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Fluid Inclusions in Epidote Minerals and Fluid Development in Epidote-Bearing Rocks

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INTRODUCTION

The widespread occurrence of epidote minerals in metamorphic and igneous rocks as well as in many ore deposit types makes it a promising candidate for fluid inclusion studies. Apart from high- to very high-temperature and low- to intermediate-pressure conditions, epidote minerals are stable over a wide range of pressure and temperature in the continental and oceanic crust (e.g., Poli and Schmidt 1998). Yet fluid inclusion studies on epidote minerals are surprisingly scarce, even in fluid-saturated environments like certain vein-type deposits or hydrothermal-volcanic vugs and druses. For example, epidote minerals are not mentioned in the subject index of Roedder's (1984) outstanding summary and review of fluid inclusion studies and occurrences, which lists more than sixty different host minerals for fluid inclusions. Nonetheless, more recent studies showed fluid inclusions in epidote minerals to be the only direct witness of the physiochemical and compositional fluid evolution during certain geodynamic processes mainly found in fossil geothermal systems, ore deposits and high-pressure to ultra-high pressure rocks.

The aim of this review is to outline and summarize some aspects and interpretations of geodynamic processes, which are based on temperature (T), pressure (P), molar volume (V) and composition (X) data from fluid inclusions in epidote minerals as well as associated host minerals from various geological environments.

The review starts with a chapter on some typical mixed volatile solid-fluid equilibria involving epidote minerals, which are relevant for the here discussed environments. This is followed by a short introduction into the basic concepts of fluid inclusion research and the role of epidote minerals. The next section covers fluid inclusion studies on epidote minerals from active and fossil geothermal systems as well as low-grade metamorphic rocks and constraints on the P-T-X properties of the fluids present in these systems. This is followed by a short introduction on skarn deposits and the role of ore-forming fluids during the prograde and retrograde skarn evolution, with the focus on those skarn deposits, in which epidote minerals were investigated for fluid inclusions. In addition fluid inclusion studies on epidote minerals are described from other ore deposits and plutonic rocks. The next part deals with high pressure (HP) and ultra-high pressure (UHP) metamorphic rocks, which frequently preserve prograde and retrograde epidote minerals containing fluid inclusions. The presence and composition of a free fluid phase during HP and UHP metamorphism is discussed in terms of the consequences for mineral stabilities, P-T conditions, fluid-phase equilibria and fluid flow mechanisms.

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MIXED VOLATILE REACTIONS INVOLVING EPIDOTE MINERALS

In addition to pressure and temperature, epidote mineral stability also depends on the Al/Fe^{3+} ratio, the oxygen fugacity, the bulk and fluid composition and the solution pH. Here the emphasis is mainly placed on some typical mixed volatile solid-fluid equilibria involving epidote minerals, which are relevant for the subsequent chapters, so that the composition and development of the fluid phase in equilibrium with the epidote-bearing mineral parageneses can be discussed and compared with the composition of the fluid inclusions in epidote minerals.

Hydrothermal and low-grade conditions

Epidote occurs in active geothermal systems at temperatures <200°C as well as under low-grade conditions at temperatures below 360°C (Deer et al. 1986; Bird and Spieler 2004). Epidotization is usually interpreted to be a result of mass transport via a fluid phase in such low temperature environments. Epidote is therefore often found to have precipitated in open fractures and cavities, but also to have replaced the immediate country rocks. It is typically associated with laumontite, heulandite, wairakite, prehnite, pumpellyite, illite, anorthite, chlorite, calcite, quartz and hematite. Some -under the above mentioned conditions- important general reactions in the CaO-FeO-Fe_2O_3-Al_3O_3-H_2O-system occur during the transition to greenschist-facies conditions (summarized in Deer et al. 1986):

pumpellyite = epidote + H_2O (1)

pumpellyite = epidote + actinolite + H_2O (2)

pumpellyite + chlorite + quartz = epidote + actinolite + H_2O (3)

prehnite = epidote + grossularite + H_2O (4)

prehnite + hematite = epidote + H_2O (5)

laumontite + hematite = epidote + quartz + Al_2O_3 + H_2O (6)

wairakite + hematite = epidote + quartz + H_2O (7)

Metamorphism frequently proceeds directly into the greenschist-facies without the development of lower grade minerals such as prehnite, pumpellyite, Fe-poor epidote or laumontite. The reason for this being that even small amounts of CO_2 in the fluid phase suppress the formation of these lower grade facies minerals (e.g., Thompson 1971; Bird and Helgeson 1981; Yardley 1989). However in the presence of quartz and calcite, epidote solid solutions of intermediate composition form over a wide range of X_{CO_2} values at low-pressure conditions as was shown by Bird and Helgeson (1981). For example, the mineral assemblage epidote-K-feldspar-muscovite-calcite-quartz is common in the Salton Sea geothermal system. Bird and Helgeson (1981) demonstrated that the epidote of this mineral assemblage displays an increase in Fe with increasing X_{CO_2} under constant pressure and temperature conditions. The following reaction (Arnason et al. 1993) represents the equilibrium conditions of the mineral assemblage:

muscovite + calcite + quartz = epidote$_{ss}$ + K-feldspar + CO_2 + H_2O (8)

Greenschist-facies conditions

Epidote minerals are characteristically associated with chlorite, quartz, albite, actinolite, muscovite, biotite, garnet, corundum and calcite. Typical mixed volatile reactions (summarized in Tracy and Frost 1991; Labotka et al. 1988) in the CaO-Al_2O_3-CO_2-H_2O (CASCH)-system are:

2 zoisite + 1CO_2 = 3 anorthite + 1 calcite + 1H_2O (9)

4 zoisite + 1 quartz = 1 grossularite + 5 anorthite + $2H_2O$ (10)

6 zoisite = 2 grossularite + 6 anorthite + 1 corundum + $3H_2O$ (11)

2 zoisite + 2 calcite = 1 corundum + 2 grossularite + $2CO_2$ + $1H_2O$ (12)

2 zoisite + 2 quartz + corundum = 4 anorthite + $1H_2O$ (13)

2 zoisite + $4CO_2$ = 4 calcite + 6 quartz + 3 corundum + $1H_2O$ (14)

2 zoisite + 5 calcite + 3 quartz = 3 grossularite + $1H_2O$ + $5CO_2$ (15)

and in the CaO-(FeO,MgO)-Al_2O_3-CO_2-H_2O (C(FM)ASCH)-system:

5 vesuvianite + 1 clinozoisite + 4 quartz = 29 grossularite + 10 diopside + $23H_2O$ (16)

3 chlorite + 10 calcite + 21 quartz = 3 actinolite + 2 clinozoisite + $10CO_2$ + $1H_2O$ (17)

The fluid phase in all of these reactions has a relatively low X_{CO_2}. This is demonstrated by a T-X_{CO_2} projection in the CASCH end-member system at a constant pressure of 2 kbar and with an excess fluid phase (Fig. 1). The T-X_{CO_2} projection was calculated for $0 < X_{CO_2} < 0.3$ and with temperatures of between 300 and 650°C using the internally-consistent thermodynamic dataset of Holland and Powell (1990) with the endmembers zoisite, grossularite, quartz, wollastonite, corundum, anorthite, calcite and an H_2O-CO_2 fluid (computer program THERMOCALC v.3.1; Powell and Holland 1988). The zoisite-bearing assemblages, which are stable only at $X_{CO_2} < 0.1$ between 280 and 580°C, are delimited by reactions (9), (11) and (14).

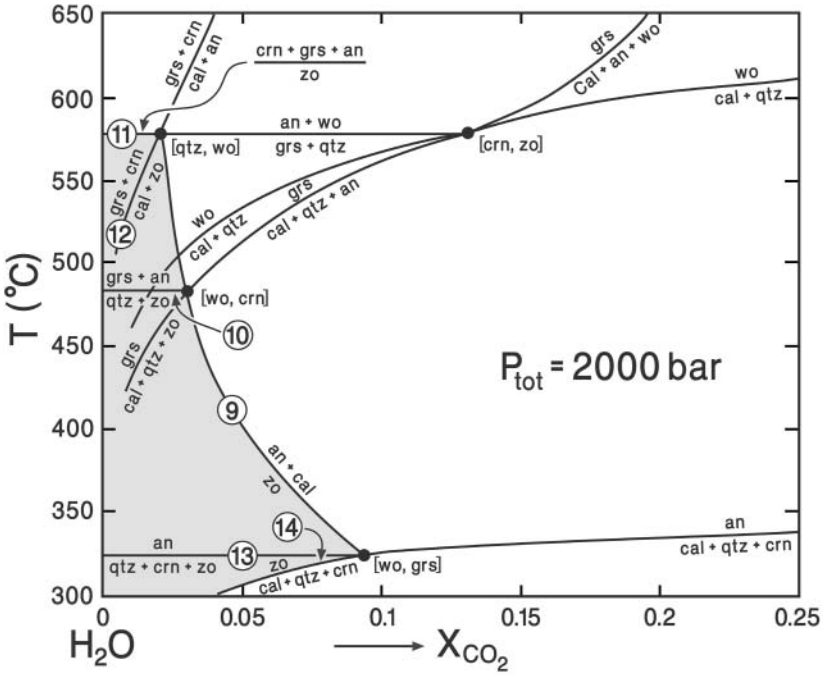

Figure 1. T-X_{CO_2} projection calculated at 2000 bar in the system CASCH and with an excess fluid phase. Pure endmember compositions were used. Shaded field outlines zoisite stability. Numbers refer to reactions listed in the text. Abbreviations follow Kretz (1983).

A similar result was obtained by Will et al. (1990), who calculated a T-X_{CO_2} petrogenetic grid for the system CFMASCH with quartz and fluid in excess at a fixed pressure of 2 kbar and with temperatures of between 380 and 510°C involving the minerals amphibole, chlorite, anorthite, clinozoisite, dolomite, chloritoid, garnet, margarite, andalusite and calcite. In this diagram the stability field of Fe-free clinozoisite-bearing assemblages was restricted to $X_{CO_2} < 0.15$, which is also shown by a pseudosection for a specific bulk composition (Will et al. 1990). Even when adding Na (mainly to plagioclase) and Fe^{3+} (mainly to epidote) to the system the divariant field of the clinozoisite-epidote-bearing assemblage is restricted to a very narrow field and a low X_{CO_2}. However, temperature and X_{CO_2} values increase with pressure.

