

Variation of Fe and Mg in Hydrothermal Altered Chlorite

Niniek Rina Herdianita

*Research Group of Petrology, Volcanology and Geochemistry, Faculty of Earth Sciences and Technology,
Bandung Institute of Technology (ITB) - Indonesia. Email: herdianita@itb.ac.id*

Abstract

Chlorite is the most common clay mineral present in the hydrothermal system. It occurs as a replacement of phenocrysts and groundmass and in veins. Chlorite occurs over a wide range of temperatures, i.e. from 120 to 330°C and it is classified in terms of Si, Fe and Mg. This paper reveals that the compositions of hydrothermal minerals record information about the physicochemical conditions and processes prevailing during their formation, sometimes including temperature, pressure and fluid composition.

The occurrence of chlorite is confirmed using petrography and X-ray diffraction (XRD) analyses. Chemistry of chlorite is determined using electron microprobe (EM). The result shows that there is zoning of replacement chlorite. It might indicate an equilibrium process during water and rock interactions.

Keywords: ferromagnesian, clay mineral, hydrothermal, electron microscope.

Introduction

Chlorite is the most common clay mineral in the hydrothermal system. It replaces almost all primary minerals and also occurs as vein-filling mineral. Chlorite is typically green in color with streak of pale green to grey. It has a great range in composition, mainly Fe-rich (e.g. chamosite, ripidolite (prochlorite) and brunsvigite) or Mg-rich (e.g. clinocllore and penninite). Kerr (1959) showed that under petrography microscope Fe-rich chlorite is green, greenish gray, pale brown to almost colorless, whereas Mg-rich chlorite is typically green or greenish.

Chlorite is also indicated by the appearance of X-ray diffraction (XRD) peaks at about 14, 7.1, 4.7 and 3.55 Å identified as chlorite (001), (002), (003) and (004) reflections respectively. In some cases, the odd chlorite peaks are weak or absent and this probably reflects the amount of Fe in chlorite (Moore & Reynolds, 1989). Therefore, the intensity ratio between the (001) and (002) peaks can be used to determine the relative amounts of Fe in chlorite. The higher the ratio of the chlorite (001) and (002) peaks, the lower the amount of Fe in chlorite.

Chlorite commonly appears in sub prophyllitic to prophyllitic alteration zones. It occurs over a wide range of temperatures, i.e. from 120 to 330°C (Reyes, 2000). Variation of the chlorite chemical composition could be used as a geothermometer estimating the chlorite formation temperature (e.g. de Caritat et al., 1993; Maydagán et al., 2018 and Wilkinson et al., 2015). Generally, the lower the Fe content in chlorite, the higher the chlorite formation temperature (Maydagán et al., 2018).

This paper discusses the characteristics of chlorite in a geothermal well. The chlorite compositional zoning can be seen from the results of petrography, XRD and mineral chemistry analyses from various sample depths. Furthermore, based on the chemical compositions of chlorite, the temperature of its formation was calculated using geothermometers mentioned in de Caritat et al. (1993).

Data and Method

Chlorite mineral was taken from 300, 900, 1000, 1200, 1250, 1300 and 1320 m depths. Hostrock and association of alteration mineral were confirmed using petrography and XRD analyses. Chlorite is present in lithology of brecciated andesite lava and microdiorite. Mostly chlorite replaced groundmass and plagioclase phenocryst. Alteration of chlorite from 300 m is associated with smectite, whereas at the other depths chlorite is associated with illite. Below 1000 m depth chlorite is associated with quartz, epidote and sometimes with garnet and calcite.

Forty (40) electron microprobe (EM) analyses were used to determine the chemical composition of chlorite. The EM determinations of SiO₂, TiO₂, Al₂O₃, FeO, MnO, MgO, CaO, Na₂O, K₂O, P₂O₅, Cl, SO₃, Cr₂O₃ and NiO are on a wt.% basis; the chlorite elemental compositions were then calculated from their oxides based on 36 oxygens

Result and Discussion

From petrography and XRD analyses, chlorite is mostly well crystallised and Fe-rich, except samples from 300 and 900 m depths, where they are poorly crystallised and Mg rich.

