VOLCANIC STRATIGRAPHY AND GEOCHEMISTRY OF THE LOS AZUFRES GEOTHERMAL CENTER, MEXICO

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SUBMITTED TO THE DEPARTMENT OF GEOLOGY AND THE COMMITTEE ON GRADUATE STUDIES OF STANFORD UNIVERSITY IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF MASTER OF SCIENCE

By Patrick F. Dobson May 1984 I certify that I have read this thesis and that in my opinion it is fully adequate, in scope and quality, as a dissertation for the degree of master of science.

(Principal Advisor)

Approved for the University Committee on Graduate Studies:

Dean of Graduate Studies & Research

ABSTRACT

The Los Azufres volcanic center, located 200 km northwest of Mexico City, is one of a number of Pleistocene silicic volcanic centers with active geothermal systems that lie north of the axis of the Mexican Neovolcanic Belt. This calc-alkaline suite overlies a thick pile of Miocene to Pliocene volcanic rocks dominated by andesitic lava flows. Three main episodes of volcanism have been documented at the Los Azufres center. Silicic volcanism began approximately 1 m.y. ago with eruption of the Agua Fria rhyodacite to high-silica rhyolite lava domes and flows. They are covered by rhyodacite and dacite lava domes and flows of the San Andres volcano. One of the San Andres dacites has been dated at 0.3 m.y. All these lavas are cut by high-angle normal faults. A north- to northeast-trending set is cut by a younger and more prominent east-trending set that parallels the principal regional structural trend. These faults do not cut the youngest volcanic rocks of the center, the Yerbabuena rhyodacites to high-silica rhyolites. These morphologically well-preserved lava domes are dated at approximately 0.15 m.y. and are probably associated with air-fall tuffs that blanket the western portion of the volcanic center.

Los Azufres is the site of a producing geothermal system. Comparison of the results of thermodynamic calculations, observed geochemical water-rock relations, and stable-isotope systematics in several wells suggests that partial equilibrium conditions existed in the Los Azufres system in its preproduction state.

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The alteration assemblages of five drill-core samples from stratigraphic levels corresponding to measured temperatures between 200° and 300°C of the wells Az-1 and Az-6 contain quartz, Mn-rich calcite, and septachlorite; the two deepest samples (1685 and 1827 m) contain epidote, and all but the deepest sample contain sericite.

Data for chemical analyses on gas and water from the wells Az-1 and Az-5 were recast into species to model downhole conditions using an iterative program based on the ionasable proton total. The aquifer water compositions and the observed mineral assemblages are in agreement with the theoretically predicted mineral-fluid phase relations of Helgeson and his coworkers.

Isotopic data for meteoric waters and well discharges suggest that recharge to the system occurs both locally and regionally. Isotopic evidence further indicates that boiling occurs within the reservoir, causing steam to separate at depth and mix in varying amounts with the liquid phase. This process results in well discharges that range from steam-only to liquid-only.

The calculated oxygen isotope composition of reservoir water (-4.5 permil) is in equilibrium at 300° C with calcite and quartz separates from the two deepest drill-core samples. The δ^{18} O values for separates of secondary calcite and quartz in samples taken from depths of 594 to 875 m are isotopically heavier than would be predicted by the calcite-water and quartz-water fractionation curves. This relation suggests that mineral-water equilibration took place at these intermediate depths at lower temperatures than those presently observed.

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Chapter I

VOLCANIC STRATIGRAPHY OF THE LOS AZUFRES GEOTHERMAL AREA

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1.1 INTRODUCTION

The purpose of this chapter is to outline the geology of a silicic volcanic center associated with an important geothermal field for which there are numerous internal reports but little published information. The Los Azufres area has long been recognized for its thermal manifestations (Waitz, 1906; Maldonado, 1956; Alonso et. al., 1964; Mooser, 1964), but only recently has its geothermal potential prompted further study. Regional mapping and petrologic studies by Demant et al. (1975) and Silva Mora (1979) have been augmented by more detailed investigations of the geothermal area itself under the auspices of Mexico's Comision Federal de Electricidad (CFE) (Garfias and Gonzalez, 1978; Camacho, 1979, de la Cruz et. al., 1982). CFE has drilled over 30 wells to depths of up to 2900 m, providing good subsurface geologic information. Five well-head generators were installed in August of 1982 and are currently producing a total of 23 megawatts of electricity.

1.2 REGIONAL SETTING OF THE LOS AZUFRES VOLCANIC FIELD

The Los Azufres volcanic center is located along the northern edge of the east-west-trending Mexican Neovolcanic Belt, 200 km northwest of Mexico City (Figure 1). It is one of a number of Pleistocene silicic volcanic centers, including Los Humeros, La Primavera, Huichapan, and Amealco, that lie behind the zone of active andesitic stratovolcances (Ferriz and Mahood, in press). The nearest exposures of prevolcanic basement are 35 km southwest of Los Azufres and consist of gently folded shales, sandstones, and conglomerates of Eccene to Oligocene age

(Mauvois et al., 1976). Extensive Neogene volcanic rocks dominated by basaltic and andesitic lavas unconformably overlie these sedimentary rocks. Two K-Ar dates of 18 and 13.5 m.y. (Table 1) have been obtained on andesite flows from the upper part of this sequence. Similar lava flows, comprised mostly of phenocryst-poor andesite, form the local basement for the Los Azufres center. These andesite lavas, with minor intercalated pyroclastic deposits and basalt, porphyritic andesite, and dacite lava flows, have a minimum aggregate thickness of 2900 m as measured in well Az-20 (Garfias and Casarrubias, 1979c). A minimum age of 10.2 ± 0.6 m.y. for the oldest volcanic rocks underlying the Los Azufres center is based upon a K-Ar whole-rock date on a drill-core sample from well Az-20 at 2700 m depth. Drill-core samples collected from higher stratigraphic levels yielded K-Ar dates of 5.9, 5.0, and 3.1 m.y. A whole-rock sample from a surface lava flow gave a K-Ar age of 1.0 ± 0.2 m.y. (Table 1), thus providing a minimum upper age limit for this dominantly andesitic volcanism.



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FIGURE 1: Regional location map. Stippled pattern: Mexican Neovolcanic Belt (modified from Demant and Robin, 1975; Demant, 1978); Quaternary calderas: La Primavera (LP), Amealco (A), Huichapan (H) and Los Humeros (LH); M: Mexico City. Box gives location of Fig. **6**.

TABLE 1: Summary of K-Ar dates for the Los Azufres region.

