An empirical phase diagram for the clinozoisite-zoisite transformation in the system
\[ \text{Ca}_2\text{Al}_8\text{Si}_3\text{O}_{12}(\text{OH})-\text{Ca}_2\text{Al}_7\text{Fe}^{3+}\text{Si}_3\text{O}_{12}(\text{OH}) \]

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**ABSTRACT**

The effects of pressure, temperature, and \( \text{Fe}^{3+} = \text{Al} \) exchange on the transformation from orthorhombic zoisite to clinozoisite are examined using thermodynamic data and analyses of naturally coexisting mineral pairs. Theoretical considerations indicate a steep transformation loop in the \( T-X \) sections, with the Al end-member reaction occurring at low temperature and the Fe end-member reaction at high temperature; the orthorhombic phase is the high-temperature form. The position of the two-phase zoisite-clinozoisite area in a \( T-X \) section varies with pressure. Equilibrium mineral pairs from low- to intermediate-pressure regimes indicate a smaller two-phase area (between approximately 8-15 mol\% \( \text{Al}_2\text{Fe} \) in zoisite and 25-40 mol\% in clinozoisite) than those from high-pressure regimes (same variation in zoisite, 35-55 mol\% in clinozoisite). The width of the two-phase region also depends on minor elements, such as the rare earth elements. The effect on the phase diagram of a possible low-temperature miscibility gap in the monoclinic series is also discussed. Disequilibrium textures, such as complex zoning patterns and multiple generations of grains, are common features in naturally coexisting clinozoisite-zoisite pairs. Owing to the sluggish reaction behavior of the epidote minerals, these can serve as important petrogenetic indicators of prepeak or relict metamorphic conditions in a wide range of bulk compositions.

**INTRODUCTION**

The epidote mineral group, like the pyroxenes and feldspars, exhibits both chemical and structural variations. The principal isomorphous substitution \( \text{Al} = \text{Fe}^{3+} \) is continuous over a wide range of compositions and operates in both orthorhombic and monoclinic crystals. The structural transformation from the orthorhombic to the monoclinic form thus potentially depends on pressure, temperature, and chemical composition. This transformation is petrologically significant in a variety of metamorphic environments: zoisite is part of the high-pressure assemblage that replaces lawsonite and anorthite and is common in many eclogites; epidote minerals are ubiquitous in mafic rocks throughout the blueschist, green schist, and epidote amphibolite facies; and zoisite and clinozoisite both occur in calc-silicate rocks from a variety of \( P-T \) environments. Despite its petrologic importance, however, the effects of structural and chemical variations on reactions involving epidote group minerals are not well understood.

The controversy concerning the zoisite-clinozoisite phase diagram can be summarized as follows. Enami and Banno (1980) analyzed coexisting zoisite-clinozoisite mineral pairs from rocks of different metamorphic grade. They arranged the analyses by increasing metamorphic grade (i.e., temperature) and suggested that, with increasing temperature, both the monoclinic and the orthorhombic forms become enriched in \( \text{Fe}^{3+} \). However, Ackermann and Raase (1973) observed that clinozoisite and zoisite showed prograde core to rim zoning toward Fe-poor compositions. Prunier and Hewitt (1985) presented experimental evidence that at high temperatures both forms are relatively Fe rich and thus verified Enami and Banno's hypothesis. Comparing the loop proposed by Prunier and Hewitt (1985) with the data of Enami and Banno (1980) still leaves considerable uncertainty about the exact position in \( P-T \) space of the two-phase loop and its form in \( T-X \) and \( P-X \) projections. The aim of this study is to present new data on coexisting zoisite and clinozoisite mineral pairs in order to construct an empirical phase diagram that stresses the important influence of pressure on the phase transformation.

**THEORETICAL CONSIDERATIONS**

This investigation is restricted to the system
\[ \text{Ca}_3\text{Al}_8\text{Si}_3\text{O}_{12}(\text{OH})-\text{Ca}_3\text{Al}_7\text{Fe}^{3+}\text{Si}_3\text{O}_{12}(\text{OH}) \]; the influence of other potentially important substitutions involving Mn, Cr, and rare earth elements is only briefly discussed. In addition, we restrict it to the Al-rich part of the system, where only up to one-third of the total Al is replaced by \( \text{Fe}^{3+} \) (and we assume that \( \text{Fe}^{2+} \) is not important). Higher Fe contents are only rarely reported in the literature (e.g.,
rather low critical temperature or both. Their possible influence is discussed in a subsequent section.