The EM analysis shows that the compositions of replacement and vein chlorites are similar. Chlorite from 300 m depth is Al-chlorite (Figure 1). It contains 45-50 wt.% SiO₂ and 32-38 wt.% Al₂O₃. The amounts of MgO and FeO are very low, i.e. up to 6 and less than 0.5 wt.% respectively. The other chlorites from 900, 1000, 1200, 1250, 1300 and 1320 m depths contain lower SiO₂ and Al₂O₃ and higher MgO and FeO compared to chlorite from 300 m depth. The SiO₂ and Al₂O₃ contents are 28-38 and 13-21 wt.% respectively and the MgO and FeO contents are 17-31 and 3-22 wt.% respectively. Figure 1 shows that these chlorites are Mg-chlorites. All chlorites could contain up to 1.4 wt.% MnO; the amounts of CaO and K₂O are less than 1 wt.% each and the amount of Na₂O is only less than 0.25 wt.%.

Based on the amounts of Si and Fe atom in the 36 oxygen structure formulae, chlorite from 900 m depth is penninite (Figure 2) having ratio Mg/Fe+Mg of above 0.9 (Figure 3). Chlorites from 1000, 1200 and 1250 m depth are pynochlorite (Figure 2) and have the ratio Mg/Fe+Mg of 0.7-0.8 for sample from 1000 m depth and 0.6-0.7 for samples from 1200 and 1250 m depth (Figure 3). Chlorites from 1300 and 1320 m depth are mixture of talc-chlorite, penninite, pynochlorite and diabantite; they have the ratio Mg/Fe+Mg between 0.7 and 0.9 (Figure 2 and 3).

Temperature of chlorite formation was estimated using geothermometer mentioned in de Caritat et al. (1993). Cathelineau (1988 in de Caritat et al., 1993) suggested the chlorite geothermometer relating to the content of aluminium in tetrahedral structure (Al^{IV}):

$$t (^{\circ}\text{C}) = - 61.92 + 321.98 \text{ Al}^{\text{IV}} \dots\dots\dots (1)$$

This geothermometer is generally applicable for chlorite in diagenetic, hydrothermal and metamorphic settings (Cathelineau, 1988 in de Caritat et al., 1993).

Kranidiotis and MacLean (1987 in de Caritat et al., 1993) modified the Cathelineau and Nieva (1985 in de Caritat et al., 1993) geothermometer by calculating a corrected Al^{IV} (Al^{IV}_{cor}) value using Fe and Mg contents:

$$t (^{\circ}\text{C}) = 106 \text{ Al}^{\text{IV}}_{\text{cor}} + 18 \dots\dots\dots (2)$$

where,

$$\text{Al}^{\text{IV}}_{\text{cor}} = \text{Al}^{\text{IV}} + 0.7 (\text{Fe}/[\text{Fe} + \text{Mg}]) \dots\dots\dots (3)$$

Jowett (1991 in de Caritat et al., 1993) suggested a similar type of correction, derived from an isothermal Fe/(Fe+Mg) normalization, the chlorite

geothermometer and the Al^{IV} correction are as follow:

$$t (^{\circ}\text{C}) = 319 \text{ Al}^{\text{IV}}_{\text{cor}} - 69 \dots\dots\dots (4)$$

where,

$$\text{Al}^{\text{IV}}_{\text{cor}} = \text{Al}^{\text{IV}} + 0.1 (\text{Fe}/[\text{Fe} + \text{Mg}]) \dots\dots\dots (5)$$

Jowett (1991 in de Caritat et al., 1993) claimed that this Fe-Mg-modified geothermometer is applicable to a variety of systems in the temperature range of 150 to 325°C for chlorites with Mg/(Fe+Mg) values of more than 0.4.

