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COMPOSITIONAL DIFFERENCES IN CHLORITE FROM HYDROTHERMALLY ALTERED ROCKS AND HYDROTHERMAL ORE DEPOSITS

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ABSTRACT

We report on the composition of chlorite in altered rocks from active and fossil geothermal systems, and from Neogene hydrothermal Cu–Pb–Zn vein-type and Kuroko deposits of Japan. Values of $Fe^{2+}/(Fe^{2+} + Mg)$ in chlorite from the ore deposits are more variable than in chlorite from the altered rocks of the geothermal systems. The value Fe^{2+}/Mg of chlorite from the latter is positively correlated with that of the fresh rock, and thus seems controlled by the composition of the original rock. The variability in Fe^{2+}/Mg of chlorite from the Kuroko and Neogene vein-type deposits is attributed to a control by the fluid phase (Fe^{2+}/Mg, pH, ΣS, temperature). The influence of movement and mixing of fluid phases may also be important.

Keywords: chlorite, stability, chemical composition, Kuroko deposits, vein-type deposits, geothermal system, oxygen fugacity, propylitic alteration, water–rock interaction, Japan.

SOMMAIRE

On décrit la composition de la chlorite dans les roches altérées des systèmes géothermiques actifs et fossiles, des gisements néogènes de Cu–Pb–Zn en remplissage de fissures et des gisements de type Kuroko, au Japon. Les valeurs du rapport $Fe^{2+}/(Fe^{2+} + Mg)$ pour la chlorite des gîtes minéraux sont plus variables que pour celle des roches lessivées des systèmes géothermiques. La valeur du rapport Fe^{2+}/Mg pour la chlorite dans ces roches altérées montre une corrélation positive avec sa valeur dans les roches saines, ce qui indiquerait l'influence importante de la composition de la roche originelle sur celle de la chlorite. Quant aux gîtes de Kuroko et de Cu–Pb–Zn néogènes, la grande variabilité du rapport Fe^{2+}/Mg dans la chlorite serait due aux propriétés des fluides (Fe^{2+}/Mg, pH, ΣS, température). L'influence des flux et des mélanges de fluides auraient aussi une certaine importance.

(Traduit par la Rédaction)

Mots-clés: chlorite, stabilité, composition chimique, gîtes de type Kuroko, gîtes en remplissage de fissures, système géothermique, fugacité d'oxygène, altération propylitique, interaction roche–eau, Japon.

INTRODUCTION

Chemical compositions of chlorite from various geological environments are given, for example, by Hey (1954), Foster (1962), Albee (1962), Shirozu (1959, 1967, 1969) and Nakamura (1970). Chlorite is one of the most abundant and widespread products of alteration in geothermal and hydrothermal systems. Large numbers of analytical data have been accumulated over recent years on the chlorite from these hydrothermal environments. No one has as yet attempted to summarize the chemical composition of such chlorite, which displays wide compositional variation, probably reflecting the variations in fluid and rock chemistry, gas fugacities and temperature. These relationships between the composition of chlorite and gas fugacities, chemical compositions and temperature of hydrothermal fluids, respectively, have been considered by several investigators (Ellis 1971, Shikazono 1974a, 1978a, Barton *et al.* 1977, Giggenbach 1980, McDowell & Elders 1980, Walshe & Solomon 1981, D'Amore & Gianelli 1984, Reed 1984, Cathelineau & Nieva 1985, Walshe 1986).

In this paper we consider the possible causes for the compositional variation in chlorite from geothermal and hydrothermal environments. Attention is focused on Fe and Mg contents and on the importance of the composition of the hydrothermal fluid and original (*i.e.*, fresh) rock as factors in controlling the chemical composition of chlorite. Differences in the different sites of hydrothermal systems (*e.g.*, discharge zone *versus* recharge zone) are also evaluated.

CHEMICAL COMPOSITION OF HYDROTHERMAL CHLORITE

Natural chlorite contains Mg, Fe, Al and Si as major elements, and Ca, Cr, Ti and Mn as minor elements. Data on concentrations of minor elements in chlorite are scarce, and therefore not taken into account in this investigation.

