AN OXYGEN-ISOTOPE STUDY OF HYDROTHERMALLY ALTERED ROCKS AT THE LOS AZUFRES GEOTHERMAL FIELD, MEXICO

Ignacio Torres-Alvarado, Muharrem Satir, Steven Fortier and **Paul** Metz

Institut fur Mineralogie, Petrologie und Geochemie
Wilhelmstr. 56,72074 Tubingen, F. R. Germany

Keywords: Hydrothermal alteration, oxygen isotopes, ^{18}O-shift, Los Azufres, Mexico.

ABSTRACT

The $\delta^{18}O$ systematics of the Los Azufres geothermal field (Mexico) were investigated on **44** whole rock samples and 18 authigenic quartz and calcite samples from different depths from wells Az-26 and Az-52. The $\delta^{18}O$ values of the analysed whole rock samples vary from +2.2‰ to +16.7‰. These values show a temperature-dependent isotope exchange, shifting the rock isotopic composition to heavier $\delta^{18}O$ values at temperatures lower than ≈90°C and to lighter values at temperatures higher than 90°C. The $\delta^{18}O$ range of the analysed quartz samples is **+3.93‰** to +20.23‰. The analysed calcite samples yield values between +3.38‰ and +12.23‰. Some of the analysed quartz samples have $\delta^{18}O$ values that are not in isotopic equilibrium with present thermal or meteoric water at ***in*** *situ* temperatures. The majority of the analysed calcites have isotope ratios close to or in isotopic equilibrium with present thermal or meteoric water at ***in situ*** temperatures. Some of the analysed minerals may have precipitated from waters significantly enriched in ^{18}O relative to present geothermal fluids.

1 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 (Fig. 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 and Verma, 1987; Mooser, 1972; Robin, 1982).

Los Azufres has been intensively investigated and developed since 1970. Almost 60 wells have been drilled, and with **a** production of 98 MW it represents the second most important geothermal field in Mexico.

Studies of hydrothermal alteration at Los Azufres have been carried out by different authors using mainly petrographical techniques (Cathelineau and Izquierdo, 1988; Cathelineau, ***et al.,*** 1985; González Partida and Nieva Gómez, 1989; Robles Camacho, ***et al.,*** 1987). These studies have shown that partial to complete hydrothermal metamorphism with mineral paragenesis from greenschist to amphibolite facies has occurred (Cathelineau, ***et al.,*** 1991). Various stable isotope studies on meteoric and geothermal fluids from the field (Giggenbach and Quijano, 1981; Ochoa Pérez and Meza de Luna, 1989; Ramirez Dominguez, *et al.*, 1988; Tabaco Chimal, 1990), indicate that the $\delta^{18}O$ values of present day meteoric and geothermal water are ≈ -9‰ ± 1‰ and ≈ -4‰ ± 1‰, respectively. Oxygen isotope systematics of altered rocks and authigenic minerals, in contrast, have received little attention.

The purpose of the present study was to obtain **a** better understanding of the waterhock interaction processes occurring in the field and to investigate the state of equilibrium between water and minerals in the active hydrothermal system from Los Azufres.

2 GEOLOGICAL SETTING AND SAMPLES

The volcanism at Los Azufres is made up of two principal units (Fig. 1): (1) a silicic sequence of rhyodacites, rhyolites and dacites with ages between 1.0 and 0.15 m.y. and a thickness up to 1000 m, and (2) a 2700 m thick interstratification of lava flows and pyroclastic rocks, of andesitic to basaltic composition with ages up to 18 **m.y.**, forming the local basement (Dobson, 1984). The thermal fluids are sodium-chloride rich waters with high C02 and H_2S contents, pH 7-8.

The samples studied were drill cuttings and cores from different depths of the wells Az-26 and Az-52 (Fig. 1). The well Az-26 (1241 m in depth) includes the whole volcanic sequence, with the first 500 m an interstratification of rhyolites and dacites (from here on called felsic rocks) overlying andesites which extend down to the bottom. The well Az-52 (1936 m in depth), though completely drilled through andesites (from here on called mafic rocks), shows a wide range of hydrothermal alteration **as** well **as** interesting hydrothermal paragenesis (Huitrón Esquivel, ***et al.,*** 1987; Rodriguez Salazar and Garfias, 1981).