Table 1 shows results on chlorite geothermometer calculation using equations (1) to (5). The result shows that sample from 300 m depth cannot be used because the unreasonable temperature. The results on Table 1 also shows that the formation temperatures estimated using the Cathelineau (1988) and Jowett (1991) in de Caritat et al. (1993) geothermometer can reach 600 to 750°C. These temperatures are too overestimated and cannot be used. On the other hand, the Kranidiotis and MacLean (1987 in de Caritat et al., 1993) geothermometer seems to give reasonably result; the chlorite formation temperatures range between 130 and 280°C, corresponding to the formation of chlorite mineral (Table 1). Figure 4 shows that the chlorite formation temperatures are appropriate with the well temperature measurement and fluid inclusion homogenization temperature given by Herdianita (2012).

Table 1. Estimation of formation temperature of chlorite.

mD	Chlorite Geothermometer (°C)		
	Cathelineau (1988)* - Equation (1)	Kranidiotis and MacLean (1987)* - Equation (2)	Jowett (1991)* - Equation (4)
300	1980 – 2470	20 – 35	- 60 – - 68
900	700 – 740	160 – 200	420 – 460
1000	670 – 740	260 – 280	600 – 640
1200	700 – 710	250 – 270	570 – 600
1250	630 – 690	210 – 250	440 – 550
1300	600 – 650	130 – 230	210 – 540
1320	620 – 670	190 – 220	400 – 500

* In de Caritat et al., 1993

Conclusions

Chlorite geothermometers are suitable for both Mg- and Fe-rich chlorites. When using this geothermometer, it is better to make a correction to

Al content by taking into account the amount of Fe and Mg. This research shows that the chlorite geothermometer by Kranidiotis and MacLean (1987 in de Caritat et al., 1993) provides a reasonable and appropriate temperature. Of course, more data is needed to test the validity of this conclusion.

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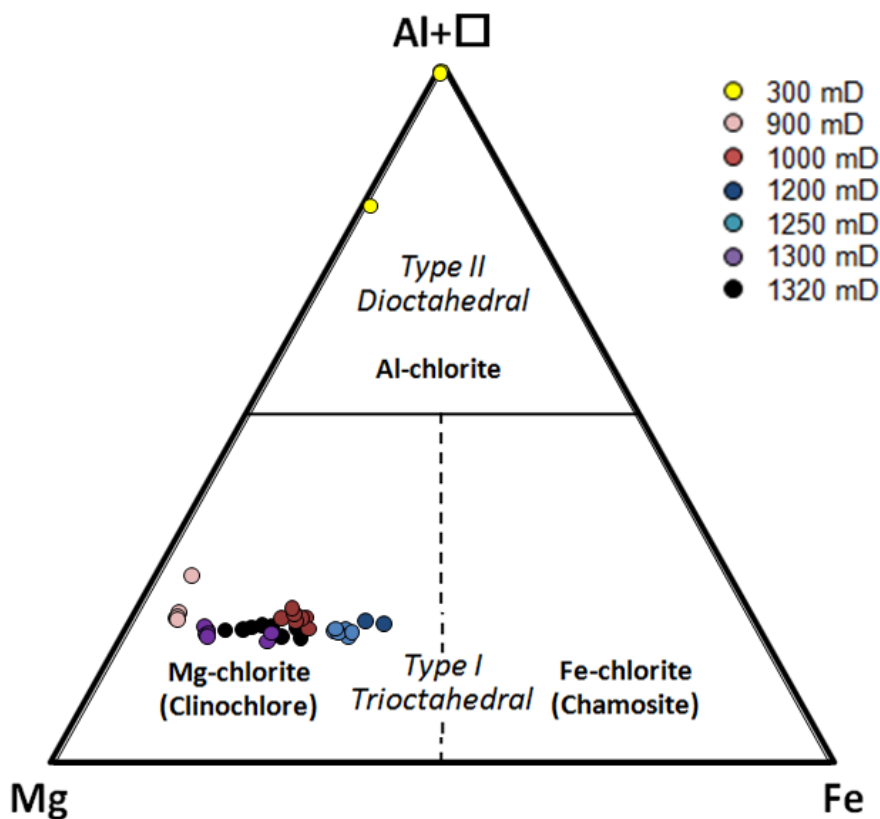


Figure 1. Classification of chlorites based on the amounts of Al, Mg and Fe in the 36 oxygen structure formulae.

