, 1983) or a sub-continental mantle magmatic source ($R/R_a = 6.5$; e.g., Gautheron and Moreira, 2002). These lower values can be explained by mixing between the mantle component ($R/R_{a,mantle} = 8$) and that of a crustal, radiogenic He component ($R/R_{a,crustal} = 0.02$). The radiogenic helium fraction (He_{rad}) can be estimated by using a simple binary mixing equation and it ranges from 23 to 58% of the total measured helium. The neon isotopic composition is atmospheric within uncertainties (Table 5). Except for the $^{40}\text{Ar}/^{36}\text{Ar}$ ratios measured in the Cerro Prieto which show the presence of radiogenic/mantle $^{40}\text{Ar}^*$ ($302 \leq ^{40}\text{Ar}/^{36}\text{Ar} \leq 313$; Table 5), all other argon isotopic ratios are atmospheric but have undergone mass-dependent fractionation (see Fig. 1a in appendix; Marty, 1984). Although distinction between a mantle and a crustal source of argon is not straightforward, Mazor and Truesdell (1984) had previously noticed the possible occurrence of $^{40}\text{Ar}^*$ in excess of the atmospheric composition in Cerro Prieto geothermal fluids ($^{40}\text{Ar}/^{36}\text{Ar}$ up to 321.9).

Assuming that the radiogenic portion of ^4He is produced *in-situ*, i.e., in the aquifer reservoir rock, and then released in the liquid phase, the fluid residence time (t) in the field can be estimated using a simple age model (e.g., Torgersen and Clarke, 1985; Kulongoski and Hilton, 2011):

$$t = \frac{[^4\text{He}]}{\rho \times \Lambda \times \{1.19 \times 10^{-13}[\text{U}] + 2.88 \times 10^{-14}[\text{Th}]\} \times \left(\frac{1-\phi}{\phi}\right)} \quad (7)$$

where $[^4\text{He}]$ is the measured radiogenic ^4He concentration in the liquid phase. The denominator of equation (7) is equivalent to the rate of ^4He accumulation in the liquid phase expressed in $\text{cm}^3\text{STP He g}^{-1} \text{H}_2\text{O a}^{-1}$; Λ is the fraction of He produced in the rock that is released into the liquid phase assumed to be unity; ρ is the bulk density of the aquifer rock ($\text{g}_{\text{rock}}/\text{cm}^3$); $[\text{U}]$ and $[\text{Th}]$ are the

concentrations of U and Th in ppm; $1 - \phi/\phi$ is the void ratio ($\text{cm}^3_{\text{rock}}/\text{cm}^3_{\text{water}}$).

Because we are measuring the ^4He concentration in the steam phase and not in the liquid phase at depth, we can estimate the latter from the simple relation:

$$[^4\text{He}] = F(^4\text{He}) \times \left(\frac{^4\text{He}}{^{36}\text{Ar}}\right)_{\text{air}} \times [^{36}\text{Ar}]_{\text{recharge}}^{\text{ASW}} \quad (8)$$

where the $[^{36}\text{Ar}]_{\text{recharge}}^{\text{ASW}}$ is the amount of dissolved atmospheric argon at the recharge conditions (ASW or Air Saturated Water) which is calculated using solubility data from Smith and Kennedy (1983) and $^4\text{He}/^{36}\text{Ar}$ is the ratio in the atmosphere equal to 0.16675 (Ozima and Podosek, 1983). The term $F(^4\text{He})_{\text{ASGW}}$ is the F -notation value for helium corrected for the effect of boiling and steam separation, following the equation:

$$F(^4\text{He})_{\text{ASGW}} = f \left(1 - \frac{K_{\text{He}}^{\text{He}}}{K_{\text{Ar}}^{\text{Ar}}}\right) \times F(^4\text{He})_i \quad (9)$$

Using f values obtained from steam separation simulations in Figs. 5 and 6 (0.03–0.04 for CP-507 and 0.14–0.15 for CP-509) lead to $F(^4\text{He})_{\text{ASGW}}$ values varying between 557 and 640 for CP-507 and between 1295 and 1950 for CP-509. Because at very high temperatures the solubility coefficients of He and Ar are very close, i.e., the fractionation between He and Ar during boiling is minimal (Potter and Clyne, 1978; Crovetto et al., 1982), correction of equation (9) can be neglected.

In the case of the LTV wells which are contaminated by the atmosphere, we need to recalculate the $F(^4\text{He})$ prior to the atmospheric contamination using the measured $^3\text{He}/^4\text{He}$ ratios (Table 4). Resulting $F(^4\text{He})$ values for LTV wells corrected for air contamination would range from 18 to 28 (1.1 to 9.6 prior of air correction; Table 4). ^4He abundances recalculated from equation (4) taking into account air contamination range from 1.2 to $2.5 \times 10^{-6} \text{ cm}^3\text{STP}/\text{cc}_{\text{water}}$ for LTV wells and from 1.24×10^{-4} to $3.14 \times 10^{-5} \text{ cm}^3\text{STP}/\text{cc}_{\text{water}}$ for CP wells.

In Las Tres Virgenes, the production zone for wells LV-4A, LV6 and LV-11 is in a Cretaceous granodiorite (Télló-López and Rodríguez, 2015) related to the great Baja California batholith (López-Hernández et al., 1994). To calculate U–Th/ ^4He residence times of geothermal fluids contained in the granodiorite, we assumed typical U and Th concentrations of 2.7 and 7.9 ppm, respectively (e.g., Fiala et al., 1982), and typical granodiorite densities of 2.7–2.8 g/cm^3 . Assumed porosities are based on measured effective porosity values of 1.1–5.0% for granodiorite samples from LV-5 and LV-8 (sample depths of 1700 and 1000 m, respectively) (Portugal et al., 2000).

The larger uncertainties on the calculated U–Th/ ^4He residence times derive from the porosities (i.e., the void ratio between rock producing ^4He and fluid accumulating it). For the granodiorite as representative of the LTV reservoir, we obtain U–Th/ ^4He residence

Table 4
Elemental composition of noble gases in Las Tres Virgenes and Cerro Prieto wells.