For this investigation 44 whole rock samples and 18 hydrothermal minerals (quartz and calcite) were analysed for their $\delta^{18}O$ composition. The analysed whole rock samples showed hydrothermal alteration to differing extents, varying with the amount of hydrothermal alteration relative to primary minerals from 0 to 70%. The quartz and calcite separates were from fracture- or vug-filling deposits or when present, complete fragments from drill cuttings.

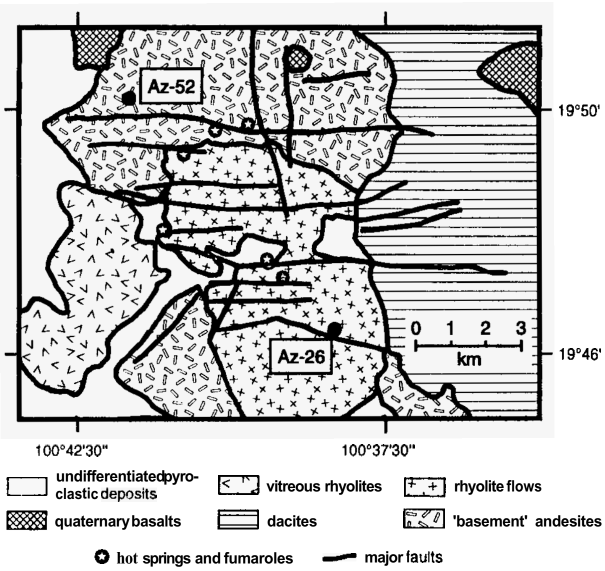

Fig. 1. Geologic map of the Los Azufres area, simplified after Dobson, 1984. Az-26 and Az-52 = studied wells.

3 ANALYTICAL METHODS

Minerals were separated by mechanical methods, heavy fluids, and finally by hand picking. Oxygen isotope analyses of whole rock and quartz samples were obtained by the BrF_5 method (Clayton and Mayeda, 1963). Oxygen and carbon isotope analyses of calcite were obtained by the phosphoric acid method (McCrea, 1950). Oxygen isotope ratios are reported relative to VSMOW (Vienna Standard Mean Ocean Water) in the δ notation, $\delta=[(R_{sample}/R_{standard})-1)\times 1000$, where R is $^{18}O/^{16}O$. The precision of the $\delta^{18}O$ measurements is better than ±0.2‰.

4 RESULTS AND DISCUSSION

The analytical results are shown in Figures 2 to **4,** along with *in situ* temperatures for each sample, measured by geophysical methods (Huitrón Esquivel, *et al.*, 1987; Rodriguez Salazar and Garfias, 1981). These *in situ* temperatures were derived by linear interpolation with depth between measurements obtained approximately two months after drilling. The time delay is that needed to achieve underground thermal stability, based on experience in this field. The temperatures are considered accurate to ±5°C.

4.1 Whole rock samples

The relation of $\delta^{18}O$ values for whole rock samples from Los Azufres drill cuttings from wells Az-26 and Az-52 to depth and *in situ* temperatures is shown in Fig. 2. The $\delta^{18}O$ values range from +2.2‰ to +16.7‰. In well Az-52 $\delta^{18}O$ values decrease with increasing depth, showing **a** continuous correlation with temperature. Az-26, on the other hand, shows **a** different correlation: from the surface to 400 m depth the $\delta^{18}O$ values are around +9‰ with a very small variation; after this depth the $\delta^{18}O$ shifts abruptly to ≈ +17‰, decreasing after 400 m to values = +4‰, in continuous correlation with temperature.

The initial $\delta^{18}O$ value of the investigated rocks can not be measured directly because of the hydrothermal alteration which has acted to some extent in **all** samples. However according to the values obtained from the least altered samples and from the relations observed in Fig. 2, we can assume an initial $\delta^{18}O_{rock}$ ≈ +8 ‰ for mafic rocks and ≈ +9 ‰ for felsic ones. These values are typical for fresh rocks from other volcanic systems (Hoefs, 1980).

