Stable Isotope Composition of Hydrothermally Altered Rocks and Hydrothermal Minerals at the Los Azufres Geothermal Field, Mexico

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Abstract: The Los Azufres geothermal field is the second most important geothermal field for electricity production in Mexico, with a total installed capacity of 188 MW. Hydrothermal alteration studies have been an important tool for geothermal exploration and development of the field, but little attention has been given to the geochemical and isotopic characterization of hydrothermal minerals. $\delta^{18}O$, $\delta^{2}H$, and $\delta^{13}C$ systematics at Los Azufres geothermal field were investigated using whole rock samples, as well as hydrothermal minerals separates, obtained from different depths in the wells Az-26 and Az-52. Most $\delta^{18}O$ values reproduce well the present in-situ field temperatures and isotopic composition of geothermal fluids or local meteoric water. Temperature seems to be the most important factor controlling the oxygen isotope composition of reservoir rocks. A vertical correlation with decreasing $\delta^{18}O$ values and increasing temperature is given for both well profiles. Most analyzed calcites have isotope ratios close to or in isotopic equilibrium with present geothermal or meteoric water at in-situ temperatures. A good correlation between lower calcite $\delta^{18}O$ values and high W/R ratios indicate that oxygen isotopic composition of calcite might constitute a tool for identifying areas of high permeability in the geothermal system of Los Azufres. In contrast, the disequilibrium for some quartz samples suggests the presence of reservoir fluids significantly enriched in ^{18}O ($\delta^{18}O$ values about 8‰ higher than those of present geothermal fluids) at the time of quartz deposition.

Key Words: hydrothermal alteration, hydrothermal minerals, oxygen, hydrogen and carbon stable istotopes, geothermal systems, Los Azufres

Los Azufres Jeotermal Alanında (Meksika) Hidrotermal Alterasyona Uğramış Kayaç ve Minerallerin Kararlı İzotop Bileşimleri

Özet: Meksika elektrik üretimi için ikinci en önemli jeotermal bölge olan Los Azufres jeotermal alanı toplam 188 MW kurulu güce sahiptir. Hidrotermal alterasyon çalışmaları jeotermal araştırma ve jeotermal alanın geliştirilmesi için önemli bir araç olmasına karşın hidrotermal minerallerin jeokimyasal ve izotopik karakterizasyonu daha az dikkat çekmiştir. Los Azufres jeotermal alanındaki $\delta^{18}O$, $\delta^{2}H$ ve $\delta^{13}C$ sistematiği Az-26 ve AZ-52 kuyularının farklı derinliklerden elde edilen tüm kaya örneklerinin yanı sıra hidrotermal mineraller kullanılarak incelenmiştir. En $\delta^{18}O$ değerleri jeotermal akışkanların ya da yerel meteorik suların yerindeki mevcut sıcaklıkları ve izotopik bileşimlerini iyi yansıtmaktadır. Sıcaklık, rezervuar kayaçlardaki oksijen izotop bileşimini kontrol eden en önemli faktör olarak gözükmektedir. Azalan $\delta^{18}O$ değerleri ve artan sıcaklık ile dikey bir ilişkinin varlığı her iki iyi profiller içinde verilmiştir. Analiz edilen kalsitlerin büyük bir bölümü mevcut jeotermal veya meteor suların yerindeki sıcaklıkları ile izotopik dengede veya dengeye yakın izotop oranlarına sahiptirler. Düşük kalsit $\delta^{18}O$ değerleri ve yüksek W/R oranları arasındaki iyi korelasyon kalsit oksijen izotopik bileşimlerinin Los Azufres jeotermal sisteminde yüksek geçirgenliği olan alanları tanımlamak için kullanılabilecek iyi bir parametre olabileceğine işaret etmektedir. Buna karşılık, bazı kuvars örneklerindeki dengesizlik, kuvars oluşumu sırasında rezervuar akışkanlarının ^{18}O değerlerinin önemli ölçüde zenginleştiğine ($\delta^{18}O$ değerleri mevcut jeotermal akışkanlara göre ‰8 daha fazladır) işaret eder.

Anahtar Sözcükler: hidrotermal alterasyon, hidrotermal mineraller, duraylı izotoplar, oksijen, hidrojen, karbon, jeotermal sistemler, Los Azufres

Introduction

The Los Azufres geothermal field is located in central Mexico, approximately 200 km northwest of Mexico City. It is one of a number of Pleistocene silicic volcanic centres with active geothermal systems that lie in the Mexican Volcanic Belt (MVB, Figure 1). This belt extends from the Gulf of Mexico to the Pacific Coast, and comprises Late Tertiary to Quaternary volcanics represented by cinder cones, domes, calderas and stratovolcanoes, along a nearly East–West axis (Aguilar y Vargas & Verma 1987). Los Azufres has been intensively investigated and developed since 1970. Nearly 70 wells have been drilled, and with a production of 188 MW, it represents the second most important geothermal field in Mexico (Gutiérrez-Negrín *et al.* 2010).

Hydrothermal minerals in geothermal systems are an important tool to study the structure of a geothermal reservoir, as well as the physico-chemical and hydrogeological conditions prevailing in it (e.g., Giggenbach 1981; Arnórsson *et al.* 1983). Although mineralogical studies of the hydrothermal alteration in active geothermal fields have been performed during the last 30 years, more detailed mineralogical investigations, particularly those designed to determine the chemical composition of hydrothermal minerals using modern analytical techniques, are still needed (Browne 1998). Studies of hydrothermal alteration at Los Azufres have been carried out by several authors (e.g., Cathelineau *et al.* 1985; Robles Camacho *et al.* 1987; Cathelineau & Izquierdo 1988; González Partida & Nieva Gómez 1989; Torres-Alvarado 2002). These studies have shown that partial to complete hydrothermal metamorphism, with mineral parageneses from greenschist to amphibolite facies, has occurred (Cathelineau *et al.* 1991). However, stable isotope studies on meteoric and geothermal fluids from the field (Giggenbach & Quijano 1981; Ramírez Domínguez *et al.* 1988; Tabaco Chimal 1990; Birkle *et al.* 2001) indicate that, on average, the $\delta^{18}O$ values of present day meteoric and geothermal waters are $\approx -9‰ \pm 1‰$ and $\approx -4‰ \pm 2‰$, respectively. Stable isotope (O, H, C) systematics of altered rocks and authigenic minerals, in contrast, have received little attention. The objectives of the present study were: (1) to characterize the isotopic composition (O, H, C) of altered rocks and hydrothermal minerals from the Los Azufres geothermal field; (2) to obtain a better understanding of the water/rock interaction processes occurring in the field, and (3) to use isotopic tools to investigate the state of equilibrium between water and minerals in the active hydrothermal system from Los Azufres.

Geological and Hydrogeochemical Setting

Geological Framework

Los Azufres is one of several Pleistocene silicic volcanic centres with active geothermal systems in the Mexican Volcanic Belt (MVB, Aguilar y Vargas & Verma 1987). It is located approximately 200 km northwest of Mexico City (Figure 1).

The volcanic rocks at Los Azufres have been described, among others, by Dobson & Mahood (1985), Razo Montiel *et al.* (1989), Cathelineau *et al.* (1991), Pradal & Robin (1994), and Campos-Enriquez & Garduño-Monroy (1995). Geologically, this field is distinguished by extensive Neogene volcanic activity, dominated by basaltic and andesitic lavas (Figure 1), which unconformably overlie metamorphic and sedimentary rocks of Late Mesozoic to Oligocene age. The nearest exposures of the prevolcanic basement lie about 35 km southwest of Los Azufres and consist of gently folded shales, sandstones, and conglomerates. The oldest volcanic activity reported in this area began at 18 Ma with andesite flows (Dobson & Mahood 1985). The local basement for Los Azufres is formed by a phenocryst-poor, microlithic andesite, interstratified with pyroclastic rocks of andesitic to basaltic composition, basaltic lava flows, and subordinate dacites. This 2700-m-thick unit has been dated by K/Ar between 18 and 1 Ma (Dobson & Mahood 1985). This massive unit constitutes the main aquifer, through which the geothermal fluids flow mainly using fractures and faults (Birkle *et al.* 2001). These fluids locally reach the surface as thermal springs and fumaroles (Figure 1).