Sample name	Depth m	T °C	TDI g/l	⁴ He ccSTP/ cc	²⁰ Ne ccSTP/ cc	³⁶ Ar ccSTP/ cc	⁸⁴ Kr ccSTP/ cc	¹³² Xe ccSTP/ cc	F(⁴ He) ±	F(²⁰ Ne) ±	F(⁸⁴ Kr) ±	F(¹³² Xe) ±									
LV-4A	2413	275	11.68	7.19E-07	1.08E-08	2.79E-08	2.15E-06	5.20E-08	7.92E-08	1.19E-09	3.02E-09	6.65E-11	1.08	0.02	1.025	0.019	0.956	0.019	1.014	0.026	
LV-6	n.r.	260	14.71	5.48E-06	8.22E-08	1.97E-08	1.52E-06	4.47E-08	7.34E-08	1.10E-09	2.82E-09	6.21E-11	9.55	0.19	0.842	0.015	1.032	0.020	1.102	0.028	
LV-11-1	1974	260	15.33	1.77E-06	2.66E-08	8.16E-09	6.28E-07	1.82E-08	2.96E-08	4.45E-10	1.13E-09	2.48E-11	7.60	0.15	0.858	0.016	1.026	0.020	1.084	0.028	
LV-11-2	1974	260	15.33	4.52E-07	6.78E-09	2.83E-09	2.18E-07	6.23E-09	1.02E-08	1.53E-10	3.82E-10	8.41E-12	5.65	0.11	0.868	0.016	1.030	0.020	1.071	0.027	
CP-507	2400	319	0.36	9.79E-07	1.47E-08	3.66E-11	2.81E-09	2.03E-08	7.42E-10	1.11E-11	6.32E-11	1.39E-12	290	6	0.265	0.005	1.773	0.035	4.191	0.107	
CP-509	2395	304	25.74	1.18E-06	1.78E-08	2.35E-11	1.81E-09	1.06E-08	3.57E-10	5.36E-12	2.19E-11	4.82E-13	668	13	0.325	0.006	1.626	0.032	2.764	0.071	
	-2650	-314																			

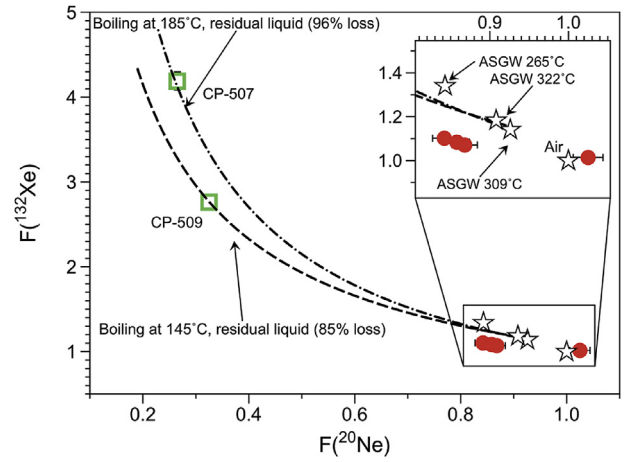


Fig. 5. $F(^{20}\text{Ne})$ vs. $F(^{132}\text{Xe})$ values for LTV and CP wells. Curves represent the evolution of $F(i)$ values in a residual fluid after boiling and steam separation. Initial $F(i)$ compositions (ASGW or Air Saturated Geothermal Water) are calculated from average borehole temperatures (309 and 322 °C for CP wells and 265 °C for LTV wells). Green squares are CP fluids while red-filled dots are LTV fluids. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

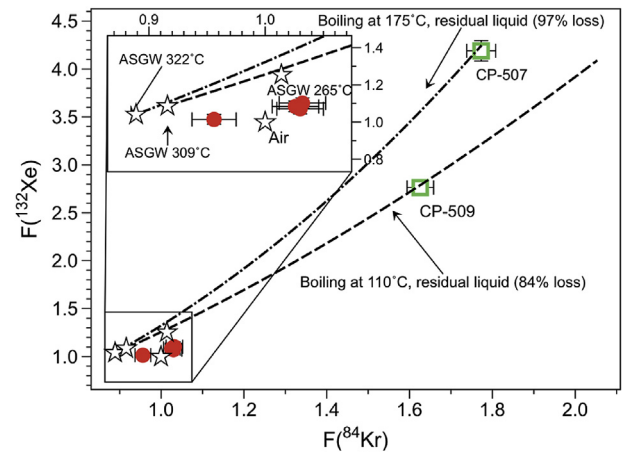


Fig. 6. $F(^{84}\text{Kr})$ vs. $F(^{132}\text{Xe})$ values for LTV and CP wells. Curves represent the evolution of $F(i)$ values in a residual fluid after boiling and steam separation. Symbols are as in Fig. 5.

times ranging from 8.7 to 18.0 ka ($\phi = 1.1\%$) and from 37.8 to 78.9 ka ($\phi = 5.0\%$). The calculated lower U–Th/⁴He ages are within the same range of ¹⁴C ages (fluid residence time: 4.0 to 30.0 ka BP; c.f. section 3.3.).

The recalculated lower estimates of the [⁴He] abundances for CP wells of $3.14 \times 10^{-5} \text{ cm}^3\text{STP}/\text{cm}^3_{\text{water}}$ are within the range of ⁴He concentrations previously measured by Mazor and Truesdell (1984) ($1.8\text{--}5.5 \times 10^{-5} \text{ cm}^3\text{STP}/\text{cm}^3_{\text{water}}$). The maximum estimated value, prior to steam separation, is $6.5 \times 10^{-5} \text{ cm}^3\text{STP}/\text{cm}^3_{\text{water}}$ (Mazor and Truesdell, 1984), half of the maximum estimate here obtained ($12.5 \times 10^{-5} \text{ cm}^3\text{STP}/\text{cm}^3_{\text{water}}$). U–Th/⁴He calculated residence times in CP fluids were estimated using rock densities of 2.2–2.5 g/cm³ as measured in typical sediments of the Salton Sea Through. Average U and Th concentrations in typical shale-sandstone sediments of the area are of 4.5 and 13.5 ppm, respectively (Zukin et al., 1987). Core porosities of the deltaic sandstone-siltstone-shale sequences of the CP reservoir range from 10 to 35%

Table 5
He, Ne and Ar isotopic composition of noble gases in Las Tres Virgenes and Cerro Prieto wells.

