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CHLORITES ZONING IN DRILL HOLES OF THE COPAHUE GEOTHERMAL FIELD, NEUQUEN, ARGENTINA

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ABSTRACT

Chlorites constitute one of the main hidrothermal products of the metamorphic alteration of andesites in the Copahue Geothermal Field. They show a rather wide range of variation in their structural and optical characteristics, regarded with the depth of occurrence.

The objective of this work is the study of the chlorites zoning in two drilled holes of Copahue and the relation between the zoning with temperature, by means of XRD analysis and optical study of the chloritic minerals of the COP-2 and COP-3 wells. The use of these minerals as a quick and simple mean for the thermal characterization of the drilling zone is proposed.

Key words: Copahue, chlorites, zoning.

INTRODUCTION

Secondary phyllosilicates occur in almost E, of the geothermal systems of the world and it is also an important group of authigenic minerals in the drill hole samples from the active geothermal field of Copahue.

The mineralogical studies of the drilling cores and cuttings were performed using optical microscopy, Xray Diffractometry and Scanning Electronic Microscopy. These studies show that clay minerals as a whole, and the chloritics in particular, are among the minerals which evidence stronger variations with depth.

The vertical zonation of these secondary minerals were delineated as follows:

Smectites --- swelling chlorites --- chlorites

The two former occur at temperatures below 200°C, whereas the latter, accompanied by epidote,

prehnite, garnet, chlorite and tremolite, occurs within a range of temperatures from 200°C to greater than 300°C.

STUDY AREA

The Copahue Geothermal field is located at latitude 37°50'S and longitude 71°05'W, some 1170 km WSW of Buenos Aires City, and adjoining the border with Chile. The area is connected with the city of Neuquen by national and provincial routes, covering nearly 360 km through Zapala, Las Lajas and Loncopue (figure 1). This geothermal field is on the east side of Los Andes, in the ridge which forms the watershed separating the river basins of the Pacific and Atlantic sides, as typified by Volcan Copahue and Paso Copahue in the western part of the area. This area rises to about 2000 m above sea level.

In wide view, several composite volcanos, similar to each other in terms of type and period of activity, range for about 220 km. The volcanos unconformable cover pre-Pliocene sedimentary and volcanic rocks and form stratovolcanos with a gentle dip. The volcanic activity which is considered, up to now to have started in Pliocene time is located around the tensional stress field which was formed in the North-South tectonic relief, behind a subduction zone. The volcanic activity is characterized by calc alkaline' hnd shoshonitic series (Pesce, 1987).

The Copahue-Caviahue composite volcano, in which this geothermal field is located, stands nearly at the center of the mentioned volcanic row, forming a distinguished ring shaped topography. Mountains ringing the basin are 2200 to 2400 m above sea



Fig.1: Location map.

level. In this area there are five active geothermal manifestations, which mainly consist of fumaroles, hot springs and mud pots. Four of these manifestations are placed in Argentina: Termas de Copahue, Las Máquinas, Las Maquinitas and Anfiteatro, and the fifth on the Chilean side: Chancho Co. **All** of them are on the horst northeast of Vn. Copahue, and the overall area comprises aproximately 20 km².

Three exploration wells had been drilled here, in a sector NW of the circular basin and about 6 km northeast of Vn Copahue. The well COP-I is located 2005 m above sea level on the south shore of Las Mellizas lower pond and reached a depth of 1414 m; COP-2 located about 2120 m above sea level on the north of Las Mellizas and is 1241 m in total depth: and COP-3 is located about 2011 m above sea level, at 30 m from the east shore of Las Mellizas upper pond, and is 1065 m deep. (Figure I, inset). This latter was drilled in the course of the "Northern Neuquén Geothermal Development Project" carried out by EPEN (Ente Provincial de Energia del Neuquen) and JICA (Japan International Cooperation Agency). These exploration wells confirm the occurrence of a vapor dominated reservoir below a depth of 800 m.

The three wells form a triangle with 1 km side length, placed over a predominant fault WNW-ESE which links the Chancho Co, Paso Copahue and Las Máguinas.