Silicic volcanism began shortly after eruption of the last andesites, forming a sequence up to 1000 m thick of rhyodacites, rhyolites, and dacites with ages between 1.0 and 0.15 Ma (Figure 1; Dobson & Mahood 1985). They typically build domes and short
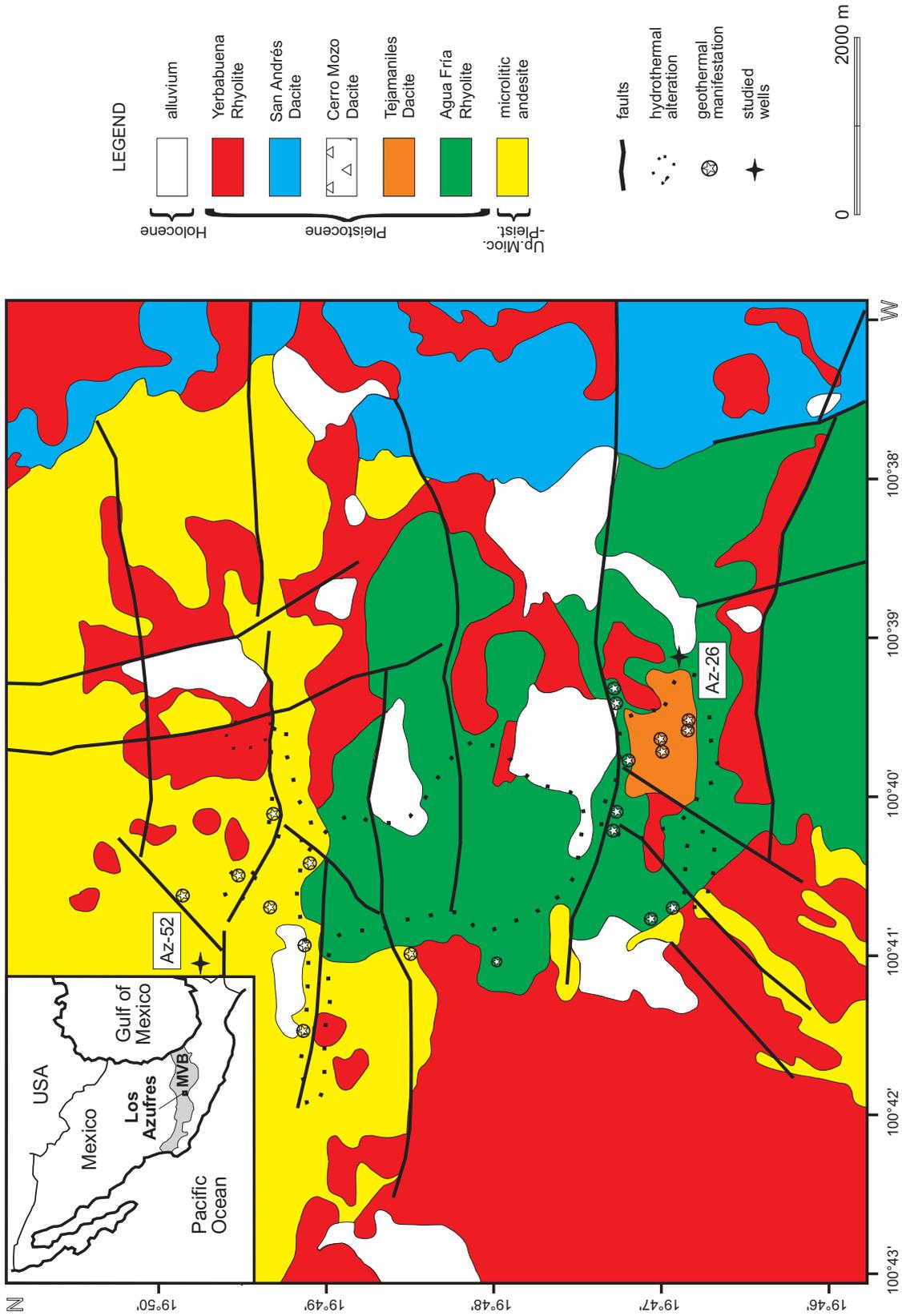
Figure 1. Geological map of the Los Azufres geothermal field (modified after Razo-Montiel *et al.* 1989). The geothermal wells studied in this work and the principal fault systems are shown. MVB– Mexican Volcanic Belt.

lava flows with glassy structures. Advanced alteration, as shown by strong kaolinization and silification, can be observed close to hydrothermal manifestations.

Three different fault systems, which confer secondary permeability to the geological units, can be distinguished in the field (Garduño Monroy 1988; Campos-Enriquez & Garduño-Monroy 1995): NE–SW, E–W and N–S. The E–W system is considered to dominate geothermal fluid circulation. Geothermal manifestations (fumaroles, solfataras, and mudpits), geophysical anomalies and important energy production zones are related to this fault system.

For this work, drill cuttings and cores from different depths of the wells Az-26 and Az-52 were selected (Figure 1). The well Az-26 (1241 m in depth) includes the whole volcanic sequence, presenting an interstratification of rhyolites and dacites (called here felsic rocks) through the upper 500 m of the drilling column, which overlie andesites that extend to the bottom. The well Az-52 (1936 m in depth), though almost completely drilled through andesites (called here mafic rocks), shows a wider range of hydrothermal alteration as well as complex hydrothermal paragenesis (Torres-Alvarado 2002).

Hydrogeochemical Framework

Geothermal fluids in Los Azufres are sodium chloride-rich waters with high CO_2 contents, and pH around 7.5 (Nieva *et al.* 1987; Birkle *et al.* 2001). The Cl content varies between 2000 and 4000 mg/kg. Fluids from Los Azufres show elevated B ($\approx$ 300 mg/kg) as well as low Ca concentrations ($\approx$ 14 mg/kg), compared to other geothermal fluids worldwide (Nicholson 1993). The gas phase composition is relatively homogeneous, with CO_2 up to 90% of the total gas phase and subordinate H_2S, N_2, and NH_3 (Santoyo *et al.* 1991). Reservoir temperatures range up to 320°C, but 240 to 280°C are commonly observed in the field. An approach to full equilibrium conditions for chemical reactions between volcanic host rocks and geothermal fluids is indicated by the location of most well fluids along the full equilibrium line in the Na-K-Mg classification diagram (Giggenbach 1988; Torres-Alvarado 2002).

In contrast to the relatively homogeneous chemical composition of deep geothermal fluids, thermal and cold springs in the Los Azufres area show significant chemical differences. Based on the chemical composition of thermal springs (T= 30–89°C), Ramírez Domínguez *et al.* (1988) recognized four different chemical groups: SO_4^-, Cl^-, and HCO_3^- rich springs, along with a mixed group. All spring samples are classified as immature waters on the Na-K-Mg triangle (Giggenbach 1988), indicating their shallow origin. However, Cl-type spring waters may represent a mixture between deep geothermal fluids and shallower waters (Ramírez Domínguez *et al.* 1988).

The stable isotopic (O and H) composition of springs and geothermal fluids show significant discrepancies as well (Figure 2). Cold springs, HCO_3-rich springs, and most mixed thermal waters show $^{18}O/^{16}O$ ratios between –8 and –10‰ and δ^2H values from –60 to –72‰ close to the local meteoric line, demonstrating their meteoric origin (Figure 2; Ramírez Domínguez *et al.* 1988). However, geothermal fluids show a tendency towards higher $\delta^{18}O$ values (–2 to –6‰), but with D/H ratios similar to local meteoric waters (–61 to –67‰). This positive ^{18}O-shift trend towards heavier oxygen isotopic ratios has been observed in many geothermal systems, interpreted as the result of isotopic exchange at high temperature between fluids and primary rock minerals enriched in ^{18}O (e.g., Gerardo-Abaya *et al.* 2000). The isotopic composition of SO_4-rich waters shows higher $\delta^{18}O$ and δ^2H values (Figure 2). SO_4-rich springs with higher $\delta^{18}O$ and δ^2H values are interpreted as a mixture of shallow meteoric water with H_2S enriched geothermal gases, along with evaporation, as these springs present highest temperatures (up to 89°C; Ramírez Domínguez *et al.* 1988).

