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THE OCCURRENCE OF CO_2-ENRICHED FLUIDS IN ACTIVE GEOTHERMAL SYSTEMS: DATA FROM FLUID INCLUSIONS

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ABSTRACT

The condensation of CO_2 and steam in groundwaters above zones of boiling is thought to produce the CO_2-enriched fluids that are commonly found on the margins of high-temperature geothermal systems. Evidence for significant CO_2 flux has been found in fluid inclusions from the geothermal systems at Los Azufres, Mexico, and Zunil, Guatemala. These geothermal fields have measured temperatures close to 300°C.

CO_2-enriched fluid inclusions are widely distributed in both geothermal systems. These inclusions define a cap over each system that thickens outward from the main upwelling zones. Fluid inclusions from the upper portions of the caps frequently produce CO_2 clathrate upon freezing that melts at temperatures above 0°C. These inclusions have calculated CO_2 contents that range up to 5 weight percent. Ice-melting temperatures indicate that inclusions from the lower portions of the caps are also enriched in gas but contain less than 4 weight percent CO_2. The concentrations of CO_2 in the clathrate-bearing inclusions require trapping at pressures above hydrostatic. These pressures may have developed intermittently as fracture permeabilities were reduced by mineral deposition.

INTRODUCTION

CO_2-rich waters are frequently found on the flanks of geothermal systems associated with young volcanism. Their high bicarbonate-to-chloride ratios and low to moderate temperatures has led to the conclusion that these fluids represent shallow reservoirs produced by the steam-heating of local groundwaters (Mahon et al., 1980). Despite the common occurrence of shallow CO_2-enriched fluids, little data has been published on the compositional and thermal structure of the reservoirs they form. In this paper we present fluid inclusion data from the geothermal systems at Los Azufres, Mexico, and Zunil, Guatemala, where CO_2-rich reservoirs are well developed. The use of fluid inclusions has allowed us to obtain information on regions of the geothermal reservoirs that cannot be sampled directly.

GENERAL FEATURES OF THE GEOTHERMAL SYSTEMS

The Zunil Geothermal System

Zunil is located approximately 200 km west of Guatemala City adjacent to the active volcanoes at Cerro Quemado and Santa Maria (Fig. 1). Since 1978, six production wells and eleven thermal gradient coreholes have been drilled into a narrow graben developed on the flanks of the volcanoes (Fig. 2). In the production wells, which were drilled to depths ranging from 872-1300 m, temperatures were encountered as high as 288°C. Most of the present fluid production comes from the lower parts of a thick sequence of altered andesite and dacite lava flows, breccias and ash-flow tuffs that unconformably overlie Cretaceous(?) granodiorite. Additional drilling is planned to test fracture zones within the crystalline basement complex.

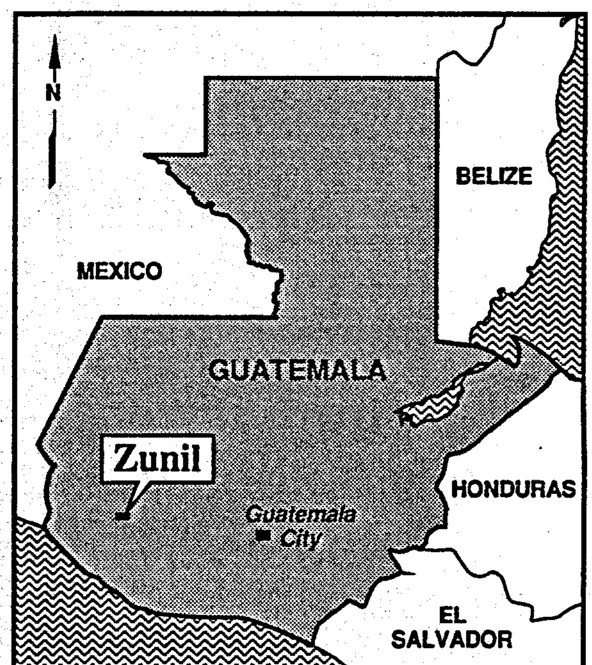

Fig. 1. Location map of the Zunil geothermal area.