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Eruptive unit	Locality	Material	Sample wt.(g)	K,0%	40^{+} (10 ⁻¹³ mol/g)	40 Ar Atm (%)	age(m.y)
"Basement" rocks	near Querendaro, Michoacan						18 ²
	19 [°] 39' • 100 [°] 57'	WR(?)	-	1.722		66.0	13.8 ± 0.7^3
-	19 [°] 45'23" 100 [°] 41'10" (2700 в)	WR		1.648		87.5	10.2 <u>+</u> 0.6 ⁴
	unknown drill hole	WR		2.129		9 5.2	5.9 <u>+</u> 0.4 ⁴
	19 ⁰ 46'47" 100 ⁰ 40'00" (900 m)	WR		2.167		87.7	5.0 <u>+</u> 0.4 ⁴
	19 ⁰ 45'23" 100 ⁰ 41'10" .(720-1000 m)	WR 1		4.260		93.7	3.1 ± 0.2^4
	19 ⁰ 49'48" 100 ⁰ 38'11"	WR	- 2.6500	2.68	41.3	89.6	1.03 ± 0.20^{5}
Agua Fria	unknown	WR		4.401		94.6	1.2 ± 0.4^4
Rhyolites	19 ⁰ 46'21" 100 ⁰ 39'26"	glass	4.1217	4.6 7 4.71	69.6	47.1	1.03 ± 0.02 ^{5,0}
	19 ⁰ 46'58" 100 ⁰ 39'46"	WR	6.6280	4.50 4.66	61.1	87.0	0.93 ± 0.04 ⁵
	19 ⁰ 48'46" 100 ⁰ 40'22"	glass	4.1003	4.6 6 4.70	56.9	49.7	0.84 <u>+</u> 0.02 ⁵
San Andres Dacites	19 ⁰ 46'38" 100 ⁰ 37'30"	plagioclase	9.9638	1.87 1.81	8.66	95.5	0.33 <u>+</u> 0.07 ⁵
Yerbabuena Rhyolites	19 [°] 45'32" 100 [°] 42'52"	biotite	2.0765	6.85 7.27	31.0	96.8	0.30 ± 0.07 ⁵
	19 ⁰ 47'41" 100 ⁰ 42'27"	biotite	0.3525	6.64	14.0	98.5	0.15 <u>+</u> 0.05 ^{5,7}
	19 ⁰ 48'05" 100 ⁰ 43'15"	glass	6.4385	4.72 4.73	9.61	81.7	0.14 ± 0.02^5

¹Value in parentheses gives depth below surface for drill-core samples.

²Camacho, 1979 (old decay constants). Dash indicates data not reported.

³Demant et al., 1975 (old decay constants).

⁴Aumento and Gutierrez, 1980. Dates recalculated using new decay constants. This study. Decay constants are: = $0.581 \times 10^{-10} \text{ yr}^{-1}$ = $4.692 \times 10^{-10} \text{ yr}^{-1}$ $40 \text{ K/K} = 1.161 \times 10^{-4} \text{ atom/atom}$

⁶PDLA 82-50 (Table 3) 7 PDLA 82-52 (Table 3)

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1.3 VOLCANIC HISTORY OF THE LOS AZUFRES VOLCANIC CENTER

Silicic volcanism began shortly after eruption of the last andesites. Three major eruptive groups have been identified at Los Azufres: the Agua Fria rhyolites, the San Andres dacites, and the Yerbabuena rhyolites (Figures 2 and 3).

The Agua Fria rhyolites consist of lava domes and stubby flows totalling approximately $10-15 \text{ km}^3$ in volume that cover 35 km² in the central part of the Los Azufres center. Outcrops of the lavas are typically blue-gray, flow-banded, and devitrified, with well-developed spherulites. A remnant of pumiceous carapace was observed at Cerro Pizcuaro, one of seven topographically expressed domes (Figure 2). The domes vary in composition from rhyodacite to high-silica rhyolite, and contain phenocrysts of plagioclase/sanidine=quartz/ biotite/Fe-Ti oxides ± hornblende ± orthopyroxene. The principal phenocrysts range in size from 1 to 5 mm and comprise 1-15% of the rock, with the more mafic compositions being more crystal rich. Nonhydrated obsidian samples from cerro El Gallo and Cerro Chinapo yielded K-Ar dates of 0.84 ± 0.02 and 1.03 ± 0.02 m.y.; these glass dates provide a minimum age range for the Agua Fria volcanics. Three sets of paleomagnetic measurements on lavas gave reversed field orientations, corresponding well with the K-Ar dates. A fourth set of measurements, on the porphyritic Las Humaredas dome dated at 0.93 ± 0.04 m.y. (whole rock), gave a normal field orientation, which corresponds to the Jaramillo subchron of 0.92 - 0.97 m.y. (Tables 1 and 2).



FIGURE 2: Geologic map of the Los Azufres volcanic center. Heavy lines with hachures indicate high-angle normal faults. Cerro El Gallo (EG), Cerro El Chino (CEC), Cerro Pizcuaro (CP), Cerro La Providencia (CLP), Cerro Las Humaredas (LH), Cerro El Jilguero (CEJ), and Cerro Chinapo (CCH) are Agua Fria rhyolite domes. Mesa El Carpintero (MEC), Mesa El Bosque (MEB), Mesa El Rosario (MER) and Cerro El Guangoche (CEG) are Yerbabuena rhyolite domes. Cerro de San Andres (CSA) is a vent complex for the San Andres dacites. Stars mark hot springs and fumaroles. A-B-C-D and E-F mark cross section locations.



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FIGURE 3: Geologic cross sections of the Los Azufres center. No vertical exageration. Vertical scale in meters above sea level. Symbols as in Fig. 2. Numbers mark Well locations; data from Garfias (1981), Garfias and Casarrubias (1979a, b, c), Garfias and Gonzalez (1978), Garfias and Rivera (1980a, b, c), Izaguirre and Garfias (1981), and Rodriguez and Garfias (1981).

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Eruptive Unit	Location	# Samples	Field Orientation	Interpreted Polarity Chron/Subchron
"Basement" rocks	19 ⁰ 45'49" 100 ⁰ 41 '43 "	5	reversed	unknown
	19 ⁰ 45'51" 100 ⁰ 41'32"	5	reversed	unknown
Agua Fria Rhyolites	19 ⁰ 47'16" 100 ⁰ 37'47"	5	reversed	Matuyana
	19 ⁰ 48 '33" 100 ⁰ 38'55"	5	reversed	Matuyana
	19 ⁰ 48'06' 100 ⁰ 40'44"	6	reversed ¹	Matuyana
	19 ⁰ 46'58" 100 ⁰ 39'46"	5	normal	Matuyama/Jaramillo
San Andres Dacites	19 ⁰ 44 ' 49" 100 ⁰ 33 ' 14"	5	normal	Brunhes
	19 ⁰ 47 ' 3 7" 100 ⁰ 36 ' 0 9"	6	normal	Brunhes
	19 ⁰ 48'23" 100 ⁰ 36'23"	6	normal	Brunhes
Yerbabuena Rhyolites	19 ⁰ 47 '41" 100 ⁰ 42'27"	5	normal	Brunhes

TABLE 2: Results of flux-gate magnetometry measurements.

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1 Additional samples were measured using alternating field demagnetization. The measured inclinations correspond with the flux-gate deflections observed in the field. The next major eruptive group is the San Andres dacite and rhyodacite lava domes and flows. These lavas cover 70 km² east of the Agua Fria rhyolites and comprise an estimated volume of 15-20 km³. In contrast to the other volcanic edifices of the Los Azufres center, the San Andres lavas form a large vent complex, the 700-m-high Cerro de San Andres. These porphyritic hornblende dacites and rhyodacites are dark gray to blue gray in color and commonly display flow-banding. They consist of 20-40% phenocrysts of plagioclase (1 cm in size), hornblende, clinopyroxene, orthopyroxene and minor biotite and quartz (1-5 mm), and Fe-Ti oxides (<1 mm). Rounded grayish-red aphyric inclusions up to 4 cm in diameter are common, and may be altered andesite from the "basement". Plagioclase from one of the San Andres lavas yielded a K-Ar date of 0.33 \pm 0.07 m.y., which agrees with the normal field orientation measured at two sites (Tables 1 and 2).

