	125 Jahre Knappenwand – 125 years Knappenwand Proceedings of a Symposium held in Neukirchen am Großvenediger (Salzburg/Austria) September 1990			Editors: Volker Höck Friedrich Koller	
	Abh. Geol. B.-A.	ISSN 0378-0864 ISBN 3-900312-85-0	Band 49	S. 7–16	Wien, Juni 1993

Stabilities of Natural Epidotes

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With 8 Text-Figures and 2 Tables

Epidote
Phase relations
Stability
O₂-fugacity
Occurrence

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Stabilität natürlicher Epidote

Zusammenfassung

Die unterschiedlichen geologischen Vorkommen der Epidotminerale sind mit dem weiten P-T- f_{O_2} -Stabilitätsfeld der Epidotgruppe konsistent. Sowohl Geländebefunde als auch experimentelle Ergebnisse haben gezeigt, daß Epidot in tiefen granitischen und granodioritischen Plutonen auch als magmatische Phase auftritt. In regionalmetamorphen Bereichen und geothermalen Systemen kann Epidot schon bei Temperaturen von 170 bis 200°C auftreten. Er ist auf niedriges X_{CO_2} beschränkt. Die obere Druckstabilität des Epidots ist unbekannt. Epidot sollte aber mit Coesit bei extrem hohen Drucken stabil sein, da Einschlüsse von Coesitpseudomorphosen in Epidot aus Eklogiten in Zentralchina beschrieben wurden. Die Variation in der Zusammensetzung des Epidots mit steigender Metamorphose hängt stark vom Gesteinschemismus und vom Chemismus der fluiden Phase ab. Lediglich in einfach zusammengesetzten Paragenesen variiert die Mineralchemie des Epidots mit den intensiven Variablen und wird durch kontinuierliche Reaktionen kontrolliert. Die Zusammensetzung der Epidote kann dann als P-T-Indikator benutzt werden.

Abstract

The diversity of geologic environments in which the epidote minerals occur is consistent with the large P-T- f_{O_2} stability range for this important mineral group. Both field and experimental evidence have led to acceptance of epidote as a magmatic phase in deep-seated granitic and granodiorite rocks. In regional metamorphic terranes and geothermal systems, epidote together with hematite may occur at temperatures as low as 170–200°C. Epidote is restricted to very low X_{CO_2} environments. The maximum pressure limit of natural epidote is not known; however, epidote is believed to be stable with coesite in ultrahigh-pressure metamorphism as inclusions of coesite pseudomorphs in epidote occur in eclogitic rocks in central China. Compositional variation of epidote with increasing metamorphic grade is highly dependent on rock and fluid chemistry. Only the compositions of epidotes from low-variance assemblages vary systematically with intensive variables and are controlled by continuous reactions, hence can be used as P or T indicators.

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1. Introduction

Epidote occurs in a wide range of geologic environments; it has been recorded as a primary magmatic phase in deep-seated granitic plutons and as an index mineral in low- to medium-grade regional and contact metamorphic rocks. It is also common in skarns, as a hydrothermal alteration product in veins and vugs, and as a deuteric phase in some igneous rocks. Epidote is the most common calc-silicate mineral in active geothermal systems and occurs together with quartz as epidotes in ophiolite sequences. The diversity of geologic environments in which epidote occurs has promoted extensive study of the crystal chemistry and phase relations of this important mineral group (for a review, see DEER et al., 1986). Its parageneses in magmatic, metamorphic and hydrothermal systems and compositional variations are controlled by P, T, and rock and fluid compositions; this paper reviews some of the physico-chemical controls of natural epidotes in geologic environments.

Compositional ranges of natural epidotes are best described by the binary solid solution end-members clinozoisite $\text{Ca}_2\text{Al}_3\text{Si}_3\text{O}_{12}(\text{OH})$ and pistacite $\text{Ca}_2\text{Fe}_3\text{Si}_3\text{O}_{12}(\text{OH})$. Epidote composition is normally expressed in terms of mole fraction of pistacite [$\text{Ps} = 100 \times \text{Fe}^{3+}/(\text{Fe}^{3+}+\text{Al})$]. Natural epidotes range in composition essentially from pure clinozoisite to Ps_{33} (DEER et al., 1986; KEPESHINSKAS & KHLESTOV, 1971). However, extreme Fe-rich epidote with Ps_{53} has been reported (p.57 of DEER et al., 1986; EDWARDS et al., 1956). The existence of miscibility gap within the epidote series was first suggested by STRENS (1965) at between Ps_{12} and Ps_{22} . Subsequently the gap was reported for natural epidotes from greenschist to amphibolite facies metamorphic rocks (HOLDAWAY, 1965; HIETNAN, 1974; RAITH, 1976). However, LIU et al. (1983) plotted available composition of epidotes from rocks of PP, PA, and GS facies and concluded that the epidote solid solution is continuous at least in the range of Ps_{10} to Ps_{33} . Compositions of epidotes from active and fossil geothermal systems

range from Ps_{11} to Ps_{40} and do not show a miscibility gap (BIRD et al., 1984; ROSE & BIRD, 1988). On the other hand, coexistences of orthorhombic zoisite and clinozoisite have been observed in several high-P terranes (ENAMI & BANNO 1980 in the Sanbagawa, FRANZ & SELVERSTONE, 1992 in Tauern Window and YOKOYAMA et al., 1986 in New Caledonia) and experimentally produced (PRUNIER & HEWITT, 1985). Both phases increase in Al_2Fe component with increasing temperature. The compositional difference becomes most apparent with increasing pressure. For low P and T terrane (e.g., $<400^\circ\text{C}$), phase relations of zoisite-clinozoisite are complex and the occurrence of monoclinic miscibility gap may intersect the transformation loop; such configuration is proposed by FRANZ & SELVERSTONE (1992).

The Ps content of epidote from metamorphic terranes and geothermal systems varies, depending on fluid composition, metamorphic grade and oxidation state of the rock. In addition, Mn^{3+} can substitute for Fe^{3+} or Al^{3+} , and trivalent REE elements can substitute for Ca^{2+} , with charge balance achieved by substitution of ferrous for ferric iron. Mn-rich varieties are called piemontite, and REE-rich varieties are called allanite.

2. P-T Stability of Epidote

Examining the general formulae $\text{Ca}_2\text{Al}_{3-x}(\text{Fe}^{3+},\text{Mn})_x\text{Si}_3\text{O}_{12}(\text{OH})$ for natural epidotes, one can conclude that epidote stability depends on X_{CO_2} and f_{O_2} in addition to P_{total} , T, PH_2O and $\text{PH}_2\text{O}/P_{\text{total}}$. The effects of these variables on epidote stability have been extensively investigated from hydrothermal experiments (e.g., HOLDAWAY, 1972; LIU, 1973, natural parageneses of minerals (e.g., SEKI, 1972; MARUYAMA et al., 1983) and thermodynamic calculations (e.g., HELGESON et al., 1978; BIRD & HELGESON, 1981; BIRD et al., 1984). Stabilities, parageneses and compositions

of natural epidotes are highly dependent on fluid and rock compositions. The maximum P-T- f_{O_2} limit of an epidote mineral of its own composition has been well experimentally determined (e.g., HOLDAWAY, 1972; LIU, 1973); this together with the effect of rock bulk composition (e.g., granite vs. basaltic) on epidote stability and composition will be examined in this review.