Trioctahedral chlorite occurs commonly in geothermal and hydrothermal areas, whereas the occurrence of dioctahedral chlorite is very limited. For instance, donbasite does not occur in geothermal and hydrothermal areas, but sudoite (Al-chlorite) commonly does occur in the Kuroko area (*e.g.*, Tsuzuki & Honda 1977). Dioctahedral chlorite has not been reported from the Neogene Cu-Pb-Zn vein-type deposits of Japan; instead, trioctahedral chlorite is common (Shirozu *et al.* 1975). In the Kuroko area, the common chlorite is trioctahedral Mg chlorite. The structural formula for trioctahedral chlorite is represented by $(Mg_{6-x-y}Fe^{2+}_{y}Al_{x})[Al_{x}Si_{4-x}]O_{10}(OH)_8$. It is convenient to plot a diagram of $Fe^{2+}/(Fe^{2+} + Mg)$ (in atomic fraction) against $^{IV}Al/(Si + {}^{IV}Al)$ to display compositional variations in chlorite (*e.g.*, Hey 1954, Foster 1962, Nagasawa *et al.* 1976).

In Figures 1 and 2, we show the analytical data on chlorite from hydrothermally altered rocks and hydrothermal ore deposits (Japanese Neogene Cu-Pb-Zn vein-type and Kuroko deposits). It can be seen in Figure 2 that the $Fe^{2+}/(Fe^{2+} + Mg)$ values vary very widely (0 to 0.99), ^{IV}Al varies from 0.8 to 1.7, and the $Fe^{2+}/(Fe^{2+} + Mg)$ value of chlorite from different geological environments is different. The $Fe^{2+}/(Fe^{2+} + Mg)$ value of chlorite from the Kuroko deposits in Japan is usually very low, ranging from 0 to 0.1. Its value in propylitically altered rocks in areas of vein-type mineralization ranges from 0.25 to 0.45, and that in chlorite from the Neogene Cu-Pb-Zn vein-type deposits in Japan is high, in the range from 0.26 to 0.45. Chlorite from terrestrial and submarine geothermal systems has a $Fe^{2+}/(Fe^{2+} + Mg)$ value in the range from 0.25 to 0.74.

