

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 Fe³⁺-Al³⁺-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 CO₂-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 Fe³⁺ und Al³⁺ 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 epidotführender 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 Fe³⁺-Al³⁺ 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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Temperature, oxygen fugacity, and carbon dioxide fugacity appear to be the most important intensive variables controlling epidote composition. The functional relationships among changes in these variables and changes in epidote solid solution composition depend on the enthalpies and stoichiometries of reactions. In addition, aqueous complexing of Fe³⁺ and Al³⁺ by OH⁻ causes epidote composition to be a sensitive function of pH in near-neutral aqueous solutions of low ionic strength.

The sensitivity of epidote composition to fluid chemistry and the multivariance of many epidote-bearing mineral assemblages makes chemically zoned epidote crystals unreliable indicators of the evolution of chemical and physical variables during metamorphism.

1. Introduction

Epidote (Ca₂ Fe_x AI_{3-x} Si₃ O_{12} (OH)) is formed in a wide variety of geological environments. It occurs in prograde mineral assemblages of regional metamorphic terranes of the prehnite-actinolite, greenschist, blueschist, and epidote-amphibolite facies. Amphibolite, granulite, and eclogite facies rocks frequently contain epidote most likely as retrograde alteration. In many active geothermal systems, epidote forms as a result of reactions between hot agueous solutions and host rocks of various bulk compositions. The appearance of epidote as an alteration mineral in plutonic rocks, ophiolites, and skarns is evidence for similar hydrothermal activity in the past. Compositional zoning, caused by variable Fe³⁺-Al³⁺ substitution, is a common characteristic of epidote in these systems. This zoning records a complex sequence of irreversible chemical reactions under changing conditions of temperature, pressure, and fluid composition. In some cases epidote zoning has been used to infer the evolution of physical and chemical conditions during regional metamorphism (e.g. RAITH, 1976) and hydrothermal metamorphism (e.g., Ki-TAMURA, 1975; EXLEY, 1982).

The present study focuses on the variables that control epidote composition in low-temperature (200–400°C) and low-pressure (<5 kb) conditions characteristic of geothermal systems in subvolcanic environments and low-pressure greenschist or prehnite-actinolite facies regional metamorphism. The purpose of this communication is to provide a systematic analysis of the major thermodynamic variables that affect Fe³⁺ -Al³⁺ substitution in epidote solid solutions in such environments.

2. Chemical Composition and Site Occupancy

The major compositional variation in natural epidote solid solution involves the exchange of six-coordinated Fe³⁺ and Al³⁺ on octahedral sites. In the monoclinic epidote structure (P21/m), there are 3 octahedral sites: M(1), M(2), and M(3), of which the M(2) site contains only Al³⁺ (e.g. DOLLASE, 1971; GABE et al., 1973). Ferric iron can occupy the M(1) and the M(3) sites, although the larger and more disorted M(3) site is energetically more favorable for Fe³⁺ substitution. Results of Mössbauer spectroscopy indicate that minor amounts of Fe³⁺ are found in the M(1) site of relatively Fe-rich epidotes thought to have formed at temperatures >400°C (DOLLASE, 1973).

Most epidote solid solutions in geologic systems fall within the compositional range between $Ca_2 AI_3 Si_3 O_{12}$ (OH) (clinozoisite) and $Ca_2 FeAI_2 Si_3 O_{12}$ (OH) (epidote) (DEER et al., 1986; KEPESHINSKAS & KHLESTOV, 1971). Consequently, natural epidote solid solution (epidote-ss) is treated here as a binary system, and the terms epidote and clinozoisite are used as thermodynamic components. In this communication, the composition of epidote-ss will be represented either by the mole fraction of the epidote component (X $_{ep})$ or by the mole fraction of the clinozoisite component (X $_{cz}$ = 1 – X $_{ep}).$

In order to relate the composition of epidote-ss to the physical and chemical conditions that are present in geologic systems, it is necessary to have expressions that relate chemical compositions to thermodynamic activities for the components. BIRD & HELGESON (1980) have developed an activity-composition model that combines ideal intrasite mixing of Al3+ and Fe3+ on the M1 and M3 octahedral sites with explicit provisions for the temperature dependence of substitutional order-disorder. It is consistent with Mössbauer spectral data, observed mineral compositions in geologic systems, and experimental phase equilibria. The model suggests that at T <400°C, ideal mixing of Al3+ and Fe3+ on the M(3) site can be used to predict the observed mineral compositions and phase relations in active geothermal systems. Consequently, in the present study epidote-ss is approximated as an ideal solution, and the activities of the epidote and clinozoisite components are equal to their mole fractions (ie., $a_{ep} = X_{ep}$ and $a_{cz} = X_{cz}$).

