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MINERAL CHEMISTRY OF HYDROTHERMAL SILICATES IN LOS AZUFRES GEOTHERMAL FIELD, MEXICO

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ABSTRACT

The chemical composition of hydrothermal silicates at Los Azufres geothermal field (Mexico) was studied using microprobe techniques. The main objective of this study was to study the compositional variations of secondary silicates in relation to changes of the physico-chemical parameters in the field, in order to obtain a better understanding of the water/rock interaction processes occurring in this active hydrothermal system. The most abundant minerals are chlorite, epidote, quartz, calcite und sericite. Zeolite, several types of clay minerals, potassium feldspar, albite, prehnite, amphibole, hematite, pyrite and hydrothermal garnet are also present. Chlorites show a relatively homogenous Fe-clinochlore composition. Epidotes are solid solutions with Fe-epidote as the dominant end member. Hydrothermal garnets are grossular-rich solid solutions with higher andradite content in core areas. Amphiboles show an Fe-rich tremolite composition.

On the basis of the investigated hydrothermal minerals and their changes with depth it is possible to delimit three zones in the altered rocks from Los Azufres. Using the stability conditions of significant mineral assemblages it is also possible to stimate the temperatures of these zones.

Zone I. Main paragenesis: stilbite + chlorite + calcite; max. depth approx. 500 m; temperature lower than 170°C and pressure lower than 50 bar.

Zone II. Main paragenesis: heulandite + chlorite + calcite or wairakite + chlorite + calcite; max. depth 1500 m approx; temperature between about 170°C and 250°C and pressure up to 150 bar.

Zone III. Main paragenesis: epidote + tremolite + chlorite; max. depth 3000 m approx; temperature higher than 250°C and pressure between about 150 and 200 bar.

1. INTRODUCTION

Hydrothermal minerals in geothermal systems are an important tool to reveal the structure of the geothermal reservoir, as well as the physico-chemical and hydrogeological conditions prevailing in it. Although mineralogical studies of the hydrothermal alteration in active geothermal fields have been performed during the last 30 years, more detailed mineralogical investigations, particularly those oriented to determine the chemical composition of hydrothermal minerals using modern analytical techniques, are still to be done (Browne, 1998).

We report in this work the results of petrographical and chemical studies carried on hydrothermally altered cores and cuttings from Los Azufres geothermal field. The objectives of these studies were (1) to characterise the chemical composition of hydrothermal silicates, (2) to study the compositional variations of secondary minerals in relation to changes of the physico-chemical parameters in the field and (3) to obtain a better understanding of the water/rock interaction processes occurring in this active hydrothermal system.

2. GEOLOGICAL SETTING

Los Azufres is one of several Pleistocene silicic volcanic centres with active geothermal systems in the Mexican Volcanic Belt (MVB, Aguilar y Vargas and Verma, 1987). It is located approximately 200 km Northwest of Mexico City (Fig. 1). With an electricity production of 98 MW, it represents the second most important geothermal field in Mexico (Quijano León and Gutiérrez Negrín, 1995).

The volcanic rocks at Los Azufres have been described by different authors (Cathelineau *et al.*, 1987; De la Cruz *et al.*, 1982; Dobson and Mahood, 1985; Huitrón Esquivel and Franco Serrano, 1986; López Hernández, 1991; Razo Montiel *et al.*, 1989). Geologically, two principal units can be distinguished:

(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 (Dobson and Mahood, 1985);

(2) a 2700 m thick interstratification of lava flows and pyroclastic rocks, of andesitic to basaltic composition with ages between 18 and 1 m.y., forming the local basement. This unit provides the main aquifer with fluid flow through fractures and faults, sometimes reaching the surface.

Three different fault systems, which confer secondary permeability to the geological units, can be distinguished in the field (Garduño Monroy, 1985; Garduño Monroy, 1988): NE-SW, E-W and N-S. The E-W system is the most important one for geothermal fluid circulation. Geothermal manifestations (fumaroles, solfataras and mudpits), geophysical anomalies and important energy production zones are related to this fault system.

