

CHEMICAL VARIATIONS IN CHLORITE AT THE LOS HUMEROS GEOTHERMAL SYSTEM, MEXICO

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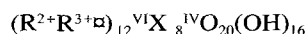
Abstract—The chemical composition of hydrothermal chlorite was determined by means of more than 200 electron microprobe analyses (EMPA) in almost all of the 70 chlorite-bearing samples taken from 5 boreholes in a study of the active geothermal system of Los Humeros, Mexico. Bulk rock composition of 6 different volcanic lithologies, as well as available *in situ* temperatures and chemical compositions of chlorite, were analyzed by principal component analysis (PCA) in order to test the dependence of chlorite composition on physicochemical parameters. The results show that chlorite minerals display a wide range of chemical compositions in this hydrothermal system that reflect the particular conditions of crystallization episodes: The Na + K + 2Ca values are low (from 0 to 0.6) and they show no correlation patterns with octahedral vacancies (\square) in chlorite, indicating that compositional variations are not due to the intergrowth of smectite and/or illite. The octahedral occupancy of most chlorite is relatively high (from 11.3 to 11.95), especially that from a high-temperature range, as is the case of metamorphic chlorite. The octahedral occupancy seems not to be related to other chemical variables of chlorite from the G3, G4 and G5 lithologic units, suggesting that the lack of complete occupancy is not dependent on “contamination” by other silicates (such as quartz). Cationic substitution in tetrahedral sites in chlorite is small and via a Tschermak exchange ($\text{Mg}^{\text{VI}}\text{Si}^{\text{IV}} \leftrightarrow \text{Al}^{\text{VI}}\text{Al}^{\text{IV}}$). To preserve a charge balance in the structure, an octahedral substitution of R^{2+} by Al^{3+} accompanies the Tschermak exchange. The chemical composition of hydrothermal chlorite is very similar to that of metamorphic chlorite but slightly different from equivalent phases found in diagenetic environments. In hydrothermal chlorite the Si^{IV} , Al^{VI} and \square decrease, whereas the Al^{IV} and Fe^{2+} contents increase with the degree of alteration and depth, the same way as in chlorite formed in diagenetic high-temperature environments. The ferrous iron content, in general, increases with depth and temperature; however, whole-rock chemistry affects the iron distribution in chlorite of Los Humeros. Changes in the oxygen fugacity of fluids at depth also affect the iron distribution in chlorite, $X_{\text{Fe}} = \text{Fe}/(\text{Fe} + \text{Mg})$, which ranges from 0.30 to 0.38 in oxidizing conditions and from 0.39 to 0.60 in reducing conditions. Finally, the chemical composition of chlorite in Los Humeros appears to change with temperature, but the correlations of \square and Al^{IV} with temperature are more variable than in another nearby active geothermal system located in Los Azufres, Mexico. This implies that geothermometers based on chlorite composition and empirically calibrated in some geothermal systems cannot be generalized and it is necessary to consider other physicochemical variables.

Key Words—Chlorite, Geothermal System, Hydrothermal, Mexico, Octahedral Occupancy, Phyllosilicate.

INTRODUCTION

Chlorite is stable over a large range of temperatures and pressures (40–400 °C, according to Hillier and Velde 1991, and up to a few kilobars), and in a large variety of geological environments (Deer et al. 1962), including sedimentary, low-grade metamorphic and hydrothermal altered rocks (Foster 1962; McDowell and Elders 1980; Bevins et al. 1991; Hillier and Velde 1991). In most hydrothermal systems, chlorite is a major mineral occurring as an alteration of the surrounding rocks, particularly in volcanic environments (Walshe 1986). This phyllosilicate can either replace preexisting ferromagnesian minerals or precipitate directly in cavities or veins from hydrothermal solutions. The structure of chlorite is characterized by regularly alternating octahedral “brucite-like” layers and tetrahedral-octahedral-tetrahedral “talc-like” layers (Mc

Murphy 1934; Engelhardt 1942; Bailey 1988). In the crystallochemical formula for chlorite:



R^{2+} generally represents Fe^{2+} or Mg^{2+} , R^{3+} generally represents Al^{3+} or Fe^{3+} , \square represents structural vacancies in octahedral sites (VI) and X represents Si^{4+} or Al^{3+} in tetrahedral sites (IV).

Variations in chlorite composition may reflect changes in the physicochemical properties in the environment of crystallization such as temperature (Cathelineau and Nivea 1985; Cathelineau 1988), oxygen and sulfur fugacities (Bryndzia and Scott 1987) and whole-rock chemistry (Bevins and Merriman 1988; de Caritat et al. 1993). The composition of chlorite is therefore of great interest in studies of alteration mechanisms, temperature-related variations (geother-

mometers) and physicochemical conditions of the environment.

Because of the fine grain sizes and complex textural relations, it is extremely difficult to obtain analyses of single chlorite crystals in low-grade rocks with EMPA techniques (Peacor 1992; Warren and Ransom 1992). Mineral coatings, inclusions, mixed layering and complex intergrowths may occur at scales that cannot be detected by standard microprobe analysis or any other classic analytical method. Such analyses could be interpreted as being caused by solid solution, leading to errors in interpretation. Therefore, Jiang et al. (1994) and Essene and Peacor (1995) concluded that the use of a geothermometer based on the tetrahedral Al content of chlorite or some related parameter is not appropriate because of compositional variations and the lack of well-defined analyses.

At the Los Humeros (Mexico) geothermal field, chlorite is a major alteration mineral in the vein network and replaces preexisting ferromagnesian minerals (Martínez-S. 1993). This geothermal field is composed of different lithologies (andesites, dacites, rhyolites and related pyroclastic materials) and chlorite is associated with a variety of calc-silicate minerals.

The purpose of the present study is to examine and assess the correlation between variations in chlorite and whole-rock composition, temperature and physicochemical conditions of alteration in an active hydrothermal system.

GEOLOGICAL SETTING

The Los Humeros geothermal system is located in a complex volcanic caldera system less than 500,000 y old at the eastern end of the Plio-Pleistocene Trans Mexican Volcanic Belt (Figure 1) (Ferriz 1982; Ferriz and Mahood 1984; Negendank et al. 1985; Torres-R. et al. 1988). Thermal manifestations as well as most exploration boreholes are located in a small area (5 × 7 km) called Colapso Central-Xalapazco, in a system of coalesced calderas (Figure 1). Studies of cores and drill cutting samples and surface geology from the system have shown that the basement of the region is formed of Late Cretaceous limestone sequences (Viniestra-O. 1965). Most boreholes penetrate a hydrothermally altered sequence more than 2200 m thick consisting of andesites, dacites, rhyodacites, rhyolitic tuffs, rhyolites and minor basalts, all less than 500,000 y old (Table 1), as well as the Cretaceous basement (Ferriz and Mahood 1984; Martínez-S. 1993). The most recent event was the eruption of an olivine basalt lava less than 20,000 y ago. The volcanic rock sequences of Los Humeros were separated into 6 lithologic units on the basis of their petrographic features (Table 1), in order to determine how chlorite composition relates to bulk rock chemistry.

The subsurface structure in the Los Humeros system has been inferred from geophysical studies by Cam-

pos-E. and Arredondo-F. (1992). It consists of sequences of blocks bounded by fractures and faults forming grabens and horsts associated with the process of caldera formation. Petrographic and geochemical studies carried out in the Los Humeros system (Vig-giano-G. and Robles 1988; Prol-L. 1990; Martínez-S. 1993; Martínez-S. and Alibert 1994) show that the volcanic rock sequences were affected by the circulation of hot water (>290 °C) with less than 2500 mg kg⁻¹ of total dissolved salts, transforming the primary minerals into phases stable under new physicochemical conditions. Geochemical analyses of the present-day fluids discharged from the boreholes suggest that they probably are the result of mixing between a deep geothermal fluid and meteoric water, with the addition of a high percentage of steam (between 30 and 80%) at shallow depths (Barragán et al. 1991; Martínez-S. 1993). The geothermal system presently behaves as a mixed system of high enthalpy with 2 coexisting fluid phases (vapor and liquid).