High- and ultra-high pressure metamorphic conditions

Experimental data indicate that orthorhombic zoisite is the Fe-free epidote mineral at *experimentally and geologically relevant conditions* (Poli and Schmidt 1998). Nevertheless, in natural rocks clinozoisite as well as epidote are believed to occur at low to intermediate pressure (Poli and Schmidt 1998). Furthermore, besides zoisite clinozoisite and/or epidote are frequently reported to occur in eclogite-facies rocks (e.g., Holland 1979; Giaramita and Sorensen 1994; Klemd et al. 1994; Scambelluri et al. 1998; Fu et al. 2001, 2003). Several (mixed) volatile reactions involving epidote minerals occur under high- to very-high pressure conditions. The transition of very-low grade rocks to blueschist-facies conditions is displayed by the following general reaction, which involves zoisite (Spear 1993):

$$\text{prehnite} + \text{calcite} = \text{lawsonite} + \text{zoisite} + H_2O + CO_2. \tag{18}$$

The transition of greenschist- to blueschist-facies conditions is marked by the NCFMASH divariant reaction (Maruyama et al. 1986; Will et al. 1998):

$$\text{actinolite} + \text{chlorite} + \text{albite} = \text{glaucophane} + \text{zoisite (or epidote)} + \text{quartz} + H_2O \tag{19}$$

Blueschist facies can be subdivided into a lawsonite- and epidote-bearing subfacies, which is displayed by the following NCFASCH reactions (Franz and Althaus 1977; Winkler 1979; Heinrich and Althaus 1988):

$$4\ \text{lawsonite} + 1\ \text{albite} = 1\ \text{paragonite} + 2\ \text{zoisite} + 2\ \text{quartz} + 6H_2O \tag{20}$$

$$4\ \text{lawsonite} + 1\ \text{jadeite} = 1\ \text{paragonite} + 2\ \text{zoisite} + 1\ \text{quartz} + 6H_2O \tag{21}$$

$$3\ \text{lawsonite} + 1\ \text{calcite} = 2\ \text{zoisite} + 1CO_2 + 5H_2O \tag{22}$$

$$5\ \text{lawsonite} + 1\ \text{albite} = 1\ \text{margarite} + 2\ \text{zoisite} + 2\ \text{quartz} + 8H_2O \tag{23}$$

At high pressure and with increasing temperatures the following important reactions, which are relevant for epidote minerals, occur in the NCMASH system (Gao and Klemd 2001; Poli and Schmidt 2004):

$$6\ \text{zoisite} + 4\ \text{pyrope} + 7\ \text{quartz} = 13\ \text{kyanite} + 12\ \text{diopside} + 3H_2O \tag{24}$$

$$13\ \text{lawsonite} + 3\ \text{diopside} = 8\ \text{zoisite} + 1\ \text{pyrope} + 5\ \text{quartz/coesite} + 22H_2O \tag{25}$$

$$15\ \text{diopside} + 12\ \text{zoisite} = 13\ \text{grossularite} + 5\ \text{pyrope} + 12\ \text{quartz/coesite} + 6H_2O \tag{26}$$

$$13\ \text{glaucophane} + 5\ \text{zoisite} = 26\ \text{jadeite} + 12\ \text{diopside} + 9\ \text{pyrope} + 19\ \text{quartz} + 15H_2O \tag{27}$$

$$12\ \text{lawsonite} + 1\ \text{glaucophane} = 2\ \text{paragonite} + 1\ \text{pyrope} + 6\ \text{zoisite} + 5\ \text{quartz} + 20H_2O \tag{28}$$

All of these reactions are believed to occur under very low X_{CO_2} conditions (e.g., Franz and Spear 1983; Klemd et al. 1994; Gao and Klemd 2001; Boundy et al. 2002). This is supported by experimental investigations by Poli and Schmidt (1998) who came to the conclusion that at low temperature (<800°C)-high pressure conditions lawsonite or zoisite coexist with an H_2O-rich fluid phase. Boundy et al. (2002) suggested three reasons for the low X_{CO_2} of the fluid phase present during eclogite-facies metamorphism: 1) Lack of progress of decarbonation reactions during subduction with depths less than 100 km; 2) Dehydration reactions dominate during subduction; and 3) CO_2 fractionation into solid phases during eclogite-facies conditions.

However, several fluid inclusion studies on eclogite-facies rocks (see below) indicate the presence of considerable amounts of dissolved salts in primary aqueous fluid inclusions in high-pressure minerals, which implies that at least some eclogite-facies fluids will have reduced water-activities and increased SiO_2 solubilities (e.g., Shmulovich and Graham 1999).

Low-pressure contact metamorphic-metasomatic fluids in skarn deposits

Typically, epidote minerals are associated with contact metamorphic/metasomatic open-system processes, as is the case of skarn deposits. Due to advecting hydrothermal solutions, which are at least partly derived from nearby magmatic intrusions, a compositional gradient is established in addition to the thermal gradient. Typical minerals of many skarn deposits are—besides the epidote minerals—diopside-hedenbergite-rich pyroxene, grossularite-andradite-rich garnet, actinolite, wollastonite, vesuvianite, anorthite, phlogopite, calcite, dolomite, magnetite and other Ca-Al-Fe-Mn-Mg silicates (see below). In addition to the reactions above, in skarns and skarn deposits epidote minerals are the result of several other mixed volatile reactions, as for example in the CFMASCH-system (Labotka et al. 1988):

5 vesuvianite + 1 clinozoisite + 4 quartz = 29 grossularite + 10 diopside + 23H_2O (16)

3 vesuvianite + 14CO_2 =
9 grossularite + 6 diopside + 5 clinozoisite + 14 calcite + 11H_2O (29)

3 vesuvianite + 87CO_2 =11 clinozoisite + 85 calcite + 9 quartz + 6 diopside + 8H_2O (30)

These phase equilibria indicate very low X_{CO_2}, as is derived from T-X_{CO_2} diagrams (Labotka et al. 1988). The authors suggested that almost CO_2-free aqueous fluids were in equilibrium with calcareous argillites in the Big Horse Limestone, west-central Utah, which had locally undergone contact metamorphism.

However, even more characteristic for skarn deposits is the involvement of Fe^{3+}-bearing phases in mixed volatile reactions, which occur almost in all types of skarn deposits and are generally related to the ore-forming process (Einaudi et al. 1981; see below). Some characteristic epidote-involving reactions in the CaO-Fe_2O_3-Al_2O_3-SiO_2-CO_2-H_2O (CF^*ASCH) system are:

2 epidote + 1 grossularite + 1CO_2 = 1 calcite + 3 anorthite + 1 andradite + 1H_2O (31)

2 epidote + 1 calcite + 1 quartz = 2 anorthite + 1 andradite + 1CO_2 + 1H_2O (32)

2 epidote + 1 calcite + 1 hedenbergite =
2 grossularite + 2 quartz + 1 magnetite + 1CO_2 + 1H_2O (33)

2 epidote + 5 calcite + 3 quartz = 2 grossularite + 1 andradite + 5CO_2 + 1H_2O (34)

4 epidote + 1 quartz + 1 grossularite = 5 anorthite + 2 andradite + 2H_2O (35)

8 epidote + 1 hedenbergite =
1 quartz + 8 anorthite + 1 magnetite + 3 andradite + 4H_2O (36)

2 epidote + 3 calcite + 1 hedenbergite + 3CO_2 =
3 calcite + 2 anorthite + 1 magnetite + 4 quartz + 1H_2O (37)

These oxygen-conserving mixed volatile reactions are displayed on a T-X_{CO_2} projection for the

$CF^{*}ASCH$ end-member system at a constant pressure of 1 kbar (Fig. 2). The T-X_{CO_2} projection was calculated for $0 < X_{CO_2} < 0.45$ and temperatures between 300 and 650°C using the internally-consistent thermodynamic dataset of Holland and Powell (1990) and the computer program THERMOCALC v.3.1 (Powell and Holland 1988). The diagram is calculated for zoisite, grossularite, quartz, wollastonite, andradite, hedenbergite, anorthite, magnetite, calcite and quartz and the fluid phase as excess phases. The diagram is highly schematic seeing that solid solutions between Fe^{3+} and Al in epidote and garnet were neglected, but it still serves to show the principles of the phase relations. Epidote is clearly stable up to much higher X_{CO_2} values as in the CASCH-system.

Metasomatic reactions of epidote can be formulated as exchange reactions with a fluid of the type

$$3\ \text{anorthite} + 1CaCl_2 + 1H_2O = 2\ \text{zoisite} + 2HCl \qquad (38)$$

$$3\ \text{anorthite} + 1CaF_2 + 1H_2O = 2\ \text{zoisite} + 2HF \qquad (39)$$

$$3\ \text{anorthite} + 1Ca^{2+} + 1CO_3^{2-} + 1H_2O = 2\ \text{zoisite} + 2CO_2 \qquad (40)$$

On the one hand these reactions show that epidote becomes less stable with increasing acidity, on the other hand that $CaCl_2$ can be an important salt in fluids, which are responsible for the formation of epidote minerals. This is supported by the fluid inclusion studies below.

In summary it can be stated that Fe-poor epidote is a good indicator for low X_{CO_2} values, at both low- and high-pressure conditions. However, Poli and Schmidt (1998) also suggested that zoisite can coexist with a CO_2-rich fluid phase at very high pressures of 40 kbar and temperatures above 800°C. Furthermore, epidote solid solutions of intermediate composition may be stable over a wide range of CO_2 concentrations in the fluid phase of hydrothermal, low-pressure environments as proposed by Bird and Helgeson (1981). In addition, under

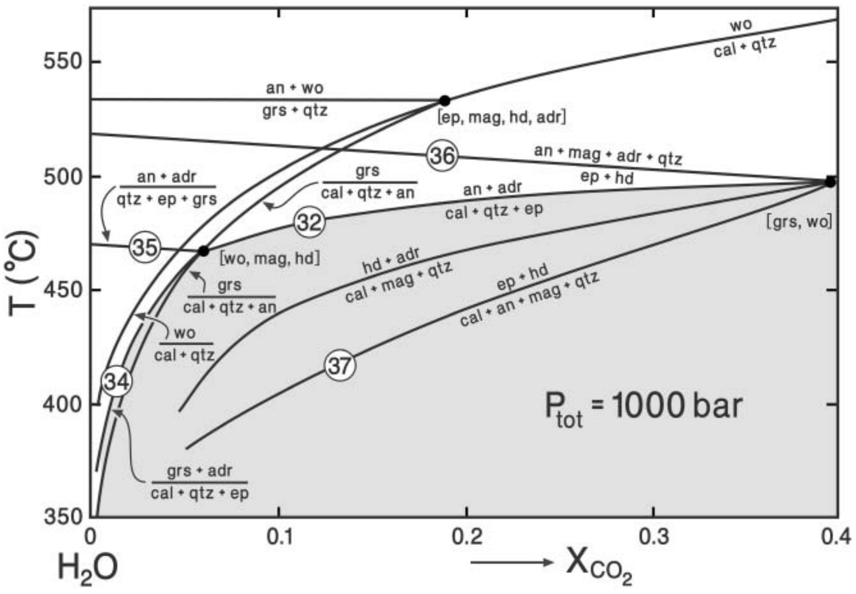

Figure 2. T-X_{CO2} projection calculated at 1000 bar in the system $CF^{*}SCH$ and with quartz and the fluid phase in excess. Pure endmember compositions were used. Shaded field outlines epidote-calcite-quartz stability. Numbers refer to reactions listed in the text. Abbreviations follow Kretz (1983).

highly oxidizing conditions, as is the case in skarns, epidote shows an enlarged stability range with respect to X_{CO_2} (Fig. 2). These results contradict the findings of Taylor and Liou (1978) and Liou (1993) who after evaluating the stability of epidote in the CaO-Al_2O_3-SiO_2-FeO_x-H_2O-CO_2-system at 2 kbar concluded that epidote together with quartz can not be stable at $X_{CO_2} < 0.2$. These contrasting conclusions are the consequence of the use of different thermodynamic datasets, different endmembers as well as different chemical systems. However, fluid inclusions found in epidote minerals in low-grade rocks are usually H_2O-salt rich and CO_2 poor (see below). The dissolved salts frequently result in a considerable decrease in the H_2O-activity. Therefore the low X_{CO_2} value—as displayed by the epidote minerals' stability in the T-X_{CO_2} projection—of the above discussed CASCH-example do not necessarily indicate that pure H_2O fluids were in equilibrium with the epidote minerals.