The Yerbabuena rhyolite forms the youngest major eruptive group of the Los Azufres center. It consists of five biotite-bearing high-silica rhyolite to rhyodacite domes and associated air-fall tuffs. The dome field covers 40 km² west of the older Agua Fria rhyolites and has an estimated volume of 8 km³. The domes are well-preserved with pumiceous carapaces still intact. The lavas are light gray in color, with 5-15% phenocrysts of plagioclase, quartz, sanidine, biotite, orthopyroxene, Fe-Ti oxides, and minor hornblende set in a glassy pumiceous matrix. The more mafic lavas are richer in phenocrysts. A glass separate from the dome El Carpintero yielded a K-Ar age of 0.14 \pm 0.02 m.y., and biotite separates from the domes Mesa El Bosque and Mesa El Rosario yielded less precise dates of 0.15 \pm 0.05 and 0.30 \pm 0.07 m.y., respectively, all in agreement with the normal field magnetization (Tables 1 and 2). Associated air-fall tuffs are at least 15 m thick near the domes and thin outward. The tuffs have been reworked, forming tuffaceous sediments that crop out south of the domes.

1.4 <u>COMPOSITIONS OF LOS AZUFRES VOLCANIC ROCKS</u>

The Los Azufres eruptive products can be classified as calc-alkaline they fall within the calc-alkalic field of an AFM diagram (Figure 4) and satisfy the major-element and Ba/La-ratio criteria of Gill (1981, p. 139) for a high-K suite. Possible mafic end-members of the Los Azufres suite are approximated by samples of the youngest "basement" andesites as well as a basaltic andesite from an outlying Pleistocene cinder cone. The relatively high Ti concentrations of the andesites are comparable to those observed elsewhere in the Mexican Neovolcanic Belt (Gunn and Mooser, 1970, Gill, 1981, p. 111). Chemical analyses from selected samples of the Los Azufres center are presented in Table 3.

It is not possible to model differetiation mechanisms for the Los Azufres suite because of lack of control on parental compositions. We simply note that concentrations of Al_2O_3 , FeO^* , MgO, MnO, CaO, TiO_2, P_2O_5 and V all decrease with increasing SiO_2, while Rb and K increase (Figure 5). Drops in Sr and Ba concentrations after initial increases may reflect the importance of plagioclase and sanidine, respectively, as separating phenocryst phases. Declines in FeO^* , TiO_2 , and V concentrations are consistent with the presence of Fe-Ti oxides in all of the Los Azufres volcanic units. Rb is the most incompatible element

					Fe	0				
					/					
22552222225232			/	/		13.4 9.7 1.1 4.3 4.3 4.3 4.3 4.3 4.3 4.3 4.3 4.3 4.3		8.3 8.3 1.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0	91.3 8.32 8.31 8.39 8.30 8.30 8.30 8.30 8.30 8.30 8.30 8.30	
Seed S S S S S S S S S S S S S S S S S S	/		00					* * * * * * * * *		16.02 15 15 10 10 10 10 10 10 10 10 10 10 10 10 10
0+/	6°°	11.5 11.5 10.5 10.5 10.5 10.5	Korte-te Sor	NATUR MARTA MARTA MARTA MARTA	10-10-00 10-10-00 10-10-00 10-10 10-10 10-10 10-10	an Maria Maria Maria	Alter-Sati Balan Karah Malan Karah Malan Karah Malan Karah Malan Malan Malan Malan			

FIGURE 4: AFM diagram.

Dashed line marks boundary between calc-alkaline and tholeiitic fields of Irvine and Barager (1971). Squares: basaltic andesite and andesites; circles: Los Azufres volcanics; triangles: outlying ash-flow tuffs. Analyses from Table 3 recalculated to 100% anhydrous.

	Outlying andesite FDLA \$2-29	PDLA \$2-37	" andesites	PDLA 82-24	San Andr PDLA 82-34	es lavas 943	968	POLA 62-38	PDLA 82-48	PDLA 82-50
	19 ⁶ 42'09" 100 ⁶ 34'03"	19 ⁰ 48'25" 100 ⁰ 37'46"	19 ⁶ 45'21" 100 ⁶ 41'15"	19 ⁰ 46'02" 100 ⁰ 37'18"	19 ⁰ 47'32" 100 ⁰ 36'18"	19 ⁰ 62'10" 100 ⁰ 35'58"	39 ⁰ 52110" 100 ⁰ 37100"	19 ⁰ 48'33" 100 ⁰ 38'55"	19 ⁰ 46'16" 100 ⁰ 38'53"	19 ⁰ 66'21" 100 [°] 39'26'
\$10,	- 54.4	58.0	56.6	69.4	67.0	65.8	66.1	76.2	71.2	73.5
T102	1.77	0.92	1.38	0.43	0.45	0.79	0.67	0.05	0.22	0.06
A1,0,	16.7	17.0	17.7	14.9	15.5	14.5	15.2	12.7	14.1	13.5
F#2 ⁰ 3*	9.17	6.27	1.50	3.33	3.44	1.50	1.50	1.01	2.24	1.60
Fe0			5.47	Tableto:		2.57	2.47	-		
ta 0	0.17	0.13	0.34	0.07	0.07	0.07	0.06	0.03	0.05	0.05
10	3.98	4.51	3.46	0.76	1.09	1.97	1.47	0.10	0.40	0.10
0 e 0	7.56	6.73	6.17	2.39	2,80	3.97	3.48	D. 34	1.31	0.54
4a20	3.47	3.68	4.22	3.97	3.71	4.12	4.29	3.62	3.86	4.39
K20	1.63	1.74	2.03	3.59	3.43	3.01	2.95	4.55	4.22	4.61
P205	0.32	0.24	0.33	0.11	0.13	0.17	0.16	0.05	6.07	0.05
លរ	0.66	0.14		0.35	2.91			0.89	1.11	Ø. 26
n₂0 [™]			0.93			0.93	0.48			
120 ⁻			0.07			0.13	0.33			
Fotal	99.80	99.33	100.03	99.28	99.51	99.50	99.14	99.53	98.77	98.65
v	200	120	140	30	39	75	65	10	11	10
Rb .	43	46	54	- 119	190	75	78	167	140	136
Br	456	651	500	241	327	367	459	12	141	23
r	32	22		30	26			28	34	41
Lr.	203	194		191	192			120	197	267
ilb.	14	10		13	13			21	17	22
le .	450	490	385	750	66 0	468		20	20	580
	36	20		31	30			20		37
					·			•		
	Agus Fr	is domes		Terbabus	na dones		Air-fall tuff	Ant-flo	w tuff	
	PDLA 82-64	PDLA 82-70	70LA 82-52	PDLA \$2-74	389	447	PDLA 82-19a	A-80-5	A-80-7	
	19 ^{°°} 47 <i>'27</i> " 100 ^{°°} 39' 36"	19°47'15" 100° 39'52"	19"47'41" 100 ⁶ 42'27"	19°43'13" 100°42'47"	19"47'06" 100 [°] 41'14"	19"43'21" 100 [°] 43'03"	100 40'20"	19 59 05	15"42"54" 100 ⁰ 44"37"	
	70.1	71.3	72.9	74.7	73.7	74.7	71.1	72.8	74.6	
T10.	0.36	0.16	0.07	Q.08	0.12	0.30	0.15	0.05	0.09	
A1_0	34.6	23.7	12.4	12.5	12.7	12.9	12.8	12.2	11.8	
7*,0,*	3.02	0.95	1.25	1.17	0.35	9.19	1.63	1.02	1.17	
FeO				_	3.15	\$.9 7				
lin0	0.00	0.04	0.04	0.44	0.06	0.04	8.85	0.04	9.04	
NgO	0.35	0.10	8.15	0.13	0 59	0.33	0.2 5	0.10	0.12	
CeO	1.08	0.57	0.53	0.52	0.01	0.46	0.72	0.36	0.50	
He_O	3.83	3.14	3. 32	3.44	3.40	3.97	2.80	2.07	3.19	
ĸ,6	4.21	4.66	4.29	4.74	4.68	4.85	4.68	5.93	4.87	
, 0,	0.05	8.05	0.05	8.0 5	9.03	0.01	8.05	0.85	0.05	
	1.74	4.35	4.67	2.82			4.68	4.87	2.20	
1.,0 ⁴	<u></u>			-	2.55	1.69				
n_0 [−]			-		6.20	0.14				
Total	99.4 1	99.40	99.05	99.37	99.93	100.70	98.89	99.49	98.61	
*	21	10	10	10		24	10	10	30	