The Zunil area contains numerous hot springs and fumaroles. At the highest elevations, near the production wells, the thermal features consist mainly of active fumaroles, acid altered ground, and boiling acid-sulfate springs (Fig. 2). At lower elevations along the Samala River, sodium bicarbonate springs that are depositing travertine are common, although a few acid-sulfate and sodium chloride springs are also present. The deep fluids tapped by the production wells are relatively dilute sodium chloride waters (Table 1). Chloride-enthalpy relationships indicate that dilution of the deep fluids increases from the west to the east and southeast of the well field.

The Los Azufres Geothermal System

Los Azufres is a large, high-temperature geothermal system located approximately 80 km east of Moralia, Michoacan in central Mexico (Fig. 3). Fifty-two wells ranging in depth from 452 to 3544 m have been drilled in an area covering approximately 30 sq km (Fig. 4). Temperatures in these wells are close to 300°C. Regional geologic, geochemical, and geophysical studies, combined

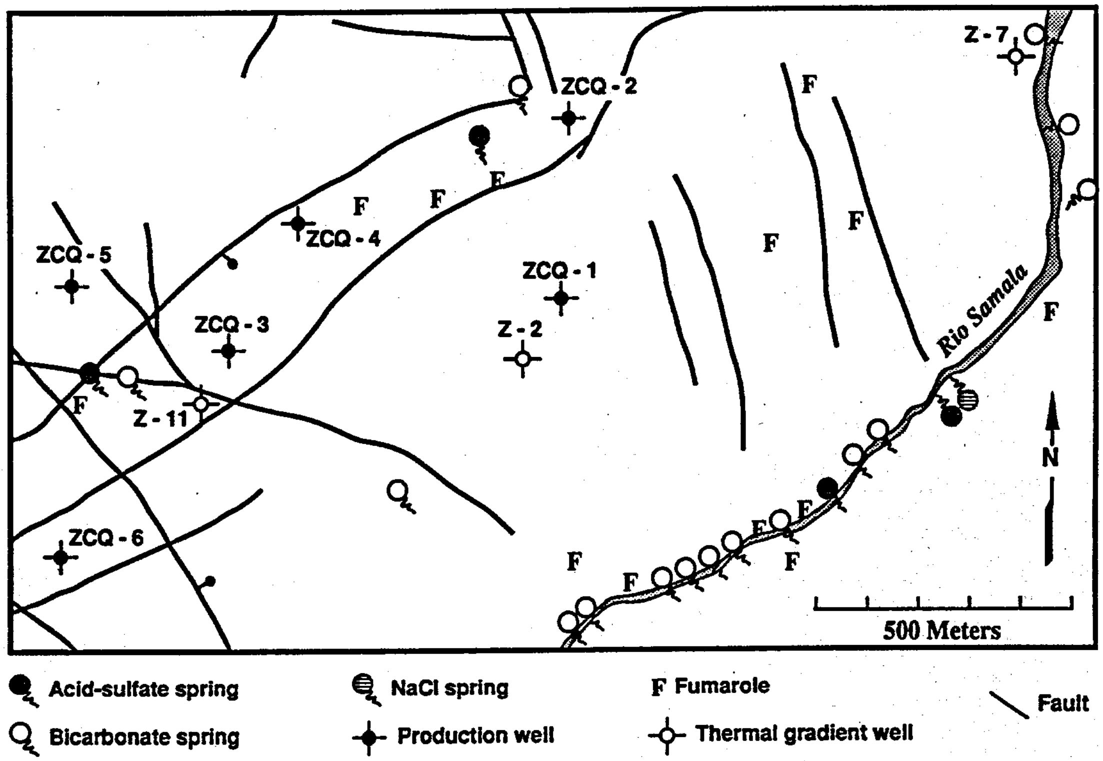

Fig. 2. Locations of the wells and major thermal features in the Zunil Geothermal area.

with investigations of fluid and rock samples from the wells and numerical modeling of the production data have led to the development of a very detailed model of this complex system. Summaries of these data are presented by Quijano (1985), and Nieva et al., (1986). The field presently produces 80 MW.