More recently, Birkle *et al.* (2001) proposed a different spring classification based on stable isotopes (O, H) and tritium. They distinguished four different spring water types (Figure 2): Type A: high mineralized (Cl, B, and F) spring waters with high δD (–24 to –34‰) and $\delta^{18}O$ (3.4 to 5.6‰) values, indicating the direct exposure of geothermal fluid on the surface. Type B: spring waters with missing ^3H (0 T.U.), quite high δD (–24 to –39‰) and $\delta^{18}O$ values (–1.7 to 5.4‰), along with low Cl-concentrations (16–29 mg/l) and enrichment in SO_4 (640–660
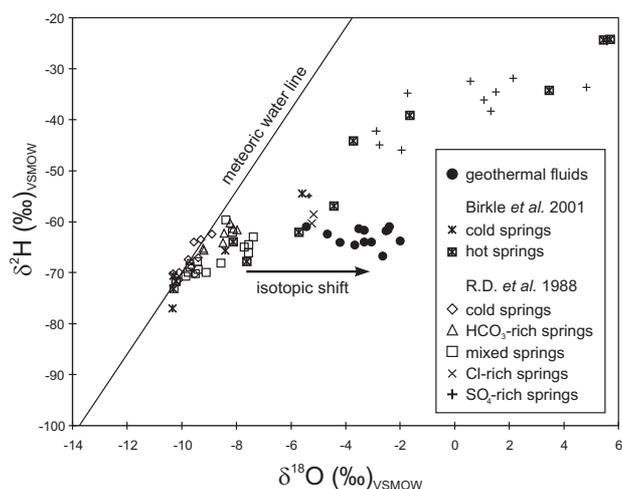
Figure 2. Oxygen and hydrogen isotopic composition of geothermal fluids and some spring waters from the area of Los Azufres. Data for spring waters are from Ramírez Domínguez *et al.* (1988) and Birkle *et al.* (2001). The isotopic composition of geothermal fluids was taken from Ramírez Domínguez *et al.* (1988).

mg/l), reflecting the mixing of geothermal H$_2$S-rich gases with shallow groundwater. Type C: waters characterized by elevated ^{3}H values (5.1–8.3 T.U.), low mineralization rate, and the deviation of the δD (–57 to –62‰) and δ^{18}O (–4.5 to –5.8‰) values from the meteoric water composition, indicating the heating of a shallow aquifer (residence time of more than 10 years) by ascending vapour. Type D: hot springs with δ^{18}O and δD composition close to the meteoric water line and ^{3}H values close to the recent atmospheric composition (3.5–6.0 T.U.), indicating recent, heated meteoric water. The isotopic composition of spring waters and geothermal fluids might be explained by mixing between a meteoric and magmatic component, along with evaporation, which may account for most δ^{18}O- and δ^{2}H-enriched samples (Birkle *et al.* 2001).

Important regional physicochemical differences have been found between the northern and the southern part of Los Azufres. In the northern part (Marítaro zone) geothermal fluids contain a mixture of gases and liquid, with temperatures around 300 to 320°C. In the southern part (Tejamaniles zone), the gas phase generally dominates over the liquid phase, and temperatures are lower than in the north (260–280°C). Regional elevation, permeability, and pressure differences, as well as different boiling rates may account for this zoning (Nieva *et al.* 1987).

Hydrothermal Alteration

Studies of hydrothermal alteration at the Los Azufres geothermal system have been carried out, among others, by Cathelineau *et al.* (1985), González Partida & Barragán (1989), Torres-Alvarado & Satır (1998), and Torres-Alvarado (2002). These studies showed that partial to complete hydrothermal alteration has affected the primary geochemical composition of most host rocks, producing dominantly propylitic mineral assemblages at higher temperatures (deeper zones) and important argillization within lower temperature zones and at the surface.

Systematic mineralogical changes occur with increasing temperature and pressure (increasing depth). The most important alteration assemblages with increasing depth are argillitization/ silicification, zeolite/calcite formation, sericitization/ chloritization, and chloritization/epidotization. Mafic rocks show an alteration succession, directly related to the crystallization temperature of the primary mineral (Torres-Alvarado 2002). Olivine alters rapidly, followed by augite, hornblende, and biotite. These minerals are commonly altered to antigorite, chlorite, calcite, hematite, quartz, and to a lesser extent, amphibole (tremolite). Plagioclase alteration can be divided into three different types, depending on the temperature. The first alteration products are fine-grained phyllosilicates (sericite, muscovite, clay minerals, and chlorite), followed by carbonates. At higher temperatures (> 180°C), plagioclase is preferably altered to zeolite and epidote. Vesicles and fractures are filled mainly by chlorite, quartz, chalcedony, and amorphous silica, as well as calcite and epidote. Zeolites (stilbite, heulandite, laumontite, and wairakite), hematite, pyrite, and sericite can also be observed replacing the primary matrix. Amphiboles, prehnite, and garnet are sporadically present, indicating temperatures > 250°C.

Samples and Analytical Procedures

In the present study, 43 whole rock samples (Table 1) and 44 hydrothermal mineral separates from different depths of wells Az-26 and Az-52 (calcite, quartz, epidote, and chlorite; Tables 2 & 3) were analyzed for their stable isotope (O, H, C) composition. The studied minerals were mainly present as fracture- or

Table 1. O and H-isotope data for hydrothermally altered rocks from the Los Azufres geothermal reservoir, Mexico. Sample name indicates the well number followed by the approximate depth in meters from which the sample was recovered.

Sample	Rock type	$SiO_{2(adj)}$ (wt%)	T (°C)	Alteration (%)	LOI (wt%)	$\delta^{18}O$ (‰)$_{VSMOW}$	W/R$_{closed}$	W/R$_{open}$	δ^2H (‰)$_{VSMOW}$
26-20	R	75.71	38	0	2.02	9.8*	0.13	0.12	–
26-60	D	67.45	38	0	5.54	10.5	0.28	0.25	–77
26-120	R	73.13	38	11	0.89	9.2*	0.03	0.03	–140
26-220	R	75.18	38	10	1.20	8.9	–	–	–122
26-280	R	75.98	38	10	1.72	9.2*	0.04	0.03	–127
26-340	R	74.80	38	15	0.45	8.5*	–	–	–136
26-380	R	77.02	38	15	4.50	16.7	–	–	–
26-440	R	76.56	52	31	2.13	15.1*	–	–	–76
26-480	R	78.01	58	15	1.58	12.1	9.30	2.33	–77
26-540	D	64.00	78	33	4.74	10.5*	–	–	–79
26-620	BA	53.79	90	22	4.52	7.6*	0.22	0.20	–93
26-700	D	63.29	110	34	5.17	9.0	–	–	–92
26-740	D	63.00	132	78	4.44	5.4	0.88	0.63	–94
26-780	D	63.23	140	66	5.37	6.3	0.38	0.32	–
26-800	D	63.05	132	73	6.83	4.2	2.13	1.14	–72
26-840	D	63.07	140	73	6.13	5.9	0.51	0.41	–88
26-940	A	59.48	150	75	9.03	6.7	0.23	0.20	–90
26-1000	D	68.07	177	80	5.38	7.7	0.03	0.03	–88
26-1080	D	65.34	180	73	5.32	5.6	0.38	0.32	–
26-1160	BA	55.88	180	58	6.06	4.7	0.63	0.49	–92
52-60	A	62.07	60	30	1.31	9.9	–	–	–
52-100	A	62.57	77	40	2.08	10.6	–	–	–112
52-220	A	62.24	135	15	2.44	9.7	–	–	–120
52-300	BA	56.10	135	25	3.96	6.6	0.33	0.28	–
52-380	BA	54.95	175	25	4.47	4.9	0.60	0.47	–
52-420	A	62.87	182	30	4.02	4.5	0.67	0.51	–111
52-520	D	69.48	197	50	1.68	6.2*	0.44	0.36	–
52-600	R	70.87	208	60	1.23	5.1	0.68	0.52	–103
52-720	A	60.13	210	25	2.89	4.4	0.91	0.65	–92
52-820	A	58.81	214	25	4.07	4.0	0.64	0.50	–
52-940	A	61.37	220	35	3.32	4.7	0.47	0.38	–111
52-1120	A	62.77	226	20	3.08	5.1	0.38	0.32	–
52-1180	A	62.03	230	30	2.20	3.2	0.81	0.59	–91
52-1220	A	62.53	232	15	2.33	2.9	0.87	0.63	–
52-1320	TA, ben	61.27	238	30	1.58	3.5	0.68	0.52	–99
52-1400	A	61.14	240	35	2.55	2.3	1.03	0.71	–
52-1480	A	62.68	242	10	2.11	5.3	0.32	0.28	–88
52-1600	D	63.39	247	30	1.90	3.2	0.73	0.55	–
52-1640	TA, ben	61.35	250	35	2.08	2.2	1.02	0.70	–
52-1680	D	64.79	253	20	2.18	2.7	0.84	0.61	–94
52-1780	A	62.91	258	30	2.02	6.6	0.14	0.13	–
52-1860	A	62.83	260	30	2.11	4.5	0.41	0.35	–95
52-1920	A	62.90	260	20	1.78	4.5	0.42	0.35	–