The transformation from monoclinic to orthorhombic forms can be described in terms of two end-member reactions:

\[
\text{mcl } \text{Ca}_2\text{Al}_3\text{Si}_3\text{O}_{12}(\text{OH}) = \text{orh } \text{Ca}_2\text{Al}_3\text{Si}_3\text{O}_{12}(\text{OH})
\]

(1)

\[
\text{mcl } \text{Ca}_2\text{Al}_3\text{Si}_3\text{O}_{12}(\text{OH}) = \text{orh } \text{Ca}_2\text{Al}_3\text{FeSi}_3\text{O}_{12}(\text{OH}).
\]

(2)

The structures of the orthorhombic and monoclinic forms are similar. They consist of SiO₄ and Si₂O₇ groups linked by octahedral chains occupied by Al and Fe³⁺. The two forms are related to each other by a glide-twin operation, but the types of octahedral chains in the two forms are essentially different: in zoisite only one type of chain occurs, whereas in clinzoisite there are two types of chains (Dollase, 1968). The transformation can also be described as cation shuffle or synchroshear (Ray et al., 1986) with a rearrangement of (Al,Fe) and Ca on the M3 site. Such a transformation is probably of first order with a two-phase region in a T-X or P-X section. It cannot be described as a miscibility gap, which would be a function only of cation ordering. In the epidotes, ordering of octahedrally coordinated Al and Fe³⁺ is almost complete in zoisite (Fe³⁺ in the Al3 site; Ghose and Tsang, 1971) and less perfect in clinzoisite (Fe³⁺ in the M3 site, with small amounts in the M1 site; Dollase, 1971).

Both Enami and Banno (1980) and Prunier and Hewitt (1985) argued that pressure has no influence on the transformation loop, owing to the very small difference in molar volumes of the orthorhombic and monoclinic forms \( V_{\text{orh}} = 135.9 \text{ cm}^3/\text{mol}, V_{\text{mcl}} = 136.2 \text{ cm}^3/\text{mol} \), Helgeson et al., 1978; \( V_{\text{orh}} = 135.58, V_{\text{mcl}} = 136.73 \), Holland and Powell, 1990; \( V_{\text{orh}} = 135.88, V_{\text{mcl}} = 136.76 \), Berman, 1988). However, the \( P-T \) slope of a reaction depends on both \( \Delta V \) and \( \Delta S \), and since the entropy values for the epidote minerals are also similar \( S_{\text{orh}} = 296.1 \text{ J/K-mol}, S_{\text{mcl}} = 295.7 \text{ J/K-mol} \), Helgeson et al., 1978; \( S_{\text{orh}} = 295, S_{\text{mcl}} = 291 \), Holland and Powell, 1990; \( S_{\text{orh}} = 297.58, S_{\text{mcl}} = 287.08 \), Berman, 1988; \( S_{\text{orh}} = 296.58, S_{\text{mcl}} = 294.06 \), Gottschalk, 1990), it is possible that pressure exerts a significant effect on the position and shape of the two-phase region. The reported molar-volume value with the smallest error in determination of the lattice constants for synthetic orthoziolite was given by Langer and Lattard (1980) as 135.77 cm³/mol, which is in good agreement with the data from the above mentioned data sets. No reliable data for synthetic Fe-free clinzoisite are known. Pistorius (1961) reported identical values for zoisite and clinzoisite (within the limits of error) of 136.4 ± 0.7 cm³/mol. Extrapolation of data for Fe-bearing clinzoisites presented by Myer (1966), Bird and Helgeson (1980), and Seki (1959) yields a value of 136.2 cm³/mol. Linearly extrapolated data from Hörmann and Raith (1971) in-
dicate a slightly higher value of 136.5, but they suggest that a linear extrapolation is probably not correct, and their given line would extrapolate toward a value of 137.5 cm$^3$/mol.

Reaction 1 has a negative slope in $P-T$ space, although there is a large range in the magnitude of the slope obtained with different data sets ($-124$ bars/$^\circ$C, Berman, 1988; $-13.3$ bars/$^\circ$C, Helgeson et al., 1978; $-34.8$ bars/$^\circ$C, Holland and Powell, 1990). If an average value of $-50$ bars/$^\circ$C is accepted, a pressure increase of 2 GPa would shift the equilibrium temperature for Reaction 1 by $400^\circ$C. No thermodynamic data for Reaction 2 are available. If we assume that the change in entropy arising from the exchange of Fe$^{3+}$ for Al is essentially the same regardless of whether the exchange occurs in an orthorhombic or a monoclinic crystal, the $P-T$ slope of Reaction 2 depends only on the molar volumes and the entropy contribution from order-disorder phenomena. Bird and Helgeson (1980) compiled data on lattice constants and calculated molar volumes. In their Figure 2 it can be seen that, with increasing Fe$^{3+}$ contents, the difference in the molar volumes of the orthorhombic and monoclinic forms may get smaller.