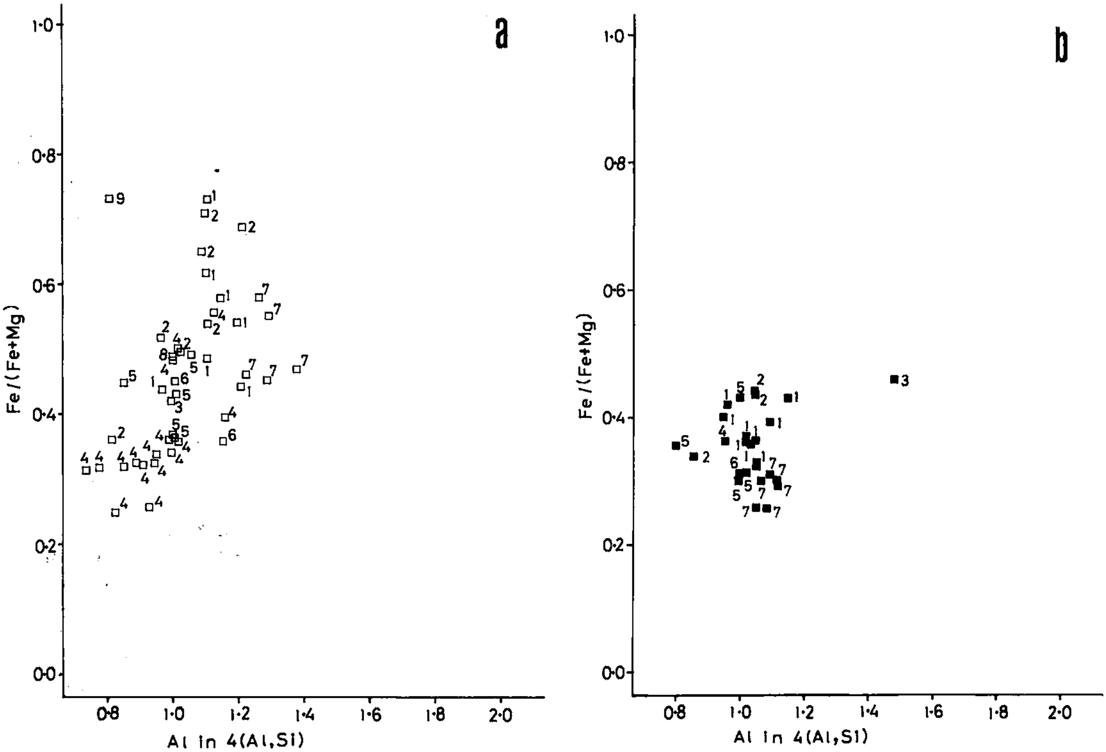

FIG.1.a. Variation of $Fe^{2+}/(Fe^{2+} + Mg)$ as a function of tetrahedral Al in 4(Al, Si) (both expressed as atomic fractions) in chlorite from hydrothermally altered rocks (altered rocks in terrestrial and submarine geothermal areas). Localities: 1 Salton Sea (McDowell & Elders 1980), 2 Iceland (Exley 1982), 3 Wairakei (Steiner 1977), 4 Costa Rica Rift (Kawahata 1984, Alt & Honnorez 1984), 5 Mid-Atlantic Ridge (Humphris & Thompson 1978), 6 Ohtake (Hayashi 1973), 7 Larderello (Cavaretta *et al.* 1982), 8 Svartsengi (Ragnarsdóttir *et al.* 1984), 9 Reydarfjördur (Viereck *et al.* 1982). b. Variation of $Fe^{2+}/(Fe^{2+} + Mg)$ and tetrahedral Al in chlorite from hydrothermally altered rocks (propylitically altered rocks in the mining area). Localities: 1 Seigoshi (Hattori 1974, Shikazono 1985), 2 Yugashima (Fujiwara 1957, Fujii 1976), 3 Budô (Sudo & Sekine 1951), 4 Kushikino (Takeuchi 1979), 5 Hosokura (Konno & Matsueda 1985), 6 Toyoha (Shikazono 1974a, Sawai 1984), 7 Furutobe basalt (Shikazono, unpubl. data).

EFFECT OF THE ORIGINAL CHEMICAL COMPOSITION OF THE ROCKS ON THE Fe^{2+}/Mg RATIO IN CHLORITE

Although a large body of analytical data on hydrothermal chlorite from geothermal and hydrothermal areas is available, there are few data on the chemical composition of original fresh volcanic rocks. The relationship between the ratio MgO/FeO in chlorite and that in the fresh host-rocks is shown in Figure 3; the chemical compositions of chlorite from the geothermal areas in which sedimentary rocks predominate (*e.g.*, Salton Sea, Larderello, Cerro Prieto) are not included.

The value MgO/FeO of chlorite generally satisfies a line of 1:1 slope. The correlation between MgO/FeO in the host rock and that in the chlorite implies that the MgO/FeO value of chlorite from propylitically altered rocks associated with the mining areas and from altered rocks in terrestrial and submarine geothermal areas is largely affected by MgO/FeO ratio of original fresh rocks. However, most of the data from Kuroko and Neogene Cu-Pb-Zn vein-type deposits deviate significantly from this line.

EFFECT OF THE CHEMISTRY OF FLUIDS ON Fe^{2+}/Mg IN CHLORITE

Effect of Fe^{2+}/Mg^{2+} of fluid

Chlorite compositions from some mining areas (Toyoha, Kuroko) deviate significantly from a line of 1:1 slope (Fig. 3). This deviation implies that the Fe^{2+}/Mg value of chlorite from these areas is controlled not only by the FeO/MgO value of the fresh host-rocks, but also by factors such as the ratio of Fe^{2+} to Mg^{2+} in the fluid phase.

Several investigators have shown isotopically that seawater played an important role in the formation of the Kuroko deposits (*e.g.*, Sakai *et al.* 1970, Kajiwara 1971, Hattori & Sakai 1979, Farrell & Holland 1983). Mg-rich chlorite occurs in gypsum-anhydrite bodies in many Kuroko deposits. Farrell & Holland (1983), Shikazono *et al.* (1983), and Kusakabe & Chiba (1983) suggested the involvement of large amounts of seawater or seawater-dominated hydrothermal fluid in the formation of the gypsum-anhydrite bodies. It is reasonable to assume from the large number of experimental studies on rock-seawater interaction at elevated temperatures that the seawater-dominated fluid phase, which interacted with volcanic rocks at a high water/rock ratio, contained appreciable amounts of Mg but very small amounts of Fe (Seyfried & Mottl 1982). Therefore, it is likely that Mg-rich chlorite precipitated from a solution with a high proportion of Mg^{2+} to Fe^{2+}. In contrast to the Kuroko hydrothermal system, there is no evidence for the involvement of seawater in the hydrothermal system associated with the Cu-Pb-Zn vein mineralization. Results of hydrogen and oxygen isotopic studies indicate that large amounts of meteoric water were incorporated into the ore fluids responsible for these vein-type deposits (Hattori & Sakai 1979).

