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## Variables Controlling Epidote Composition in Hydrothermal and Low-Pressure Regional Metamorphic Rocks

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With 4 Text-Figures

*Epidote*  
*Phase relations*  
*Stability*  
*Thermodynamic data*  
*Fluid composition*

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### Welche Variablen kontrollieren die Epidotzusammensetzung in hydrothermalen und niedrigdruckmetamorphen Gesteinen?

#### Zusammenfassung

Epidotminerale in hydrothermalen Systemen und Niedrigdruck-Niedrigtemperatur-Metamorphiten zeigen einen weiten Bereich der Fe<sup>3+</sup>-Al<sup>3+</sup>-Substitution und bilden im allgemeinen chemisch zonierte Kristalle. Experimentelle, theoretische und petrologische Studien haben gezeigt, daß die Zusammensetzung von Epidoten eine komplexe Funktion von Temperatur, Druck, Sauerstoff-Fugazität, Mineralparagenese, Pauschalzusammensetzung des Gesteins und Chemie der fluiden Phase ist.

Temperatur und Sauerstoff-Fugazität sowie CO<sub>2</sub>-Fugazität sind die wichtigen intensiven Variablen, die für die Epidotzusammensetzung verantwortlich sind. Die funktionalen Beziehungen zwischen den Änderungen dieser Variablen und der Änderung in der Epidot-Mischkristallzusammensetzung hängen von der Enthalpie und Stöchiometrie der entsprechenden Reaktion ab. Zusätzlich verursachen wässrige Hydroxid-Komplexe von Fe<sup>3+</sup> und Al<sup>3+</sup> eine empfindliche Reaktion der Epidotzusammensetzung auf den pH-Wert in fast neutralen wässrigen Lösungen geringer Ionenstärke.

Die Empfindlichkeit der Epidotzusammensetzung im Hinblick auf die Chemie der fluiden Phase und die komplexe Zusammensetzung vieler epidot-führender Paragenesen macht chemisch zonierte Epidote zu unverlässlichen Indikatoren der Entwicklung chemischer und physikalischer Variabler während der Metamorphose.

#### Abstract

*Epidote minerals in hydrothermal systems and low-pressure, low-temperature regional metamorphic rocks exhibit a wide range in Fe<sup>3+</sup>-Al<sup>3+</sup> substitution and commonly form chemically-zoned crystals. Experimental, theoretical, and petrological studies have shown that epidote composition is a complex function of temperature, pressure, oxygen fugacity, mineral assemblage, bulk rock composition, and fluid chemistry.*

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$a_{\text{Fe}^{3+}}/a_{\text{Al}^{3+}}$  in turn depends on pH, oxygen fugacity, total Al and Fe concentration, and the concentrations of complexing ligands.

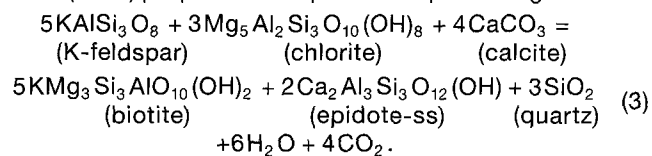
In the following discussion, we will examine the various effects of temperature, pressure, and fluid composition on the composition of natural and synthetic epidote solid solutions. Using equilibrium thermodynamic relations, we derive quantitative expressions relating changes in epidote-ss composition to changes in these variables.

### 3.1. Temperature

Experimental observations of coexisting prehnite, epidote, and grandite garnet solid solutions with hematite and excess quartz at a fluid pressure of 2 kbars and buffered oxygen fugacity (hematite-magnetite) demonstrated that epidote-ss composition becomes more aluminous with increasing temperature, in the temperature range 325°C to 405°C (LIU et al., 1983). Synthetic epidotes produced from basaltic glass at 7 kb and fixed oxygen fugacity (Ni-NiO) also became more aluminous with increasing temperature, from  $X_{\text{Cz}} = 0.28$  at 400°C to  $X_{\text{Cz}} = 0.49$  at 650°C (APTED & LIU, 1983).

Observations from geothermal systems and regional metamorphic rocks suggest that, in general, epidote-ss composition is a complex function of temperature and mineral assemblage. The mineral assemblage epidote-ss + albite + K-feldspar + K-mica + quartz is common in several active geothermal systems in rhyolitic and intermediate volcanic rocks including Wairakei, New Zealand (STEINER, 1977), Otake, Japan (HAYASHI & YAMASAKI, 1976), Pauzhetka, USSR (NOBOKO, 1970, 1976), and Miravalles, Costa Rica (ROCHELLE et al., 1989) BIRD & HELGESON (1981) calculated epidote-ss composition as a function of fluid composition and temperature for this mineral assemblage. Their calculations are in agreement with measured temperatures and fluid compositions, and they determined that epidote-ss would become more aluminous with increasing depth and temperature. They also predicted that epidote-ss coexisting with K-feldspar, K-mica, calcite, and quartz would become more aluminous with increasing temperature at constant carbon dioxide fugacity. Both predictions are consistent with observations from the Salton Sea geothermal system, where matrix epidotes coexisting with these minerals become more aluminous with increasing depth and temperature (BIRD et al., 1988).