Hydrothermal alteration has affected most rocks in the geothermal field to varying extent. Studies of hydrothermal alteration at Los Azufres have been carried out, among others, by Cathelineau *et al.* (1985), González Partida *et al.* (1989) Robles Camacho *et al.* (1987) and Torres-Alvarado (1996). These studies have shown that partial to complete hydrothermal metamorphism has occurred. Most important alteration assemblages with increasing depth are:

argillitization/silicification, zeolite/calcite formation, sericitization/chloritization, and chloritization/epidotization. For a complete description of alteration characteristics see Cathelineau *et al.* (1985) and Torres-Alvarado (1996).

3. SAMPLES AND ANALYTICAL PROCEDURES

Drill cuttings and cores from different depths of the wells Az-3, Az-25, Az-26, Az-29, Az-49 and Az-52 (Fig. 1) were used for petrographical and microprobe analyses. Most of these wells were drilled through andesites, andesitic tuffs, and to a lesser extent through basaltic units. An exception to this are the wells Az-25 and Az-26, which penetrated an intercalation of rhyolites and dacites in the first 400 to 500 m depth, and andesites down to the bottom. For a complete description of the lithological sequences cutted by the wells see Torres-Alvarado (1996).

Electron microprobe analyses were carried out for major elements at the University of Tuebingen, using an ARL-SEMQ microprobe, with 15 kV acceleration potential and a beam size of 5-10 µm. Data were recorded during approximately 180 s (three iterations) and corrected using the ZAF procedure. Analytical errors are better than 5%.

4. RESULTS

4.1 Primary minerals

The most important primary minerals in the two most important lithological units are (Torres-Alvarado, 1996):
Basaltic andesites and andesites: labradorite-bytownite (Ab_{22-48}), ± andesine (Ab_{50-57}) and augite. Accessory minerals are mainly olivine, biotite, hornblende, zircon, and apatite.
Rhyolites and rhyodacites: quartz, anorthoclase-sanidine ($Ab_{87}Or_{13}$ to $Ab_{58}Or_{42}$), ± oligoclase-andesine. Biotite, and apatite are accessory constituents.

4.2 Hydrothermal minerals

In Los Azufres hydrothermal minerals appear both, as alteration of the primary minerals and of the rock matrix, as well as filling vesicles and fractures. Although hydrothermal alteration has changed the primary minerals in different ways and magnitude, often the original textures and mineral components are still recognisable. Table 1 shows the most important hydrothermal minerals, and their precursors.

Minerals filling vesicles and fractures are mainly chlorite, quartz, chalcedony and amorphous silica, as well as calcite and epidote. Zeolite (stilbite, heulandite, laumontite and wairakite), hematite, pyrite, and sericite are also observed. Rarely amphiboles, sulfates (anhydrite and/or barite?), prehnite, and garnet are present. Mineral associations in vesicles are frequent; they consist of chlorite plus quartz, quartz plus epidote, and more rarely chlorite plus calcite.

4.3 Chemistry of hydrothermal minerals

Secondary feldspars, chlorites, epidotes, garnet, and amphiboles were analysed with the electron microprobe. Clay minerals were investigated using X-ray diffractometry by Izquierdo *et al*., (1995). For each mineral group a brief description is presented below.

Feldspar

Secondary feldspars are the product of plagioclase substitution and sometimes related to epidote. Unlike other geothermal fields, where hydrothermal feldspars can be found filling fractures and vesicles (Browne, 1984), they are rarely observed that way in Los Azufres. Compositionally, secondary feldspars are albite-rich plagioclases (Ab_{87-98}) and alkali-feldspars with a chemical composition $Ab_{80}Or_{20}$ and $Ab_{8-11}Or_{92-89}$ (adularia).

Chlorite

Chlorite in Los Azufres shows a wide distribution and a big variability of colors, forms, and textures. It varies in color from pale to dark olive green; it has low birefringence and occasionally shows anomalous purple interference colors. It may fill vesicles and fractures, or it may form banded, concentric, or radial structures, and sometimes idiomorphic crystals occur. Within veins, chlorite occurs as microspherules enclosed within epidote, but it may also replace primary pyroxene, biotite, and the matrix.