The production wells at Los Azufres discharge low salinity fluids that are characterized by a wide range of gas contents and enthalpies (Nieva et. al, 1983, 1985; Truesdell et al., 1987; Quijano et al., 1989). The presence of excess steam has greatly complicated calculation of the reservoir liquid compositions. For the purpose of this communication, we have taken the composition of Az-13 (assuming reservoir steam) presented by Truesdell et al. (1987) as being representative of the deep liquid. Well Az-13 is located in the northern part of the field near the wells that we studied in detail. Fluid from Az-13 would have an ice-melting temperature of approximately -0.2°C (Table 1).

GENERAL CHARACTERISTICS OF THE FLUID INCLUSIONS

Fluid inclusions are common in the vein minerals occurring at both Los Azufres (Combredet and Guilaumou, 1987; Gonzales et al., 1989; Lemieux et al., 1989) and Zunil. Although the majority of the measurements from these fields were made on quartz and calcite, inclusions suitable for study have also been found in anhydrite, epidote, wairakite, and barite at Los Azufres. With the exception of a single sample from Zunil, all of the data are from two phase inclusions that contained only liquid and vapor at room temperature. Three phase inclusions, containing various proportions of a miceaceous mineral, were found in quartz crystals from Zunil. However, the phase relationships suggest that the solid may have been accidently trapped.

TABLE 1
Fluid Compositions (in ppm)

	Zunil		Los Azufres	
	ZCQ-3	Spring Z-16	Az-13	Az-13
Source	1	2	3	4
Na	683	273	767	462
K	144	37	228	132
Ca	9.1	45	3.6	0.3
Mg		60	0.01	
SiO_2	610			
H_4SiO_4			708	398
Cl	1149	162	1390	881
SO_4	22	169	5.3	
HCO_3	60	669	35	46
CO_2	1005		400	3600
Tm-ice(°C)	-0.16	-0.06	-0.16	-0.22

1. Cordon y Merida/Morrison-Knudsen Engineers, 1989. Calculation of fluid composition by D. Michels.
2. JICA, 1977
3. Truesdell et al., 1987: calculated using WATCH assuming reservoir steam
4. Truesdel et al., 1987: calculated using EQQYAC assuming reservoir steam

The microthermometric measurements reported in this paper were made on primary and secondary liquid-rich inclusions. Because no systematic differences were observed in our study between the primary and secondary inclusions, we have not distinguished between them in the discussion below. In general the homgenization temperatures of the inclusions correspond closely to the

Table 2
Fluid Inclusion Data from Zunil[1]