A revised petrogenetic grid for low-grade metabasites using the internally consistent thermodynamic database of BERMAN (1988) and the GEO-CALC program of PERKINS et al. (1986) and BERMAN et al. (1987) has recently been established (FREY et al., 1991). The calculated stability fields are shown in Figs. 1 and 2 for the system $\text{CaO} - \text{Al}_2\text{O}_3 - \text{SiO}_2 - \text{H}_2\text{O}$

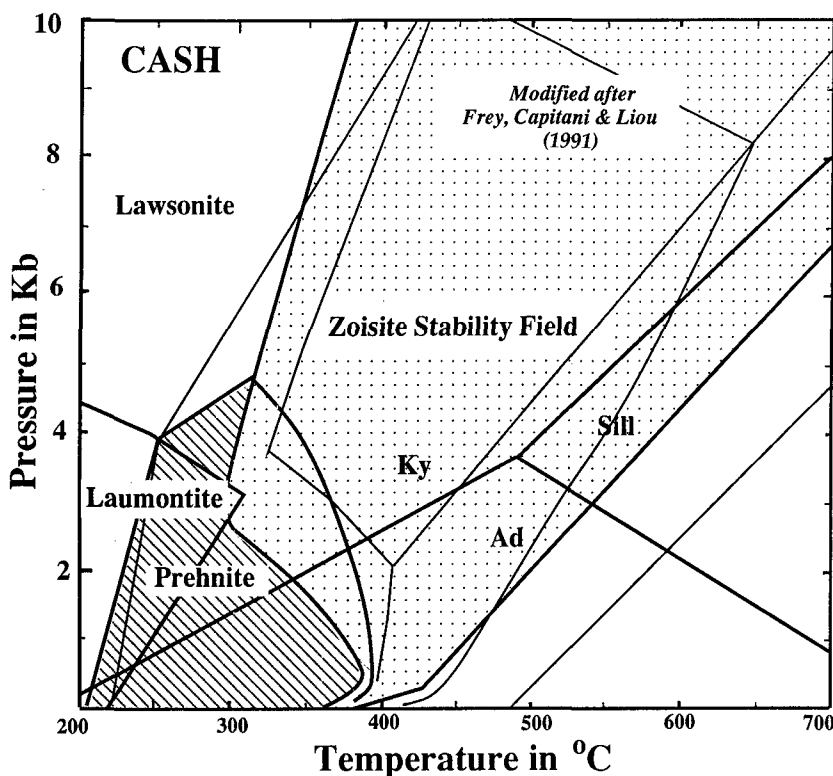
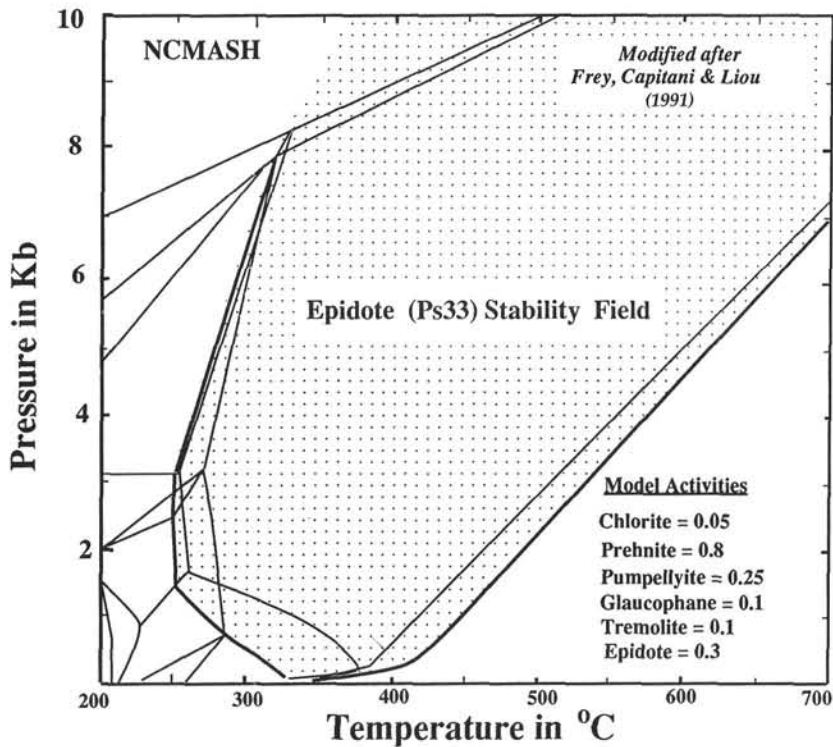


Fig. 1. P-T stability fields of zoisite and other Ca-Al silicates (+ excess H_2O and quartz) in the system $\text{CaO} - \text{Al}_2\text{O}_3 - \text{SiO}_2 - \text{H}_2\text{O}$ (CASH), calculated using the GEO-CALC program of BERMAN et al. (1987) (for details see FREY et al., 1991).



(CASH) and $\text{Na}_2\text{O} - \text{CaO} - \text{MgO} - \text{Al}_2\text{O}_3 - \text{SiO}_2 - \text{H}_2\text{O}$ (NCMASH) (for details see EVANS, 1990; FREY et al., 1991). In the simpler CASH system, P-T positions of all reactions involving zoisite, lawsonite, prehnite, laumontite, anorthite, wollastonite and three Al_2SiO_5 polymorphs are shown Fig. 1. Compared to other Ca-Al silicates, zoisite has wider P-T stability field, ranging in temperature from 300 to 700°C and pressure from one atmosphere to more than 10 kb. At lower temperatures, its P-T field overlaps those of prehnite, laumontite and lawsonite.

In the system NCMASH of Fig. 2, some common Fe-Mg silicates including chlorite, pumpellyite, glaucophane and tremolite occur together with epidote. In order to model phase relations more closely related to natural parageneses, average activity values for clinocllore, prehnite, pumpellyite, glaucophane, actinolite and epidote were derived from published mineral chemical data and used for construction of a petrogenetic grid for metabasites (FREY et al., 1991). The calculated stability of Ps_{33} epidote is shown in Fig. 2. Compared to zoisite, epidote expands its stability field toward lower temperatures from about 300 to 250°C. The P-T stabilities of zoisite and epidote were calculated assuming $P_{\text{H}_2\text{O}} = P_{\text{total}}$, unit activity of H_2O , and fixed activity terms for involving silicates. The metamorphic fluid may contain appreciable amounts of other dissolved species, resulting in reduced H_2O activity. Naturally, if we change the activities of these

Fig. 3. T- XCO_2 stability fields of epidote, zoisite and other phases in the system $\text{CaO} - \text{Al}_2\text{O}_3 - \text{SiO}_2 - \text{FeO}_x - \text{H}_2\text{O} - \text{CO}_2$ at $P_{\text{fluid}} = 2000$ bars (modified after TAYLOR & LIOU, 1978).