FLUID INCLUSION STUDIES: INTRODUCTION OF SOME BASIC CONCEPTS

Fluid inclusions are minute samples of fluids trapped in cavities generally smaller than 100 μm in diameter. These fluids were trapped at a certain event in the geological history of the host rock. Such inclusions may therefore provide information on the *P-V-T-X* properties of the fluid at the time of trapping. All of these variables are significant for application in a variety of geological and mineralogical fields, such as the study of ore deposits, igneous and metamorphic petrology, structural geology, sedimentology and gemology, to name just a few (for a more comprehensive list see Roedder 1984). In order to determine *P-V-T-X* variables during trapping conditions microthermometric studies of fluid inclusions have to be undertaken. However, before conducting microthermometric measurements with a heating-cooling stage a detailed petrographic description and classification of the fluid inclusion occurrences is imperative. Some fluid inclusions—usually H_2O-salt and/or CO_2—are trapped during crystal growth and are referred to as primary or pseudosecondary (for textural criteria see Roedder 1984). Secondary fluid inclusions form by sealing and healing of fractures subsequent to the growth of the host mineral. They occur in minerals and rocks that have been exposed to tectonic and/or thermal stresses. Temperatures of phase transitions (microthermometry) in fluid inclusions are determined with heating-freezing stages. If the composition of an inclusion fluid is known, then its density can be calculated from the homogenization temperature (T_h) of the different phases into one fluid phase. Thereafter an isochore¸ which is defined as line of constant volume and hence constant density for a homogenous fluid, can be plotted on a *P-T* diagram. Homogenization temperatures are the entrapment temperatures of fluids, only if the hydrostatic pressure did not exceed their equilibrium vapor pressure. In this case a "pressure correction" is necessary to obtain true entrapment temperatures. After freezing the fluid inclusions are heated to obtain the initial and final melting temperature, both of which provide information on the composition of the inclusion fluid. In the case of a H_2O-salt solution, the final ice melting temperature (T_m) corresponds to the freezing point depression of pure H_2O, while the initial melting temperature may correspond to the eutectic temperature for the respective salt system. The salinity of aqueous inclusions is inferred from the temperature of final ice melting and given as weight % NaCl equivalent (wt. % NaCl eq.). A detailed description of microthermometrical techniques and basic information concerning the application of the microthermometric data are summarized in several publications (Hollister and Crawford 1981; Roedder 1984; Shepherd et al. 1986; Goldstein and Reynolds 1994; Andersen et al. 2001). Two requirements have to be fulfilled before unambiguous *P-T-X* conditions can be determined from fluid inclusion studies: Firstly, the fluid inclusions must have remained a chemically closed system throughout the geological history of the host mineral, and secondly, the molar volume of the fluid inclusion must have remained constant throughout the geological history of the host mineral. Both assumptions have been shown to be violated for certain soft, easily-cleaved host minerals such as halite, barite, fluorite and carbonates when exposed to mechanical or thermal stress (e.g., Shepherd et al. 1986). Nonetheless, the widespread occurrence of quartz allows fluid inclusion studies in various geological fields to be conducted such as ore petrology, igneous and metamorphic petrology, structural geology and sedimentology. This is due to the fact that fluid inclusions are most commonly observed in quartz, although fluid inclusions have also been observed in other minerals such as apatite, halite, carbonate, topaz, barite, fluorite, olivine and less commonly in garnet, pyroxene, amphibole, kyanite, feldspar and epidote minerals.

Most fluid inclusions in epidote minerals are texturally primary or pseudosecondary. They are either aligned with their long dimension parallel to the b-axis of the epidote host or occur as large isolated single inclusions (Fig. 3). However secondary fluid inclusions occurring along healed microfractures, which crosscut grain boundaries, are also observed in epidote minerals. The shape of all inclusions ranges from irregular to tabular and negative crystal shapes are also common. Most fluid inclusions display a large range in size from <3 to 100 μm, while some of the isolated larger inclusions may reach up to 300 μm in size. All reported fluid inclusions in epidote minerals are aqueous and consist of a liquid and a vapor bubble. In addition one or more solid phases such as rutile, apatite, quartz, zircon and calcite were found in these inclusions. These solids are usually believed—according to the criteria established by Roedder (1984)—to have been accidentally trapped. However, especially in metamorphic rocks some of these solids may have formed from "back reactions" of the trapped inclusion fluid with the epidote mineral host (cf. Heinrich and Gottschalk 1995). Consequently, quartz seems to be a perfect host mineral since it does not react with the entrapped fluid to form daughter minerals by "back reactions". In addition it almost always contains fluid inclusions and has a widespread stability. Frequently a mismatch between pressure and compositional estimates—from mineral geothermobarometry and fluid-phase equilibria with fluid inclusion data (mainly from quartz)—is encountered in amphibolite-facies to high-grade metamorphic rocks (e.g., Crawford and Hollister 1986; Touret 1992). This is the result of decrepitation (fluid inclusions loose fluid along fractures in the host mineral during implosion or explosion), leakage (form of compositional and physical re-equilibration in which parts of the inclusion fluid is lost) or stretching (non-elastic volume change which is accommodated by plastic deformation of the host mineral) due to pressure differences between internal pressure (within inclusions) and confining pressure e.g., during exhumation of the host rock (e.g., Crawford and Hollister 1986; Bodnar et al. 1989; Sterner et al. 1995; Touret 1992; Küster and Stöckhert 1997).

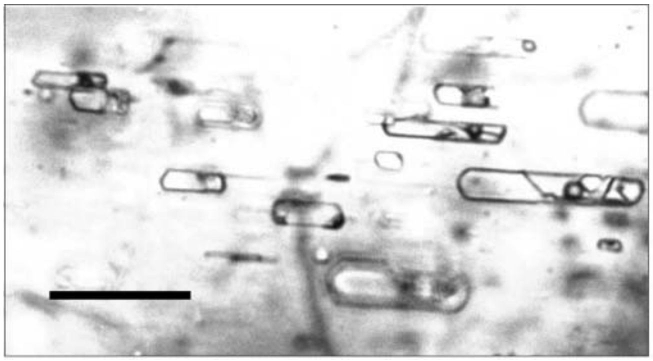

Figure 3. Photomicrograph show-ing primary high-salinity fluid inclusions parallel to the b-axis of epidote in the Sujiahe eclogites from the NW Dabie Shan HP-belt in China (Fu 2002). The inclusion contains—besides a liquid as well as a vapor-bubble—one or more unidentified solid phase, which did not dissolve during heating (for further explanation see text). Scale bar = 20 μm.

In contrast to other high-pressure minerals such as garnet and omphacite, epidote for example was suspected to be susceptible to H-diffusion (leakage) during eclogite-facies metamorphism (Giaramita and Sorensen 1994), which was however not verified in various fluid inclusion studies on epidote-group minerals from HP-UHP rocks (see discussion on HP and UHP metamorphism below). Besides primary fluid inclusions in syn-metamorphic vein minerals, fluid inclusions in metamorphic rocks are usually secondary and mainly occur along healed fractures in matrix quartz. Syn-metamorphic quartz veins represent fractures—ranging in size from microcracks to veins—along which fluid flow was accommodated and channelized (e.g., Walther and Orville 1982; Yardley 1986). The fluid in secondary inclusions along healed fractures in the matrix quartz and the quartz veins may have been derived by prograde devolatilization reactions of the immediate adjacent rock and, thus, would have been in equilibrium with the source rock at this *P-T* condition. These inclusions may therefore preserve the same information as texturally primary inclusions formed during the growth of syn-metamorphic vein minerals, which formed at sites of hydraulic fracturing. Nonetheless, it is also possible that fluids were trapped far away from the source rock and postdate the devolatilization of the host rock (e.g., Crawford and Hollister 1986; Yardley 1986). This is supported by the solubility of SiO_2 in H_2O-salt solutions, which decreases with decreasing temperatures, and thus allows the formation of quartz veins as the fluid approaches cooler rocks (e.g., Yardley 1986; Newton and Manning 2000). In addition to these uncertainties and the above described post-entrapment modifications in high-grade metamorphic rocks, quartz is also highly susceptible to recrystallization by grain boundary migration under low-grade conditions (e.g., Johnson and Hollister 1995). This recrystallization favors entrapment of CO_2 inclusions, whereas microfracturing favors entrapment of aqueous inclusions. CO_2 can therefore only be removed by hydrofracturing, while H_2O ± salt due to its strong polarity wets the quartz surface and remains outside the advancing crystal front during recrystallization. Due to the low dihedral angle of H_2O ± salt ($<60°$) it can migrate along quartz-quartz grain boundaries, whereas CO_2 with high dihedral angles ($>60°$) will stay behind (e.g., Holness 1993). Therefore, pure CO_2 inclusions in quartz in low- to high-grade metamorphic rocks as well as in deformed and heated hydrothermal/metamorphic quartz veins are most likely to represent the residue of a deformation and recrystallization process rather than a primary hydrothermal or metamorphic fluid (e.g., Johnson and Hollister 1995; Klemd 1998). As a result fluid inclusion investigations on metamorphic rocks should preferentially be conducted on matrix and vein minerals, which are less susceptible to post-trapping modifications such as garnet, pyroxene, kyanite and epidote minerals, or on quartz inclusions in these minerals, in order to obtain more accurate *P-T-X* information for peak metamorphic fluids. However, daughter minerals in fluid inclusions of these minerals may result from "back reactions" of the host mineral with the entrapped fluid, which may have altered the density and composition of the remaining fluid (cf. Heinrich and Gottschalk 1995; Kleinefeld and Bakker 2002).

One of the most significant achievements of fluid inclusion studies is that it has shed new light on the major role of fluid immiscibility, for example in the formation of ore deposits and oil fields, in the fractionation of siliceous melts and during metamorphism. Hollister (1981) summarized three types of fluid immiscibility based on the composition of the fluid phase:

I. The first type is boiling of predominantly aqueous fluids, which results in simultaneous entrapment of liquid-water and/water-rich vapor. In order to prove that boiling had occurred, both types of inclusion have to homogenize at the same temperature. Fluid inclusion investigations on epidote have revealed that boiling had occurred in active and fossil geothermal systems (e.g., De Vivo et al. 1989; Kelley et al. 1993) as well as in skarn deposits (e.g., Bukharev et al. 1982).

II. The presence of NaCl and/or other electrolytes in the H_2O-CO_2 system on the one hand enlarges the solvus between CO_2- and H_2O-rich fluids (Fig. 4) and on the other

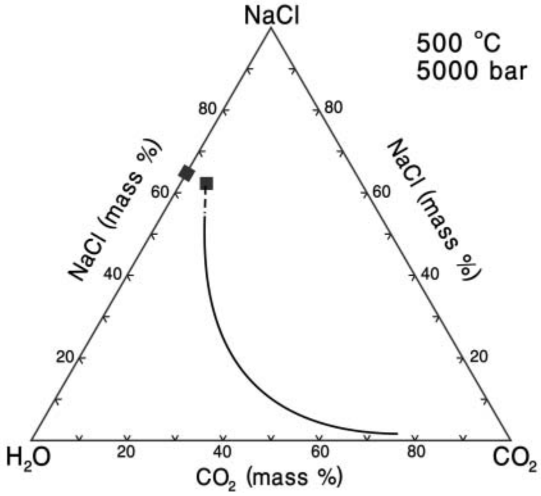

Figure 4. Isobaric isothermal phase diagram of the H_2O-CO_2-NaCl system at 5000 bar and 500°C. The thick solid line shows the interpreted immiscibility boundary between the one-fluid field and the two-fluid field for the H_2O-CO_2-salt system. Increasing NaCl content raises the immiscibility boundary considerably. Filled squares = halite saturation under experimental conditions (modified after Shmulovich and Graham 2003).

hand increases the non-ideality of H_2O-CO_2 fluid mixing. Thus mineral assemblages that are stable at low temperature in the presence of a pure H_2O-CO_2 fluid may also be stable at higher temperature in the presence of an H_2O-CO_2-salt fluid. Furthermore fluid-phase equilibria will fail to reveal the correct fluid composition at immiscibility conditions if the additional presence of electrolytes in the H_2O-CO_2 system are not recognized (Bowers and Helgeson 1983). A similar effect exists in the H_2O-CH_4 system, where the addition of salts dramatically increases the immiscibility field of H_2O- and CH_4-rich fluids towards higher *P-T* conditions (Goldstein and Reynolds 1994). Fluid inclusions found in epidote minerals in low-grade rocks are usually H_2O-salt rich and CO_2 poor (e.g., Stalder and Rykart 1980), which is in accordance with fluid-phase equilibria under these *P-T* conditions (see discussion above). Yet in some low-grade metamorphic rocks epidote seems to occur in textural equilibrium with other minerals, which contain H_2O-CO_2-rich fluids with a CO_2-content ranging from 60 to 90 mol % (Kreulen 1980, 1989). This may indicate epidote growth during or after loss of CO_2 due to unmixing (i.e., the mole fraction of H_2O is increased in the fluid phase)

III. The third type concerns the separation of a low-density fluid from a silicate melt. The solubility of an aqueous fluid is higher in silicate melts when compared to the solubility of a carbonic fluid. Accordingly a CO_2-rich fluid phase can separate early from a crystallizing melt. Hollister (1981) suggests that this is a possible explanation for the common occurrence of nearly pure CO_2 occurring with glass (quenched silicate melt) inclusions in phenocrysts and xenocrysts. However, another possibility is that CO_2 in glass inclusions are formed by the trapping of external CO_2 through melt migrating along grain boundaries (Witt-Eickschen et al. 2003). This type of immiscibility as well as melt inclusions have not yet been described for inclusions in epidote.