Well	Mineral	Depth (m)	Th (°C)	Tm-ice (°C)	Tm-clath (°C)	Max CO_2 (wt. %)	delta CO_2 (wt %)
ZCQ-1	Cc	250	184 to 233 (7)		+0.2 to +0.6 (2)	4.1	--
	Cc	455	140 to 213 (12)	0.0 (10)		--	--
	Cc	500	185 to 231 (10)		0.0 to +0.3 (8)	4.0	--
	Cc	535	145 to 224 (13)	0.0 to -0.1 (11)		--	--
	Cc	585	204 to 229 (3)		+0.3 (3)	4.1	--
	Cc	655	229 to 248 (6)	0.0 to -0.2 (5)		--	--
	Cc	795	178 to 244 (9)		+0.1 to +0.5 (12)	4.1	--
	Cc	1020	e	-0.2 to -1.6 (5)		--	3.7
	Cc	1170	195 to 235 (7)	0.0 to -0.1 (5)		--	--
	Cc	1220	196 to 241 (14)	0.0 to -0.2 (12)		--	--
ZCQ-3	Cc	210	152 to 199 (9)		+0.3 (6)	4.0	--
	Cc	245		0.0 (3)		--	--
	Cc	310	e		+0.3 (1)	3.9	--
	Cc	335	198(1)	-0.2 (1)		--	--
	Cc	400	160 to 214 (18)	0.0 to -0.1 (13)	+0.1 (2)	4.0	--
	Cc & Qtz	550	216 to 264 (19)	0.0 to -0.4 (18)		--	0.5
	Cc	750	248 to 300 (12)	-0.1 to -0.5 (10)		--	0.9
	Cc	890	260 to 290 (7)	-0.0 to -1.1 (9)		--	2.5
	Cc	930	254 to 262 (3)	-0.1 to -0.5 (3)		--	0.8
ZCQ-5	Cc	200	151 to 206 (7)	-0.1 to -0.4 (4)		--	0.5
	Qtz	230	209 to 241 (5)		+0.1 to +0.3 (5)	4.1	--
	Cc	260	213 to 227 (8)	-0.1 to -0.2 (6)		--	--
	Qtz	300	157 to 211 (14)	0.0 to -0.5 (5)		--	0.8
	Qtz	445	210 to 265 (14)	0.0 to -0.3 (15)	+0.3 (5)	4.0	0.3
	Cc	550	216 to 237 (22)	-0.3 to -0.7 (22)		--	1.3
	Cc	900	258 to 282 (15)	0.0 to -0.7 (15)		--	1.4
	Cc	940	258 to 276 (15)	0.0 to -0.1 (12)		--	--

Table 3
Fluid Inclusion Data from Los Azufres[1]

Well	Mineral	Depth (m)	Th (°C)	Tm-ice (°C)	Tm-clath (°C)	Max CO_2 (wt. %)	delta CO_2 (wt. %)
Az-3	Cc	396	170 to 189 (6)		+0.1 to +0.6 (6)	4.0	--
	Cc	468	200 to 259 (13)		+0.2 to +0.3 (13)	4.3	--
	Cc	564	242 to 257 (5)		+0.4 to +0.6 (4)	4.3	--
	Ep	912	254 to 255 (7)	-0.1 to -0.2 (7)		--	--
	Ep	1278	273 to 277 (2)	-0.1 (1)		--	--
	Qtz	1968	263 to 301 (8)	-0.2 to -1.4 (7)		--	3.4
	Qtz	2028	263 to 332 (6)			--	--
	Cc	2196	251 to 253 (7)	0.0 (2)		--	--
						--	--
Az-28	Cc	120	184 to 196 (10)	-0.4 to -0.5 (8)		--	0.8
	Cc	492	242 to 254 (3)			--	--
	Qtz	1404	259 to 281 (8)	-0.0 to -0.1 (3)		--	--
	Qtz	1566	241 to 264 (9)	0.0 (4)	+0.1 to +0.3 (3)	4.2	--
	Qtz	1680	249 to 261 (4)	-0.2 to -0.6 (4)		--	1.1
Az-29	Qtz	996	255 to 267 (10)	-0.0 to -0.9 (10)		--	1.9
	Cc	996	251 to 280 (6)	-0.2 to -0.3 (6)		--	0.3
	Cc	1308	266 to 274 (3)			--	--
	Cc	2466	255 to 256 (4)	0.0 to -0.1 (3)		--	--
Az-48	Cc	198	183 to 185 (2)			--	--
	Cc	318	184 to 217 (4)		+1.1 to 2.6 (4)	4.5	--
	Cc	420	175 to 234 (10)		+0.9 to 2.0 (9)	4.6	--
	Qtz	1092	232 to 267 (14)	-0.1 to -0.2 (11)		--	--
	Qtz	1458	298 to 307 (6)	0.0 (1)		--	--
	Qtz	1482	310 to 312 (7)			--	--
Az-51	Anhy	798	213 to 258 (14)		+0.2 to +1.0 (6)	4.5	--
	Cc	798	192 to 240 (5)	-0.1 to -0.5 (5)		--	0.8
	Qtz	798	210 to 219 (11)	-0.7 to -1.4 (11)		--	3.2
	Cc	960	199 to 233 (8)		+1.2 to +1.8 (7)	4.4	--
	Cc	1152	236 to 285 (16)	0.0 (2)	+0.2 to 1.5 (9)	4.7	--
	Qtz	1368	253 to 278 (12)		+0.2 to +0.6 (7)	4.4	--
	Cc	1572	255 to 284 (6)		+1.3 to +1.6 (5)	4.7	--