Based on prograde phase relations observed in the State 2-14 Well of the Salton Sea geothermal system, CHO et al. (1988) proposed the epidote-ss-producing reaction



Assuming that the activities of all minerals except epidote-ss are unity, the logarithm of the law of mass action for reaction (3) is written as,

$$\ln K_3 = 2\ln a_{\text{Cz}} + 4\ln f_{\text{CO}_2} + 6\ln a_{\text{H}_2\text{O}}, \quad (4)$$

where  $K_3$  is the equilibrium constant for reaction (3),  $a_{\text{H}_2\text{O}}$  is the activity of water, and  $f_{\text{CO}_2}$  is the fugacity of carbon dioxide. Substitution of  $X_{\text{Cz}}$  for  $a_{\text{Cz}}$  in equation (4) and differentiation with respect to temperature at constant total pressure and fluid composition yields

$$\left( \frac{\partial X_{\text{Cz}}}{\partial T} \right)_{P, f_{\text{CO}_2}, a_{\text{H}_2\text{O}}} = \frac{X_{\text{Cz}}}{2} \cdot \frac{\Delta H_3^\circ}{RT^2}, \quad (5)$$

where  $\Delta H_3^\circ$  is the standard enthalpy of reaction (3),  $R$  is the universal gas constant, and  $T$  is temperature in Kelvins. At constant pressure and fluid composition, the temperature derivative of  $X_{\text{Cz}}$  is directly proportional to epidote-ss composition and the enthalpy of reaction (3) and inversely proportional to  $T^2$ . In Figure 1,  $\Delta H_3^\circ$  is plotted as a function of temperature over a range of pressures. At all pressures,  $\Delta H_3^\circ$  is positive, and therefore, from equation (5)  $X_{\text{Cz}}$  will increase with increasing temperature at constant pressure and fluid composition. For example, at 300°C, 86 bars, and  $X_{\text{Cz}} = 0.15$ ,  $X_{\text{Cz}}$  will increase by 0.01 deg<sup>-1</sup>. Due to the properties of water near its critical point,  $\Delta H_3^\circ$  approaches infinity and epidote-ss composition is extremely sensitive to temperature changes near the critical point (Figure 1).

Equation (5) can be applied even when the activities of K-feldspar, chlorite, calcite, and biotite in reaction (3) are not unity, so long as their compositions are relatively constant compared to that of epidote-ss over a range of temperature.

In the State 2-14 well, changes in the compositions of these minerals are small over the temperature range 250 to 350°C (CHO et al., 1988). If these observations are taken into account in equations (4) and (5), the result remains the same:  $X_{\text{Cz}}$  increases with increasing temperature.

In epidote-bearing veins of the Salton Sea geothermal system, the assemblage epidote-ss + calcite + quartz + hematite is common (CARUSO et al., 1988). Equilibrium among these minerals and a fluid can be represented by the reaction

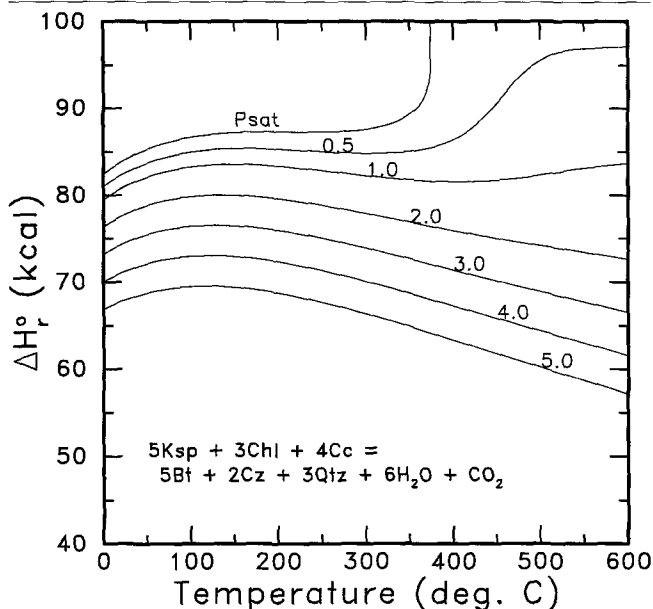
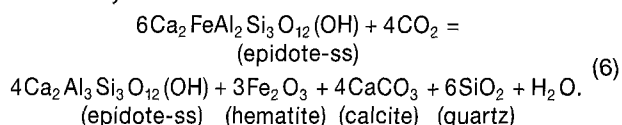


Fig. 1. Standard molal enthalpy of reaction (3) as calculated by the program SUPCRT.

$P_{\text{sat}}$  represents the liquid-vapor equilibrium pressure for pure water. Pressure contours in kilobars. Thermodynamic data for minerals are from HELGESON et al. (1978). Data for aqueous species and gases are from HELGESON & KIRKHAM (1974a,b; 1976) and HELGESON et al. (1981). Ksp = K-feldspar; Chl = chlorite; Cc = calcite; Bt = biotite; Cz = clinozoisite component of epidote-ss; Qtz = quartz.

Assuming unit activity for all minerals except epidote-ss the logarithm of the law of mass action for reaction (6) is

$$\ln K_6 = 4 \ln a_{cz} - 6 \ln a_{ep} + \ln a_{H_2O} - 4 \ln f_{CO_2}. \quad (7)$$

Substitution of  $X_{cz}$  for  $a_{cz}$  and  $1-X_{cz}$  for  $a_{ep}$  in equation (7) and differentiation with respect to temperature at constant pressure and fluid composition yields

$$\left( \frac{\partial X_{cz}}{\partial T} \right)_{P, f_{CO_2}, a_{H_2O}} = \frac{X_{cz}(1-X_{cz})}{(2X_{cz}+4)} \cdot \frac{\Delta H_6^\circ}{RT^2}, \quad (8)$$

where  $\Delta H_6^\circ$  is the standard enthalpy of reaction (6). In Figure 2 the standard enthalpy of reaction (6) is plotted as a function of temperature at constant pressure.  $\Delta H_6^\circ$  is negative for temperatures between 0 and 600°C and pressures between 1 and 5000 bars. The factor preceding  $\Delta H_6^\circ/RT^2$  in equation (8) is positive for all values of  $X_{cz}$ . Hence, at constant  $f_{CO_2}$  and  $a_{H_2O}$ ,  $X_{cz}$  will decrease with increasing temperature in the assemblage epidote + calcite + quartz + hematite. At 300°C, 86 bars, and  $X_{cz}=0.5$ ,  $X_{cz}$  decreases by 0.004 deg<sup>-1</sup>.

