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Magmatic Epidote

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INTRODUCTION

Epidote was first recognized as a magmatic mineral in the alpine Bergell tonalite by Cornelius (1915). Field observations and microscopic textures let Cornelius to conclude "... the only possibility is, that epidote is a primary mineral in our tonalite, crystallizing early from the magma, i.e., before (in part also contemporaneous with) biotite" *(translated from German, Cornelius (1915), p. 170)*. This knowledge disappeared and for the following 70 years, epidote and zoisite were categorized as metamorphic minerals. The petrologic significance of magmatic epidote was then rediscovered when Zen and Hammarstrom (1984) identified epidote as an important magmatic constituent of intermediate calc-alkaline intrusives in plutons of the North American Cordillera. Zen and Hammarstrom (1984) also suggested that epidote indicates a minimum intrusive pressure of about 0.5 to 0.6 GPa. Subsequently, magmatic epidote was described from many granodioritic to tonalitic plutons, but also from monzogranite (e.g., Leterrier 1972), dikes of dacitic composition (Evans and Vance 1987), and orbicular diorite (Owen 1991, 1992). Furthermore, epidote was not only recognized in crystallizing plutons or dikes but also in high pressure migmatites and pegmatites derived from eclogites (Nicollet et al. 1979; Franz and Smelik 1995).

The role of epidote during magmatic crystallization is relatively well understood, and crystallization temperatures and sequences involving epidote in intermediate magmas (granodiorite-tonalite-trondhjemite, TTG) are experimentally determined and confirmed from natural intrusives. In contrast, little attention is directed towards the inverse process, i.e., melting of epidote bearing lithologies. Epidote is omnipresent in eclogite of intermediate temperature (Enami et al. 2004) and denominates three subfacies (i.e., epidote-blueschist, epidote-amphibolite, and epidote-eclogite facies). Indeed the epidote-amphibolite facies intersects the wet granite solidus near 0.5 GPa at 680°C, defining the pressure above which epidote may be present during melting processes. Experiments on natural compositions have confirmed that epidote is stable above the wet granite solidus in the pressure range 0.5 to 3.0 GPa (Poli and Schmidt 1995, 2004), and thus is involved in partial melting processes. Unfortunately, it is difficult to recognize the participation of epidote during partial melting in nature, as epidote is one of the first phases to "melt out." On the other hand, it is exactly the relatively narrow temperature interval of epidote + melt, which makes epidote a significant provider for H_2O during fluid-absent melting (Vielzeuf and Schmidt 2001).

In this chapter we use the term "epidote" or "epidote minerals" in a general sense for all minerals of the epidote group including zoisite, and "epidote$_{SS}$" for the monoclinic solid solution between $Ca_2Al_3Si_3O_{12}(OH)$ and $Ca_2Al_2Fe^{3+}Si_3O_{12}$ (OH) ("ps"). Solid solutions with significantly more than one Fe per formula unit have not been reported as magmatic epidote. "Zoisite" is used only to specifically designate the orthorhombic polymorph. The review is limited to epidote with relatively low REE contents. The stability and role of allanite, a common early accessory mineral in granitoid intrusions, is discussed by Gieré and Sorensen (2004). We first review natural occurrences of magmatic epidote starting with criteria to identify a magmatic origin of epidote. Our compilation of magmatic epidote occurrences focuses on the oddities, i.e., the <5% of magmatic epidote which are not part of the widespread "epidote in TTG" (i.e., tonalite-trondhjemite-granodiorite) plutons. We then review experimentally determined phase relations of epidote minerals in coexistence with melt. This includes melting and crystallization reactions as well as the bulk composition effect on the magmatic occurrence. The factors influencing the variation in "minimum pressure" indicated by magmatic epidote in intrusions receive particular intention. Finally we investigate the role of epidote during fluid-absent melting processes.

MAGMATIC EPIDOTE IN INTRUSIVES

Epidote crystallizes from intermediate magmas above a certain pressure (Zen and Hammarstrom 1984) that, mainly in function of bulk composition and oxygen fugacity, may vary from 0.3 to 0.7 GPa. The dependence of epidote crystallization on magma composition is somewhat masked by the very uniform chemistry of tonalite-granodiorite intrusions. These account for >90% of the magmatic epidote occurrences and result in the inappropriate impression that their 0.5 GPa minimum pressure for magmatic epidote is generally applicable, which, as will be discussed below, is not the case. The fairly late rediscovery of the possible magmatic character of epidote is mainly due to the unfounded assumption that epidote is a low temperature mineral and thus metamorphic or hydrothermal, but also it is indeed not always easy to distinguish epidote as magmatic on a textural basis. Textural criteria play a central role, as compositional criteria are not very helpful to distinguish magmatic from metamorphic epidote: the metamorphic compositional array (ps_0 to ps_{100}) encompasses the magmatic compositional array (typically ps_{30} to ps_{70}), and the only deviations from the pseudobinary epidote$_{SS}$ chemistry, such as high concentrations of Ce and other REE, are characteristic for a magmatic origin, though they modify the pressure-temperature range of crystallization. If available, stable isotope data can help to distinguish magmatic from subsolidus epidote (see discussion in Morrison 2004).

Textural evidence for magmatic epidote

Several features are considered to be characteristic of a magmatic origin of epidote (Zen and Hammarstrom 1984; Moench 1986; Tulloch 1986; Zen and Hammarstrom 1986; Zen 1988):

- A reliable indication is strong zonation with allanite-rich cores. However a lack of such a zonation does not exclude a magmatic origin.

- An ophitic texture is considered to be typically magmatic. In the crystallization sequence epidote seems to appear in tonalite after hornblende but before or contemporaneous with biotite.

- Magmatic epidote is sometimes embayed where in contact with the quartzofeldspatic matrix, pointing towards not being stable at the final crystallization of the magma.

- Magmatic epidote may be embedded as single euhedral crystals in a quartz-feldspar matrix which shows graphic intergrowths.

- The lack of biotite alteration to chlorite and a fresh appearance of plagioclase mostly exclude a later retrograde greenschist facies or hydrothermal overprint and therefore make it unlikely that epidote formed through a subsolidus reaction.

A few examples of such textural features are shown in Figure 1. Of course both primary magmatic and secondary metamorphic epidote might occur together and, in particular cases, an unequivocal identification can be difficult. However, for an estimate of intrusion conditions, the presence of magmatic epidote represents a powerful tool. In tonalite and granodiorite epidote is macroscopically easily identifiable - and its presence excludes a shallow intrusion level for the tonalitic or granodioritic magma.

Natural magmatic epidote – the crowd

Since magmatic epidote has been revived, a large number of intermediate to deep seated plutons were described to contain magmatic epidote. Intrusion pressures for these plutons were derived by means of the Al-in-hornblende barometer (Hammarstrom and Zen 1986; Schmidt 1992) and by contact aureole pressures. In the context of this chapter, we focus on pressures from the magmatic systems and thus rely on the Al-in-hornblende barometer (see below), with the advantage that these are directly comparable for all TTG compositions. Such intrusion pressures yield in most cases 0.5 to 0.8 GPa, in accordance with the experimental studies discussed in the subsequent sections. Reactions and observed textures of the "common" magmatic epidote are discussed in the section "Epidote in H_2O saturated magmas" below. Typical volumetrically dominant granodiorite-tonalite suites of large calc-alkaline intrusions containing epidote are described from the following regions (non-exhaustive list):

Europe:

- Bergell, Central Alps (Cornelius 1915; Davidson et al. 1996; Fig. 1a)
- Porhorje Mountains, Slovenia (Altherr et al. 1995)
- Retezat and Mala Fatra granitoids, Carpathians, Slovakia-Romania (Broska et al. 1997)
- Syrostan and Verkhisetsk batholiths, Ural, Russia (Bea et al. 1997; Montero et al. 2000; Popov et al. 2001)
- Velfjord, Norway (Barnes and Prestvik 2000)
- Jerissos and Verdikoussa plutons, Greece (Pepiper et al. 1993; Frei 1996)

Africa:

- Bas Draa, Anti-Atlas, Marocco (Mortaji et al. 2000)

New Zealand:

- Ridge, Table Hill, and Campsite plutons, New Zealand (Allibone and Tulloch 1997; Tulloch and Challis 2000)

North America:

- Alaska (>10 batholiths, Zen and Hammarstrom 1984; Cook et al. 1991; Zen 1988)
- British-Columbia (at least 5 batholiths, Hammarstrom and Zen 1986; Hollister et al. 1987; Ghent et al. 1991, Zen 1988)
- Washington, Oregon, Idaho (at least 5 batholiths, Zen and Hammarstrom 1984; Zen 1985, 1988)
- California (at least 5 batholiths, Zen and Hammarstrom 1984; Anderson et al. 1988; Keane and Morrison 1997)
- Santa Catalina batholith, Arizona (Anderson et al. 1988)
- Minto block, Canada (Bedard 2003)
- Kaipokak domain and Cape-Breton highlands, Novia Scotia and Labrador, respectively (Farrow and Barr 1992; Barr et al. 2001)
- Appalachians (several plutons, Vynhal et al. 1991)
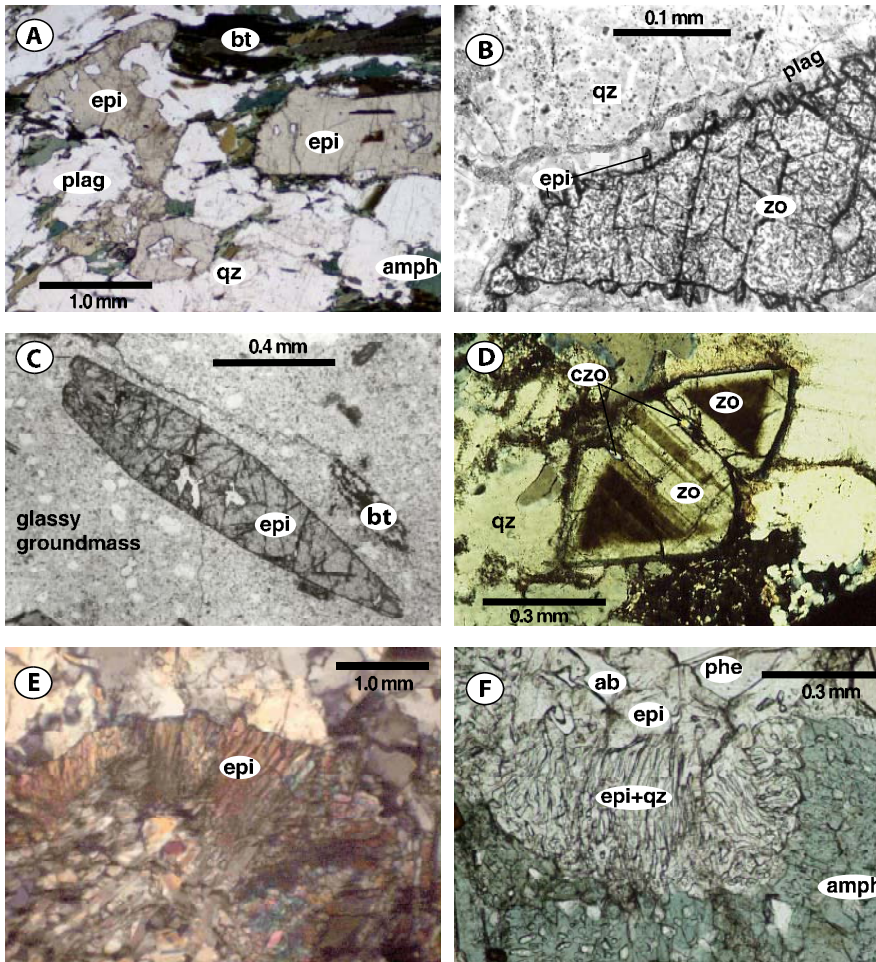
Figure 1. Photographs of natural magmatic epidote. (a) Tonalite of the Bergell intrusion, CH/I, where magmatic epidote was first identified by Cornelius (1915). Typical texture of magmatic epidote in the TTG series. In this case, epidote is idiomorphic where growing into amphibole and sometimes embayed where in contact with the quartzo-feldspatic matrix. (b) Magmatic zoisite with overgrowth of subsolidus epidote (small shortprismatic crystalls almost perpendicular to the zoisite grain) and with an oligoclase corona. The photograph represents a migmatite formed in eclogites from the Massif Central, France (Nicollet et al. 1979). (c) Epidote phenocryst in fine-grained matrix from a dacite dike in Boulder County, Colorado. The matrix contains quartz and plagioclase phenocrysts and partly chloritized biotite (Evans and Vance 1987). (d) Zoned zoisite from the Weissenstein pegmatite, Münchberg Massiv, Germany. This pegmatite is derived from high pressure melting of eclogite at ≈2.0 GPa (Franz and Smelik 1995). (e) Corona of fibroradial to vermicular magmatic epidote within an orbicule, from an orbicular diorite from the Greenville Front zone in Labrador (Owen 1991, 1992). (f) Vermicular epidote-quartz intergrowth from the Sanagawa-gabbro. The intergrowth occurs interstitially and consists, beside of epidote and quartz, also of albite and phengite indicating an envolved bulk composition of the last crystallizing melt. Thin section (a) and photographs (b) to (f) courtesy of C. Nicollet, B. Evans, G. Franz, J.V. Owens, and P. Ulmer, respectively.

Abbreviations for all figures: amph: amphibole$_{ss}$, an: anorthite, bt: biotite$_{ss}$, cor: corundum, cpx: clinopyroxene$_{ss}$, cs: coesite, epi: epidote$_{ss}$, gar: garnet$_{ss}$, gr: grossular, hbl: hornblende, ky: kyanite, mgt: magnetite, ms: muscovite, or: orthoclase, omph: omphacite, opx: orthopyroxene$_{ss}$, ph: phlogopite, phe: phengite$_{ss}$, plag: plagioclase$_{ss}$, qz: quartz, tr: tremolite, v: vapor = aqueous fluid, wo: wollastonite, zo: zoisite.

Middle America:

- Cuzahuico granite, Oaxacan complex, Mexico (Elias-Herrera and Ortega Gutierrez 2002)

South America:

- Argentina-Chile (at least 5 plutons, Saavedra et al. 1987; Cerredo and De Luchi 1998; Sial et al. 1999a; Dahlquist 2001a,b)
- Serra Negra do Norte Pluton, Borborema Province, and Rio Grande do Norte State, NE Brazil (Galindo et al. 1995; Sial et al. 1999a,b; Campos et al. 2000)

For almost all of the intrusions in these batholiths and plutons, the features described above apply and intrusions with such magmatic epidote shall not be discussed any further. The above list contains mostly intrusions from orogenic settings, pointing to the common occurrence of deep seated intrusions in such settings. In contrast, epidote-bearing intrusions in Archean shields are rare.

Natural magmatic epidote – the odd one's

This section focuses on the out-of-the-normal natural occurrences of magmatic epidote that we divide into those, where pressures are such that magmatic epidote in TTG's should not occur, unusual bulk compositions with magmatic epidote (e.g., dacite, diorite) sometimes occurring in dikes, and epidote occurrences during migmatisation processes.