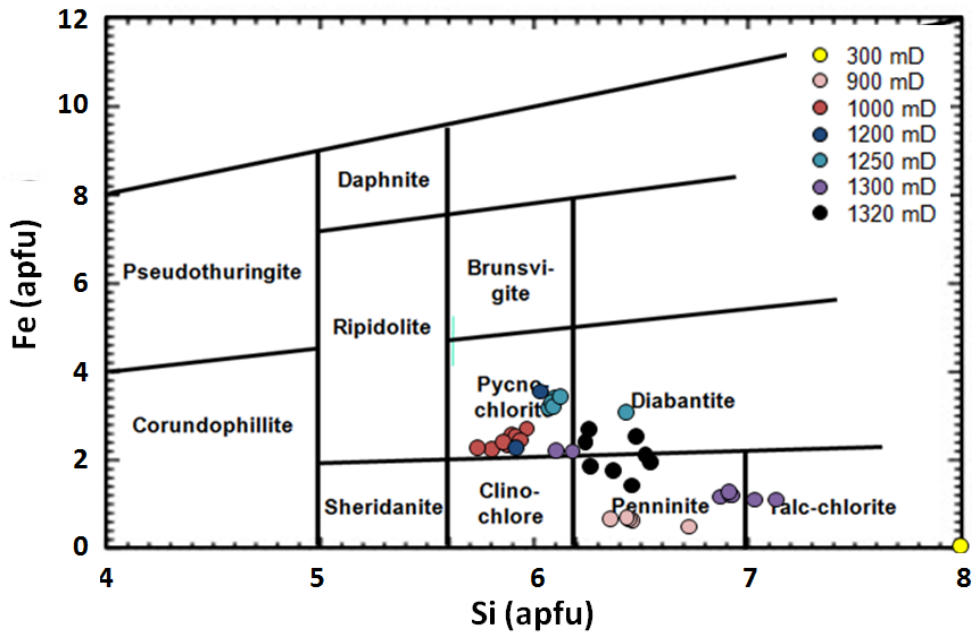


Figure 2. Classification of chlorites based on the amounts of Si and Fe (apfu = atoms per formulae unit) in the 36 oxygen structure formulae.