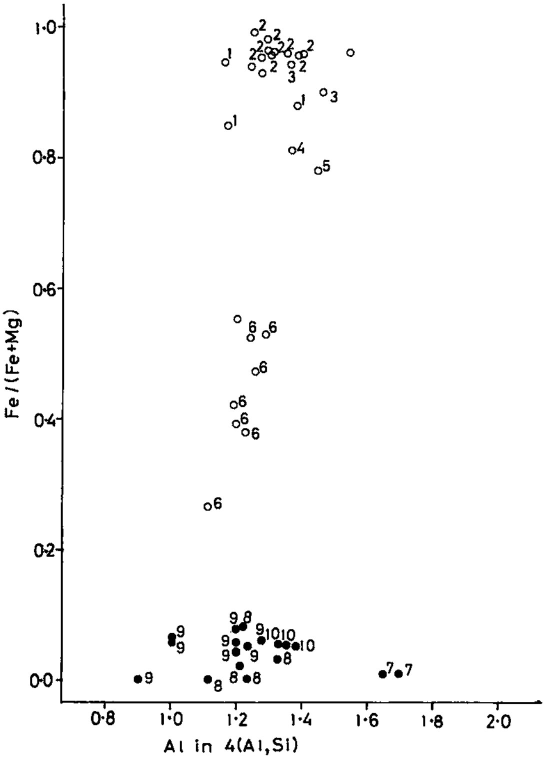

FIG.2. Variation of $Fe^{2+}/(Fe^{2+} + Mg)$ and tetrahedral Al of chlorite from hydrothermal ore deposits: Japanese Neogene Cu-Pb-Zn vein-type (open circle) and Kuroko deposits (solid circle). Localities: 1 Ashio (Nakamura 1960, 1963), 2 Yatani (Hattori 1974), 3 Toyoha (Shikazono 1974a, Sawai 1984), 4 Kishu (Shirozu 1958), 5 Sayama (Shirozu 1958), 6 Mikawa (Nagasawa 1961), 7 Furutobe (Shirozu *et al.* 1975), 8 Hanaoka (Hayashi 1961, Hayashi & Oinuma 1965, Tsuzuki & Honda 1977, Shirozu *et al.* 1975), 9 Wanibuchi (Sakamoto & Sudo 1956, Iwao & Minato 1959, Katsumoto & Shirozu 1973) 10 western Bergslagen (Baker & De Groot 1983).

Effects of oxygen fugacity $f(O_2)$, pH and total concentration of dissolved sulfur Σ S

If Fe-Mg chlorite is assumed to be in equilibrium with a fluid phase and pyrite, the ratio of Fe^{2+} to Mg^{2+} in the fluids may be related to factors such as pH, $f(O_2)$, temperature and Σ S. This relationship can be derived from the following chemical reactions:

