

EPIDOTE CHARACTERISATION IN A MEXICAN GEOTHERMAL FIELD

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ABSTRACT

Epidote is a common mineral in geothermal fields. A dating process using epidote has been established. However, it requires determining degree of crystallinity, elemental composition and impurities in the epidote. Epidote characterization was performed in eleven drill core drillings from three production areas in the Los Azufres geothermal field in México. Epidote minerals were separated from samples at depths between 250m and 2500m. X-ray diffraction analysis allowed us to identify three kinds of crystallographic groups: epidote, piemontite and clinozoisite. Quartz, albite, clinocllore, calcite and anorthite were also identified, No epidotes were present before the first 1100m, after that depth all samples contained epidotes. Morphology of all epidote minerals, observed under a low vacuum scanning electron microscope (SEM) showed well shaped crystals, and an X-ray microprobe attached to the SEM, permitted to identify elemental composition of single crystals in areas, as small as 1 μm^2 . The aluminium concentration is indicative of both epidote and clinozoisite, whereas manganese indicative of piemontite could not be identified for being in concentrations below the detection limit (0.1%). Manganese and other metal impurities, in the range of a few ppb and ppm, were assessed in same samples by means of neutron activation analysis.

1.0 INTRODUCTION

México is the third main geothermal energy producer in the world, with a total amount of 855 MW. The main fields are Cerro Prieto 720 MW, Los Azufres 93 MW, Los Humeros 42 MW/h, and Tres Virgenes with 10 MW.

Nuclear techniques (Balcázar, 1997) have been applied by the Instituto Nacional de Investigaciones Nucleares in the study of geothermal fields, in collaboration with La Gerencia de Proyectos Geotermoeléctricos engaged in producing geothermal energy in México. Among these techniques are fission-track dating of obsidians (Gutiérrez-Negrin, 1984), radon mapping for active faults location (López, 1987; Balcázar, 1990), radon measurements in heat-producing geothermal fields (Balcázar, 1991), radon studies for extending a geothermal field (Tavera, 1999) and real-time geogases-determination (Streil, 2000). Some of these techniques have also been applied in the Chipilapa geothermal field in El Salvador (Balcázar, 1993a, 1993b).

The fission track dating technique will be applied to hydrothermal epidotes in rock core samples in order to obtain an absolute age of Los Azufres hydrothermal system. Epidote is a monoclinic mineral elongated parallel to the b crystallographic axis. It has a particular yellow-green to pistachio green colour, which distinguishes it from other minerals. To this group of minerals belong Clinozoisite $\text{Ca}_2\text{Al}_3(\text{SiO}_4)(\text{Si}_2\text{O}_7)\text{O}(\text{OH})$, Piemontite $\text{Ca}_2\text{Al}_2\text{Mn}(\text{SiO}_4)(\text{Si}_2\text{O}_7)(\text{O},\text{OH})_2$ and Epidote $\text{Ca}_2\text{Al}_2\text{Fe}(\text{SiO}_4)(\text{Si}_2\text{O}_7)\text{O}(\text{CH})_2$.

In addition, its clear registration of fission tracks and its high closure temperature allow reliable age dating for epidotes subjected to high geothermal temperatures.

The closure temperature or effective retention temperature refers to the temperature at which 50% of spontaneous fission tracks are retained in the mineral. For epidote, Reimer and Wagner (1971), Haack (1976), and Harrison *et al.* (1979) suggested a value of 240°C, and a partial

annealing zone of 200-280°C *i.e.*, a range of temperature in which there is no annealing of fission tracks below the low limit while total annealing occurs above the upper limit.

Wagner (1992) gave a comprehensive summary of fission-track work in epidote pointing out that "apart from being used as a geothermo-chronometer, epidote fission-track ages have also been applied for dating Cretaceous and Tertiary movements with accompanying epidotization along fault and fissures in the Sinai peninsula". Wagner also discussed the problems encountered in dating epidote. The discrepancy between experimental prediction and geological evidence of the effective retention temperature may be caused by variation of the chemical composition, by accumulated alpha-radiation damage in the crystal lattice, or even by low-temperature growth of the epidote crystals.

2.0 EXPERIMENTAL PROCEDURE

2.1 Sample Preparation

Twenty pieces of rock core samples were obtained from eleven drill holes at depths of 306m down to 2495m (Table I). In some wells, as in Az-57, samples were taken at three depths: 1497m, 1499m and 1725m; in others as in Az-55, depth was defined in the range 1409-1414 m. The characteristic green colour of epidote made easy its separation from the rock matrix.