Hydrothermal alteration observed in the drill cutting samples consists of a shallow argillic zone (0–600 m) with mostly clay minerals, zeolites, calcite and oxides, and an intermediate propylitic zone (600–1700 m) formed by epidote, chlorite, calcite, quartz and sulfides. Calc-silicate alteration, including amphibole, garnet, clinopyroxene and biotite, is observed in the deeper zones of the system (>1700 m) where temperatures exceed 320 °C. Pyrite is the most ubiquitous sulfide mineral throughout the altered volcanic sequences (Martínez-S. et al. 1996). Alteration mineralogy depends on the local geothermal gradient, hydrothermal fluid composition and type of country rocks. Figure 2 shows the distribution of hydrothermal minerals in borehole H15. Andesitic and dacitic volcanic rocks located at depths of 1000 to 1900 m are generally considered to be the reservoir (porous and permeable) formations of the hydrothermal system (López-M. and Munguía-B. 1989).

Borehole Temperatures

Temperature data from different levels of the geothermal system were obtained from fluid inclusion studies and some direct measurements during the first drilling works. The use of cationic geothermometers was not possible, considering the fact that the intensive exploitation of the geothermal system has widely modified the geochemical patterns of the fluids at the present time (Martínez-S. 1993). Hydrothermal fluids sampled on the surface at the boreholes (Barragán et al. 1991; Tello 1992) have geochemical patterns indicating that the boiling process occurs between 1300 and 1600 m depth (López-M. and Munguía-B. 1989). This is confirmed by fluid inclusion studies carried out in quartz associated with alteration minerals (for example, chlorite, epidote, calcite) (González-P. et al. 1991). These authors showed that, in samples from the an-

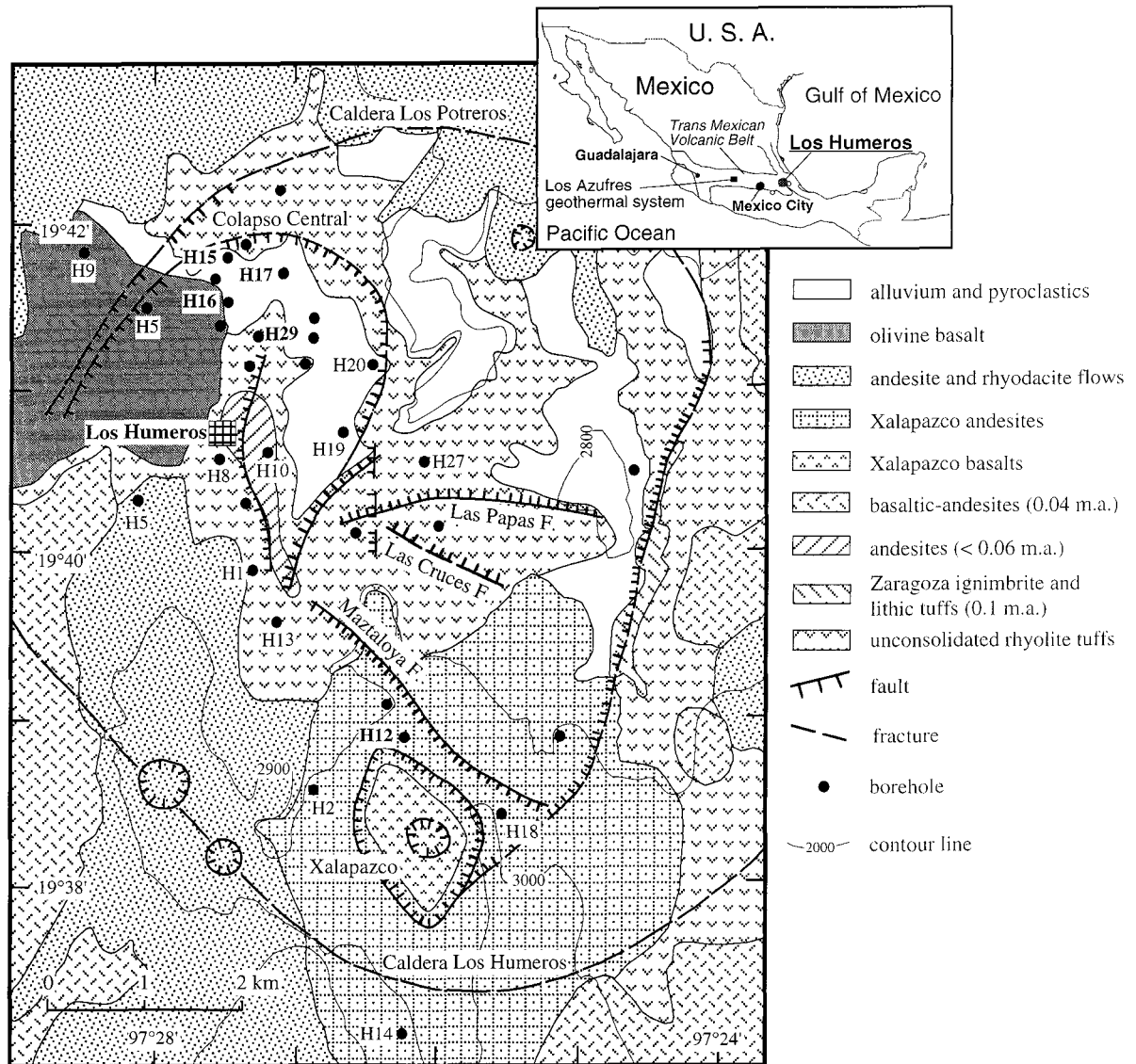


Figure 1. Geologic map and location of the boreholes at the Los Humeros caldera system, Mexico (modified after Martínez-S. et al. 1996).

Table 1. Lithologic composition and temperature range of the Los Humeros geothermal system. Abundant chlorite alteration is found between 850 and 1700 m (units G3 to G6). Temperature data from fluid inclusions (González-P. et al. 1991).

Depth interval (m)	Lithologic unit	Composition	Temperature range (°C)
<100	G1	Basaltic-andesite	<120
100–850	G2	Rhyolite	140–150
850–1000	G3	Microlitic andesite	200–220
1000–1100	G4	Rhyolitic tuffs	220–240
1100–1250	G5	Andesites and dacites	220–280
1250–1700	G6	Porphyric andesite-dacites	>270

desitic sequence (between 1000 and 1600 m depth), both liquid-rich and vapor-rich inclusions coexist, a clear evidence of the boiling process. Homogenization temperatures of both separated end-member inclusions can be used as a direct indicator of *in situ* temperatures (Ramboz et al. 1982). The temperature range observed in the geothermal system is shown in Table 1 for different stratigraphic levels.

SAMPLES AND METHODS

Only drill-cuttings are available in the Los Humeros geothermal system. They do not represent exact horizons, but rather a limited depth range. However, with careful selection the data are considered to show real