RESULTS

The sequence penetrated by drilling is dominated by basaltic andesite to andesite lavas, with minor' pyroclastics rocks. The host rock at the reservoir depth is a strongly altered andesite whose original phenocrystals mainly comprised andesine and augite, in a vitroclastic matrix now altered to a fine-grained! assemblage of chlorite, quartz, albite, and minor illite, pyrite and leucoxene. Primary plagioclase was replaced by epidote, albite and K-feldspar. Filled veins of wairakite, quartz, prehnite, epidote and some garnet cut the rock, and coarsely crystalline wairakite (up to 3 mm in diameter) coats surfaces of what were once cracks and open veins filled with fluid.

The degree of alteration changes from surface to the bottom of the wells. It is rather weak above 600 m of (depth on the whole, and mainly consists of comparatively strong montmorillonitization and chloritization, and it is stronger below 600 m, with chloritization and epidote filling cracks. Below 800m of depth it can be distinguished: -a wide chloritization, which affects almost the whole rock; - Ca silicate minerals, such as epidote, prehnite, garnet and tremolite occurring specially in cracks, although

they can be found also as a replacement: and -quartz and/or prehnite and epidote lining veins filled by later crystals of wairakite.

Chlorites are characteristically found at depths greater than 80 m. These minerals shows a rather wide range of variation in their structural and optical characteristic, related to the depth of occurrence. Therefore it was decided to studied them with the aims of analyzing their use as a quick method for the thermal characterization of the drilling zone.

X Ray Diffractometry:

The preliminar XRD identification of chlorites is rather simple by means of the basal reflection between 14,2 and 14,4 Å, with a series of reflections up to (005). When this mineral was mixed with kaolinite or montmorillonite the sample was treated with ethyleneglycol (to expand the smectite) and heated up to 550° C (to colapse the kaolinite). In order to confirm the presence of chlorites, the samples with mixtures where treated with ClH 1N during an hour at 90°C. This treatment destroys the chlorite, besides the calcite and wairakite.

The following mineral groups were identified:

Smectites: very common in the upper levels of the well and inmediately below the fractured and intensively altered reservoir zone. They are characterized for a basal reflection doo1 between 14,3Å and 15,0Å under dry conditions and between 16,6 **8**, and 18,0 **8**, when they are glycolated.

Chlorite-smectite interstratified: they are the most common phyllosililicates at depth greater of 150 m. In these minerals d001, between 14,0 Å and 15,0 Å expanded up to 3,0 Å after the ethylene-glycol treatment. The degree of expansion increases with the increase of smectite component. Also d002 reflections suffer the effects of glycolation, with a diminution of the intensity and the increasing of the peak breadth.

The diagram of fig.2 shows the relation between d001 values from 30 dry samples of COP-3 well and their glycolated equivalent. The diagonal line ties points of equal d001 values (without expansion:). Area (a) comprises the non-swelling chlorites; (b) swelling chlorites; and (c) smectites. It can be seen in the graphic that expansion increase with increasing dooi values, and that a small gap exists between smectites and smectites/chlorites interstratified minerals, whereas

a continuous series occurs between the latters and chlorites.





Fig.2: dooi dry) - dooi (ethylene glycol) diagram of chlorites(a), swelling chlorites (b) and smectites (c).

The relative intensities of the 148, and **78**, reflection can be used to roughly estimate the relative proportion of expandable layers (Liou et al., 1985). With increasing chlorite content the peak height ratio of 14Å/7Å decreases continuously from -1.5 to -0.4, and d001 changes from 15 Å to 13.5Å.. Fig.3 shows 'the graphic that related I001/I002 vs d001, made up with the same samples.



Fig.3: d001 vs l001/l002 diagram of smectites, chlorites and swelling chlorites.

It can be seen in the diagram the mentioned tendency: samples with dooi smaller than 14.5 Å have predominantely I001/I002 ratios smaller than 1, and this ratio progressively dimished with the decreasing basal spacing, eg. with the increasing of choritic components. In the opposite direction, with the d001 increasing grows the intensities ratio, pointing out an increment of the smectitic phase. As a whole the intensities ratio decreased with increasing depth in wells.