TABLE 3: Chemical analyses of Los Azufres volcanic rocks.

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of those analysed, showing a five-fold increase in concentration with increasing differentiation.

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= 0.8 for samples for which FeO was not determined). Symbols as in Analyses from Table 3 recalculated to 100% anhydrous (with Fe $_{2}$ O_3* recalculated to FeO and Fe $_{2}$ O_3 assuming Fe $^{2+}/(Fe^{2+} + Fe^{3+})$ FIGURE 5: Harker diagrams. Fig. 3.

1.5 STRUCTURAL ASPECTS OF THE LOS AZUFRES VOLCANIC FIELD

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The Lo3 Azufres center is structurally bound on the north by a large east-trending graben presently filled by Laguna de Cuitzeo (Figure 6). The orientation and style of faulting at the Los Azufres center are similar to large-scale regional features. East-striking high-angle normal faults cut the Agua Fria rhyolite and the San Andres dacite units, but do not disturb the younger Yerbabuena domes. Thus the last major episode of fault movement occurred between approximately 0.4 and 0.15 m.y. ago. Minimum offsets as determined by scarp heights within the Los Azufres center are on the order of 100 m for the principal faults. Movement is mainly dip-slip; little lateral offset of volcanic units is observed.

The principal faults cut and partially obscure an older set of high-angle normal faults that strike north to northeast. Both sets of faults serve as primary conduits for hydrothermal fluids, as shown by alignments of hot springs and fumaroles (Figure 2).



FIGURE 6: Regional structural map. Heavy lines with hachures indicate high-angle normal faults. Stippled areas show locations of towns. Box gives location of Fig. 2.

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1.6 <u>COMPARISON OF THE LOS AZUFRES VOLCANIC CENTER WITH OTHER SILICIC</u> <u>CENTERS IN THE MEXICAN NEOVOLCANIC BELT</u>

The Los Azufres silicic volcanic center differs in both eruptive style and magma compositions erupted from the well-studied Pleistocene silicic centers within the Mexican Neovolcanic Belt, La Primavera and Los Humeros. La Primavera rhyolitic center is located just west of Guadalajara. It is dominated by an 11-km-diameter caldera that formed 95,000 years ago on eruption of 40 km³ of magma as ash-flow tuffs (Mahood, 1980, 1983). The tuff and succeeding lava domes are all mildly peralkaline, high-silica rhyolites (Mahood, 1981). The Los Humeros system (Yanez and Casique, 1980; Ferriz and Yanez, 1981; Ferriz, 1982; Ferriz and Mahood, in press) is located 180 km east of Mexico City. Three caldera-forming eruptions have occurred, the largest of which produced the 115 km³ rhyodacite to rhyolite Xaltipan ash-flow tuff 0.50 m.y. ago. Since silicic volcanism began 0.51 m.y. ago, there has been a general trend toward eruption of increasingly mafic magmas as volumetric eruption rates increased with time.

The Los Azufres center is older than these two systems and magma compositions show a different evolution over time. At Los Azufres, approximately 10-15 km³ of rhyodacite to high-silica rhyolite lavas were erupted over a period of at least 200,000 years starting 1 m.y. ago, followed by 15-20 km³ of dacitic to rhyodacitic lavas perhaps one half m.y. later, and finally an additional 8 km³ of rhyodacite to high-silica rhyolite magma were erupted around 0.15 m.y. ago. These estimates of magma volumes are based on areal distribution and thickness of the volcanic units as determined by field mapping and drill-core data (Figures 2 and 3). These calc-alkaline products differ substantially from the slightly peralkaline, high-silica rhyolite products of the Primavera system, and do not span the wide range of compositions that includes significant amounts of mafic lavas at the Los Humeros center.

During the course of this reconnaissance field study, no caldera was identified. Ash-flow tuff does, however, crop out in the vicinity of the Los Azufres center. We were not successful in dating the phenocryst-poor, pumiceous ash-flow tuffs. Chemical analyses of samples from two outcrops located north and west of the center (A-80-5 and A-80-7 in Table 3) indicate that the ash-flow tuffs are more evolved than any of the Los Azufres rhyolites sampled, having higher Rb and lower Ba, Cu, and Zr concentrations than either the Agua Fria or the Yerbabuena rhyolites. Ash-flow tuffs are commonly more evolved than cogenetic domes (e.g. Smith, 1979), thereby making Los Azufres a chemically plausible source. Significant accumulations of ash-flow tuff are not seen at the surface within the Los Azufres area proper and have not been identified in drill holes. Although an unusual thickness (>1000 m) of rhyolite was cut by well Az-23 (Figure 3), thin sections from drill core samples do not exhibit the vitroclastic textures, lithic inclusions, or broken phenocrysts typical of densely welded ash-flow tuffs. We interpret it as a feeder for the Cerro La Providencia dome.

One important feature shared by these three centers is the presence of an associated active geothermal system. The fact that all three

centers have undergone significant silicic volcanism within the last 0.2 m.y. emphasizes that high-level silicic magma chambers are important as heat sources for the corresponding geothermal systems (Smith and Shaw, 1975). The reservoirs for all three of these geothermal systems are hosted by andesitic rocks that are capped by younger, altered, silicic volcanic rocks which act as a seal for the geothermal system (Ferriz, 1982, Mahood et al., 1983). The centers have fracture-controlled permeability, a feature demonstrated by the localization of hot springs and fumaroles along major faults, and by the close correlation of resistivity anomalies with principal structural features (Palma, 1982; Ferriz, 1982; Templos, 1982). The deep fluids of all of these systems are boron-rich chloride waters. Measured downhole temperatures of approximately 300°C in the Los Azufres system (Dobson and Janik, in prep.) are comparable to the deep water conditions of La Primavera (Mahood et al., 1983, Dominguez and Lippmann, 1983) and Los Humeros (Ferriz, 1982).

1.7 LINKS BETWEEN GEOTHERMAL ACTIVITY AND VOLCANISM AT LOS AZUFRES

The active geothermal field currently being exploited by the Comision Federal de Electricidad is centered within the highly fractured Agua Fria rhyolites and their underlying andesitic basement rocks. Hydrothermal activity is noticeably absent from the zone of most recent silicic volcanism, the Yerbabuena rhyolites.