ZONE	WELL	DEPTH (m)
North	Az-5	1004; 1165
	Az-29	902; 2498
	Az-48	306-306.35
	Az-57	1497; 1499; 1725
	Az-59	904
Centre	Az-25	1300
	Az-30	1851
	Az-54	1055; 2196
South	Az-2	2197-2200
	Az22	800-802; 1262
	Az47	1400-1400.35
	Az-55	1409-1414

All samples were washed three times with distilled water in an ultrasonic bath, then dried in an oven for one hour at 100°C. Thin sections of rocks with abundant epidote crystals were made

for SEM analysis. Other portion of the epidote crystals was crushed in an agate mortar to obtain a fine powder of 100 µm size for X-ray diffraction and neutron activation analysis. Although well-formed epidote crystals were observed, most of them were small, in the range of 20-50 µm long and a few were in the range of 500-1500 µm. Big crystals were mounted on a slide glass and then polished until a good petrographic section allows observation under an optical microscope for dating.

2.2 X-ray diffraction

Samples were analysed using a Siemens X-ray diffractometer model 05000. It has a copper X-ray tube with a wavelength of 1.5 Å, 60 kV voltage and 30 mA beam current and a gas scintillation detector which allows a resolution of <1°. All samples were classified into two groups, the crystalline fraction where yellowish-green material indicated presence of epidote, and the matrix fraction surrounding the green material. The mineral diffraction pattern or diffractogram provides characteristic peaks whose position in the 2θ horizontal axis, intensity, shape and breadth is determined by Bragg's Law. Chemical composition and position of atoms in the unit cell define the relative intensities of the XRD peaks. A library of mineral spectrums, stored in the attached computer permits mineral identification of samples under analysis.

2.3 Scanning Electron Microscopy

A low-vacuum scanning electron microscope (SEM), with a resolution of 3nm and amplifications up to 300,000X, was used to analyze morphology and elemental composition of the samples. The low vacuum characteristic of this SEM allow analysis of non-conductive samples. Like minerals without unwanted interference of gold or carbon covers required in other types of SEM. Elemental composition in percentage, is achieved on the surface of the samples analysing the de-excitation characteristic X-rays of atoms composing the sample under the electron beam. The electron beam can be focused on an area as small as 1µm², allowing the possibility of performing elemental analysis of small single crystals. Both morphology and elemental composition of individual crystals allow the identification of different species of epidotes: zoisite (gemstone variety, tanzanite), clinozoisite, epidote and piemontite (manganiferous epidote).

24 Neutron Activation Analysis

A few milligrams of both matrix and crystalline fractions of the samples were subjected to neutron irradiation in a Triga Mark III Research Reactor. The samples were encapsulated and sealed in a 2-cm long polyethylene tube with 1-cm diameter, introduced in a 3-cm long Perspex tube with 2-cm diameter, and then exposed to a neutron flux of 1.3×10^{13} neutrons/cm²s for three different times: one second, five minutes and two hours to assess short lived, medium lived and long lived radioisotopes, respectively.

Due to lack of electric charge, neutrons are able to cross the whole volume of the sample with few interactions with the nuclei composing the sample. Those neutrons interacting with the nuclei of the sample produce nuclear excitation and the formation of a radionuclei which emit characteristic γ -rays during the de-excitation process allowing a quantitative elemental composition. The γ -energy determination from samples was performed in a low-background GeH(p) immediately, for one second irradiation and after a cooling time of 2 days and 8 days, for five minutes and two hours irradiation, respectively, to allow the induced radioactivity to decay to safety levels. A qualitative analysis of the samples showed the presence of metals and rare earths (Table 2). The quantitative neutron activation analysis (NAA) is shown in Table 3.