Electron microprobe analyses of chlorites occurring in veins (i.e. crystallized from a hydrothermal solution) and of chlorites replacing the groundmass are shown in Fig. 2, classified according to Hey (1954). Most chlorites in Los Azufres are Mg-rich, showing compositions principally on the pycnochlorite, diabantite, rhipidolite, and clinochlore field.

Epidote

The first appearance of this mineral is between 500 and 1200 m depth, above the 200ºC isotherm. Epidotes are more abundant in the northern part of the field, due to its higher temperatures and lower vapor fraction in its fluids. Epidotes show a systematic textural development with increasing depth. First crystals are anhedral and form fine grained aggregates. In deeper zones they are idiomorphic, tabular, radiated, or fibrous; here epidote achieves its biggest abundance with a wide variety of textures, and forms. Furthermore epidotes can be found filling fractures, vesicles, and replacing primary plagioclase and pyroxene. Frequently epidote forms mineral associations with quartz, chlorite and sometimes with calcite, wairakite and pyrite. Rarely it may be found in contact with amphibole and/or prehnite at temperatures higher than 250ºC.

Microprobe analyses of epidotes are shown in Fig. 3. These minerals are a solid solution with the epidote (Fe-rich), clinozoisite (Fe-poor) and Mn-piemontite as end members. Most epidotes in Los Azufres are Fe-rich, the clinozoisite content can increase only rarely up to 60%.

Garnet

Garnet in Los Azufres has been observed rarely. Garnet crystals associated to quartz in well Az-29, at 2220 m depth, were analysed with microprobe analytical techniques. The analysed hydrothermal garnet has a grossular composition, with a core having andradite up to 20 wt% (Fig. 4).

Amphiboles

In the altered rocks from Los Azufres secondary amphiboles are encountered occasionally. They are difficult to determine because of their small crystal size and intergrowth with epidote. Texturally they form radial, fibrous and sometimes tabular aggregates. The analysed amphiboles are tremolite rich solid solutions between tremolite and ferro-actinolite. Gedrite has been rarely observed in Los Azufres. Amphiboles are in so far important as they indicate high temperatures in the field (> 250ºC).

5. MINERAL PARAGENESES

On the basis of the hydrothermal minerals and their changes with depth it is possible to delimit three specific mineral zones in the altered rocks from *Los Azufres*:

Zone I. Typical hydrothermal minerals in this zone are smectite, zeolite, calcite and chlorite. In addition some other clay minerals such as kaolinite and minor amounts of illite may be found (Izquierdo *et al.*, 1995). Furthermore, amorphous silica, and quartz are also present. Regarding zeolites stilbite may be the principal mineral (Torres Alvarado, 1996). Petrogenetically the paragenesis stilbite + chlorite + calcite is significant. Zone I reaches maximal depths of about 500 m, corresponding to a pressure of 50 bars; from bore hole measurements the temperature is lower than 170°C.

Zone II. This zone contains zeolites as well, but due to its higher temperatures, they are possibly not stilbite, but heulandite and wairakite. Chlorite, calcite, and quartz are common, and reach their maximal abundance. Albite, sphene, pyrite, hematite, illite, and sometimes laumontite and anhydrite are also present. The first appearance of epidote and prehnite belongs to this zone. The petrogenetically important mineral assemblages are: heulandite + chlorite + calcite or wairakite + chlorite + calcite. The physical conditions for Zone II are depths below 1500 m, i.e. pressures lower than 150 bars and temperatures between about 170°C and 250°C.

Zone III. This zone is characterised by the mineral association of epidote and amphibole. Besides those chlorite, quartz, pyrite, hematite, prehnite, and garnet are also present. The main paragenesis for this zone is epidote + tremolite + chlorite. Typical depths for this zone are between 1500 and 3000 m, i.e. pressures between 150 and 300 bars, and temperatures are higher than 250°C, when the fluid consists of H_2O.

6. CONCLUSIONS

There is a wide variety of hydrothermal minerals in Los Azufres geothermal field. The alteration follows propylitic characteristics, chemically and texturally similar to other geothermal fields. Although hydrothermal minerals show larger textural variations, chemically they are relatively homogeneous, as was shown by the microprobe analyses carried out on hydrothermal chlorites, epidotes, amphiboles, and garnet.