Well	R/Ra	±	$^4\text{He}/^{20}\text{Ne}$	(R/Ra) _c	±	$^{20}\text{Ne}/^{22}\text{Ne}$	±	$^{21}\text{Ne}/^{22}\text{Ne}$	±	$^{38}\text{Ar}/^{36}\text{Ar}$	±	$^{40}\text{Ar}/^{36}\text{Ar}$	±
LV-4A	0.999	0.016	0.335	n.c.	n.c.	9.80	0.01	0.0289	0.0002	0.1884	0.0008	294.4	1.1
LV-6	4.570	0.068	3.613	4.490	0.068	9.82	0.01	0.0288	0.0002	0.1863	0.0009	293.3	0.8
LV-11-1	2.833	0.141	2.820	2.728	0.141	9.83	0.02	0.0285	0.0002	0.1867	0.0010	295.2	0.8
LV-11-2	4.080	0.045	2.074	3.932	0.049	9.83	0.01	0.0287	0.0001	0.1871	0.0010	293.3	0.7
CP-507	4.769	0.139	347.78	4.768	0.139	9.86	0.14	0.0278	0.0003	0.1872	0.0014	302.5	5.5
CP-509	4.622	0.124	653.81	4.622	0.124	9.91	0.03	0.0284	0.0002	0.1876	0.0010	313.1	2.2
Air/ASW	1.000		0.267			9.80		0.0290		0.1880		295.5	

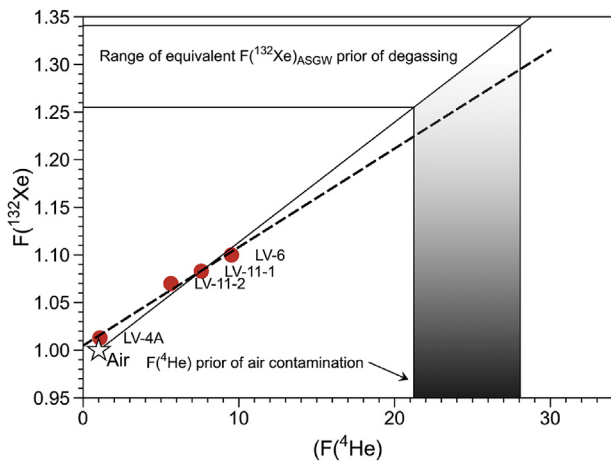


Fig. 7. $F(^4\text{He})$ vs. $F(^{132}\text{Xe})$ in LTV wells. Thick dotted line is the regression line passing through the measured points. The thinner line has been forced through the air composition (F_i) = 1 for definition. Shaded area represents the expected range of $F(^4\text{He})$ values prior to the air contamination (see text for details).

with an approximate average of 22% on 55 cored wells (Vonder Haar, 1984). Westwood and Castanier (1981), on the other hand, suggest porosities of 15–35% for CP sands and sandstones. The calculated U–Th/ ^4He residence times range from 1 to 6 Ma ($\phi = 10\%$) and from 2 to 7 Ma ($\phi = 35\%$). Using Mazor and Truesdell (1984) measured ^4He abundances lead to U–Th/ ^4He ages ranging from 0.7 to 2.5 Ma ($\phi = 10\%$) and from 2 to 7 Ma ($\phi = 35\%$) at Cerro Prieto, consistent with those calculated here. These apparent ages are two orders of magnitude older than those calculated from ^{14}C activities.

4. Discussion

4.1. Paleotemperatures and fluid sources

The relationship between climate and precipitation's mean annual stable isotopic composition can provide significant insights into paleoclimatic conditions (Rozanski et al., 1992). As a working hypothesis, fluctuating climatic conditions in northwestern Mexico and southwestern U.S., with temporary cooler and more humid conditions during Late Pleistocene and/or Early Holocene might have enhanced meteoric water recharge into the Las Tres Virgenes geothermal reservoir. Late Pleistocene groundwater from the Ojo Alamo and Nacimiento aquifers in the central San Juan Basin, New Mexico are about 25‰ lighter in D and 3‰ lighter in ^{18}O than modern precipitation and groundwater (Phillips et al., 1986). In contrast, the replacement of sustained winter rains by hurricane-derived rainwater in Early Holocene seems to have caused a positive isotope shift of precipitation in Baja California (Eastoe et al., 2015). The decrease of δD and $\delta^{18}\text{O}$ in Colorado River water

during Holocene could be related to temporal variations of the rainfall isotopic ratios, but also to wetter climatic conditions at lower altitude, as shown along the Rio Grande in New Mexico (Plummer et al., 2004).

4.1.1. Las Tres Virgenes

The LTV fluid composition (vapor + liquid) is derived from mixing of meteoric water with a non-evaporated seawater component. Reconstructed meteoric δD -value end-member ($\sim -81\%$ to -92% ; Fig. 8) appears to be 20‰–44‰ lower than present precipitation values of -60.0% to -61.8% for the Imperial and Mexicali Valleys and -48.0% to -61.0% for Jacumba and Brawley stations in southern California (Coplen, 1972; Coplen and Kolesar, 1974; Friedmann et al., 1992), supporting the occurrence of Late Pleistocene meteoric recharge under cooler than present-day climatic conditions. This is consistent with the occurrence of glacial period-related precipitation water from central San Juan Basin, where the isotopic depletion is attributed to colder mean annual air temperatures, with a temperature decrease of 5° to 7 °C during the late Wisconsin accompanied, perhaps, of increased winter precipitation (Phillips et al., 1986). Similarly, Dutton (1995) reported isotopic evidence for paleo-recharge in the US High Plains during Late Pleistocene with temperatures 5–8 °C cooler than Holocene.