If there is significant order-disorder of Al and Fe in the epidotes, it is likely that the degree of disorder in clinozoisite is higher than in zoisite (Dollase, 1971; Ghose and Tsang, 1971), which results in a decrease in $\Delta S$ for Reaction 2. Bird and Helgeson (1980) give an entropy difference for ordered-disordered epidote of 0.3 J/K mol. Changing the value of $\Delta S$ and a decreasing $\Delta V$ will have a large effect on the slope of the reaction, but unfortunately uncertainties in the available entropy and volume data and lack of data concerning their sensitivity to substitution and order-disorder phenomena do not allow us to distinguish with confidence between a positive and negative slope for Reaction 2.

For the construction of a schematic $P-T$-$X$ diagram, it is also necessary to have some information about the temperature range in which Reactions 1 and 2 are located. Jenkins et al. (1985) determined Reaction 1 experimentally and located it at temperatures below 350 $^\circ$C; calculations with the data of Berman (1988) yield a temperature near 200 $^\circ$C at 1 bar. Despite the uncertainties in the absolute temperatures, there is no doubt that the orthorhombic form is the high-temperature form. Reaction 2 is probably metastable because it must lie at temperatures well above 600 $^\circ$C. This was demonstrated experimentally by Holdaway (1972) and empirically by the common occurrence of monoclinic epidote near its upper stability limit in amphibolite facies rocks.

Figure 2 shows $T-X$ sections for Reactions 1 and 2, with the assumption of both positive and negative slopes for Reaction 2 and extreme temperature differences between the two reactions. In a $T-X$ diagram the limbs of the two-phase region are very steep, and their position changes with pressure and the changing slope of Reaction 2. If a negative slope for Reaction 1 is correct, it is clear that pressure has a large effect on the composition of coexisting phases. With the assumption that the model with a positive slope for Reaction 2 is correct, coexisting zoisite and clinozoisite would exhibit different types of zoning, depending upon the $P-T$ path they had followed during metamorphism: a simple prograde path with simultaneous burial and heating would result in increasing Fe contents from core to rim of both phases (path a in Fig. 2B), whereas isothermal uplift (path b) and isobaric cooling (path c) would result in decreasing Fe contents; heating during uplift (path d) would also cause a rimward decrease in Fe content of both minerals. If Reaction 2 has instead a negative $P-T$ slope, the two-phase region is shifted with increasing pressure toward lower temperatures. Qualitatively, the change in composition of coexisting pairs would be the same for the $P-T$ paths discussed for Figure 2B, but the change would be much more pronounced for both minerals, in contrast to the small changes in zoisite composition illustrated in Figure 2B.

**Naturally Coexisting Zoisite-Clinozoisite Pairs**

In order to constrain the position of the two-phase region, we analyzed coexisting minerals from a variety of $P-T$ regimes. This approach has some inherent problems. The first problem is that epidotes, especially Fe-rich clinozoisite, can preserve extremely complicated zoning patterns, which show up clearly in backscattered electron images and indicate slow diffusion rates at metamorphic temperatures. In theory, slow Fe$^{3+}$-Al diffusion should make the epidote minerals suitable for an empirical study of the two-phase region because their sluggish reaction behavior inhibits retrograde reequilibration. In practice, however, epidotes can form over a wide range of $P-T$
Fig. 3. Distribution of Fe$_2$O$_3$ between clinozoisite and zoisite (only analyses of grains in contact with one another are plotted); clinozoisite is strongly enriched in Fe$_2$O$_3$.

In most samples, other optical features, such as anomalous interference colors, crystal shape and size, and inclusion patterns, were also helpful in distinguishing between zoisite and clinozoisite. Additional transmission electron microscopy was done on two samples; a detailed report on this work is in preparation (Smelik and Franz).