REFERENCES

Aguilar y Vargas V. H. and Verma S. P. (1987) Composición química (elementos mayores) de los magmas en el Cinturón Volcánico Mexicano. In Special volume on the Mexican Volcanic Belt - Part 3B, Vol. 26 (ed. S. P. Verma), pp. 195-272. Geofísica Internacional.

Browne P. R. L. (1984) Lectures on Geothermal Geology and Petrology. National Energy Authorithy of Iceland & United Nations University-Geothermal Training Programme.

Browne P. R. L. (1998) Hydrothermal alteration in New Zealand geothermal systems. In Water-rock Interaction (ed. G. B. Arehart and J. R. Hulston), pp. 11-17. Balkema.

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 14, 49-57.

Cathelineau M., Oliver R., and Nieva D. (1987) Geochemistry of volcanic series of the Los Azufres Geothermal Field. Geofísica Internacional 26-2, 273-290.

De la Cruz V. M., Aguilar J. S., Ortega D. G., and Sandoval J. M. (1982) Estudio geológico-estructural a detalle del campo geotérmico de Los Azufres, Mich. Comisión Federal de Electricidad.

Dobson P. F. and Mahood G. A. (1985) Volcanic stratigraphy of the Los Azufres Geothermal Area, Mexico. Journal of Volcanology and Geothermal Research 25, 273-287.

Garduño Monroy V. H. (1985) Análisis estructural de la zona norte del campo geotérmico de Los Azufres, Michoacán. Comisión Federal de Electricidad.

Garduño Monroy V. H. (1988) La caldera de Los Azufres y su relación con el sistema regional E-W. Geotermia, Revista Mexicana de Geoenergía 4(1), 49-61.

González Partida E. and Barragán R. M. (1989) Estudio detallado de las inclusiones fluidas en el sistema hidrothermal activo del campo geotérmico de Los Azufres, Mich. Geotermia, Revista Mexicana de Geoenergía 5(1), 126-152.

Hey M. H. (1954) A new review of chlorites. Mineralogical Magazine 30, 277-292.

Huitrón Esquivel R. and Franco Serrano A. (1986) Carta geológica del campo geotérmico de Los Azufres, Mich., México. Geotermia, Revista Mexicana de Geoenergía 2(3), 211-213.

Izquierdo G., Cathelineau M., and García A. (1995) Clay minerals, fluid inclusions and stabilized temperature estimation in two wells from Los Azufres Geothermal Field, Mexico. World Geothermal Congress, 1083-1086.

López Hernández A. (1991) Geología de Los Azufres. Geotermia, Revista Mexicana de Geoenergía 7(3), 265-275.

Quijano León J. L. and Gutiérrez Negrín L. C. A. (1995) Present situation of geothermics in Mexico. World Geothermal Congress, 245-250.

Razo Montiel A., Huitrón Ezquivel R., and Moore J. N. (1989) Geología del campo geotérmico de Los Azufres, Mich. Preliminary Proceedings of the Final Symposium on the Agreement between U.S. Department of Energy and the Comisión Federal de Electricidad de México in the field of Geothermal Energy, 7-15.

Robles Camacho J., Izquierdo Montalvo G., and Oliver Hernández R. (1987) Alteración hidrotermal en el Módulo Marítaro, Los Azufres, Michoacán. Geotermia, Revista Mexicana de Geoenergía 3(2), 131-143.

Torres-Alvarado I. S. (1996) Wasser/Gesteins-Wechselwirkung im geothermischen Feld von Los Azufres, Mexiko: Mineralogische, thermochemische und isotopengeochemische Untersuchungen. Tuebinger Geowissenschaftliche Arbeiten Reihe E(Band 2), 181.

Table 1. Summary of the most important hydrothermal minerals in Los Azufres and their precursors (Cathelineau *et al*., 1985; Torres-Alvarado, 1996; clay minerals are described by Izquierdo *et al*., 1995).