GEOTHERMAL SYSTEMS

Introduction

Many geothermal systems are associated with active or recently active volcanism and plutonism, which act as heat sources to enhance fluid circulation and, thereby, mass transport in the continental and oceanic crust (e.g., Norton 1977, 1987; Cathles 1997). Irreversible reactions between hydrothermal fluid and immediate host rocks produce mineral alteration in order to reach equilibrium between fluid and rock (e.g., Helgeson 1979; Norton 1987). The presence or absence of certain minerals in the alteration assemblage depends on factors such as CO_2 and O_2 fugacities, solution pH as well as bulk rock composition (e.g., Henley and Ellis 1983; Hedenquist and Henley 1985; Barnes 1997). Fluid inclusions are often trapped during the growth of the alteration minerals, and are therefore able to give direct evidence on the physicochemical properties of the hydrothermal fluid responsible for the alteration. In active hydrothermal systems fluid inclusion data allow a comparison with directly measured temperature and fluid composition in order to assess short time scale variations (De Vivo et al. 1989; Hedenquist et al. 1992; Lecuyer et al. 1999). Fluid inclusion data from minerals of fossil geothermal systems provide direct evidence concerning the composition and the evolution of the hydrothermal fluids (Kelley et al.1993; Barnes 1997).

This review is restricted to studies involving fluid inclusions in epidote minerals from several well-known geothermal systems, including those associated with active magmatic hydrothermal systems as well as submarine hydrothermal systems. For more details on geothermal systems along with extensive reference lists see Barnes (1997) and Bird and Spieler (2004).

ACTIVE MAGMATIC HYDROTHERMAL SYSTEMS

World-wide numerous active geothermal systems are formed by penetrating hydrothermal fluids, which are driven by the heat of associated volcanic or plutonic activity. The hydrothermal solutions are usually mixtures of meteoric and magmatic fluids as revealed by stable isotope investigations. All described occurrences document the physicochemical properties and composition of inclusion fluids, which represent pristine samples of the hydrothermal fluids and, if possible, its evolution in time and space.

Los Azufres geothermal fields, Mexico

The Los Azufres geothermal field is a well-described geothermal system in the Trans-Mexican volcanic belt and has been the subject of several geothermal fluid and fluid inclusion studies (Cathelineau and Nieva 1986; Cathelineau et al. 1989, Izquierdo et al. 1997; Torres-Alvarado 2002) conducted on rock samples from different wells and depths. The up to 3 km thick stratigraphy of the geothermal field consists of andesitic lavas, which are overlain by rhyolitic and dacitic lavas and a volcano-sedimentary sequence (Cathelineau and Nieva 1986; Cathelineau et al. 1989). The authigenic minerals quartz, calcite, epidote and anhydrite have primary inclusions with low salinity (1–7 wt. % NaCl eq.) aqueous fluids. Homogenization temperatures are in close agreement with downhole temperatures, with some local evidence for cooling (30−40°C) since peak thermal conditions (Cathelineau and Nieva 1986; Cathelineau et al. 1989). A mineralogical sequence from the surface to the deepest levels of four temperature zones was established by a combination of fluid inclusion data and mineral assemblages (Izquierdo et al. 1997):

alunite-amorphous silica-gypsum-native sulfur (80–150°C),

kaolinite-smectite-clinoptilolite-laumontite (100–180°C),

illite-chlorite-calcite-pyrite-wairakite-anhydrite (190–250°C), and

chlorite-mica-quartz-epidote-hematite-diopside-prehnite-adularia (220–320°C)

Epidote is part of the high-temperature mineral assemblage and occurs in vesicles and veins and appears to have formed together with chlorite, quartz, prehnite, and hematite. Reaction (5) represents the equilibrium conditions of this mineral assemblage.

Chipilapa geothermal field, El Salvador

The Chipilapa geothermal volcanic field is located in western El Salvador and resulted from the subduction of the Cocos plate under the Caribbean plate (Molner and Sykes 1969). Geothermal activity is displayed by fumaroles and solfatares (Bril et al. 1996; Patrier et al. 1996). Mineral assemblage and fluid inclusion studies were undertaken on eight drill cores, which revealed the following vertical zoning of alteration (Papapanagiotou 1994; Bril et al.1996): an early propylitic alteration (epidote-chlorite-quartz-prehnite-adularia) followed by a clay-phyllic alteration (illite/smectite-chlorite/saponite-calcite), which is prominent in the upper part of the drill core. Fluid inclusions were investigated in early and late quartz, calcite and epidote. All three minerals contain two-phase primary and secondary aqueous inclusions, while quartz and calcite additionally contain one-phase vapor inclusions. Homogenization into the liquid ranges from 196 to 300°C for the two-phase inclusions in all of the minerals, while final melting temperatures range between –1.5 and –0.4°C. Average T_h values are 260°C for quartz, 230°C for epidote and 220°C for calcite. Bril et al. (1996) interpreted the fluid inclusion data to display successive crystallization events of quartz, epidote and calcite all of which had precipitated from a low-salinity/low-temperature hydrothermal fluid. Quartz deposition was interpreted to have started at about 270°C, whereas calcite crystallized at about 230°C. Epidote precipitated before calcite at temperatures just above 230°C. Authigenic quartz and epidote commonly precipitated from the low-salinity/low-temperature hydrothermal fluids as vug-fillings with increasing grain size towards greater depth (Fig. 5). Prehnite and adularia are associated with quartz and epidote at the greatest depth (2556 m), while wairakite additionally occurs at shallower depths (above 1400m). The homogenization temperature in the primary and secondary fluid inclusions was found to be higher than the temperature measured directly in the drill holes. This was considered as evidence for the cooling of the geothermal field. The presence of the one-phase vapor-rich secondary inclusions was considered to record local boiling events. The reconstruction of the geothermal evolution in the Chipilapa area was achieved by combining the alteration and fluid inclusion data (Bril et al. 1996; Patrier et al. 1996): Initially the propyllitic alteration was formed by a conductive thermal gradient, which was followed by the influx of meteoric water, thus causing local boiling (Fig. 5). During the last stage a new geothermal gradient was formed and clay minerals were converted to illite/chlorite (Fig. 5).

Dixie Valley Geothermal system, Nevada

The Dixie Valley geothermal system in west-central Nevada is a fault-related geothermal system (e.g., Parry et al. 1991). The fluids from wells have maximum temperatures of 265−275°C and were formerly believed to be of meteoric origin only (Nimz et al. 1999; Blackwell et al. 2000). The source of the heat for the geothermal system was thought to be due to the circulation of the hydrothermal fluids through an area with an anomalously high geothermal gradient (Blackwell et al. 2000). Fluid inclusion microthermometry and gas analysis by quadropole mass spectrometry were used in order to gain information on the P-T condition and composition of the hydrothermal fluid phase (Lutz et al. 2002). The relationship between CO_2/CH_4, N_2/Ar, and H_2S in fluid inclusions from epidote-bearing fault-gauges, and hematite- and actinolite-bearing veins indicates a mixing of meteoric and magmatic fluids, which was further supported by N_2/Ar ratios of up to 300. Consequently, the hydrothermal fluids of the Dixie Valley geothermal system must have been at least partially related to Miocene volcanism (Lutz et al. 2002).

Phlegrean geothermal field, Italy

The geothermal field of Phlegrean is located west of Naples in southern Italy within Pliocene graben structures of the Campanian Plain of the western Apennines. This geothermal system formed subsequently to the opening of the Tyrrhenian Basin (e.g., De Vivo et al. 1989).

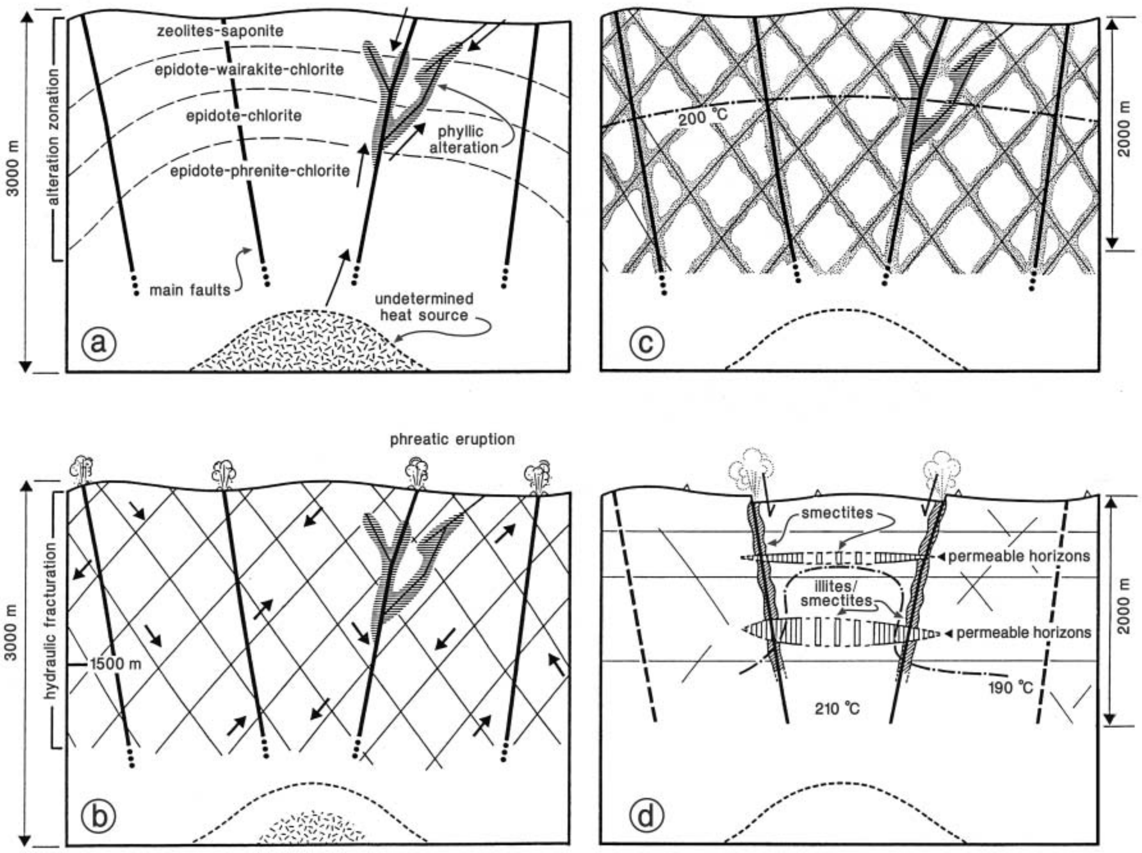

Figure 5. The evolution of the Chipilapa geothermal system as determined by the alteration mineralogy and fluid inclusion data. (a) The first stage involves a propylitic alteration and quartz crystallization. (b) The second stage shows an influx of meteoric water. (c) The third stage displays a self-sealing of the fracture-network by carbonate and clays and the formation of a new geothermal gradient. (d) The last stage indicates active fluid circulation controlled by fault systems, along which smectite precipitated independently of the temperature (modified after Bril et al. 1996).