In many low-grade regional metamorphic rocks the average Fe-content of epidote-ss decreases with increasing metamorphic grade (MIYASHIRO & SEKI, 1958; HOLDAWAY, 1965; RAITH, 1976; LAIRD, 1980; SMITH et al., 1982; FRANK, 1983; ERNST, 1983; MARUYAMA et al., 1983). Assuming that these epidotes grew during prograde metamorphism, their zoning is consistent with a decline in  $X_{ep}$  with increasing metamorphic grade. In addition, MIYASHIRO & SEKI (1958) observed an increase in compositional variation with increasing metamorphic grade. In some instances, however, there appears to be no correlation between average epidote composition and metamorphic grade (LAIRD & ALBEE, 1981a,b; COOPER, 1972). In a contact metamorphic environment, SEKI (1961) noted that the Fe-content of epidote in calcareous hornfels decreased with increasing temperature in the metamorphic aureole of a granodiorite pluton.

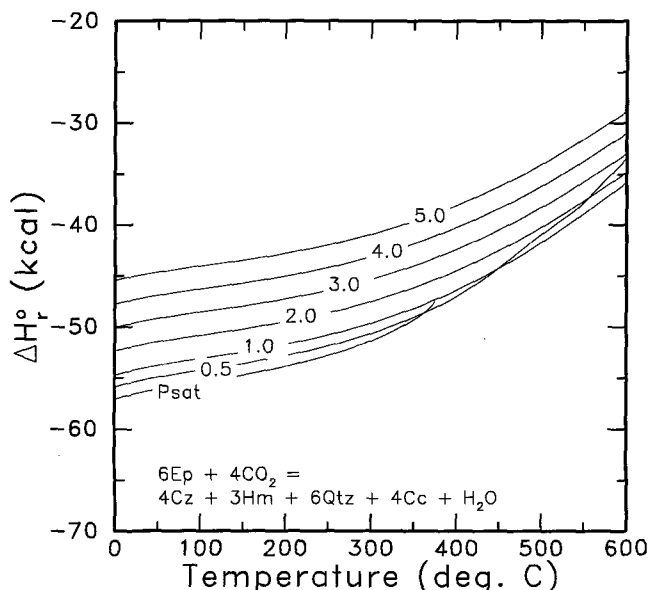


Fig. 2. Standard molar enthalpy of reaction (6) as calculated by the program SUPCRT.  $P_{sat}$  represents the liquid-vapor equilibrium pressure for pure water. Pressure contours in kilobars. See Fig. 1 for the thermodynamic data sources. Ep = epidote component of epidote-ss; Cz = clinozoisite component of epidote-ss; Hm = hematite; Qtz = quartz; Cc = calcite.

In higher grade metamorphic rocks where epidote coexists with plagioclase, epidote often becomes more Fe-rich with increasing metamorphic grade. Theoretical phase relations calculated by BIRD & HELGESON (1981) among epidote and plagioclase solid solutions and an aqueous solution at 500°C and 5 kb predict that epidote in equilibrium with pure anorthite, hematite, quartz, and an aqueous fluid becomes more Fe-rich with increasing temperature. However, for epidote in equilibrium with plagioclase solid solution, Fe-content decreases with increasing activity of the anorthite component in plagioclase ( $a_{CaAl_2Si_2O_8}$ ). In many regional metamorphic rocks,  $a_{CaAl_2Si_2O_8}$  in plagioclase increases with increasing metamorphic grade (e.g., TURNER, 1981). Thus, rising temperature and increasing  $a_{CaAl_2Si_2O_8}$  would have competing effects on the composition of coexisting epidote solid solution. Field and petrographic observations, however, indicate that in metamorphic rocks of amphibolite facies or higher, the Fe-content of epidote coexisting with plagioclase typically increases with increasing metamorphic grade (e.g. RAMBALDI, 1973; TURNER, 1981). Although correlations between epidote composition and metamorphic grade imply that temperature may control epidote composition in these rocks, other intensive thermodynamic variables such as oxygen fugacity and the activity of water change with metamorphic grade. Therefore, it is difficult to isolate the effect of one variable such as temperature on epidote composition in multivariant natural assemblages.