$SiO_{2(adj)}$ concentrations are from Torres-Alvarado & Satır (1998), adjusted to a 100% anhydrous basis. Rock types are named after the TAS classification (total alkalis vs silica; Le Bas *et al.* 1986) calculated using the SINCLAS computer program (Verma *et al.* 2002). A– andesite; BA– basaltic andesite; D– dacite; R– rhyolite; TA, ben– trachyandesite, benmoreite. T– in-situ measured temperature. Alteration is the amount of secondary minerals expressed as a percentage of the total area observed under a petrographical microscope. LOI = loss on ignition, after Torres-Alvarado & Satır (1998). Data marked with an asterisk (*) were taken from Verma *et al.* (2005). W/R ratios are intentionally reported with two digits for comparison purposes. See text for explanation related to the W/R ratios calculations.

vesicle-fills and, in some cases, as complete fragments from drill cuttings. Minerals were separated by mechanical methods, heavy fluids, and finally by hand picking.

Oxygen isotope analyses for whole rock and silicate samples were carried out by reacting samples with BrF_5 in externally heated nickel reaction vessels (Clayton & Mayeda 1963), and converting O_2 to CO_2 gas by reaction with heated carbon rods. Whole rock samples for H isotope analyses were prepared following the methodology proposed by Venneman & O'Neil (1993). For this, rock samples were heated in a vacuum at 150°C for 4 hours, and then fused to drive off water, which was sealed in a quartz tube with Zn metal. H_2 gas generated during sample fusion was converted to H_2O by reaction with hot CuO, and total water was reacted with Zn for 10 minutes at 500°C to generate hydrogen gas for mass spectrometric analysis. Oxygen and carbon isotope analyses of calcite were obtained by the standard phosphoric acid method (McCrea 1950).

O, H, and C isotope ratios were measured using a Finnigan MAT 252 mass spectrometer at the Laboratory for Isotope Geochemistry of the University of Tübingen, Germany. A mean $\delta^{18}O$ value of 9.6‰ (±0.2, 1s) was measured for the NBS28 quartz standard, compared to the reported standard value of 9.58‰. Uncertainties for $\delta^{13}C$ were better than ±0.2‰ (1s). Absolute reproducibility for whole rock δD values was generally about ±2‰ (1s).

Isotope ratios are reported in the notation (Tables 1 to 3), where $\delta= [(R_{sample}/R_{standard})-1]\times1000$, and R represents the isotopic ratios $^{18}O/^{16}O$, $^{13}C/^{12}C$ or $^{2}H/H$. Oxygen and hydrogen isotope ratios are reported relative to VSMOW (Vienna Standard Mean Ocean Water). Carbon isotope ratios are reported relative to PDB (Peedee belemnite) standard.

In-situ temperatures for each sample (Tables 1 to 3) were obtained from Az-26 and Az-52 drilling reports (Rodríguez Salazar & Garfias 1981; Huitrón Esquivel *et al.* 1987), derived by linear vertical interpolation of geophysical measurements obtained two months after drilling. Although the temperatures are considered to be accurate within ±10°C, the time interval between drilling and temperature measurement could be insufficient for achieving thermal stability.

Results and Discussion

The $\delta^{18}O$, $\delta^{13}C$, and $\delta^{2}H$ values obtained for whole rock samples and hydrothermal minerals are reported in Tables 1 to 3, along with in-situ temperatures for each sample.
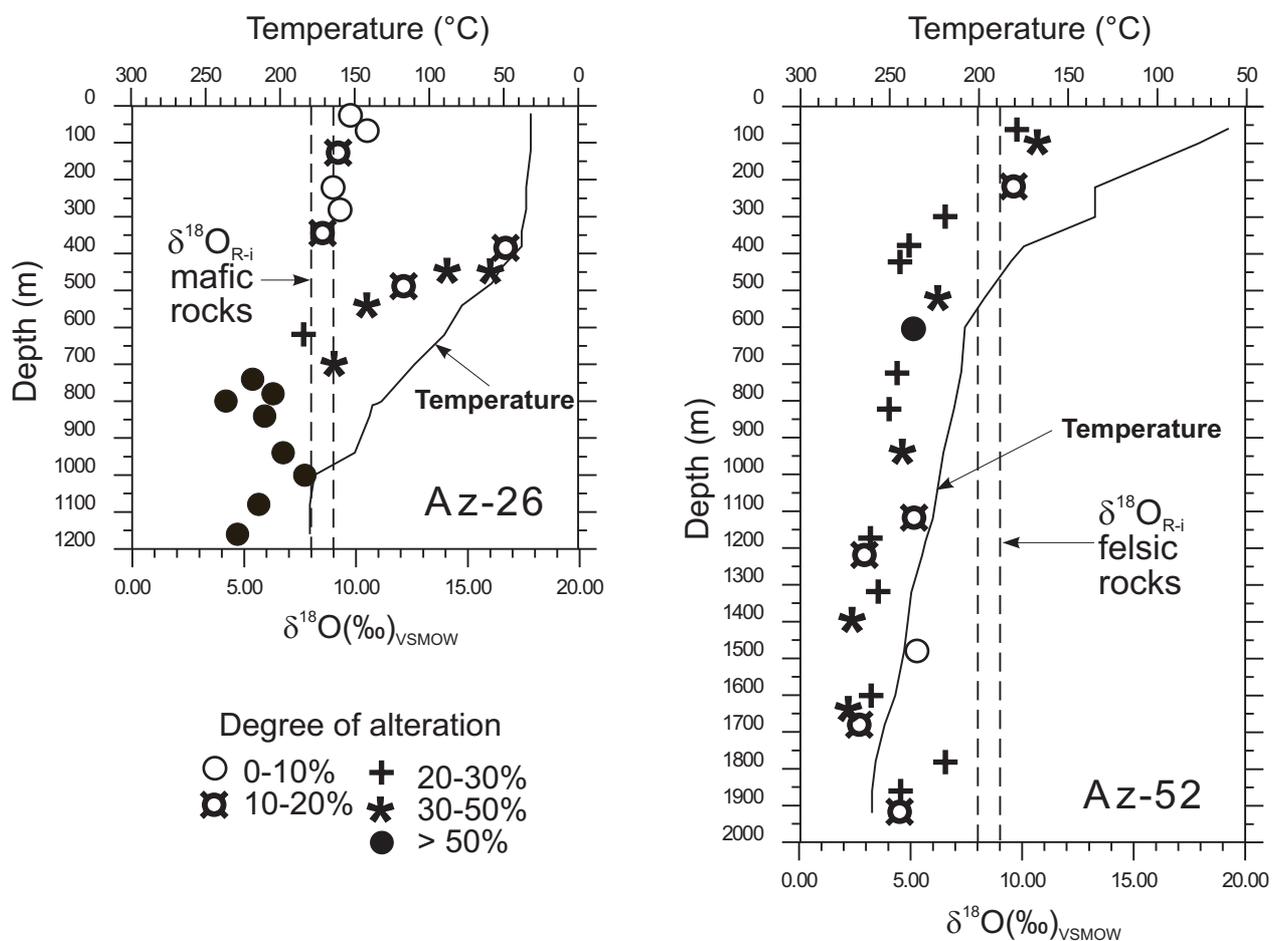
Whole Rock Samples

The analyzed whole rock samples showed differing extents of hydrothermal alteration, with a variable degree of hydrothermal alteration relative to primary minerals (quantified using petrographical techniques) from 0 to 80% (Table 1). Figure 3a shows the relation between the volumetric amount of hydrothermal minerals and the oxygen isotopic composition of altered whole rock samples. For comparison, loss on ignition (LOI, wt%) is also presented in Table 1 and Figure 3b, considering that water content in an altered rock might be correlated to the alteration degree, as hydrothermal minerals such as clays and micas contain water molecules in their atomic structure. Unexpectedly, there is no clear relation between the amount of alteration or LOI and the $\delta^{18}O$ values obtained for altered rock samples from the Los Azufres geothermal field. Only in some samples from well Az-26 does there seem to be a negative tendency between $\delta^{18}O$ values and the amount of alteration or LOI, although these data show significant dispersion. The lack of correlation between $\delta^{18}O$ values and the amount of alteration or LOI may indicate that the hydrothermal alteration of the rocks does not completely account for the final oxygen isotopic composition of altered rocks at Los Azufres.