Gutierrez and Aumento (1982) found that most alteration minerals in drill-core samples form two or more distinct zones that are spatially

subparallel. They take this as evidence for two periods of hydrothermal activity which they attribute to two magmatic cycles. Oxygen isotope data on secondary quartz and calcite in drill-core samples supports an earlier stage of hydrothermal activity at Los Azufres (Janik and Dobson, 1983). These hydrothermal minerals are significantly out of isotopic equilibrium with present-day geothermal fluids at all but the lowest stratigraphic levels. Equilibration probably took place with an isotopically heavier fluid and at lower temperatures than are presently observed.

Abundant Pleistocene basaltic cinder cones that surround the Los Azufres center but do not occur within it are suggestive of a basaltic "shadow zone" within the Los Azufres center, implying that a high-level silicic magma chamber is currently present. A new influx of silicic magma to high levels between 0.4 and 0.15 m.y. could have rejuvenated the hydrothermal system and and culminated in eruption of the Yerbabuena rhyolite domes. Faulting appears to be a prerequisite for the movement of hydrothermal fluids. This may explain the absence of geothermal activity in the zone of the unfaulted younger domes.

Chapter II

THERMODYNAMIC, ISOTOPIC, AND CHEMICAL EVIDENCE FOR EQUILIBRIUM IN THE LOS AZUFRES GEOTHERMAL SYSTEM

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2.1 INTRODUCTION

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The Los Azufres geothermal field is located within the Pleistocene Los Azufres volcanic center, 200 km northwest of Mexico City (Figure 7). Rocks in the geothermal reservoir are composed of Miocene to Pliocene andesites, which are overlain by Pleistocene dacitic to rhyolitic lavas (Dobson, 1983, Dobson et al., submitted). High-angle normal faults cut all but the youngest volcanic units and consist of a prominent set striking east-west and a subordinate and older set striking north to northeast. The alignment of acid-sulfate hot springs along these faults and the intersection of production zones with the faults at depth indicate that fluid movement is largely fracture-controlled.

Chemical and isotopic analyses of geothermal fluids and drill-core samples taken from several wells before production began in August of 1982 provide a test of thermodynamic models of mineral-solution interaction. Geothermal fluid samples from the wells Az-1, Az-2, Az-4, Az-5, Az-6, Az-13, Az-17, and Az-19 (Figure 7) were collected in August 1982. Comision Federal de Electricidad (CFE)

supplied five drill-core samples from the wells Az-1 and Az-6. Oxygen isotope compositions from carbonate, quartz, and total silicate separates from these drill cores were compared with experimentally determined fractionation curves. The alteration mineral assemblages of the drill-core samples were studied by petrographic, X-ray diffraction, and microprobe techniques.



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FIGURE 7: Location map of the Los Azufres geothermal field. Only wells sampled in this study are shown; over 35 wells have been drilled to date by CFE.

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2.2 ALTERATION MINERALOGY

Quertz, calcite, chlorite, sericite and epidote were identified in the drill-core samples through petrographic and X-ray diffraction analyses. A summary of the alteration mineralogy is given in Table 4. The assemblages are consistent with those found during the more comprehensive alteration studies of Gutierrez and Aumento (1982) and Cathlineau et al. (1983). X-ray analysis revealed 7A chlorite; 14A peaks were generated after a 12 hour heat treatment at 550°C. Microprobe analyses of epidote from the drill core P1-3 yielded an average composition of pistacite 30.6 (Table 5), and qualitative EDS scans suggest that as much as 10 percent MnCO₃ is present in carbonate veins. The downhole alteration mineralogy from the production zone of well Az-5 was reported by Gutierrez and Aumento to be calcite, chlorite, epidote, quartz, and oxides.

TABLE 4: Alteration mineralogy.

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Sample	Depth(m)	Rock type	Alteration minerals
Az-1			
P1-2	594	andesite	cc., qtz., septachlorite, sericite, hematite
P1-3	1685	andesite	cc., qtz., septachlorite, sericite, epidote, tr. pyrite
P1-4	1827	basalt	cc., qtz., septachlorite, tr. epidote
Az-6			
P6-1	604	andesite	cc., qtz., septachlorite, sericite
₽6-2	875	andesite	cc., qtz., septachlorite, sericite

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TABLE 5: Microprobe analyses of epidote from vein of drill-core sample P1-3, well Az-1.

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1	2	3
38.2	39.4	37.8
22. 2 ⁻	21.8	21.6
14.8	15.4	15.1
•08	.02	•05
.10	.07	•05
22.06	22.5	21.8
97. 5	99. 2	96.4
	1 38.2 22.2 14.8 .08 .10 <u>22.06</u> 97.5	1 2 38.2 39.4 22.2 21.8 14.8 15.4 .08 .02 .10 .07 22.06 22.5 97.5 99.2

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2.3 <u>THERMODYNAMIC ANALYSIS OF MINERAL-ELECTROLYTE SOLUTION</u> INTERACTIONS

Thermodynamic modeling of water-rock equilibria has been applied in studies of the Salton Sea, Cerro Prieto, and Broadlands geothermal fields to determine if equilibrium has been attained in these systems (Bird and Norton, 1981; Truesdell and Henley, 1982, Seward, 1974). These models involve the comparison of experimentally determined mineral-fluid relations to observed mineral assemblages and their corresponding fluid compositions. This study similarly uses available chemical analyses of geothermal fluids, the mineral assemblages observed in drill cores, and the predicted mineral-fluid phase relations from calculated equations and data reported by Helgeson et al. (1978, 1981) to evaluate fluid-mineral reactions.

Chemical analyses of Los Azufres gas and water samples are presented in Tables 6 and 7. Data for well Az-1 (Molina et. al., 1978, Molina and Templos, 1978a,b) and an analysis from well Az-5 were furnished by CFE. Gas data for the wells Az-5, Az-6, and Az-17 are for samples collected in 1982 and analysed at the U. S. Geological Survey in Menlo Park, California. These analyses indicate that the separated liquid phase is a chloride-rich, near-neutral water with unusually high boron levels. Early gas analyses by CFE show much lower CO₂ gas contents and correspondingly higher steam/gas ratios than 1982 samples. The very low CO₂/H₂S ratio of the CFE Az-1 analysis strongly suggests that the CO₂ value is incorrect, due either to analytical error or to improper

sampling. This value has been recast using the CO₂/H₂S gas ratio obtained for the analysis of Az-5 to predict downhole fluid compositions. The 1982 analyses are similar to those reported for Cerro Prieto, New Zealand, and Krafla (Nehring and D'Amore, 1984; Giggenbach, 1980; 1982).

The chemical data in Tables 6 and 7 were used to calculate reservoir conditions using an iterative calculator program, pH (Henley et al., 1984). This program uses analyses of well-discharge fluids to calculate pH as well as aquifer concentrations and activities of species for high temperature electrolyte solutions. For concentrations of species such as Na+ and K⁺, a simple calculation of aquifer fluid compositions was made based on the steam fraction. The calculated aquifer compositions are shown in Table 8.

Activity diagrams of log aK⁺/aH⁺ vs. log aSiO₂ and log aCa⁺⁺/(aH⁺)² vs. log aSiO₂ were constructed for 300°C (the maximum measured downhole temperature) using the data of Helgeson et al. (1978, 1981). Microprobe data for epidote in the core P1-3 were used to calculate the clinozoisite activity using the equations of Bird and Helgeson (1980). The calculated water compositions plot near the quartz-saturation line within the muscovite and epidote solid solution stability fields shown in Figures 8 and 9, respectively.