### 3.2. Pressure

Because most univariant reactions involving epidote are hydration-dehydration reactions with large positive Clapeyron slopes, total pressure should have a small effect on epidote composition and stability. Experimental investigations have shown, however, that high pressures (>3 kb) favor nucleation and growth of epidote in the laboratory (LIU, 1973). The standard molar volume of clinozoisite is 136 cm<sup>3</sup>/mole as compared to 139 cm<sup>3</sup>/mole for epidote ((Ca<sub>2</sub>FeAl<sub>2</sub>Si<sub>3</sub>O<sub>12</sub>(OH))), and the volume of intermediate compositions does not appear to depart notably from a linear trend between the two end members (BIRD & HELGESON, 1980). The effect of pressure on reaction (1) is dependent on the volume of reaction by the relationship

$$\left( \frac{\partial \ln K_1}{\partial P} \right)_T = \frac{-\Delta V_1^\circ}{RT}, \quad (9)$$

where  $\Delta V_1^\circ$  is the standard molar volume of reaction (1). In Figure 3,  $\Delta V_1^\circ$  is plotted as a function of temperature and pressure at pressures between 500 and 5000 bars and temperatures between 50 and 600°C. Outside the P and T region of the critical point of water,  $\Delta V_1^\circ$  has a small absolute value, which indicates that pressure would have little effect on the compositions of epidote solid solutions. Near the critical point of water, however,  $\Delta V_1^\circ$  becomes large and negative due to the effects of the changing properties of the solvent on the partial molal properties of Al<sup>3+</sup> and Fe<sup>3+</sup>. Thus, small variations in pressure may be important in determining epidote composition near the critical point of water.

### 3.3. Bulk Rock Composition

Experimental studies have shown that Fe<sup>3+</sup>-Al<sup>3+</sup> substitution in epidote-ss is dependent on the bulk composi-

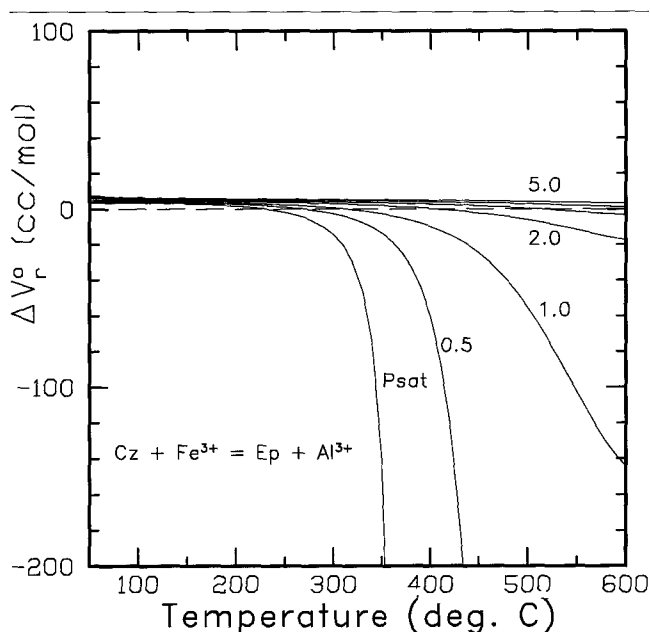


Fig. 3. Standard molal volume of reaction (1) as calculated by the program SUPCRT. Dashed line represents  $\Delta V_r^0 = 0$ .  $P_{sat}$  represents the liquid-vapor equilibrium pressure for pure water. Pressure contours in kilobars. See Fig. 1 for the thermodynamic data sources and mineral abbreviations.

tion of the starting material used. Epidotes experimentally synthesized by LIU (1973) from starting material with a high  $Fe_2O_3/Al_2O_3$  ratio are significantly higher in  $Fe_2O_3$  than epidotes synthesized by HOLDAWAY (1972) from material with a lower initial ratio. This dependence on bulk composition is also supported by petrologic investigations that have demonstrated that the compositions of natural epidotes can be correlated with the bulk composition and mineralogy of the protolith. Summarizing data from active and ancient geothermal systems, SHIKAZONO (1984) determined that there is a positive correlation between the  $Fe_2O_3$  content of the original rocks and that of epidote-ss. This correlation is also observed in regional metamorphic rocks. For example, MIYASHIRO & SEKI (1958) report a similar relationship from the Kanto Mountains of Japan where epidotes of pelitic and psammitic schists contain less  $Fe_2O_3$  than those of adjacent metabasalts. Bulk composition also correlates with zoning patterns in epidotes. In a study of epidote zoning patterns in active and fossil hydrothermal systems, ARNASON & BIRD (1992) found a correlation between host rock type and epidote-ss zoning patterns. In basalt-hosted systems epidotes become depleted in Fe toward their rims, whereas in calcareous sediment-hosted systems they become enriched in Fe towards their rims.

### 3.4. Fluid Composition

In the preceding discussion, we have seen that the composition of epidote-ss in equilibrium with an aqueous fluid depends on temperature, pressure, and bulk rock composition. As reaction (1) indicates, epidote-ss composition also depends directly on the ratio of the activities of  $Fe^{3+}$  and  $Al^{3+}$  in the fluid. Aqueous complexation of  $Fe^{3+}$  and  $Al^{3+}$  with  $OH^-$ ,  $Cl^-$ ,  $HS^-$ ,  $SO_4^{2-}$ ,  $CO_3^{2-}$ , and other anions may cause epidote-ss composition to depend on pH, chloride concentration, sulfur fugacity ( $fS_2$ ), and car-

bon dioxide fugacity ( $fCO_2$ ) in the fluid phase. Changes in fluid composition during the formation of epidote-ss may result in variations in  $Fe^{3+}$  and  $Al^{3+}$  substitution that do not reflect changes in temperature or pressure.

Isothermal growth of epidote-ss and other secondary minerals probably occurs in many hydrothermal systems. In the Salton Sea geothermal system, primary fluid inclusions in calcite which have the same homogenization temperatures often have significantly different salinities (ROEDDER & HOWARD, 1988). These data indicate that fluid composition changed during isothermal growth of the calcite crystals. The micron scale of zoning in epidote from many hydrothermal systems suggests a similar process: compositional zoning may be a result of small variations in the composition of the fluid at constant temperature and pressure.