4.1.2. Cerro Prieto

Based on δD and Cl trends, Truesdell et al. (1981) reconstructed the evolution of CP fluids as resulting from mixing evaporated seawater with Colorado River water ("CP: Mixing trend" in Fig. 8). Chlorine is used as a representative conservative element with little alteration by potential boiling, fractionation, or steam loss. Recent water samples collected during 2000–2005 and in 2011 are chemically more diverse with an increased contribution of meteoric water. Measured values were re-calculated to reservoir concentrations using the heat and mass balance equation from Henley et al. (1984) to correct for the effect of steam removal during separation and sample collection. More likely, Colorado River water represents the primary component of CP geothermal water with minor dissolution of halite during infiltration through the unsaturated zone. The position on the left side of the SET with slightly elevated Cl/Br ratios (Fig. 2) for highest saline Cerro Prieto samples explains the minor salinization of infiltrating river water by salt dissolution.

4.1.3. Salton Sea

The elevated mineralization of Salton Sea geothermal fluids results entirely from dissolution of evaporites by meteoric water and a hypothetical initial δD of $\sim -70\%$, which represents an intermediate value between present-day precipitation in the Imperial Valley (-60% ; Coplen and Kolesar, 1974), reconstructed fossil recharge for LTV fluids (~ -81 to -92%) and present Colorado river water (-95% to -101% ; Dettman et al., 2004; Payne et al., 1979).

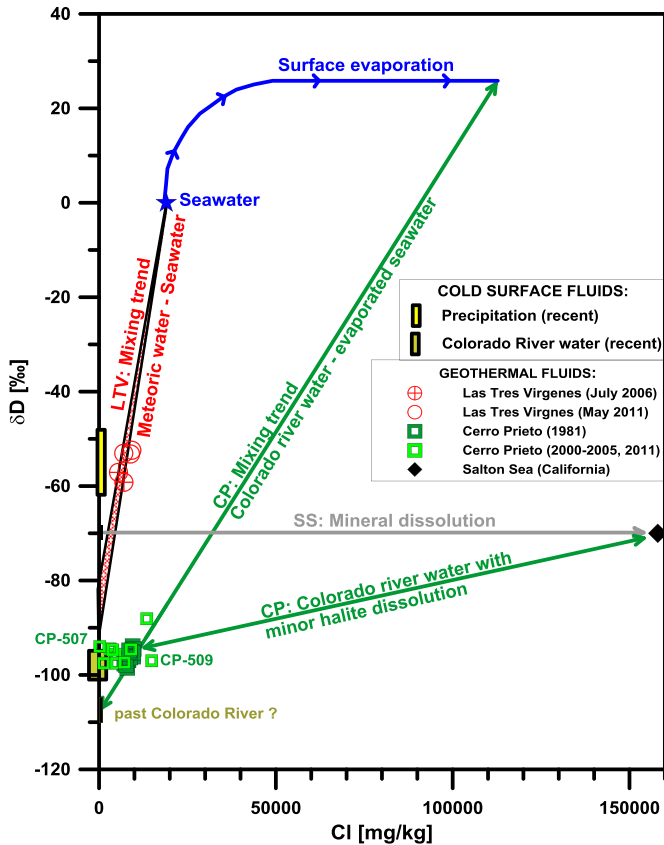


Fig. 8. Mixing models for: a) Glacial meteoric water with seawater to produce the LTV geothermal fluid; b) Cerro Prieto geothermal fluids with 15 samples from 1976 to 1977 (Truesdell et al., 1981) and 10 samples from September 2008 and May 2011 (present study), composed of Colorado River water mixed with evaporated seawater (hypothesis from Truesdell et al., 1981) or Colorado River water with minor contributions of dissolved halite during infiltration (present hypothesis), and, c) evaporite dissolution by meteoric water to form Salton Sea geothermal fluid (Coplen and Kolesar, 1974).

In order to reconstruct the paleo-temperature T of the glacial meteoric component for LTV fluids, the calculated δD end-member for meteoric water (Fig. 8) was incorporated into the following equation (Phillips et al., 1986):

$$\delta D = 4.15T - 127\text{‰} \quad (10)$$

where the paleotemperature is given in °C. The validity of this relationship has been confirmed for similar continental regions in North America (e.g., New Mexico: Goff et al., 1982; Phillips et al., 1986) and Europe (e.g., Austria: Andrews et al., 1985). Calculated annual average paleotemperatures between 8.4 °C ($\delta D = -92\text{‰}$) and 11.1 °C ($\delta D = -81\text{‰}$) are 6.9–13.6 °C lower than present average annual air temperatures in the Baja California Peninsula (18–22 °C) (<http://cuentame.inegi.gob.mx>). The calculated decrease of Baja California paleotemperatures (6.9° – 13.6 °C) lies within the lower range of the late Wisconsin paleotemperature's decline estimated in the central San Juan Basin (5–7 °C).

Primary $\delta^{18}O$ -values for the glacial meteoric water range from –11.5 to –13.5‰ and were determined through (Phillips et al., 1986):

$$\delta^{18}O = 0.604T - 18.2\text{‰} \quad (11)$$

In the next section, the calculated paleo-composition of primary end-members is used to reconstruct the temporary stages of fluid

evolution for the LTV and CP geothermal reservoirs.

4.2. Stages of fluid evolution and quantification of involved fluid types

4.2.1. Las Tres Virgenes

Mixing between seawater and meteoric water leads to fluids with intermediate $\delta^{18}O$ and δD values between these two end-members (Sakai and Matsubaya, 1974). Such a simple mixing process between seawater and meteoric water cannot reproduce the isotopic composition of the LTV reservoir fluids, since the $\delta^{18}O$ composition for LTV fluids has shifted from ~4 to 6‰ with respect to the expected value for a δD specific composition (Fig. 9). The LTV isotopic composition appears to be the result of two combined processes: (1) mixing between Late Pleistocene-Early Holocene meteoric water ($\delta D -81$ to -92‰ ; $\delta^{18}O -11.5$ to -13.5‰) and non-evaporated seawater in suitable proportions to provide the present hydrochemical and deuterium composition (Stage 1 in Fig. 9); and (2) subsequent water-rock interactions at 200–300 °C which caused a shift in $\delta^{18}O$ composition by mineral-water exchange (Stage 2, Fig. 9). This $\delta^{18}O$ exchange depends on temperature, water residence time, and water mass (Clayton and Steiner, 1975).