Calculated compositions of the geothermal fluids on a calcite solubility diagram indicate that the fluids are supersaturated with respect to calcite (Figure 10). The chemical affinity for the reaction, $CaCO_3 + H^+ = Ca^{++} + HCO_3$ - is -9.3 kcal/mol at the calculated pH of 5.9

TABLE 6: Gas analyses: total dry gas, mole percent.

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4	<u>Az-1</u> 7 Apr. 1978 ⁴	<u>Az-1</u> b	<u>Az-5</u> 16 Aug. 1982	<u>Az-6</u> 16 Aug. 1982	<u>Az-17</u> 16 Aug. 1982
	68.07	98.14	97.74	98.65	98.13
H ₂ S	14.40	1.41	1.40	0.80	1.23
NH ₃ He		·	0.03 1.45×10^{-3}	0.02 5.06x10 ⁻⁴	0.03 5.82x10 ⁻⁴
H ₂	0.62	0.06	0.29	0.14	0.24
Ar		-	4.44×10^{-3}	1.20×10^{-3}	1.97×10^{-3}
0,	0.00	0.00	0.00	0.00	0.00
N_2	3.70	0.36	0.43	0.34	0.33
CH	0.31	0.03	0.09	0.05	0.03
Steam/gas	2378	232	73.5	48.7	67.0

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^aave. of two analyses performed by CFE. ^brecast analysis using CO_2/H_2S ratio of Az-5 to correct for low CO_2 analysis by CFE. Samples from wells Az-5, Az-6, and Az-17 were analyzed by C. J. Janik.

TABLE 7: Water analyses by CFE.

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	<u>Az-1</u> ave. of 5, 7 Apr. 1978 ppm	<u>Az-5</u> 22 July 1982 ppm
Na	2268	2376
ĸ	596	711
Li		39
Ca	9.6	9.1
SiO,	1117	1195
NH3	9.3	.19
so,	13.6	34.0
Rb		8.8
Cs		4.0
В	290	426
As		32.8
Has	en 8	13.5
F		1.3
C1	3859	4400
total C as HCO,	119	454
p H	6.98	7.24

TABLE 8: Recalculated downhole water compositions.

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Molalities determined by "pH" iterative program Temperature dependent dissociation constants are from

Arnorsson et al.	(1980).	Activity coefficients are
determined using	the exten	ded Debye-Huckel equation.

	<u>Az-1</u>	<u>Az-5</u>
ns	1.68×10^{-2}	7.75×10^{-2}
BOa	1.25×10^{-2}	1.48×10^{-2}
SIO(OH)	4.80×10^{-3}	4.20×10^{-3}
NHA	1.27×10^{-2}	2.00×10^{-4}
нсо	0.708	3.17
co,	4.46×10^{-6}	2.10×10^{-5}
pH	5.90	5.94

Molalities	determined	by a s	imple	concentra	tion	assumption

	Az-1	<u>Az-5</u>
	$(x_{w} = 0.58)$	$(x_{W} = 0.44)$
5i0_	1.08×10^{-2}	8.75×10^{-3}
к ⁺ 2	8.83×10^{-3}	8.00 x 10 ⁻³
Na .	5.71×10^{-2}	4.55×10^{-2}
2+ Ca ²⁺	1.39×10^{-4}	1.01×10^{-4}

Downhole concentration = X_{W} (surface concentration)

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FIGURE 8: Activity diagram of K^+/H^+ versus SiO₂. Diagram constructed using the data of Helgeson et al. (1978, 1981) assuming unit activities for mineral phases. Water compositions from Table 8.



FIGURE 9: Activity diagram of Ca⁺⁺/H⁺² versus SiO₂. Diagram constructed using the data of Helgeson et al. (1978, 1981). Expanded clinozoisite stability field has been constructed using equations of Bird and Helgeson (1980) and average measured epidote composition of pistacite 0.306; all other mineral phases are assumed to have unit activities. Water compositions from Table 8. for Az-1 at 300° C(based on thermodynamic data from Helgeson et al. (1978, 1981)). Considering the observed MnCO₃ component and assuming 10 mole percent MnCO₃ and an ideal mixing model, the affinity (- Δ G reaction) would be only slightly changed. Supersaturation with respect to calcite has also been observed at Cerro Prieto (Truesdell and Henley, 1982), and is attributed to loss of CO₂ gas by boiling in zones near the well, causing the pH of the fluids to rise and calcite supersaturation to increase. Discharge from well Az-1 has a lower steam fraction then does Az-5, which shows greater calcite supersaturation. These results are consistent with the observed calcite scaling in the steam well, Az-17, at Los Azufres.

Using the fluid data in Table 8, the partial pressures of CO_2 for the wells Az-1 and Az-5 were calculated to be 6.5 and 7.6 bars, respectively, from the reaction: $2H^+ + CaCO_3 = Ca^{++} + H_2O + CO_2$ (log K = 8.404 at 300°C (Helgeson et al., 1978, 1981)). The calculated fugacities of CO_2 for the two wells are 6.9 and 28 bars, respectively, using the equation:

 $fCO_2 = KhX(CO_2)$, where:

$$X((O_2) = \frac{Y X_{S}(\mathfrak{H})i}{100(1+YX_{S})}$$

with Y = molar gas/steam ratio

Xs = steam fraction

(%)i= mole % of CO₂ gas and using a Henry's Law constant (Kh) for CO_2 at $300^{\circ}C$ of 3890 bars/mole fraction (Glover, 1982). Considering that the saturation pressure of H₂O at the reservoir temperature of



FIGURE 10: Calcite saturation curve. Diagram constructed using data of Helgeson et al. (1978, 1981) assuming unit activity for calcite. Water compositions from Table 8. 300° C is only 86 bars, the higher P(CO₂) value seems unreasonable (e.g. Grant, 1982).

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Because many of the well discharges contain excess steam, temperatures calculated from enthalpy data are unrealistically high. Therefore, aquifer temperatures were calculated using chemical and isotope geothermometers (Table 9). The SiO_2 temperature (conductive cooling) for the well Az-1 and the sulfate-water 8¹⁸0 temperature for the well Az-5 are in good agreement with the maximum downhole measurement of 300°C. The Na-K-Ca and Na/K temperatures are somewhat higher for both wells. Quartz geothermometers may yield anomalously low temperatures (e.g. well Az-5) for high temperature () 250°C) fluids with correspondingly high silica contents due to the rapid precipitation of amorphous silica as the fluid rises and cools. Calculated Na-K-Ca temperatures that are too high may result from boiling in the aquifer which causes loss of CO_2 and subsequent removal of aqueous Ca^{++} as $CaCO_3$ is precipitated. Gas geothermometers commonly yield high temperatures because of their slow reaction rates (Fournier, 1981; Henley et al., 1984).

TABLE 9: Geothemometry results, T(°C).