#### 3.4.1. Oxygen Fugacity

Several experimental studies have shown that the Fe content of epidote-ss is a direct function of oxygen fugacity ( $fO_2$ ). In epidotes synthesized from oxide mixtures the maximum  $Fe^{3+}$  content is found to depend on  $fO_2$ , with the higher  $X_{ep}$  occurring at hematite-magnetite and Cu-CuO buffers and the lower  $X_{ep}$  occurring at the Ni-NiO and quartz-fayalite-magnetite buffers (HOLDAWAY, 1972; LIU, 1973). Using a conventional cold-seal hydrothermal apparatus and solid oxygen buffer techniques, APTED & LIU (1983) determined that at 7 kb the maximum temperature of epidote stability increases with increasing  $fO_2$ . At  $fO_2$  buffered by quartz-fayalite-magnetite, epidote breaks down at  $652^\circ C$ , whereas at  $fO_2$  buffered by hematite-magnetite epidote breaks down above  $700^\circ C$ . In addition, at  $525^\circ C$ , the composition of epidote formed varied with  $fO_2$  from  $X_{ep} = 0.81$  (hematite-magnetite) to  $X_{ep} = 0.54$  (quartz-fayalite-magnetite).

Theoretical phase relations between epidote solid solutions and an aqueous solution in the system  $CaO - FeO - Fe_2O_3 - Al_2O_3 - SiO_2 - HCl - H_2O$  as a function of  $fO_2$  were calculated by BIRD & HELGESON (1981). These calculations predict that epidote-ss composition is most sensitive to changes in  $fO_2$  in the quartz-fayalite stability field, is less sensitive at higher  $fO_2$  where magnetite is stable, and is insensitive to  $fO_2$  when epidote and aqueous solution are in equilibrium with hematite. Also, Fe-rich epidotes ( $X_{ep} \sim 1$ ) are stable primarily with fluids in equilibrium with hematite or magnetite.

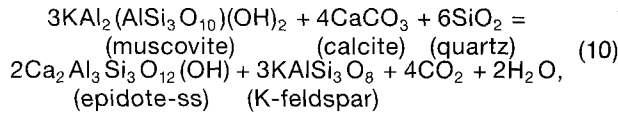
These experimental and theoretical phase relations are in agreement with many field observations. In the Salton Sea geothermal system, Fe-rich epidote commonly occurs with hematite, consistent with the relatively high oxygen fugacity ( $\sim$  hematite-magnetite) calculated for that geothermal system by BIRD et al. (1984). The occurrence of Fe-poor epidote, the abundance of organic matter, and the absence of hematite in the Cerro Prieto geothermal system are observations consistent with the low oxygen fugacity ( $<$  quartz-fayalite-magnetite) calculated for that system (SCHIFFMAN et al., 1985). RAITH (1976) shows a clear correlation between the average Fe-content of epidote and the inferred oxidation state of schists from the Tauern Window, Austria. As expected, oxidized assemblages contain the most Fe-rich epidotes, whereas reduced assemblages contain the most Fe-poor epidotes.

#### 3.4.2. Carbon Dioxide Fugacity

Theoretical calculation suggest that epidote solid solutions of intermediate composition are stable over a wide

range of CO<sub>2</sub> concentrations in the fluid in the presence of calcite and quartz, whereas Fe-poor epidote and Fe-rich epidote are only stable in H<sub>2</sub>O-rich fluids (BIRD & HELGESON, 1981). These calculation also suggest that epidote-ss composition is highly sensitive to small changes in carbon dioxide fugacity ( $fCO_2$ ) in H<sub>2</sub>O-rich fluids. BIRD & HELGESON (1981) propose that this extreme dependency may account for complex compositional zoning observed in epidote in many geologic systems.

Although epidote-ss composition is sensitive to the amount of carbon dioxide in the fluid, the effect of changing  $fCO_2$  on epidote-ss composition depends on the mineral assemblage and the stoichiometry of the epidote-forming reaction. The mineral assemblage epidote + K-feldspar + K-mica + calcite + quartz is common in the Salton Sea geothermal system where modal abundances of calcite and K-mica decrease with depth and temperature while abundances of epidote and K-feldspar increase with depth (MCDOWELL & MCCURRY, 1977). BIRD & HELGESON (1981) demonstrated that at constant temperature and pressure, epidote in this mineral assemblage will increase in Fe content with increasing carbon dioxide fugacity ( $fCO_2$ ). Equilibrium between these minerals can be represented by the reaction



for which the logarithm of the law of mass action can be written

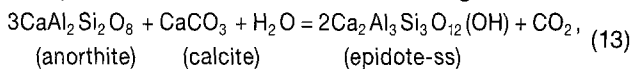
$$\ln K_{10} = 2\ln a_{cz} + 4\ln fCO_2 + 2\ln a_{H_2O} \quad (11)$$

assuming that all minerals but epidote-ss are pure. For water-rich solutions ( $a_{H_2O} > 0.90$ ), it is convenient to use the gas standard state for CO<sub>2</sub>, i.e. unit fugacity of the pure gas at 1 bar and any temperature. Thus, the activity of CO<sub>2</sub> is equal to its fugacity ( $a_{CO_2} = fCO_2$ ) at any pressure and temperature. At constant temperature, pressure, and activity of water, differentiation of equation (11) with respect to  $fCO_2$  yields

$$\left( \frac{\partial X_{cz}}{\partial fCO_2} \right)_{P,T,a_{H_2O}} = -2 \frac{X_{cz}}{fCO_2}, \quad (12)$$

Because  $X_{cz}$  and  $fCO_2$  will always have values  $\geq 0$ , it is apparent that the right hand side of equation (12) will always be  $\geq 0$ , and  $X_{cz}$  will decrease with increasing  $fCO_2$ . Note that epidote-ss solution will be highly sensitive to changes in  $fCO_2$  when  $fCO_2$  is small, i.e. water-rich solutions.