Compositions of coexisting phases

The Fe$_2$O$_3$, TiO$_2$, MnO, MgO, and Cr$_2$O$_3$ contents of all coexisting clinozoisite-zoisite pairs from all rock types are given in Figures 3 and 4. All analyses are compiled in Table 1. Figure 3 shows that Fe$_2$O$_3$ is preferentially incorporated into the monoclinic form. TiO$_2$ (Fig. 4) is also preferentially incorporated in clinozoisite, up to a maximum value of 0.4 wt%. MnO and MgO are also enriched in clinozoisite (up to 0.2 wt%), whereas Cr$_2$O$_3$ partitioning behavior is unclear (Fig. 4). Preferential incorporation of the minor elements into the monoclinic crystals will contribute to the uncertainty in position and slope of the two-phase loop in the Al-Fe system, but because the absolute amounts are small, they are probably of minor importance. This is not the case, however, if these elements are present in large amounts, as is demonstrated for the rare earth elements. Sample BP I 119 (metagranite from the Granatspitzkern Zentralgneis, Tauern Window, Austria; Fig. 5) contains zoisite blasts with small (approximately 20-100 mm) clinozoisite inclusions, which have variable amounts of REE. The zoisite has a constant composition with 6–8 mol% Al$_2$O$_3$, but the Fe
Fig. 5. Analytical results for the investigated samples of clinzoisite-zoisite pairs; squares = orthorhombic; diamonds = monoclinic; rotated squares = structural state uncertain; triangles = rare earth-bearing clinzoisite. Lines connect coexisting minerals; analyses were made a few micrometers away from the grain boundary. Sample BP 119: REE-bearing and REE-free inclusions of clinzoisite in zoisite; the width of the two-phase area widens with increasing REE content. N 13-3: Matrix and vein assemblage in a low-grade amphibolite; filled symbols indicate core compositions. Sample NR 125: Tourmaline-epidote segregation from contact metamorphic environment; filled symbols indicate core compositions. Sample RW 103: Calc-silicate nodules from a polymetamorphic granulite to amphibolite facies terrane. Solid symbol indicates Fe-poor granulite facies zoisite with overgrowth of Fe-rich zoisite during amphibolite facies metamorphism. Sample 1266: Low-grade calc-silicate rock. Closed and open squares represent core and rim analyses, respectively, of grains determined optically to be orthorhombic; closed and open diamonds are core and rim analyses from clinzoisite, with a continuous range of intermediate compositions (no analysis points shown). Closed diamonds (lower two rows) represent monoclinic intergrowths (two crystals determined with TEM) that contain 8–32 mol% Al$_2$Fe in one case and 22–46 mol% Al$_2$Fe in the other. The compositional gap between 15 and 24 mol% in one crystal does not indicate a miscibility gap, since microprobe analyses of other crystals fall into this range. Samples 85-1 and 85-2: Pegmatoid vein in eclogite with formation of clinzoisite in core of zoisite, secondary clinzoisite near and at the rim of zoisite, secondary clinzoisite in cracks in zoisite. The samples show both equilibrium and disequilibrium pairs and also the alteration of primary zoisite into clinzoisite with increasing Fe content. Newly formed crystals with <1 mol% Al$_2$Fe are too small for structural determination; an orthorhombic structure is consistent with the proposed phase diagram, but not proved. Sample St 1: Quartz-zoisite vein from eclogites, showing the same type of alteration of primary zoisite as in samples 85-1 and 85-2. Core compositions of the zoisite (filled symbols) is Fe rich, rims are Fe poor, but near to alteration products Fe content increases. Samples DT 8 and FT 1 are from eclogites, filled symbols indicate core compositions. Both clinzoisite and zoisite show a wider range of compositions compared to the low-P rocks. Dashed line connects core compositions of two adjacent crystals. Sample RM 71 is an epidote + garnet + albite vein in an eclogite. The high Fe rims of clinzoisite is only 5–10 µm wide (open diamonds), inside of this rim (filled diamonds) the clinzoisite is homogeneous.
content in the clinozoisite varies from 25 mol%, where the REE are below the detection limit (0.5 wt%), to 51 mol%, where the REE total is 11 wt% (estimated from Ca deficiency and deviation of ideal anhydrous total of 98.5 wt%; semiquantitative energy dispersive analysis). The REE end-member of the epidote group, allanite, contains Fe2+ in large proportions (Dollase, 1971), and therefore these high Fe contents do not reflect the true Al1Fe mol%, and clinozoisite of this type cannot be used to constrain the two-phase loop.

**Petrographical description**

Owing to the problems mentioned above (complex zoning, growth at different P-T conditions) each sample is different and must therefore be described separately.

Sample N 13-3 (Fig. 5) comes from an ophiolite complex in the Gebel Rahib area, Darfur, northwestern Sudan (Abdel Rahman et al., 1990). Temperatures near 550 °C at 0.2 GPa are assumed to represent the equilibration conditions. There is no significant zoning in the epidote minerals, and tourmaline inclusions in the epidote cores are similar in composition as the matrix tourmaline crystals. Zoisite contains 10–13 mol% Al1Fe, clinozoisite 32–37 mol%.

Samples 85-1 and 85-2 (Figs. 5, 6, 7) are quartz-albite(An0)-zoisite-phengite segregations in the Weissenstein eclogite, Münchberg Massif (Germany). Although these rocks subsequently underwent Tertiary Alpine metamorphism, the Paleozoic contact metamorphism is well preserved and is characterized by the mineral assemblage calcite + wollastonite + quartz + diopside. Temperatures near 550 °C at 0.2 GPa are assumed to represent the equilibration conditions. There is no significant zoning in the epidote minerals, and tourmaline inclusions in the epidote cores are similar in composition as the matrix tourmaline crystals. Zoisite contains 10–13 mol% Al1Fe, clinozoisite 32–37 mol%.