Magmatic epidote at <0.5 GPa. Using the calibration of Johnson and Rutherford (1989) for the Al-in-hornblende geobarometer, Vyhnal et al. (1991) concluded a minimum pressure of around 0.28 GPa for epidote formation in epidote-bearing Appalachian monzogranites. However, the Johnson and Rutherford calibration was performed with a CO_2-H_2O-fluid that raised solidus temperatures, and should only be applied were evidence is pointing towards an elevated solidus temperature (see "Al-in-hornblende barometer" below). Recalculating the intrusion pressures with the calibration for water-saturated systems by Schmidt (1992), the data of Vynhal et al. (1991) suggest that in monzogranite magmatic epidote appears between 0.32 and 0.40 GPa, still significantly lower than in average tonalite and granodiorite. In the case of the Appalachian monzogranite, this might be attributed to the monzogranitic bulk composition but possibly also to an elevated oxygen fugacity as epidotes are very Fe rich (up to ps_{100}). Also the Querigut intrusion in the French Pyrenees has epidote in monzogranite but neither in granodiorite nor in tonalite (Leterrier 1972; Roberts et al. 2000). Tulloch (1986) and Tulloch and Challis (2000) discuss many New Zealand epidote-bearing plutons, part of them also monzonitic, which were emplaced between 0.31 and 0.5 GPa. Tulloch (1986) underlines the corroded appearance of epidote where it is not enclosed in biotite in many of these plutons, and points out that substantial upraise of a partially crystallized magma that already contained epidote might lead to the relatively low pressure of solidification, which might then be mistaken as apparent low pressure of epidote crystallization. In fact, as will be discussed below, a discrepancy between epidote crystallization pressure and final intrusion pressure is limited in tonalite, as epidote crystallizes relatively late, but is more probable in granodiorite, and definitively possible towards trondhjemitic compositions where epidote becomes a liquidus phase.

Unusual bulk compositions. Magmatic epidote is also reported from bulk compositions outside the monzogranite to TTG range. Dacite and rhyodacite dikes with up to 71 wt% SiO_2 from the Front range of Colorado have idiomorphic epidote phenocrysts (ps_{63}), magmatic garnet and muscovite (Fig. 1c) in a very fine grained matrix (Evans and Vance 1987; Dawes and Evans 1991). The unusual phase assemblage, that also includes biotite and plagioclase, together with xenoliths in the magma, were employed to derive a magma chamber pressure of 0.72 to 1.2 GPa (Dawes and Evans 1991).

Magmatic epidote was also found in alkaline granite from the Bhela-Rajna complex, Orissa, India (Pattnaik 1996). Some of the intrusions in this complex contain riebeckite and riebeckite + epidote coexist in one rock type. It is likely that these magmas were relatively oxidized, leading to a potential expansion of the epidote-field in *P-T* space. On the SiO_2-poor end of the compositional spectrum, magmatic epidote is contained in an orbicular diorite and interstitially in a coarse grained gabbro. The shell structure of the orbicules in the orbicular diorite from the Grenville Front zone, Labrador (Owen 1991) is built by alternately enriched and depleted biotite, epidote, and magnetite (Fig. 1e). Idiomorphic epidote crystals are enclosed by plagioclase or hornblende, or occur in a vermicular texture. Owen (1991) suggested that the orbicules originated from supercooled water saturated globules within the dioritic magma, and that supercooling suppressed the crystallization of hornblende. The coarse grained garnet and rutile containing amphibole-plagioclase-clinopyroxene Saranga-gabbro, which is part of the lower crust of the Kohistan arc, Northern Pakistan, exhibits interstitial areas with vermicular intergrowth of quartz, albite, and epidote together with muscovite (P. Ulmer, pers. comm.; Fig. 1f). This interstitial intergrowth is interpreted as the crystallization product of the very last melt fraction of intermediate composition formed at high pressure probably under water rich conditions. However a detailed study is not available.

Epidote in subvolcanic dikes. This category is represented by two occurrences. The first one consists of ~20 dacitic to rhyodacitic dikes from Colorado, as already mentioned above (Evans and Vance 1987). The truly remarkable fact is that these dikes were emplaced and quenched at no more than 0.2 GPa and 250°C (conditions derived from the country rock), and thus idiomorphic epidote (ps_{59} to ps_{72}) was conserved in a holocrystalline, aphanytic groundmass (Dawes and Evans 1991). The dikes contain 65 to 75 vol% groundmass with phenocrysts of plagioclase, quartz, biotite, and epidote (1.5 to 1.8 vol%). This modal distribution provides evidence that at around 1.0 GPa, epidote crystallizes near the liquidus in dacitic compositions. The crystallization conditions of the magma before injection into the dikes (≥800°C, 0.72 to 1.2 GPa) were determined from 2-feldspar, garnet-plagioclase-biotite-muscovite, and garnet-hornblende equilibria, as well as from the Al-in-hornblende geobarometer (in this case, i.e., at elevated temperatures compared to the granitic solidus, the calibration of Johnson and Rutherford (1989) is appropriate). The second occurence is consituted by idiomorphic epidote (ps_{71} to ps_{81}) in a late lamproitic dike that intruded a tonalite of the southern Adamello, N-Italy (J. Blundy, pers. comm.). The intrusion pressure of the epidote-free tonalite host is around 0.3 ± 0.1 GPa (by Al-in-hornblende barometry, P.Ulmer, pers. comm.) which suggests that phenocrysts of epidote have been transported from significantly larger depths.

Epidote in high pressure migmatites and related dikes. Epidote-bearing partial melts from eclogites or high pressure granulites are observed in a few high pressure migmatitic terranes. These include migmatites derived from amphibole-bearing eclogites from the Rouergue complex in the French Massif Central (Nicollet et al. 1979; Fig. 1b), from the Niedewitz amphibolite massif in Poland (Puziewicz and Koepke 2001), the Eseka migmatites from Cameron (Nedelec et al. 1993), and migmatized xenoliths contained in the Cuzahuico granite in the Oaxaca terrane, Mexico (Elias-Herrera and Ortega-Gutierrez 2002). In all of these cases, epidote and/or zoisite occur in leucocratic bands, schlieren, or veins that are mostly constituted by quartz and oligoclase with some minor biotite present. These leucosomes are often trondhjemitic in composition and represent typical minimum melts from metabasalt at high pressure. Pressure estimates are 1.3 to 2.0 GPa for the granulites from the Rouergue complex, 1.3 GPa for the Niedewitz amphibolites, and 0.9 GPa for the Eseka migmatites. Furthermore, Franz and Smelik (1995) described pegmatites that are segregated leucosomes of eclogite melting in the Münchberg Massif, Germany. Franz and Smelik (1995) showed that these melts were formed during decompression from 2.5 to 1.0 GPa and have zoisite coexisting with clinozoisite (Fig. 1d) in a leuco-tonalitic bulk composition.

These high pressure melts have an enormous significance for the initial formation of melts during anatexis of mafic bulk compositions. They testify that epidote is involved in high pressure melting, and experimental stability relations in metabasalt (discussed in the last two sections of this chapter) support that epidote might indeed be critical for dehydration melting in the pressure range 1.0 to 3.0 GPa. The natural and experimental evidence on the involvement of epidote clearly demonstrates that metabasalt melting models uniquely based on amphibole are missing the critical phase responsible for the first occurrence of melt at elevated pressures.

## MELTING REACTIONS AND ZOISITE STABILITY AS DEDUCED FROM EXPERIMENTAL STUDIES IN Fe-FREE MODEL SYSTEMS

Experiments in simple systems outline the potential pressure-temperature and f_{O_2} limits of magmatic zoisite and/or epidote. The maximum temperature stability of at least 1182°C occurs in the CaO-Al_2O_3-SiO_2-H_2O system and a minimum melting temperature of 680°C, i.e., close to the granitic minimum in natural complex systems, is observed in the K_2O-CaO-Al_2O_3-SiO_2-H_2O system. Many melting reactions can be unambiguously defined in four or five component systems (e.g., in CaO-MgO-Al_2O_3-SiO_2-H_2O), which then serve as model reactions for natural systems. In the latter, melting reactions are often obscured by extensive solid solutions in, e.g., amphibole, clinopyroxene, garnet, and by little mass transformation achieved with epidote involving reactions due to relatively low modal abundances of epidote in most rock types (typically <10 vol%).

CaO-Al_2O_3-SiO_2-H_2O (CASH)

The phase diagram outlining the stability of zoisite + melt (Fig. 2) in the most simple system in which epidote-group minerals appear, is well defined in the low-pressure region to 2.5 GPa (Boettcher 1970) and along the wet solidus to 7.0 GPa (Poli and Schmidt 1998). The subsolidus reaction limiting the low pressure stability of zoisite + quartz (Fig. 2a, Nitsch and Winkler 1965; Newton 1966) is

$$\text{zoisite} + \text{quartz} = \text{anorthite} + \text{grossular} + H_2O \tag{1}$$
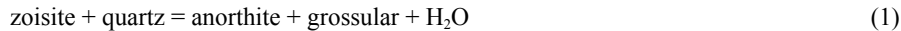
According to Boettcher (1970), this reaction intersects the appropriate eutectic H_2O-saturated solidus reaction near 0.9 GPa, 775°C (Fig. 2); the eutectic melting reaction at lower pressure being

$$\text{anorthite} + \text{grossular} + \text{quartz} + H_2O = \text{melt} \tag{2}$$
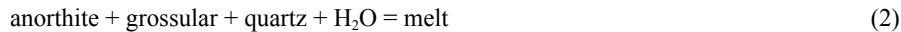
and at higher pressure, i.e., at pressures above Reaction (1),

$$\text{zoisite} + \text{anorthite} + \text{quartz} + H_2O = \text{melt} \tag{3}$$

The system CASH, serving also as a model for metamorphism and melting in some calc-alkaline assemblages, apparently generates eutectic melt compositions (at SiO_2- and H_2O-saturated conditions) projecting slightly to the SiO_2-side of the join anorthite - zoisite (Boettcher 1970, Reaction 13c) at crustal conditions. At pressures above 1.1 GPa, anorthite + H_2O are unstable and

$$\text{zoisite} + \text{kyanite} + \text{quartz/coesite} + H_2O = \text{melt} \tag{4}$$
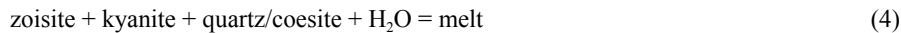
is the eutectic melting reaction. This reaction remains valid until the maximum pressure stability of zoisite is reached at 7 GPa (Poli and Schmidt 1998) where melting occurs at 1070°C. The highest temperature for zoisite was determined to 1180°C at 2.6 GPa by Boettcher (1970), the final breakdown reaction results in anorthite + grossular + corundum + melt (Fig. 2a). Between this reaction and the intersection of the zoisite pressure stability with the wet solidus
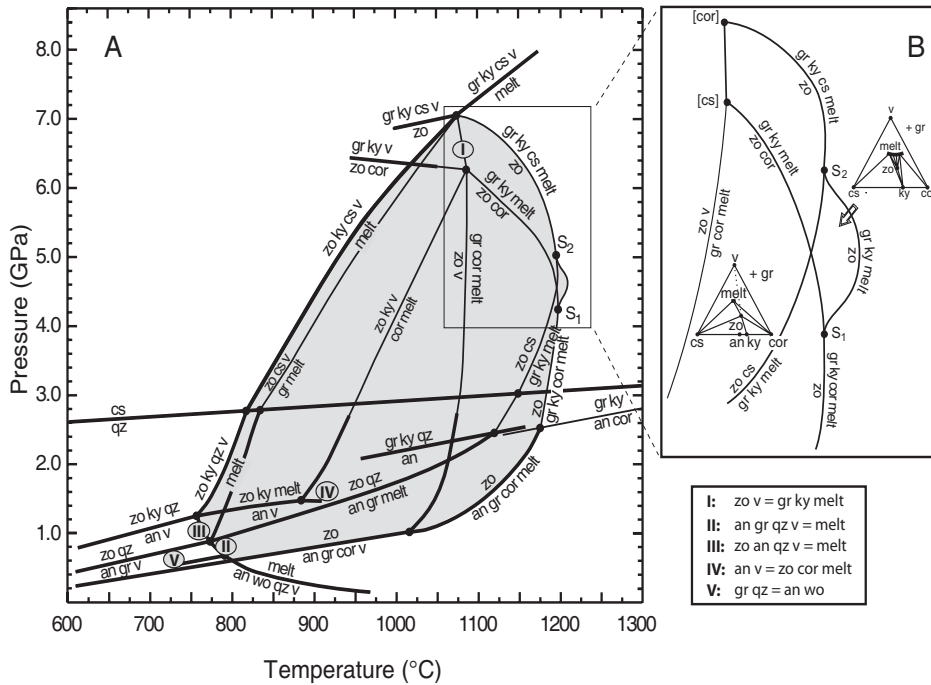
Figure 2. (a) Zoisite + melt stability field (grey) in CASH; thick lines are experimentally determined, others result from Schreinemakers' analysis and are uncertain in temperature. (b) Detail of the singular points in (a) where both corundum-saturated and coesite-saturated melts become possible. Abbreviations see Figure 1.

in CASH at 7 GPa, the limit of magmatic zoisite was drawn fairly conservative in Figure 2, as this high pressure - high temperature portion remains experimentally undetermined. Reactions delimiting the magmatic zoisite region (thin lines) under these conditions are derived from Schreinemakers analysis.

The occurrence of the H_2O-conserving fluid-absent melting reactions

$$\text{zoisite} = \text{grossular} + \text{kyanite} + \text{corundum} + \text{melt} \tag{5}$$
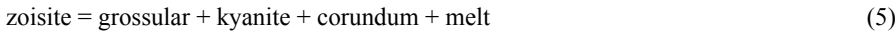
at pressures above the equilibrium anorthite + corundum = grossular + kyanite (see Fig. 2), and

$$\text{zoisite} = \text{grossular} + \text{kyanite} + \text{coesite} + \text{melt} \tag{6}$$

at ca. 7 GPa implies that the terminal zoisite breakdown with temperature produces Al_2O_3-saturated melts at low pressures but also SiO_2-saturated melts at higher pressures. This can be easily explained assuming that singularities occur along the terminal zoisite melting reactions (Fig. 2b). The location of such singular points is unknown and the width of the two phase zoisite + melt field defined by Schreinemakers' rules (chemography on the right in Fig. 2b) is purely speculative. Nevertheless it is appealing to formulate a degenerate reaction as the extreme temperature limit for zoisite:

$$\text{zoisite} = \text{grossular} + \text{kyanite} + \text{melt} \tag{7}$$

K$_2$O-CaO-Al$_2$O$_3$-SiO$_2$-H$_2$O (KCASH)

In the KCASH-system the relatively high temperature for minimum melting in CASH is reduced by about 100°C and consequently, the temperature interval of zoisite + melt is shifted to lower temperature (Fig. 3). In KCASH, the eutectic melting reaction at pressures below the zoisite + muscovite + quartz stability is (Johannes 1980; Schliestedt and Johannes 1984)

$$\text{anorthite + muscovite + orthoclase + quartz + H}_2\text{O = melt} \tag{8}$$
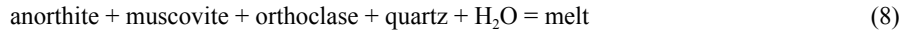
and above 0.8 GPa at 680°C it is

$$\text{zoisite + muscovite + orthoclase + quartz + H}_2\text{O = melt} \tag{9}$$

The latter reaction is studied experimentally to 2 GPa, but phase relations at higher pressure are unknown in KCASH. Reaction (9) represents an eutectic minimum melting reaction close to that in natural systems. Additional components such as Na$_2$O causes involvement of plagioclase on the left hand side of Reaction (9), and, together with Fe- incorporation in zoisite and muscovite, slightly lowers the melting temperature.
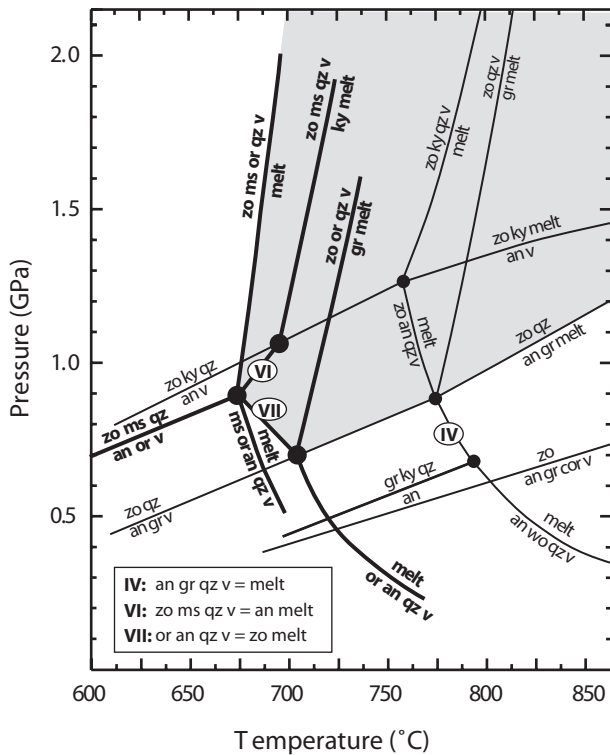
Figure 3. Zoisite-melting reactions in CASH and KCASH for pressures to 2 GPa; bold lines from Schliestedt and Johannes (1984) with some reactions added through Schreinemakers' analysis. The grey area denotes the field of possible coexistence of zoisite + quartz + melt. Abbreviations see Figure 1.