CHO et al. (1988) demonstrated a similar relationship between  $fCO_2$  and epidote-ss compositions for the assemblage epidote + plagioclase + calcite + quartz. The equilibrium reaction for this assemblage is



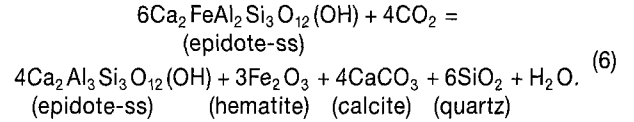
for which the dependence of epidote composition on  $fCO_2$  at constant pressure, temperature, and activities of water and anorthite component ( $a_{An}$ ) in plagioclase is given by

$$\left( \frac{\partial X_{cz}}{\partial fCO_2} \right)_{P,T,a_{An},fH_2O} = -\frac{1}{2} \cdot \frac{X_{cz}}{fCO_2}, \quad (14)$$

In both reactions (10) and (13)  $X_{cz}$  decreases with increasing  $fCO_2$ , but the sensitivity of  $X_{ep}$  to  $fCO_2$  depends on the stoichiometry of the reactions. For a given  $X_{cz}$  the Fe-content of epidote-ss in reaction (10) will change by a

factor of four over that in reaction (13) for each unit change in  $fCO_2$ .

For the vein mineral assemblage epidote + hematite + calcite + quartz, found in the Salton Sea, CARUSO et al. (1988) calculate that an increase in  $fCO_2$  at constant temperature and pressure, or an increase in temperature at constant  $fCO_2$  and pressure will result in an increase in Al-content of epidote, according to reaction (6):



For this reaction, the dependence of epidote-ss composition on  $fCO_2$  at constant temperature, pressure, and  $a_{H_2O}$  is given by

$$\left( \frac{\partial X_{cz}}{\partial fCO_2} \right)_{P,T,a_{H_2O}} = \frac{2}{fCO_2} \cdot \frac{X_{cz}(1-X_{cz})}{X_{cz}+2}, \quad (15)$$

The right hand side of the equality in (15) is positive or zero for all values of  $X_{cz}$ . Thus, for the mineral assemblage epidote-ss + hematite + calcite + quartz,  $X_{cz}$  decreases with increasing  $C_{CO_2O}$ , whereas for the assemblages epidote-ss + plagioclase + calcite + quartz and epidote + K-feldspar + K-mica + calcite + quartz, the opposite relation applies.

### 3.4.3. Aqueous Complexing

From equation (2) we see that at constant temperature and pressure, the composition of epidote solid solution is a function of the activities of Fe<sup>3+</sup> and Al<sup>3+</sup> in the aqueous solution. Except in very acid solutions, the concentrations of these ions are exceedingly small, and the majority of Fe and Al in solution occurs as aqueous complexes. Using the notation of HELGESON (1969), a generalized reaction representing equilibrium between a cation and an aqueous complex of that cation can be written as



where  $\varepsilon$  is the cation, L is the complexing anion, and  $\varepsilon L_y$  is the y<sup>th</sup> aqueous complex. The relationship between the activity of the cation ( $a_\varepsilon$ ) and its total concentration in solution ( $m_{t,\varepsilon}$ ) is given by

$$a_\varepsilon = m_{t,\varepsilon} \left( \frac{1}{y^* \varepsilon} + \sum_y \frac{a_y}{\beta_y \gamma_y} \right)^{-1}, \quad (17)$$

where  $y^*$  is the true individual ion activity coefficient of the cation,  $a_L$  is the activity of the anion,  $\beta_y$  is the overall dissociation constant of the y<sup>th</sup> complex, and  $\gamma_y$  is the activity coefficient of the y<sup>th</sup> complex (HELGESON, 1969). The activity of the cation is directly proportional to the total concentration of the element and inversely proportional to the activities of the complexes. The logarithm of the law of mass action for reaction (16) is

$$\ln \beta = \ln a_\varepsilon + y \ln a_L - \ln a_y. \quad (18)$$

Differentiation of equation (18) at constant temperature and pressure with respect to  $a_L$  gives an expression for the change in concentration of the activity of the cation as a function of the activity of the complexing anion:

$$\left( \frac{\partial \ln a_\varepsilon}{\partial \ln a_L} \right)_{P,T} = -y + \frac{\partial \ln a_y}{\partial \ln a_L}. \quad (19)$$

The rate of change of the activity of the cation with respect to the complexing anion is proportional to the stoi-

chiometry of the aqueous complex ( $y$ ) and to the change in the activity of the complex ( $a_y$ ) with the activity of the complexing ion ( $a_L$ ). The first term in equation (19) is always negative, whereas the second term will usually be positive: the activity of a ligand complex will increase as the activity of the ligand increases. Therefore, it is difficult to predict what the effect of increasing the activity of the ligand will be on the activity of the cation *a priori*.