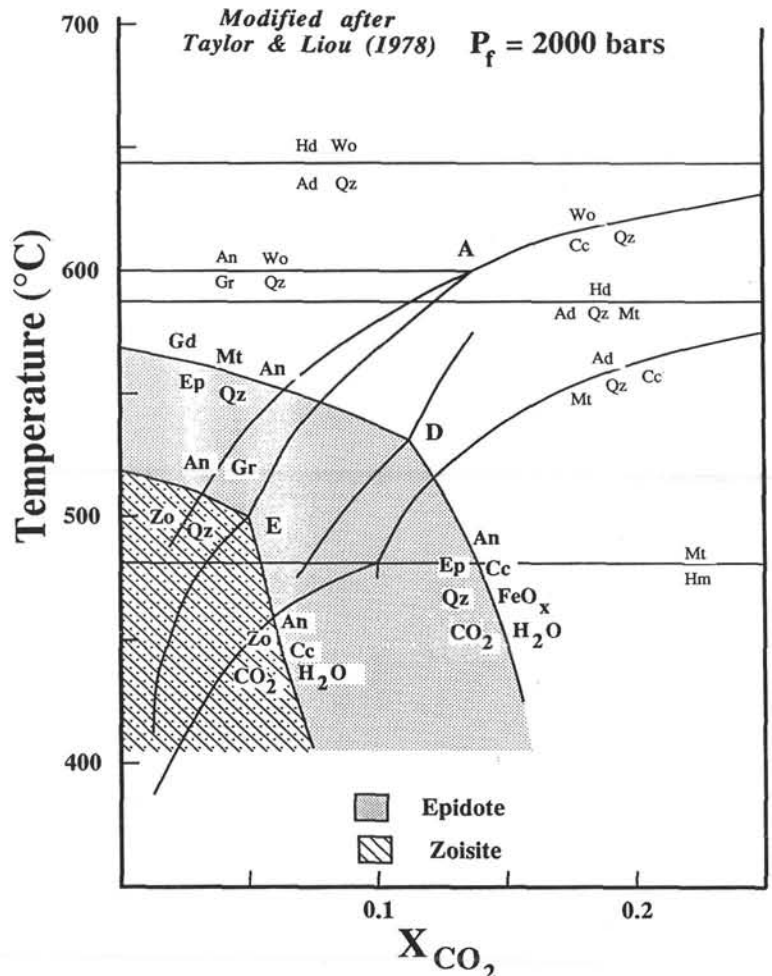
Fig. 2. P-T stability fields of epidote (Ps_{33}) and other Ca-Al silicates in the system $\text{Na}_2\text{O} - \text{CaO} - \text{MgO} - \text{Al}_2\text{O}_3 - \text{SiO}_2 - \text{H}_2\text{O}$ (NCMASH) calculated using the GEO-CALC program of BERMAN et al. (1987) and fixed activity values for other involving phases (for details see FREY et al., 1991).

phases, the stability field for epidote and other phases could be significantly modified. Moreover, in natural processes such as in geothermal systems, H_2O pressure may be considerably less than total pressure; in cases where $P_{\text{fluid}} < P_{\text{total}}$, the equilibria shown in Figs. 1 and 2 will be shifted toward lower temperatures.

Nevertheless, these two diagrams indicate a wide P-T range for crystallization of epidote, consistent with its wide geologic occurrences at magmatic conditions, in eclogites at extreme pressures, in regional metamorphic terranes at moderate pressures and temperatures, and in geothermal fields at low

temperatures. Some of these occurrences are discussed below.

CO_2 Control on the Stability of Epidote



The stability and maximum P_s content of epidote depend strongly on oxygen fugacity (e.g., LIU, 1973). For the fO_2 defined by the HM and more oxidizing buffers, epidotes are saturated with Fe_2O_3 , have compositions approaching Ps_{33} , and are stable at higher temperatures compared to those with Ps_{25} stable along the QFM buffer curve. At $P_{H_2O} = P_{total}$, epidote decomposes according to a typical dehydration reaction; at high P_{H_2O} , epidote is stable at higher temperatures at greater depths. Moreover, in voids or fissures where P_{fluid} is less than P_{total} or the fluid contains another component such as CO_2 , epidote will be stable only at much lower temperatures. In essence, the experimentally determined curve provides the maximum temperature limit under which epidote may crystallize.

The effect of introduction of CO_2 on the stability of epidote and zoisite at constant P_{H_2O} of 2 kb and fO_2 values between the HM and NNO buffer has been evaluated (e.g., TYLOR & LIU, 1978). An example at $P_{fluid} = 2$ kb is shown in Fig. 3 together with the stability fields of andradite, grossular, epidote and zoisite in the presence of quartz. Both zoisite and epidote are restricted to very low X_{CO_2} environments and zoisite has a very limited T- X_{CO_2} stability field.

Zoisite and epidote breakdown at lower temperatures when the fluid contains important amounts of CO_2 , and may not be stable under any geologic condition where X_{CO_2} is greater than 0.2.

3. High-T Stabilities and Magmatic Epidotes in Granitic Systems

The stability (ZEN & HAMMARSTROM, 1977, 1983), who crystallized epidote (together with plagioclase + biotite + melt) at temperatures above the solidus for a synthetic granodiorite with > 4 wt % H_2O at 8 kb. With decreasing temperature, the assemblage changed from plagioclase + hornblende + biotite + melt to plagioclase + epidote + biotite + melt. This paragenesis is consistent with the observed resorption of hornblende in epidote-bearing granitic rocks (ZEN & HAMMARSTROM, 1984).

Epidote was also observed above the solidus in studies of hydrous trondhjemite at 15 kb (JOHNSTON & WYLLIE, 1988). Fig. 4 shows the maximum P-T stabilities of Ps_{33} and Ps_{25} epidotes of LIU (1973), the disappearance of hornblende and biotite, and the solidus for granitic and granodioritic compositions of NANEY (1977). For granodiorite compositions, epidote crystallizes from melt as a primary phase, and in H_2O -saturated systems, the isobaric crystallization sequence is first hornblende, then biotite joined by epidote together with quartz and feldspar. On the basis of these experimental studies, ZEN and HAMMARSTROM (1984) described the significance of magmatic epidotes in deep-seated granitic plutons. In fact, magmatic epidotes are quite common in the northwestern North American Cordillera where minimum depths of 25 km for the emplacement of epidote-bearing granodiorite and tonalite have been documented (ZEN, 1985).

Magmatic epidotes tend to have compositions in the range from Ps_{25} to Ps_{28} and are commonly associated with Al-rich hornblendes (ZEN & HAMMARSTROM, 1984). Textural evidence for the occurrence of magmatic epidotes includes

- grain size similar to other mafic minerals;
- euhedral boundaries with biotite and myrmekitic contacts with plagioclase and quartz;
- inclusions of rounded to embayed hornblende; and
- occurrence of allanite cores in some epidote crystals.