An intermediate hydrochemical position of LTV water samples between meteoric water and seawater composition (Fig. 2: log Br vs. log Cl, Fig. 8: Cl vs. δD , TDS = 9550–15,300 mg/L) suggests a minimum contribution of two end-members to reconstruct the provenance for LTV geothermal fluids. The presence of modern ^{14}C in all recovered samples (1.89–35.61 pmC) confirms the impact of young surface water within the potential ^{14}C dating range from recent to about 45,000 years. Magmatic or andesitic water, as initially proposed by Giggenbach (1992), is a frequently mentioned component of reservoir fluids, such as postulated for Larderello (Italy), the Geysers (California) (D'Amore and Bolognesi, 1994) and the Los Azufres (Mexico) geothermal field (Pinti et al., 2013). Assuming an hypothetical ^{14}C - and 3H -concentration of 100 pmC and 2.0 T.U., respectively, for the current LTV atmospheric input (e.g., 1.8 T.U. for precipitation in SE-Mexico in June 2001; Birkle et al., 2006), mixing with a ^{14}C - and 3H -free magmatic fluid leads to a magmatic contribution between 64 and 98%. While the latter would fit measured ^{14}C -values of LTV geothermal fluids (1.86–35.6 pmC), a contribution of 2–36% of a present atmospheric component would result in unrealistic elevated 3H -concentrations of up to 0.72 T.U. Similarly, a hypothetical contribution of 19–31% atmospheric input could explain measured ^{14}C CP fluids values, but 3H concentrations close to detection limit (max. 0.06 ± 0.05 T.U.) exclude recent atmospheric input. The assumption of a natural tritium background between 4.7 and 6.7 T.U. as reported for the Tucson Basin precipitation in Arizona (Eastoe et al., 2004) between 1991 and 2002, would increase the hypothetical input concentration and herein contribution of the recent meteoric water end-member.

A more conclusive model to reconstruct the provenance of current geothermal water is the mixing of two end-members, fossil seawater and Quaternary meteoric water (c.f. section 4.1., Fig. 8: Cl vs. δD). Herewith, TDS concentrations between 9550 mg/L and 15,300 mg/L of LTV geothermal water can be traced back by mixing 25%–42% of standard seawater (TDS = 35,000 mg/L) with 58%–75% of average meteoric water (TDS = 1000 mg/L) ((1) in Fig. 10). Assuming absence of ^{14}C in the fossil seawater component, total ^{14}C accumulation must have been provided by the meteoric end-member. Using a minimum salinity (TDS = 9550 mg/l) and the measured ^{14}C range from 1.86 pmC to 35.61 pmC for LTV geothermal water, the reconstructed meteoric end-member must have an initial pmC value between 2.48 and 47.5 ((2) in Fig. 10). For highest saline fluids (15,300 mg/L), the volumetric input of meteoric water decreases from 75% to 58%, resulting in reconstructed

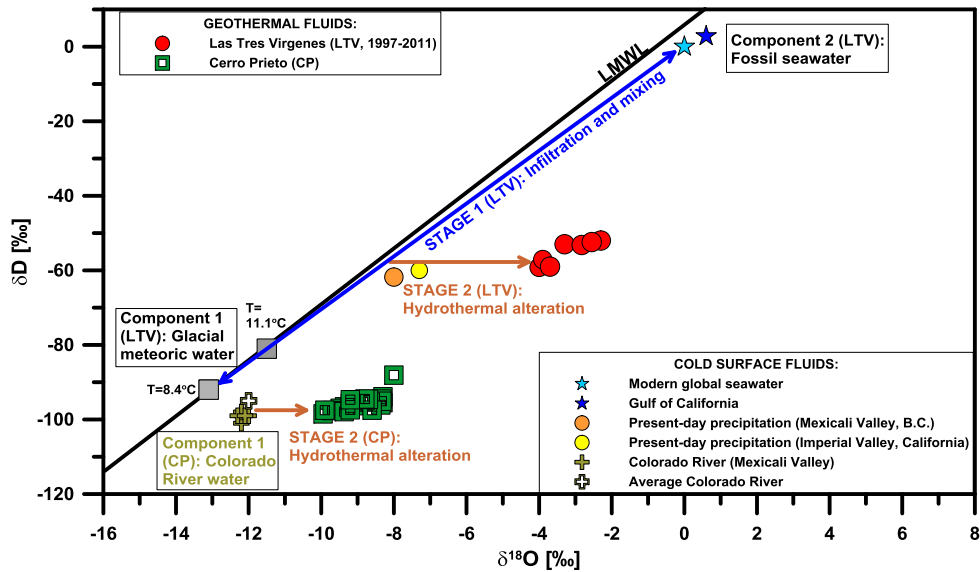


Fig. 9. Evolution stages for, a) Las Tres Virgenes with the Late Glacial infiltration of meteoric water and mixing with (fossil) seawater (Stage 1) and subsequent water-rock interaction (Stage 2), and b) Cerro Prieto fluids with the infiltration of Colorado River water (Stage 1) and minor dissolution of halite (Stage 2). Hydrothermal alteration is affecting the primary $\delta^{18}\text{O}$ aqueous composition.

pmC values between 3.22 pmC and 61.6 pmC for the meteoric end-member ((3) in Fig. 10). The wide range of ^{14}C composition can be converted into corrected ^{14}C -residence times varying between 3892 ± 36 yr BP ($^{14}\text{C} = 61.6 \pm 0.28$ pmC) and $29,697 \pm 349$ yr BP ($^{14}\text{C} = 2.48 \pm 0.11$ pmC) for the meteoric end-member.

As the atmospheric concentration of ^{14}C fluctuated in the past, a modification of the initial atmospheric activity A_{50} from the present 100 pmC to an average 110 pmC during Early Holocene (applied to sample LV-11 from 2006) and 125 pmC (applied to sample LV-4A) during Late Pleistocene (Clark and Fritz, 1997) resulted in a modified residence time between $31,490 \pm 349$ yr BP and 4658 ± 36 yr BP for the meteoric end-member. In the event that uncertainties associated to pmC values may reach 20% due to potential minor contamination during well sampling, corrected ^{14}C concentrations which vary from 1.49 pmC ($1.86 \text{ pmC} \pm 20\%$) to 42.73 pmC ($35.61 \text{ pmC} \pm 20\%$) would still provide a Quaternary (Late Pleistocene – Early Holocene) residence time for the meteoric component.