CaO-MgO-Al$_2$O$_3$-SiO$_2$-H$_2$O (CMASH)

Addition of MgO to CASH provides a model system appropriate to the melting of mafic bulk compositions (e.g., Ellis and Thompson 1986; Thompson and Ellis 1994). Eutectic melting in this system (Fig. 4) involves zoisite only at pressures above the breakdown of anorthite + H$_2$O to zoisite + kyanite + quartz. From the intersection of this latter reaction with
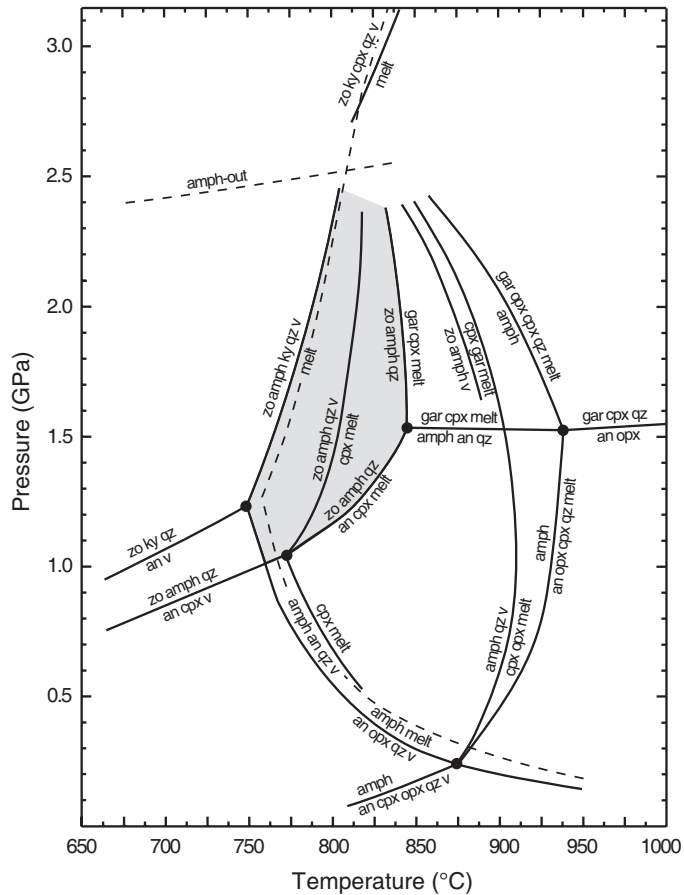
Figure 4. Amphibole + zoisite + quartz reactions (grey area) and amphibole stability in CMASH (after Thompson and Ellis 1994 and Quirion and Jenkins 1998). Stippled line: CASH solidus for comparison. Note that a large number of reactions focus into an area near 2.5 GPa, 800°C and at present, the experimental data are insufficient to select between a large number of possible topologies (e.g., Thompson and Ellis 1994). Nevertheless, zoisite exceeds amphibole in pressure stability as depicted by the eutectic solidus reaction at >2.8 GPa. Abbreviations see Figure 1.

the solidus to the pressure stability limit of amphibole, the eutectic melting reaction is then

$$\text{zoisite} + \text{amphibole} + \text{kyanite} + \text{quartz} + H_2O = \text{melt} \tag{10}$$
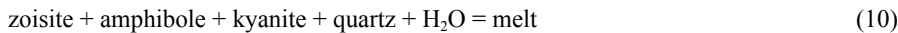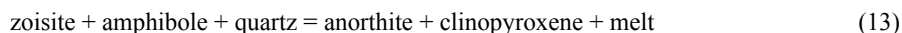
In bulk compositions representative of mafic rocks, the limiting assemblage for zoisite stability is zoisite + amphibole + quartz. Fluid-saturated melting in such compositions takes place at 770 to 820°C when the reaction

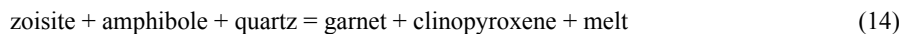$$\text{zoisite} + \text{amphibole} + \text{quartz} = \text{anorthite} + \text{clinopyroxene} + H_2O \tag{11}$$
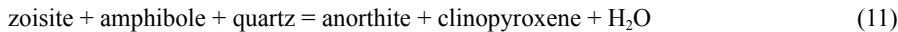
(Quirion and Jenkins 1998) encounters the wet solidus at 1.0 GPa, 780°C (Fig. 4) and transforms into the peritectic melting reaction

$$\text{zoisite} + \text{amphibole} + \text{quartz} + H_2O = \text{clinopyroxene} + \text{melt} \tag{12}$$

valid at moderate pressures of 1.0 to 1.5 GPa. The upper temperature stability and the fluid-absent solidus in systems which have amphibole + quartz in excess relative to zoisite and zoisite-excess relative to fluid is then defined by

$$\text{zoisite} + \text{amphibole} + \text{quartz} = \text{anorthite} + \text{clinopyroxene} + \text{melt} \tag{13}$$

which transforms into

$$\text{zoisite} + \text{amphibole} + \text{quartz} = \text{garnet} + \text{clinopyroxene} + \text{melt} \tag{14}$$

above 1.5 GPa. In quartz + kyanite saturated mafic model compositions, fluid saturated eutectic melting through Reaction (10) takes place about 40°C lower, but the minimum pressure for zoisite + melt in such systems is raised by 0.3 GPa to about 1.2 GPa (see Fig. 4).

The upper pressure limit of amphibole + zoisite + quartz is delimited through amphibole breakdown. However, reactions in the region around 2.5 GPa, 800°C are extremely complicate and at present it is not possible to decide which of the many possible topologies is the stable one as within a narrow region of 0.3 GPa and 100°C at least 10 phases occur in this five component system. A number of possible solutions were presented by Thompson and Ellis (1994) who also point out, that further complexity arises from talc that becomes stable instead of orthopyroxene + quartz in the region of interest. Nevertheless, from the experiments in CMASH (Thompson and Ellis 1994) it is certain that the zoisite pressure stability exceeds amphibole stability and that the melting reaction above 2.5 GPa will contain zoisite but not amphibole (or talc) as a hydrous phase. As discussed in Poli and Schmidt (2004), this is confirmed by experiments in more complex systems (KCMASH, Hermann 2002), natural systems (Poli and Schmidt 1997; Schmidt and Poli 1998), and from natural eclogites (Enami et al. 2004).

## K_2O-CaO-MgO-Al_2O_3-SiO_2-H_2O (KCMASH)

Reactions in KCMASH were studied by Hoschek (1990) at 1.0 to 2.1 GPa and by Hermann (2002) at 2.0 to 4.5 GPa. With respect to KCASH, minimum melting temperatures remain almost identical (Fig. 5) at pressures up to 2.5 GPa but melting reactions now involve tremolite$_{ss}$ and phlogopite$_{ss}$. In this system, the orthoclase absent melting reaction between 1.4 and 2.1 GPa (Fig. 5) produces zoisite (Hoschek 1990), whereas in all of the previous systems, zoisite is consumed by melting reactions. Hermann (2002) found zoisite + amphibole + quartz to coexist with melt just above the solidus to 2.5 GPa in a KCMASH system containing traces of Fe and Ti and in part being enriched in REE. In this particular bulk composition, zoisite (containing minor REE-contents) is delimited to about 800°C, which is 20 to 50°C above the amphibole melting temperature (at pressures of 2.0 to 2.5 GPa). However, the interpretation of phase relations in this latter study is complicated by the possible occurrence of non-quenchable K-rich melts and by the persistence of allanite + melt to pressures of 3 GPa and temperatures to 850°C.

EPIDOTE IN FLUID-SATURATED MAGMAS

In this contribution we deal only with H_2O fluids, as the amount of CO_2 soluble in silicic magmas at pressures typical for crustal settings is negligible. As a consequence a "fluid" is always intended here as an aqueous fluid with some silicates dissolved in it.

The wet solidus of tonalite and granodiorite

The wet (saturated in an aqueous fluid) solidus of tonalite was determined experimentally by Piwinskii (1968) at 0.1 to 0.3 GPa, by Lambert and Wyllie (1974) at 1.0 to 3.0 GPa, and slightly modified by Schmidt (1993). The wet liquidus of tonalite (Fig. 6) was determined by Eggler (1972) at 0.05 to 0.63 GPa, and by Allen and Boettcher (1983) at 1.0 to 2.5 GPa.
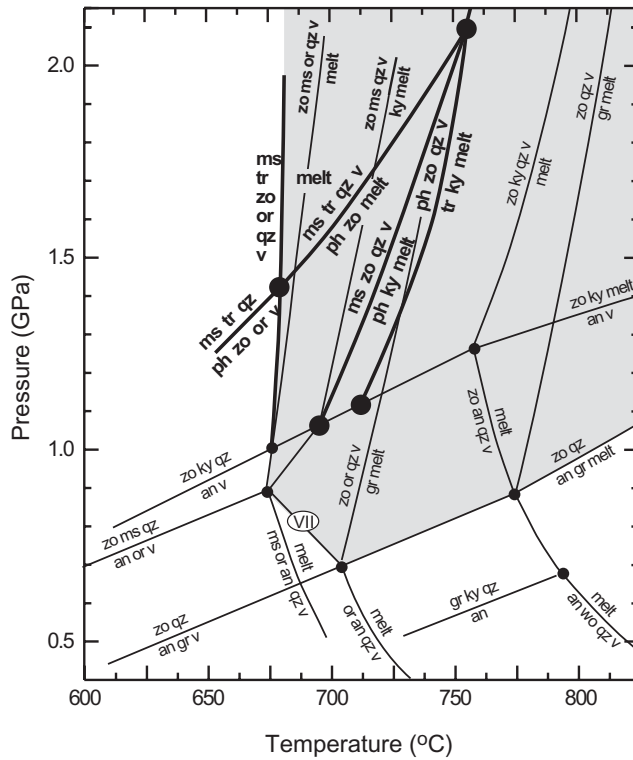
Figure 5. Zoisite-melting reactions from Hoschek (1990) in KCMASH for pressures to 2 GPa; thin lines as in Figure 2, grey area denotes possible coexistence of zo + qz + melt. Abbreviations see Figure 1, for reaction VII see Fig. 3.

Most of the reported experiments on tonalitic compositions are generally consistent, however, because similar but not identical bulk compositions were investigated, small differences are to be expected. In addition, many of the earlier experiments have problems with Fe-loss to the capsule material and uncontrolled f_{O_2} (see discussions in Lambert and Wyllie 1974 and Allen and Boettcher 1983), and this resulted in large uncertainties on the phase relations of Fe-Mg phases.

Experiments on the granodiorite solidus are limited to 1.0 GPa. Piwinskii (1968, 1973) determined the solidus of natural amphibole bearing and amphibole free granodiorites at 0.1 to 1.0 GPa to be about 20°C lower than for a tonalite. Naney (1983) found a solidus at 0.2 and 0.8 GPa again 20°C lower for a synthetic granodiorite.

Epidote-out in tonalite with increasing pressure

The wet solidus for tonalite intersects the subsolidus epidote dehydration reaction near 0.5 GPa, 660°C. Mass balance calculations (Schmidt 1993), using mineral compositions obtained in the close vicinity of the fluid-saturated solidus, suggest that the subsolidus epidote dehydration reaction appropriate to tonalite bulk compositions is
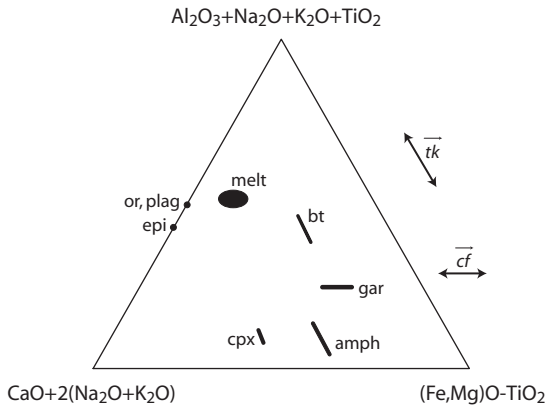
epidote + biotite + quartz =
$$\text{hornblende + K-feldspar + plagioclase + magnetite + H}_2\text{O} \qquad (15)$$
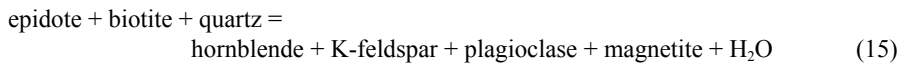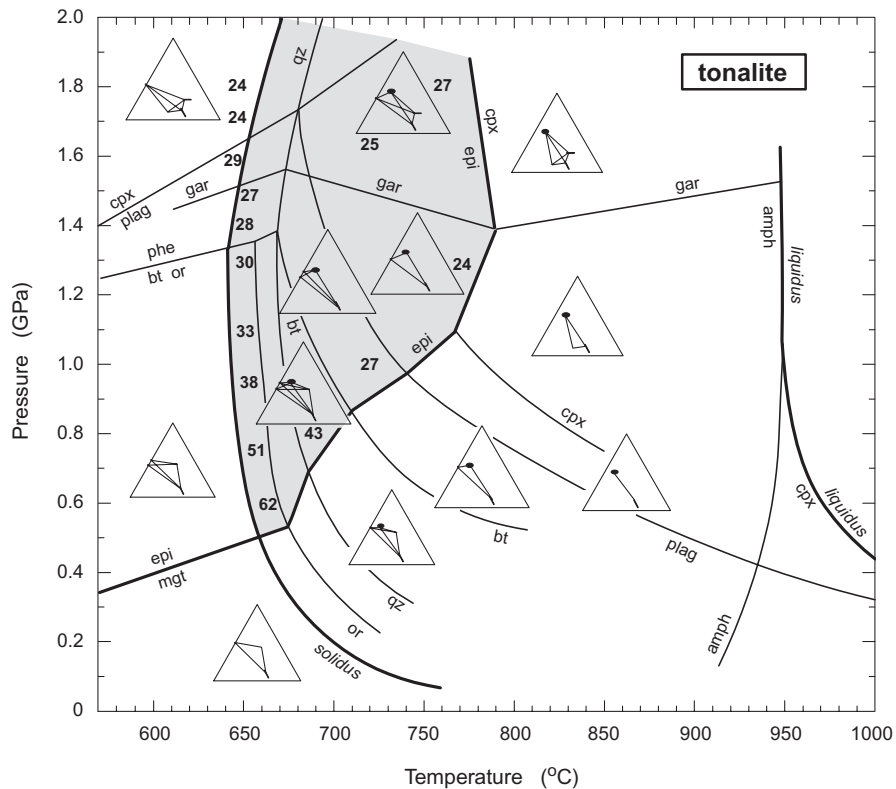
Figure 6. Pressure-temperature diagram for the magmatic domain of epidote in tonalite (grey field) to 1.9 GPa. Triangles are ACF-deluxe projections after Thompson (1982, see Fig. 7) and give tielines for coexisting phases in the different stability fields (projected from quartz). Numbers are experimental epidote compositions in terms of Fe pfu; after Schmidt and Thompson (1996). Abbreviations see Figure 1.