Assuming this range for the initial $\delta^{18}O_{rock}$, processes controlling isotope exchange appear to be basically temperature dependent. Thus in lower temperature regions (**up** to ≈ 90°C, 600 m depth, Az-26 and 300 m depth, 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.

A color key is used in Fig. 2 to show the relation between the relative amount of hydrothermal alteration observed microscopically and the oxygen isotope ratios. Although Az-52 samples do not show any apparent relation between $\delta^{18}O$ values and percentage of hydrothermal alteration, samples from well Az-26 show a correlation between lighter oxygen isotopes ratios, higher amounts of alteration, and higher temperatures.

4.2 Quartz

The $\delta^{18}O$ values of quartz are shown in relation to *in situ* temperatures in Fig. 3. Two coloured bars are also plotted

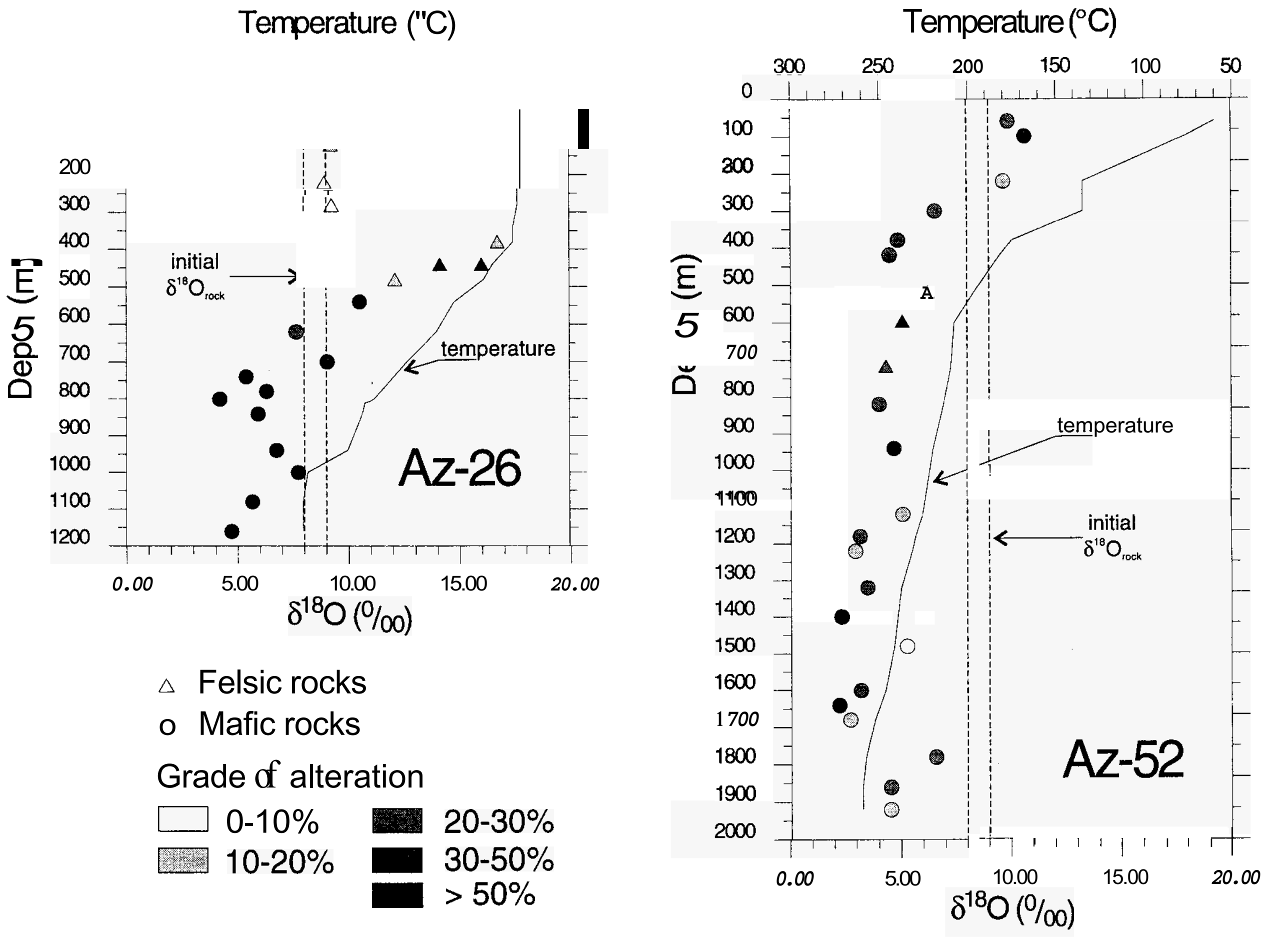

Fig. 2. $\delta^{18}O$ values of whole rock samples *vs.* depth and in *situ* temperatures from wells Az-26 and Az-52.

representing the area where theoretical quartz samples would plot if they were in isotopic equilibrium with present meteoric or geothermal water, respectively. For these calculations an extrapolation of the 200 to 500°C quartz-water fractionation factors of Clayton, ***et al.*** (1972) was used. The range of the analysed quartz samples is +3.93‰ to +20.23‰.

From the 10 analysed specimens, three appeared 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 rest of the samples are not in equilibrium, suggesting that changes in temperature and/or $\delta^{18}O_{H_2O}$ have occurred since quartz deposition. Considering that the samples in disequilibrium are from the deepest (and thus from the hottest) zones of well Az-52, the measured $\delta^{18}O_{quartz}$ can 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 time