1. Abbreviations: Cc = calcite; Qtz = quartz; Ep = Epidote; Anhy = Anhydrite; Th = homogenization temperature; e = temperature of trapping estimated to calculate CO_2 contents; Tm-ice = ice melting temperature; Tm-clath = clathrate melting temperature; Max CO_2 = maximum CO_2 content of inclusions based on Tm-clath; delta CO_2 = maximum enrichment in CO_2 relative to reservoir fluid in Table 1. Numbers in parenthesis indicate number of inclusions studied.

downhole measurements. The majority of these inclusions had maximum dimensions ranging from 2 to 10μ.

Planes of secondary, vapor-rich inclusions were also found in many samples. The distribution of vapor-rich inclusions is different, however, in the two reservoirs. At Zunil, these inclusions are found mainly in the upper several hundred meters of the geothermal system. In contrast, vapor-rich inclusions are found to depths of 1500 m at Los Azufres. Because of the small size of these inclusions (less than 10μ), it was generally not possible to observe phase changes in them during heating or freezing. Nevertheless, planes of vapor-rich inclusions provide unequivocal evidence of boiling within the reservoirs.

The liquid-rich inclusions can be grouped into two types on the basis of their behavior during freezing. In most of the inclusions the final solid phase to melt was ice. The ice-melting temperatures of these inclusions are shown in Tables 2 and 3. A prominent feature of these data is the relatively large range of ice-melting temperatures displayed by different inclusions in the individual samples. This contrasts with the relatively narrow range of homogenization temperatures shown by the same inclusions. These relationships suggest that the variations in the freezing point depressions of the inclusions are due to differences in their gas contents (Hedenquist and Henley, 1985). Significantly, few inclusions have ice-melting temperatures between -0.1° and -0.2°C which would be expected from the compositions of the spring and well discharges (Table 1). The differences in the CO_2

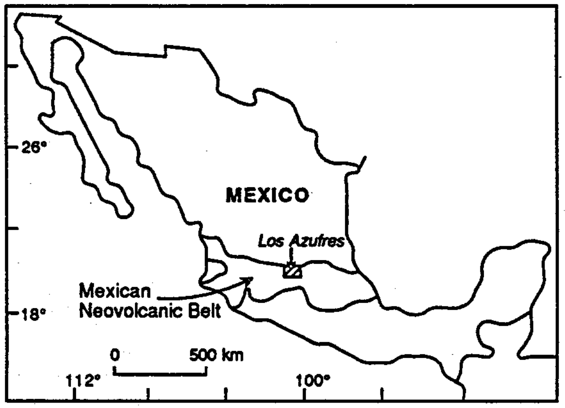

Fig. 3. Location map of Los Azufres.