In the present study, the intercrystalline standard state for minerals is one of unit activity of the pure component in its stable state at any pressure and temperature. The standard state for pure gases is one of unit fugacity at 1 bar and any temperature, and the standard state for ions is unit activity of a 1 molal aqueous solution referenced to infinite dilution at any pressure and temperature.

3. Variables Controlling Epidote Composition

Epidote solid solution composition is a complex function of temperature, pressure, and the bulk compositions of rock and fluid. The relationship between $Fe^{3+}-Al^{3+}$ substitution in epidote solid solution and the equilibrium composition of the fluid can be represented by the heterogeneous exchange reaction among the components epidote (Ca₂ FeAl₂ Si₃ O₁₂ (OH)) and clinozoisite (Ca₂ Al₃ Si₃ O₁₂ (OH)) in epidote-ss and the aqueous species Fe³⁺ and Al³⁺:

$$\begin{array}{c} Ca_2 FeAI_2 Si_3 O_{12} (OH) + AI^{3+} = Ca_2 AI_3 Si_3 O_{12} (OH) + Fe^{3+}. \\ (epidote-ss) & (epidote-ss) \end{array}$$
(1)

In logarithmic form, the law of mass action for reaction (1) is written as

$$\ln K_1 = \ln \frac{a_{cz}}{a_{ep}} + \ln \frac{a_{Fe}^{3+}}{a_{AI}^{3+}}, \qquad (2)$$

where K_1 is the equilibrium constant of reaction (1), a_{cz} and a_{ep} represent the activities of $Ca_2 Al_3 Si_3 O_{12}$ (OH) and $Ca_2 FeAl_2 Si_3 O_{12}$ (OH) in epidote-ss, respectively, and a_{Al}_{3+} and a_{Fe}_{3+} are the activities of the aqueous ions Al^{3+} and Fe^{3+} , respectively. From equation (2), it is apparent that solid solution composition depends on ratio of a_{Al}_{3+} to a_{Fe}_{3+} in the fluid, as well as the temperature and pressure dependence of the equilibrium constant. The ratio $a_{Fe^{3+}}/a_{Ai^{3+}}$ 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 (Liou 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 $X_{cz} = 0.28$ at 400°C to $X_{cz} = 0.49$ at 650°C (APTED & LIOU, 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, Сно et al. (1988) proposed the epidote-ss-producing reaction

$$5 \text{KAISi}_{3} O_8 + 3 \text{Mg}_5 \text{AI}_2 \text{Si}_3 O_{10} (\text{OH})_8 + 4 \text{CaCO}_3 = (\text{K-feldspar}) \quad (\text{chlorite}) \quad (\text{calcite})$$

$$5 \text{KMg}_3 \text{Si}_3 \text{AIO}_{10} (\text{OH})_2 + 2 \text{Ca}_2 \text{AI}_3 \text{Si}_3 O_{12} (\text{OH}) + 3 \text{SiO}_2 \quad (\text{biotite}) \quad (\text{epidote-ss}) \quad (\text{quartz}) \quad (3) + 6 \text{H}_2 \text{O} + 4 \text{CO}_2.$$

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,

$$\ln K_3 = 2\ln a_{cz} + 4\ln f CO_2 + 6\ln a_{H_2O}, \qquad (4)$$

where K_3 is the equilibrium constant for reaction (3), a_{H_2O} is the activity of water, and fCO_2 is the fugacity of carbon dioxide. Substitution of X_{cz} for a_{cz} in equation (4) and differentiation with respect to temperature at constant total pressure and fluid composition yields

$$\left(\frac{\partial X_{cz}}{\partial T}\right)_{P,fCO_{2},a_{H2O}} = \frac{X_{cz}}{2} \cdot \frac{\Delta H_{3}^{2}}{RT^{2}}, \quad (5)$$