4.2.2. Cerro Prieto

Cerro Prieto geothermal fluids experienced a sustained ^4He flux from a granitic basement, evidenced by calculated U–Th/ ^4He residence times ranging between 1 and 7 Ma, mixed with meteoric water from the Colorado River (Component 1 in Fig. 9) followed by subsequent water-rock interaction with a positive $\delta^{18}\text{O}$ -shift between 2 and 4‰ (Stage 2 in Fig. 9). Relatively low δD values for Colorado River water (~ -95 to -101 ‰) result in lighter deuterium ratios for CP reservoir water in comparison to LTV fluids. The measured ^{14}C concentration of 19.04 ± 0.33 pmC (Table 2) for formation water from CP-509, which results mostly of Colorado River water, reflects an averaged time span for the infiltration into the CP reservoir. The elevated ^{14}C concentration of 30.93 ± 0.63 pmC for the vapor-dominated sample from CP-507 suggests partial input and mixing of Colorado River water with ascending vapor from deeper resources.

Independently of potential age correction models, measured ^{14}C concentrations from 19.04 pmC to 30.93 pmC for these geothermal fluids point to a Late Pleistocene to Early Holocene (~ 9000 – $13,000$ yr

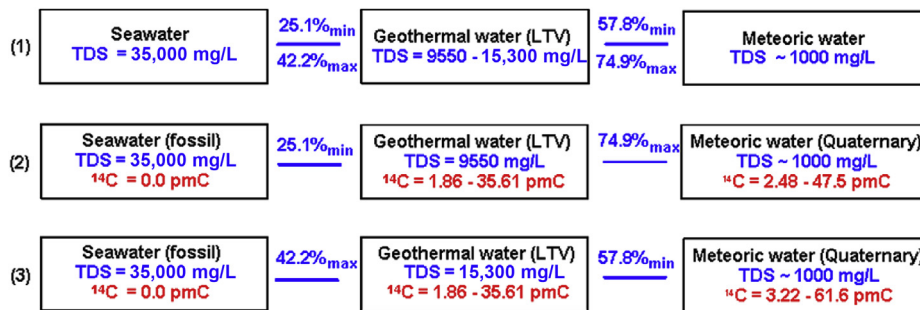


Fig. 10. Mixing model for geothermal fluids from the Las Tres Virgenes reservoir. The known salinity of geothermal fluids is applied to reconstruct the volumetric contribution for meteoric and seawater end-members (1). ^{14}C concentrations of the meteoric component are reconstructed by measured ^{14}C concentrations for geothermal LTV fluids (1.86 – 35.61 pmC), combined with an assumed lack of ^{14}C for fossil seawater. Depending on the salinity of LTV fluids, two scenarios with a meteoric ^{14}C concentration between 2.48 and 47.5 pmC (Mixing model (2)), and between 3.22 and 61.6 pmC (Mixing model (3)) were reconstructed.

BP) recharge of the CP reservoir by Colorado River water. The observed variability in ^{14}C composition together with lack of tritium can be explained by sustained infiltration of Colorado River water during the Late Pleistocene and Early Holocene.

Below we provide support for a potential link of the meteoric feeding of LTV and CP geothermal reservoirs to cooler and more humid climatic conditions in southwestern U.S. and northwestern Mexico during the Last Glacial Maximum.

4.3. Paleoclimate and volcanism as recharge triggers

4.3.1. Paleoclimatic evidence for Late Pleistocene and Early Holocene recharge

The postulated infiltration of meteoric water into the Las Tres Vírgenes and Cerro Prieto geothermal reservoirs occurred during the final stage of Late Pleistocene to Early Holocene period. The calculated range of apparent ^{14}C -residence times from about 30,000 yr BP to 4000 yr BP for the studied reservoir fluids is likely to be related to recharge events during major periods of increased humidity under cooler climatic conditions. In contrast to present arid conditions in Baja California and southwest U.S., Canada, as well as part of northern U.S. were covered by the Laurentide ice sheet (LIS) during the Last Glacial Maximum (LGM) at around 18,000 yr BP. That led to abundant rainfall in the southwestern United States, typically an arid to semi-arid region, during that period. This contrasts to most other parts of the world which became exceedingly dry.

A variety of paleoclimatic studies confirm the existence of significant climatic changes in southwestern U.S. and northern Mexico during the LGM period (e.g., Keigwin and Jones, 1990; Romero-Mayen et al., 2007). Variations in $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values of tufa deposits in the Salton Basin, southern California, ranging from -8.52‰ to -2.50‰ (PDB) and from 0.8‰ to 3.76‰ , respectively, reflect changes in the relative humidity in the Salton Basin and variations in the Colorado River inflow and hence, climatic conditions in the Colorado River drainage basin (Li et al., 2008). Ortega et al. (1998) observed two major periods of increased humidity recorded by lake-level variations of the Laguna Babicora, near the Chihuahuan Desert in NW-Mexico, during the Late Wisconsinan and Early Holocene. These periods of increased humidity were related to jet stream migration to southerly latitudes and the influence of the mobile polar high. Based on ^{14}C , Roy et al. (2007) determined high inflow rates and high lake stands from core studies from the Laguna San Felipe, Sonoran Desert, NW-Mexico, at $\sim 14,000$ – $13,000$ yr BP, $12,000$ – 8500 yr BP and 6000 – 3000 yr BP, intercalated with drier periods ($27,000$ – $14,500$ yr BP; $13,000$ – $12,000$ yr BP; 7000 yr BP) with higher evaporation in the basin and increased aeolian activity. Pollen, diatoms, sediment chemistry and isotopes ($\delta^{18}\text{O}$, ^{14}C), packrat middens and glacial records, suggest that the modern summer precipitation regime collapsed around the LGM ($\sim 21,000$ years ago), although northern Mexico was much wetter than today due to increased winter rainfall (Metcalf et al., 2000).