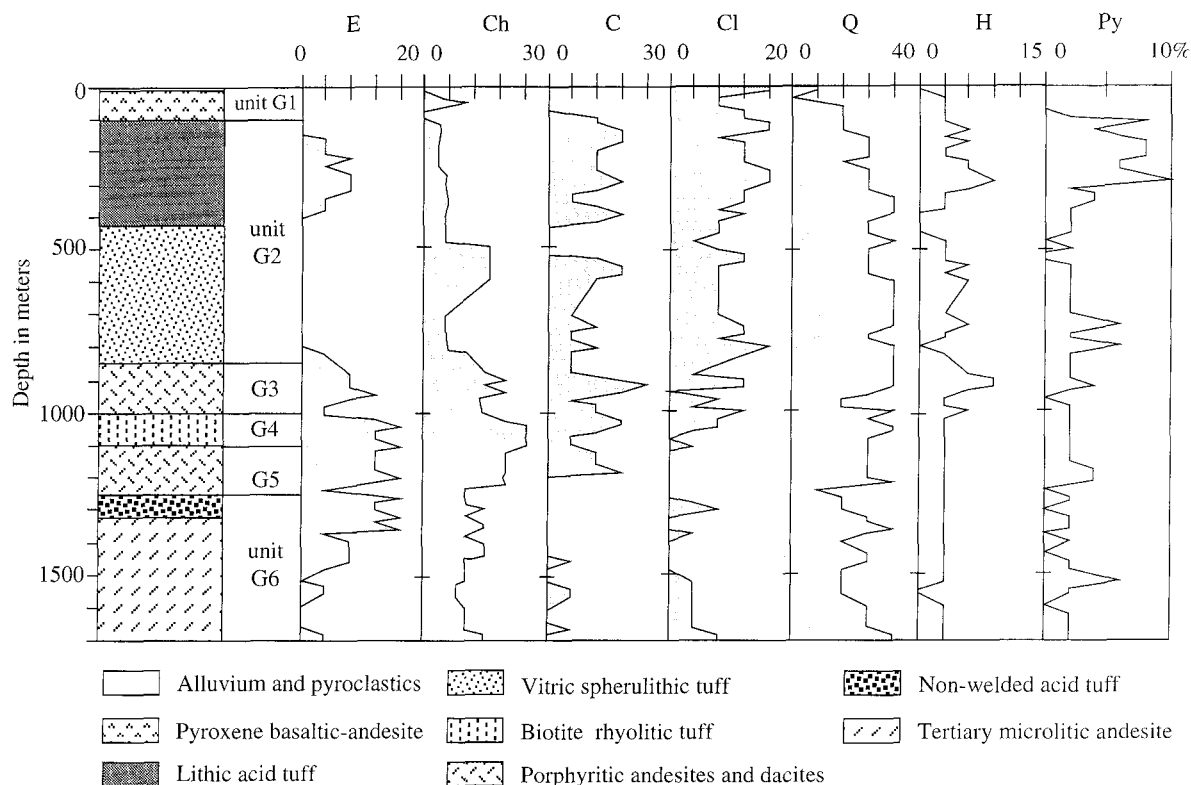


Figure 2. Stratigraphic profile and alteration distribution in borehole H15. Lithologic compositions were grouped into 6 units on the basis of their petrographic features (units G1 to G6). Modal percentage of alteration was estimated by means of petrographic observations and X-ray diffraction analyses: E = epidote, Ch = chlorite, C = calcite, Cl = clay minerals, Q = quartz, H = hematite and Py = pyrite.

assemblages. Most of the 70 chlorite-bearing samples were selected from 5 boreholes (H12, H15, H16, H17 and H29) between 400 and 1700 m depth of geothermal system (Figure 1). Polished thin sections were prepared from the cuttings. Chlorite appears to be present all along the stratigraphic sequence but is more abundant at depths greater than 500 m, except in 1 particular zone at 80 m in borehole H15 (Figure 2). The chlorite crystals located at 80 m result from the alteration of clinopyroxene and olivine at low temperature. At depths ranging between 500 and 650 m and 900 and 1700 m, high concentrations of chlorite were observed in the boreholes (Figure 2). The analyzed samples are light- to dark-green and are present in 2 different forms. In the upper levels of the volcanic sequences, chlorite appears in small intergranular patches whereas, in the deepest levels, chlorite crystallizes in idiomorphic shapes (radial aggregates) in veinlets and as vug filling in association with quartz, calcite, epidote, amphibole and iron minerals (pyrite, pyrrhotite, magnetite or some hematite). Hydrothermal chlorite of Los Humeros displays the formation of larger booklets of phyllosilicates with increasing temperature grade, similar to what as was observed in argillaceous rocks studied by Ahn and Peacor (1985) and Lee et

al. (1985). These authors observed a progressive decrease in fine scale intergrowths of phyllosilicates accompanied by an increased segregation into large booklets with increasing diagenetic grade.

More than 200 individual spot analyses in chlorite samples were obtained with an automatic electron microprobe Camebax (Department of Microanalysis, University of Nancy I), under conditions similar to those indicated by Velde (1984). All data were obtained at 15 kV (acceleration voltage); excitation current varied from 8 to 10 nA and the counting time was 7 s. The ZAF program was used to correct analytical data and the standard minerals used in the calibration were corundum (Al), albite (Na, Si), orthoclase (K), wollastonite (Ca), forsterite (Mg), hematite (Fe) and rutile (Ti). The maximum analytical error in major oxides is less than 3% of the total.

All analyses were recalculated as chlorite structural formulae on the basis of 28 oxygen equivalents, assuming an ideal anion framework of $O_{20}(OH)_{16}$. With EMPA, the oxidation state of Fe is not determinable; therefore, structural formulae were calculated by assuming all iron to be Fe^{2+} . Ferric iron is a minor constituent of low-grade chlorite (Black 1975; Shirozu 1978) and its presence in small amounts has little ef-

fect when compositions are compared. Hillier and Velde (1991) suggested that Fe^{3+} in chlorite is only likely to be present in small amounts, following comparison between trends of metamorphic chlorite, from Foster (1962), and diagenetic chlorite.

RESULTS AND DISCUSSION

Contamination Problems and Classification

Examples of mean chemical analyses and the standard deviations of chlorite from Los Humeros are given in Table 2. The concentrations of Al_2O_3 , FeO and MgO are variable from one chlorite sample to another, while the chemical composition in several spots on the same sample is relatively homogeneous (Table 3). This indicates that the chemical composition is very constant in a given idiomorphic crystal and small quantities of contaminating phases, if present, are distributed homogeneously in each sample.

A common criterion for the selection of EMPA of chlorite is that:

$$\text{Na}_2\text{O} + \text{K}_2\text{O} + \text{CaO} < 0.5 \text{ wt\%} \quad [1]$$

(Foster 1962; Hillier and Velde 1991). High concentrations of Na, K and Ca in some chlorite analyses indicate contamination. However, Jiang et al. (1994) calculated that the limiting value of 0.5% is attained with less than 4 wt% muscovite, 6 wt% illite or 12 wt% saponite mixed with chlorite. These phases produce an increase in Si and a decrease in tetrahedral Al that allow us to consider the possibility of low octahedral occupancy in an analysis cast as chlorite. Chemical data in the Los Humeros system show values of <0.5 wt% in alkaline oxides for chlorite minerals, indicating only small amounts of possible contamination with other phases. Furthermore, $\text{Na} + \text{K} + 2\text{Ca}$ plotted against \square (Figure 3) show no correlation, suggesting that the compositional variations for hydrothermal chlorite are not due to intergrowths of smectite and/or illite. One exception is for samples found at <100 m of depth, where Na, K and Ca values suggest the presence of minerals intergrown with chlorite.

Most chlorite from Los Humeros falls in the brunsvigite field in a plot of Si^{IV} vs. $\text{Fe}^{2+}/\text{R}^{2+}$ (classification proposed by Foster 1962), with Si^{IV} values of between 5.45 and 6.40 formula position units (fpu) (Figure 4). For metamorphic chlorite, a similar Si^{IV} range of between 4.7 and 6.5 fpu is observed by Foster (1962). Diagenetic chlorite (Hillier and Velde 1991) shows a large range of Si^{IV} (between 4.6 and 7.0 fpu). Minerals intergrown with chlorite, sampled at <100 m in borehole H15 (Figure 4), display higher Si^{IV} contents (6.81 to 7.73 fpu) and fall in the diabantite field. The brunsvigite type was also found at the Los Azufres geothermal system, Mexico, by Cathelineau and Nieva (1985). Chlorite in the G1, G2, G3 and G4 units shows a slight decrease in the Si^{IV} content and an increase in

the Al^{IV} and Fe^{2+} content with burial depth (Figure 4). This confirms the observations proposed by de Caritat et al. (1993) and other workers, that the effects of increasing burial depth or hydrothermal alteration upon chlorite composition show similar trends in the Si, Al and Fe contents. The chlorite phases present in the G5 and G6 lithologic units do not show a similar trend; therefore, we must consider the effect of other variables such as whole-rock chemistry or geothermal fluid composition.