3.0 RESULTS

Each of the twenty core samples indicated in Table 1 was subjected to several SEM, NAA and X-ray diffraction analysis. The best epidote

Table 2. Qualitative neutron activation analysis

Samples from Wells (m)	ELEMENTS
AZ-54 (2196) CRYSTALS	Al, As, Ca, Ce, Cr, Eu, Fe, Ga, La, Mn, Na, Sb, Sc, Sm, V, Yb.
AZ-54 (1055) CRYSTALS	Ag, Al, As, Ca, Ce, Cr, Eu, Fe, Ga, La, Mn, Na, Sb, Sc, Sm, V, Yb.
AZ-55 (1409) CRYSTALS	Ag, Al, As, Ca, Ce, Eu, Fe, Ga, La, Mn, Na, Sb, Sc, Sm, V, Yb.
AZ-54 (2196) MATRIX	Al, As, Ca, Ce, Eu, Fe, Ga, La, Mn, Na, Sb, Sc, Sm, V, Yb.
STANDAR SM-7	Ag, Al, As, Br, Ca, Ce, Eu, Fe, Ga, La, Mn, Na, Sb, Sc, Sm, V, Yb.

samples were obtained from two wells located in the center of the field (Az-56 and Az-54) and one well at the southern part (Az-55). As an example, Figure 1 shows the results of epidote analysis in well Az-55 at a depth of 1409-414m. 1A is the SEM image of epidote crystals at 1000X magnification, 1B is the corresponding x-ray fluorescence, 1C is the quantitative analysis, and 1D is the X-ray diffraction analysis. Figure 2 shows the same kind of analysis for epidote sample in well Az-56 at 2495 m.

A cross-section line through wells Az-48, Az-5 and Az-29 in the north of Los Azufres geothermal field is shown in Figure 3. Small squares on each well indicate depths of core samples referred to sea level (msl). The symbols near each square indicate relative abundance of minerals, abundant at the top and rare at the bottom. The letters on the symbols TR, M and C, means that samples were total rock, matrix and crystals, respectively. Isotherms are also indicated in Figure 3.

No epidote crystals were found in core samples analysed in the northern part of the field (except Az-59). In all depths, anorthite is

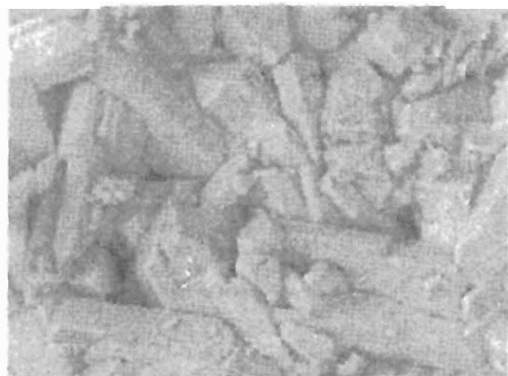
Table 3. Concentration of elements determined by neutron activation analysis

WELL (m)	Mn (ppm)	Sm (ppb)	Cr (ppb)	Eu (ppb)	Yb (ppb)	As (ppb)	Sb (ppb)	Sc (ppb)	La (ppb)
AZ-54 (2196)C	1532±39	4005±63	5928±76	2321±48	3590±60	10624±103	4531±67	14620±38	33649±483
AZ-54 (2196)M	461±21	6161±78	394±85	1405±37	4999±71	6470±80	1553±39	23369±153	44114±210
AZ-55 (1409)C	1169±34	5012±70	10596±102	2304±48	3157±56	11900±109	1332±36	9543±98	52918±230
AZ-55 (1409)M	14864±122	2097±45	101596±318	1532±39	1917±43	365±19	1407±37	11476±107	32628±181
AZ-5 (1165)C	907±30	4616±67	103827±322	1220±35	2085±46	1511±39	2301±48	9310±96	36114±190
AZ-5 (1165)M	409±20	3380±58	182668±427	1369±37	1511±38	1437±38	1725±41	5743±76	20700±144
AZ-5 (1004)C	693±26	5602±81	178075±422	3927±62	2525±50	795±28	392±20	11820±109	34563±186
AZ-5 (1004)M	481±22	5522±74	126228±355	1322±36	2610±51	3776±61	446±21	14418±120	24945±158
AZ-29 (902)C	490±22	4615±68	203649±451	1466±38	1948±44	8288±91	1205±35	16346±128	34181±185
AZ-22 (1262)C	579±24	5942±77	100753±317	2568±51	3369±58	13388±115	1459±38	20830±144	31771±78
AZ-22 (1262)M	40±6	4717±69	203256±451	1633±40	2571±51	8356±91	1077±33	28960±170	26505±163
AZ-54(1055) R	599±0.6	5345±73	116897±342	4379±66	2089±46	12173±110	1120±34	39052±198	24364±156
AZ-22 (800) R	73±8	4688±68	119158±345	3760±61	2274±48	8663±93	802±28	31046±176	24981±158
AZ-29(2498) R	105±10	5641±75	131034±362	3776±61	1847±43	10413±102	811±28	15762±125	28719±169