where ΔH_3° 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_{cz} is directly proportional to epidote-ss composition and the enthalpy of reaction (3) and inversely proportional to T². In Figure 1, ΔH_3° is plotted as a function of temperature over a range of pressures. At all pressures, ΔH_3° is positive, and therefore, from equation (5) X_{cz} will increase with increasing temperature at constant pressure and fluid composition. For example, at 300°C, 86 bars, and X_{cz} =0.15, X_{cz} will increase by 0.01 deg⁻¹. Due to the properties of water near its critical point, ΔH_3° 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_{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

$$6Ca_2 \operatorname{FeAl}_2 \operatorname{Si}_3 \operatorname{O}_{12} (OH) + 4CO_2 =$$
(epidote-ss)
$$4Ca_2 \operatorname{Al}_3 \operatorname{Si}_3 \operatorname{O}_{12} (OH) + 3\operatorname{Fe}_2 \operatorname{O}_3 + 4CaCO_3 + 6\operatorname{SiO}_2 + \operatorname{H}_2 O.$$
(epidote-ss) (hematite) (calcite) (guartz)



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

 P_{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; ChI = 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

$$\ln K_6 = 4 \ln a_{cz} - 6 \ln a_{ep} + \ln a_{H^2O} - 4 \ln f CO_2.$$
 (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

$$\left(\frac{\partial X_{cz}}{\partial T}\right)_{P,fCO_2,a_{H_2O}} = -\frac{X_{cz}(1-X_{cz})}{(2X_{cz}+4)} \cdot \frac{\Delta H_6^6}{RT^2} , \quad (8)$$

where ΔH_3° 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. ΔH_3° 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 fCO_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⁻¹.

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 & SE-KI (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 molal 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 ($a_{\text{CaAlzSizOs}}$). In many regional metamorphic rocks, a CaAl2Si2O8 in plagioclase increases with increasing metamorphic grade (e.g., TURNER, 1981). Thus, rising temperature and increasing a_{CaAl2Si2O8} 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 (LIOU, 1973). The standard molar volume of clinozoisite is 136 cm³/mole as compared to 139 cm³/mole for epidote ((Ca₂ FeAl₂ Si₃ O₁₂ (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

$$\left(\frac{\partial \ln K_1}{\partial P}\right)_{T} = \frac{-\Delta V_1^2}{RT} , \qquad (9)$$

where ΔV_1° is the standard molar volume of reaction (1). In Figure 3, ΔV_1° 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, ΔV_1° 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, ΔV_1° becomes large and negative due to the effects of the changing properties of the solvent on the partial molal properties of Al³⁺ and Fe³⁺. 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 Fe³⁺-Al³⁺ substitution in epidote-ss is dependent on the bulk composi-



Standard molal volume of reaction (1) as calculated by the program SUPCRT.

Dashed line represents $\Delta V_1^{\circ} = 0$. 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 LIOU (1973) from starting material with a high $Fe_2 O_3 /Al_2 O_3$ ratio are significantly higher in $Fe_2 O_3$ 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 Fe₂O₃ 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 Fe₂O₃ 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 epidotess 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 Fe³⁺ and Al³⁺ in the fluid. Aqueous complexation of Fe³⁺ and Al³⁺ with OH⁻, Cl⁻, HS⁻, SO₄²⁻, CO₃²⁻, and other anions may cause epidote-ss composition to depend on pH, chloride concentration, sulfur fugacity (*f*S₂), 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 Fe³⁺ and Al³⁺ 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 Fe³⁺ 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; LIOU, 1973). Using a conventional cold-seal hydrothermal apparatus and solid oxygen buffer techniques. APTED & LIOU (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°C, whereas at fO_2 buffered by hematitemagnetite epidote breaks down above 700°C. In addition, at 525°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 – Fe₂O₃ – Al₂O₃-SiO₂ – HCl – H₂O 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} ~ 1) are stable primarily with fluids in equilibrium with hematite.