Primary minerals	Secondary minerals
Olivine	Chlorite, hematite, clay minerals ± antigorite, iddingsite
Pyroxene/ amphiboles	Chlorite, epidote, hematite, calcite, clay minerals ± sphene
Biotite	Chlorite, hematite, clay minerals ± epidote
Feldspar	Sericite, calcite, albite, adularia, chlorite, epidote, zeolite ± clay minerals
Matrix	Quartz, calcite, chlorite, hematite, pyrite, sericite, clay minerals, zeolite ± sphene

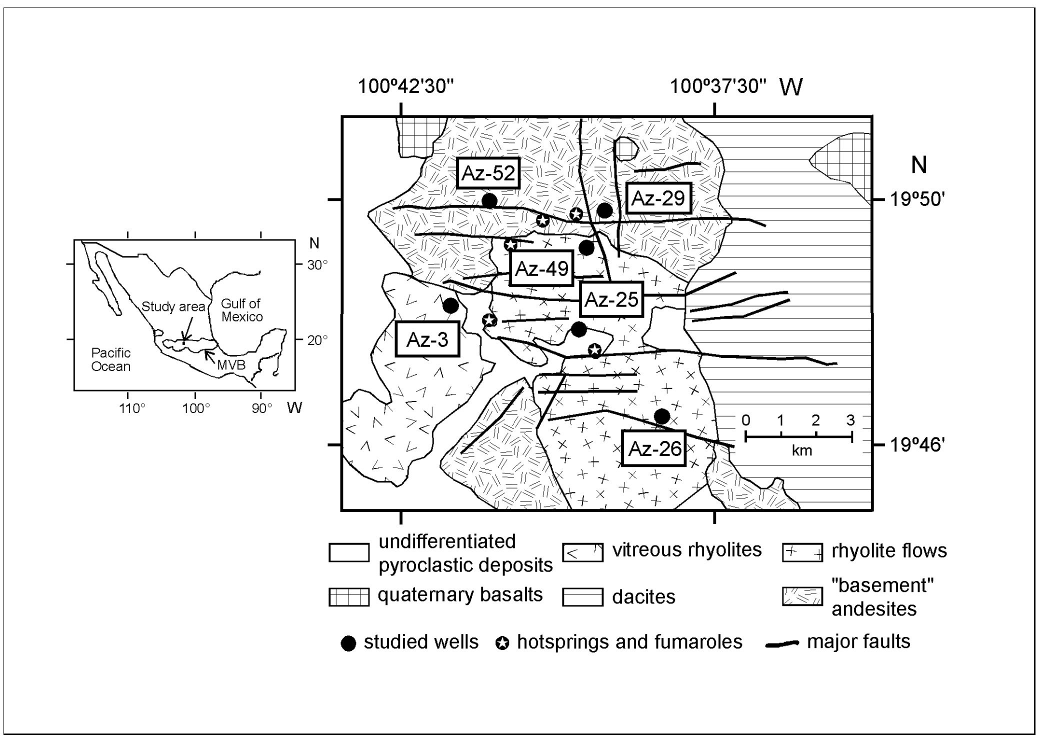

Fig. 1. Simplified geological map of the Los Azufres geothermal field (after Dobson and Mahood, 1985). The geothermal wells studied on this work and the principal fault systems are shown. MVB = Mexican Volcanic Belt.