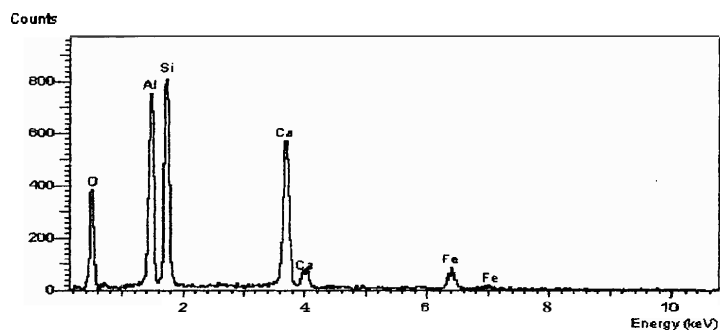
C: CRYSTALS

M: MATRIX

R: ROCK



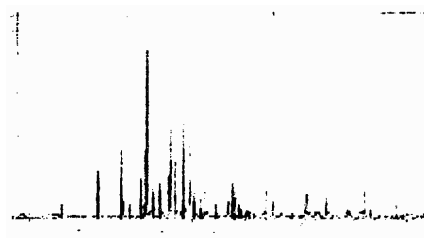
(1A) SEM image of epidote crystals (1000x)



(1B) X-ray fluorescence of image 1A

Well AZ55 (1409-1414m) 1000x			
Elmt	Element %	Sigma %	Atomic %
O	45.78184	0.872131	63.22417
Al	13.52278	0.351862	11.07323
Si	17.29594	0.414375	13.60619
Ca	18.241	0.448923	10.05599
Fe	5.157482	0.444311	2.040423

(1C) Quantitative analysis of image 1A

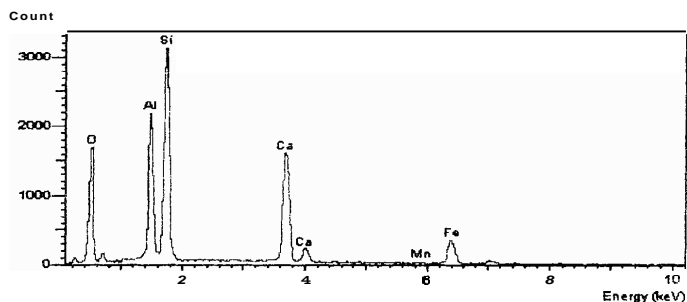


(1D) X-ray diffractogram of image 1A

Figure 1. Epidote sample from well AZ-55 (1409-1414m)

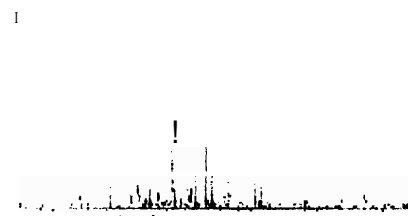


(2A) SEM image of epidote crystals (1000x)



(2B) X-ray fluorescence of image 2A

Well AZ56 (2495m) 500x			
Elmt	Element %	Sigma %	Atomic %
O	38.02524	0.583901	56.81693
Al	11.31255	0.211753	10.0227
Si	19.25927	0.282452	16.39263
Ca	19.74908	0.303494	11.77926
Fe	11.6534	0.384607	4.988486



(2D) X-ray diffractogram of image 2A

Figure 2. Epidote sample from well AZ-56 (2495m)