Bulk Chlorite Composition

In order to find a reasonable number of variables that describe the relations between the chemical composition of chlorite and parameters such as depth, octahedral vacancies and temperature, a statistical method known as factor analysis was chosen. This method takes variances and covariances into account. PCA is a kind of factor analysis which was used in this study to reduce the number of chemical variables of chlorite. It has the advantage that a large number of variables may be reduced to a few uncorrelated variables or factors, so that a variation diagram may contain information about a large number of variables instead of the usual 2 or 3. The method is well described by Le Maitre (1982). PCA examines the total variability represented in the data and describes this variability in terms of a set of factors. Each factor will account for a proportion of the original variability and will not be correlated with other factors to be found. Graphic representation of PCA is a quick means of establishing correlations among several variables. The analysis was carried out by means of a program developed by Royer and Mezgache (1989, unpublished report). Six lithologic units were distinguished (Table 1) for the PCA in order to take into account the whole-rock chemistry and to optimize the statistical analysis.

Figure 5 shows the PCA results of the chlorite data for the G3 to G6 lithologic units. The statistical analysis for the G1 and G2 units was not carried out because of the small number of samples studied.

1) Diagram of the G3 unit shows that Al^{IV} , Al^{VI} , Fe^{2+} and $\text{Fe}^{2+}:\text{R}^{2+}$ are moderately intercorrelated and exhibit a slight negative correlation with Si^{IV} and Mg^{2+} for factor F1. The \square are independent of all variables and represented by the factor F2 (the total variance is 86%). The temperature seems to show a slight positive correlation with Al^{IV} and a negative correlation with the \square , but the temperature range (from 200 to 220 °C) is almost constant between 850 and 1000 m, so this latter correlation probably does not exist.

2) The total variance of the G4 unit is represented by 96% for the 2 factors. F1 is represented by a strong intercorrelation between the Fe^{2+} , $\text{Fe}^{2+}:\text{R}^{2+}$, Al^{IV} and Al^{VI} variables and by a negative correlation with Si^{IV} and Mg^{2+} . F2 is an independent variable and is only

Table 2. Examples of mean analyses of chlorite from 5 boreholes of the Los Humeros geothermal system.

Sample Depth (m) T (°C)	H12a 980 145	(6)	H12b 1100 175	(4)	H15a 80 100	(2)	H15b 1620 315	(3)	H16a 1040 240	(4)
		σ		σ		σ		σ		σ
Chemical composition (wt %)										
SiO ₂	28.68	0.42	28.93	0.63	33.68	0.18	28.80	0.60	28.16	0.49
Al ₂ O ₃	17.47	0.63	18.26	0.83	12.03	0.09	17.20	0.25	16.93	0.14
FeO	26.89	0.54	24.74	0.33	20.14	0.47	23.75	0.75	26.94	0.60
MgO	13.73	0.32	14.63	0.22	21.22	0.25	17.15	0.54	14.61	0.11
MnO	0.19	0.09	0.26	0.04	0.54	0.03	0.34	0.10	0.49	0.13
CaO	0.12	0.05	0.07	0.02	0.72	0.09	0.12	0.02	0.18	0.11
K ₂ O	0.00		0.00		0.00		0.00		0.00	
Na ₂ O	0.00		0.03		0.00		0.00		0.00	
TiO ₂	0.00		0.14		0.00		0.00		0.00	
Total	87.08		87.06		88.33		87.36		87.31	
Structural formulae										
Si ^{IV}	6.10		6.08		6.82		6.02		6.02	
Al ^{IV}	1.90		1.92		1.18		1.98		1.98	
Al ^{VI}	2.50		2.61		1.68		2.27		2.28	
Fe ^{VI}	4.78		4.35		3.40		4.15		4.80	
Mg ^{VI}	4.36		4.58		6.40		5.35		4.64	
Mn ^{VI}	0.04		0.05		0.10		0.06		0.08	
Ca	0.02		0.02		0.16		0.03		0.04	
K	0.00		0.00		0.00		0.00		0.00	
Na	0.00		0.01		0.00		0.00		0.00	
Ti	0.00		0.02		0.00		0.00		0.00	
R ²⁺	9.18		8.98		9.90		9.56		9.52	
□	0.30		0.36		0.26		0.14		0.16	
F/(FM)	0.52		0.49		0.69		0.44		1.02	

Key: The number of spot analyses is shown in parentheses after the sample name. All analyses recalculated on the basis of a chlorite structure formula involving 28 O,OH. FeO = total iron, □ = octahedral vacancies, F/(FM) = Fe/(Fe + Mg) and R²⁺ = Fe²⁺ + Mg²⁺ + Mn²⁺. σ = Standard deviation of chlorite mean composition.

represented by the □. The temperature range (from 220 to 240 °C) in this lithologic interval shows the same compartment that was observed in the G3 unit.

3) The diagram for the G5 unit is represented by 2 factors with a good total variance (86%). There is a strong intercorrelation between Si^{IV}, Al^{VI} and □, and a slight negative correlation with temperature and Al^{IV} for F1. F2 (independent variable) shows intercorrelation between Fe²⁺ and F²⁺:R²⁺, and a negative correlation with Mg²⁺.

4) Finally, the diagram for the G6 unit shows that F1 is represented by a strong intercorrelation between Al^{VI}, Fe²⁺, Fe²⁺:R²⁺ and temperature, and by a negative correlation with Mg²⁺. The independent variable (F2) shows a very slight intercorrelation between the Si^{IV} and □ but a negative correlation with Al^{IV}.

Table 4 shows the main correlation coefficients among chemical variables of chlorite in the G3, G4, G5 and G6 units, and these confirm the observations of the PCA representations. The □ of chlorite studied are systematically independent variables for samples of the G3, G4 and G6 units, suggesting that the lack of a complete octahedral occupancy in these minerals is not a result of contamination by other silicates (such as quartz). However, the chlorite sampled in the G5 unit (between 1100 and 1250 m) shows a different

behavior in comparison with phyllosilicates of other units (Figure 5, Table 4). For example, the □ of chlorite are positively correlated with Si^{IV} content, suggesting a possible contamination by silicates.

Tetrahedral Occupancy

Statistical analysis and chemical interpretation indicate that cationic substitution in tetrahedral sites of chlorite is small (from Si_{2.72}-Al_{1.28} to Si_{3.18}-Al_{0.82}), suggesting a substitution of Si⁴⁺ by Al³⁺, accompanied by a limited octahedral substitution of R²⁺ by Al³⁺ in order to preserve the charge balance (Tscheramak exchange). The Al^{IV} is negatively correlated with Al^{VI} in chlorite of the G1, G2 and G5 lithologic units. A similar correlation was observed in the Los Azufres geothermal system, Mexico, by Cathelineau and Nieva (1985). These authors have associated this negative correlation with changes in temperature: if temperature increases in the geothermal system, Al^{IV} also increases. Chlorite in the G3, G4 and G6 units shows a positive correlation between Al^{IV} and Al^{VI} (Figure 6). This apparent correlation may represent a well-known fact, that the Fe-rich chlorite tends to be more aluminous than the Mg-rich phases. Chlorite from units G1, G2 and G5 show a smaller range in the Fe²⁺:R²⁺ ratio

Table 2. Extended.