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Sample NR 125 (Fig. 5) is a tourmaline-epidote segregation. It comes from the contact of a granitoid with metasediments, the so-called Hüllserie (“Seetörl” locality, Granatspitz Zentralgneiskern, Tauerl Window, Austria). Although these rocks subsequently underwent Tertiary Alpine metamorphism, the Paleozoic contact metamorphism is well preserved and is characterized by the mineral assemblage calcite + wollastonite + quartz + diopside. Temperatures near 550 °C at 0.2 GPa are assumed to represent the equilibration conditions. There is no significant zoning in the epidote minerals, and tourmaline inclusions in the epidote cores are similar in composition as the matrix tourmaline crystals. Zoisite contains 10–13 mol% Al1Fe, clinozoisite 32–37 mol%.

**Fig. 6.** Photomicrograph of equilibrium intergrowth of clinozoisite (34–36 mol% Al1Fe) in the core of a zoisite (12 mol% Al1Fe), together with (sericitized) albite (sample 85-1, crossed polars).

**Fig. 7.** Photomicrograph of zoisite with 10–12 mol% Al1Fe with alteration zones parallel to (100) (dark because of anomalous interference colors) with 15 mol% Al1Fe, intergrown with albite (ab; sample 85-1, crossed polars).
A second type of clinozoisite (with 31–53 mol% Al₁Fe) occurs along irregular cracks in zoisite (see Fig. 9 in Hammerschmidt and Franz, 1992) and also parallel to (100) and (010) planes of the host zoisite (Fig. 7), where it is accompanied by a slight change in interference colors of the adjacent zoisite. The clinozoisite formation and modification of the zoisite took place at a later stage, probably below 350 °C at low pressure. A late (postmetamorphic) hydrothermal stage that might have been responsible for the features shown in Figure 7 has been documented by Hammerschmidt and Franz (1992) for the Münchberg Massif. The modified zoisite crystals vary between 12 and 26 mol% (analyses at points where interference colors changed or immediately adjacent to the secondary clinozoisite). We were unable to determine by optical methods whether these crystals are monoclinic or orthorhombic, but preliminary transmission electron microscopy results show deviations from orthorhombic symmetry in these areas (a detailed description of these results will be presented elsewhere). We were also unable to determine the symmetry of small crystals approximately 5 μm in diameter that are located in the albite matrix parallel to (100) of zoisite (Fig. 7) and in altered pegmatitic plagioclase next to the pegmatitic zoisite crystals. These small crystals have Al₁Fe contents near 1 mol%. Assuming that the latter are orthorhombic and the zoisite modifications are monoclinic, a compositional gap between 1 and 12 mol% exists. The rocks from this locality provide an excellent example of the variety of epidote minerals that form during cooling. Only the primary intergrowths were used in determination of the transformation loop, although the secondary clinozoisite crystals give some constraints about the position of the loop at low P and T.

Sample 1266 (Figs. 5, 8) is also from the Münchberg area, but from the border zone adjacent to very low-grade sediments (locality Schwingen, near Schwarzenbach/Saaale, Germany). This so-called prasinite-phyllite series did not experience temperatures in excess of 350 °C (the stable assemblage is stiplnomelane + actinolite + chlorite + calcite + albite; pressures are not determined, but there is no indication of high pressures). The specimen is a calcite-phengite rock with minor amounts of epidote, titanite, and tourmaline, from a greenschist-metapelitic contact. Zoisite occurs as needle-shaped crystals 5–20 μm, with 4–12 mol% Al₁Fe mostly restricted to the calcite-rich part of the sample, whereas large clinozoisite grains (300 μm) with 7–46 mol% Al₁Fe occur mainly in the phengite-rich part of the sample. They were not found in clear grain contact but were within a few micrometers of each other. Closer inspection of these crystals with backscattered electron images revealed zoning from core to rim toward Fe-rich compositions in both the monoclinic and the orthorhombic grains, although zoning in the clinozoisite was less regular (Fig. 8). The monoclinic nature of those parts of the crystals with very low Fe content (8 mol%, determined by analytical electron microscopy) was verified by selected area diffraction analysis of two crystals. The analyses clearly demonstrate that, at low P-T conditions, low to intermediate Al₁Fe clinozoisites exist, indicating that there is no obvious miscibility gap, and that there can be an overlap in compositions of zoned clino- and orthozoisite that grew during a prograde burial and heating event.