the left hand side corresponding to the higher pressure and lower temperature side (Fig. 6). Figure 6 gives *P-T* conditions of the delimiting reactions in the tonalite-H_2O system (after Schmidt and Thompson 1996) and draws assemblages for each field in the ACF-deluxe projection of Thompson (1982, Fig. 7). As concluded from experiments (Schmidt 1993) and as indicated by field evidence (Hammarstrom and Zen 1992; see also Ishihara 1981), magnetite is significantly more abundant in epidote-free than in epidote-bearing granitoids. This was also reported by Drinkwater et al. (1991) for the Coast Plutonic-Metamorphic Complex near Juneau, Alaska, and indicates that at low pressure, magnetite is the principal phase containing Fe^{3+} at temperatures above epidote stability. Between 0.5 to 0.9 GPa, melting reactions involving similar phases as in Reaction (15) occur at temperatures above the fluid-saturated tonalite solidus and Schmidt and Thompson (1996) suggested that, in this pressure range, the reaction delimiting epidote stability in tonalite melts with excess H_2O is

epidote + biotite + (quartz$_{melt}$) + H_2O =
 hornblende + (K-feldspar$_{melt}$) + plagioclase + magnetite + melt   (16)

Quartzofeldspathic components are written in parentheses because at fluid-saturated conditions these minerals sequentially melt at temperatures not much higher than the fluid-

Al$_2$O$_3$+Na$_2$O+K$_2$O+TiO$_2$

melt

or, plag
epi

$\overrightarrow{tk}$

bt

$\overleftrightarrow{cf}$

gar

cpx amph

CaO+2(Na$_2$O+K$_2$O) (Fe,Mg)O-TiO$_2$

Figure 7. ACF-deluxe diagram after Thomson (1982, see Fig. 6). **tk**: *tschermak*-exchange vector (Mg$_{-1}$Si$_{-1}$Al^{VI}Al^{IV}), *cf.* Ca$_{-1}$Fe, other abbreviations see Figure 1.

saturated solidus. More difficult to ascertain is the nature of the multisystem epidote-melting reactions between biotite-out (ca. 0.9 GPa, 720°C), plagioclase-out (ca. 1.0 GPa, 740°C), and clinopyroxene-in (ca. 1.1 GPa, 770°C). In fact discontinuous Reaction (16) removes biotite from the tonalite bulk composition such that epidote would be stabilized in more mafic (quartz-diorite to gabbro) compositions. The clinopyroxene-in reaction in tonalite-H$_2$O melts intersects the epidote-melting reaction near 1.1 GPa, 770°C (Fig. 6). Melting of epidote at pressures above the clinopyroxene- in reaction is directly related to the appearance of clinopyroxene. With increasing temperature, modal increase in clinopyroxene is directly proportional to epidote decrease. The appropriate multisystem discontinuous reaction can be considered as

epidote + hornblende + H$_2$O = clinopyroxene + melt (17)
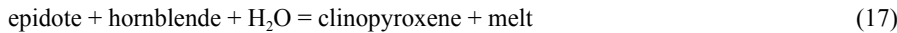
This reaction is analogous to the peritectic melting Reaction (12) in the model system CMASH (Thompson and Ellis 1994; Fig. 5), only that in wet tonalite quartz disappears at about 30°C above the solidus. At pressures along the epidote melting curve for H$_2$O-saturated tonalite, amphibole has changed from the high temperature side (Rxn. 16) to the low temperature side (Rxn. 17) when clinopyroxene appears.

In water-saturated tonalite, garnet is formed at pressures ranging from 1.4 to 1.6 GPa through a series of different reactions from 600 to 950°C. The maximum temperature stability of 790°C of magmatic epidote in tonalite is reached near 1.4 GPa, i.e., at the intersection with the mostly pressure dependent garnet-in reaction. This maximum temperature results from the change in Clapeyron slopes (dP/dT) of the epidote-melting reactions from positive at low pressure, to negative at higher pressure when garnet + clinopyroxene become a product of epidote-melting (Fig. 6) through the reaction

epidote + amphibole + H$_2$O = garnet + clinopyroxene + melt (18)
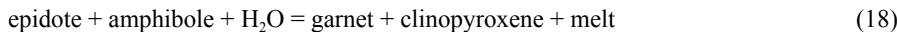
that is analogous to Reaction (13) in the simple CMASH system. The magmatic domain of epidote in tonalite ends, when the epidote delimiting reaction at high pressure intersects the solidus at 3.2 GPa. This is about 0.7 GPa higher than the amphibole breakdown reaction (Poli and Schmidt 1995). The implications of the relative pressure stabilities of epidote and amphibole are discussed in the section on melting of zoisite bearing eclogites.

Interpreting textural features of epidote-bearing tonalites. The reactions derived from experimental results can be applied to the following petrographic observation. The epidote-melting Reaction (16) in the range 0.5 to 0.9 GPa for tonalite-H$_2$O (f_{O_2} = NNO) may also

be considered, in reverse, as the crystallization of epidote + biotite contemporaneous with peritectic resorption of some hornblende by the melt. Cornelius (1915) and Hammarstrom and Zen (1986) observed such crystallization textures in natural tonalite. At pressures below 0.9 GPa, biotite begins to crystallize before epidote (Fig. 6). Hornblende is consumed by reaction with the melt (Rxn. 16), and its modal decrease should be mirrored by proportional increase in modes of epidote and biotite. Consequently, the local resorption of hornblende through the appearance of epidote and growth of biotite does not imply a general destabilization of hornblende in the tonalite melt (Fig. 6), but a decrease in modal abundance.

Epidote-out in granodiorite and granite

Experiments by Naney (1983) first demonstrated that epidote is stable above the solidus in granite and granodiorite (Fig. 8). At 0.8 GPa, synthetic granodiorite was found to crystallize epidote up to 700°C under fluid-saturated conditions (>12 wt% H_2O). Synthetic granite has epidote present to about 610°C, i.e., 20°C above its solidus. At H_2O-undersaturated conditions, the epidote-out reaction was lowered by approximately 20°C. In experiments at 0.2 GPa, epidote did not occur (Fig. 8). Schmidt and Thompson (1996) also performed some experiments on a granodiorite composition. In the range from 0.7 to 1.0 GPa the assemblage hornblende + plagioclase + biotite + melt is the same in granodiorite and tonalite, and the locations of the epidote melting reactions are also almost identical. In this pressure range, a reaction similar to that in tonalite (Rxn. 16) is probable for the granodiorite. At 1.0 to 1.5 GPa, the stability limit
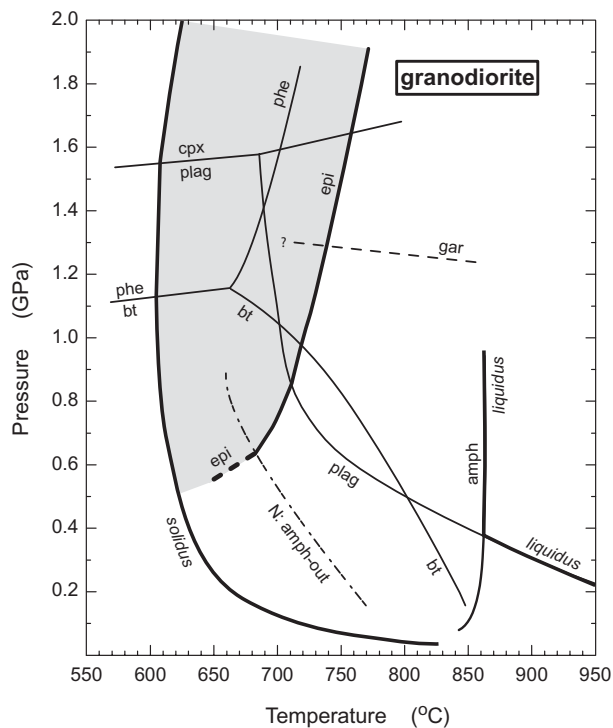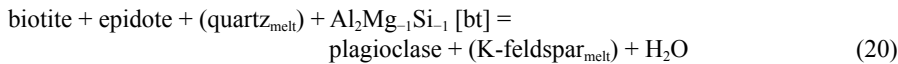

Figure 8. Pressure-temperature diagram for the magmatic domain of epidote in granodiorite (grey field) to 1.8 GPa. Compiled from experiments of Naney (1983) and Schmidt and Thompson (1996). Note that in the granodiorite of Naney (N), amphibole reacts out before the magma reaches the solidus. Abbreviations see Figure 1.

of epidote is about 30°C lower in granodiorite than in tonalite. However, the experimental data are not sufficient to constrain the epidote melting reactions in granodiorite at high pressures under H$_2$O-saturated conditions. Differently to tonalite, clinopyroxene does not appear to 1.8 GPa, but garnet appears at and above 1.3 GPa. It is above 1.8 GPa, that granodiorite again contains the same assemblage as tonalite, i.e., hornblende + garnet + clinopyroxene ± epidote + melt. Thus it is expected that around 1.8 GPa the epidote-melting reaction in the granodiorite will also change to a negative slope in *P-T* space. At low temperature, the experiments of Naney (1983) on a synthetic granodiorite composition indicate that hornblende is not stable below approximately 680°C (stippled line marked "N" in Fig. 8). This would mean that at low temperature there are fundamental differences in the fluid-saturated melting reactions in granodiorite and tonalite (at least for Naney's synthetic granodiorite). In tonalite, amphibole forms part of the subsolidus assemblage, whereas in Naney's granodiorite, amphibole is only generated above the solidus (both at 0.2 and 0.8 GPa) by reactions involving biotite + feldspar + quartz. The experiments by Piwinskii (1968) and Schmidt and Thompson (1996), however, showed amphibole to be stable down to subsolidus temperatures in several granodiorite compositions, pointing towards a strong compositional dependence of amphibole-occurrence when moving towards more granitic compositions. Because of the paucity of experiments near the fluid-saturated granodiorite solidus between 0.2 and 0.8 GPa, it is not yet possible to identify the precise epidote melting reaction in granodiorite in this pressure range.
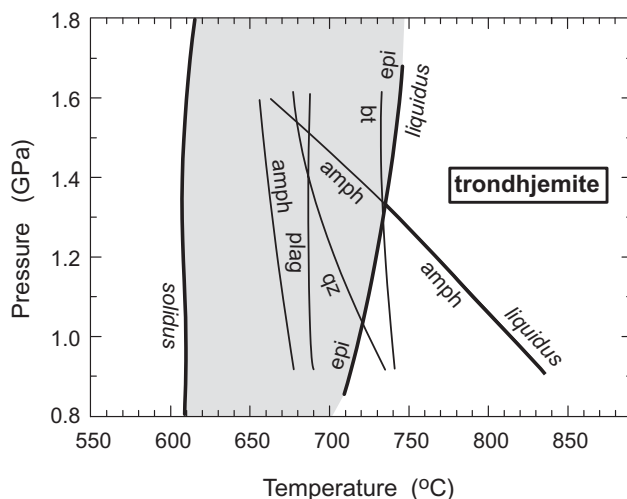
Epidote-out in trondhjemite

Johnston and Wyllie (1988) investigated experimentally an Archean trondhjemite at 1.5 GPa. Under water saturated conditions, epidote + biotite were observed to be the liquidus phases (approximately 740°C) and amphibole-only crystallized in a narrow field 100 to 130°C below the liquidus. At moderately water undersaturated conditions (>9 wt% H$_2$O), epidote remained present up to 775°C. Van der Laan and Wyllie (1992) studied the same trondhjemite at 1.0 GPa, the experiments yielded epidote to 700°C at fluid-saturated conditions (>10 wt% H$_2$O, solidus at 675°C). Both studies presented phase relationships in isobaric sections with varying temperature and water content. No particular emphasis was placed on epidote stability in these calc-alkaline magmatic rock compositions, and oxygen fugacity was left to what the experimental apparatus might or might not impose. The results of these two studies can be assembled into a coherent *P-T* diagram (Fig. 9) outlining the stability of magmatic epidote in trondhjemitic composition from about 0.9 to 1.6 GPa. Interestingly, the results of Naney (1983) at 0.8 GPa on a synthetic granodioritic composition are also coherent with the above results of Wyllie and coworkers. The crystallization temperatures of epidote in trondhjemite and granodiorite magmas are almost identical and in the granodiorite used by Naney (1983), amphibole dissolves through a peritectic reaction before the magma reaches its solidus temperature. In the absence of amphibole, the most likely reaction for the melting out of epidote in granodiorite and trondhjemite is the amphibole-absent continuous reaction

$$\text{biotite} + \text{epidote} + (\text{quartz}_{melt}) + \text{Al}_2\text{Mg}_{-1}\text{Si}_{-1} \, [bt] =$$
$$\text{plagioclase} + (\text{K-feldspar}_{melt}) + \text{H}_2\text{O} \qquad (20)$$

which forms plagioclase from epidote by consuming Al$_2$Mg$_{-1}$Si$_{-1}$ (*tschermak*-exchange) in biotite. This reaction also acts in the subsolidus region, where quartz + feldspars + epidote buffer *tschermak*-exchange in biotite. In any particular multisystem (e.g., KCMASH as in Rxn. 16), this amphibole-absent continuous Reaction (20) will occur at higher pressure and lower temperature than the discontinuous Reaction (16) in tonalite. Field evidence indicates that below 0.7 GPa epidote is less stable in trondhjemite than in granodiorite than in tonalite because in many intrusions epidote bearing tonalite is found adjacent to epidote free granodiorite (e.g., Bergell, Moticska 1970) or epidote bearing tonalite and granodiorite adjacent to epidote free trondhjemites (Archean Minto Block, Canada, Bedard 2003).

Figure 9. Pressure-temperature diagram for the magmatic domain of epidote in trondhjemite between 0.9 and 1.6 GPa (grey field). Compiled from experiments of Johnston and Wyllie (1988) and Van der Laan and Wyllie (1992). Note that epidote is the liquidus phase above 1.3 GPa. The experiments on granodiorite at 0.8 GPa of (Naney 1983, Fig.8) would also be compatible with the experiments at 1.0 GPa presented here. Abbreviations see Figure 1.