Other evidence includes

- lack of alteration of minerals in epidote-bearing granitic rocks;
- involvement of epidote in flow banding;
- epidote as a "phenocryst" in chilled margins of plutons; and
- pluton emplaced in high-P country rocks (e.g., kyanite).

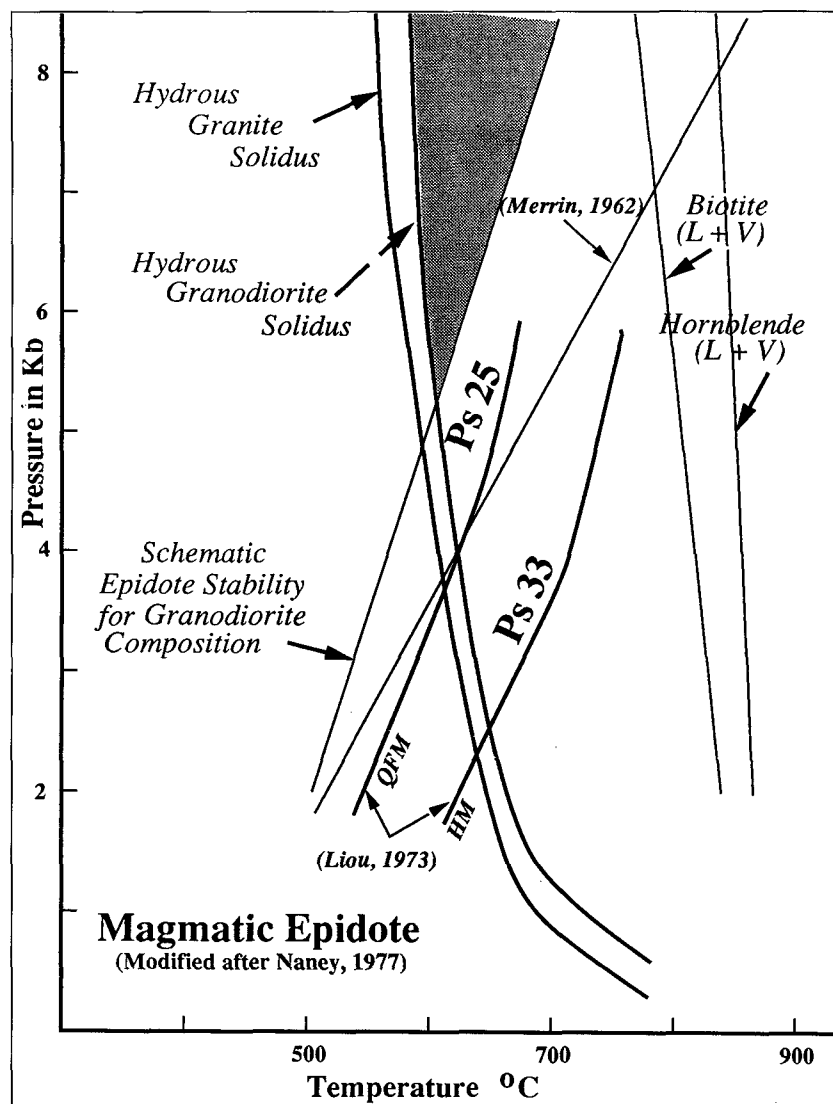


Fig. 4. P-T diagram showing stability of Ps_{33} and Ps_{25} epidotes (MERRIN, 1962; LIU, 1973) and magmatic epidote in granodiorite with excess H_2O (NANEY, 1977). Solidi for granite and granodiorite and disappearance of biotite and hornblende for granodioritic composition (NANEY, 1977) are also shown.

Barometric information from metamorphic assemblages in the wall rocks of two epidote-bearing plutons confirm emplacement at great depths (CRAWFORD et al., 1987; SELVERSTONE et al., 1987). However, the use of magmatic epidote as a barometer has been controversial because some epidote-bearing plutons invade wall rocks of low-metamorphic grade, suggesting emplacement at shallow crustal levels (see discussion in ZEN et al., 1986). For example, MOENCH (in ZEN et al., 1986) describes epidote-bearing plutons in New England with wall rocks indicating burial only to pressures between 2 and 4 kb.

The minimum pressure for crystallization of epidote from granitic melt is defined by the intersection of the P-T stability curve of epidote (LIOU, 1973) and the solidus curve of a granitic magma (e.g., about 6 kb for tonalite at fO_2 of the QFM buffer). At more oxidizing fO_2 the minimum P may be as low as 3 kb; magmatic epidotes may have compositions up to Ps_{33} . Plutonic rocks bearing magmatic epidotes of Ps_{23-28} described by ZEN & HAMMARSTROM (1984) must have crystallized under fairly oxidizing condition and moderately high pressures, corresponding to middle to lower crustal depths.

However, as shown in Fig. 4, this intersection depends on bulk composition, H_2O content and fO_2 . In H_2O -deficient tonalite melt, the solidus shifts toward high temperature and the maximum stability of epidote shifts toward lower temperature, hence, magmatic epidote may appear only at much greater depths. On the other hand, for a granitic melt at more oxidizing conditions, magmatic epidotes are stable at higher temperatures and may crystallize at depths less than 20 km.

Some problems related to the magmatic epidote barometer include:

- 1) Epidote in many plutonic granites is deuteric, not magmatic;

- 2) epidote may have crystallized at greater depths then be carried upward to shallow depths during pluton emplacement;
- 3) metamorphic assemblages in country rocks may not indicate the depths of emplacement;
- 4) magmatic epidote is not really a reliable indicator of high-P crystallization; and
- 5) there is a lack of systematic experiments for the stability of magmatic epidotes as function of bulk rock composition, H_2O content and fO_2 .

4. High-T Stability of Epidote in Metabasites

High-T stabilities of epidote define the transitions within the greenschist and amphibolite facies assemblages for basaltic bulk compositions; they have been investigated both from field and laboratory standpoints (e.g., LIOU et al., 1974, 1985a; SPEAR, 1981; APTED & LIOU, 1983; MARUYAMA et al., 1983). Mineral assemblages such as albite + epidote + chlorite + actinolite + sphene (greenschist facies), albite + epidote + chlorite + hornblende (epidote amphibolite facies), hornblende + plagioclase ± garnet (amphibolite facies), and plagioclase + actinolite + chlorite (Ca-plagioclase-actinolite facies) have been assigned to specific P-T fields. For the transition of epidote amphibolite or greenschist to amphibolite facies assemblages, the epidote-out reaction albite + chlorite + epidote + quartz = oligoclase + tschermakite + Fe_3O_4 + H_2O was experimentally determined at low pressures (e.g., 2 kb) by LIOU et al. (1974), and the reaction epidote + albite + hornblende + quartz = oligoclase + hornblende_{II} + H_2O was investigated at high-P (e.g., 5 kb) by APTED & LIOU (1973). These reactions involve complex compositional and modal variations among several coexisting phases, as well as disappearance and production of new phases. These epidote-out reactions are highly dependent on fO_2 and bulk rock compositions. They shift to higher temperatures with increasing fO_2 .