Sample St 1 (Fig. 5) is another example of modifications to primary zoisite during retrograde development. This sample comes from the eclogite zone (Knappenhaus locality, Frosnitztal, Tauern Window, Austria), from a zoisite-quartz segregation in a banded eclogite (Thomas and Franz, 1989). Following eclogite facies metamorphism, these rocks underwent subsequent alteration in the P-T range from the lower amphibolite facies down to temperatures below 350 °C (Spear and Franz, 1986). The
centimeter-sized zoisite crystals of the segregation are replaced along their rims by clinozoisite, paragonite, albite, and calcite, and adjacent to these newly formed minerals, zoisite changes its composition from 6–10 mol% Al$_2$Fe at the rim (cores are 11–15 mol%) to 16–21 mol%. The secondary clinozoisite ranges from 39 to 47 mol% Al$_2$Fe. Samples FT-1 and DT-8 (Figs. 5, 9) are from the same area as sample St 1. They are both from banded eclogites (localities Frosnitztal, southern margin of the eclogite zone, and Dorfer Tal, western end of the Gastacher Wände). The eclogites experienced pressures near 2.0 GPa, at temperatures near 590 °C (Holland, 1979; Frank et al., 1987; Spear and Franz, 1986) with some subsequent reequilibration to lower greenschist facies conditions. The FT sample shows no signs of this reequilibration, whereas the DT sample is slightly retrograded (as indicated by the beginning of symplectite formation of some omphacite and the scattering of $K_p$ values for garnet clinopyroxene). The mineral assemblage in both samples is epidote + garnet + omphacite + amphibole + phengite + dolomite + magnetite + rutile + quartz. Clinozoisite is in most cases strongly zoned with increasing Fe contents from core to rim; in coexisting zoisite the trend is similar but less pronounced. The zoisite composition ranges from 10 to 15 mol% Al$_2$Fe (one exception with 18 mol%), the clinozoisite from 34 to 52 mol%, with core compositions between 29 and 38 mol%. There are two average compositions of clinozoisite, one near 34, the other near 45 mol%. Figure 9 shows that omphacite inclusions are in textural equilibrium with both of these compositions. We use this observation to argue that the clinozoisite grains with the high Al$_2$Fe component are not late-stage overgrowths but rather formed during prograde metamorphism.

Sample RM 71 (Figs. 5, 10) is a garnet amphibolite with strong indications that it is a retrograded eclogite (symplectite of amphibole and plagioclase, corroded garnet; the main mineral assemblage is amphibole + plagioclase + chlorite + epidote + titanite). It comes from the basement complex of the Tauern Window, Maurer Tal. Eclogites within this basement record lower pressures (1.2
GPa) and temperatures (500 ± 50 °C; Zimmermann and
Franz, 1989) than those within the eclogite zone. The
coeexisting zoisite-clinozoisite minerals occur in a small
layer in the sample, coexisting with albite and garnet (+
paragonite), with good indications for textural equilibrium.
The zoisite crystals are embedded in clinozoisite and
albite but also have inclusions of clinozoisite. These in-
cclusions show the same type of zoning as the matrix cli-
nozoisite, with very narrow rims of Fe-rich composition
(42–54 mol% Al₂Fe), central parts with 31–34 mol% (Fig.
10b). This is again taken as an argument for prograde
zoning of the minerals not modified by retrogression. The
zoisite ranges from 8 to 16 mol% Al₂Fe, with core to rim
zoning toward Fe-rich compositions.

Sample RW 103 (Fig. 5) is a calc-silicate nodule in an
amphibolite. It comes from the Nubian Desert basement,
approximately 30 km west of Delgo (20°N, Nile River)
in the northern province of Sudan. This basement is char-
acterized by a main stage of mineral formation in the
upper amphibolite facies (P near 0.5 GPa, T near 650
°C), but contains relics of granulite facies metamorphism
(P = 0.8 GPa, temperatures near 800 °C; Bernau et al.,
1987; Huth et al., 1984). The calc-silicate nodule consists
of grossular + zoisite + diopside + anorthite + quartz,
separated by a small reaction zone of clinozoisite + zois-
ite + diopside + anorthite from the amphibolite (mainly
plagioclase + amphibole). Zoisite is strongly zoned from
2 to 12 mol% Al₂Fe, with Fe-rich rims, but zones of all
compositions coexist with clinozoisite. The variations in
clinozoisite composition (36–42 mol% Al₂Fe) occur in
sharp zones parallel to the b axis. It is assumed that the
zoisite formed during granulite facies conditions above
the upper stability limit of clinozoisite, which is near 650
°C (Holdaway, 1972). During the amphibolite facies event,
epidote component was formed, changing the zoisite
composition and also forming separate clinozoisite crys-
tals. Although both minerals are in grain contact and
present in equal grain sizes, the large range in zoisite
rim compositions coexisting with clinozoisite indicates
disequilibrium.

**DISCUSSION**

A primary observation in nearly all of the samples that
we have studied is that both zoisite and clinozoisite com-
monly show disequilibrium features, such as complex
zoning patterns (especially in rocks of high-pressure ori-
gin), formation of texturally and chemically different types,
and modifications of earlier minerals. Within a single grain
the composition can vary widely and often irregularly,
that minor elements can influence the width of the gap.
This is evident for the REE (Fig. 5) and has also been
shown for Sr by Maaskant (1985).