Atmospheric noble gas measurements of Late Pleistocene groundwater indicate a 5 – 6 °C decrease in mean average temperature relative to modern values in the southwestern U.S. (e.g., Stute et al., 1992; Castro et al., 2000). Noble gas derived temperatures in the Mojave Desert, California averaged 4.2 ± 1.1 °C cooler in the Late Pleistocene (from ~ 43 to ~ 12 ka BP) compared to the Holocene (from ~ 10 to ~ 5 ka BP) (Kulongoski et al., 2009). As an analogous case for the recharge of deep aquifers (>1000 mbsl) at the end of the LGM, “late glacial” formation water with residence times varying between 7 and 40 ka BP are described for oil reservoirs from the Gulf Coast sedimentary basin in SE-Mexico (Birkle et al., 2002, 2009; Birkle and Angulo, 2005). The isotopic content of

geothermal systems in the Great Basin likely reflects the isotope geochemistry of precipitation in the Great Basin during the Late Pleistocene, 40,000 to 10,000 years BP, suggesting an extended period of recharge in response to lower mean-annual temperatures (Flynn and Buchanan, 1990).

4.3.2. Co-genetic volcanic activity and reservoir recharge during Late Pleistocene and Early Holocene

In addition to the proxies mentioned above suggesting enhanced recharge during the occurrence of periodic cooler and humid climatic conditions in northwestern Mexico during the Late Pleistocene and Early Holocene periods, volcanic activity in the LTV region seems to have triggered additional hydrologic processes. Late Pleistocene tectonic–volcanic activity in the Las Tres Vírgenes region is evidenced by (U–Th)/ ^4He zircon dating of 30.7 ka (± 1.8 ka; -1.4 ka) for the ultimate eruptive phase of La Virgen volcano (Schmitt et al., 2010). A sequence of fall and hydromagmatic surge horizons from the El Mezquital formation (Capra et al., 1998) deposited during this volcanic episode represents a co-genetic process to the postulated meteoric recharge of the adjacent LTV geothermal reservoir. Increased precipitation by humid climatic conditions in NW-Mexico at the end of the LGM together with increased fracture permeability caused by tectonic extensional processes during volcanic eruptions might have enabled and accelerated an ultimate event of fossil pore fluids displacement in the geothermal reservoir by glacial-periodic recharge with surface-derived fluids. Similar to the La Virgen eruptive event, a young eruptive, intermittent cycle from 110,000 to 10,000 yr BP was reported for the Cerro Prieto volcano, based on paleomagnetic data (de Boer, 1980).

In case of the Salton Trough, obsidian hydration ages for Salton buttes are 250–8400 yr (Friedman and Obradovich, 1981), and recent zircon analyses for a granophyre ejecta clast from the Red Island rhyolite dome indicate a very recent eruption age of 2480 ± 470 years (Schmitt et al., 2012). Previously published estimates for the age of the Salton Sea geothermal system range from a few thousand years (Heizler and Harrison, 1991) to at least 100,000 years (Williams and McKibben, 1989). Kasameyer et al. (1984) suggest a reservoir age of 3000–20,000 years for the Salton Sea geothermal field, while numeric modeling from Hulen et al. (2002) indicates that static temperature profiles for selected Salton Sea wells could have taken 150,000–200,000 years to develop. Although the modern geothermal anomaly is recent and likely related to Holocene volcanism in Salton Sea, deep-reaching precursor hydrothermal systems must have existed during Pleistocene, as evidenced by U–Pb zircon ages of 420 ± 8 ka and 479 ± 38 ka for rhyolite volcanism (Schmitt and Hulen, 2008). The combination of recent volcanological and climatic events is pointing toward a common young age for the initiation of hydrothermal fluid migration into deep reservoirs of southern California and northwestern Mexico.

4.4. Tracing fluid migration – U–Th/ ^4He versus ^{14}C ages

4.4.1. Cerro Prieto

Calculated U–Th/ ^4He ages of 0.7–7 Ma for Cerro Prieto fluids from wells CP-507 and CP-509 and data from Mazor and Truesdell (1984) are far higher than apparent ^{14}C ages of 10–50 ka BP (Truesdell et al., 1979) and 9–13 ka BP (this study) for these same wells. This discrepancy could be related to the presence of externally produced ^4He (e.g., Torgersen and Clarke, 1985; Patriarche et al., 2004), which is not accounted for in these calculations. However, the occurrence of radiogenic $^{40}\text{Ar}^*$ associated with ^4He (see appendix and Mazor and Truesdell, 1984) is a clear indication of prolonged water-rock interactions and long water residence times

in the aquifer. Interestingly, the lower age estimates correspond to the depositional age of the Colorado River sediments that constitute the CP reservoir (Lippmann et al., 1999). The U–Th/⁴He age model might indicate the occurrence of a minor fraction of connate pore water in the reservoir. Alternatively, we should assume the occurrence of a sustained ⁴He flux from the deeper, fractured basement, possibly through faults bordering the field and controlling fluid circulation (Lippmann et al., 2000). This “excess He” (Torgersen and Clarke, 1985) would have the effect of “ageing” fluids in the CP reservoir that will then result from mixing between “recent” recharge water with a potential ¹⁴C age range from 9 to 13 ka BP (this study) and older water enriched in ⁴He and residing in the fractured crystalline basement. All along the pull-apart basins of Southern California created by the movement of the transform San Andreas Fault, such as the Salton Through, extensional stresses favor the upward flux of volatiles, including helium (e.g., Kennedy et al., 1997; Kulongoski et al., 2013; Evans, 2013). Recently, Evans (2013) calculated a sustained flux of ⁴He in the Salton Sea basin, NW of Cerro Prieto, of $5.88 \times 10^{-6} \text{ cm}^3 \text{STP cm}^{-2} \text{ yr}$, i.e. $1.8 \times$ the average continental crust flux of helium of $3.30 \times 10^{-6} \text{ cm}^3 \text{STP cm}^{-2} \text{ yr}$ (O’Nions and Oxburgh, 1983). This flux is largely sufficient to explain the helium anomalies and “older” ages calculated for the CP fluids. Although the water and salts in the Cerro Prieto geothermal fluid may have originated from Colorado River water and minor halite dissolution, noble gas results suggest a different origin for gases in the fluid.

Regarding the meteoric component, the Colorado River was - prior to construction of upstream dams - the main recharge source of the Mexicali and the Imperial Valley aquifers (Portugal et al., 2005; Payne et al., 1979), reflecting the ongoing dynamic of vertical and lateral hydraulic pathways.