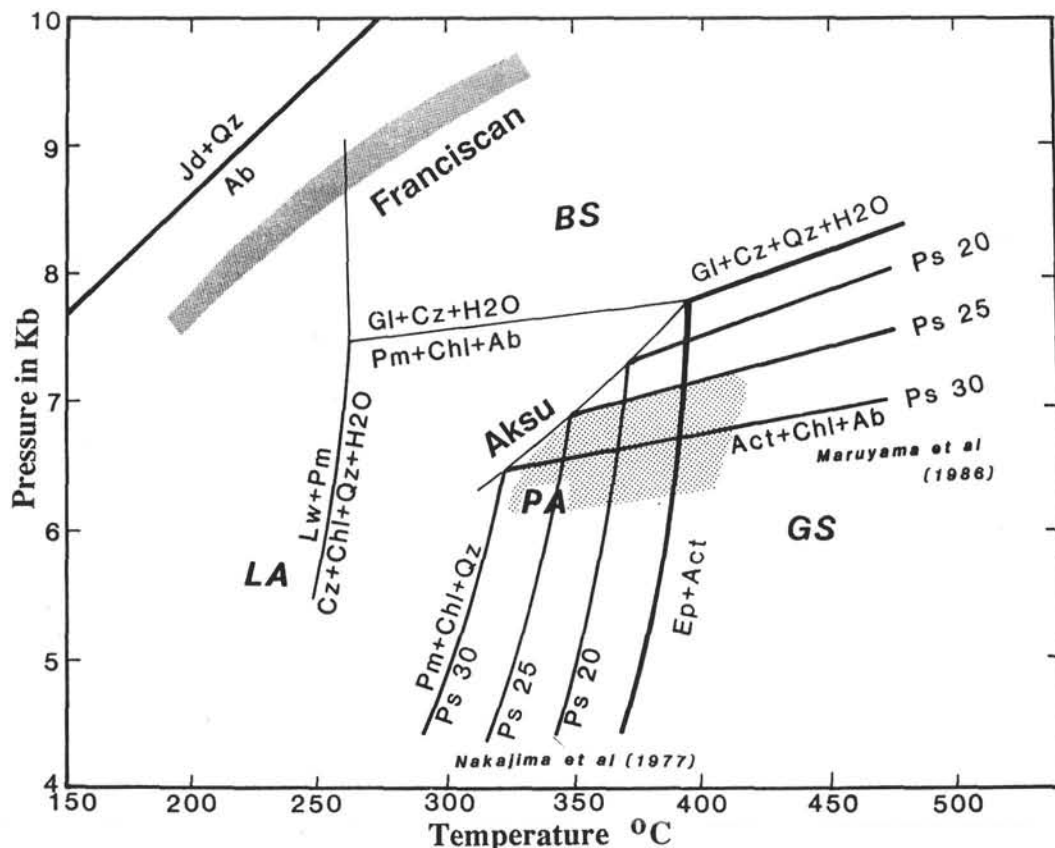


Fig. 5. P-T diagram showing isopleths of epidotes from two buffered assemblages (+ Chl + Qz + Ab + H_2O): (1) sodic amphibole + epidote + actinolite; and (2) pumpellyite + epidote + actinolite. P-T fields of the blueschist (BS), lawsonite albite (LA), pumpellyite-actinolite (PA) and greenschist (GS) facies are also shown.

whereas the chlorite-out reactions of the transition shift to lower temperatures.

In consequence, the effect of increasing fO_2 is to expand the P-T boundaries of the epidote-amphibolite stability field and decreases the maximum pressure for the occurrence of the actinolite-plagioclase assemblage. These experimental data indicate that epidote is a common phase in epidote amphibolite facies rocks; the temperature for its disappearance increases with increasing pressure and increasing fO_2 . They may also explain why epidote is rather uncommon in dredged oceanic gabbros except for epidotes which are metasomatized diabasic rocks that form at temperatures of 325–375°C and pressures of 300–400 bars (SCHIFFMAN et al., 1990).

Compositions of epidotes from metabasites and active geothermal systems indicate that epidote solid solution is continuous at least in the range of Ps_{10} to Ps_{40} and does not show a miscibility gap. The Ps value of epidote depends on metamorphic grade, mineral assemblage, fO_2 , and pH (ARNASON et al., 1989; this issue). Domain equilibrium prevails in very low-grade metamorphism, hence, compositions of epidote in a single thin section may vary according to occurrence such as replacement after plagioclase or mafic minerals, or as fillings in vesicles or fractures. However, the Ps value of epidote from a low-variance assemblage varies systematically either with temperature or pressure but is insensitive to rock chemistry (LIU et al., 1987). For example, the composition of epidote in the buffered assemblage epidote + pumpellyite + actinolite + (Chl + Ab + Qz) systematically changes from Ps_{33} at 260°C to nearly pure clinozoisite at about 370°C and 5 kb (NAKAJIMA et al., 1983) as shown in Fig. 5. Similarly, epidote in another buffered assemblage, epidote + sodic amphibole + actinolite (+ Chl + Qz + Ab) in the transition from the blueschist to greenschist facies decreases in Ps content with increasing pressure (MARUYAMA et al., 1987). Hence, the composition of epidotes in the assemblage epidote + sodic amphibole + actinolite + pumpellyite (+ Ch + Ab + Qz) in metabasaltic rocks must form at unique P-T conditions as shown in Fig. 5.

5. Low-T Stabilities of Natural Epidotes

In regional metamorphic terranes, epidote first appears in the higher grade part of the zeolite facies and is stable together with laumontite. With increasing pressure, epidote occurs in prehnite-pumpellyite and blueschist facies rocks. Some simplified chemical reactions for the first appearance of epidote in low-T metamorphism are listed in Table 1. Similar to the high-T stability limit of epidote discussed in the previous sections, its low-T stability limit

also depends on fluid and bulk rock compositions in addition to P, T, fO_2 , and P_{fluid}/P_{total} . The minimum temperature for its appearance was estimated from its association with laumontite or wairakite in active geothermal systems, with laumontite ± prehnite ± pumpellyite in zeolite-facies metabasites, and with lawsonite ± pumpellyite in blueschists. Table 2 lists temperatures for the first appearance of epidote recorded in several active geothermal systems. Most reported minimum temperatures for occurrence of epidote in active geothermal systems range from 200 to 250°C but temperatures as low as 170–200°C have been recorded in Onikobe (SEKI et al., 1983; LIU et al., 1985b), Tatun, Taiwan (LAN et al., 1983) and Reykjanes, Iceland (MEGHAN et al., 1982). In these geothermal fields, epidote is stable with hematite and has a high Ps content. In other words, epidote appears at lower temperatures in highly oxidized environments.

The transition from the zeolite to prehnite-pumpellyite facies has been investigated (e.g., LIU et al., 1987). The P-T positions of several continuous reactions related to the transition have been determined based on experimental data and the P-T grid predicted in a model basaltic system (LIU et al., 1985a; CHO et al., 1986).