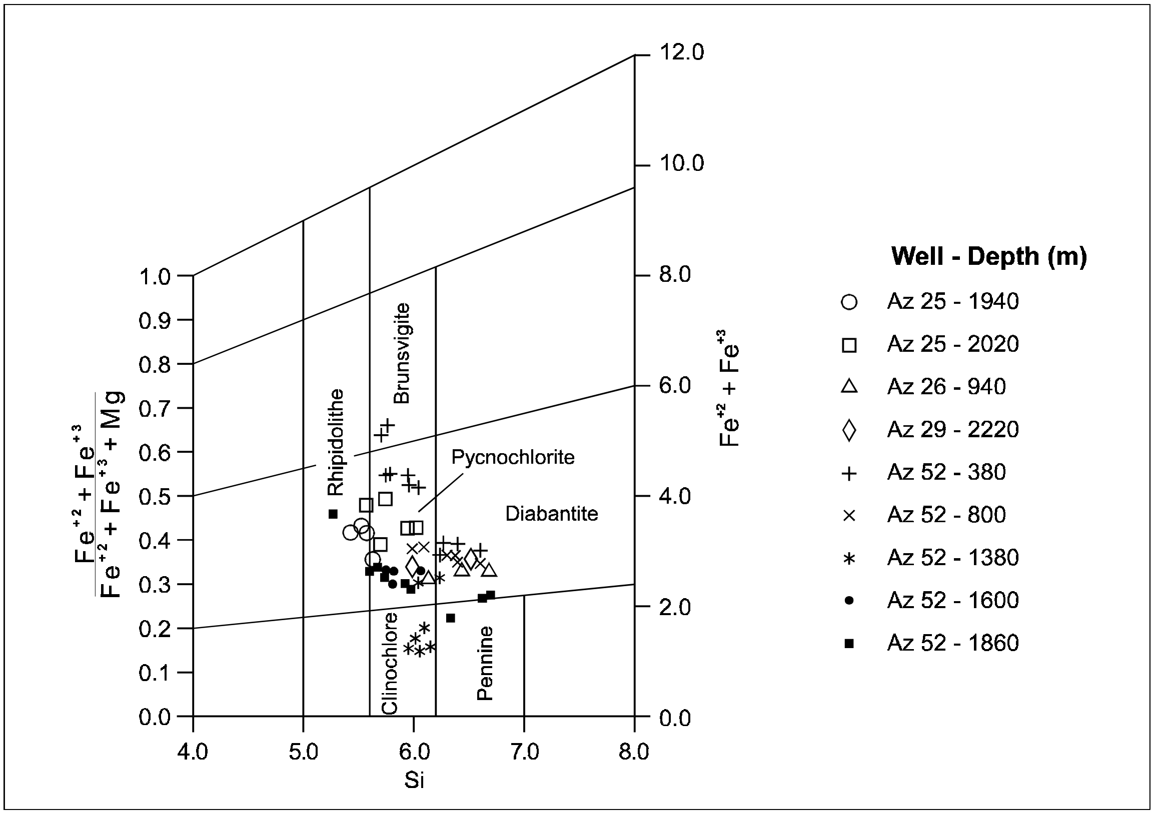

Fig. 2. Chemical composition of hydrothermal chlorites from Los Azufres geothermal field, according to the classification of Hey (1954). Despite their wide variety in textures and colours they show a very homogeneous composition.