4.4.2. Las Tres Vírgenes

The lack of post-bomb tritium in the geothermal fluids discards the hypothesis of present seawater inflow, although only trace concentrations for modern tritium would be expected due to little fresh water input, well-documented upwelling of deep water, and effective mixing because of strong tides at the northern end of the Gulf of California. Therefore, current hydraulic communication between the Las Tres Vírgenes and the Gulf of California (with a minimum lateral distance of 8–10 km), as proposed by Verma et al. (2006), seems unlikely. More likely, vertical tectonic structures of major NNW-SSE trending extensional faults (Portugal et al., 2000) form principal conduits for groundwater migration. The dominance of vertical pathways was also confirmed for the Boléo Cu–Co–Zn mining district (Conly et al., 2006), whose northwestern boundary is controlled by the LTV-region. Metal distribution, tectonic relationships, mineral textures, and geochemical and Pb-isotopic composition of conglomerate units support evidence for the downward filtration of metalliferous brine (Conly et al., 2006). The proximity of highly altered, clay facies conglomerates to fault zones indicates also that migration of hydrothermal fluids did occur in the vicinity of basin faults.

4.5. Time-scale of hydrothermal alteration processes

Reconstructed ¹⁴C- residence times within a time span from ~30,000 to ~4000 yr BP for a meteoric component suggest Quaternary recharge of the LTV reservoir by surface water. Consequently, hydrothermal alteration of reservoir host rock by water–rock interaction must have occurred within a time period of less than ~30,000 years. Elevated geothermometer temperatures from 260 to 300 °C in the liquid-dominated reservoir (Portugal et al., 2000) accelerated the alteration, resulting in an equilibrated water–rock isotopic composition within a relatively short time period.

Apparent ages of 7340–33,168 yr BP for petroleum in the Guaymas Basin, Gulf of California, point to fast conversion of organic matter to hydrothermal petroleum within the last ~4–6 ka (Peter et al., 1991). Fast infiltration processes and current hydrothermal alteration are also documented for the Yellowstone National Park (YNP). YNP isotopic and chemical data suggest that hydrothermal water, being currently discharged from YNP, was recharged in the Gallatin and northern Absaroka Ranges during the Little Ice Age (1350–1870 AD) by cooler meteoric water with lighter δD (–149‰) and $\delta^{18}\text{O}$ (–19.9‰) values (Kharaka et al., 2002).

5. Conclusions

The Las Tres Vírgenes geothermal reservoir appears to be so far the only reported case in which the recharge event of a geothermal reservoir was genetically linked to tectonic–volcanic activity by radiogenic age dating, including as (U–Th)/⁴He zircon dating (30,700 yr BP; Schmitt et al., 2010). The latter supports a similar age for the most recent volcanic eruptions from the La Virgen volcano, located adjacent to the LTV geothermal field, and ¹⁴C-based residence times (~4000–30,000 yr BP) for the infiltration period of surface water into the geothermal reservoir. Na/Cl- and Br/Cl-ratios as well as mixing calculations with several elements (Na, Ca, Cl, Br) suggest a mixing contribution of 58%–75% for primary meteoric water and 25%–42% for a potential fossil seawater component. Indeed, such a mixing allows us to reconstruct the present LTV reservoir fluid composition. The δD -values of the modeled meteoric end-member appear to be 20‰–44‰ lower with respect to present-day precipitation (–60.0‰ and –61.8‰ for the Imperial and Mexicali Valley, Coplen and Kolesar, 1974; Coplen, 1972), providing strong support for cooler and more humid climatic conditions in NW-Mexico during the Late Pleistocene and Early Holocene time periods. As demonstrated analogously for the central San Juan Basin in New Mexico, USA, isotopic depletion is attributed to colder mean annual air temperatures, with a temperature decrease of 5° to 7 °C during the late Wisconsin and perhaps to increased winter precipitation (Phillips et al., 1986).

The commercial lifespan of any geothermal field depends on the presence of recharge sources to feed the reservoir. Isotopic analysis of the Las Tres Vírgenes and Cerro Prieto reservoirs indicate the existence of infiltration processes during the Late Glacial Maximum period in Late Pleistocene and pluvial phases in Early Holocene, whereas no evidence was found for present-day recharge. Therefore, unknown hydrological parameters for these glacial aquifer systems, especially available fluid volumes, require careful management planning for future exploitation. The production history of each geothermal well should continuously be monitored, combined with routinely performed chemical and isotopic fluid analyses to detect any anthropogenic-induced hydraulic alterations in the geothermal reservoir.

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Appendix

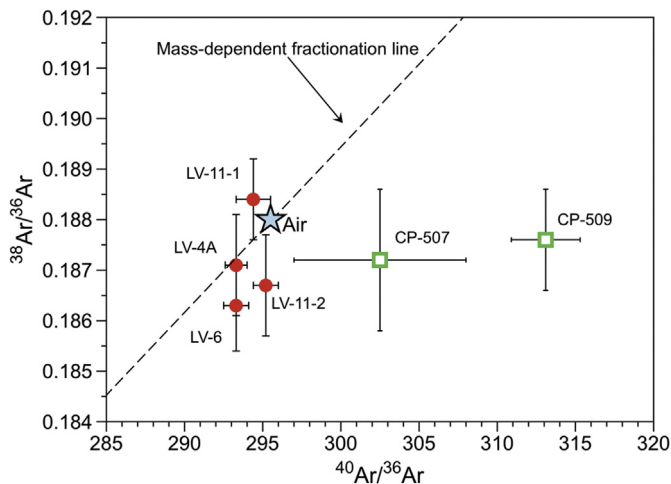


Fig. 1A. The three-isotope plot of argon ($^{40}\text{Ar}/^{36}\text{Ar}$ vs. $^{38}\text{Ar}/^{36}\text{Ar}$) for the CP and LTV fluids (symbols as in Fig. 5). The star indicates the air composition ($^{38}\text{Ar}/^{36}\text{Ar} = 0.1880$; $^{40}\text{Ar}/^{36}\text{Ar} = 295.5$; Ozima and Podosek, 1983). The dashed line represents the evolution of the Ar isotopes during a closed-system batch isotopic fractionation. Values calculated using relevant equations from Marty (1984).

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