of quartz deposition. Gonzalez Partida and Barragán (1989) measured homogenisation temperatures of fluid inclusions in hydrothermal minerals from both wells, obtaining temperatures on average 30°C higher than present ***in situ*** temperatures, supporting our interpretation. The corresponding range in $\delta^{18}O_{water}$ for these quartz samples would have been -2.3‰ to +4.3‰, ≈ 4‰ heavier than present thermal water.

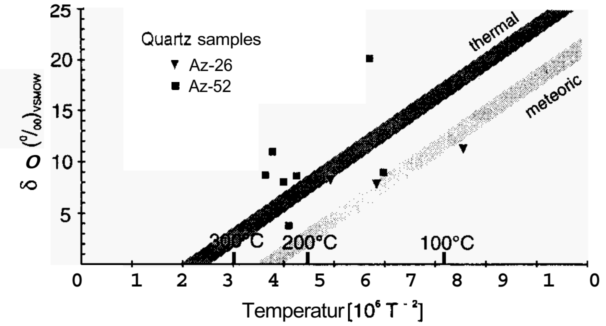

Fig. 3. $\delta^{18}O$ values of analysed quartz samples ***vs. in situ*** temperatures. The bars represent the areas of isotopic equilibrium between quartz and present meteoric water ($\delta^{18}O$ ≈ -8 to -10‰) and thermal fluids ($\delta^{18}O$ = -3 to -5‰).

4.3 Calcite

The $\delta^{18}O$ values of calcite are shown in relation to ***in situ*** temperatures in Fig. 4. Also shown in this figure are the areas representing calculated $\delta^{18}O$ for calcite in equilibrium with water with the present isotopic composition of meteoric and geothermal fluids (according to the calcite-water fractionation factors of ONeil, ***et al.,*** 1969). Calcite samples yield $\delta^{18}O$ values from +3.38‰ to +12.23‰.

Most of the analysed 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 the results of other studies showing that carbonate minerals tend to equilibrate readily with fluids in zones with relatively high waterhock ratios (Clayton, ***et al.***, 1968; Clayton and Steiner, 1975; Sturchio, ***et al.***, 1990; Williams and Elders, 1984). One sample appeares to be enriched in ^{18}O. It could have equilibrated with a thermal fluid of an isotopic composition of +1.6‰, possibly indicating calcite precipitation from ^{18}O-enriched water and/or a region with small waterhock ratios (very low permeability), explaining the disequilibrium with present thermal water.