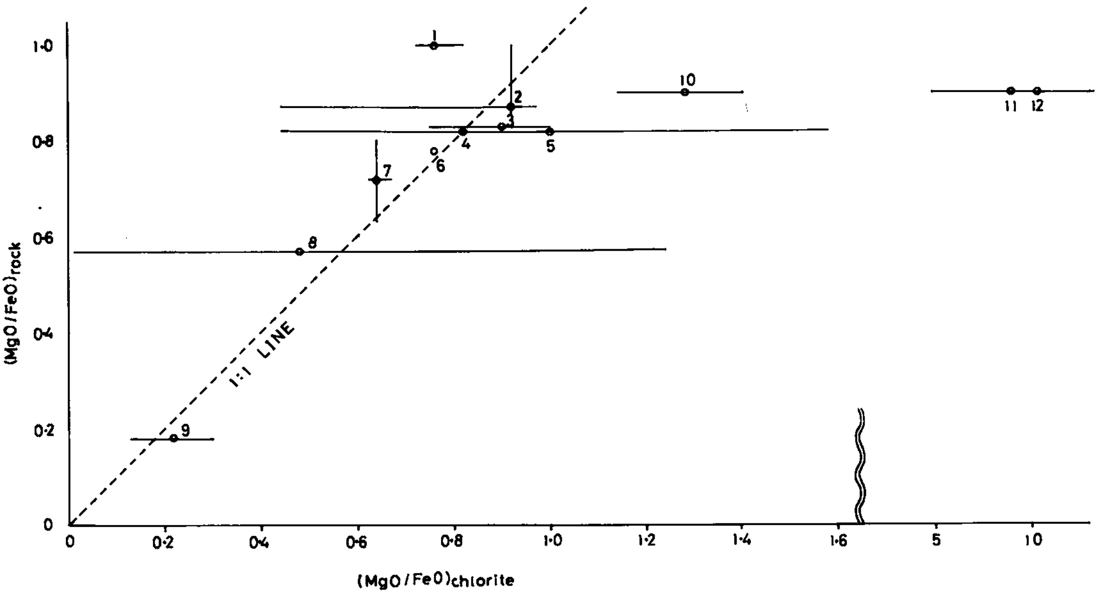

FIG. 3. Relationship between MgO/FeO of chlorite and that of original fresh volcanic rocks. Localities: 1 Seigoshi (Hattori 1974, Shikazono 1985), 2 Mid-Atlantic Ridge (Humphris & Thompson 1978), 3 Ohtake (Hayashi 1973), 4 Yugashima (Iwao 1949, Fujiwara 1957, Fujii 1976), 5 Costa Rica Rift (Kawahata 1984, Honnorez *el al.* 1983, Alt & Honnorez 1984), 6 Wairakei (Steiner 1977), 7 Svartsengi (Ragnarsdóttir *et al.* 1984), 8 Toyoha (Shikazono 1974a, Okabe & Bamba 1976, Sawai 1984), 9 Mitsuishi (Nabetani 1981), 10 Kuroko basalt (MMAJ 1979, Shikazono, unpubl. data), 11 Hanaoka (Hayashi 1961, Hayashi & Oinuma 1965, Tsuzuki & Honda 1977, Shirozu *et al.* 1975), 12 Wanibuchi (Sakamoto & Sudo 1956, Iwao & Minato 1959, Suzuki *et al.* 1971, Date & Tanimura 1973, Katsumoto & Shirozu 1973, Date *et al.* 1983).

$$Mg_5AlSi_3AlO_{10}(OH)_8 + 5Fe^{2+} = Fe_5AlSi_3AlO_{10}(OH)_8 + 5Mg^{2+} \quad (1)$$

$$FeS_2 + 2H^+ + H_2O = Fe^{2+} + 2H_2S + \tfrac{1}{2}O_2 \quad (2)$$

where $Mg_5AlSi_3AlO_{10}(OH)_8$ and $Fe_5AlSi_3AlO_{10}(OH)_8$ represent Mg-chlorite and Fe-chlorite, respectively.

Equilibrium constants for reactions (1) and (2) are represented by

$$K_1 = (a_{Fe\text{-}chl}a^5_{Mg^{2+}})/(a_{Mg\text{-}chl}a^5_{Fe^{2+}}) \quad (3)$$

$$K_2 = (a_{Fe^{2+}}f(O_2)^{1/2}a^2_{H_2S})/a^2_{H^+} \quad (4)$$

where a denotes activity, and Fe-chl and Mg-chl represent Fe-chlorite and Mg-chlorite, respectively. Generally, activities of liquid H_2O and FeS_2 do not deviate from unity; thus these values are assumed to be unity.

From equations (3) and (4), we obtain, for the H_2S-dominant region,

$$\log (a_{Fe\text{-}chl}/a_{Mg\text{-}chl}) = \log K_1 + 5\log K_2 - 5\log a_{Mg^{2+}} - 10\log \Sigma S - 10\log \gamma_{H_2S} - (5/2)\log f(O_2) - 10pH \quad (5)$$

where γ is the activity coefficient. For the SO_4^{2-}-dominant region,

$$\log (a_{Fe\text{-}chl}/a_{Mg\text{-}chl}) = \log K_1 + 5\log K_2 - 5\log a_{Mg^{2+}} + 10\text{ pH} - 10\log \Sigma S - 10\log \gamma_{SO_4^{2-}} + 35/2\log f(O_2) + 10\log K_7 \quad (6)$$