The relation between depth (and consequently in-situ temperatures) and the $\delta^{18}O$ values analyzed for whole rock samples from wells Az-26 and Az-52 is given in Figure 4. The $\delta^{18}O$ values for rock samples range from +2.2‰ to +16.7‰ (Table 1). For well Az-52 (Figure 4, right), a slight depletion of $\delta^{18}O$ values from the surface to a depth of 500 m is followed by a relatively homogenous distribution of $\delta^{18}O$ values of reservoir rocks, showing a continuous correlation with temperature. However, isotopic and hydrothermal trends allow three reservoir zones for the Az-26 well to be distinguished (Figure 4, left):
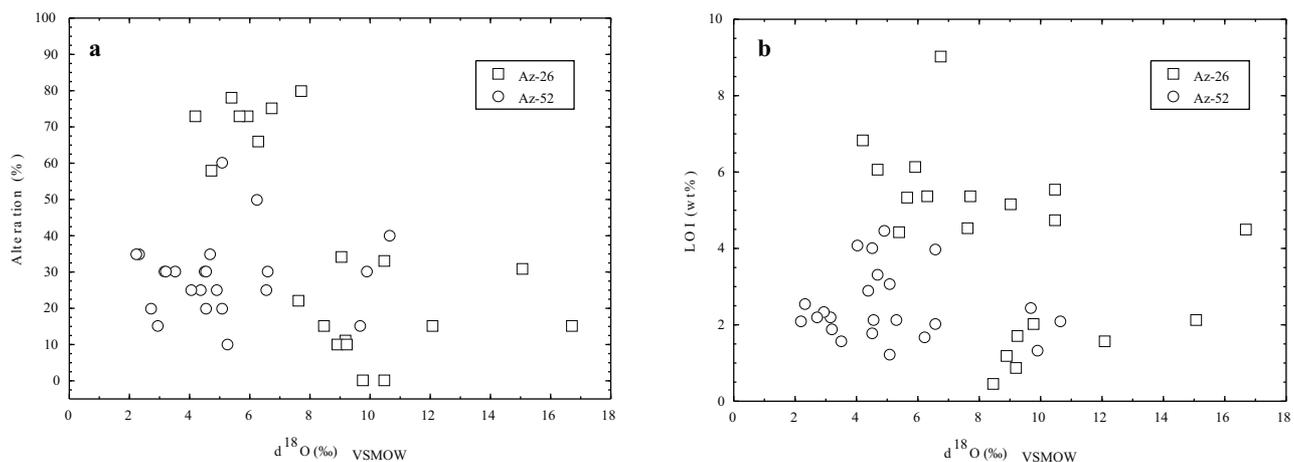
Figure 3. **(a)** Relation between the amount of alteration minerals (%) and $\delta^{18}O$ values of whole rock samples; **(b)** relation between the loss on ignition (LOI, wt%) and $\delta^{18}O$ values of whole rock samples.

Figure 4. $\delta^{18}O$ values of whole rock samples vs depth and in-situ temperatures for the wells Az-26 and Az-52. The amount of alteration minerals (%) is also represented by different symbols.

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(i) From the surface to 400 m depth, $\delta^{18}O$ values for Az-26 host rocks are close to +9‰, representing the unaltered primary composition of the felsic caprock.

(ii) Beginning with an abrupt shift of +17‰, a second zone from 400 to 700 m shows increasing hydrothermal alteration (from 0 to 50%) and decreasing $\delta^{18}O$ values due to increasing temperature conditions towards the upper part of the geothermal reservoir (Birkle *et al.* 2001).

(iii) From the upper part of the reservoir (700 m depth) towards the reservoir bottom (1200 m), stable isotope values are becoming homogenized ($\approx$ +4‰), in continuous correlation with increasing temperature. Comparing the vertical trend of $\delta^{18}O$ values in geothermal waters from different wells in Los Azufres to the host rock composition from Az-26, the approaching values between both phases in the main production zone suggest a maximum intensity of water-rock interaction process at a depth of 1200 m (Birkle *et al.* 2001; Birkle 1998). The closest $\delta^{18}O$ values of −2.0‰ and +4.7‰ for the fluid and rock phase, respectively, suggest maximum water-rock interaction process at this depth with hydrothermal alteration degrees above 50%. Below the reservoir zone, homogenous $\delta^{18}O$-values for geothermal fluids from 1300 to 2250 m depth indicate that increasing temperature conditions do not exceed the maximum degree of water-rock interaction, reached at a depth of 1200 m in the main reservoir zone (Birkle *et al.* 2001).

Different symbols are used in Figure 4 to investigate the relation between the relative amount of hydrothermal alteration and the oxygen isotope ratios. Whereas the rock column from the well Az-52 in the northern Los Azufres reservoir zone (Marítaro) does not show a clear relation between $\delta^{18}O$ values and percentage of hydrothermal alteration, deeper samples from well Az-26 from the southern Tejamaniles zone seem to show a correlation between lower oxygen isotopes ratios, higher amounts of alteration, and higher temperatures.

Due to the hydrothermal alteration, which has to some extent affected all samples, the initial $\delta^{18}O$ value of the investigated rocks cannot be directly measured. However, using values obtained from the least altered samples and from observed trends in Figure 4, we can assume an initial $\delta^{18}O \approx +8$ ‰ for mafic rocks and $\approx +9$ ‰ for felsic ones. These values correspond well to fresh rocks outcropping at Los Azufres (Verma *et al.* 2005) and for unaltered material from other volcanic systems (Hoefs 1980). Assuming this range for initial $\delta^{18}O$ values for volcanic rocks at Los Azufres, processes controlling isotope exchange appear to be basically temperature dependent. In lower temperature regions (up to $\approx$ 90°C or $\approx$ 600 m depth for Az-26, and $\approx$ 300 m depth for Az-52) isotope exchange between rock and thermal fluids causes a shift to heavier oxygen isotope ratios. At higher temperatures the isotope exchange produces lighter $\delta^{18}O$ values for the rock phase.

In order to further examine this hypothesis, mass balance water/rock ratios (W/R) were calculated on the basis of molar oxygen for individual whole rock samples using the equation of Taylor (1979), assuming open and closed systems:

$$W/R_{closed} = (\delta^{18}O_{R-f} - \delta^{18}O_{R-i}) / (\delta^{18}O_{W-i} - \delta^{18}O_{R-f})$$
$$W/R_{open} = \ln[\ (\delta^{18}O_{W-i} + \Delta - \delta^{18}O_{R-i}) /$$
$$(\delta^{18}O_{W-i} - \delta^{18}O_{R-f} + \Delta)\ ]$$

where the subscripts i and f refer to the initial and final isotope ratios, respectively, of water (W) and rock (R), and Δ is the water-rock isotope fractionation for individual in-situ temperatures. Δ is assumed to be approximately equal to that of plagioclase-water, since plagioclase is the most abundant mineral in fresh rocks. The plagioclase-water fractionation factors of O'Neil & Taylor (1967) were used for these calculations, using the average plagioclase composition of the felsic and mafic rocks in the field (An$_{25}$ and An$_{65}$, respectively; Torres-Alvarado 2002). The present isotopic composition of the local meteoric water (−9‰) was used as $\delta^{18}O_{W-i}$ and +9‰ and +8‰ as $\delta^{18}O_{R-i}$ for felsic and mafic rocks, respectively.