In Figure 11 we have arranged the data on coexisting
clinozoisite-zoisite pairs (outer rim analyses) in a T-X
diagram, using average values (mean of the analyses), but
also showing the range of analyses, together with an es-
timate of the temperature of formation of the epidote
minerals. The rocks were split into two groups, one with
low to intermediate pressure of formation (<1 GPa), the
other with high pressure (>1 GPa). These estimates are
rather uncertain: even when rigorous thermobarometric
calculations are made, the timing of equilibration of the
epidote minerals is still unknown. Error boxes in the T-X
diagram would be large, but several key features are evi-
dent despite these uncertainties: (1) The overall chemical
variation in zoisite is much smaller than in clinozoisite,
but both show an increasing Al₂Fe component with in-
creasing temperature. This supports the previous findings
of Enami and Banno (1980), Maaskant (1985), and Pru-
nier and Hewitt (1985). (2) The largest compositional
variations, in both zoisite and clinozoisite, were consis-
tently observed in rocks of high-pressure origin. High-
pressure rocks necessarily have a complex metamorphic
history with more possible stages of mineral growth than,
for example, during simple contact metamorphism. (3)
Clinozoisite samples from the high-pressure terranes are
significantly higher (by approximately 10 mol%) in Al₂Fe
component than those from low-pressure terranes, al-
though their estimated formation temperatures are sim-
ilar. The same trend can be observed in Enami and Ban-
no’s (1980) data: Their FU and OM samples (their Fig.
4) come from low-pressure terranes, whereas their TO,
NI, and IR samples are from eclogites; the compositional
gap for the high-pressure rocks is significantly wider.

These observations provide evidence that pressure ex-
erts an important influence on the position of the clino-
zoisite limb. This is supported by observations of Spencer et al. (1988), who described pairs of zoisite and clinozoisite with 13-14 and 40-51 mol% Al$_2$Fe, respectively, from eclogites of the Western Gneiss Region (Norway), and Maaskant (1985), who reported a zoisite-clinozoisite pair (16.5 and 45 mol% Al$_2$Fe) from the high-pressure rocks of Galicia (northwestern Spain). We cannot distinguish unambiguously between the two possibilities discussed in Figure 2 because of the large variation in the compositions, but a configuration similar to Figure 2B seems quite likely.

At temperatures below approximately 400 °C the two-phase region is not well constrained. Our sample 1266 (see Fig. 5) shows that intermediate compositions for monoclinic crystals lying within the two-phase region at higher temperatures do exist. Therefore at low P-T conditions, the limb restricting the monoclinic phase area extends toward very Al-rich compositions, but its exact position is still uncertain. An equilibrium temperature for Reaction 1 near 200 °C at low pressures is likely, in agreement with calculations using the Berman (1988) data set and with the experimental determination of Jenkins et al. (1985).

The secondary epidote minerals formed in samples 85-1, 85-2, and St 1 show a large variation of compositions and textures within a single thin section, reflecting prolonged cooling of the rocks. The primary zoisite crystals with 10-12 mol% Al$_2$Fe were transformed during a hydrothermal event into grains with up to 26 mol%, typically without changing the morphology and the straight extinction of the crystal. The increasing Fe content is visible in narrow zones with increasing birefringence. Preliminary TEM data suggest that these zones consist of intergrowths of monoclinic and orthorhombic domains (Smelik and Franz, in preparation). Secondary clinozoisite crystals precipitated in cracks range from 30 to 54 mol%. This indicates that at low P-T conditions (approximately 0.3 GPa, 350 °C) no miscibility gap is apparent. The existence of almost Fe-free epidote minerals (symmetry not determined) in altered plagioclase, only a few micrometers away from the primary Fe-bearing zoisite and the secondary high-Fe clinozoisite, is typical of the disequilibrium preserved among neighboring grains of the epidote minerals. An orthorhombic symmetry of these Fe-free epidotes would be consistent with the transformation temperature for Reaction 1 near 200 °C, as mentioned above.