In order to conduct a geothermal exploration program, several shallow and deep (~3 km) wells were drilled in areas displaying a high thermal gradient (Belkin and De Vivo 1987; De Vivo et al. 1989). The wells penetrated hydrothermally altered volcanic rocks, such as trachytic lavas, volcaniclastics and sedimentary rocks in shallow depths. Below about 900 m the effect of thermometamorphism was encountered. Five studied drill cores contain four main alteration zones as a function of decreasing depth: 1) Argillic zone, 2) Illite-chlorite zone, 3) Ca-Al-silicate zone, and 4) Thermometamorphic zone. Hydrothermal minerals usually occur as open fracture- and vug-filling. Fluid inclusion and Sr isotope studies were undertaken on the drill core in order to constrain the evolution of the fluid composition and the geothermal field (Barbieri et al. 1986; Belkin et al. 1986; Belkin and De Vivo 1987; De Vivo et al. 1989). Primary fluid inclusions were observed in hydrothermal quartz, K-feldspar, calcite and epidote. The fluid inclusions are aqueous and occur as two-phase (liquid- and/or vapor-rich) and multiphase inclusions (liquid + vapor + solids). The contemporaneous occurrences of liquid- and vapor-rich fluids were found to represent boiling conditions. Salinity determined by ice and halite dissolution temperatures range from 0.1 to 49 wt. % NaCl eq. The initial melting temperatures range from –52 to –22°C indicating the presence of $CaCl_2$, in addition to NaCl and KCl. Reactions (38) and (40) have already shown that $CaCl_2$ can be an important salt in fluids from which epidote minerals are formed. This salinity range corresponds to the composition of the encountered fluid from the wells (Carella and Guglielminetti 1983). In general homogenization temperatures increase with depth and are consistent with those in the wells. It should be mentioned that temperatures derived from one well are lower than those from the fluid inclusions. This was found to be related to the cooling of the geothermal system. The $^{87}Sr/^{86}Sr$ study on carbonate and leached residue suggested an interaction with seawater, which was probably introduced along aquifers at depth.

FOSSIL SUBMARINE HYDROTHERMAL SYSTEMS

Circulation of seawater through mid-ocean ridges is believed to account for at least 25% of the heat flux from the interior of the earth (e.g., Thompson 1983; Scott 1997). Large-scale circulation of heated seawater in the vicinity of ocean or back-arc ridges results in wide spread alteration of the oceanic crust. In order to extend our knowledge on the relationship between hydrothermal and magmatic systems at oceanic ridges microthermometric investigations were undertaken on fluid inclusions in alteration minerals such as epidote and anhydrite. Such investigations reveal the composition of the hydrothermal fluid and give information on the evolution of the magmatic-hydrothermal fluid. Fluid expelled from hydrothermal vents on the ocean floor exhibits a salinity ranging from 0.1 to 200% of the seawater value (e.g., von Damm et al. 1985, 1997). The composition of the fluid rising to the surface is mainly determined by fluid/rock interaction in the deep high-temperature reaction zones of the geothermal system (Bischoff and Rosenhauer 1989; Seyfried et al. 1991; Seyfried and Ding 1995). The process, which is responsible for the large spread of salinity in the hydrothermal fluids emanating from the vents is still a matter of discussion. Phase separation and/or fluid mixing may play an important role in fixing the fluid chemistry (Bischoff and Rosenbauer 1984, 1989; Butterfield et al. 1990; Nehlig 1991; Kelley and Robinson 1990; Kelley et al.1993; Lecuyer et al. 1999; Lüders et al. 2002).

Ophiolites

Ophiolites are tectonically obducted mafic and ultramafic rocks, which are understood to represent relics of oceanic or back arc basin crust (Coleman 1977). They form at crustal rifts, which are associated with extensive magmatism and related geothermal systems. Accordingly, hydrothermal alteration due to fluid circulation has been observed in ophiolites world-wide (e.g., Gillis and Bangerjee 2000). The hydrothermally altered rocks—including epidosites—

were the subject of numerous fluid inclusion studies in order to contribute to the current discussion on the evolution of submarine hydrothermal systems.

Nehlig (1991) conducted an extensive fluid inclusion study on quartz, epidote, plagioclase, amphibole, anhydrite and sphalerite from hydrothermally altered plutonic and volcanic rocks of the Semail (Oman) and Trinity (California) ophiolites. The plagiogranites of the ophiolite sequence were almost completely altered to epidosites, which were formed due to metamorphic equilibrium reactions such as reaction (9), or to metasomatic exchange reactions such as reactions (38) and (40), which require the introduction of $CaCl_2$. The salinity of primary aqueous fluid inclusions in all minerals in the plagiogranites show a wide range from 0.3 to 52 wt. % NaCl eq. However, more than 60% of the mean are within the range of seawater. Most minerals have inclusions with a salinity somewhat higher than seawater, for example that of primary fluid inclusions in secondary epidote, quartz and sphalerite ranges between 3.9 and 10.3 wt. % NaCl eq., while some secondary inclusions in quartz have salinity of up to 52 wt. % NaCl eq. The very high salinity is restricted to rocks occurring in the transition zone between the magma chamber and the sheeted dyke complex. Homogenization of the low-salinity inclusions occurs between 213 and 452°C into the liquid or the vapor phase. High-salinity fluid inclusions with halite always homogenize into the liquid phase by halite dissolution between 333 and 446°C (T_h (V $\rightarrow$ L) < Tm_{halite}). One measured initial melting temperature occurred at temperatures <26.7°C indicating the presence of $CaCl_2$, apart from NaCl in the inclusion fluid. This supports the theory that the hydrothermal fluids, which were responsible for the epidotisation of the plagiogranites, were enriched in $CaCl_2$. Nehlig (1991) interpreted the fluid inclusion data to reflect phase separation in hydrothermal or magmatic fluids at a temperature in excess of 500°C within the transition zone of the hydrothermal system and the magma chamber.

Further fluid inclusion studies on plutonic and diabase samples from the Troodos ophiolite (Cyprus) were conducted by Kelley and Robinson (1990) and Kelley et al. (1992). These authors observed high-salinity (30−61 wt. % NaCl eq.) fluid inclusions in quartz and epidote from plagiogranites and associated epidosites. Halite dissolution always occurred into the liquid phase at a temperature between 400 to 500°C. Low- salinity (2−7 wt. % NaCl eq.) liquid- and vapor-dominated aqueous inclusions occur in secondary fluid inclusion trails, which often crosscut high-salinity inclusion trails. The former have T_h values from 200 to 400°C. Initial melting temperatures range from –76 to –61°C indicating the possible presence of $CaCl_2$, $FeCl_2$ and $MgCl_2$, in addition to NaCl and KCl in the inclusion fluid. However, Kelley et al. (1992) found the low initial melting temperatures to be related to the presence of mainly $CaCl_2$, in addition to NaCl and KCl. They suggested that this fluid represented the hydrothermal fluid, which was responsible for the extreme epidote alteration of the plagiogranites. Kelley and Robinson (1990)—in accordance with Nehlig (1991)—interpreted the high-salinity inclusions to have resulted by phase separation of seawater or an exsolved magmatic aqueous fluid phase at >500°C. The low-salinity fluid inclusions however were considered to have their origin in seawater circulating along microfractures in the upper crust. Hydration reactions with primary magmatic minerals and/or mixing with the already phase-separated fluids resulted in the salinity enrichment of these seawater-derived fluids. Although phase separation of brine and vapor seemed to have been a well established model to explain the occurrence of the high- and low-salinity fluids (see above), Kelley et al. (1992) preferred the model of direct exsolution of the high-salinity fluids from a magmatic source. They suggested that these brines were trapped as high-salinity inclusions while migrating along microfractures in the deep-seated, high temperature portion of the hydrothermal system. The later low-salinity fluids were interpreted as seawater-derived fluids trapped at a temperature of >200−400°C.

Mid-Atlantic Ridge (MARK area)

Kelley et al. (1993) undertook a fluid inclusion study on hydrothermally altered gabbros, quartz-breccias and basalts from the western intersection of the Mid-Atlantic Ridge and the Kane Fracture Zone in order to shed some light on the thermal and compositional evolution of hydrothermal fluids in oceanic-rift magma-hydrothermal systems. Multiple generations of primary and secondary fluid inclusions occur in plagioclase, clinopyroxene, amphibole, epidote and apatite. Apatite in plutonic rocks contains the most complex fluid inclusion inventory (Kelly and Delaney 1985, 1986; Kelley et al. 1993). Type 1 are primary vapor- and liquid-dominated, halite ± pyrite-bearing inclusions. Total homogenization occurs at a temperature of >700°C, while halite dissolves between 352 and 408°C indicating a salinity of 41−47 wt. % NaCl eq. Some vapor-dominated, halite-bearing inclusions contain CO_2 in variable amounts as indicated by their freezing behavior and confirmed by Raman spectroscopy. Associated with the brine inclusions are Type 2 low-salinity (1−2 wt. % NaCl eq.) vapor-dominated H_2O-CO_2 inclusions, which homogenize between 364 and 420°C, and Type 3 are liquid-dominated, low-salinity, secondary inclusions which homogenize between 263 and 309°C and have a salinity of 0.4–7.6 wt. % NaCl eq. Epidote, which mainly formed at the expense of plagioclase (see reactions (9) or (38)) or occurs in veins, contains primary Type 2 and Type 3 inclusions, both of which homogenize at about 400°C and have a salinity of between 4.4 and 5.9 wt. % NaCl eq. Secondary Type 2 and 3 inclusions mainly occur in plagioclase and may contain up to four solids. Quartz from the quartz-breccias also contains secondary to primary Type 3 inclusions with somewhat lower T_h values from 187 to 343°C and a salinity from 3.5–6.5 wt. % NaCl eq., when compared with the fluid inclusion data from the plutonic rocks.

As a consequence of these fluid inclusion data, Kelley et al. (1993) suggested the following scenario (Fig. 6): During solidification and cooling of the magma a CO_2-rich vapor (Type 1, vapor-rich inclusions) was initially exsolved. This was followed by H_2O-CO_2 vapor-rich fluids (Type 2 inclusions) and formation of a cogenetic H_2O-NaCl ± CO_2 ± Fe-rich immiscible brine (Type 1, liquid-rich inclusions). The exsolution of an early vapor-rich fluid phase may have initiated fracturing close to the magma chamber at a temperature >700°C. The transition from magmatic to hydrothermal conditions was marked by initial penetration of low-salinity seawater-like fluids (Type 3 inclusions) at a temperature >400°C. The fluid flow came to an end at a temperature of 180–340°C represented by Type 3 inclusions in plagioclase and quartz.

Discussion

All fluid inclusion studies were conducted on oceanic or back arc basin crust, which formed in the vicinity of crustal rifting due to extensive magmatism. The magma chamber acted as a heat source in order to keep up the fluid flow in the geothermal system. Consequently all microthermometric studies from the different localities revealed inclusion fluids with low and high salinity. The high-salinity fluid inclusions contain $CaCl_2$ besides NaCl and KCl and are thought to be responsible for the extreme epidotization of the plagiogranites. These fluids—whether or not derived by phase separation and/or fluid unmixing—were always considered to reflect the participation of a magmatic component in the seawater-dominated hydrothermal systems. This is in accordance with many other fluid inclusion studies from other localities with similar geotectonic settings (e.g., Vanko 1988; Vanko et al. 1992; Lecuyer et al. 1999) as well as with “segregation of brine and vapor” processes in natural vent emanations (von Damm et al. 1997). Nevertheless, in this context it is interesting to note that the combined use of Cl/Br ratios and δ^{37}Cl values of inclusion fluid in sphalerite from fracture fillings in felsic igneous rocks with massive sulfide mineralization from the Jade field (Central Okinawa Trough) and the North Fidji basin exclude any significant magmatic component (Lüders et al. 2002). These authors consequently interpreted the salinity variations in the fluid inclusions of sphalerite to be the result of phase separation of seawater only.