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Geothermometer	Az-1	<u>Az-5</u>	<u>Az-6</u>	<u>Az-17</u>	Reference
SiO, (conductive cooling)	299	264	-	-	Fournier and Potter, 1982
SiO, (adiabatic cooling)	257	233	-	-	Fournier and Potter, 1982
Na/K	317	333	-		Fournier, 1979
Na/K	322	346	-	-	White, 1970
Na-K-Ca	311	321	-	-	Fournier, 1981
Methane	-	335	349	362	Henley et al., 1984
NH3	-	333	341	345	Henley et al., 1984
6 ¹⁸ 0 (SO4-H2O)	_	304	-	-	McKenzie and Truesdell, 1977

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2.4 STABLE ISOTOPE SYSTEMATICS OF THE LOS AZUFRES GEOTHERMAL SYSTEM

Stable isotope studies of active geothermal fields have been used to examine equilibrium states between hydrothermal fluids and alteration minerals (Clayton et al., 1968; Clayton and Steiner, 1975; Eslinger and Savin, 1973; Blattner, 1975; Lambert, 1975; Olson, 1979; Truesdell et al., 1979, 1984; Williams and Elders, 1981, 1984; Williams, 1982). These studies have compared experimentally determined fractionations of oxygen isotopes between minerals and water to isotopic analyses of alteration minerals and geothermal fluids which are constrained by downhole temperature measurements.

Table 10 contains chloride and isotopic analyses on steam and water samples as well as physical data specific to the collection. The analytical results have been converted to total well discharge compositions for Cl-, 6¹⁸0, and 6D(also shown in Table 10) using the equations:

> $\delta^{18}\text{Otd} = \delta^{18}\text{Ow} - X\text{sE}\delta^{18}\text{O}$ Dwtd = Dw - XsED

where

and

ED = 68 - 0.4t

 $E8^{18}0 = 9.2 - 0.04t$

at temperatures (t) from 80° to 100° C (Siggenbach, pers. comm., 1983) with Xs = steam fraction, Xw = water fraction, td = total discharge, and w = measured water composition.

samples. and calculated total discharge compositions of well fluids. TABLE 10: Collection data, Cl and isotope data of steam and water

411	Date	Collection	S ep	Collection		Hear	sured				Calcula	ted Total	Discharge
		Point	T(•C)	T(°C)	E(J/E)	4 ¹⁸ 0	ą	Cl(ppm)	3	x1(300°C)	6 ¹⁶ 0	0 \$	cl(ppm)
As-1	8/21/82	Weir	92	Bà	1582	4.0-	7	3416	0.475	0.831	-3.3	-57	1626
As-2	8/21/82	Weir	92	87	1210	-1.9	-54.5	2204	0.638	1.000	-3.9	-66	1406
17	8/21/82	Wair	92	78	1421	-1.0	-52.5	2644	0.545	0.945	-3.5	-67	1441
4-14	8/28/82	Wair	92	78	1421	-0.95	-51	2728	0.545	0.945	-3.5	-65	1487
A=-5	8/16/82	Separator: Water	164	1	1814	-2.5	Ŧ	1983	0.458	0.666	0. †	-67	806
		Bteam	1	1	١	-3.5	-70	0.19	1	ł	ł	ł	ł
A1-5	8/31/82	Neir	92	78	1014	-1.35	-57	24.35	C/C.O	0.666	8.4-	11-	906
Az-5	8/31/82	Weir	92	11	1814	-1.6	-57.5	2697	0.373	0.666	-5.0	-17	1006
Az-5	8/31/82	Steam line to turbine	١	Ļ	1814	-5.4	۰. ۱	0.04	ł	ł	1	ł	ł
4-14 V	8/16/82	fteem line to turbine	ł	ł	2660	5.4	-61.5	0.02	0.00	0.000	n. †	-61.5	ł
Az-6	8/16/82 (2hre later)	Steam line to turbine	ł	1	2660	9. T	9 1	0	0.000	0.000	9.4	-60	1
Ar-6	0/31/82	Steem line to turbine	1	1	2660	7.6	Ŧ	0	0.000	0.000	59.4	7	1
As-13	8/21/82	Weir	92	R	2173	1.1+	67	2650	0.215	014.0	-3.2	-63.5	570
As-13	8/28/82	Their	92	18	2173	+0.7	42.5	2319	0.215	0.410	-3.6	67	667
As-13	\$/31/62	Weir	92	8	2173	+1.2	-39	2634	0.215	0.410	1.6-	-63.5	566
(1-sy	20/12/0	Steam line to turbine	1	1	2173		-67	1	ł	ł	1	ł	:
As-17	8/16/82	Steam line to turbine	!	1	2660	e. T	-63.5	0.01	0.00	0.000	• 7	-63.5	ł
As-17	8/31/82	Steam line to turbine	ł	i	2660	£.7	-64.5	0	0.000	0.000	-4.95	-4.5	ł
As-19	8/21/82	Weir	92	£	1418	-1.05	-50	2459	0.547	0.947	-3.55	Ŧ	54C1
As-19	8/28/82	Neir	92	"	1418	-1.3	7	4622	0.547	0.947	-3.8	-63	1222
A1-19	8/31/82	Weir	92	8	1418	-1.6	-56.5	2798	0.547	0.947	17	11-	1681
As-19	8/31/82	Steam line	1	1	1418	-5.3	-70.5	0	ł	1	ł	ł	;
		to turbine											

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X_y = vater fraction at the separation temperature. X₁ = liquid vater fraction in the deep fluid feeding the well, assuming a reservoir temperature of 300°C. An₁ysts: 4D by C. Kandall, U. S. Geological Survey, Reston, Virg.; 4¹⁰0 and Cl by A. Brown, U. S. Geological Survey, Menlo Part, Calif. Isotope values are given in permit relative to VSMOW. The analytical precision of 1s for reported value is: 4D1.0; 4¹⁰0.10.1.

The isotopic composition of the reservoir fluids exhibit an apparent oxygen isotope shift of +5 to 6 permil from local meteoric waters, as illustrated in a plot of 6D versus 6^{18} O (Figure 11). The linear trend of the well discharge compositions which parallels the meteoric water line is possibly due to a mixture of recharge fluids that are derived from both local and regional sources. The scatter of data points along this trend may result from admixture of deep steam to the liquid phase.

The composition of high-enthalpy fluids at Los Azufres appears to be most affected by aquifer boiling and underground steam separation. This deep steam may feed wells directly, forming vapor-enriched, high-enthalpy discharges (e.g. wells Az-6 and Az-17), or may mix in variable amounts with the liquid phase. Wells that discharge vapor-depleted, low-enthalpy discharges (e.g. wells Az-2, Az-4, and Az-19) are fed primarily by the deep liquid.

Underground steam separation and addition of deep steam are illustrated by the the relation of enthalpy and isotope data with chloride compositions of the total discharges (Figure 12). Dilution of deep fluids by meteoric waters and addition of deep steam are modeled with mixing lines using the average composition of the local meteoric waters (6D = -68, $6^{10}O = -9.7$, Cl < 10 ppm (Giggenbach and Quijano, 1981; Combredet, 1982)) and the isotopic fractionation between steam and water at $300^{\circ}C$ (Δ ws ($6^{10}O) = 0.94$, Δ ws(6D) = -3.4 (Truesdell et al., 1977)). The mixing lines for the addition of deep steam were calculated assuming a temperature of $300^{\circ}C$. However, the fact that some data points fall off of the mixing lines suggests an addition of steam



FIGURE 11: Relationship between 6D and δ^{10} for Los Azufres geothermal fluids. Calculated total discharge of separated and weirbox waters (O, \Box) and separated steam (\odot, \boxdot) and meteoric waters are from Giggenbach and Quijano (1981) and this study. Two groups of meteoric waters consist of local waters (\triangle) from the high Los Azufres region and waters of the low-lying Laguna de Cuitzeo area (\triangle). separated at temperatures between 220°C (where 6D (H_2O liquid - H_2O vapor) = 0) and the discharge temperature. This process results in anomalously light D values for the total discharge fluids. Removal of steam from the reservoir causes heavier oxygen isotope compositions in the remaining liquid, and if this loss occurs between 220° and 300°C, the deuterium concentrations would not shift more than -4 permil. Other data scatter may be due to evaporation of water between the time of flashing and collection in the weirbox.