There is also evidence to suggest that miscibility gaps might occur in the monoclinic series at low temperatures or high pressures. Apparent miscibility gaps have been reported by several authors (Strens, 1965; Holdaway, 1972; Hietanen, 1974; Raith, 1976; Selverstone and Spear, 1985) on the basis of coexisting compositions of monoclinic epidotes in natural rocks. Our own analyses and backscattered electron images of epidotes show that disequilibrium textures are commonly preserved in single grains and even in coexisting monoclinic and orthorhombic forms; it is thus possible that published reports of miscibility gaps in the monoclinic series are merely an artifact of complex growth histories. On the other hand, such effects as ordering of Al and Fe$^{3+}$ in M1 and M3 sites may create structural variations leading to miscibility gaps. We hope that detailed TEM studies will resolve this problem. Because most of the reported miscibility gaps are located at high Al$_2$Fe contents (between 35 and 75 mol%) and close at temperatures near 550 °C (Raith, 1976) or even lower (450 °C; Selverstone and Spear, 1985), they probably have no influence on the steep orthorhombic to monoclinic transformation loop reported here. However, if the clinozoisite limb is significantly shifted toward Fe-rich composition with increasing pressure, as indicated in Figure 11, the suggested monoclinic miscibility gaps might intersect the transformation loop. Such a configuration is shown in Figure 12 for the miscibility gap proposed by Selverstone and Spear (1985), with a critical temperature of 450 °C.

**Conclusions**

This study supports the previous findings of Enami and Banno (1980), Maaskant (1985), and Prunier and Hewitt (1985) that the transformation loop between clinozoisite and zoisite depends strongly on temperature and that Fe$^{3+}$ (as well as the minor elements Ti, Mn, and Mg) is preferentially distributed into clinozoisite. In addition, we show that pressure may also be a significant variable and that in high-pressure rocks clinozoisite is enriched in Fe$^{3+}$ compared to low-pressure rocks (at the same temperature, coexisting with zoisite) at intermediate temperatures between 400 and 600 °C; zoisite-clinozoisite relations remain uncertain at lower temperatures, although a narrowing of the compositional gap is likely, and at higher temperatures do exist.
temperatures the upper stability limit of clinozoisite disturbs the simple binary phase relations.

The phase diagram that we present for the orthorhombic to monoclinic transformation can be used as an aid in the calculation of reactions involving epidote minerals. For example, if the pressure-sensitive reaction anorthite + $\text{H}_2\text{O} = \text{zoisite}-\text{clinozoisite} + \text{kyanite} + \text{quartz}$ is considered, its position in a $P$-$T$ diagram depends on the structural state, as well as on the composition of the epidotes. Calculations involving such a reaction at high $P$-$T$ conditions (eclogite facies) should consider zoisite at bulk $\text{Al}_2\text{Fe}$ compositions from 0 to 15 mol%, coexisting zoisite and clinozoisite in the range 15-45 mol% $\text{Al}_2\text{Fe}$, and clinozoisite only at $\text{Al}_2\text{Fe}$ contents greater than 45 mol%.

At low $P$-$T$ conditions (green schist to amphibolite facies) the compositional gap is small and of only minor effect. Hence, at these conditions clinozoisite should be used in the calculations for all bulk rock compositions that might yield more than 10-15 mol% $\text{Al}_2\text{Fe}$; zoisite would be the appropriate phase only for very Fe$^{3+}$-poor compositions.

For a more temperature-sensitive reaction such as lawsonite = zoisite + kyanite + quartz + $\text{H}_2\text{O}$, the pressure influence is more pronounced: at low $P$ and $T$, 5-10 mol% $\text{Al}_2\text{Fe}$ can be incorporated in zoisite, and the coexisting clinozoisite has around 20 mol%, whereas at low $T$ and high $P$ the clinozoisite has around 40 mol% $\text{Al}_2\text{Fe}$. The likelihood of forming zoisite in addition to clinozoisite increases with rising pressure because of the wider compositional gap. This provides an explanation for the relative abundance of zoisite in high-pressure rocks, although zoisite itself is also stable at low pressure.

Epidote minerals, owing to their stability over a wide range of $P$-$T$ conditions, can be produced in many different stages during the metamorphism of a single rock; the apparently slow diffusion rates of $\text{Al} = \text{Fe}^{3+}$ exchange result in preservation of complex zoning patterns in individual grains. The epidote minerals thus have the potential to provide a wealth of petrologic information relevant, for example, to the reconstruction of $P$-$T$ paths, provided that quantitative data on $P$-$T$-$X$ relations in the epidote series are available. Though this is not yet the case, the empirical phase diagram presented in Figure 11 should serve as a starting point for future work. More analyses of coexisting mineral pairs from areas with well-known metamorphic histories are necessary to refine this diagram further. For fine-grained rocks, this will require simultaneous determination of crystal structure and chemical composition by transmission electron microscopy.

Ultimately, single epidote grains might be useful candidates for radiometric age determinations with a microbeam technique, both because they can contain high concentrations of trace elements such as REE, Sr, Pb, U, and Th and because they can record different stages of growth during complex metamorphic events; in this regard, they may eventually serve the same purpose in geochronologic studies of intermediate-temperature metamorphic rocks that zircon does in higher temperature (e.g., magmatic) rocks. Such studies have the possibility to yield timing information on the prograde paths of high-pressure rocks and thereby provide useful data for geodynamic studies of paleosubduction environments.

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