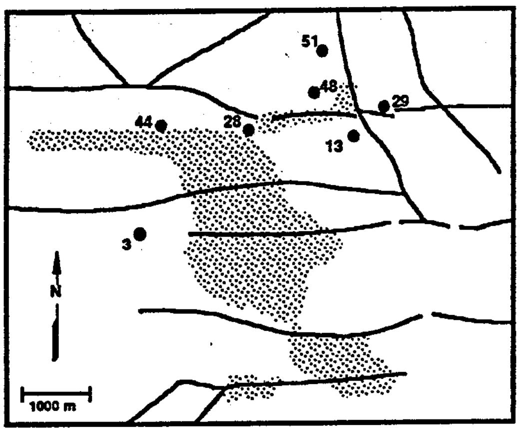

Fig. 4. General features of the Los Azufres geothermal field. Wells discussed in this paper are shown by solid circles. Solid lines show the location of faults. The stippled pattern shows the distribution of hydrothermal alteration. Geologic data from Razo et al. (1989) and unpublished CFE maps.

contents of the inclusions relative to a reservoir fluid with an ice-melting temperature of -0.2°C are shown in Tables 2 and 3. In contrast to inclusions with low ice-melting temperatures, melting temperatures between 0.0° and -0.1°C indicate that the inclusion fluids have less than .17 equivalent weight percent NaCl. The high homogenization temperatures of these inclusions suggest they represent condensed steam or steam that has mixed with small quantities of reservoir fluid.

Some of the liquid-rich inclusions had sufficient CO_2 to generate CO_2 clathrate upon freezing. These inclusions are characterized by positive melting temperatures ranging up to 2.6°C and an obvious phase change during freezing at temperatures near -30°C. The CO_2 contents of the inclusions calculated from the melting temperatures of the clathrate are presented in Tables 2 and 3. These data indicate that CO_2 contents of clathrate-bearing inclusions range from 3.8 to 4.8 weight percent.

Many of the samples from Zunil and Los Azufres were crushed to test the hypothesis that the inclusions are indeed enriched in CO_2. Samples that contained inclusions characterized by large variations in ice-melting temperatures or by positive values typically released a gas which expanded when the samples were crushed in glycerine. This expansion indicates that the gas must have been trapped at pressures above 1 atmosphere. When the inclusions were crushed in alkaline $BaCl_2$, the bubbles disappeared instantly indicating that the gas was composed of CO_2 (Roedder, 1984).

DISCUSSION

The compositional variations displayed by the inclusion fluids can be used to develop geochemical cross sections of the upper portions of the geothermal systems at Zunil and Los Azufres. At Zunil, four groups of inclusions can be distinguished on the basis of the microthermometric measurements. The distribution of these groups in 3 production wells, ZCQ-5,-3, and -1, and the measured downhole temperatures are shown in Figure 5. The fluid inclusions in the uppermost portion of the reservoir are characterized by low salinities, low gas contents, and temperatures up to 200°C. These inclusions extend to depths of approximately 200 m. Below this zone is a thick region that is variably enriched in CO_2 relative to the deep reservoir fluids discharged from the production wells. The highest CO_2 contents occur at the top of this region. Some of the inclusions from this part of the reservoir form CO_2 clathrate and have CO_2 contents up to 4.3 weight percent. Lower but significant contents of CO_2 characterize the underlying inclusions. Here, inclusions have CO_2 concentrations of up to 2.8 weight percent. The high flux of CO_2 in this region of the reservoir indicates that steam-heating is occurring and that a secondary bicarbonate reservoir has developed. Fluid inclusions similar in composition to those discharged from the production wells have low CO_2 contents and low salinities. These inclusions are characterized by ice-melting temperatures ranging from 0.0 to -0.4°C.

Figure 5 indicates that the region of CO_2-enriched fluid inclusions thickens from the western to eastern portion of the well field. The inclusion data and the temperature patterns suggest that both upwellling of the deep reservoir fluid and downwelling of the cooler CO_2-enriched fluids are occurring. Zones of upwelling are indicated by the presence of inclusions with high temperatures and low CO_2 contents. Incursion of the CO_2-enriched fluids into deeper portions of the reservoir occurs near ZCQ-3 and on the eastern edge of the cross section near ZCQ-1. The presence of bicarbonate-rich springs along Rio Samala demonstrate that these CO_2-enriched fluids continue to the east beyond the limit of the cross section.