Epidote-out in dioritic and gabbroic compositions

There is no apparent compositional reason, why epidote should be less stable in diorite or basalt than in tonalite. Indeed, subsolidus experiments (Poli 1993) show a slightly lower pressure in MORB than in tonalite necessary for epidote stability in the subsolidus. Nevertheless, to our knowledge, there is only one diorite (Owen 1991) described, that contains magmatic epidote, in addition, this diorite is orbicular and very heterogeneous. There is also the Saranga-gabbro with magmatic epidote (from the Kohistan arc, see above; Ulmer pers. comm.), but epidote only crystallized in a very late stage from a quartz + albite + muscovite saturated interstitial melt which had an intermediate or even granodioritic bulk composition. Apart from these two exceptions, to our knowledge, epidote is not reported from other dioritic or gabbroic intrusions. However, this is likely to be a mere consequence of the high temperature of solidification of such intrusions (typically 800°C), which exceeds the stability field of epidote, and inadequate *P-T* trajectories during the crystallization history. Only a few experiments provide constraints on the magmatic stability field for epidote in mafic rocks. Some experiments on metabasalt yielded zoisite + melt + amphibole + garnet + clinopyroxene at 2.0 to 2.5 GPa, 700 to 750°C (Pawley and Holloway 1993; Poli and Schmidt 1995). These authors did not report supersolidus experiments at lower pressure. In a gabbroic composition, zoisite was found to coexist with melt in five experiments in the range 1.5 to 2.0 GPa, 685 to 775°C (Lambert and Wyllie 1972).

Epidote-out in granites and granitic dikes

With decreasing CaO-content, normative anorthite component, and anorthite activity in plagioclase and melt, the epidote stability field retracts to higher pressure. The experiments of Naney (1983) show an extremely narrow (20°C) epidote + melt field in granite at 0.8 GPa, which evidently represents the minimum pressure for magmatic epidote in granites. Epidote does occur in some high pressure granitic dikes but, to our knowledge, has not been reported in massive granites.

The temperature stability of epidote: the role of anorthite component in magmas

The epidote-melting reactions are located at similar *P-T* conditions in H_2O-saturated experiments on tonalite, granodiorite, and trondhjemite (Fig. 10). Nevertheless, a systematic variation of epidote-stability with bulk normative anorthite for the investigated tonalite (an^{CIPW} = 27 wt%), granodiorites (an^{CIPW} = 22 to 18 wt%), trondhjemite (an^{CIPW} = 14 wt%) and granite (an^{CIPW} = 7 wt%) is evident (Fig. 10). On the very anorthite-normative end is an anorthosite (an^{CIPW} = 41 wt%), which was investigated by Selbekk and Skjerlie (2002). This composition has plagioclase with an_{70} to an_{84} and crystallized zoisite with 0.13 Fe pfu. The high normative anorthite contents, anorthite-rich plagioclase compositions, and Fe-poor zoisite cause an extension of the magmatic epidote$_{ss}$ stability field to extreme temperatures (but still far below temperatures in the CASH system), which cannot be expected in most crustal rock compositions and in particular not in the TTG series.

The correlation of epidote stability with normative anorthite content may be understood if we accept that normative anorthite contents grossly correlates with anorthite activity in plagioclase and melt. Considering subsolidus and melting reactions such as Reactions (12) and (13), decreasing anorthite activities in plagioclase (and melt) shift these reactions to lower temperature and thus cause the magmatic epidote field to shrink with decreasing
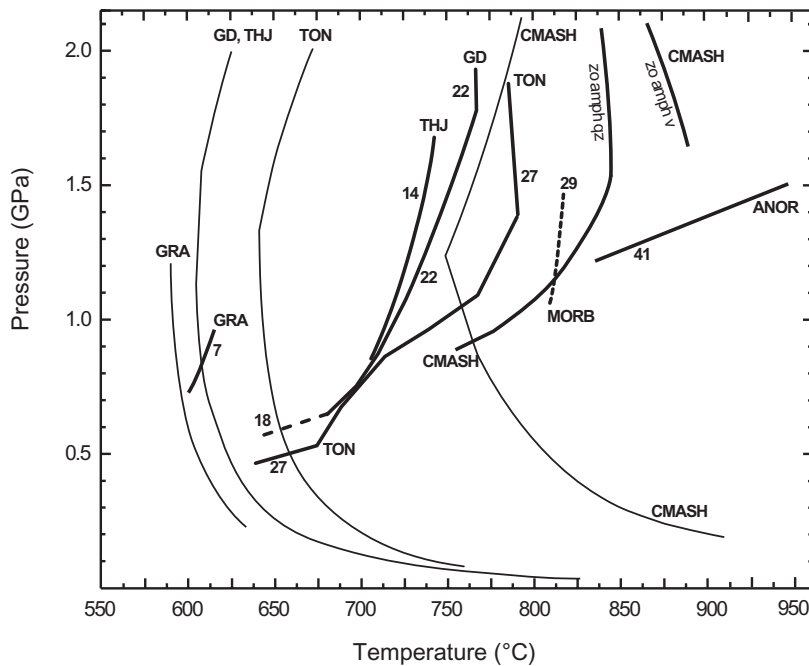
Figure 10. Solidi (thin lines) and reactions delimiting magmatic epidote stability (bold lines) at H_2O-saturated conditions, except for MORB. There is a clear correlation between the temperature of the epidote-out melting reaction and the normative anorthite content of the bulk composition (numbers are CIPW-normative anorthite contents in wt%). Note that from 1.0 to 1.8 GPa a different granodiorite was used than below 1 GPa. The solidus for trondhjemite is within error identical to that of granodiorite. ANOR: anorthosite, GD: granodiorite, GRA: granite, MORB: mid-ocean ridge basalt, THJ: trondhjemite, TON: tonalite, CMASH: synthetic system CaO-MgO-Al_2O_3-SiO_2-H_2O. Epidote$_{ss}$ is stable towards the low temperature side of each bold line. For details see Figures 4, 6, 8, and 9.

anorthite activity. However, this qualitative approach has to be cautioned: in a natural granite-trondhjemite-granodiorite-tonalite-diorite-gabbro series, not only normative anorthite content decreases with SiO_2-content but also a number of other compositional parameters vary systematically (which for example lead to a decrease of hornblende content). Thus, synthetic systems must not necessarily comply to the normative anorthite content scheme. The synthetic greywacke used by Singh and Johannes (1996b) with $an^{CIPW} = 23$ wt% has epidote slightly more stable than the tonalite with $an^{CIPW} = 27$ wt%. Whether this is because of variation of compositional parameters other than normative anorthite, or to a slight expansion of the epidote field due to H_2O-undersaturated conditions, or due to an unbuffered and possibly higher oxygen fugacity than NNO in the experiments by Singh and Johannes (1996b), cannot be decided without additional experiments.

Below 0.8 GPa, the nature of the epidote-out reaction will depend on the stability of amphibole in the various rock compositions. In trondhjemite (Johnston and Wyllie 1988; van der Laan and Wyllie 1992) and in granodiorite of Naney (1983) ($an^{CIPW} = 18$ wt%), amphibole is not stable at the H_2O-saturated solidus. In contrast, in Piwinskii's (1968) and Schmidt and Thompson's (1996) granodiorite ($an^{CIPW} = 16$ wt% and 22 wt%, respectively) amphibole appears at the fluid-saturated solidus. In the presence of amphibole, the epidote-out reactions in granodiorite will be similar to that discussed above for tonalite.

How likely is epidote fractionation?

Modal abundances of epidote in tonalite are generally low near the epidote-out reactions (1 to 5 vol%, Schmidt and Thompson 1996), but increase to 11 to 14 vol% near the solidus (Fig. 12 in Schmidt 1993) The amount of melt is in the order of 60 to 70 vol% when epidote starts to crystallize. Thus, fractionation of epidote in tonalite would be possible at water saturated conditions, however, epidote contents are low and a significant effect of epidote fractionation on bulk composition appears to be unlikely. By contrast, fractionation of LREE enriched epidote or allanite may modify the trace element patterns in specific cases. The possibility of REE-fractionation through fractionation of early crystallizing epidote was discussed by Johnston and Wyllie (1988). In trondhjemite, the amphibole crystallization field is retracted with respect to tonalite and granodiorite and epidote becomes the liquidus phase at 1.3 GPa, thus improving the chances of epidote to be fractionated.

## THE ROLE OF OXYGEN FUGACITY AND Fe^{3+} IN CONTROLLING EPIDOTE IN MAGMATIC SYSTEMS

Oxygen fugacity in granitoid bodies

Intermediate (calc-alkaline) granitoid magmas mostly crystallize quartz, magnetite, and titanite. Quartz + magnetite define the lower limit of f_{O_2} close to the quartz-fayalite-magnetite (QFM) buffer. An upper limit of oxidation is provided by the presence of ilmenite in many intermediate granitoids (Ishihara 1977, 1981; Murata and Itaya 1987; Hammarstrom and Zen 1992), which defines an f_{O_2} below the magnetite-ilmenite-rutile buffer (MIR). Wones (1989) showed that the assemblage quartz + magnetite + titanite requires f_{O_2} slightly above QFM. Thus, for most granitoid intrusions, the intrinsic oxidation conditions are experimentally reproduced by the NNO-buffer and the results from these experiments are therefore directly applicable to most natural tonalite intrusions. However, more oxidizing conditions might occur in some plutons (documented by Fe-Ti-oxides, or in extreme cases by the presence of hematite, e.g., Ishihara 1981). While f_{O_2} conditions are not likely to fluctuate extremely during magma crystallization, the f_{O_2} may step from buffer to buffer as particular Fe^{3+}-bearing minerals are replaced by others, e.g., magnetite by epidote (Rxn. 15 and references above), or in some extreme cases by acmite or riebeckite (magmatic riebeckite + epidote is reported from

Pattnaik 1996). Alternatively, f_{O_2} could change when the fluid composition changes drastically (physically by phase separation, or chemically through C-O-H-S reactions) during late stage crystallization. This latter effect is most likely to happen at the borders of intrusions where interaction with the surrounding country rock is facilitated.

Oxygen fugacity, Fe oxidation state and the stability field of magmatic epidote

Experiments on the CaO-FeO-Al$_2$O$_3$-SiO$_2$-H$_2$O-O$_2$ system at subsolidus temperatures have been performed by Holdaway (1972) and by Liou (1973) at 0.2 to 0.5 GPa and are discussed in Poli and Schmidt (2004). For our purpose here, it should be noted that in both studies the thermal stability of epidote increases with increasing f_{O_2}. Furthermore, not only the *P-T* location but also the stoichiometry of epidote subsolidus dehydration reactions (e.g., Rxns. 1,11,15,20), as well as epidote composition, strongly depend on f_{O_2}. As minimum pressure of magmatic epidote is defined by the intersection of the latter reactions with the solidus, a shift of these reactions in *P-T*-space is of direct significance for the interpretation of natural phase relations. The breakdown reaction of epidote as determined by Holdaway (1972) and Liou (1973) for f_{O_2} buffered to NNO would intersect the granitic solidus at around 0.5 GPa (Fig. 11), which would then be the lower pressure limit of magmatic epidote; the breakdown reaction of epidote for f_{O_2} buffered to HM is shifted to higher temperature by about 100°C and would thus intersect the wet granite solidus at around 0.3 GPa. This pressure difference indicates the amplitude of the effect of oxidizing a magma on the minimum pressure necessary for magmatic epidote. Schmidt and Thompson (1996) found for natural tonalite at a temperature above the water-saturated solidus that the stability and composition of epidote strongly depends on f_{O_2}. They determined the epidote-out reaction to intersect with the wet tonalite solidus at 0.3 instead of 0.5 GPa (Fig. 11) when f_{O_2} changes from NNO to HM. Both epidote melting reactions in the tonalite at NNO and at HM, with excess H$_2$O, lie close to extrapolated epidote subsolidus dehydration reactions in the synthetic CFASH-system at equivalent f_{O_2} (as determined by Holdaway 1972 and Liou 1973). The experimental f_{O_2}-range corresponds to the range expected for somewhat oxidized calc-alkaline magmas (Ishihara 1981). The inverse effect in anomalously reduced magmas could explain a possible absence of epidote in intrusions that otherwise should contain magmatic epidote.
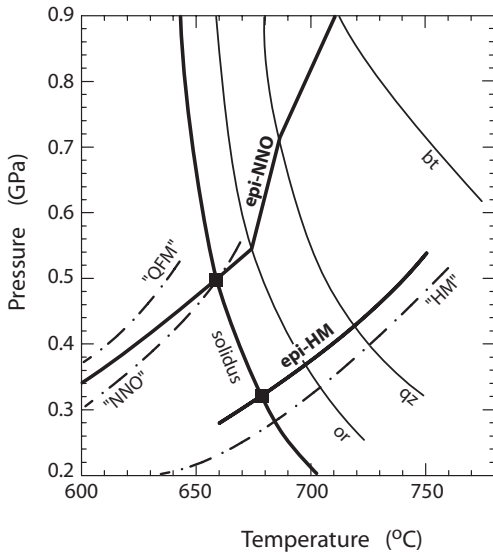
Figure 11. Pressure temperature diagram depicting the epidote-out reaction near the lower intersection with the solidus for varying oxygen fugacities (QFM = quartz-fayalite-magnetite, NNO = nickel-bunsenite, HM = hematite-magnetite). Solid lines are from Schmidt and Thompson (1996), stippled lines represent subsolidus epidote-out reactions from Liou (1973) and Holdaway (1972) for a synthetic CaO-FeO-Al$_2$O$_3$-SiO$_2$-H$_2$O-O$_2$ system.

More oxidizing conditions favor a higher temperature of epidote and thus an intersection of the epidote stability with the wet solidus at lower pressure. In the presence of Fe^{3+}, Reaction (1) is displaced to lower pressure because epidote has a higher Fe^{3+}/Al ratio compared to garnet. This effect was anticipated by Strens (1965) and demonstrated experimentally by Holdaway (1972), Liou (1973), and Brunsmann et al. (2002). The same effect of an increasing Fe^{3+}-fractionation is expected for epidote-melt equilibria where Fe^{3+} strongly partitions into epidote and thus enlarges its stability. Thus while epidote in many intermediate calc-alkaline plutons is a pressure indicator, its exact pressure significance cannot be assessed without determining the f_{O_2} of the crystallizing magma (which in most intrusions is possible through oxide mineral equilibria).

Singh and Johannes (1996a,b) investigated fluid-absent melting of biotite-plagioclase-quartz starting mixtures. One mixture had synthetic Fe-free phlogopite, while the others had Fe present; all mixtures employed the same plagioclase (An_{45}) such that normative anorthite contents are identical ($an^{CIPW} = 23$ wt%). This study isolates the effect of Fe on the magmatic occurrence of epidote: in the Fe-free system, epidote occurs between 1.0 and 1.2 GPa at 750°C, whereas the minimum pressure for magmatic epidote is lowered to between 0.8 and 0.9 GPa at 750°C in the Fe-bearing starting materials.

EPIDOTE PHASE RELATIONSHIPS AS A TOOL FOR EXTRACTING THE INTRUSION DEPTH

Crawford and Hollister (1982) predicted magmatic epidote to occur at a minimum pressure of approximately 0.6 GPa on the basis of the intersection of Liou's (1973) low pressure subsolidus curve for epidote stability (Fig. 11) with the melting curve for H_2O-saturated granite. Zen and Hammarstrom (1984) established that epidote appears in moderate to high pressure intrusions and estimated a minimum pressure for the crystallization of magmatic epidote between 0.6 and 0.8 GPa on the basis of Naney's (1983) experiments. The low pressure limit of 0.6 to 0.8 GPa for magmatic epidote was questioned by Moench (1986), who described several epidote bearing intrusions where pressure estimates from the contact aureoles yielded around 0.4 GPa.

The Al-in-hornblende geobarometer. This geobarometer is based on the total Al-content in magmatic hornblende buffered by the 8-phase assemblage plagioclase + K-feldspar + quartz + biotite + epidote or magnetite + rutile + ilmenite + melt. If all of these phases are present, the 9 component system is fully buffered, and all exchange vectors in hornblende are buffered (in particular *tschermak*, plagioclase, and *edenite* exchange), the Al-content should then only depend on pressure (as the wet solidus is almost constant in temperature). This barometer has been invented and calibrated on the basis of pressures from the contact aureole of intrusions by Hammarstrom and Zen (1986), improved by including additional intrusions by Hollister et al. (1987), and experimentally calibrated for a mixed-volatile, "high"-temperature (i.e., 100-150°C above the wet solidus) situation by Johnson and Rutherford (1989) and for a fluid-saturated situation by Schmidt (1992).