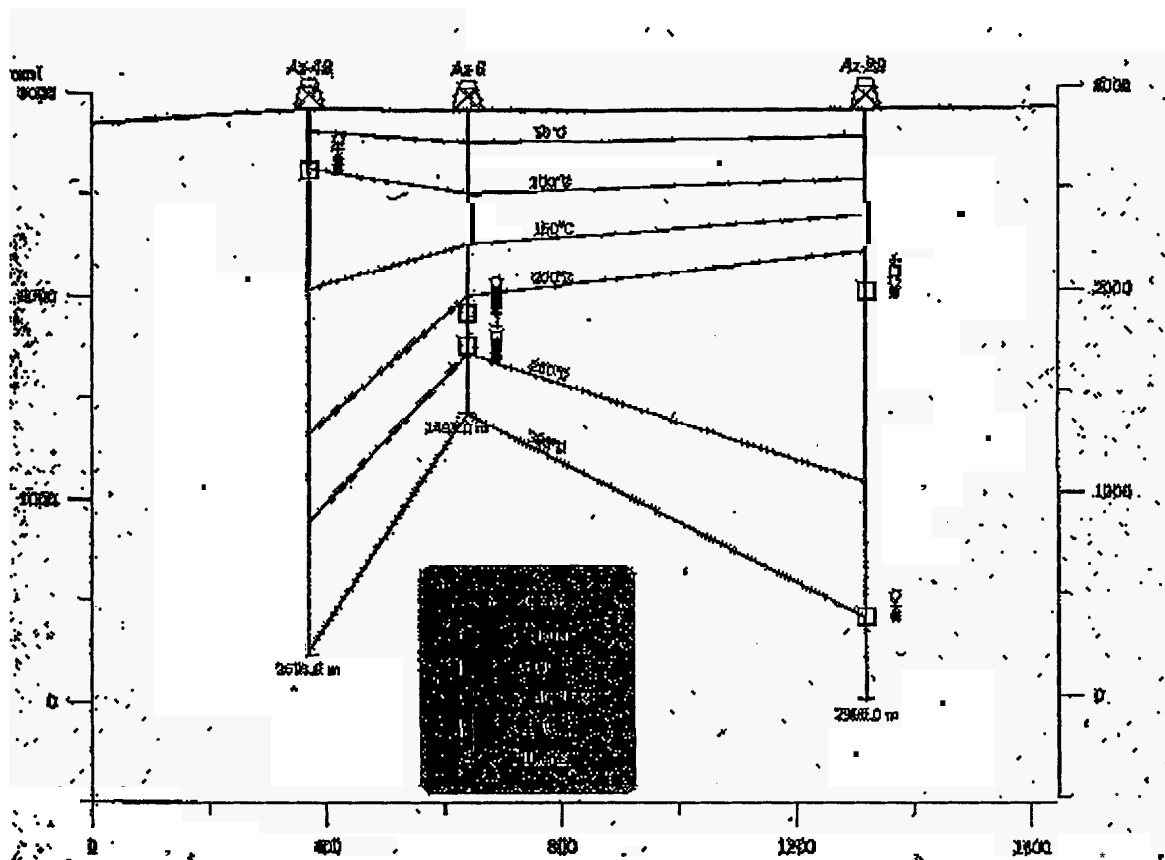


Figure 3. Line across wells Az-48, Az-5 and Az-29. Squares indicate core samples

the most abundant crystal present followed by quartz and clinoclorite. Albite is absent at depths near 2600 msl and at 400 msl in the northern wells.

A cross-section line through wells Az-2, Az-22, Az-47 and A-55 in the south of the field is shown in Figure 4. Epidote (in three varieties) is present in all wells at depths greater than 1500 msl. Albite is present at well depths in all wells, with exception of Az-55. Quartz is the most abundant at depth up to 1500 msl and scarce at depths of 3000 msl.

Similarly, a cross-section line across wells Az-59, Az-54, Az-56 and Az-25 from northwest to southeast of the field is shown in Figure 5. Epidote is present in all wells at depths greater than 1800 msl. Quartz is the most abundant crystal in all wells; while albite is determined in one well (Az-54) at 1800 msl, but absent at greater depths. Calcite is found in all cases at depths down to 1500 msl.

Epidote is found in all regions of the Los Azufres geothermal field, at the centre and southern part, at temperatures above 200°C , well Az-59 is the only well in the northern sector where epidote occurs above the 200°C temperature.

4.0 CONCLUSIONS

Epidote was found in the drill-cores below 1100 m, SEM analysis identified the degree of crystallization in each sample. Two wells located at the center of the field (Az-56 and Az-54) and one well in the southern part (Az-55) have epidotes with well-defined structures. However, it is not possible to define the exact proportion of epidote and clinozoisite. In contrast, the piemontite concentration is low, in these wells, as determined from the low concentration of Mn in comparison with Fe and Al. The best epidote crystals found in these three wells will be subject of efficiency calibration to apply the population fission-track dating-method.