In almost all the samples interstratification is rather disordered. Few swelling chlorites show a undoubtly reflection at 31Å for 001, which pointed out their regularly interstratified character.

Chlorites:Chlorites with non-swelling doo1 spacing are also present in the Copahue field, although they are less common than the former and restrained to the zones of greater temperatures and most intensively altered.

In the samples where well crystallized chlorite is abundant, the XR diffractograms can give some chemical and structural additional information (Brindley & Brown, 1984). It was determined that the crystallographic constant b_o ranges between 9,294 Å and 9,252 Å, suggesting a tendency to decrease with depth. Simultaneously the ratio Fe/Fe+Mg, calculated in function of b_o , ranges between 0,55 and 0,32.

On the other hand the $Al^{\Gamma V}$ ratio is rather constant, between 1,0 and 1,2, and it does not show any aparent relation with depth. All the analyzed chlorites correspond to the IIb and Ib polytypes, with a little prevailing of the former.

Crystals thickness normal to the basal planes is greatly variable in these minerals. The amount of expandable layers was determined by means of the Scherrer equation (Brindley y Brown, 1984) which related the angular breadth, measured at half the maximum intensity, with the number of layers in the crystal.

These are some of the results:

120 m -	number of basal planes randomly variable
620 m -	number of basal planes regularly variable
660 m -	21 basal layers
790 m -	11 basal layers
880 m -	27 basal layers

Differences are greater when the thickness determined for each basal reflection in chlorites, and in the smectite/chlorite minerals from the upper levels are compared. In the latters, the number of basal planes is different for each basal reflection, with random or regular variations in accordance with the character of the interstratification. On the other hand, non-swelling chlorites show almost constant values for all the series of basal planes in each sample.

The number of basal planes increase with depth up to the most intensively altered level where this number remains nearly constant, ranging between 27 and 30 basal layers. At aproximately 790 m of depth there are a thin level where the number of basal layers dimishes; this fact coincides with the presence of swelling chlorites besides the well crystallized chlorites.

Table 1 resumes the results obtained by means of the XRD analysis of the clay fractions from the samples between 20 and 1064 m of depth in the COP-3 well.

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Table	
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Depth	S	S/Ch.	3.Ch.	Ch/S.Ch.	Ch	I
20	x		*		-	
- 50 - 80	*		x			*
120		x				
170			x			
200				x		
250				x		
280		x				
294					х	
320			X			
400			X			
420				x		* 1
450	Į.			x	v	
480					~	0
560			Ŷ			*
600	l		x			*
620		x				*
660					x	*
120					х	*
760					х	
790			x			
810					х	
830			х		х	
850	1	1			Х	
865					х	
880	l				х	
900		0			Х	0
960					X	*
1002	-				×	*
1013				*	x	*
1022	1			x	Â	0
1045			0	x		
1055	x		-	х		*
1064	x			х		*
x : dominant o : subordinate *: scarce S: smectite; S.Ch: swelling chlorite;						
Ch: chlorite; I: illite						

It can be seen there, that:

- montmorillonite prevails in the upper lev accompanied by very subordinated illite;
- from 80 m to 620 m of depth aproximately, predominate the chlorite/smectite minerals, formed by swelling chlorites and/or mix layer chlorite /swelling chlorites. Some of the samples show a

small contraction during heating which indicated the presence of a little montmorillonite.

- between 450 m and 660 m of depth, there is a little illite, subordinated to chloritic minerals;
- from that temperature and up to 1022 m, the nonswelling chlorite is the only clayed mineral present, with the exception of the thin level between 780 and 790 m; and
- There is **an** inversion in this progresive sequence below 1022 m of depth. In the last 40 m of the well swelling chlorites, interstratified chlorite /smectite and smectite appear successively.

Fig.4 shows the diffractograms of the phyllosilicates present in the last portion of the well with the mentioned succession.



Fig.4: diffractograms of clay fractions from the deepest portion of COP-3 well.