Discrepancies between estimated intrusion depths and minimum pressure conditions recorded by epidote-bearing assemblages

The minimum pressure for magmatic epidote of 0.5 GPa was criticized by several authors investigating epidote bearing granitoids where both Al-in-hornblende barometry and pressures derived from the contact aureole indicate intrusion levels significantly less than 15 km. This apparent contradiction to the experimental results may result from several differences between the natural and experimental systems:

- The crystallization depth of 70 to max. 80% of the crystals within a magma does

not necessarily correspond to the emplacement depth. Examples of liquid state deformation of an intrusion and possible uplift of a crystal-melt mush are observed in the Bergell intrusion (Davidson et al. 1996), in New Zealand (Tulloch 1986), and in the Archean Minto block, Canada (Bedard 2003; see also discussion on the Great tonalite sill at Mount Juneau, Alaska by Drinkwater et al. 1991). In the Bergell tonalite, amphibole, biotite, plagioclase, and epidote, but not intergranular quartz and K-feldspar are deformed, pointing to late stage crystallization of quartz and K-feldspar after upraise and deformation of a crystal-melt mush. In this case, the Al-in-hornblende barometer yields slightly higher pressure than suggested by the contact aureole (e.g., the western end of the Bergell intrusion, where regional metamorphism indicates 0.6 to 0.7 GPa and Al-in-hornblende intrusion pressures 0.75 to 0.8 GPa), although differences of <0.15 GPa are at the resolution limit of geobarometrical methods. Nevertheless, such a difference might be taken as an indication that the Al-in-hornblende barometer may sometimes document pressures of crystallization of a crystal melt mush rather than final solidification and that occasionally, such crystal-melt mushes could have moved to somewhat higher levels.

- If cooling is rapid enough, epidote may not react with the remnant melt. The kinetics of epidote dissolution was investigated by Brandon et al. (1996) and was found to be relatively rapid. At the relevant temperature of 700 to 800°C grain sizes of 0.2 to 3 mm would need 2 to 2000 years for dissolution.

- In many plutons, epidote shows resorption textures. Armoring of epidote within later crystallized biotite or plagioclase (as described by Tulloch 1986) or other minerals may prevent equilibration of a higher pressure epidote during final full crystallization of a magma.

- An increased f_{O_2} increases the stability field of epidote. This might be testified by Fe-Ti-oxides or by an increased Fe-content in epidote. Magmatic epidote from the Appalachian monzogranites have ps_{73} to ps_{100} (Vynhal et al. 1991), i.e., compositions that are at the Fe-rich end of the solid solution, and which are likely to have formed at elevated f_{O_2}.

- Bulk composition outside the TTG series may result in a shift of the intersection of epidote-in and wet solidus to lower pressure (see next paragraph).

It is conspicuous that several plutons that lead the investigators to challenge the minimum epidote-pressure of 0.5 GPa were monzogranites (Appalachian granitoids, Vynhal et al. 1991; Querigut-complex, French Pyrenees, Leterrier 1972; Roberts et al. 2000; partly also in the Median batholith in New Zealand, Tulloch 1986; Tulloch and Challis 2000). The particular role of monzogranites is evident in the Querigut massif, which consists of about 10 individual intrusions. In Querigut, only the monzogranites, but not the granodiorites and tonalites bear epidote. Epidote-bearing monzogranites have normative anorthite contents of 13 to 17 wt% and in most cases, oxidation states appear to be within the average range. On the basis of the bulk composition of monzogranites, there is no evident reason, why monzogranites should have a distinctly lower pressure stability of magmatic epidote, and it is necessary to investigate this systematically.

Epidote in the crystallization sequence: a sensitive tool for estimating pressure conditions

The first appearance of epidote during the crystallization history of a cooling magma could provide a more detailed geobarometer. At fluid-saturation and pressures to about 1.1 GPa (Fig. 6) the sequence of crystallization in tonalite is

above 1.0 GPa   hornblende → **epidote** → plagioclase → biotite → quartz → K-feldspar;

1.0 to 0.8 GPa   hornblende → plagioclase → **epidote** → biotite → quartz → K-feldspar;

0.8 to 0.6 GPa   hornblende → plagioclase → biotite → **epidote** → quartz → K-feldspar;

0.6 to 0.5 GPa   hornblende → plagioclase → biotite → quartz → **epidote** → K-feldspar.

The position of epidote moves from left to right in this sequence as pressure decreases. Some of these various crystallization sequences for epidote have been reported from natural rocks in the literature (for example the references cited by Tulloch, by Moench, and by Zen and Hammarstrom in their exchange of correspondence in 1986). The above pressures result from H_2O-saturated experiments with f_{O_2} buffered to NNO. The actual temperature of epidote crystallization would be increased in oxidized magmas, such that, at a given pressure, epidote might move to the left in the crystallization sequence.

PHASE RELATIONSHIPS IN H$_2$O-UNDERSATURATED SYSTEMS

The maximum temperature limit of magmatic epidote in tonalite has been experimentally determined at fluid-saturated conditions to about 750°C. H_2O-undersaturated crystallization of epidote has been investigated at 0.8 GPa in a granite and granodiorite (Naney 1983), and at 1.0 GPa (van der Laan and Wyllie 1992) and 1.5 GPa (Johnston and Wyllie 1988) in a trondhjemite. These studies have defined *T*- H_2O sections (Fig. 12) and show that the H_2O-saturated melting temperature changes only slightly at H_2O-undersaturated conditions, i.e., decreases by about 20°C in Naney's (1983) granodiorite at 0.8 GPa, and increases from 740 to 775°C in the trondhjemite at 1.5 GPa. Experiments above 0.8 GPa on a hornblende-bearing dacite (very similar in composition to the granodiorites studied by Naney 1983 and Schmidt and Thompson 1996) at 3 and 5 wt% water content (Green 1992) did not produce epidote down to 800°C. This indicates that in granodioritic compositions (at 1.5 GPa) the epidote stability field does not substantially enlarge with decreasing water content. Experiments on an epidote-bearing tonalite with no water added (Skjerlie and Johnston 1993) did not result in stable epidote down to 875°C at 1.0 GPa. Two experimental brackets at H_2O-undersaturated conditions exist: Singh and Johannes (1996b) in a synthetic bulk composition (biotite-plagioclase-quartz, 0.8 wt% bulk H_2O) defined zoisite and epidote to melt out between 750 and 800°C at 1.0 to 1.5 GPa, in both an Fe free and an Fe bearing system, respectively. Lopez and Castro (2001) studied an amphibolite *sensu strictu* of MORB composition and formed new epidote at 800°C, 1.1 to 1.2 GPa but epidote had melted out at 850°C. Thus, epidote was found to be unstable in experiments on natural or close-to-natural compositions at temperatures above 800°C (Lambert and Wyllie 1972; Winther and Newton 1991; Pawley and Holloway 1993; Skjerlie and Johnston 1993; Sen and Dunn 1994; Poli and Schmidt 1995; Schmidt and Thompson 1996; Lopez and Castro 2001) and there is no evidence for a significantly enlarged stability field of epidote + melt at H_2O-undersaturated conditions. Further comments on epidote stability in the H_2O-undersaturated region cannot be made without additional experiments. Unfortunately, it is a difficult experimental task to perform fluid-absent experiments at $\approx$ 800°C. Skjerlie and Patino-Douce (2002) suggested zoisite to be stable up to 1000°C at 2.6 GPa. However, this interpretation of their experiments is at odds with any other study on basaltic compositions in this *P-T* region (Lambert and Wyllie 1972; Winther and Newton 1991; Pawley and Holloway 1993; Sen and Dunn 1994; Poli and Schmidt 1995; Schmidt and Thompson 1996). Skjerlie and Patino-Douce (2002) (i) had zoisite in their starting material and did not reverse their experiments, (ii) the zoisite present in their experimental products had a composition identical to the one in the starting material, (iii) they used a very low H_2O content of 0.2 wt% leading to fluid-absent conditions, and (iv) employed a very coarse grained starting material (>50 μm). Thus, Skjerlie and Patino-Douce (2002) had an extremely unfavorable setup for reaching equilibrium and their interpretation of zoisite-remnants in experimental charges is incompatible with other studies. Further experimental
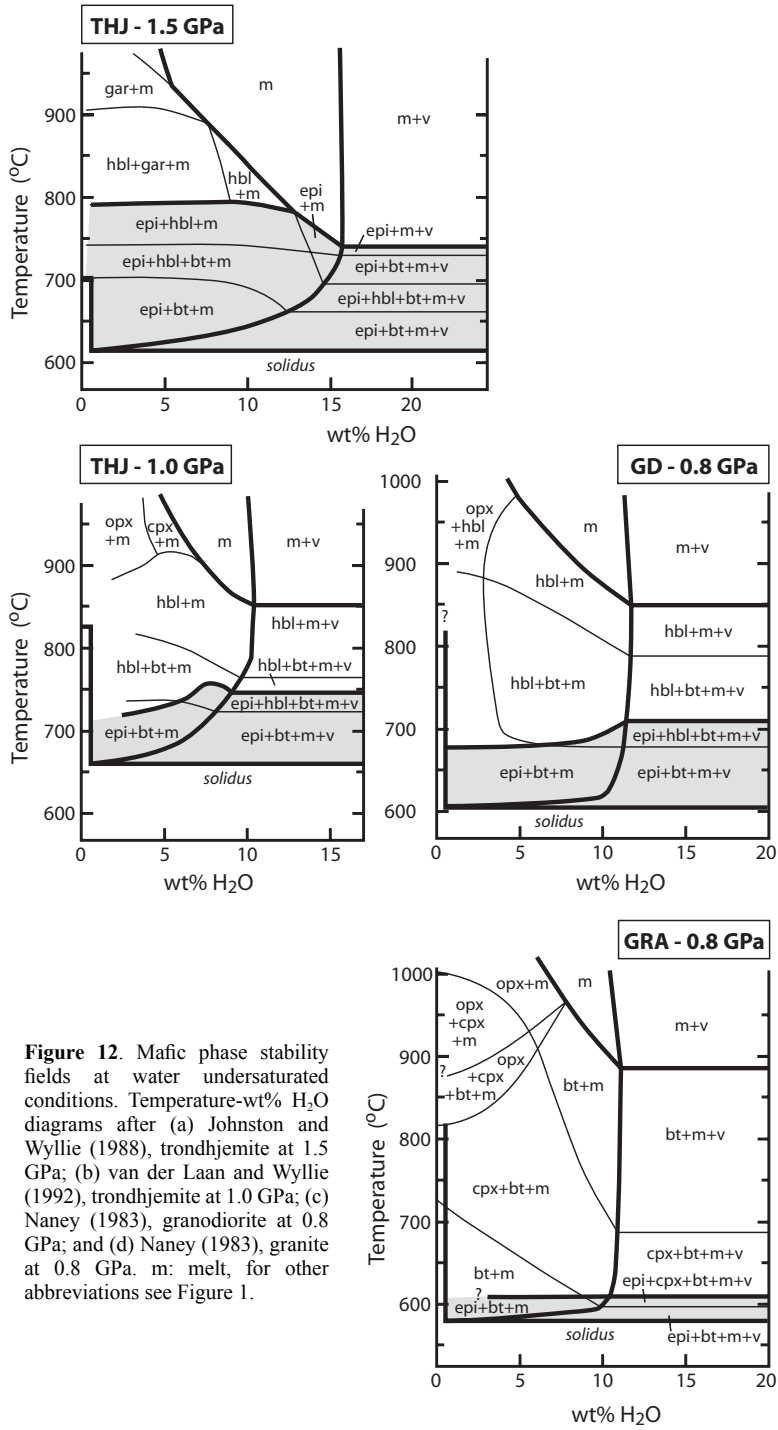
Figure 12. Mafic phase stability fields at water undersaturated conditions. Temperature-wt% H$_2$O diagrams after (a) Johnston and Wyllie (1988), trondhjemite at 1.5 GPa; (b) van der Laan and Wyllie (1992), trondhjemite at 1.0 GPa; (c) Naney (1983), granodiorite at 0.8 GPa; and (d) Naney (1983), granite at 0.8 GPa. m: melt, for other abbreviations see Figure 1.

work, demonstrating equilibrium, is required before accepting an extension of epidote stability at H_2O-undersaturated conditions.

It was suggested that epidote inclusions in biotite (e.g., in high level oxidized granitoids; Tulloch 1986) and epidotes, which crystallized when the melt proportion was 50 to 80 vol% (as in the rhyodacite dykes described by Evans and Vance 1987), are xenocrysts carried from depth. Between 1.0 to 1.5 GPa epidote crystallizes before biotite in tonalite-H_2O (f_{O_2} = NNO, Fig. 6) and in granodiorite-H_2O (f_{O_2} = NNO, Fig. 8). However, in the early stages of magmatic crystallization it is not likely that fluid-saturation is reached, so the question arises as to the (yet unknown) crystallization sequences at H_2O-undersaturated conditions.

Epidote in fluid-absent melting processes

Nicholls and Ringwood (1973) and Vielzeuf and Schmidt (2001) suggested involvement of epidote in fluid-absent melting reactions between 0.8 and 3.0 GPa. Vielzeuf and Schmidt (2001) compiled available experiments on melting of basaltic compositions into a melting phase diagram, and showed that epidote is indeed the hydrous phase responsible for the first occurrence of fluid-absent melting in basaltic to andesitic bulk compositions.

Hydrous phases at the wet solidus. In the early nineties, several experimental studies investigated the fluid-absent melting of metabasalts (Beard and Lofgren 1991; Rapp et al. 1991; Rushmer 1991; Winther and Newton 1991; Wolf and Wyllie 1994). In these studies, the appearance of first melts in mafic compositions is attributed to the decomposition of amphibole as the only hydrous phase. However, above ca 1.0 GPa this interpretation is no longer valid as epidote is present at the solidus (compare to Poli and Schmidt 2004; Enami et al. 2004). With increasing pressure, the succession of stable mineral assemblages in MORB at the fluid-present solidus is (Vielzeuf and Schmidt 2001):

- to approximately 0.8 GPa, metabasalts are amphibolites sensu stricto composed of amphibole + plagioclase + quartz;

- at 0.8 to 1.0 GPa epidote and garnet crystallize (Apted and Liou 1983; Poli 1993) leading to an assemblage of amphibole + plagioclase + epidote + quartz ± garnet, defining the epidote-amphibolite facies;

- omphacite forms near 1.5 GPa and amphibolite transforms into amphibole-eclogite with an assemblage of amphibole + epidote + clinopyroxene + garnet + quartz (Lambert and Wyllie 1972; Poli 1993);

- around 2.5 GPa, amphibole decomposes, leaving a zoisite-eclogite with a characteristic assemblage of zoisite + clinopyroxene + garnet + quartz/coesite (Pawley and Holloway 1993; Poli 1993);

- finally, near 3.0 GPa, zoisite decomposes (Poli and Schmidt 1995) and a K-poor metabasalt transforms into an eclogite sensu stricto with the anhydrous mineral assemblage omphacite + garnet + coesite.