H16b 1260 270	(3)	H16c 1360 300	(4)	H17a 1120 180	(6)	H17b 1320 255	(4)	H17c 1380 260	(2)	H17d 1700 295	(2)	H29b 1140 280	(5)
σ		σ		σ		σ		σ		σ		σ	
28.16	0.57	29.90	0.77	28.46	0.11	31.21	0.47	28.93	0.36	29.85	0.31	28.89	0.20
17.60	0.29	17.52	0.36	16.90	0.33	17.59	0.20	18.96	0.23	15.75	0.11	17.68	0.07
23.95	0.36	21.09	0.53	27.53	0.88	13.59	0.41	19.50	0.03	24.47	0.84	24.17	0.17
16.60	0.40	18.62	0.35	14.44	0.69	24.87	0.48	19.45	0.27	17.38	0.10	16.59	0.25
0.53	0.07	0.50	0.09	0.22	0.04	0.35	0.09	0.76	0.08	0.36	0.02	0.47	
0.12	0.07	0.03		0.14		0.24		0.15		0.19		0.09	
0.00		0.00		0.00		0.00		0.02		0.04		0.00	
0.00		0.00		0.00		0.00		0.02		0.04		0.00	
0.00		0.00		0.00		0.00		0.00		0.00		0.00	
86.96		87.66		87.69		87.85		87.79		88.08		87.89	
5.94		6.12		6.05		6.13		5.89		6.21		6.02	
2.06		1.88		1.95		1.87		2.11		1.79		1.98	
2.31		2.36		2.29		2.21		2.44		2.08		2.35	
4.22		3.62		4.90		2.23		3.32		4.26		4.20	
5.22		5.68		4.58		7.28		5.90		5.39		5.14	
0.09		0.08		0.04		0.06		0.13		0.06		0.08	
0.03		0.01		0.03		0.05		0.03		0.04		0.02	
0.00		0.00		0.00		0.00		0.01		0.01		0.00	
0.00		0.00		0.00		0.00		0.01		0.02		0.00	
0.00		0.00		0.00		0.00		0.00		0.00		0.00	
9.53		9.38		9.52		9.57		9.35		9.71		9.42	
0.13		0.25		0.16		0.17		0.16		0.14		0.21	
0.45		0.78		0.52		0.23		0.36		0.44		0.45	

(between 0.27 and 0.56) than chlorite found in units G3, G4 and G6 (between 0.23 and 0.73) (Figure 4).

Al^{VI} is greater than Al^{IV} for all chlorite data of Los Humeros (Figure 6). Cathelineau and Nieva (1985) have found a similar behavior for Los Azufres, Mexico. This behavior is slightly different compared to that of metamorphic chlorite reported by Foster (1962), but very similar to chlorite of the Precambrian Belt Supergroup, Montana (Hillier and Velde 1991), composed of alternating carbonate and siliciclastic formations. Maxwell and Hower (1967) suggested that these rocks have been subjected to conditions varying from high-grade diagenesis to low-grade metamorphism, with paleotemperatures ranging from 225 to 330 °C (Esligner and Savin 1973). This temperature range is similar to that observed in the Los Humeros geothermal system. Shau et al. (1990) found that most

chlorite occurring in diagenetic and low-grade metamorphic rocks contains interlayers of corrensite that produce Al^{VI} \gg Al^{IV}, and high concentrations of Ca, Na and/or K. These workers noted that many of the chlorite analyses of Cathelineau (1988) have similar chemical characteristics and suggested that these chlorite data reflect variable amounts of corrensite packets rather than representing a monotonic solid solution of a single phase responding to increasing temperature. At Los Humeros we did not find anomalous quantities of Ca, Na and K in chlorite analyses, so probably the chlorite does not contain corrensite packets in its structure.

Octahedral Occupancy

Total (Fe + Mg) in chlorite of Los Humeros shows values of 8.38 to 9.9 with a mean value of 9.28 fpu.

Table 3. Examples of individual spot analyses for chlorite of the Los Humeros geothermal system.

Borehole Depth (m)	H29 1140					H12 980						
FeO	25.83	26.29	26.46	24.49	25.83	25.95	26.77	26.86	27.67	27.35	26.75	
Na ₂ O	0.00	0.02	0.00	0.00	0.05	0.09	0.00	0.01	0.00	0.00	0.00	
K ₂ O	0.02	0.00	0.00	0.03	0.01	0.45	0.00	0.00	0.06	0.00	0.00	
SiO ₂	28.99	28.87	29.03	29.00	29.29	29.11	29.26	28.34	28.15	28.34	28.88	
MnO	0.33	0.48	0.62	0.44	0.67	0.06	0.31	0.15	0.31	0.14	0.14	
CaO	0.15	0.05	0.07	0.10	0.13	0.12	0.21	0.04	0.10	0.13	0.10	
Al ₂ O ₃	16.74	17.46	17.15	17.42	17.16	17.63	16.75	17.30	18.58	17.75	16.78	
TiO ₂	0.00	0.04	0.03	0.00	0.01	1.00	0.63	0.03	0.00	0.01	0.00	
MgO	15.05	14.53	14.49	14.66	14.93	13.36	14.37	13.79	13.51	13.60	13.73	
Sum %	87.11	87.74	87.85	86.14	88.08	87.77	88.30	86.52	88.38	87.32	86.38	

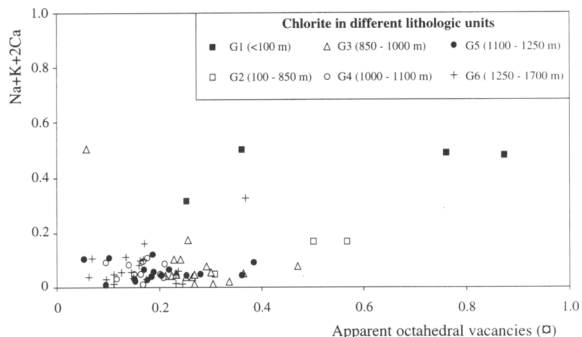


Figure 3. Diagram showing relations between Na + K + 2Ca and apparent \square of chlorite from 6 lithologic units of the Los Humeros geothermal system (full unit cell).

These values are relatively high compared to the diagenetic low-grade metamorphic chlorite studied by Hillier and Velde (1991), which showed values of 6.23 to 9.45 with a mean value of 8.23. Iron content in chlorite from Los Humeros increases with depth and temperature (Figure 7), whereas Mg-rich varieties of chlorite are found at shallow depths (<1000 m). Similar behavior was observed in phyllosilicates from Los Azufres by Cathelineau and Nieva (1985). However, in the G5 lithologic unit, iron decreases slightly with depth. Whole-rock chemistry strongly affects the iron content in chlorite (Cathelineau and Nieva 1985; Bevins and Merriman 1988), although other workers (Liou 1979; Ishizuka 1985; Cho and Liuo 1987) have suggested that chlorite composition may be affected more by the effective bulk composition at the particular growth site. At Los Humeros there are both chlorite and whole-rock data for 40 samples (Martínez-S. and Alibert 1994). Figure 8 displays an excellent positive correlation between $X_{\text{Fe}}^{\text{chlorite}}$ and $X_{\text{Fe}}^{\text{whole rock}}$ for the G1, G3, G4 and G5 units which is not so strong for the rhyolitic G2 unit. Data from Los Azufres, Mexico, plot on Los Humeros trend line (A in Figure 8). This evidence confirms that X_{Fe} ratios, in chlorite, are controlled in part by the initial bulk rock chemistry, as stated previously by Cathelineau and Nieva (1985) and Bevins et al. (1991).

Change in the oxygen fugacity (fO_2) conditions of fluids at depth can also affect the Fe distribution in chlorite phases (de Caritat et al. 1993). Geochemical fluid studies, carried out at the Los Humeros geothermal field by Martínez-S. (1993), suggest that boiling processes occurring between 1300 and 1600 m depth affect the fO_2 conditions. Bryndzia and Scott (1987) observed, in experiments on synthetic chlorite phases, that oxygen and sulfur fugacities produced changes in Fe-Mg occupancy. Variations observed in X_{Fe} for a given lithologic unit in Los Humeros, can be explained by means of redox reactions: the chlorite of the G1 and G2 units presents an X_{Fe} of 0.30 to 0.38 under oxidizing conditions (hematite and minor pyrite quan-

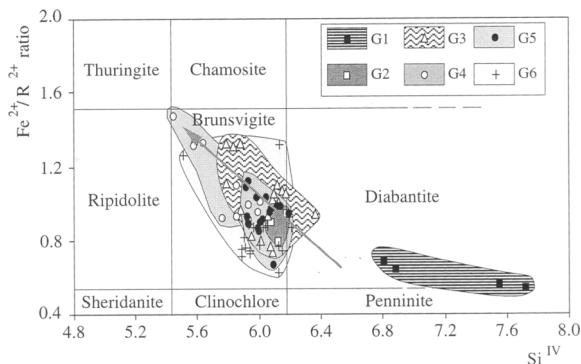


Figure 4. Classification of chlorite from Los Humeros, based on the 2 types of ionic replacement (total unit cell) (Foster 1962). The 6 lithologic units are: G1 (<100 m), G2 (100–850 m), G3 (850–1000 m), G4 (1000–1100 m), G5 (1100–1250 m) and G6 (1250–1700 m). The arrow indicates the chemical variations in chlorite for the G1 to G4 unit with burial depth.

tities were observed), whereas chlorite for the G3 and G4 units shows an X_{Fe} from 0.39 to 0.60 in reducing conditions (pyrite, pyrrhotite and minor magnetite were observed).