where K_7 is equilibrium constant for the following reaction,

$$H_2S + 2O_2 = SO_4^{2-} + 2H^+ \quad (7)$$

Equations (6) and (7) imply that the $a_{Fe\text{-}chl}/a_{Mg\text{-}chl}$ of chlorite depends on $f(O_2)$, $a_{Mg^{2+}}$, ΣS, pH, temperature and ionic strength. From equations (6) and (7), it can be shown that the $a_{Fe\text{-}chl}/a_{Mg\text{-}chl}$ of chlorite in equilibrium with pyrite decreases with increasing $f(O_2)$ at constant temperature, pH, $a_{Mg^{2+}}$, ionic strength, and ΣS in the region where H_2S is dominant, whereas it increases with increasing $f(O_2)$ in the SO_4^{2-}-dominant region. Previous studies on the estimates of $f(O_2)$, $f(S_2)$, pH, ΣS and temperature for Kuroko ore deposition have been reported, for instance, by Kajiwara (1971), Shikazono (1976) and Ohmoto *et al.* (1983), who showed that the $f(O_2)$ of the Kuroko ore fluids lies in the region close to the $\Sigma SO_4^{2-}/\Sigma H_2S$ boundary (in this expression, ΣSO_4^{2-} and ΣH_2S represent the concentration of the total dissolved oxidized sulfur species and total dissolved reduced sulfur species, respectively). These estimates seem consistent with the low Fe^{2+}/Mg value of chlorite from the Kuroko deposits. Chlorite from the Toyoha deposits is associated with sphalerite, pyrite and, rarely, pyrrhotite (Shikazono 1974a). The iron content of the sphalerite associated with chlorite is 1.2 - 2.9 wt.%. The temperature of formation of chlorite in the Toyoha deposits is estimated to be 200 - 250°C from fluid-inclusion data (Shikazono 1974b, 1975, Yajima & Ohta 1979), which indicates that the chlorite was formed in a relatively reducing environment, *i.e.*, one in which reduced sulfur species predominate. This estimate seems consistent with the composition of chlorite from the Toyoha deposits and from the other Neogene Cu-Pb-Zn vein-type deposits in Japan, which contains up to 40 wt.% FeO (Nakamura 1960, 1963, Shirozu 1969, Shikazono 1974a, Hattori 1974). Shikazono (1974a, c, 1977, 1978b) and Hattori (1975) showed that these deposits formed in environments where species of aqueous reduced sulfur predominated. This estimated range of oxidation state and ratio of concentration of aqueous reduced sulfur species to oxidized sulfur species appears to be in agreement with the chemistry of chlorite from these deposits. However, the Fe^{2+}/Mg of chlorite also depends on the other factors, such as ΣS, pH and $a_{Mg^{2+}}$. From equations (5) and (6), it is obvious that increasing ΣS and $a_{Mg^{2+}}$ also causes a lower Fe^{2+}/Mg in chlorite.

The Fe^{2+}/Mg and Fe^{3+}/Fe^{2+} values of chlorite from the Kuroko deposits and Neogene Cu-Pb-Zn vein-type deposits differ greatly (Fig. 4). Chlorite from the Kuroko deposits contains lower Fe^{2+}/Mg and higher Fe^{3+}/Fe^{2+} values than those from the Neogene vein-type deposits in Japan. The most likely explanation for these differences is that these two types of deposit formed at different states of oxidation, although other variables such as pH, temperature, $a_{Mg^{2+}}$ and ΣS are also possibly important factors, as discussed above.

Effects of temperature, site of chlorite formation and fluid movement

Generally, the Fe^{2+}/Mg value of chlorite from a given geothermal or hydrothermal area is variable. The Fe^{2+}/Mg value of chlorite in the Toyoha mining district varies widely (Fig. 3). Sawai (1984) has shown that the iron content of chlorite decreases away from the Pb-Zn veins. Iron content of chlo-