The pressures in the succession above are valid for MOR basalts, but are very similar in intermediate tonalitic compositions (Schmidt 1993; Poli and Schmidt 1995). The upper pressure limit of epidote in tonalite as defined by Schmidt (1993) is in error, because the critical experiment of Schmidt (1993) at 2.6 GPa, 650°C, that did not yield epidote, was inconsistent with subsequent experiments (Poli and Schmidt 1995) and was thus repeated. The second experiment at the same conditions did then yield 12 wt% epidote. The reason for the inconsistency of the first experiment is unclear (and was not searched for).

The sequence of assemblages from the experiments is in agreement with natural observations. Lardeaux and Spalla (1991) describe coronae of clinopyroxene and zoisite (± garnet) at the boundaries between plagioclase and amphibole in amphibolites metamorphosed

under Alpine eclogite facies conditions (Sesia Zone, Western Alps). The upper pressure stability of amphibole relative to zoisite in metabasalts is documented in coesite bearing rocks: coesite coexists with zoisite but never with barroisitic amphibole (e.g., Dabie-Shan, Zhang et al. 1995). This confirms that zoisite is stable to higher pressure than amphibole at the wet solidus. Between 1.0 and 2.5 GPa, epidote is the first hydrous phase to decompose and thus to melt on a prograde *P-T* path (Fig. 13).

The amount of epidote in a metabasalt at subsolidus conditions can be estimated between 5 and 15 wt% (Poli 1993) and thus, only a small amount of melt will be formed by the
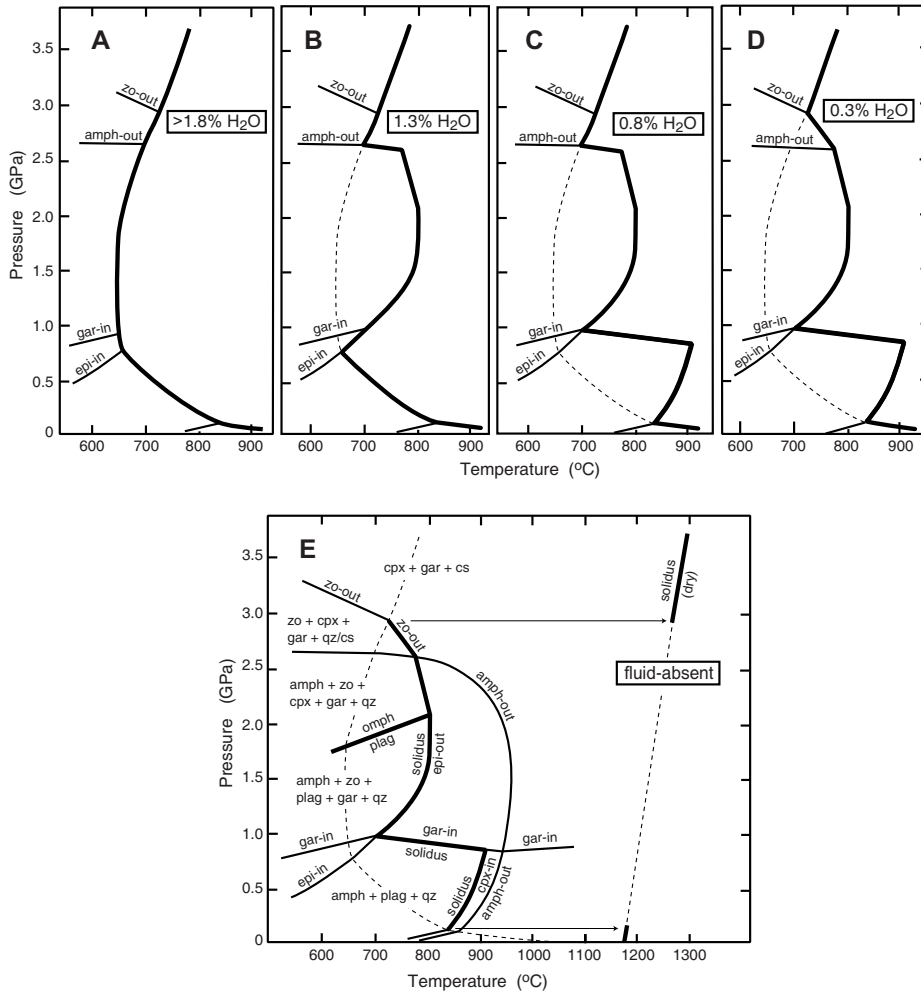
Figure 13. Melting in an epidote bearing MOR basalt. (a-d): Solidi for MOR basalt with fixed bulk water contents: (a) >1.8 wt% H$_2$O, fluid-saturated at all pressures (b) 1.3 wt% H$_2$O, assemblages with epidote + amphibole are not fluid saturated; (c) 0.8 wt% H$_2$O, assemblages with amphibole are generally fluid-undersaturated; (d) 0.3 wt% H$_2$O, any assemblage containing hydrous phases is water undersaturated. (e) System open to volatiles: MOR basalt fully water saturated below the wet solidus but following a prograde *P-T* path along which a fluid-absent situation is strictly maintained. Abbreviations see Figure 1.

incongruent epidote melting reaction. Evidence for high pressure melting in eclogite areas has been documented by Nicollet et al. (1979), Franz and Smelik (1995), Puziewitcz and Koepke (2001), and Elias-Herrera and Ortega-Gutierrez (2002). At 2.5 to 3.0 GPa, i.e., beyond the amphibole-out curve, epidote is the major hydrous phase present in metabasalt.

A generalized phase diagram for partial melting of metabasalt. The phase relationships outlined above result in a generalized phase diagram for the melting of SiO_2-saturated metabasalt (Fig. 13e; Vielzeuf and Schmidt 2001). The upper sequence of diagrams (Fig. 13a-d) delineates the solidus for fixed bulk H_2O-contents. The rational of these diagrams is: the H_2O-content stored in amphibole and epidote is subtracted from the bulk H_2O-content, the difference resulting in a fluid-present or fluid-absent melting situation. If fluid is present, the wet solidus is responsible for the first occurrence of melt, if no free fluid phase results, fluid-absent melting reactions of epidote and amphibole are designated as part of the solidus. From this series of diagrams it is evident that between 1.0 and 3.0 GPa, the fluid-absent melting of epidote marks an intermediate step. The shape of the solidus (Fig. 13c) was confirmed by the experimental study of Lopez and Castro (2001). Their experiments with amphibolite containing 1 wt% H_2O resulted in a strong depression of the solidus temperature when overstepping the garnet-in reaction with pressure, and in epidote-melting above 1.0 GPa.

Nevertheless, such a fixed bulk H_2O is fairly hypothetical. A more realistic endmember situation is, that any significant amount of fluid-phase produced during prograde metamorphism will leave the rock volume in question, thus maintaining at subsolidus conditions a fluid-absent situation. The melting curve for such a process is designated in Figure 13e. The maximum temperature for the stability of epidote (at 1.5 to 2.0 GPa) was modified from Vielzeuf and Schmidt (2001) and now placed at 800°C in agreement with the study of Lopez and Castro (2001). This latter upper temperature limit of epidote was chosen (Fig. 13) irrespective of the bulk fluid-content. Although this temperature must vary at least slightly with H_2O-activity in the melt, this is consistent with the absence of epidote in the fluid absent melting experiments conducted above 800°C. We conclude, that during high pressure melting of basaltic to intermediate bulk compositions, epidote will be involved in the melting process. Whereas in tonalite, the fluid-absent melting of potassic hydroxylated phases (i.e., micas) results in a complex interplay with the fluid-absent melting of calcic hydroxylated phases (i.e., epidote and amphibole), epidote will be dominant for forming the first high-pressure melts in potassium-poor rocks. Nevertheless, the amount of melt formed by reactions involving epidote is small (generally <10%), a more significant melt volume is formed by the decomposition of amphibole.

OPEN PROBLEMS

Whereas the "Deer-Howie-Zussmann" (Deer et al. 1986, section "clinozoisite-epidote", p. 121-123) still casts a dubious eye on the possibility of magmatic epidote, field and experimental petrologists are now accustomed to the coexistence of epidote with silicate melts. Although epidote minerals are omnipresent near the solidus, a quantitative appreciation of their role during melting is still lacking. Experimental studies did not yet define the

- upper temperature stability of zoisite from 1 to 7 GPa;

- zoisite melting relations in simple systems more complex than CASH above 2 GPa (apart from studies by Thompson and Ellis 1994 and Hermann 2002);

- influence of oxygen fugacity in relevant simple systems;

- fluid-absent melting relations of zoisite at temperatures between the wet solidus and ca. 800°C.

The latter appears to be the most interesting and rewarding task, however, will have to overcome the kinetic problems in fluid-absent systems below 800°C and any result will only be credible when truly reversed. One way to go might be seeded and unseeded starting materials, possibly involving seeded or/and unseeded gels. As such experiments are difficult, much information could be gained by field studies of migmatitic terranes that contain epidote. It appears to us, that the few reported involvements of epidote in natural melting processes would not constitute a close-to-complete list. Defining conditions and reactions of epidote melting in prograde amphibolite to granulite facies terrains would complete one of the major deficiencies in natural melting processes.

A further task that remains wide open is to understand epidote compositions and the relation of epidote and plagioclase compositions as a function of bulk composition, intrusion pressure and oxygen fugacity. For this purpose, plagioclase compositions in equilibrium with epidote need to be known (which is obviously not always straightforward in plutons), and thus a detailed comprehensive study would be necessary.

EPILOGUE

This chapter has a sad history. Initially it was planned to be written together with Kjell Skjerlie from University of Tromsø, Norway. Tragically, our colleague Kjell Petter Skjerlie died last summer in an accident during a mountain hike. He was hit by a falling rock and died immediately. Kjell would just have become 42 years, he is survived by his wife and their three children.

ACKNOWLEDGMENTS

We thank G. Franz, A.Wittenberg and T. Fehr for reviews of this chapter.

REFERENCES

Allen JC, Boettcher AL (1983) The stability of amphibole in andesite and basalt at high pressures. Am Mineral 68:307-314
Allibone AH, Tulloch AJ (1997) Metasedimentary, granitoid, and gabbroic rocks from central Stewart Island, New Zealand. New Zeal J Geol Geop 40(1):53-68
Altherr R, Lugovic B, Meyer HP et al. (1995) Early-miocene postcollisional calc-alkaline magmatism along the easternmost segment of the periadriatic fault system (Slovenia and Croatia). Miner Petrol 54:25-247
Anderson JL, Barth AP, Young ED (1988) Mid-crustal cretaceous roots of Cordilleran metamorphic core complexes. Geology 16:366-369
Apted MJ, Liou JG (1983) Phase relations among greenschist, epidote-amphibolite, and amphibolite in a basaltic system. Am J Science 283-A:328-354
Barnes CG, Prestvik T (2000) Conditions of pluton emplacement and anatexis in the Caledonian Bindal Batholith, north-central Norway. Norsk Geol Tidsskr 80:259-274
Barr SM, White CE, Culshaw NG (2001) Geology and tectonic setting of Paleoproterozoic granitoid suites in the Island Harbour Bay area, Makkovik Province, Labrador. Can J Earth Sci 38:441-463
Bea F, Fershtater G, Montero P (1997) Generation and evolution of subduction-related batholiths from the central Urals: constraints on the P-T history of the Uralian orogen. Tectonophys 276:103-116
Beard JS, Lofgren GE (1991) Dehydration melting and water-saturated melting of basaltic and andesitic greenstones and amphibites at 1, 3, 6.9 kb. J Petrol 32:365-401
Bedard JH (2003) Evidence for regional-scale, pluton-driven, high-grade metamorphism in the Archaen Minto Block, northern Superior Province, Canada. J Geol 111:183-205
Boettcher AL (1970) The system CaO-Al₂O₃-SiO₂-H₂O at high pressures and temperatures. J Petrol 11:337-379
Brandon AD, Creaser RA, Chacko T (1996) Constraints on rates of granitic magma transport from epidote dissolution kinetics. Science 271:1845-1848

Broska I, Petrik I, Benko P (1997) Petrology of the Mala Fatra granitoid-rocks (Western Carpathians, Slovakia). Geol Carpath 48:27-37

Brunsmann A, Franz G, Heinrich W (2002) Experimental investigation of zoisite-clinozoisite phase equilibria in the system CaO-Fe$_2$O$_3$-Al$_2$O$_3$-SiO$_2$-H$_2$O. Contrib Mineral Petrol 143:115-130

Campos TFC, Nieva AMR, Nardi LSV (2000) Geochemistry of granites and their minerals from Serra Negra do Norte Pluton, northeastern Brazil. Chem Erde-Geochem 60:279-303

Cerredo ME, De Luchi MGL (1998) Mamil Choique Granitoids, southwestern North Patagonian Massif, Argentina: magmatism and metamorphism associated with a polyphasic evolution. J Am Earth Sci 11:499-515

Cook RB, Crawford ML, Omar GI et al (1991) Magmatism and deformation, southern Revillagigedo Island, southeastern Alaska. Geol Soc Am Bull 103:829-841

Cornelius HP (1915) Geologische Beobachtungen im Gebiet des Forno-Gletschers (Engadin). Centralblatt für Mineral Geol Paläontol 1913, 8:246-252

Crawford ML, Hollister LS (1982) Contrast of metamorphic and structural histories across the Work Channel lineament, Coast Plutonic Complex, British Columbia. J Geophys Res 87:3849-3860

Dahlquist JA (2001a) Low-pressure emplacement of epidote-bearing metaluminous granitoids in the Sierra de Chepes (Famatinian Orogen, Argentina) and relationships with the magma source. Rev Geol Chile 28:147-161

Dahlquist JA (2001b) REE fractionation by accessory minerals in epidote-bearing metaluminous granitoids from the Sierras Pampeanas, Argentina. Mineral Mag 65:463-475

Davidson C, Rosenberg C, Schmid SM (1996) Synmagmatic folding of the base of the Bergell pluton, Central Alps. Tectonophys 265:213-238

Dawes RL, Evans BW (1991) Mineralogy and geothermobarometry of magmatic epidote-bearing dikes, front range, Colorado. Geol Soc Am Bull 103:1017-1031

Deer WA, Howie RA, Zussman J (1986) Clinozoisite-Epidote. *In:* Disilicates and Ring Silicates, Rock Forming Minerals 1B. Deer WA, Howie RA, Zussman J (eds) Longman Scientific & Technical, Burnt Mill, Harlow. 44-134

Drinkwater JL, Ford AB, Brew DA (1991) Magnetic susceptibilities and iron content of plutonic rocks across the Coast Plutonic -Metamorphic Complex near Juneau, Alaska. *In:* Geologic studies in Alaska by the U.S. Geological Survey. Bradley DC, Dusel-Bacon C. (eds) U.S. Geol Survey Bull 2041:125-139

Eggler DH (1972) Water-saturated and undersaturated melting relations in a Paricutin andesite and an estimate of water content in the natural magma. Contrib Mineral Petrol 34:261-271

Elias-Herrera M, Ortega-Gutierrez F (2002) Caltepec fault zone: An Early Permian dextral transpressional boundary between the Proterozoic Oaxacan and Paleozoic Acatlan complexes, southern Mexico, and regional tectonic implications. Tectonics 21:10.1029/2000TC001278

Ellis DJ, Thompson AB (1986) Subsolidus and partial melting reactions in the quartz excess CaO+MgO+Al$_2$O$_3$+SiO$_2$+H$_2$O system under water-excess and water-deficient conditions to 10 kbar: some implications for the origin of peraluminous melts from mafic rocks. J Petrol 27:91-121

Enami M, Liou JG, Mattinson CG (2004) Epidote minerals in high P/T metamorphic terranes: Subduction zone and high- to ultrahigh-pressure metamorphism. Rev Mineral Geochem 56:347-398