Iron distribution in chlorite phases of Los Humeros results from changes in temperature-pressure conditions, but this is strongly affected by bulk rock compositions and oxygen fugacity conditions. It is very important to keep in mind the potential effect of these factors during the formation of chlorite. We cannot assume that changes in the chemical composition of phyllosilicate minerals are related simply to changes in the temperature of mineral crystallization.

In Figure 9, all analyses from Los Humeros have been plotted in the trioctahedral half of the vector representation of chlorite compositions as presented by Wiewióra and Weiss (1990) and Hillier and Velde (1991). This diagram shows the relationships between Si^{IV} , $R^{2+}(Fe^{2+} + Mg^{2+} + Mn^{2+})$, total Al and octahedral occupancy. Si^{IV} and R^{2+} are represented by the orthogonal axes, and total Al and octahedral occupancy are shown by isolines. Almost all chlorite analyses from the Los Humeros geothermal system are distributed close to the line of full octahedral occupancy ($\Sigma_{VI} = 12$), which corresponds to the variation in the amount of Tschermak substitution ($Al_2R^{2+}_{-1}Si_{-1}$). Octahedral occupancy varies from 11.4 to 11.9, very similar to metamorphic chlorite of Foster (1962). Chlorite analyzed at 80 m in borehole H15 (G1 unit) shows an octahedral occupancy lower than 11.5, similar to diagenetic phases analyzed by Hillier and Velde (1991). However, for hydrothermal chlorite the total Al is less than in diagenetic phases. Metamorphic chlorite tends to plot along, or close to, the line between the compositions corresponding to serpentine and amesite, but is restricted to Al contents from 3 to 6.4 fpu (analyses from Foster 1962). A similar trend is observed for

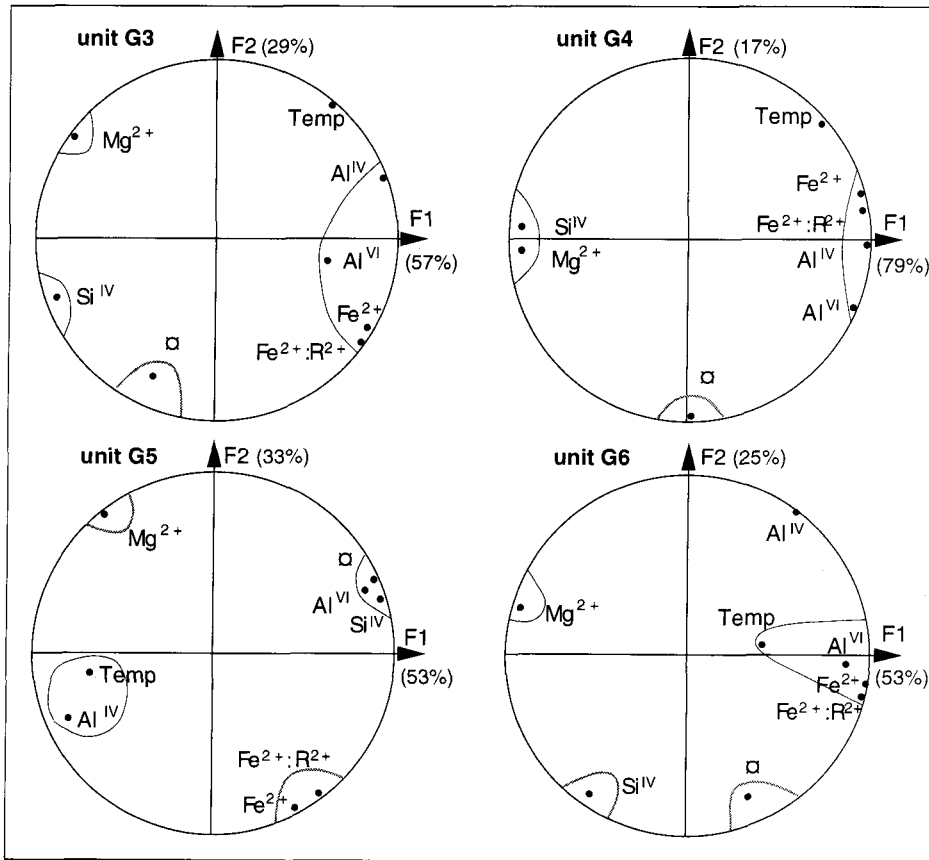


Figure 5. Representation of statistical analyses (PCA) of chlorite data for the G3 (850–1000 m), G4 (1000–1100 m), G5 (1100–1250 m) and G6 (1250–1700 m) lithologic units. The percentage values are the variance data associated with each uncorrelated factor (F1 and F2). The black line group variables with the F1 factor and dashed line shows variables associated with the F2 factor; \square = octahedral vacancies.

chlorite in the Los Humeros system where the octahedral occupancy is deficient, less than the ideal total of 12 cations for a fully trioctahedral chlorite.

Jiang et al. (1994) proposed that the high \square in most published chlorite formulae are due to inclusions of other minerals. The $\text{Na} + \text{K} + 2\text{Ca}$ and \square data from Los Humeros, presented in Figure 3, confirmed a minor presence of minerals intergrown with chlorite. The PCA showed that the \square of chlorite are systematically independent of the chemical composition for these phyllosilicates in the G3, G4, G5 and G6 units. These

results suggest that the lack of a complete octahedral occupancy is probably not due to contamination by silicate phases (such as quartz). In Figure 9, some potential effect of “contamination” trends by 10% quartz, albite-potassium feldspar and talc-saponite in chlorite, from Jiang et al. (1994), are illustrated. The data points of chlorite from Los Humeros seem not to follow these trends. Therefore, we suggest that the deficient octahedral occupancy of chlorite is not due to contamination by quartz or other phases. However, the trends of G1, G2 and G5 shown in Figure 9 may be

Table 4. Correlation coefficients present among different chemical variables for chlorite of the Los Humeros geothermal system.

Lithologic unit	$\text{Al}^{\text{IV}}\text{-Al}^{\text{VI}}$	$\text{Al}^{\text{IV}}\text{-Fe}^{2+}$	$\text{Al}^{\text{IV}}\text{-}\square$	$\text{Al}^{\text{VI}}\text{-}\square$	$\text{Fe}^{2+}\text{-Mg}^{2+}$	$\text{Al}^{\text{VI}}\text{-Mg}^{2+}$	$T\text{-}\square$	$T\text{-Al}^{\text{IV}}$
G3	0.55	0.51	-0.58	—	-0.98	—	-0.75	0.83
G4	0.93	0.86	—	—	-0.99	-0.84	—	—
G5	-0.61	—	-0.84	0.93	-0.95	—	-0.63	0.5
G6	0.54	—	—	0.58	-0.98	-0.75	—	—

Key: \square = Octahedral vacancies in chlorite, T = temperature in $^{\circ}\text{C}$, dash = no correlation.