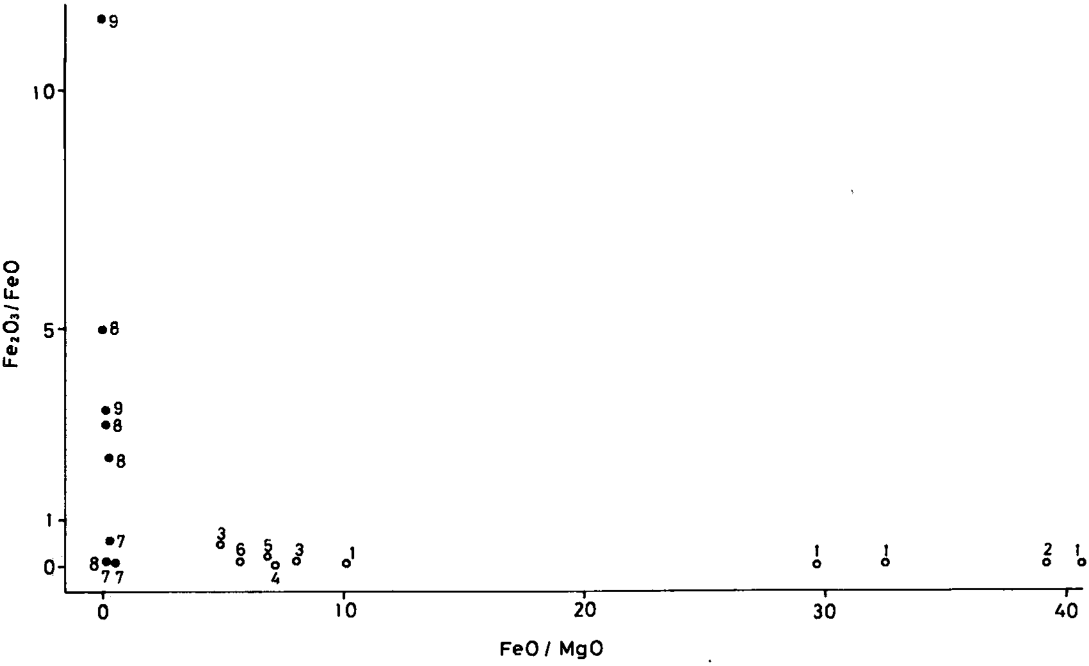

FIG. 4. FeO/MgO and Fe_2O_3/FeO of chlorite from the Kuroko (solid circles) and Neogene Cu-Pb-Zn vein-type deposits (open circles) in Japan. Localities: 1 Ashio (Nakamura 1963), 2 Yatani (Hattori 1974), 3 Ani (Sudo 1954), 4 Kishu (Shirozu 1958), 5 Arakawa (Sudo 1954), 6 Sayama (Shirozu 1958), 7 Wanibuchi (Sakamoto & Sudo 1956, Iwao & Minato 1959, Katsumoto & Shirozu 1973), 8 Hanawa (Hayashi 1961, Hayashi & Oinuma 1965, Tsuzuki & Honda 1977, Shirozu *et al.* 1975), 9 Furutobe (Shirozu *et al.* 1975).

rite in the Toyoha veins is very high (40 wt.% FeO: Shikazono 1974a, Sawai 1984). Variations in iron content of chlorite from the host rocks toward the Cu–Pb–Zn veins have also been studied for other Neogene vein-type deposits in Japan (*e.g.*, Oe, Ashio deposits: Hayashi 1979). Variations in iron content of chlorite from Japanese epithermal mining districts suggest that the iron content of chlorite in the discharge zone of a hydrothermal system is higher than that in the recharge zone. Mottl (1983) has also suggested that the Fe^{2+}/Mg value of chlorite in the discharge zone of submarine geothermal systems is higher than that in the recharge zone. The Fe^{2+}/Mg of chlorite from different parts of a geothermal system (recharge zones *versus* discharge zones) is probably not constant. In order to evaluate the effect of the fluid movement at discharge *versus* recharge zones, the temperature dependence of Fe^{2+}/Mg^{2+} in fluids in equilibrium with the isochemically recrystallized crustal rocks will be considered below. The ratio of Fe^{2+} to Mg^{2+} in the fluids is controlled by reaction (1).

By taking a value for Fe^{2+}/Mg of chlorite that is equal to that of the average andesitic and basaltic rocks (0.6), and assuming that chlorite is an ideal solid-solution of 14 Å Fe-chlorite and 14 Å Mg-chlorite, the dependence of $a_{Fe^{2+}}/a_{Mg^{2+}}$ in fluids on temperature was calculated by using thermochemical data for chlorite from Walshe & Solomon (1981). Figure 5 shows that $a_{Fe^{2+}}/a_{Mg^{2+}}$ of fluids increases with increasing of temperature. Therefore, if fluids initially in equilibrium with chlorite having the same FeO/MgO as that of average andesitic and basaltic rock at elevated temperature (for example, at point A in Fig. 5) ascend rapidly without interaction with the surrounding rocks, chlorite precipitating from fluids at lower temperature (for example, at point B) could contain appreciable amounts of Fe^{2+} compared with Mg. This mechanism could lead to the formation of chlorite having an unusually high content of iron. It is also noteworthy that the vein chlorite in the altered basalt from the Costa Rica Rift contains higher concentrations of iron than the chlorite that replaces mafic minerals in the rock (Kawahata 1984). In this case it is likely that the flow rate of ascending fluids from which vein chlorite precipitated is high compared with the rate of reaction between the ascending fluids and surrounding rocks. The Fe^{2+}/Mg value of chlorite precipitating from ascending fluids depends on the extent of deviation from equilibrium between fluids and surrounding rocks. As discussed in detail by Giggenbach (1984), a number of processes such as adiabatic and conductive cooling of fluids and mixing of fluids can cause this deviation. The above considerations suggest that chlorite occurring in the discharge zones of hydrothermal systems would contain a higher concentration of iron than that occurring in recharge zones. If a magnesium-rich solution such as seawater or a seawater-dominated hydrothermal solution was involved in the hydrothermal system, it could be expected that chlorite, even that occurring in discharge zones, would contain a high content of Mg. It is widely accepted that ascending hydrothermal