An example is shown in Fig. 6 with schematic isopleths of epidote compositions. The zeolite facies assemblage epidote (Ps_{33}) + laumontite + pumpellyite from Kartmusen, Vancouver Island, occurs at 170 to 190°C and 1.1 ± 0.5 kb (CHO et al., 1986). With increasing temperature, the pistacite content of epidote in this buffered assemblage decreases. A similar compositional trend of epidote for assemblages epidote + prehnite + laumontite, prehnite + pumpellyite + epidote and epidote + prehnite (chlorite + albite + quartz) are shown in Fig. 6. The Ps value of epidote from a low-variance assemblage can be used as geothermometer or geobarometer (for details see LIU et al., 1987).

In fact, the Al-enrichment of epidote with increasing temperature has been recorded in many metamorphic assemblages, reflecting not only the effect of temperature and total pressure but also the concomitant decrease of the oxidation state of the rocks.

Epidote has not been recognized as a neoblastic phase in metagraywackes of the Franciscan Complex but first appears in metabasites at about 290°C and 7 kb (MARUYAMA & LIU, 1988). In blueschist facies metamorphism, lawsonite occurs in low-grade blueschists, whereas epidote is common in high-grade blueschists, epidote amphibolites and, more rarely, eclogites (e.g., see Evans, 1990 for phase relations of mineral assemblages characteristics among the epidote-blueschist and its neighbouring facies). The relationship between epidote (or clinozoisite) and lawsonite has been experimentally determined (e.g., NEWTON & KENNEDY, 1967) and thermodynamically calcu-

Table 1.
Examples of Reactions for the Appearance of Epidote in Low-T Metamorphism

1)	4 CaAl ₂ Si ₄ O ₁₂ ·4H ₂ O	+ Fe ₂ O ₃	=	2 Ca ₂ Al ₂ Fe ³⁺ Si ₃ O ₁₂ (OH)	+ 10 SiO ₂	+ 2 Al ₂ O ₃	+ 15 H ₂ O
	Laumontite	Hematite		Epidote	Quartz		
2)	2 Ca ₂ Al ₂ Si ₃ O ₁₀ (OH)	+ Fe ₂ O ₃	=	Ca ₂ Al ₂ Fe ³⁺ Si ₃ O ₁₂ (OH)	+ H ₂ O		
	Prehnite	Hematite		Epidote			
3)	6 Ca ₄ (Mg,Fe)Al ₄ Fe ³⁺ Si ₆ O ₂₁ (OH) ₇	+ 4 SiO ₂	+ 3 Fe ₂ O ₃	=	12 Ca ₂ Al ₂ Fe ³⁺ Si ₃ O ₁₂ (OH)	+ (Mg,Fe) ₆ Si ₄ O ₁₀ (OH) ₈	+ 11 H ₂ O
	Pumpellyite	Quartz	Hematite		Epidote	Chlorite	
4)	4 CaAl ₂ Si ₂ O ₇ (OH)·2H ₂ O	+ Fe ₂ O ₃	=	2 Ca ₂ Al ₂ Fe ³⁺ Si ₃ O ₁₂ (OH)	+ 2 SiO ₂	+ 2 Al ₂ O ₃	+ 7 H ₂ O
	Lawsonite	Hematite		Epidote	Quartz		

Table 2.
Recorded Temperatures for the First Appearance of Epidote in Geothermal Systems.

Geothermal Field	Temp [°C]	Depth [m]	Associated Phase	Composition [PS value]	Reference
Wairakii, N.Z.	230	400-500	Wr	25-33	BROWNE, 1978
Reykjanes, Iceland	200	500	Pr	22-35	MEHEGAN et al., 1982
Onikobe, Japan	170	165	Lm	19-37	SEKI et al., 1983
Salton Sea, Calif.	<230	906	K-f	36-39	CHO et al., 1987
Tatun, Taiwan	200	500	Wr	33	LAN et al., 1980

Epidote has been reported from virtually every geothermal system at temperatures exceeding 200-250°C.

lated (e.g., Figs 2 & 3). A simple reaction such as reaction 4 of Table 1 or lawsonite + $FeO_x = \text{epidote} + \text{quartz} + \text{kyanite} + H_2O$ can be used to depict the lawsonite-epidote transition. This reaction again is a function of fO_2 and X_{CO_2} in addition to P and T. Figure 7 schematically illustrates the occurrence of lawsonite + magnetite + glaucophane assemblage (Ch + Ab + Qz) in pillow cores, epidote + crossite + magnetite in pillow rims and hematite + epidote + acmite + riebeckite (+ Qz) in overlying pelagic sediments in the Franciscan Complex (e.g., MARUYAMA & LIU, 1988). The variation in fO_2 during blueschist facies metamorphism must have been inherited from differences in the Fe^{3+}/Fe^{2+} ratio of protoliths, which in turn, may be controlled by differences in the degree of water/rock interaction and effective water/rock ratio. Metamorphic conditions were estimated at about 7 kb and 300°C. The variation in assemblage at constant P and T in a single outcrop is due to the difference in fO_2 as illustrated in Fig. 7. Under highly oxidizing conditions such as appropriate for pelagic layer se-

diments, the epidote + hematite + acmite assemblage appears in the lawsonite P-T stability field at lower temperatures.

6. High-P Stabilities of Natural Epidotes

Zoisite (with Ps value less than 5) is a common phase in eclogite as its upper pressure stability limit is known to reach at least 35 kb at 800°C (BOETTCHER, 1970). It coexists with garnet and omphacite in many zoisite-kyanite eclogites and even in coesite-bearing eclogites. Compared to zoisite, epidote (with Ps >14) is less common in eclogitic rocks. The maximum pressure limit of epidote is not known. However, in a regionally developed ultrahigh pressure metamorphic terrane in central China, pseudomorphs of fine-grained quartz aggregates after coesite have been discovered as inclusions in an euhedral epidote