Optical Microscopy

Under the microscope swelling chlorites appear mainly as replacement of mafic phenocrysts while the ordered chlorites fill fractures and vesicles.

Chlorite texture varies between very thin and desordered laminar in samples where swelling chlorite prevail to parallel plates, with crystals up to 100μ m of length and greater in veinlets and radial aggregates for the ordered chlorites. It is common that both varieties coexist in a same level, but the relative ratio changes with depth. Table 2 resume the optic characteristics of these minerals.

Type (001)	Grain	Interfer.	Pleocr.	Orient/
orientation	size	color		Opt. sign

Swellling Chlorite	Random and poorly	<2 µm	l°order grey	debil to	+1?
	developed laminar habit			none	
Ordered Chlorite	Parallel, ordered	>100µm	grey to anomalous blue	llght green	+ / -

DISCUSION

Chlorites are among the most common secondary silicates in geological environments under moderate thermobarometric conditions (between 150° y 450°C and few Kb of pressure); and their crystallochemidal characteristics change as a function of pressure and temperature conditions.

In the geothermal field Copahue the following vertical zonation has been determined:



Smectites occur at rather low temperature, of about 120-130°C, and at depth that generally not exceed 100 m. Swelling chlorite and mix layer chlorite / smedtite pointed out a higher temperature, of about 200°C. These minerals occur between 50 m and 650 m aproximately. Finally, chlorite occurs in deeper levels, and it is stable at temperatures higher than 250" C.

In accordance with the graphics proposed by Cathelineu & Nieva (1985), the determined Al^{IV} ratio (1,0-1,2) pointed out temperatures of about 250° to 300°C aproximately.

The number of basal plane increases with de h, implying a better crystallization degree. The preserve of the IIb and/or Ib polytypes, confirm this tendency. Hayes (in Bailey, 1988) pointed out that temperatures higher than 200°C are required to reach the Ib to IIb transition and Walker (1989) stated that chlorite IIb is the final product of thermic metamorphism, and the transition should occurred at a temperature between 150" and 250°C. Secondary minerals assocciated to the clays, which vary between cristobalite and calcic zeolites near the surface to calcic secondary minerals (epidote, prehnite, actinolite, etc) in the lower levels, confirm this zonation.

On the other hand, this tendency is similar to which Kristmannsdottir (in Browne, 1990) described in Reykjanes, Island, where smectites are discret phases at temperatures lower than 200°C, they turned ramdomly interstratified with chlorites, between 200° and 270°C, and chorites is the only clayed mineral where the temperature is upper than 270°C.

Fujishima & Fan (1977) stated that in Keolu Hills the increasing of temperature and pressure with depth results in a smaller incidence of the swelling chorites.

The sporadic occurrence of smectite, swelling chorites and interstratified minerals in the deepest levels of Copahue, can be correlated with a temperature inversion caused by the entrance of colder fluids through the system of fractures, eg. a strong horizontal component of flux.

On the other hand, the restringed presence of illite only in few thin levels, seems to be more related with the pH of the fluids rather than with temperature. This mineral should indicated the occurrence of sporadic boiling levels that unmix an acid fluid phase of low density, or a mixing of two different fluids.

Taking into account these considerations, it can be concluded:

- The hidrothermal altered rocks in a geothermal field act as temperature register of the thermal flux they have suffered;
- These minerals can be used as correlation criteria between wells. They are useful in the definition of the areal extension of reservoir;
- The detailed XRD and optical studies of the chorites and other clayed minerals allow to proposed a progresive sequence of hidrothermal alteration zones;
- In accordance with their characteristics and the assocciated minerals, a temperature between 250"

and 300°C is suggested for the ordered chorite zone.

- This sector of higher temperature coincide with the zone of reservoir recognized in the three geothermal wells, which is besides, exploted for geothermal energy production in the plant in COP-1 well;
- On the other hand, the invertion of alteration in the last portion of the wells points out that this is not the main reservoir of the system, but only a fractured zone which has acted as a path for the solutions that cause the intense alteration.

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