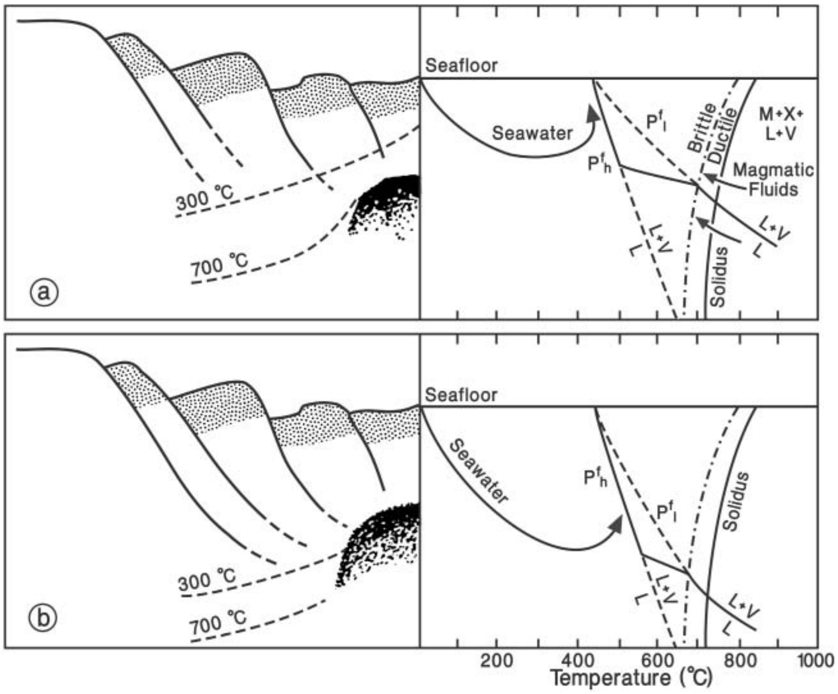

Figure 6. Model of the fluid evolution in the MARK-geothermal system. (a) Crossection with the 300 and 700°C isotherms adjacent to an axial magma chamber. The right side of the sketch shows the two-phase curves for NaCl-bearing fluids under hydrostatic (p^f_h) and lithostatic (p^f_l) conditions. Also shown is the solidus. The intersection of the solidus and the two-phase curves determines the field of the magmatic fluids coexisting with melt (M) and crystals (X). Fracturing near the solidifying magma chamber allowed the migration of exsolved brine and vapor phases at temperatures >700°C. (b) Brittle fracturing occurred during cooling at 400–550°C and allowed the penetration of seawater-derived hydrothermal fluids (modified after Kelley et al. 1993).

LOW-GRADE METAMORPHIC ROCKS

Kreulen (1980) undertook fluid inclusion studies in a succession of metamorphic rocks in the metamorphic core complex on Naxos (Greece). He reported the presence of mainly CO_2-rich inclusions of varying density in quartz segregations and matrix quartz from metamorphic rocks. About 70% of all fluid inclusions have an optically estimated CO_2-content of between 60 to 70 mol. %, which is independent of metamorphic grade and lithology. CO_2-rich inclusions were found besides in quartz in various other minerals such as kyanite, andalusite, corundum, feldspar and dolomite. However, Kreulen (1980, 1989) also observed pure aqueous inclusions in epidote from associated lower-grade rocks and associated lenses of vesuvianite-grossularite-diopside, which is intimately intergrown with quartz containing mainly primary CO_2-rich inclusions and only few aqueous inclusions. This indicates that epidote and quartz did not grow during different stages of metamorphism, and accordingly should have grown in contact with the same fluid phase, unless H_2O and CO_2 were immiscible under the specific low-grade metamorphic conditions (Kreulen 1980). Yet the reactions (15), (16), (29) and (30), which represent equilibrium conditions for the above described mineral assemblage, indicate in accordance with the fluid inclusions found in epidote a low X_{CO_2} content for the fluid phase.

SKARN DEPOSITS

Introduction

Fluid inclusion studies are a major tool for the investigation of all types of ore deposits, in order to determine the composition and the *P-V-T-X* properties of the ore-forming fluids. As a result of numerous fluid inclusion studies the fluid environment for certain ore deposits has been tightly constrained, and thus fluid inclusion data are used as exploration tools for these deposits (e.g., Klemd et al. 1993; Roedder 1979; Roedder and Bodnar 1997). Despite the large number of fluid inclusion studies only a few were conducted on epidote, although it is widely distributed in many ore deposits. An exception is epidote in skarn deposits, on which this brief review focuses. In the following I will describe some of the main characteristics of skarn deposits, however, for a more detailed discussion see the reviews of Einaudi et al. (1981) and Meinert (1992). The terms skarns and skarn deposits—i.e., those skarns, which have an economic ore mineralization—should be used in a purely descriptive manner, since both types are the product of regional and contact metamorphism as well as metasomatism involving metamorphic, magmatic, meteoric, and/or marine fluids (Einaudi et al. 1981; Meinert 1992). Skarns are characterized by coarse-grained Ca-Al-Fe-Mn-Mg silicates such as andraditic garnet, clinopyroxene, wollastonite, epidote and amphibole, which mainly formed by the replacement of a carbonate-rich lithology. However, skarns also may form in shale, sandstone, granite, basalt and komatiite. The terms exoskarn and endoskarn refer to a sedimentary or igneous origin, respectively. Einaudi et al. (1981) classified skarn deposits in terms of their dominant economic metals. Seven major skarn types are distinguished: Fe-, Au-, W-, Cu-, Zn-, Mo-, and Sn skarn deposits. Almost all occur in tectonic settings with igneous activity, such as magmatic arcs above subduction zones, and often along with porphyry copper deposits at convergent plate boundaries (Fig. 7a,b,c). However, Sn and some Zn skarns may be related to rift settings and

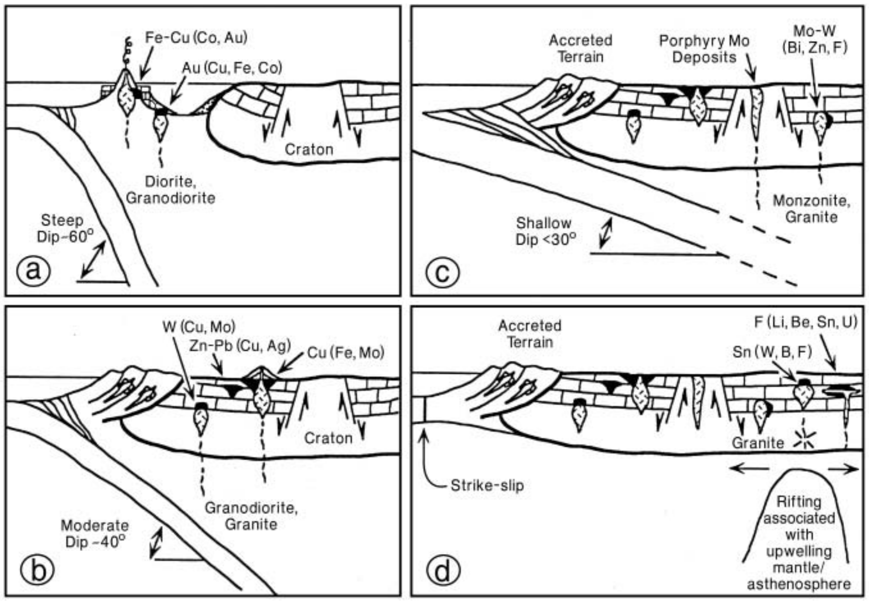

Figure 7. Tectonic models for skarn deposit formation: (a) oceanic subduction and back arc basin development; (b) continental subduction; (c) transitional low-angle subduction; (d) rifting (modified after Meinert 1992).

anorogenic magmatism (Fig. 7d). Thus skarn deposit formation is a process associated with the intrusion of a plutonic body, which is accompanied by regional to contact metamorphism and metasomatism of the immediate country rocks. Metamorphism will be most affective at deeper levels (1-3 kbar, corresponding to 3 to 10 km depth), while retrograde alteration will affect skarns at shallower depths (0.3 to 1 kbar, corresponding to 1 to 3 km depth). This dynamic process often involves an early isochemical metamorphism followed by later metasomatism, which are overprinted by a subsequent retrograde stage. A complex metasomatic fluid evolution results from the early high-temperature metamorphic stage towards the late low-temperature stages. The formation of skarn deposits involves several continuous stages, initially exceeding 700°C, during which the skarn and initial ore mineralization formed, followed by subsequent phases of cooling, which are accompanied by a retrograde stage and continued ore deposition. Depending on the geotectonic setting and the rock's composition these stages may correspond to the early potassic and later phyllic/argillic alteration.

Formation of epidote minerals can occur at the early high-temperature metasomatic stage and/or the later lower temperature retrograde stage, both of which may be associated with ore mineralization (e.g., Einaudi et al. 1981; Brown et al. 1985). Einaudi et al. (1981) suggested that epidote minerals can form at medium to high temperatures only at low X_{CO_2} values. This conclusion was based on a T-X_{CO_2} diagram, which was constructed for the CASCH system at 2 kbar. However under highly oxidizing conditions it is more appropriate (see above) to use the CF*ASCH-system when constructing a T-X_{CO_2} projection (Fig. 2), which displays some of the most characteristic epidote-involving equilibrium reactions (32)-(37) in skarns. In contrast to the results of Einaudi et al. (1981) the mineral-fluid phase reactions in Figure 2 clearly demonstrate that epidote is stable for a wide range of CO_2 concentrations in the aqueous fluid phase. However epidote in skarn deposits may also be formed by a metasomatic exchange with the infiltrating fluid phase as is shown by the simplified reaction (38), (39) and (40), which usually requires the introduction of Ca and Fe^{3+} by a magmatic/hydrothermal fluid phase.

Fluid inclusion studies on skarn deposits do not only provide information on the P-V-T-X conditions of the ore-forming fluid phase, but also on the change of these parameters from prograde to retrograde conditions as well as on the metasomatic mass transfer of elements. Summaries of the fluid inclusion literature on skarn deposits are given in Kwak (1986) and Meinert (1992).

Iron skarn deposits

Iron skarn deposits are mined exclusively for Fe, although they do have minor concentrations of other metals such as Au, Co and Cu. Magnetite is the dominant mineral in these skarn deposits, whereas silicate mineral assemblages frequently play a minor role. Calcic-Fe skarn deposits, which are formed by the replacement of limestone, display two generations of minerals: Early prograde, high-temperature minerals such as andraditic garnet, clinopyroxene, magnetite and epidote and later retrograde low-temperature minerals such as amphibole, chlorite, calcite, quartz, magnetite, epidote and ilvaite. The equilibrium relations of the early magnetite- and epidote-involving prograde mineral assemblage are represented by the reactions (33), (36) and (37). In contrast magnesian-Fe skarns, which have formed by the replacement of dolomitic country rocks, preferentially contain—besides garnet and magnetite—early forsterite, diopside, epidote and periclase. Several fluid inclusion studies were conducted on Fe skarn deposits (for summaries see Kwak 1986; Meinert 1992). T_h of primary aqueous fluid inclusions of early garnet and clinopyroxene ranges from 370 to >700°C and 300 to 690°C, respectively. Homogenization always occurred into the liquid phase. Dissolution temperature of halite and sylvite daughter minerals indicate a salinity of up to 50 wt. % NaCl eq. Crosscutting quartz veins contain epidote, in which the aqueous fluid inclusions display a somewhat lower T_h of about 250°C with a salinity <25 wt. % NaCl eq. (Meinert 1992). However, fluid inclusion data from skarn deposits vary somewhat from deposit to deposit. Beuline (1976) reported high T_h values for the Tagarsk Fe skarn deposit in Russia, between 520−610°C for primary aqueous fluid inclusions in andraditic garnet and clinopyroxene, while primary aqueous inclusions in epidote showed T_h between 140 and 330°C. Even higher T_h of 350 to 380°C for primary aqueous inclusion in epidote were reported by Vorontsov et al. (1978) and Ayshford et al. (1997) from the Korshunvskoe (Russia) and Tallaway (Tasmania) Fe skarn deposits, respectively. Primary aqueous fluid inclusions in pyroxene and garnet from the Blagodat (Ural) Fe skarn deposit revealed T_h values from 350 to 780°C, while primary aqueous fluid inclusions in epidote showed lower T_h values, between 480 and 580°C into the gas and liquid phase, indicating boiling (Bukharev et al. 1982). Li et al. (1989) and Feng and Chang (1996) observed primary aqueous fluid inclusions in prograde diopside and garnet with T_h of 540−660°C and a salinity between 25 and 65 wt. % NaCl eq. as determined by the dissolution of halite in the Fe-skarn deposits in the Shanxi province of NE-China. Epidote, which had precipitated with the magnetite ore, has an average T_h of 422°C and an average salinity of 41 wt. % NaCl eq. Besides halite and sylvite, Ca- and Fe-rich daughter minerals were observed in the high-salinity inclusions, thus indicating the introduction of these elements by the hydrothermal fluids.