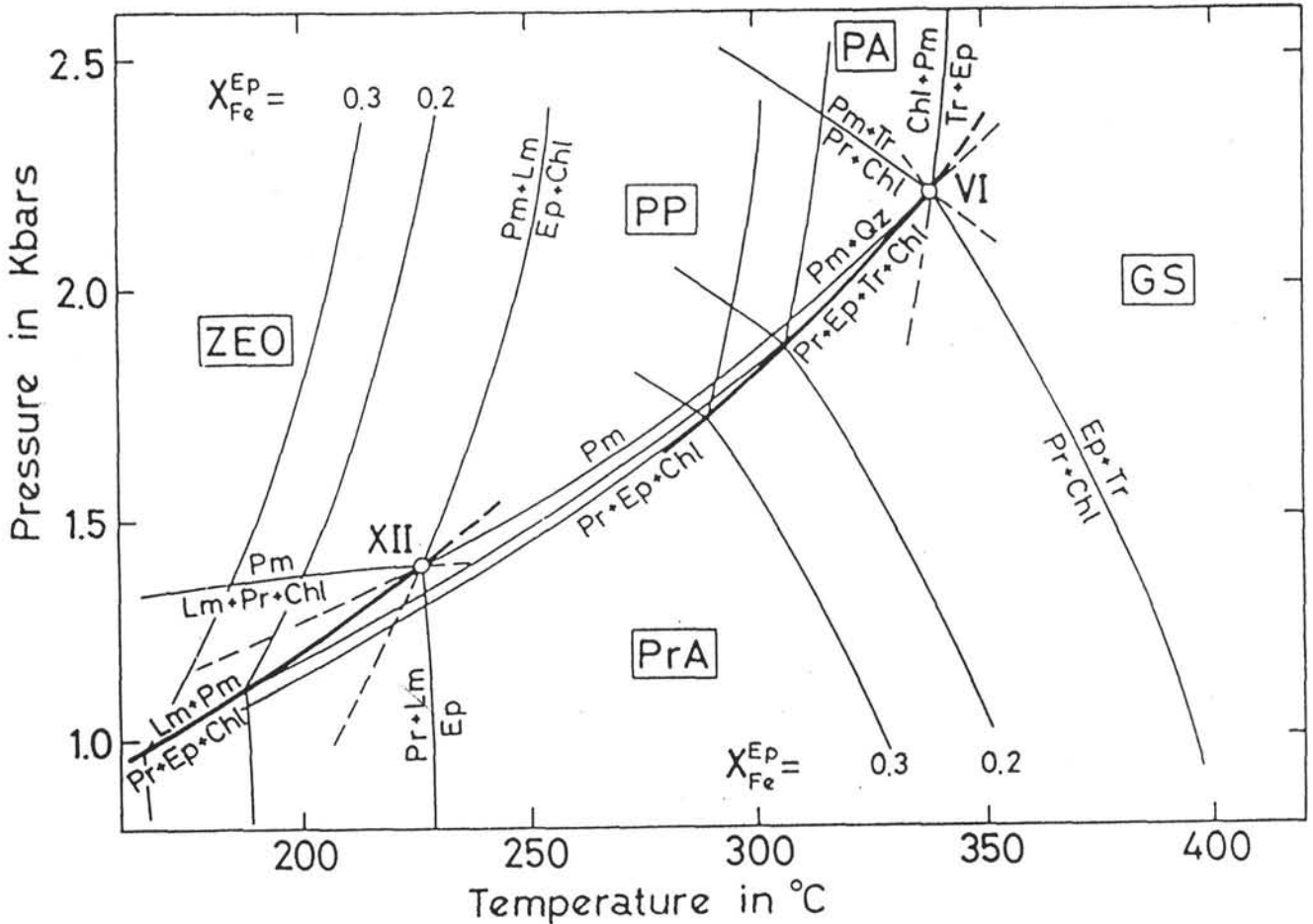


Fig. 6. P-T diagram showing various continuous reactions bordering the zeolite (ZEO), prehnite-actinolite (PrA), prehnite-pumpellyite (PP), pumpellyite-actinolite (PA) and greenschist (GS) facies. Isopleths of epidote are shown (for details, see CHO et al., 1987).

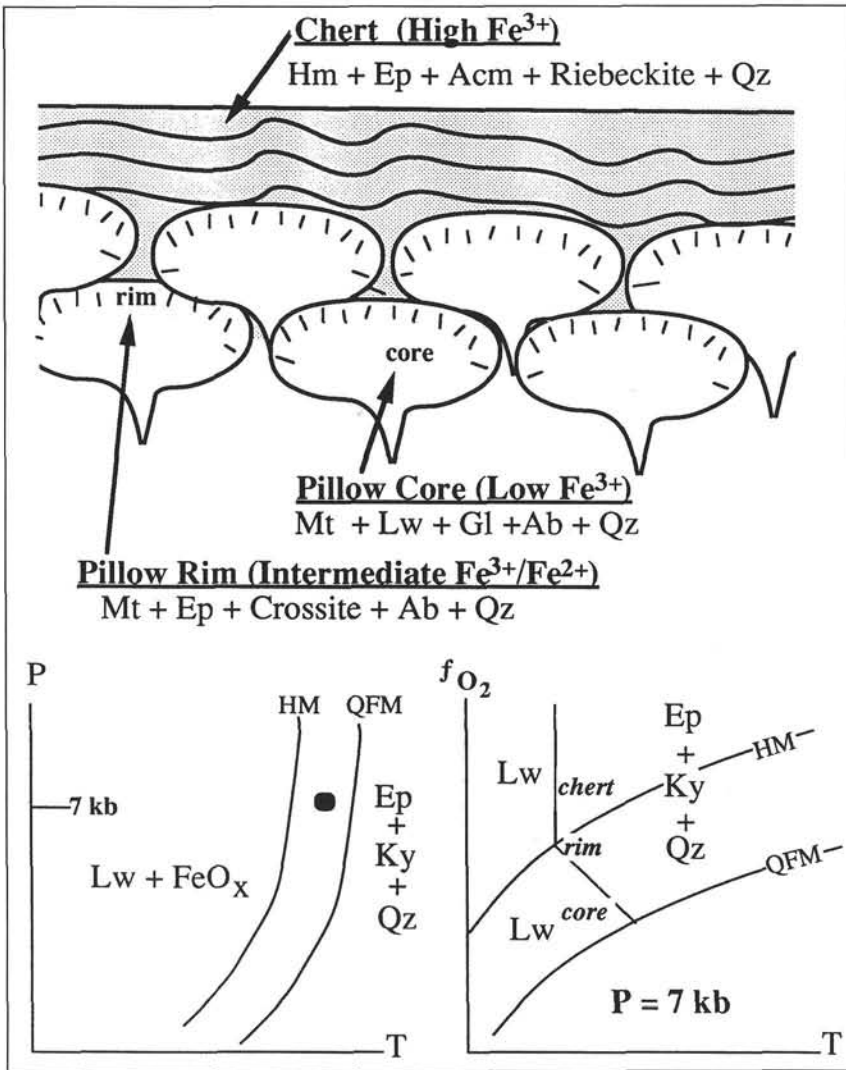


Fig. 7. Schematic diagrams illustrating the effect of fO_2 on the occurrence of lawsonite + magnetite + glaucophane + albite + quartz in pillow core, epidote + magnetite + crossite + albite + quartz in pillow rim and epidote + hematite + acmite + riebeckite + quartz in overlying chert at constant P and T.

sions. In this and adjacent eclogites in eastern China, epidote evidently was stable together with coesite, garnet, omphacite, etc; P-T conditions have been estimated to be at about 850°C and 32 kb (ZHANG, 1991). These petrologic data indicate that epidote is stable with coesite during ultrahigh-pressure metamorphism, although epidote is a very common retrograde phase after garnet and omphacite during the uplift stage of deep-seated eclogitic rocks.

7. The Effect of Mn on Epidote Stability

The effect of Mn on the stability relations (P-T- fO_2) of clinzoisite and epidote has been experimentally evaluated (KESKINEN & LIU, 1979, 1987). The introduction of Mn complicates the breakdown reactions of clinzoisite and epidote. The reactions become more dependent on fO_2 than for Mn-free epidote, hence breakdown curves have much gentler fO_2 -T slopes. The stability fields of Mn-bearing epidote and piemontite are restricted to lower T and very high fO_2 . Natural occurrences of piemontite are confined mainly to blueschist and greenschist facies metamorphism and hematite-bearing rocks. At the fO_2 defined by the HM buffer, Fe-free piemontite is not stable, whereas epidotes with Ps₁₇Pm₁₇ are stable at temperatures less than 400°C and 2 kb. Only at extremely high fO_2 (e.g., cuprite-tenorite buffer), both Fe-free and Fe-bearing piemontite can occur under amphibolite facies conditions.