5 CONCLUSIONS

Temperature represents the most significant factor controlling the $\delta^{18}O$ values of whole rock samples from wells **Az-26** and Az-52 at the Los Azufres geothermal field, with $\delta^{18}O$ paralleling temperature over most of both profiles. Oxygen isotope exchange to heavier $\delta^{18}O$ values occurs under temperatures lower than 90°C. Some of the analysed quartz samples have $\delta^{18}O$ values that are not in isotopic equilibrium with present thermal or meteoric water at ***in situ*** temperatures. On the other hand, most of the calcites analysed have isotope ratios close to or in isotopic equilibrium with present thermal or meteoric water at *in situ* temperatures. Minerals in disequilibrium may have precipitated from waters that were significantly enriched in ^{18}O relative to present geothermal fluids. The inferred ^{18}O enrichment has been preserved in quartz better than in calcite, presumably because of the resistance of the former to subsequent oxygen isotope exchange with water.

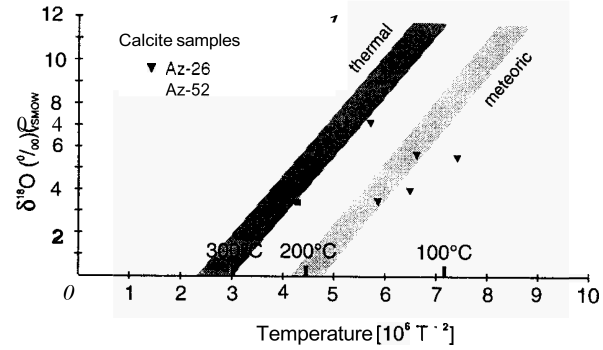

Fig. 4. $\delta^{18}O$ values of analysed calcite samples ***vs. in situ*** temperatures. The bars represent the areas of isotopic equilibrium between calcite and present meteoric water ($\delta^{18}O$ ≈ -8 to -10‰) and thermal fluids ($\delta^{18}O$ ≈ -3 to -5‰).

ACKNOWLEDGEMENTS

This work was supported by the foundations Alfried-Krupp-von-Bohlen-and-Halbach and Hans-Bockler. We thank T. Kretzschmar for reviewing the manuscript.

REFERENCES

Aguilar y Vargas, V.H. and Verma, S.P. (1987). Composición quimica (elementos mayores) de los magmas en el Cinturón Volcinico Mexicano. In Verma, S.P. (Eds.), ***Special volume on the Mexican Volcanic Belt - Part 3B. Geof. Int.***, 26, pp. 195-272.

Cathelineau, M. and Izquierdo, G. (1988). Temperature-composition relationships of authigenic micaceous minerals in the Los Azufres geothermal system. ***Contrib. Mineral. Petrol.,*** Vol. 100, pp. 418-428.

Cathelineau, M., Oliver, R., Garfias, A., and Nieva, D. (1985). Mineralogy and distribution of hydrothermal mineral zones in the Los Azufres (Mexico) geothermal field. ***Geothermics,*** Vol. 14, pp. 49-57.

Cathelineau, M., Izquierdo, G., Vázquez, G.R., and Guevara, M. (1991). Deep geothermal wells in the Los Azufres (Mexico) caldera: Volcanic basement stratigraphy based on major-element analysis. ***J. Volcanol. Geotherm. Res.,*** Vol. 47, pp. 149-159.

Clayton, R.N. and Mayeda, T. (1963). The use of bromine pentafluoride in the extraction of oxygen from oxides and silicates for isotopic analysis. ***Geoch. Cosmochim. Acta,*** Vol. 27, pp. 43-52.

Clayton, **R.N. and** Steiner, **A. (1975).** Oxygen isotopes studies of the geothermal system at Wairakei, New Zealand. ***Geoch. Cosmochim. Acta,*** Vol. 39, pp. 1179-1186.

Clayton, **R.N.**, Muffler, L.P.J., and White, D.E. (1968). Oxygen isotope study of calcite and silicates of the River Rancho No. 1 well, Salton Sea geothermal field, California. ***Am. Jour. Sci.***, Vol. 266, pp. 968-979.

Clayton, R.N., ONeil, J.R., and Mayeda, T.K. **(1972).** Oxygen isotope exchange between quartz and water. ***J. Geoph. Res.,*** **Vol. 77,** pp. **3057-3067.**

Dobson, P.F. **(1984)** ***Volcanic stratigraphy and geochemistry of the Los Azufres Geothermal Center, Mexico.*** Master Degree Thesis, Stanford University, **58** pp.