When considering epidote-ss composition, the cations of interest are  $\text{Fe}^{3+}$  and  $\text{Al}^{3+}$ . The activity of  $\text{Al}^{3+}$  will depend on the total concentration of Al and on the concentrations of the ligands which complex Al, and the activity of  $\text{Fe}^{3+}$  will depend on the total concentration of Fe and the concentrations of the ligands which complex Fe. In most hydrothermal and metamorphic fluids,  $\text{Fe}^{3+}$  and  $\text{Al}^{3+}$  will occur predominantly as aqueous complexes. Both  $\text{Fe}^{3+}$  and  $\text{Al}^{3+}$  have low polarizability ("hard spheres" of PEARSON, 1963) and complex preferentially with the flouride ion and ligands having oxygen as the donor atom. Hence,  $\text{OH}^-$  will complex preferentially over sulfide complexes, and chloro- complexes are weak and occur most readily in acid solutions under which conditions competition with  $\text{OH}^-$  is minimal (STUMM & MORGAN, 1981).

### 3.4.4. Hydrogen Ion Activity

In the State 2–14 well of the Salton Sea geothermal system, epidote-ss occurs with albite, K-feldspar, muscovite, calcite, quartz, and pyrite. For this mineral assemblage, ARNASON et al. (1989) used computer modelling of solution-mineral equilibria to show that epidote-ss composition is more sensitive to hydrogen ion activity ( $a_{\text{H}^+}$ ) than to oxygen fugacity. Their computer experiments demonstrated that local changes in pH ( $= -\log a_{\text{H}^+}$ ) produced by hydrolysis and de-carbonation reactions may result in the complex chemical zoning of epidote-ss that is observed there. The thermodynamic basis for the extreme sensitivity of epidote-ss composition to pH is summarized below.

For cations that form primarily hydroxide complexes, the concentration of the ligand  $\text{OH}^-$  can be related to hydrogen ion activity  $a_{\text{H}^+}$  and to pH. Converting equation (2) to base 10 logarithms and differentiating with respect to pH at constant temperature and pressure yields

$$\left(\frac{\partial X_{\text{ep}}}{\partial \text{pH}}\right)_{P,T} = 2.303 X_{\text{ep}} (1-X_{\text{ep}}) \left(\frac{\partial \log a_{\text{Fe}^{3+}}}{\partial \text{pH}} - \frac{\partial \log a_{\text{Al}^{3+}}}{\partial \text{pH}}\right) \quad (20)$$

In Figure 4, the predominance of various mononuclear hydroxides of  $\text{Fe}^{3+}$  and  $\text{Al}^{3+}$  are depicted graphically as functions of temperature and pH. At  $300^\circ\text{C}$  and  $\text{pH} > 5$ ,  $\text{Fe}(\text{OH})_{3(\text{aq})}$  and  $\text{Al}(\text{OH})_4^-$  are the dominant complexes of  $\text{Fe}^{3+}$  and  $\text{Al}^{3+}$ , respectively. The complete dissociation reaction for  $\text{Fe}(\text{OH})_{3(\text{aq})}$  is



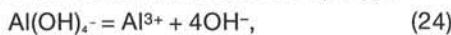
for which the logarithmic law of mass action is

$$\log K_{21} = \log a_{\text{Fe}^{3+}} + 3 \log a_{\text{OH}^-} - \log a_{\text{Fe}(\text{OH})_{3(\text{aq})}}. \quad (22)$$

For  $\text{pH} > 5$ , where  $\text{Fe}(\text{OH})_{3(\text{aq})}$  is the dominant complex of  $\text{Fe}^{3+}$  and  $(\partial a_{\text{Fe}(\text{OH})_{3(\text{aq})}} / \partial \text{pH})_{P,T} = 0$ , differentiation of equation (22) with respect to pH at constant temperature and pressure and rearrangement of terms yields

$$\left(\frac{\partial \log a_{\text{Fe}^{3+}}}{\partial \text{pH}}\right)_{P,T} = -3. \quad (23)$$