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 (~ 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 CO₂ concentrations in the fluid in the presence of calcite and quartz, whereas Fe-poor epidote and Fe-rich epidote are only stable in H₂O-rich fluids (BIRD & HELGE-SON, 1981). These calculation also suggest that epidote-ss composition is highly sensitive to small changes in carbon dioxide fugacity (fCO₂) in H₂O-rich fluids. BIRD & HEL-GESON (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 epidoteforming 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

$$3KAI_{2}(AISi_{3}O_{10})(OH)_{2} + 4CaCO_{3} + 6SiO_{2} = (muscovite) (calcite) (quartz) (10)$$

$$2Ca_{2}AI_{3}Si_{3}O_{12}(OH) + 3KAISi_{3}O_{8} + 4CO_{2} + 2H_{2}O, (epidote-ss) (K-feldspar)$$

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

$$\ln K_{10} = 2 \ln a_{cz} + 4 \ln f CO_2 + 2 \ln a_{H^2O}$$
(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_2 , ie. unit fugacity of the pure gas at 1 bar and any temperature. Thus, the activity of CO_2 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

$$\left(\frac{\partial X_{cz}}{\partial f CO_2}\right)_{P, T, a_{H2O}} = -2 \frac{X_{cz}}{f CO_2} , \qquad (12)$$

Because X_{cz} and fCO_2 will always have values ≥ 0 , it is apparent that the right hand side of equation (12) will always be ≥ 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, ie. 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

$$\begin{array}{ll} 3\text{CaAl}_2\text{Si}_2\text{O}_8 + \text{CaCO}_3 + \text{H}_2\text{O} = 2\text{Ca}_2\text{Al}_3\text{Si}_3\text{O}_{12}(\text{OH}) + \text{CO}_2, \\ (\text{anorthite}) & (\text{calcite}) & (\text{epidote-ss}) \end{array}$$
(13)

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

$$\left(\frac{\partial X_{cz}}{\partial f CO_2}\right)_{P,T,a_{An},fH_2O} = -\frac{-}{2} \cdot \frac{X_{cz}}{fCO_2} , \qquad (14)$$

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 $\int CO_2$.

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 a increase in Al-content of epidote, according to reaction (6):

$$6Ca_2FeAl_2Si_3O_{12}(OH) + 4CO_2 = (epidote-ss)$$

 $\begin{array}{l} 4\text{Ca}_2\text{Al}_3\text{Si}_3\text{O}_{12}\left(\text{OH}\right) + 3\text{Fe}_2\text{O}_3 + 4\text{Ca}\text{CO}_3 + 6\text{SiO}_2 + \text{H}_2\text{O}. \\ \text{(epidote-ss)} \qquad (\text{hematite}) \quad (\text{calcite}) \quad (\text{quartz}) \end{array}$

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

$$\left(\frac{\partial X_{cz}}{\partial f CO_2}\right)_{P, T, a_{HzO}} = \frac{2}{f CO_2} \cdot \frac{X_{cz} (1 - X_{cz})}{X_{cz} + 2} , \quad (15)$$

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_{COzO} , 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 activites of Fe³⁺ and Al³⁺ 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 aqeous 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

$$\varepsilon L_y = \varepsilon + yL$$
 (16)

where ε is the cation, L is the complexing anion, and εL_y is the yth aqueous complex. The relationship between the activity of the cation (a_{ε}) and its total concentration in solution ($m_{t,\varepsilon}$) is given by

$$\mathbf{a}_{\varepsilon} = \mathbf{m}_{t,\varepsilon} \left(\frac{1}{\mathbf{y}_{\varepsilon}^{*}} + \sum_{\mathbf{y}}^{\mathbf{z}} - \frac{\mathbf{a}_{\mathbf{y}}}{\beta_{\mathbf{y}} \gamma_{\mathbf{y}}} \right)^{-1}, \qquad (17)$$

where y_{\sharp} is the true individual ion activity coefficient of the cation, a_{L} is the activity of the anion, β_{y} is the overall dissociation constant of the yth complex, and γ_{y} is the activity coefficient of the yth 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

$$\ln\beta = \ln a_{s} + \sin a_{l} - \ln a_{v}. \tag{18}$$

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:

$$\begin{pmatrix} \frac{\partial \ln a_{\varepsilon}}{\partial \ln a_{L}} \end{pmatrix}_{P,T} = -y + \frac{\partial \ln a_{y}}{\partial \ln a_{L}} \quad . \tag{19}$$