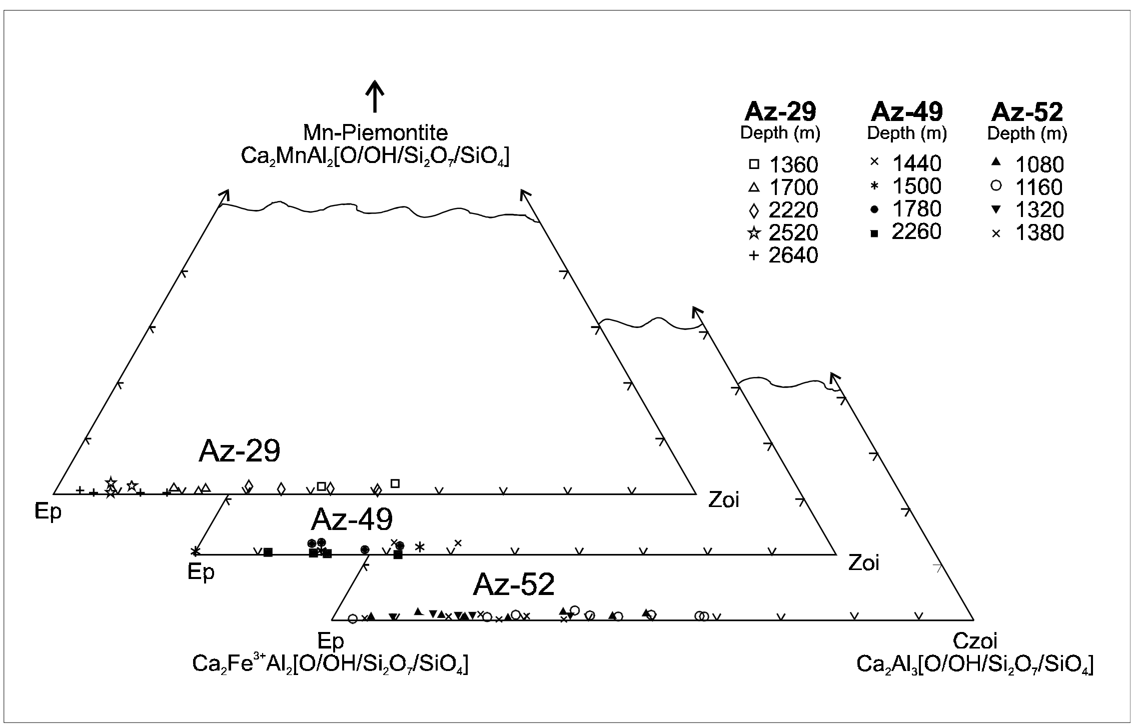

Fig. 3. Chemical analyses of secondary epidotes from Los Azufres geothermal field. Ep = epidote, Czoi = clinozoisite.

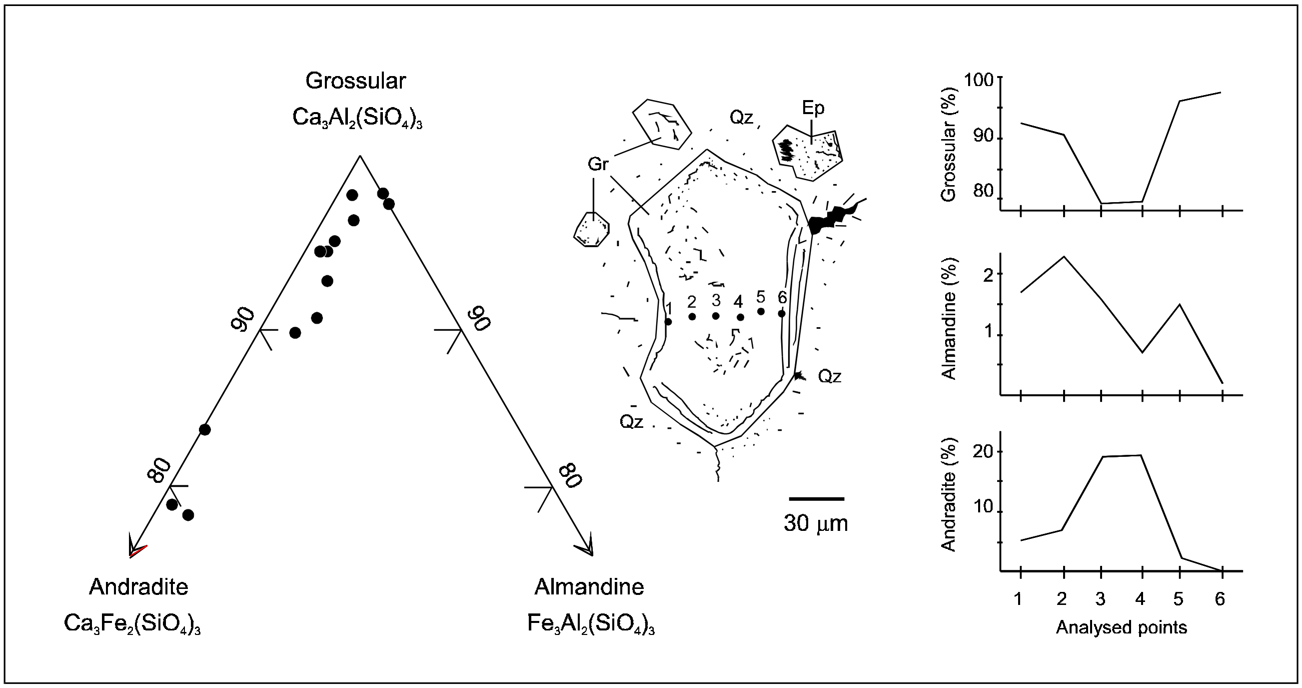

Fig. 4. Chemical composition of the garnet from well Az-29, 2220 m depth, from Los Azufres geothermal field. Gr = garnet, Qz = quartz, Ep = epidote.