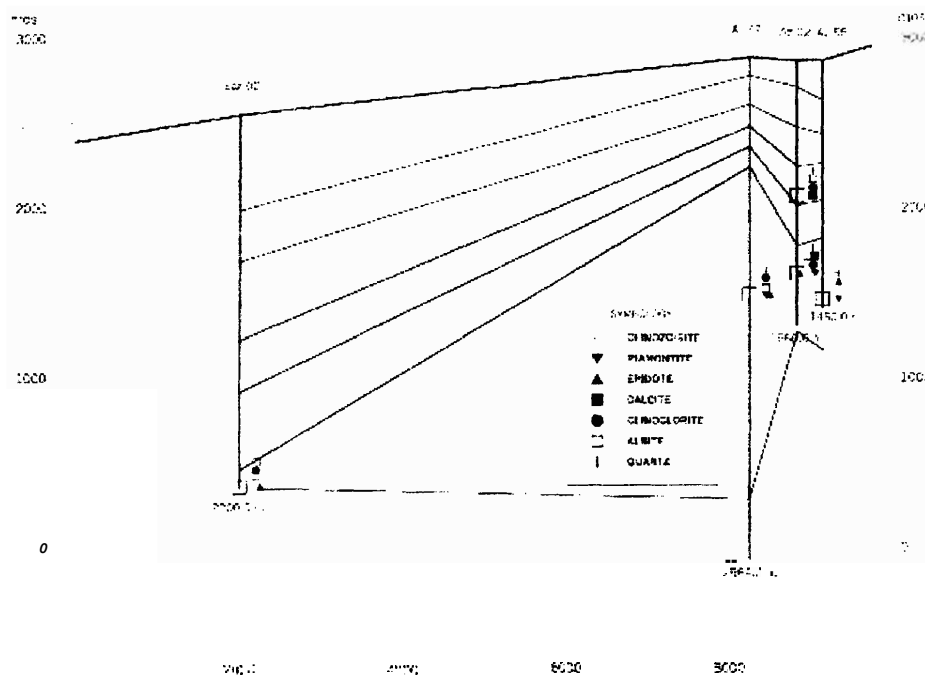


Figure 4. Wells Az-2, Az-22 Az-47 and Az-55. Depth units are referred to sea level (msl)

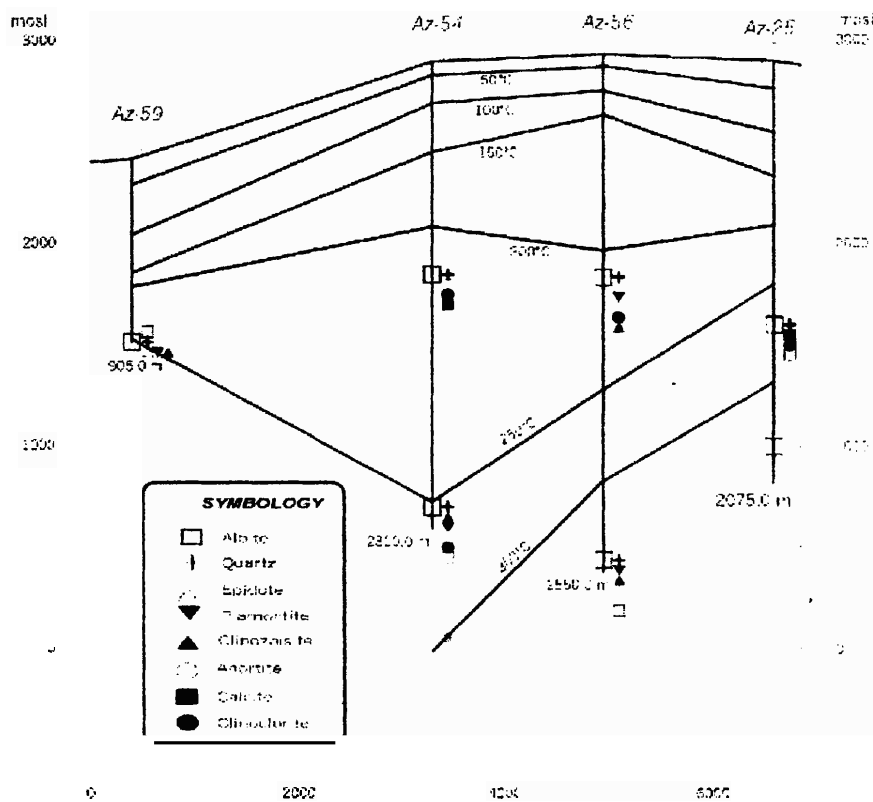


Figure 5. Wells Az-59, Az-54, Az-56 and Az-25. Symbols indicate relative abundance of minerals.

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