For comparison, Figure 6 illustrates the major compositional features of the northern portion of the Los Azufres geothermal system from its southwestern to northeastern margin. The cross section shows that the upper portion of the geothermal system is also characterized by inclusions that form CO_2 clathrate on freezing. These inclusions have CO_2 contents of up to 4.8 weight percent (Table 3). The region of the reservoir containing inclusions with CO_2 contents greater than 3.8 weight percent is thinnest (less than 120 m) in the vicinity of well Az-28. This well was drilled near the center of the upflow zone where shallow fracturing is most intense. However, CO_2-rich inclusions are found to depths in excess of 1580 m in Az-51 drilled on the northeastern margin. CO_2 clathrate-bearing inclusions from both Zunil

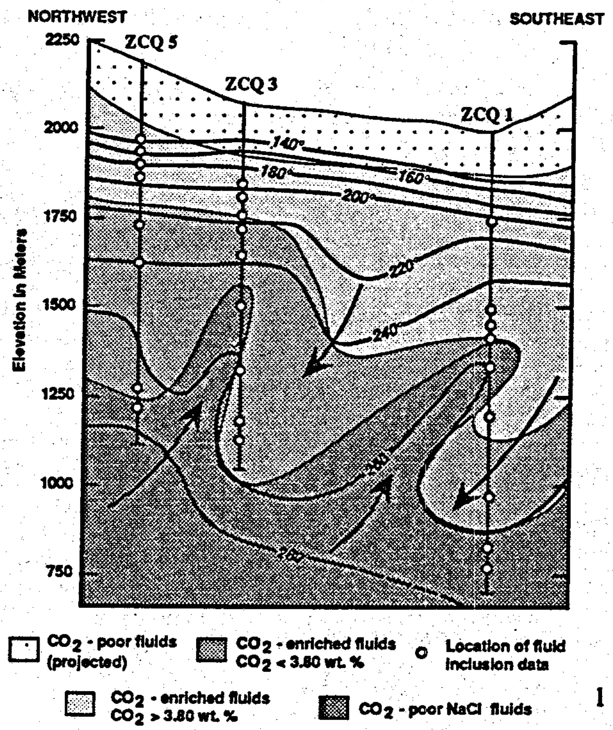

Fig. 5. Conceptual model of the Zunil geothermal system.

and Los Azufres are associated with planes of vapor-rich inclusions, suggesting that they were trapped at temperatures close to the boiling point of the fluids. In addition, our observations indicate that these inclusions trapped only a liquid phase. Comparison of the homogenization temperatures of the inclusions with boiling point to depth curves adjusted for the high CO_2 contents of the fluids shows that these inclusions plot within the vapor field if hydrostatic pressures are assumed. Thus, pressures must have been locally higher than hydrostatic in the past. Higher pressures could have developed intermittently as fracture permeabilities were reduced by mineral deposition during boiling, as well as by the deposition of clay minerals resulting from the influx of CO_2 (Hedenquist, 1990). At Zunil, regions where overpressures have developed are frequently associated with hydrothermal breccias. The effectiveness of shallow sealing at Los Azufres is reflected in the absence of any significant recharge from the surface despite high rainfall and numerous lakes (Nieva et al., 1986). The apparently steep northeastern boundary of the CO_2-enriched cap in this system suggests that its position is controlled by a steeply dipping fault.