Giggenbach, W. and Quijano, L. **(1981).** ***Estudio isotdpico de las aguas del campo geotirmico de Los Azufres, Michoacan.*** Unpublished internal report, Comisión Federal de Electricidad, Mexico, **25** pp.

Gonzfilez Partida, E. and Barragfin, R.M. **(1989).** Estudio detallado de las inclusiones fluidas en el sistema hidrothermal activo del campo geottrmico de Los Azufres, Mich. ***Geotermia, Rev. Mex. Geoenergia,*** Vol. 5(1), pp. 126-152.

Gonzfilez Partida, E. and Nieva Gómez, D. **(1989).** Caracterización mineralógica en 10 pozos del campo geothmico de Los Azufres, Mich. I: Minerales opacos. ***Geotermia, Rev. Mex. Geoenergia,*** Vol. 5, pp. **347-373.**

Hoefs, J. **(1980).** ***Stable isotope geochemistry*** (3rd ed.). Springer, Berlin, **241** pp.

Huitrón Esquivel, R., Gonzfilez, M.A., and Abad Rodriguez, A. **(1987).** ***lnforme del pozo Az-52 del campo geotérmico de Los Azufres, Michoacun.*** Unpublished internal report, Gerencia de Proyectos Geotérmicos, Comisión Federal de Electricidad, Mexico, **43** pp.

McCrea, J.M. **(1950).** On the isotopic chemistry of carbonates and a paleotemperature scale. ***J. Chem. Phys.,*** Vol. **18,** pp. 849-857.

Mooser, F. **(1972).** The Mexican Volcanic Belt: Structure and tectonics. ***Geof. Int.,*** **Vol. 12,** pp. **55-70.**

ONeil, J.R., Clayton, R.N., and Mayeda, T.K. **(1969).** Oxygen isotope fractionation in divalent metal carbonates. J. ***Chem Phys.,*** Vol. **51,** pp. 5547-5558.

Ochoa Pérez, M. and Meza de Luna, E. **(1989)** ***Determinaciones isotópicas de Deuterio, ^{18}O y ^{13}C enjluidos del campo geotérmico de Los Azufres, Michoacán.*** Tesis de licenciatura, Instituto Tecnológico de La Laguna, **120** pp.

Ramírez Dominguez, E., Verma, M.P., and Nieva, D. **(1988).** Ebullición y mezcla en procesos de formación de fuentes termales en Los Azufres, Mich. ***Geotermia, Rev. Mex. Geoenergia,*** Vol. **4(2),** pp. **59-77.**

Robin, C. **(1982).** Mexico. In Thorpe, R.S. (Eds.), ***Andesites.*** John Wiley & Sons, Chichester, pp. **137-147.**

Robles Camacho, J., Izquierdo Montalvo, G., and Oliver Hernández, R. **(1987).** Alteración hidrotermal en el Módulo Maritaro, Los Azufres, Michoach ***Geotermia, Rev. Mex. Geoenergla,*** **Vol.** 3(2), pp. **131-143.**

Rodriguez Salazar, **A.** and **Garfias,** A. **(1981).** ***Resumen geológico del pozo Az-26 del campo geotirmico de Los Azufres, Michoacan.*** Unpublished internal report, Gerencia General de Estudios e Ingenieria Preliminar, Comisión Federal de Electricidad, Mexico, **34** pp.

Sturchio, N.C., Keith, T.E.C., and Muehlenbachs, K. **(1990).** Oxygen and carbon isotope ratios of hydrothermal minerals from Yellowstone drill cores. ***J. Volcanol. Geotherm. Res.,*** **Vol. 40,** pp. **23-37.**

Tabaco Chimal, F. **(1990)** ***Estudio isotópico del Carbono-13 en fluidos hidrotermales del campo geotérmico de Los Azufres, Michoacun.*** Tesis de Licenciatura, Universidad Autónoma de Tlaxcala, **93** pp.

Williams, A.E. and Elders, W.A. **(1984).** Stable isotope systematics of oxygen and carbon in rocks and minerals from the Cerro Prieto Geothermal Anomaly, Baja California, Mexico. ***Geothermics,*** Vol. **13,** pp. **49-63.**