8. Epidotes in Geothermal Systems

Epidote is the most commonly reported calc-silicate other than zeolites from active geothermal systems. In fact, epidote has been reported from virtually every geothermal system

crystal of Ps₂₃ (Jianchange eclogite), as shown in Fig. 8 (ZHANG, 1991). Relict coesite and quartz pseudomorphs occur in this and adjacent eclogites. Characteristic features for coesite inclusions in garnet and omphacite described elsewhere in the western Alps (CHOPIN, 1984), in Norway (SMITH, 1984) and in central China (WANG et al., 1989) were observed in this sample. Polycrystalline quartz aggregates occur as oval inclusions in epidote, garnet and omphacite; they are clearly recognized by the occurrence of radial fractures in host minerals around the silica inclu-

Mn-free epidote, hence breakdown curves have much gentler fO_2 -T slopes. The stability fields of Mn-bearing epidote and piemontite are restricted to lower T and very high fO_2 . Natural occurrences of piemontite are confined mainly to blueschist and greenschist facies metamorphism and hematite-bearing rocks. At the fO_2 defined by the HM buffer, Fe-free piemontite is not stable, whereas epidotes with Ps₁₇Pm₁₇ are stable at temperatures less than 400°C and 2 kb. Only at extremely high fO_2 (e.g., cuprite-tenorite buffer), both Fe-free and Fe-bearing piemontite can occur under amphibolite facies conditions.

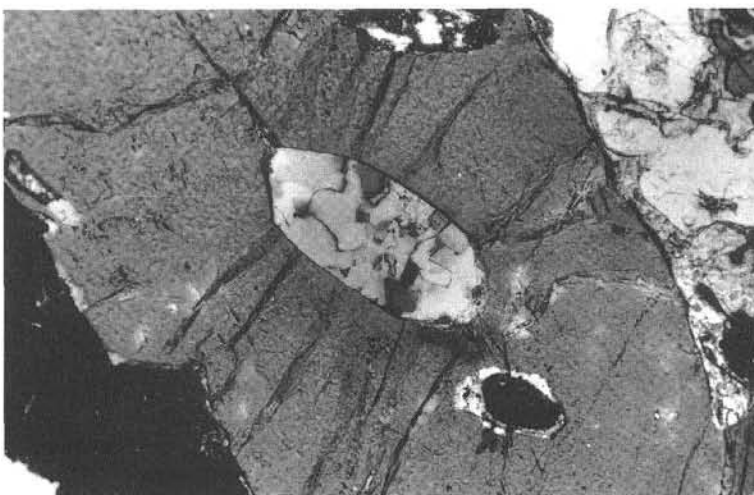


Fig. 8. Photomicrograph showing inclusion of coesite pseudomorphs in epidote (Ps₂₃) in eclogite from eastern China (long dimension = 1.28 mm).

in which measured present temperatures exceed 200 to 250°C. In addition, once epidote is encountered, it remains the dominant calc-silicate phase down the well. For example, in drill cores from the Salton Sea geothermal system in California, epidote is the most common secondary mineral in both fractures and in meta-sediments (CHO et al., 1988; BIRD et al., 1988; CARUSO et al., 1988). The first appearance of epidote (with $P_s > 35$) in metasediment is at about 200°C. With increasing depth, an overall, but irregular, decrease in P_s content of epidote has been observed; however, the epidote composition appears to be related to the associated vein mineralogy, depth, parageneses and fluid composition. In hematite-bearing assemblages, epidote tends to be more Fe-rich.

The stabilities and compositions of geothermal epidotes have been extensively investigated; they are controlled by bulk-rock composition, P , T , fO_2 , X_{CO_2} , and the activities of cations in the fluid phase, including the activity of hydrogen ions (pH) (for details, see BIRD & HELGESON, 1981; BIRD et al., 1984, 1988). Many activity – activity relations have been used to explain parageneses and the observed compositional zoning of epidotes and their relationship with measured geothermal fluids.

9. Conclusions

This paper outlines the stabilities of natural epidotes in a variety of geologic environments. Numerous field, laboratory and theoretical studies have identified several important variables controlling both stabilities and compositions of natural epidotes. In spite of these efforts, stabilities and compositional zoning of natural epidotes remain a scientific challenge. In the future, the effect of each specific intensive and extensive variable needs to be sorted out, continuous reactions for metamorphic epidotes need to be identified, and mass-transfers and disequilibrium processes for complex zoning of hydrothermal epidotes need to be determined. The main conclusions drawn from this review of previous studies are:

- ① Epidote is ubiquitous in a wide variety of geological environments; its occurrences and compositional variations are functions of P , T , PH_2O , X_{CO_2} , fO_2 , fluid and rock compositions.
- ② Most reported magmatic epidotes occur in tonalite-granodioritic rocks crystallized at depths > 25 km; they may occur at shallower depths in oxidized environments and in granitic rocks of different compositions.
- ③ The high- T stability limit of epidote in basaltic rocks defines the transition of the epidote-amphibolite to amphibolite facies at high- P and the greenschist to actinolite-oligoclase facies at low- P .
- ④ Compositions of epidote in low-variance assemblages vary systematically with P or T and are controlled by continuous reactions, hence they can be used as P - T indicators in favorable circumstances.
- ⑤ The minimum temperature for the appearance of epidote is estimated to be about 170°C in geothermal systems and the thermally metamorphosed Karmutsen metabasites; it is associated with hematite and laumontite.
- ⑥ Piemontite is restricted to very oxidized greenschist, blueschist and rare epidote amphibolite facies rocks.
- ⑦ Complexly zoned epidotes in geothermal systems may be controlled by variations in P , T , fO_2 , and fluid compositions, including pH.

- ⑧ The maximum pressure limit of epidote has not been determined; but epidote apparently coexists stably with coesite at $P > 30$ kb and $T = 800^\circ\text{C}$ in central China.

Acknowledgements

This invited contribution for the International Symposium "125 Jahre Knappenwand" during September 16–22, 1990, in Neukirchen was made possible with the support of the Austrian Naturhistorisches Museum and Austrian Mineralogie – Petrologie Society. I thank for the hospitality and exchanges given by many symposium participants, particularly by the organizers, Dr. ROBERT SEEMANN, Dr. FRIEDRICH KÖLLER and Prof. Dr. VOLKER HÖCK. Preparation of this manuscript is supported by NSF EAR 8721225 on the Salton Sea Scientific Drilling project. This manuscript was critically reviewed and materially improved by Dr. BRADLEY HACKER, Prof. W. G. ERNST and Prof. VOLKER HÖCK. I thank the above named institutes and individuals for their assistance.

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