It can be concluded that magnetite, the major ore mineral in the Fe skarn deposits, precipitated early during the high-temperature metasomatic stage as well as during an intermediate temperature stage before the onset of retrograde alteration. Fluid inclusion data derived from epidote clearly support this evolution of the ore-forming fluid, by means of decreasing salinity during decreasing temperature. Furthermore, indications for boiling (homogenization in the gas and liquid phase at the same temperature) were observed in some of the high-temperature fluids.

Gold skarn deposits

Gold skarn deposits occur in a large variety of tectonic settings and range in age between Archean and Phanerozoic (e.g., reviews by Meinert 1992, 1998). Four different types of Au skarn deposits have been distinguished:

1. reduced Au skarn deposits, which are associated with reduced (ilmenite-bearing, $Fe^{3+}/Fe^{2+} < 0.75$) dioritic to granodioritic plutons and dike/sill complexes;
2. oxidized Au skarn deposits (high garnet/pyroxene ratios; Fe-poor garnet and pyroxene; low total sulfides);
3. magnesian-Au skarn deposits replacing dolomitic country rocks;
4. metamorphic Au skarn deposits associated with shallow plutonic rocks, which intruded the sedimentary country rocks.

All of these deposits have common characteristics—besides economic Au concentrations—such as distal and early biotite ± potassium feldspar hornfels, garnet-pyroxene alteration and a Au association with various Bi and Te minerals. Epidote usually is a late stage low-temperature product.

Fluid inclusion studies in reduced and oxidized Au skarn deposits (Hickey 1990; Ettlinger et al. 1992; Brooks 1994, all of which are summarized in Meinert, 1992) revealed the presence of high-temperature brines in prograde garnet and pyroxene with T_h of between 210 to 730°C and a salinity of 5 to 40 wt. % NaCl eq. As postulated for several Fe skarn deposits some of the high temperature fluids provided evidence for boiling (see Vargunina and Andrusenko 1983). The fluid inclusions in retrograde epidote have lower T_h, of between 255 and 450°C (305−450°C pressure-corrected, Hickey 1990), and a salinity of up to 28 wt. % NaCl eq. Similar T_h-values between 380 and 390°C were measured for fluid inclusions in retrograde epidote from a Au skarn deposit from NE-Russia (Vargunina and Andrusenko 1983). Gold deposition from aqueous saline fluids was usually accompanied by sulfide mineralization and retrograde hydrous minerals such as amphibole, chlorite and epidote at a temperature of >300°C, as evidenced by the fluid inclusion studies above and several fluid-phase and mineral equilibria (summarized in Meinert 1998). Meinert (1992, 1998) interpreted these features as evidence for the transport of Au in chloride complexes at a temperature >300°C and at a high salinity.

Tungsten skarn deposits

Tungsten skarn deposits are found worldwide in Precambrian to Triassic limestone and are usually associated with calc-alkaline intrusives in orogenic belts (Fig. 7b,c). For details see the recent summary and review by Newberry (1998). W skarn deposits are almost always associated with coarse-grained granodioritic to quartz monzonitic stocks and batholiths. Newberry and Einaudi (1981) differentiated between reduced and oxidized W skarn deposits. Reduced W skarn deposits have early andradite garnet and pyroxene, which are associated with Mo-rich scheelite. Later retrograde mineral assemblages include Mn-Fe^{2+}-rich garnet, biotite, hornblende, epidote, sulfides and low-Mo scheelite. In oxidized W skarn deposits andraditic garnet dominates over clinopyroxene and the main retrograde phases are epidote and amphibole, both of which are associated with the main ore mineralization. Fluid inclusion studies of both deposit types are summarized in Kwak (1986) and Meinert (1992). Garnet and clinopyroxene in W skarns from three deposits (MacMillan, Yukon; King Island, Tasmania and Salau, Pyrenees) contain primary aqueous inclusions with a wide range of T_h values and salinity, from 290 to 800°C (with evidence of boiling) and 23 to 65 wt. % NaCl eq., respectively. Late retrograde minerals such as epidote, quartz and amphibole have lower T_h values and salinity, between 250 and 470°C and 2–28 wt. % NaCl eq., respectively. Besides NaCl and KCl, $CaCl_2$- and $NaAlCO_3(OH)_2$-minerals were observed in the high-salinity inclusions in garnet and clinopyroxene, while the low-salinity fluids are relatively $CaCl_2$-poor as is shown by the fluid inclusions in epidote, amphibole and quartz. Other observed solids in the high-salinity fluid inclusions are unidentified Zn, W and Cu minerals representing the metal characteristics of the hydrothermal, ore-forming fluid (Kwak 1986). Primary aqueous inclusions in scheelite show T_h values between 270 and 600°C and a salinity between 15 and 61 wt. % NaCl eq. (see Kwak 1986; Meinert 1992). A relative high T_h of 448°C was observed for aqueous fluid inclusions in epidote from the Sangdong W skarn deposit in Korea (Kwak 1986). Epidote and scheelite in the Yaguki W skarn deposit in Japan have primary fluid inclusions with almost identical T_h values from 220 to 330°C and 230 to 330°C, respectively (Muramatsu and Nambu 1982). Similar T_h values—from 213 to 364°C—and low salinity were obtained from primary inclusions in epidote and clinozoisite from the Copina W skarn deposit in Argentina (Ocanto et al. 2001). Consequently, the scheelite precipitation must have occurred over a large temperature range, from the waning prograde stage until the late retrograde alteration.

Zinc and tin skarn deposits

Most Zn skarn deposits are associated with continental subduction, while related rocks range from diorite to a high-silica granitic composition. Sn skarn deposits are predominantly related to high-silica granites, which were derived by partial melting of continental crust associated with rifting (Fig. 7d). A brief summary and review of both types of deposits are given by Einaudi et al. (1981) and by Kwak (1986, 1987), respectively. In contrast to most other skarn deposits Zn skarn deposits usually have low fluid inclusion T_h values (<600°C), even for the prograde mineral assemblage, which is consistent with boiling and a relatively shallow (0.2–1 kbar) and distal geotectonic setting (Kwak 1986; Meinert 1992). Fluid inclusion studies on Zn skarn deposits from four different mining districts Verladenia and Naica, Mexico (Megaw et al. 1998; Haynes and Kesler 1988); Groundhog Mine, New Mexico (Meinert 1987), and Kamioka Mine, Japan (Takeno et al. 1999) revealed T_h values from 290 to 586°C for primary inclusions in garnet and clinopyroxene with a salinity of 2–23 wt. % NaCl eq. T_h values of primary aqueous inclusions in sphalerite range from between 230 and 420°C, while T_h values of primary and secondary inclusions in epidote from the Kamioka Mine range from 240 to 300°C. Similar T_h values of between 260 and 362°C and an average salinity of 9.5 wt. % NaCl eq. were displayed by primary inclusions in epidote from the Orphid Mine Zn skarn deposit in Utah (Wilson and Parry 1986).

Fluid inclusion investigations on quartz and fluorite from five Sn Skarn deposits (summarized in Kwak 1986, and Meinert 1992) displayed T_h values (into the liquid phase only) ranging from 100 to 492°C and salinity from 6 to 40 wt. % NaCl eq. Garnet and pyroxene however accommodated fluid inclusions, which homogenized into the gas and liquid phase at a temperature of 300 to >600°C. Primary fluid inclusions in epidote of the JC mine (Yukon Territory, Canada) revealed a T_h range of 243 to 420°C and salinity between 0.27 and 34 wt. % NaCl eq., while cassiterite showed somewhat higher temperature (Layne et al. 1987; Layne and Spooner 1991). Daughter minerals in the high-salinity inclusions are mainly NaCl, KCl, CaF_2, thus reflecting the importance of metasomatic exchange reactions such as (38) and (39).

Discussion

Fluid inclusion studies in ore deposits (as well as in metamorphic rocks) usually focus on secondary inclusions in quartz. Due to the common post-trapping modifications of fluid inclusions in quartz and quartz recrystallization, the interpretation of fluid inclusion data is often problematic and ambiguous (see Introduction). In contrast, skarn deposits usually have primary fluid inclusions in prograde skarn minerals such as andraditic garnet and clinopyroxene as well as in later retrograde minerals such as epidote and amphibole. This offers a unique opportunity to study the *P-T-X* evolution of the skarn-forming fluid, which is displayed by high salinity at high temperature and declining salinity during decreasing temperature. Boiling is usually evident during the early phase of skarn formation but rare during later retrograde processes. Furthermore, systematic quantitative variations of the salt composition in single fluid inclusions from prograde and retrograde host minerals of different skarn deposits (Haynes and Kesler 1988) combined with the results of $\delta^{18}O$ and δD values of later retrograde minerals such as epidote (Layne et al. 1991) indicate mixing of multiple fluids of magmatic and meteoric origin.

OTHER ORE DEPOSITS

The geology and hydrothermal alteration of the porphyry copper deposit at Ann Mason (Yerrinton, Nevada) have been described in detail by Dilles and Einaudi (1992) and Dilles et al. (1992): The Ann Mason porphyry copper deposit contains 495 mt of 0.4 wt. % Cu and ca. 0.01 wt. % Mo, which mainly occurs within or near the contact of the Jurassic Yerrington batholith, a highly differentiated granite. At least three different hydrothermal fluids caused three alteration zones in the plutonic rocks: 1) an early potassic alteration caused by fluids of magmatic origin; 2) a contemporaneous sodic-calcic (propylitic) alteration and epidote veins, mainly caused by formation brines, and 3) a late sodic to sericitic-chloritic alteration probably as a result of seawater interaction. Primary liquid-rich aqueous inclusions (L + V + halite) in quartz from the potassic alteration zone (1) were homogenized by halite dissolution from 150 to 550°C, thus indicating a salinity of between 32 and 62 wt. % NaCl eq. This inclusion fluid is linked to the copper deposition and believed to represent relics of magmatic fluids, as is supported by stable isotope studies of K-feldspar and biotite. Epidote and quartz from the alteration zone (2) contain primary aqueous inclusions (L + V + halite), which also homogenized by halite dissolution between 170 and 340°C, thereby indicating a salinity of 31 to 41 wt. % NaCl eq. The inclusion fluids of both minerals were interpreted to be relics of elevated formation water, which circulated convectively through the granitoid, and by this means leaching elements such as K, Fe, Cu and S. Lower temperature (T_h = 100–250°C) aqueous fluid inclusions in quartz, which exhibit a salinity from 2–5 wt. % NaCl eq., are believed to be of seawater origin and to have caused the late sodic and sericite-chlorite alteration (3).