The calculated W/R_{closed} and W/R_{open} ratios for individual whole rock samples are presented in Table 1

and Figure 5. Theoretical W/R curves were calculated for different temperatures using the same initial rock and water $\delta^{18}O$ values as for the analysed samples and are presented in Figure 5 as well. The water/rock data show that water-rock oxygen isotope interaction can be satisfactorily estimated by exchange between meteoric fluid and rocks at in-situ temperatures. W/R ratios for open and closed systems are broadly similar (mostly < 1.0), even though W/R ratios under closed system assumptions are moderately higher (Table 1). For felsic rocks, W/R ratios range from 0.03 to 9.30 (mean value= 1.08) and from 0.03 to 2.33 (mean value= 0.47) for closed (W/R_{closed}) and open systems (W/R_{open}), respectively. W/R ratios for mafic rocks
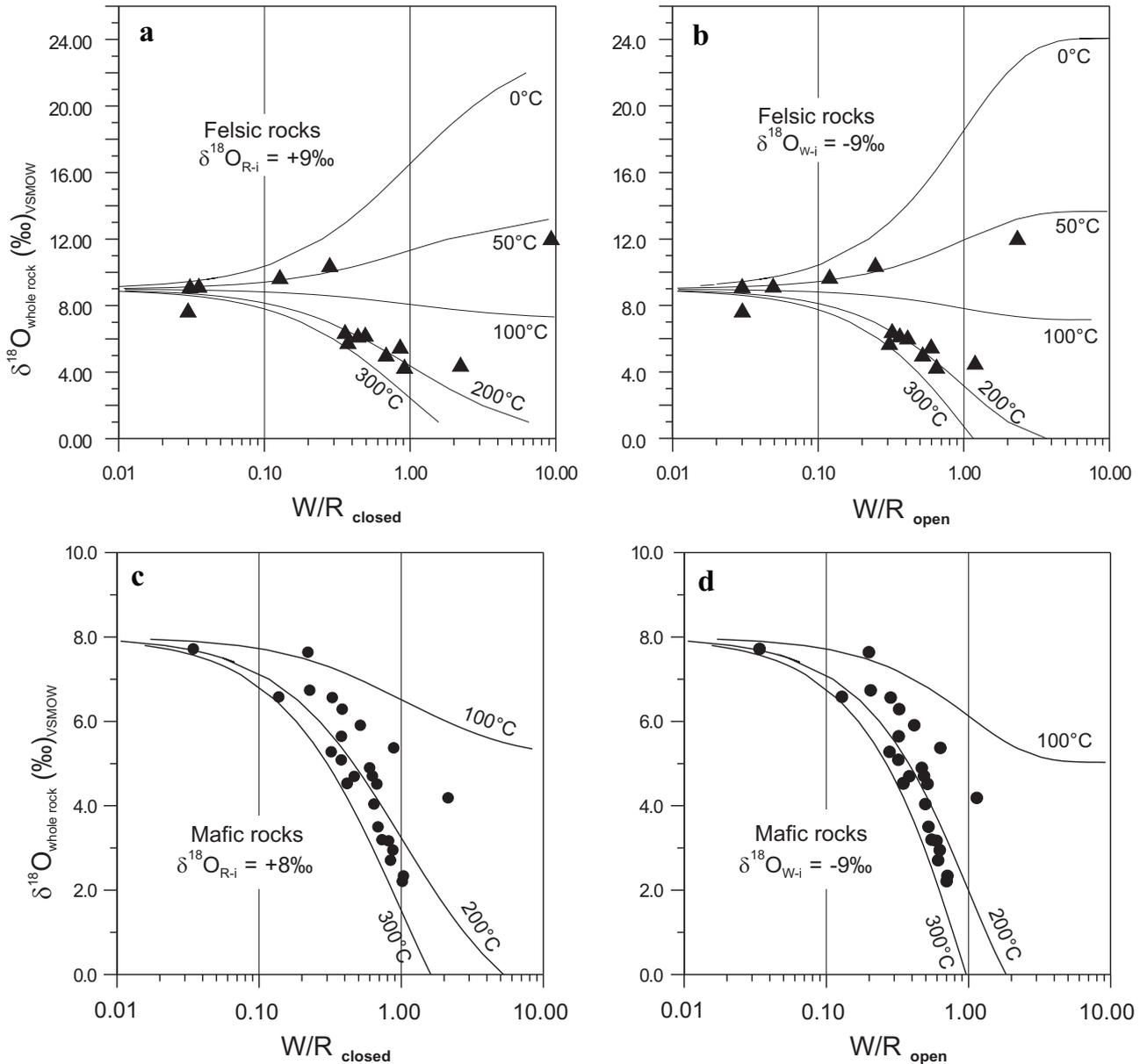

Figure 5. Water/rock ratios calculated from whole rock $\delta^{18}O$ values. The plagioclase-water fractionation of O'Neil & Taylor (1967) was used to approximate the rock-water fractionation. Results are divided in felsic **(a, b)** and mafic **(c, d)** rocks with an assumed value of −9‰ for $\delta^{18}O_{W-i}$. Theoretical W/R ratios for different temperature conditions under identical system assumptions are represented by continuous lines.

vary between 0.14 and 1.03 (mean value= 0.62), and between 0.13 and 0.71 (mean value= 0.47) for closed (W/R$_{closed}$) and open systems (W/R$_{open}$), respectively.

Figure 5a, b shows that felsic rocks exhibit two different trends. Some samples show a positive correlation between δ^{18}O$_{R-f}$ and W/R, very close to the theoretical curve for 50°C, while other rocks show a negative correlation, close to the theoretical curves for 200 and 300°C. Since the W/R ratios of these felsic rocks are of the same order of magnitude as those of mafic rocks (Figure 5c, d), temperature is considered to represent the most important factor controlling the final oxygen isotopic composition of the rocks. Furthermore, plagioclase-water fractionation provides a very useful approximation to describe the water-rock oxygen isotope exchange in Los Azufres at present field temperatures. These results are similar to those reported by Alt & Bach (2006) for hydrothermally altered oceanic crust.

Figure 6 shows the relationship between δ^{18}O and δ^{2}H values for whole rock samples from Los Azufres. δ^{2}H values range between –72 and –140‰, although most rock samples presented relatively homogeneous δ^{2}H values around –80 and –100‰ (Table 1, Figure 6). δ^{18}O values show a bigger dispersion product of the oxygen shift due to water-rock interaction. Interestingly, the lowest δ^{2}H values are present in the uppermost samples of wells Az-26 and Az-52 (Figure 6), probably demonstrating the importance of argillization in the shallowest parts of the geothermal
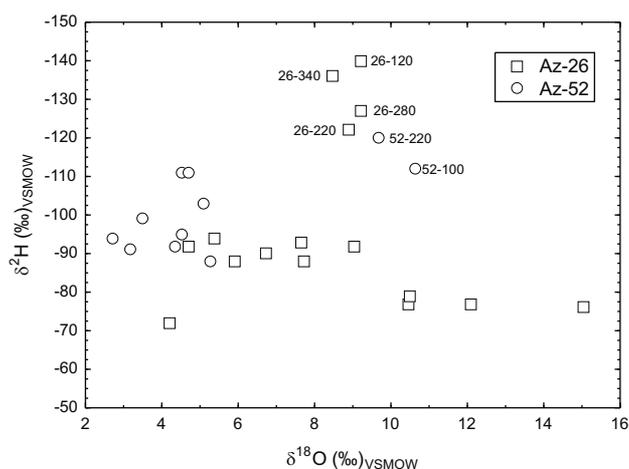
system, clearly present in the surroundings of well Az-26 (Rodríguez Salazar & Garfias 1981).