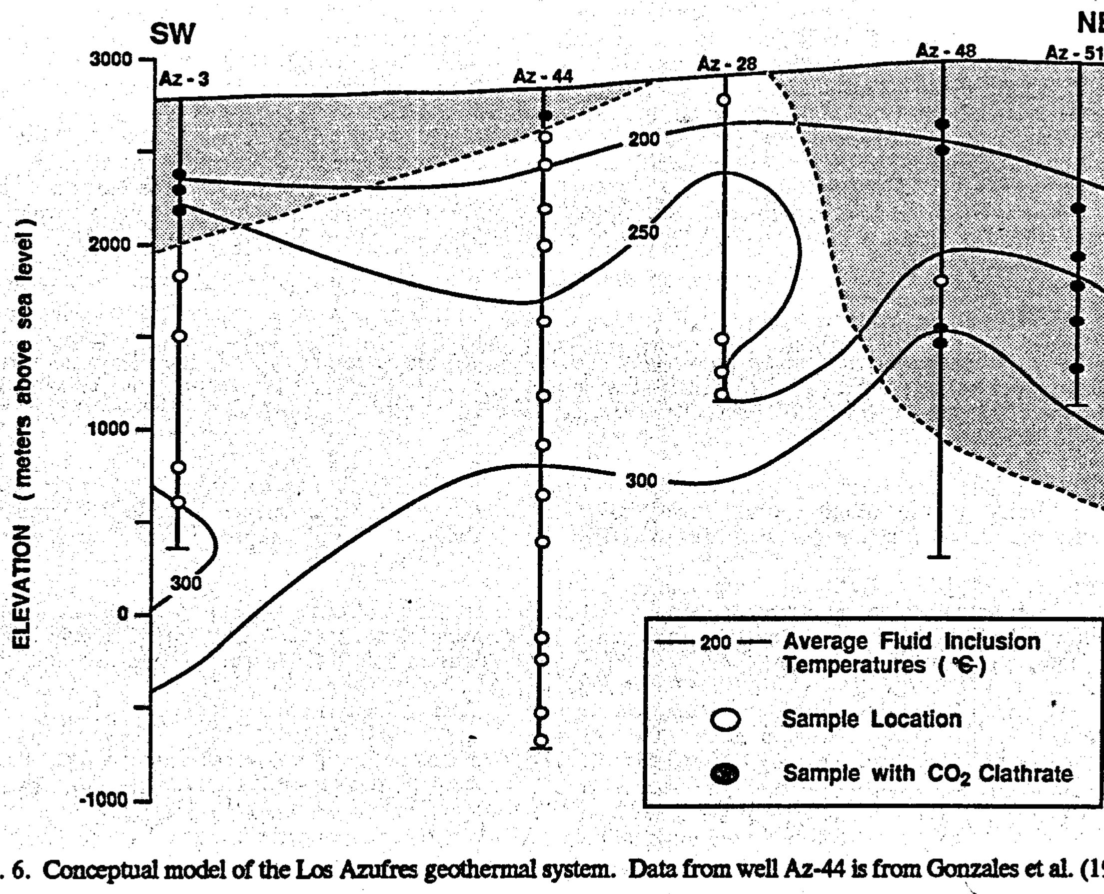

Fig. 6. Conceptual model of the Los Azufres geothermal system. Data from well Az-44 is from Gonzales et al. (1989).

CONCLUSIONS

Fluid inclusions from both Los Azufres and Zunil display systematic variations in their CO_2 contents. These inclusions define regions of the reservoirs that are enriched in CO_2 relative to the deep liquids. These regions form caps over the thermal systems that become progressively thicker towards the margins of the fields. At Zunil, the CO_2-enriched cap is overlain by heated groundwaters characterized by low salinities and low gas contents.

Some of the fluid inclusions from the upper portions of the caps in these reservoirs formed CO_2 clathrate when frozen, indicating that they contain CO_2 contents in excess of 3.8 weight percent. The lower portions of the caps contain fluids with variable but lower CO_2 contents. Comparison of the homogenization temperatures of the CO_2-enriched inclusions with appropriate boiling point curves indicates that the CO_2 was trapped at pressures greater than hydrostatic. In the upper portions of these caps, the trapping pressures exceeded hydrostatic values by up to several tens of bars. Mineral deposition accompanying boiling and the formation of clay minerals may have been responsible for decreasing permeabilities and allowing pressures to increase.

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