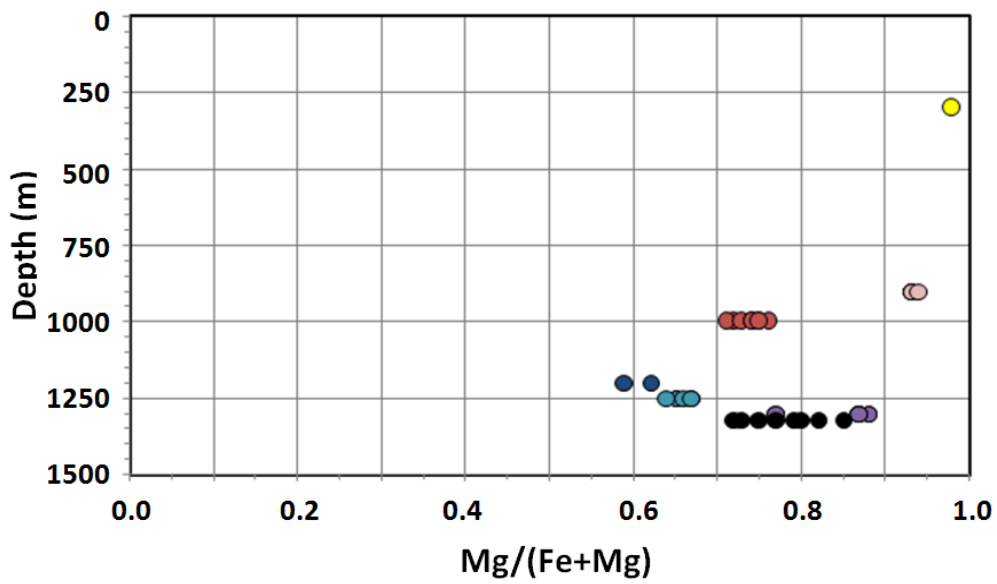


Figure 3. Variations in the ratios between Mg and Fe+Mg of chlorites with respect to depth.

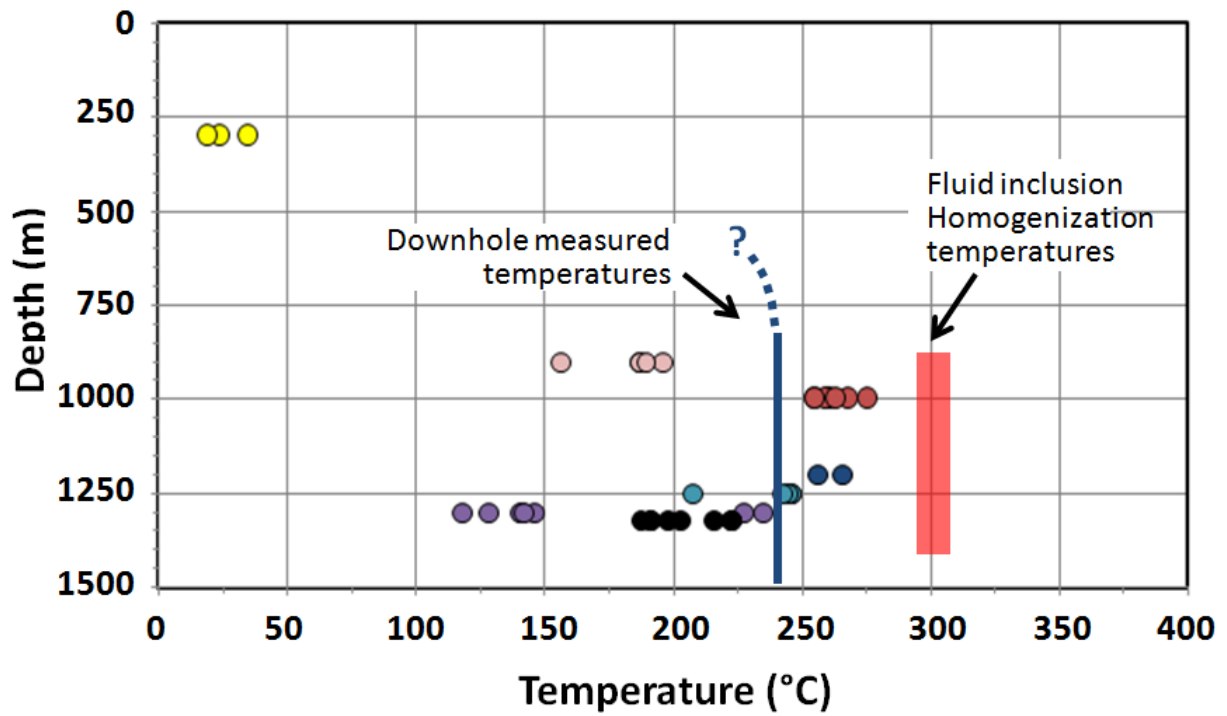


Figure 4. Variations in the chlorite formation temperature using Kranidiotis and MacLean (1987 in de Caritat et al., 1993) geothermometer with respect to depth. The temperatures are compared to downhole well temperature measurement and fluid inclusion homogenization temperature given by Herdianita (2012).