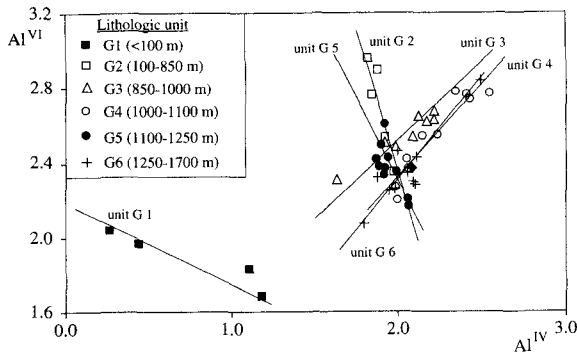


Figure 6. Correlation diagram showing variation of the tetrahedral aluminum (Al^{IV}) as a function of octahedral aluminum (Al^{VI}) for chlorite of Los Humeros. Lines show the negative or positive correlation found for chlorite present in each lithologic unit. Al^{VI} is greater than Al^{IV} for all data set (total unit cell).

due to the presence of minor “contamination” that result in slight increases in the \square of chlorite.

Temperature/Composition Relationships

The structure and composition of chlorite have been used to obtain information about the temperature of crystallization of this mineral. The chlorite structure appears to change with temperature (Bailey and Brown 1962; Hayes 1970; Curtis et al. 1985; Walker 1989); therefore, chlorite polytypism may be used as a geothermometer. However, this geothermometer is largely qualitative and lacks in-depth investigation of the processes controlling polytype transition (de Caritat et al. 1993). For example, the polytype transition in chlorite depends on other factors such as grain size, pressure and the duration of geological process. The chemical composition of chlorite used as a geothermometer has received much more attention. Some authors (Cathelineau and Nieva 1985; Cathelineau 1988; Shau et al. 1990) proposed that the simplest form of an empirical geothermometer consists of calibrating a particular quantifiable aspect of chlorite composition; for example, Al^{IV} content or \square , with temperature.

Essene and Peacor (1995) defined the requirements for a clay mineral to be useful as a geothermometer. These requirements include 1) chemically and structurally homogeneous phases, 2) systems in chemical equilibrium, 3) constraint of additional variables that affect the condition of stable equilibrium and 4) experimental calibration at compositions, pressures and temperatures comparable to those for which it is to be applied. Unfortunately, the clay mineral system, including chlorite, cannot be used as an accurate geothermometer. Any bulk chemical analyses of chlorite, including electron microprobe measurement or analytical electron microscope (AEM) analyses, represent averages over the intergrowths (Peacor 1992). Therefore, bulk analytical data on clay minerals must be

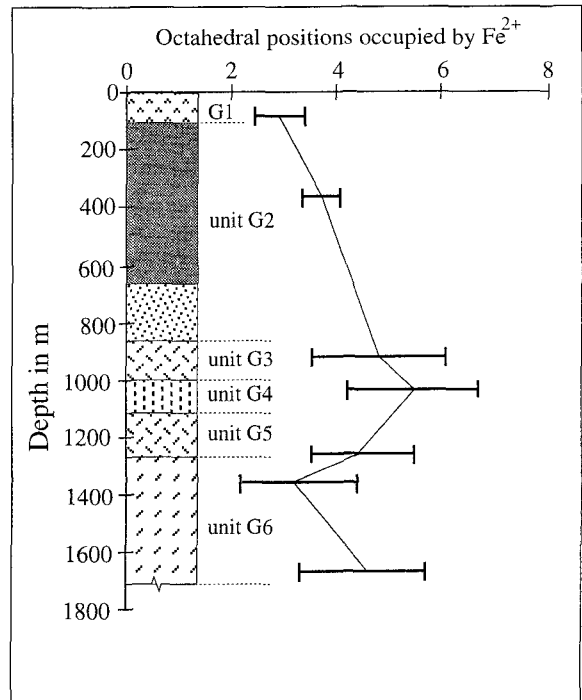


Figure 7. Octahedral Fe^{2+} content in chlorite increases in function of depth and temperature. Some iron variations may be due to changes in oxygen fugacity conditions at different depths.

used cautiously (Jiang et al. 1994). Furthermore, clay minerals, including chlorite, show a very heterogeneous nature which is inconsistent with the phase rule and therefore with attainment of stable equilibrium (Loucks 1992; Velde 1992a, 1992b). Finally, most experiments on the stability of chlorite solid solutions

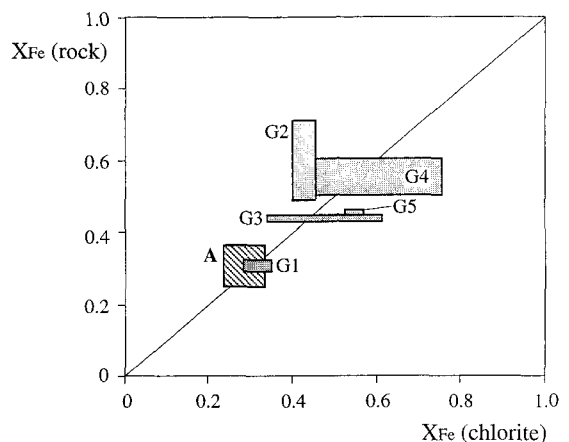


Figure 8. Diagram of X_{Fe} chlorite vs. X_{Fe} whole rock, $X_{Fe} = Fe/(Fe + Mg)$. Rectangles show range of values for lithologic units of Los Humeros: G1 (<100 m), G2 (100–850 m), G3 (850–1000 m), G4 (1000–1100 m) and G5 (1100–1250 m) and for Los Azufres, Mexico (square A).

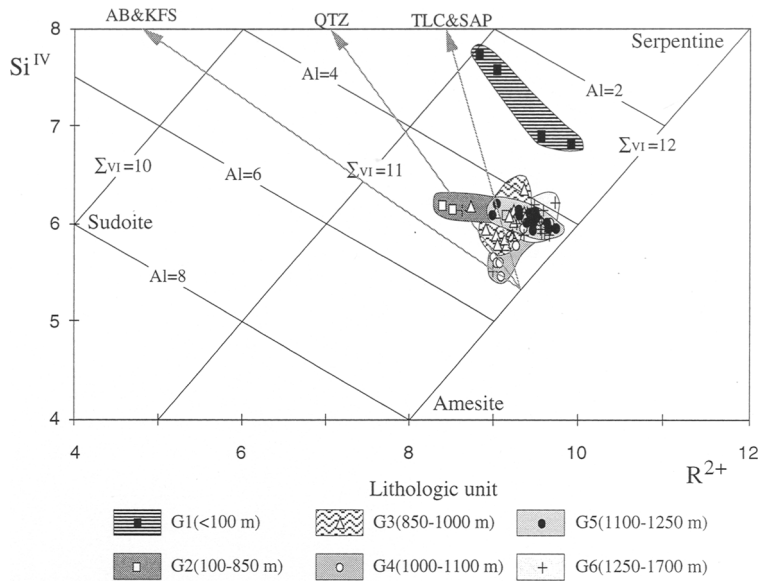


Figure 9. Chlorite compositions plotted in the vector representation of Wiewóra and Weiss (1990). Si^{IV} and R²⁺ are orthogonal axes, and total Al and octahedral occupancy (Σ^{vI}) are shown by isolines (total unit cell). Some schematic trends of compositional deviations generated from mixtures of chlorite and other minerals (10% quartz: QTZ, albite and K-feldspar: AB&KFS, and talc and saponite: TLC&SAP) are displayed from Jiang et al. (1994).

(Fawcett and Yoder, 1966; McOnie et al. 1975; Fleming and Fawcett 1976; Cho and Fawcett 1986) are based on nonreversible experiments carried out at high temperatures and have limited value for equilibrium relations. Therefore, these experimental data are not representative of real conditions.