Calcite

The δ^{18}O values of calcite separates are presented in Table 2 and correlated with in-situ temperatures in Figure 7. δ^{18}O values for calcite range from +3.4 to +21.9‰. For comparison, two grey-shaded areas represent the calculated δ^{18}O values for calcite in equilibrium with water with the present isotopic composition of geothermal fluids (grey-shaded area 'a' in Figure 7) and present meteoric water (grey-shaded area 'b' in Figure 7), according to the calcite-water fractionation factors of O'Neil *et al.* (1969).

Most of the analyzed calcites seem to be in or near equilibrium with the present isotopic composition of local meteoric water or with the isotopic composition of thermal fluid at in-situ temperatures. This agrees with other studies showing that carbonate minerals tend to equilibrate readily with fluids in regions with relatively high water/rock ratios and temperatures (Clayton *et al.* 1968; Clayton & Steiner 1975; Williams & Elders 1984; Sturchio *et al.* 1990).

Some calcite separates appear to be enriched in δ^{18}O and consequently seem to be equilibrated with a thermal fluid enriched in ^{18}O. These samples correspond to some of the deepest samples in well Az-52 (Figure 7) with very low W/R ratios (Table 1). Both ^{18}O-enriched fluids and low W/R ratios (very low permeability) may explain the isotopic disequilibrium of these samples with present thermal water. In contrast, calcite samples with the lowest δ^{18}O values coincide with the highest W/R ratios (Table 1, Figure 7), indicating that oxygen isotopic composition of calcite separates might constitute a tool for identifying areas of high permeability in the geothermal system of Los Azufres. Although this hypothesis needs more data to be validated in other areas of the field, this possibility could have important repercussions for geothermal exploration purposes.

Quartz

The δ^{18}O values of quartz separates (Table 3) are plotted in relation to in-situ temperatures in Figure 8. δ^{18}O values from analyzed quartz samples range

Figure 6. δ^{18}O vs δ^{2}H values of whole rock samples for the wells Az-26 and Az-52.

Table 2. O and C-isotope data for hydrothermal calcite samples from the Los Azufres geothermal reservoir, Mexico. Sample name indicates the well number followed by the approximate depth in metres from which the sample was recovered.

Sample	Mineral	T (°C)	$\delta^{18}O$ (‰)$_{VSMOW}$	$\delta^{18}O_{Wi}$ (‰)$_{VSMOW}$	$\delta^{13}C$ (‰)$_{PDB}$
26–60	Calcite	40	16.4*	−8.6	−13.5
26–120	Calcite	40	20.3	−4.7	−6.9
26–220	Calcite	40	21.9*	−3.1	−3.7
26–340	Calcite	40	20.7*	−4.3	−7.8
26–380	Calcite	40	10.2	−14.7	−5.5
26–440	Calcite	50	17.7*	−5.6	−3.7
26–480	Calcite	60	15.3*	−6.4	−4.8
26–540	Calcite	80	13.8*	−5.2	−3.6
26–600	Calcite	90	5.6*	−12.1	−8.3
26–700	Calcite	115	5.8*	−9.3	−7.4
26–754	Calcite	120	3.9*	−10.6	−7.9
26–802	Calcite	140	3.4*	−9.5	−7.2
26–900	Calcite	145	7.1*	−5.4	−7.4
26–1000	Calcite	160	11.9	1.6	−5.4
26–1080	Calcite	170	5.0*	−5.1	−25.2
26–1160	Calcite	180	4.9	−5.3	−25.2
52–258	Calcite	135	8.6*	−4.7	−5.5
52–380	Calcite	175	7.5*	−3.0	−7.1
52–660	Calcite	210	3.4*	−5.1	−7.5
52–720	Calcite	212	4.6*	−3.9	−7.3
52–820	Calcite	215	7.2*	−1.1	−5.9
52–1100	Calcite	225	3.9*	−3.8	−7.4
52–1220	Calcite	230	12.1	4.5	−7.30
52–1480	Calcite	245	20.9	13.9	−14.2
52–1640	Calcite	250	18.5	11.8	−10.7
52–1780	Calcite	253	19.5	12.8	−12.7
52–1920	Calcite	260	19.4	13.0	−12.3

T– in-situ measured temperature. $\delta^{18}O_{Wi}$ is the oxygen isotopic composition of the water from which the calcite crystals have presumably been precipitated, assuming the fractionation factors from O'Neil *et al.* (1969). Data marked with an asterisk (*) were taken from Torres-Alvarado (2002).

from +3.9‰ to +20.2‰. For comparison, two shaded bars represent the areas with a theoretical isotopic equilibrium of quartz samples with present geothermal fluids (dark grey-shaded area 'a') or with present meteoric water (light grey-shaded area 'b'). For these calculations an extrapolation of the 200 to 500°C quartz-water fractionation factors of Clayton *et al.* (1972) was applied.

Three of the analyzed specimens appear to be in or near equilibrium with the present isotopic composition of local meteoric water and three with

the isotopic composition of present geothermal fluids. The remaining samples (4 quartz separates) are not in equilibrium, suggesting that changes in temperature and/or $\delta^{18}O$ of the water have occurred since quartz deposition. As the samples in disequilibrium are from the deepest (and thus from the hottest) zones of well Az-52, the measured $\delta^{18}O$ values could not be explained by an entirely temperature dependent isotopic exchange. This could indicate the presence of a geothermal fluid enriched in ^{18}O relative to present thermal waters for the deepest zones of well Az-52 at
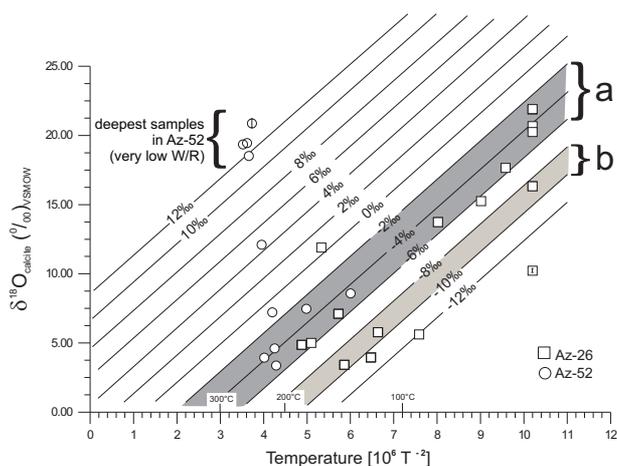
Figure 7. $\delta^{18}O$ values of analyzed calcite separates vs in-situ temperatures. The grey bars represent areas of isotopic equilibrium between calcite and present geothermal fluids (a: $\delta^{18}O \approx -2$ to $-6‰$) and meteoric water (b: $\delta^{18}O \approx -8$ to $-10‰$), considering the calcite-water fractionation factors from O'Neil *et al.* (1969).

the time of quartz precipitation. The corresponding range in $\delta^{18}O_{Wi}$ for these quartz separates would have been $-2.3‰$ to $+4.3‰$, $\approx 4‰$ higher than present thermal water, indicating that present geothermal fluids sampled at the surface of Los Azufres are in reality a mixture of fluids of different chemical and isotopic compositions contained in different units of the thick andesitic aquifer.

According to Birkle *et al.* (2001), hydrological mass balance calculations, extreme negative $\delta^{13}C$-values of formation water (see section 4.5 for $\delta^{13}C$ results), and issues from radioactive isotopes suggest recharge of the geothermal reservoir with meteoric water during the Late Pleistocene/Early Holocene, causing the mixing of different water types with a heterogeneous stratification of aquifer zones.

Chlorite and Epidote

$\delta^{18}O$ values obtained from chlorite and epidote separates are presented in Table 3, along with measured in situ-temperatures and calculated $\delta^{18}O_{Wi}$, considering the fractionation factors of Marumo *et al.* (1980) for chlorite-water, and Matthews *et al.* (1983) for zoisite-water. Due to the small crystal size and the amount of these minerals in the studied core material, only a few samples were analyzed. Unlike

Table 3. O-isotope data for hydrothermal minerals from the Los Azufres geothermal reservoir, Mexico. Sample name indicates the well number, followed by the approximate depth in meters from which the sample was recovered.