For the complete dissociation reaction of  $\text{Al}(\text{OH})_4^-$ ,



a similar expression can be derived,

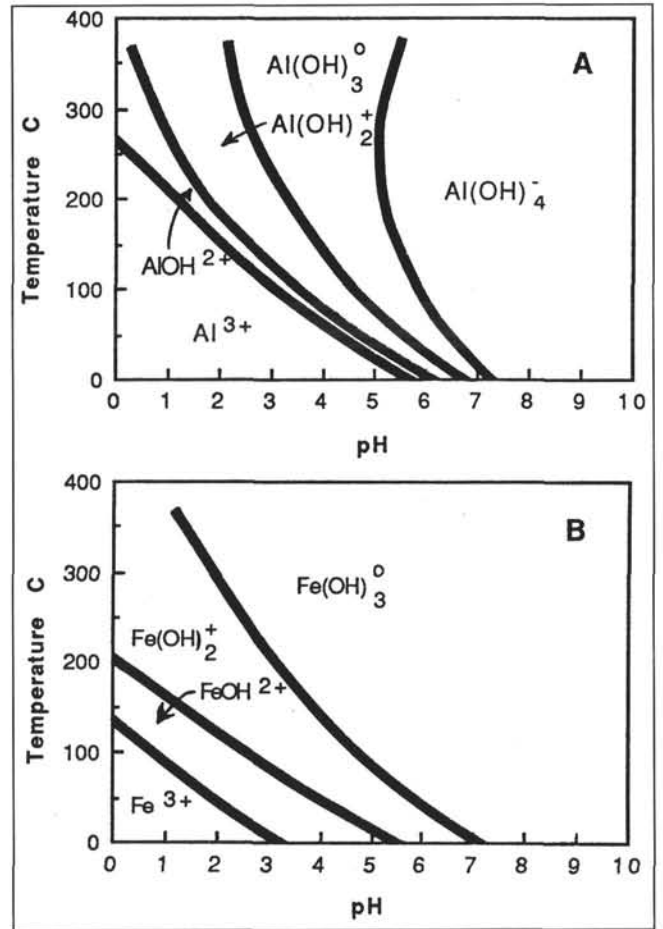


Fig. 4. A) Predominance of mononuclear hydroxides of  $\text{Al}^{3+}$  in the system  $\text{Al}_2\text{O}_3 - \text{H}_2\text{O}$  as a function of pH and temperature at pressure given by liquid-vapor equilibrium for pure water. Solid lines represent equal concentrations of complexes in adjacent fields.  $\text{Al}^{3+}$  species calculated from the equations of ARNORSSON (pers. comm.). B) Predominance of mononuclear hydroxides of  $\text{Fe}^{3+}$  in the system  $\text{Fe}_2\text{O}_3 - \text{H}_2\text{O}$  as a function of pH and temperature at pressure given by liquid-vapor equilibrium for pure water.  $\text{Fe}^{3+}$  species calculated from the equations of ARNORSSON et al. (1982).

$$\left(\frac{\partial \log a_{\text{Al}^{3+}}}{\partial \text{pH}}\right)_{P,T} = -4. \quad (25)$$

that applies when  $\text{Al}(\text{OH})_4^-$  is the dominant  $\text{Al}^{3+}$  species ( $\text{pH} > 5$ ). Equations (23) and (25) are special cases of equation (19). Substitution of equations (23) and (25) into equation (20) yields pH dependence of epidote composition

$$\left(\frac{\partial X_{\text{ep}}}{\partial \text{pH}}\right)_{P,T} = 2.03 X_{\text{ep}} (1-X_{\text{ep}}). \quad (26)$$

From equation (26), we see that  $X_{\text{Fe}}$  of epidote will increase with increasing pH, and decrease with decreasing pH when  $\text{Fe}(\text{OH})_{3(\text{aq})}$  and  $\text{Al}(\text{OH})_4^-$  are the dominant species of ferric iron and aluminum. Notice that in equation (26) epidote composition will be most sensitive to pH when  $X_{\text{ep}} = 0.5$  and insensitive to pH when  $X_{\text{ep}} = 0$  or 1. For example, when  $X_{\text{ep}} = 0.50$ ,  $X_{\text{ep}}$  will increase by  $\sim 0.05$  for each 0.1 increase in pH.

The preceding example illustrates how the composition of epidote solid solution will vary as a function of pH in high temperature aqueous electrolyte solutions of low ionic strength in which  $\text{Fe}^{3+}$  and  $\text{Al}^{3+}$  occur dominantly as hydroxide complexes. It serves to illustrate that epidote-ss composition can be controlled by aqueous speciation

of Fe<sup>3+</sup> and Al<sup>3+</sup>. Natural aqueous solutions have a wide range in ionic strength and other Fe<sup>3+</sup> and Al<sup>3+</sup> complexes such as polynuclear and chloride complexes may be significant. Nevertheless, changes in the  $a_{\text{Fe}^{3+}}/a_{\text{Al}^{3+}}$  ratio of the fluid will depend on relative differences between the complexes.

#### 4. Conclusion

Substitution of Fe<sup>3+</sup> and Al<sup>3+</sup> in epidote solid solutions is a complex function of pressure, temperature, and bulk rock and fluid compositions. Except near the critical point of water, changes in pressure probably have a negligible effect. Temperature is an important variable, because most epidote-forming reactions are of the hydration-dehydration type for which there are large heats of reaction, and thus the equilibrium constant depends strongly on temperature. Bulk rock composition affects the average composition of epidote-ss, and, in some cases, may control compositional zoning patterns in individual crystals. The effects of oxygen fugacity and carbon dioxide fugacity on epidote composition depend on reaction stoichiometry. Solubility experiments demonstrate that aluminum and ferric iron occur predominantly as hydroxide complexes in high temperature aqueous solutions of low ionic strength. If these complexes predominate in hydrothermal solutions, then slight variations in pH may cause large variations in Fe<sup>3+</sup>-Al<sup>3+</sup> substitution in epidote solid solutions. Thus, quantitative evaluation of physical and chemical variables during metamorphism based on epidote-ss composition and zoning patterns may be unreliable, due to the sensitivity of epidote-ss compositions to slight changes in fluid chemistry.

In the present study, we have assumed that epidote solid solution composition depends on differential changes in intensive and extensive thermodynamic variables under equilibrium conditions. While this approach is helpful for understanding the relationships between these quantities, many epidotes probably do not form by equilibrium processes. Many natural epidotes are chemically zoned and are metastable in terms of their compositional and ordering states, indicating that they formed by non-equilibrium, irreversible processes. Our observations of chemically zoned epidote crystals from several different hydrothermal systems, combined with computer modelling experiments, indicate that epidote-ss composition and zoning may be controlled by the relative rates of aluminum and ferric iron mass transfer accompanying the irreversible dissolution of common rock-forming minerals (ARNASON & BIRD, 1992). These results, together with previous studies described above, demonstrate the importance of bulk rock and fluid chemistry on the composition of epidote solid solutions and on the development epidote zoning patterns.

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