The relationship between temperature, at different stratigraphic levels, and chemical composition of chlorite from Los Humeros was determined by mean of statistical analyses (PCA). Correlation coefficients between the temperature and \square (Table 3) are -0.75 and -0.63 for chlorite samples from the G3 and G5

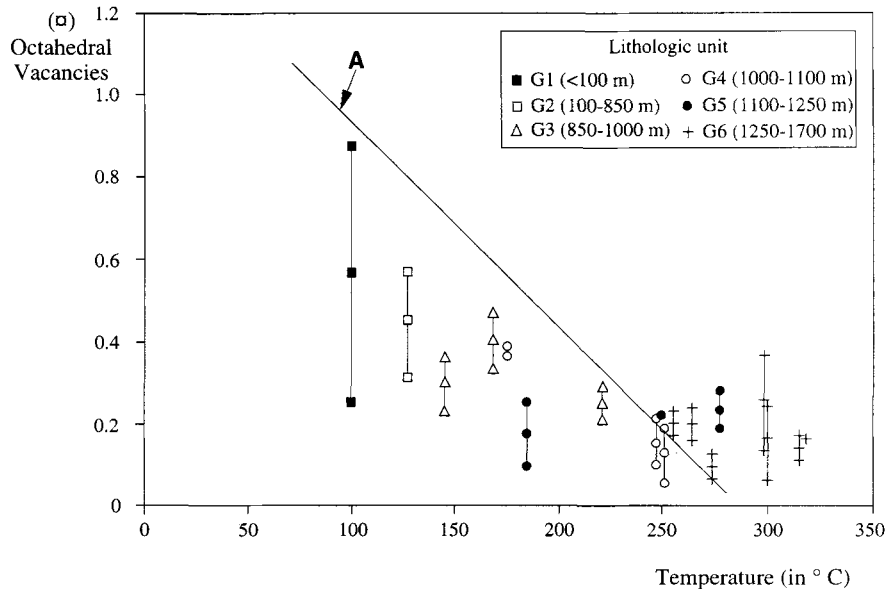


Figure 10. Relationship between \square and temperature with data represented as mean composition and compositional range for chlorite. The regression line proposed by Cathelineau and Nieva (1985) for chlorite of Los Azufres, Mexico, is also shown (line A). Chlorite of G1 unit is suspected of contamination.

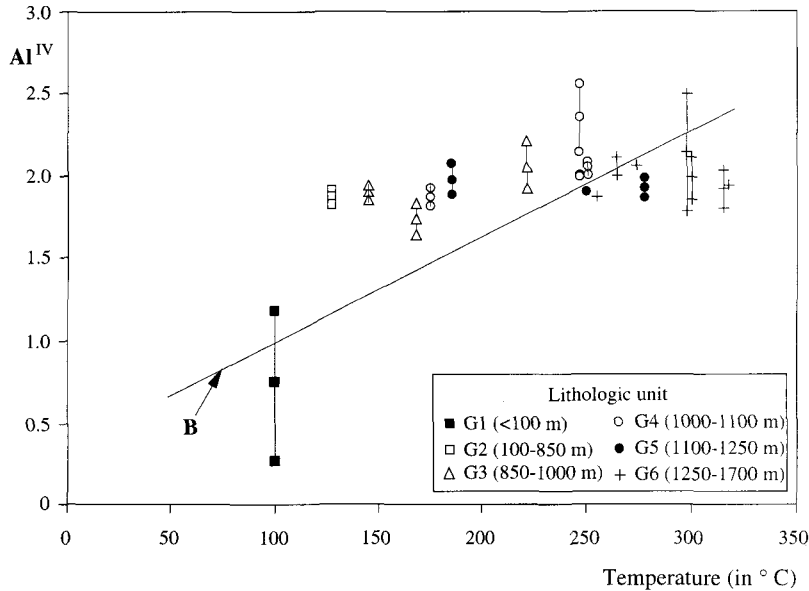


Figure 11. Relationship between Al^{IV} content and temperature with data represented as mean composition and compositional range for chlorite from Los Humeros. Also shown is the regression line calculated by Cathelineau (1988) for hydrothermal chlorite of Los Azufres, Mexico (line **B**). Chlorite of G1 unit is suspected of contamination.

groups, respectively. Unfortunately, the correlation coefficient for the G3 unit is not significant, as was mentioned above, in the PCA results. Figure 10 shows the relationship between temperature and \square for chlorite of Los Humeros. The regression line of Cathelineau and Nieva (1985) for phyllosilicates of the Los Azufres geothermal system was included in Figure 10. A general decrease in \square of chlorite with increasing temperature is observed. However, chlorite samples of each lithologic unit seem to show a particular trend. The correlation coefficient for the best-fit line through the main composition is very low (<0.4). Chlorite series with relatively abundant \square (in the G1, G2 and G3 units) plot below the line given by Cathelineau and Nieva (1985), whereas chlorite minerals of the G4, G5 and G6 lithologic units, showing relatively high octahedral occupancies, appear to plot in a zone parallel to but below or above the Los Azufres chlorite line. From the PCA studies, we conclude that \square is an independent variable and that it is not related to temperature or any other chemical variable of chlorite.

The relationship between Al^{IV} and temperature for chlorite of Los Humeros is shown in Figure 11 together with the geothermometer line calculated by Cathelineau (1988). There is a general relationship showing that the tetrahedral charge increases slightly with temperature, although the correlation coefficients between temperature and Al^{IV} for all chlorite data are relatively low (<0.6).

Our results show that the chemical composition of chlorite appears to change with temperature (Figures 10 and 11). However, the correlation of \square and Al^{IV}

with temperature is considerably more variable than those found by Cathelineau and Nieva (1985). In the Los Azufres geothermal system, the lithologic units are more homogeneous in comparison with those of Los Humeros. In the case of Los Azufres, the chlorite phases were crystallized mainly in andesitic rocks whereas, at Los Humeros, there are many lithologic units (intercalated andesites, dacites and rhyolites) with chlorite alteration. On the other hand, the hydrothermal alteration, mineral association and temperature conditions of geothermal fluids are very similar in the 2 geothermal systems. However, the whole-rock composition and other physicochemical conditions (such as oxygen and sulfur fugacities) are very important factors that cannot be ignored, as previously reported (Hillier and Velde 1991; de Caritat et al. 1993; Essene and Peacor 1995).

CONCLUSIONS

The chemical composition of almost 70 hydrothermal chlorite samples obtained by EMPA has been examined with respect to lithology, temperature (from 100 to 320 °C) and various physicochemical conditions of crystallization. Hydrothermal chlorite tends to be less siliceous, has total replacement in Fe and Mg in octahedral sites, and shows a high total (Fe + Mg) compared to diagenetic chlorite. However, the most Fe-rich hydrothermal chlorite is the most aluminous (total Al), whereas the most Mg-rich chlorite is the least aluminous, as was also observed in low-temperature chlorite by Hillier and Velde (1991). The Fe/(Fe + Mg) ratio for all sets of analyses is probably deter-

mined by the chemical environment (whole rock) and modified by oxygen fugacity conditions. The Fe-rich chlorite in Los Humeros is present at deep levels of the system, suggesting an increase in iron with degree of alteration. Most hydrothermal chlorite shows indications of only minor \square , especially those from high-temperature ranges, the same as in metamorphic chlorite. The \square are low, <0.3 per 12 octahedral sites in most trioctahedral chlorite of the G3, G4, G5 and G6 lithologic units at Los Humeros, and the PCA showed that \square are not related to temperature changes, "contamination", or other chemical variables (such as Si^{IV}). We consider that, with an increase in temperature, depth and degree of alteration, the Si^{IV} content of these phyllosilicates decreases, but the (Fe + Mg) content and octahedral occupancy increase in same way as in metamorphic chlorite. Empirical geothermometers, such as those proposed by Cathelineau and Nieva (1985) and Cathelineau (1988), may be useful if this method is used to determine temperature using chlorite of similar geologic and physicochemical conditions. However, these empirical relations appear to be very sensitive to parameters other than temperature (de Caritat et al. 1993; Essene and Peacor 1995). Finally, we suggest that chlorite formed in hydrothermal environments presents certain characteristics that are different from those of their equivalents from sedimentary and low-temperature chlorite; for example, less siliceous, more (Fe + Mg) and relatively high octahedral occupancy.

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