Temporal changes in isotope and Cl compositions of well discharges resulting from removal of reservoir fluids may be determined by repeated sampling. Changes are observed for the Los Azufres geothermal system by comparing 1982 data with 1980 and 1981 analyses reported by Giggenbach and Quijano (1981). A significant change is the shift of the liquid phase towards heavier δ^{180} values possibly due to removal of steam from the reservoir (see discussion below). Using our 1982 fluid data, the deep liquid phase has Cl = 1600 ppm, δ^{180} = -3.8, and δD = -65, whereas Giggenbach and Quijano (1981) calculated values of 1800 ppm, -4.2 and -65, respectively. Nieva et al. (1983) estimated an average reservoir chloride composition of 1650 ppm.

Fluid-mineral isotopic equilibria can be determined by comparing downhole fluid and alteration mineral compositions with predicted fractionations. Oxygen isotope compositions of quartz and calcite separates from the drill core P1-4 indicate deep Water compositions of -4.4 and -4.6, respectively, using the experimental fractionation curves of O'Neil et al. (1969) and Clayton et al. (1972) at 300°C. Therefore,

FIGURE 12: Plots of enthalpy, 61*0, and 6D values versus chlorides for Los Azufres well discharges. Predicted effects of steam addition and dilution are indicated with modeling lines. Data from Giggenbach and Quijano (1981)(() and this study([)). Filled symbols indicate estimated deep fluid and steam compositions.

a 6^{18} O value of -4.5 is estimated for the waters that equilibrated with this deepest mineral assemblage, and is assumed to represent the fluid composition at the time of drilling in 1977. The apparent shift in deep fluid composition from -4.5 to -3.8 permil between 1977 and 1982 may reflect increasing water-rock interaction in combination with steam removal as a boiling front expands into the reservoir resulting from a drop in aquifer pressure with initial flow.

Quartz and carbonate 8¹⁸0 values are plotted against 1/T2 in Figure 13 using measured downhole temperatures (Garfias and Gonzalez, 1978; Garfias and Casarrubias, 1979b). Linear trends with 1/T2 are observed for δ^{18} of both carbonate and silicate samples. However, the δ^{18} O trend for both calcite and quartz is much steeper than that predicted by the experimental fractionation curves of O'Neil et. al. (1969) and Clayton et. al. (1972), suggesting significant deviations from equilibrium for all but the deepest, highest-temperature samples. The difference may be partially due to isotopic fractionation between steam and water as the fluid boils upon rising through the reservoir (Bottinga and Craig, 1968; Truesdell et al., 1977), but water moving from the lower part of well Az-1 to the 200°C level should change in 6^{18} O by only + 0.6 permil (Truesdell et. al., 1977). This effect might be explained by interaction between the geothermal fluids and the wallrock, causing the water to shift towards higher 8180 values, depending on the water/rock ratios and whether the system is open or closed (Craig, 1963; Taylor, 1974; 1977). However, this process cannot explain the relatively heavy oxygen isotope compositions of the minerals. Water-rock reactions cause reservoir fluids to become enriched with 180

with time, and earlier episodes of equilibrium deposition would yield minerals that have lighter 6¹⁸0 values, assuming present thermal conditions.

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A probable cause for the high δ^{18} O values of calcite and quartz is that the samples reflect earlier equilibration at lower temperatures. The δ^{18} O values of quartz samples from depths of 594 to 875 m are much too high to indicate a residual primary igneous quartz signature, as Clayton and Steiner (1975) suggested for Wairakei. The observed isotopically heavy calcite and quartz from the shallower samples could only result from low-temperature (<150°C) equilibration, and perhaps with isotopically heavier waters than are currently detected. The observed large calcite-quartz fractionation indicates that, over time, secondary calcite has partially reequilibrated with the warmer geothermal fluids. The two-stage model of hydrothermal activity at Los Azufres, as proposed by Gutierrez and Aumento (1982) based on multiple subparallel alteration mineral zones, is compatible with these observations.

A plot of δ^{18} O versus δ^{13} C for calcite separates (Figure 14, data in Table 11) illustrates a general trend towards lighter isotopic compositions with increasing depths and temperatures. A similar correlation has been observed for samples from the Cerro Prieto field (Williams, 1982). Within the production zone, δ^{13} C content is relatively independent of changes in δ^{18} O content for samples taken from the well bottom.

FIGURE 13: Oxygen isotope compositions of calcite and quartz separates. Values are plotted against measured downhole temperatures. Experimental calcite-water and quartz-water fractionation trends for 61*0 water values of -4.5 (solid line) and -3.8 (dot-dash line) are indicated.

Sample	Depth	Temp °C	CaCO3 Z	6 ¹⁸ 0 Cc.	\$ ¹³ C Cc.	6 ¹⁸ 0 wh. rk. sil.	6 ¹⁸ 0 Qtz.
<u>Az-1</u>			<u> </u>				
P1-2	594	206	5.0	6.9	-7.3	9.8	19.2
₽1-3	1685	280	4.8	1.3	-7.5	2.1	5.6
P1-4	1827	292	4.5	1.0	-7.7	0.3	3.8
<u>Az-6</u>							
P6-1	604	232	10.0	3.6	-7.1	7.5	14.8
P6-2	875	248	10.6	3.5	-7.5	5.3	9.4

TABLE 11: Isotopic data for drill-core samples.

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Temperatures are from Acero (1977), Garfias and Gonzalez (1978), and Garfias and Casarrubias (1979). Quartz was separated from the drill-core samples by methods of Kiely and Jackson (1965) and Syers et al. (1968). Samples were analyzed by C. Johnson, P. F. Dobson, and J. Drotleff at the U. S. Geological Survey, Menlo Park, Calif. The average δ^{13} C of CO₂ in the three steam samples is -7.0 +/- 0.1. An equilibrium fractionation between this CO₂ and the deepest calcite sample indicates an unreasonable temperature of 205°C. Therefore, it appears that the calcite-oxygen in the production zone is nearly in equilibrium with the deep liquid, but calcite-carbon is not in equilibrium with reservoir CO₂.

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FIGURE 14: Relationship between δ^{18} C and δ^{13} C for calcite separates. Data from Combredet (1982) and this study. Sample depth given in meters next to symbol.

2.5 <u>CONCLUSIONS</u>

Isotopic and chemical data from several wells of the Los Azufres geothermal field indicate that the shallow, lower temperature levels of the system are in a state of disequilibrium. Thermodynamic mineral relationships, as expressed by activity-activity diagrams, correspond well with the observed alteration mineralogy and help constrain possible downhole pH and $f(CO_2)$ values. Observed isotopic fractionations, however, suggest that the secondary calcite and quartz equilibrated during an earlier hydrothermal regime at lower temperatures than are presently observed. Changes in the isotopic compositions of the well discharges between 1980 and 1982 are probably due to steam loss.

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