Evans BW, Vance JA (1987) Epidote phenocrysts in dacitic dikes, Boulder County, Colorado. Contrib Mineral Petrol 96:178-185

Farrow CEG, Barr SM (1992) Petrology of high-Al-hornblende-plutons and magmatic-epidote bearing plutons in the southeastern Cape-Breton highlands, Nova-Scotia. Can Mineral 30:377-392

Franz G, Smelik EA (1995) Zoisite-clinozoisite bearing pegmatites and their importance for decompressional melting in eclogites. Eur J Mineral 7:1421-1436

Frei R (1996) The extent of inter-mineral isotope equilibrium: A systematic bulk U-Pb and Pb step leaching (PbSL) isotope study of individual minerals from the Tertiary granite of Jerissos (northern Greece). Eur J Mineral 8:1175-1189

Galindo AC, Dallagnol R, McReath I et al. (1995) Evolution of Brasiliano-age granitoid types in a shear-zone environment, Umarizal-Caraubas region, Rio-Grande-Do-Norte, northeast Brazil. J S Am Earth Sci 8:79-95

Gieré R, Sorensen SS (2004) Allanite and other REE-rich epidote-group minerals. Rev Mineral Geochem 56:431-494

Green TH (1992) Experimental phase equilibrium studies of garnet-bearing I-type volcanics and high level intrusives from Northland, New Zealand. Transact Royal Soc Edinburgh: Earth Sciences 83:429-438

Ghent ED, Nicholls J, Simony PS, et al. (1991) Hornblendegeobarometry of the Nelson-batholith, southeastern British-Columbia - tectonic implications. Can J Earth Sci 28:1982-1991

Hammarstrom JM, Zen E (1986) Aluminium in hornblende: an empirical igneous geobarometer. Am Mineral 71:1297-1313

Hammarstrom JM, Zen E (1992) Petrological characteristics of magmatic epidotebearing granites of the western cordillera of America. Abstract. Transact Royal Soc Edinbourgh: Earth Sciences 83:490-491

Hermann J (2002) Experimental constraints on phase relations in subducted continental crust. Contrib Mineral Petrol 143:219-235

Holdaway MJ (1972) Thermal stability of Al-Fe-epidote as a function of f_{O_2} and Fe content. Contrib Mineral Petrol 37:307-340

Hollister LS, Grissom GC, Peters EK, Stowell HH, Sisson VB (1987) Confirmation of the empirical correlation of Al in hornblende with pressure of solidification of calc-alkaline plutons. Am Mineral 72:231-239

Hoschek (1990) Melting and subsolidus reactions in the system K_2O-CaO-MgO-Al_2O_3-SiO_2-H_2O: experiments and petrologic application. Contrib Mineral Petrol 105: 393-402

Ishihara S (1977) The magnetite-series and ilmenite-series granitic rocks. Mining Geol 27: 293-305

Ishihara S (1981) The granitoid series and mineralization. Economic Geol 75th anniversary volume: 458-484

Johannes W (1980) Melting and subsolidus reactions in the system K_2O-CaO-Al_2O_3-SiO_2-H_2O. Contrib Mineral Petrol 74:29-34

Johnson MC, Rutherford MJ (1989) Experimental calibration of the aluminium-inhornblende geobarometer with application to Long Valley caldera (California) volcanic rocks. Geology 17:837-841

Johnston AD, Wyllie PJ (1988) Constraints on the origin of Archean trondhjemites based on phase relationship of Nuk gneiss with H2O at 15 kbar. Contrib Mineral Petrol 100:35-46

Keane SD, Morrison J (1997) Distinguishing magmatic from subsolidus epidote: Laser probe oxygen isotope compositions. Contrib Mineral Petrol 126: 265-274

Lambert IB, Wyllie PJ (1972) Melting of gabbro (quartz eclogite) with excess water to 35 kilobars, with geological applications. J Geol 80:693-708

Lambert IB, Wyllie PJ (1974) Melting of tonalite and crystallization of andesite liquid with excess water to 30 kilobars. J Geol 82:88-97

Lardeaux JM, Spalla MI (1991) From granulites to eclogites in the Seisa zone (Italian Western Alps): a record of the opening and closure of the Piedmont ocean. J metam Geol 9:35-59

Leterrier J (1972) Etude petrographique et geochimique du massif granitique de Querigut (Ariege). These docteur es-sciences naturelles. Universite de Nancy, France, 292 p.

Liou JG (1973) Synthesis and stability relations of epidote, $Ca_2Al_2FeS_3O_{12}(OH)$. J Petrol 14:381-413

Lopez S, Castro A (2001) Determination of the fluid-absent solidus and supersolidus phase relationships of MORB-derived amphibolites in the range 4-14 kbar. Am Mineral 86: 1396-1403

Moench RH (1986) Comment on "Implications of magmatic epidote-bearing plutons on crustal evolution in the accreted terranes of northwestern North America" and "Magmatic epidote and its petrologic significance". Geology 14: 187-188

Montero P, Bea F, Gerdes A, et al. (2000) Single -zircon evaporation ages and Rb-Sr dating of four major Variscan batholiths of the Urals - A perspective on the timing of deformation and granite generation. Tectonophys 317:93-108

Mortaji A, Ikenne M, Gasquet D et al. (2000) Palaeoproterozoic granitoids from the Bas Draa and Tagragra d'Akka Inliers (western Anti-Atlas, Morocco): part of the jigsaw puzzle concerning the West African Craton. J Afr Earth Sci 31:523-538

Morrison J (2004) Stable and radiogenic isotope systematics in epidote group minerals. Rev Mineral Geochem 56:607-628

Moticska P (1970) Petrographie und Strukturanalyse des westlichen Bergeller Massivs und seines Rahmens. Schweiz Mineral Pet Mitt 50:355-443

Murata M, Itaya T (1987) Sulfide and oxide minerals from S-type and I-type granitic rocks. Geochim Cosmochim Acta 51:497-507

Naney MT (1983) Phase equilibria of rock-forming ferromagnesian silicates in granitic systems. Am J Sci 283: 993-1033

Nedelec A, Minyem D, Barbey P (1993) High-P-high-T anatexis of archean tonalitic gray gneisses - the Eseka migmatites, Cameroon. Precambrian Res 62:191-205

Newton RC (1966) Some calc -silicate equilibrium relations. Am J Sci 264:204-222

Nicholls IA, Ringwood AE (1973) Effect of water on olivine stability in tholeiites and the production of silica-saturated magmas in the island-arc environment. J Geol 81:285-300

Nicollet C, Leyreloup A, Dupuy C (1979) Petrogenesis of high pressure trondhjemitic layers in eclogites and amphibolites from Southern Massif Central, France. In: Trondhjemites, dacites, and related rocks. Developements in Petrology. Vol.6 Barker F (ed) Elsevier, Amsterdam Oxford New York, p.435-463

Nitsch KH, Winkler HGF (1965) Bildungsbedingungen von Epidot und Orthozoisit. Beiträge Mineral Pet 11: 470-486

Owen JV (1991) Significance of epitote in orbicular diorite from the Grenville front zone, eastern Labrador. Mineral Mag 55:173-181

Owen JV (1992) Geochemistry of orbicular diorite from the Grenville-front zone, eastern Labrador. Mineral Mag 56(385):451-458

Pattnaik SK (1996) Petrology of the Bhela -Rajna alkaline complex, Nuapara District, Orissa. J Geol Soc India 48:27-40

Pawley AR, Holloway JR (1993) Water sources for subduction zone volcanism: new experimental constraints. Science 260:664-667

Pepiper G, Doutsos T, Mporonkay C (1993) Structure, geochemistry and mineralogy of hercynian granitoid rocks of the Verdikoussa area, northern Thessaly, Greece and their regional significance. Neues Jb Miner Abh 165:267-296

Piwinskii AJ (1968) Experimental studies of igneous rock series: central Sierra Nevada batholith, California. J Geol 76:548-570

Piwinskii AJ (1973) Experimental studies of igneous rock series, central Sierra Nevada batholith, California: Part II. Neues Jb Miner 5:193-215

Poli S (1993) The amphibolite-eclogite transformation: An experimental study on basalt. Am J Sci 293:1061-1107

Poli S, Schmidt MW (1995) H_2O transport and release in subduction zones: experimental constraints on balsaltic and andesitic systems. J Geophy Res 100:22299-22314

Poli S, Schmidt MW (1997) The high-pressure stability of hydrous phases in orogenic belts: an experimental approach on eclogite-forming processes. Tectonophys 273:169-184

Poli S, Schmidt MW (1998) The high-pressure stability of zoisite and phase relationships of zoisite-bearing assemblages. Contrib Mineral Petrol 130:162-175

Poli S, Schmidt MW (2004) Experimental subsolidus studies on epidote minerals. Rev Mineral Geochem 56: 171-195

Popov VS, Nikiforova NF, Bogatov VI et al. (2001) Multiple gabbro-granite intrusive series of the Syrostan pluton, southern Urals: Geochemistry and petrology. Geochem Int 39:732-747

Puziewicz J, Koepke J (2001) Partial melting of garnet-hornblende granofels and the crystallisation of igneous epidote in the Niedzwiedz Amphibolite Massif (Fore-Sudetic Block, SW Poland) Neues Jb Miner Monat 12:529-547

Quirion DM, Jenkins DM (1998) Dehydration and partial melting of tremolitic amphibole coexisting with zoisite, quartz, anorthite, diopside, and water in the system H_2O-CaO-MgO-Al_2O_3-SiO_2. Contrib Mineral Petrol 130:379-389

Rapp RP, Watson EB, Miller CF (1991) Partial melting of amphibolite/eclogite and the origin of archean trondhjemite and tonalite. Precambrian Res 51:1-25

Roberts MP, Pin C, Clemens JD, Paquette JL (2000) Petrogenesis of mafic to felsic plutonic rock associations: the calc -alkaline Quérigut complex, French Pyrenees. J Petrol 41:809-844

Rushmer T (1991) Partial melting of two amphibolites: contrasting experimental results under fluid-absent conditions. Contrib Mineral Petrol 107:41-59

Saavedra J, Toselli AJ, Rossi de Toselli JN, Rapela CW (1987) Role of tectonism and fractional crystallisation in the origin of lower Paleozoic epidote-bearing granitoids, northwestern Argentina. Geology 15:709-713

Schliestedt M, Johannes W (1984) Melting and subsolidus reactions in the system K_2O-CaOAl$_2O_3$-SiO_2-H_2O: corrections and additional experimental data. Contrib Mineral Petrol 88:403-405

Schmidt MW (1992) Amphibole composition in tonalite as a function of pressure: an experimental calibration of the Al-in-hornblende-barometer. Contrib Mineral Petrol 110:304-310

Schmidt MW (1993) Phase relations and compositions in tonalite as a function of pressure: An experimental study at 650°C. Am J Science 293:1011-1060

Schmidt MW, Thompson AB (1996) Epidote in calc-alkaline magmas: An experimental study of stability, phase relationships, and the role of epidote in magmatic evolution. Am Mineral 81:462-474

Selbekk RS, Skjerlie KP (2002) Petrogenesis of the anorthosite dyke swarm of Tromsø, North Norway: Experimental evidence for hydrous anatexis of an alkaline mafic complex. J Petrol 43:943-962

Sen C, Dunn T (1994) Dehydration melting of a basaltic composition amphibolite at 1.5 and 2.0 GPa: implications for the origin of adakites. Contrib Mineral Petrol 117:394-409

Sial AN, Toselli AJ, Saavedra J et al. (1999a) Emplacement, petrological and magnetic susceptibility characteristics of diverse magmatic epidote-bearing granitoid rocks in Brazil, Argentina and Chile. Lithos 46:367-392

Sial AN, Dall'Agnol R, Ferreira VP et al. (1999b) Precambrian granitic magmatism in Brazil. Episodes 22: 191-198

Singh J, Johannes W (1996a) Dehydration melting of tonalites. Part I. Beginning of melting. Contrib Mineral Petrol 125:16-25

Singh J, Johannes W (1996b) Dehydration melting of tonalites. Part II. Composition of melts and solids. Contrib Mineral Petrol 125:26-44

Skjerlie KP, Douce AEP (2002) The fluid-absent partial melting of a zoisite-bearing quartz eclogite from 1.0 to 3.2 GPa; Implications for melting in thickened continental crust and for subduction-zone processes. J Petrol 43:291-314

Skjerlie KP, Johnston AD (1993) Fluid-absent melting behaviour of an F-rich tonalitic gneiss at mid-crustal pressures: Implications for the generation of anorogenic granites. J Petrol 34:785-815

Strens RGJ (1965) Stability and relations of the Al-Fe epidotes. Mineral Mag 35:464-475

Thompson AB, Ellis DJ (1994) CaO+MgO+Al$_2$O$_3$+SiO$_2$+H$_2$O to 35 kbar: amphibole, talc and zoisite dehydration and melting reactions in the silica-excess part of the system and their possible significance in subduction zones, amphibolite melting and magma fractionation. Am J Sci 294:1229-1289

Thompson JB (1982) Composition space: An algebraic and geometric approach. Mineral Soc Am Reviews 10:1-32

Tulloch AJ (1986) Comment on "Implications of magmatic epidote-bearing plutons on crustal evolution in the accreted terranes of northwestern North America" and "Magmatic epidote and its petrologic significance". Geology 14:187-188

Tulloch AJ, Challis GA (2000) Emplacement depths of Paleozoic -Mesozoic plutons from western New Zealand estimated by hornblende-Al geobarometry. New Zeal J Geol Geophys 43:555-567

van der Laan SR, Wyllie PJ (1992) Constraints on archean trondhjemite genesis from hydrous crystallization experiments on Nuk Gneiss at 10-17 kbar. J Geol 100:57-68

Vielzeuf D, Schmidt MW (2001) Melting relations in hydrous systems revisited: applications to metapelites, metagreywackes and metabasalts. Contrib Mineral Petrol 141:251-267

Vyhnal CR, McSween HY, Speer JA (1991) Hornblende chemistry in southern Appalachian granitoids: implications for aluminium hornblende thermobarometry and magmatic epidote stability. Am Mineral 76:176-188

Winther KT, Newton RC (1991) Experimental melting of hydrous low-K tholeiite: evidence on the origin of Archaen cratons. Bull Geol Soc Denmark 39:213-228

Wolf MB, Wyllie PJ (1994) Dehydration-melting of amphibolite at 10 kbar: effects of temperature and time. Contrib Mineral Petrol 115:369-383

Wones DR (1989) Significance of the assemblage titanite + magnetite + quartz in granitic rocks. Am Mineral 74:744-749

Zhang RY, Liou JG, Coney BL (1995) Talc-, magnesite- and Ti-clinohumite-bearing ultrahigh pressure meta-mafic and ultramafic complex in the Dabie Mountains, China. J Petrol 36:1011-1037

Zen E (1988) Tectonic significance of high-pressure plutonic rocks in the western cordillera of North America. *In*: Metamorphism and Crustal Evolution of the Western United States. Rubey Vol.VII. W.G.Ernst (ed) Prentice-Hall, Englewood Cliffs, New Jersey, p 41-67

Zen E (1985) Implications of magmatic epidote-bearing plutons on crustal evolution in the accreted terranes of northwestern North-America. Geology 13:266-269

Zen E-an, Hammarstrom JM (1984) Magmatic epidote and its petrologic significance. Geology 12:515-518

Zen E, Hammarstrom JM (1986) Reply on the comments on "Implications of magmatic epidote-bearing plutons on crustal evolution in the accreted terranes of northwestern North America" and "Magmatic epidote and its petrologic significance" by AJ Tulloch and by RH Moench. Geology 14:187-188