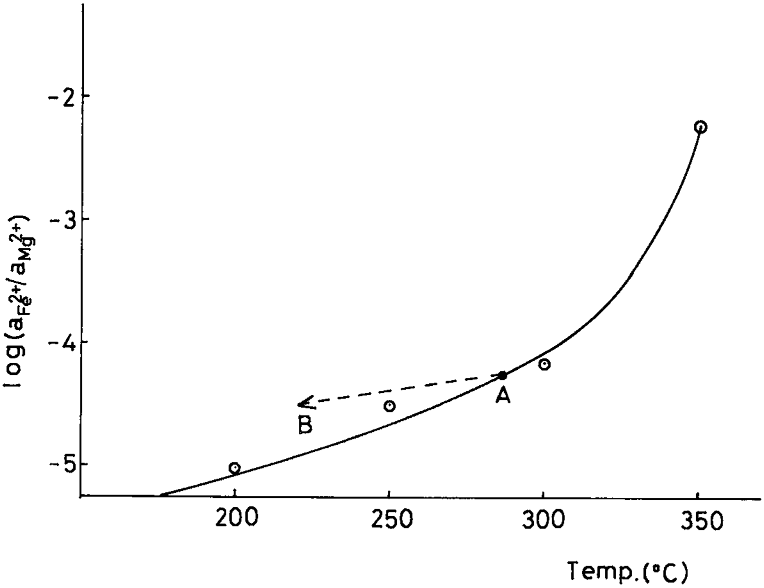

FIG. 5. Variation of $a_{Fe^{2+}}/a_{Mg^{2+}}$ of hydrothermal solution in equilibrium with chlorite having constant Fe^{2+}/Mg (=0.6), as a function of temperature. The significance of points A and B is discussed in the text.

solutions mixed with cold seawater at the time of ore formation at Kuroko (*e.g.*, Hattori & Sakai 1979, Shikazono *et al.* 1983). The Mg concentration of this hydrothermal fluid increased with higher degrees of mixing. Involvement of large amounts of seawater at the site of ore deposition could be one of the reasons why chlorite from the Kuroko deposits contains high amounts of Mg. In addition to a large concentration of Mg in the fluids, relatively high $f(O_2)$, ΣS and $\Sigma SO_4^{2-}/\Sigma H_2S$, and low pH, could lead to the large Mg-content of chlorite in the Kuroko deposits, as discussed above.

Consequently, we conclude that composition of chlorite in the discharge zone depends largely on the chemical nature of fluids (factors such as Fe^{2+}/Mg^{2+}, $\Sigma SO_4^{2-}/\Sigma H_2S$, pH, $a_{Mg^{2+}}$) and temperature. Movement of fluids may also be an important cause for the variability in the ratio of Fe^{2+} to Mg in hydrothermal chlorite. Wide compositional variations in chlorite from the hydrothermal ore-deposits in Japan, including the Kuroko and Neogene Cu–Pb–Zn vein-type deposits, are considered to reflect the variable chemical nature of ascending ore-fluids and fluids that mix with ascending ore-fluids at discharge zones.

In this paper, the variations in Fe and Mg contents of the 14Å Fe-chlorite – 14Å Mg-chlorite solid solution have been considered. However, structural formulae for chlorite are not as simple as those considered in this study. As mentioned by Walshe & Solomon (1981), Stoesell (1984), Cathelineau & Nieva (1985) and Walshe (1986), chlorite solid-solution may be represented by six components, and accurate thermochemical data on each end-member component at the hydrothermal conditions of concern are necessary to provide a far more rigorous calculation of the equilibrium between chlorite and hydrothermal solution. In this study, the polytype of chlorite and the possibility of chlorite–smectite mixed-layer minerals were also not taken into account. However, the present study demonstrates that the composition of chlorite is a highly useful indicator of physicochemical conditions of hydrothermal fluids and extent of water–rock interaction.

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