The rate of change of the activity of the cation with respect to the complexing anion is proportional to the stoichiometry 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 Fe³⁺ and Al³⁺. The activity of Al³⁺ will depend on the total concentration of Al and on the concentrations of the ligands which complex Al, and the activity of Fe³⁺ will depend on the total concentration of Fe and the concentrations of the ligands which complex Fe. In most hydrothermal and metamorphic fluids, Fe³⁺ and Al³⁺ will occur predominantly as aqueous complexes. Both Fe³⁺ and Al³⁺ have low polarizability ("hard spheres" of PEARSON, 1963) and complex preferentially with the flouride ion and ligands having oxygen as the donor atom. Hence, OH- will complex preferentially over sulfide complexes, and chloro- complexes are weak and occur most readily in acid solutions under which conditions competition with 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_{H^+}) than to oxygen fugacity. Their computer experiments demonstrated that local changes in pH (= $-loga_{H^+}$) 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 OH⁻ can be related to hydrogen ion activity a_{H^+} and to pH. Converting equation (2) to base 10 logarithms and differentiating with respect to pH at constant temperature and pressure yields

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

In Figure 4, the predominance of various mononuclear hydroxides of Fe³⁺ and Al³⁺ are depicted graphically as functions of temperature and pH. At 300°C and pH > 5, Fe(OH)_{3(aq)} and Al(OH)₄⁻ are the dominant complexes of Fe³⁺ and Al³⁺, respectively. The complete dissociation reaction for Fe(OH)_{3(aq)} is

$$Fe(OH)_{3(aq)} = Fe^{3+} + 3OH^{-},$$
 (21)

for which the logarithmic law of mass action is

$$ogK_{21} = log a_{Fe^{3+}} + 3log a_{OH^{-}} - log a_{Fe(OH)_{3(aq)}}.$$
 (22)

For pH> 5, where Fe(OH)_{3(aq)} is the dominant complex of Fe³⁺ and $(\partial a_{Fe(OH)_{3(aq)}} / \partial pH)_{P,T} = 0$, differentiation of equation (22) with respect to pH at constant temperature and pressure and rearrangement of terms yields

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

For the complete dissociation reaction of AI(OH)₄,

$$(OH)_{4^{-}} = AI^{3+} + 4OH^{-},$$
 (24)

 $AI(OH)_{a^{-}} = AI^{3+} + 4C$ a similar expression can be derived,



Fig. 4.

- A) Predominance of mononuclear hydroxides of Al³⁺ in the system Al₂O₃ - H₂O 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. Al³⁺ species calculated from the equations of ARNORSSON (pers. comm.).
- B) Predominance of mononuclear hydroxides of Fe³⁺ in the system Fe₂O₃ – H₂O as a function of pH and temperature at pressure given by liquid-vapor equilibrium for pure water. Fe³⁺ species calculated from the equations of ARNORSSON et al. (1982).

$$\frac{\partial \log a_{A^{3+}}}{\partial pH} \bigg|_{P,T} = -4.$$
(25)

that applies when $Al(OH)_4^-$ is the dominant Al^{3+} species (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

$$\frac{\partial X_{ep}}{\partial pH} \bigg|_{P,T} = 2.03 X_{ep} (1 - X_{ep}) .$$
(26)

From equation (26), we see that X_{Fe} of epidote will increase with increasing pH, and decrease with decreasing pH when Fe(OH)_{3(aq)} and Al(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 $X_{ep} = 0.5$ and insensitive to pH when $X_{ep} = 0$ or 1. For example, when $X_{ep} = 0.50$, X_{ep} will increase by ~ 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 electolyte solutions of low ionic strength in which Fe³⁺ and Al³⁺ occur dominantly as hydroxide complexes. It serves to illustrate that epidote-ss composition can be controlled by aqueous speciation of Fe³⁺ and Al³⁺. Natural aqueous solutions have a wide range in ionic strength and other Fe³⁺ and Al³⁺ complexes such as polynuclear and chloride complexes may be significant. Nevertheless, changes in the a_{Fe}^{3+}/a_{Al}^{3+} ratio of the fluid will depend on relative differences between the complexes.

4. Conclusion

Substitution of Fe3+ and AI3+ 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 stongly 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 Fe³⁺-Al³⁺ 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 senstivity of epidote-ss compostions 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 (ARNA-SON & 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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