Sample	Mineral	T (°C)	$\delta^{18}O$ (‰)$_{VSMOW}$	$\delta^{18}O_{Wi}$ (‰)$_{VSMOW}$
26-600	Quartz	90	11.4*	−10.8
26-600	Epidote	90	2.0	−14.7
26-802	Quartz	140	8.0*	−8.4
26-802	Chlorite	140	6.9	5.9
26-900	Quartz	145	20.2*	4.3
26-1000	Quartz	160	8.4	−5.0
26-1000	Chlorite	160	7.1	6.1
52-258	Quartz	135	9.0*	−7.8
52-660	Quartz	210	8.7*	−2.4
52-950	Quartz	220	3.9*	−6.6
52-950	Epidote	220	2.8	−7.5
52-1100	Quartz	226	8.2*	−2.0
52-1100	Epidote	226	0.7	−9.5
52-1392	Quartz	240	11.1*	1.7
52-1392	Epidote	240	3.7	−6.1
52-1720	Quartz	250	8.8*	−0.1
52-1720	Epidote	250	6.5	−3.0

T− in-situ measured temperature. $\delta^{18}O_{Wi}$ the oxygen isotopic composition of the water from which the calcite crystals have presumably been precipitated, assuming the fractionation factors from Clayton *et al.* (1972) for quartz-water, Mathews *et al.* (1983) for zoisite-water, and Marumo *et al.* (1980) for chlorite-water. Data marked with an asterisk (*) were taken from Torres-Alvarado (2002).

the results from calcite and quartz separates, data obtained from chlorite and epidote samples show an extensive dispersion.

Chlorite $\delta^{18}O$ values range from $+6.9$ to $+7.1‰$, which correspond to a $\delta^{18}O_{Wi}$ value of $+5.9$ to $+6.1‰$ (assuming equilibrium conditions at in-situ temperatures). These calculated $\delta^{18}O_{Wi}$ do not correspond to present meteoric or geothermal waters at Los Azufres.
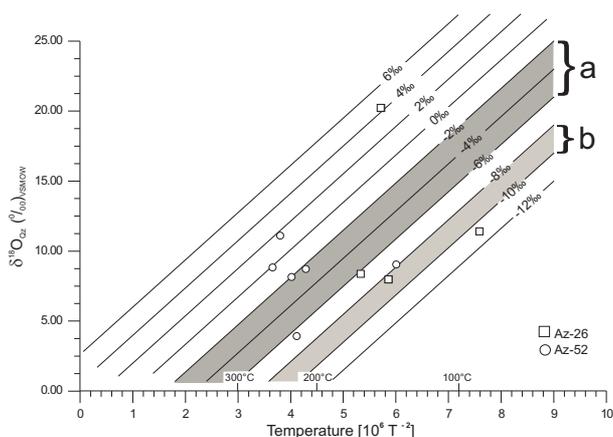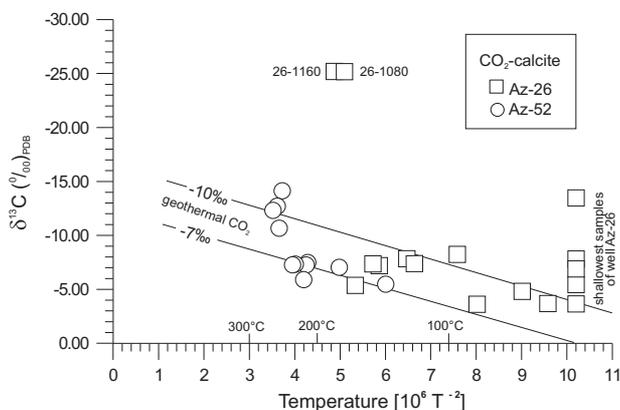
Figure 8. $\delta^{18}O$ values of analyzed quartz separates vs in-situ temperatures. The grey bars reflect areas of isotopic equilibrium between quartz and current geothermal fluids (a: $\delta^{18}O \approx -2$ to $-6‰$) and meteoric water (b: $\delta^{18}O \approx -8$ to $-10‰$), assuming the quartz-water fractionation factors of Clayton et al. (1972).

Figure 9. $\delta^{13}C$ values of analyzed calcite separates vs in-situ temperatures. The inclined bars represent the areas of isotopic equilibrium between calcite and present geothermal CO_2 ($\delta^{13}C \approx -7$ to $-10‰$), considering the calcite-CO_2 fractionation factors from Bottinga (1969).

Epidote crystals were difficult to separate, since intergrowths with quartz are common. Five samples were analyzed for their $\delta^{18}O$ values, ranging from $+0.7$ to $+6.5‰$. This isotopic composition would represent a $\delta^{18}O_{Wi}$ value from -15 to $-3.0‰$, assuming equilibrium at in-situ temperatures. However, using the fractionation factors of Mathews et al. (1983) for zoisite-quartz, the calculated crystallization temperatures for three samples are on average 30°C lower than present in-situ temperatures. Considering the accuracy of in-situ temperatures, these results may indicate isotopic equilibrium between epidote and quartz at the sampling depths in Los Azufres, emphasizing the importance of this common mineral paragenesis.

$\delta^{13}C$ Results

Carbon isotopic compositions of calcite separates are presented and plotted against in-situ temperature in Figure 9. $\delta^{13}C$ values are negative, ranging from -25.2 to $-3.7‰$.

Unfortunately, in Los Azufres not all $\delta^{13}C$ values of the dissolved carbon species have been characterized. Tabaco Chimal (1990) analyzed the $\delta^{13}C$ composition of CO_2 dissolved in the geothermal fluids from Los Azufres, reporting values between -10 and $-7.2‰$ relative to PDB. Figure 9 shows $\delta^{13}C$

values for calcite separates in comparison with the calculated equilibrium area between calcite and the isotopic composition of CO_2 in Los Azufres (values from Tabaco Chimal 1990), using the fractionation factors proposed by Bottinga (1969). Most analyzed samples fall close to or inside the area of isotopic equilibrium with geothermal CO_2. Outside this area are the uppermost samples from well Az-26, which show the lowest temperatures. As these samples were taken from felsic, rather impermeable volcanic rocks, their $\delta^{13}C$ values would indicate that the amount of CO_2 in this volcanic unit was not enough to reach isotopic equilibrium. However, even more negative $\delta^{13}C$ values from -5 to $-20‰$ for inorganic carbon in geothermal fluids, as reported by Birkle et al. (2001), suggest equilibrium conditions for most of the reservoir host rocks.

Slightly elevated $\delta^{13}C$ values for magmatic $CO_2 -5$ to $-8‰$; Taylor 1986) and the lack of organic matter throughout the lithological reservoir column (i.e. carbonate sediments) exclude both environments as potential sources for ^{13}C depletion. Therefore, the origin of extreme negative $\delta^{13}C$ values is explained by an organic input into the geothermal reservoir by meteoric water, probably originating from recharge during the Late Pleistocene–Early Holocene glacial period (Birkle et al. 2001).

Conclusions

Stable isotopes (O, H, C) are important tools for investigating the physico-chemical characteristics of geothermal systems.

Temperature represents the most significant factor controlling the $\delta^{18}O$ signatures of whole rock samples from wells Az-26 and Az-52 at the Los Azufres geothermal field, suggested by a parallel trend of $\delta^{18}O$ with temperature along both profiles. Water/rock ratios from whole rock samples show that the degree of water-rock interaction can be estimated by the isotopic exchange between present geothermal fluids and the volcanic rocks in Los Azufres, at current in-situ temperatures. Two alteration zones, controlled by temperature can be differentiated: (1) T < 90°C, causing a $\delta^{18}O_{rock}$ shift to heavier values, and (2) T > 90°C, shifting the $\delta^{18}O_{rock}$ to lighter values, governed by oxygen exchange with plagioclase.

Most of the analysed mineral samples (especially calcite) showed isotopic equilibrium with present thermal or meteoric water under in-situ temperatures. Some quartz samples are significantly enriched in ^{18}O relative to present thermal water, indicating a complex reservoir structure with a mixture of fluids with different chemical and isotopic characteristics in different lithological units.

A homogeneous degree of hydrothermal alteration above 50% and approaching $\delta^{18}O$ values for whole rock and water phases at the main geothermal production zone, as well as isotopic equilibrium conditions for most mineral phases indicate an advanced stage of water-rock alteration in the Los Azufres reservoir.

Acknowledgements

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