Hagemann et al. (1996) investigated the Wiluna lode-gold deposit in the Archean Norseman-Wiluna greenstone belt in western Australia. Using a combined microthermometric and laser Raman and ion chromatographic study on quartz and epidote from unmineralized pillow lavas, they mainly observed aqueous fluids, which were interpreted to represent unchanged relics of evolved seawater.

Gem quality zoisite ("tanzanite" = vanadiferous zoisite) from Merelani (Tanzania) has primary aqueous fluid inclusions with up to three unidentified daughter minerals (Malisa et al. 1986). Homogenization into the liquid phase occurred from 37 to 51°C, however, one vapor-rich inclusion homogenized into the vapor phase at 242°C. The daughter minerals only began dissolving at 350°C.

PLUTONIC ROCKS

The Hercynian calc-alkaline plutonic complex of Charroux-Civray (NW-Massif Central, France) displays several stages of hydrothermal alteration (Freiberger et al. 2001a,b). The primary igneous mineralogy and an early postmagmatic Ca-Al silicate alteration were overprinted by a multiphase illite-chlorite-phengite-carbonate alteration. Cooling of the calc-alkaline pluton started at a solidus temperature of about 650°C at about 4 kbar, as was indicated by the isochores of the primary aqueous fluid inclusions in subsolidus epidote (Freiberger et al. 2001a,b). These authors further observed decompressional cooling of the pluton to 2–3 kbar at 200–280°C, with a subsequent greisenization by an H_2O-CO_2-rich fluid of varying density at a temperature of between 400 to 450°C, which was indicated by primary and secondary fluid inclusions mainly in quartz. This high temperature was related to the late intrusion of one or several leucogranitic bodies, that also caused the low temperature illite-chlorite-phengite-carbonate alteration (Freiberger et al. 2001a).

Aqueous fluid inclusions in epidote of the granite-pegmatites from the Strzegom Massif and the Karkonosie Mts. in Poland indicate a late crystallization temperature between 360 to 120°C (Karwowski and Wlodyka 1981; Lendowski 1983). Kuznetzova and Gostyaeva (1982) reported very low T_h values of about 120°C for two-phase aqueous inclusions in epidote from albitized granites in the Ukranian Shield.

HIGH- AND ULTRA-HIGH PRESSURE (HP AND UHP) METAMORPHISM

Introduction

One of the problems when investigating high- and ultra-high pressure metamorphism is the effect of the possible presence of a free fluid phase. Syn-metamorphic quartz veins with coarse grained eclogite-facies minerals such as omphacite, kyanite, garnet and epidote were taken as evidence for the presence of such a free aqueous fluid phase in equilibrium with eclogite-facies conditions (e.g., Essene and Fyfe 1967; Okrusch et al. 1978; Holland 1979; Klemd 1989). Several fluid inclusion studies on syn-metamorphic high- to ultrahigh pressure vein minerals and matrix minerals of the surrounding host rocks revealed a large variety of fluid compositions. Reported fluid compositions include aqueous low-salinity fluids (e.g., Giaramita and Sorensen 1994; Vallis and Scambelluri 1996; El-Shazly and Sisson 1999; Franz et al. 2001; Gao and Klemd 2001), high-salinity aqueous fluids and/or CO_2-N_2- or N_2-rich fluids (e.g., Andersen et al. 1989; Selverstone et al. 1992; Philippot 1993; Klemd et al. 1992, 1995; Scambelluri et al. 1998; Xiao et al. 2000; Fu et al. 2001, 2002, 2003). The presence of a fluid as well as the exact composition is of primary importance when considering *P*-*T* estimates and quantitative phase diagrams such as *P*-*T* pseudosections (phase diagrams that are constructed for the specific bulk composition of a rock). Together with *P* and *T* the composition of the fluid phase is important when assessing its capability to transport and move certain major and trace elements during eclogite-facies metamorphism. The reason for this being that element transport and fluid-rock interaction during blueschist- to eclogite-facies conditions play a key-role in understanding the fluid storage and recycling during subduction and continent-continent collision (e.g., Peacock 1993; Brunsmann et al. 2000, Scambelluri and Philippot 2001). Several models based on theoretical considerations suggest that large amounts of H_2O-rich fluids, which were released by the dehydration of subducted lithospheric serpentinized mantle and/or oceanic crust—for instance during the transition from blueschist to eclogite—act as element carriers from the slab to the overlying mantle wedge and are thus responsible for the trace element signatures of island arc magmas (Fig. 8; e.g., Peacock 1993; Schmidt and Poli 1998; Mibe et al. 1999, 2003; Draper et al. 1999; Rüpke et al. 2002; John and Schenk 2003). The latter theoretical considerations concerning the dehydration of the oceanic crust are supported by recent findings in the Tianshan high-pressure belt (NW-China). Large eclogite-facies veins in blueschist were found to be the product of hydrofracturing induced by devolatilisation of minerals such as glaucophane, paragonite and epidote during blueschist-eclogite transition (see reactions (24) to (28)) and thus, represent former fluid pathways within a paleosubduction zone (Gao and Klemd 2001). However, significant differences do not only exist as far as the fluid composition is concerned but also with respect to the kind of fluid flow under eclogite-facies conditions. A first model suggests the influx of relatively large quantities of aqueous fluids in an open system on a kilometer-scale (e.g., Bebout and Barton 1993; Giaramita and Sorensen 1994; Nelson 1995), whereas a second model—based mainly on fluid inclusion, stable isotope and connectivity studies—demonstrates that fluid flow under eclogite-facies condition was limited and restricted to a millimeter to centimeter scale (e.g.,

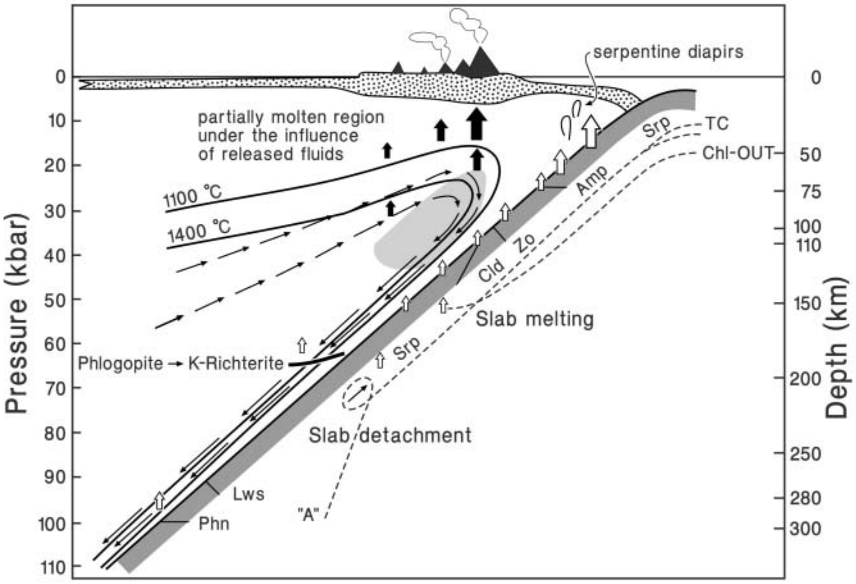

Figure 8. Schematic diagram showing the subduction of oceanic lithosphere and regions of dehydration along with partial melting in the mantle wedge as well as the associated island arc volcanism (modified after Schmidt and Poli 1998).

Philippot and Selverstone 1991; Selverstone et al. 1992; Klemd et al. 1992, 1995; Philippot 1993; Xiao et al. 2000; Mibe et al. 2003).

Some of the established results and discrepancies, which are based on fluid inclusion studies in eclogite-facies rocks, may be ambiguous given that they were conducted on fluid inclusions in quartz which are prone to post-entrapment modification during post-peak metamorphic and recrystallization processes (e.g., Bakker and Jansen 1991; Sterner et al. 1995; Johnson and Hollister 1995; Küster and Stöckhert 1997). However, even fluid inclusion studies on eclogite-facies minerals such as garnet, omphacite, kyanite and epidote, which are less susceptible to recrystallization and thus to re-equilibration and leakage, revealed fluid compositional differences and density modifications of fluid inclusions, as is shown by a mismatch between pressure estimates based on conventional geothermobarometry of silicate minerals and fluid inclusions (e.g., Philippot and Selverstone 1991; Klemd et al. 1992, 1995; Giaramita and Sorensen 1994; Selverstone et al. 1992; Scambelluri et al. 1998; Svensen et al. 1999; Xiao et al. 2000; Franz et al. 2001; Gao and Klemd 2001; Fu et al. 2001, 2002, 2003; Schmid et al. 2003).

Although the density of texturally primary eclogite-facies fluid inclusions in HP and UHP minerals (Fig. 3) may have re-equilibrated during exhumation, the peak metamorphic fluid composition can be preserved. This is indicated by the constant composition of different-sized fluid inclusions in individual as well as in different minerals such as garnet, omphacite, kyanite and epidote from single rock samples, furthermore by the preserved fluid heterogeneity between samples, which have undergone an identical *P-T* evolution but come from different localities or even from the same outcrop (see studies below). Moreover, theoretical considerations and fluid-phase equilibria based on the actual eclogite-facies mineral assemblage (Holland 1979) and model calculations in the H_2O-CO_2-NaCl-system (Selverstone et al. 1992) with the aim to establish the composition of the fluid phase during eclogite-facies metamorphism, show that these results correspond with fluid inclusion composition from eclogite-facies vein minerals. Nevertheless, Philippot and Selverstone (1991) pointed out the large uncertainty in pressure determination from inclusions with complex daughter minerals, some of which may have formed by "back reactions," thus changing the original density and the composition of the fluid (e.g., Heinrich and Gottschalk 1995; Svensen et al. 1999). The following section provides an overview on fluid inclusions in epidote in eclogite-facies rocks and can hopefully shed some light on the above described observations and discrepancies.

Tauern Window, Austria

In one of the early fluid inclusion studies on HP-metamorphic rocks Luckscheiter and Morteani (1980) investigated fluid inclusions in Alpine epidote-apatite-bearing quartz veins in amphibolites and amphibolite-facies gneisses (Zentralgneis area), in order to compare them with fluid inclusions in matrix quartz of eclogites from the lower and upper Schieferhülle of the Tauern Window in Austria. Epidote and apatite contained texturally primary aqueous inclusions with a relatively low salinity of 3 to 9 wt. % NaCl eq. Homogenization always occurred into the liquid phase, between 240 and 220°C. Secondary to pseudosecondary fluid inclusions in associated quartz display the same composition. In contrast, fluid inclusions in quartz of syn-metamorphic high-pressure veins contain secondary to pseudosecondary CO_2-H_2O-rich inclusions with a highly variable CO_2-content of between 20 and 80 vol. % and a salinity of 5 to 21 vol. % NaCl eq. for the fluid phase. The CO_2-density, which was derived exclusively from the CO_2 homogenization temperature, ranges from between 0.16 and 1.15 g/cm^3. The presence of syn-metamorphic fluids with such a high CO_2-and NaCl-content stands in direct contrast to fluid-phase equilibria considerations and a fluid inclusion study by Holland (1979), who suggested that the Tauern Window eclogites with the peak-mineral assemblage paragonite-glaucophane-epidote-talc-magnesite-dolomite in association with garnet, omphacite, kyanite and quartz necessitates the coexistence of a free aqueous fluid phase during eclogite-facies metamorphism. Furthermore, quartz-omphacite-kyanite high pressure veins and the presence of aqueous inclusions ($X_{CO_2} < 0.1$; $X_{NaCl} \leq 0.02$) in omphacite and epidote suggest that crystallization took place under conditions comprising a high water activity at ca. 19.5 kbar and ca. 620°C. The high water activity during peak metamorphic conditions was supported by fluid-phase equilibria calculations in eclogite-facies siliceous dolomites from this area (Franz and Spear 1983). Yet Selverstone et al. (1992) calculated fluid activity ratios with strongly varying H_2O activities at peak metamorphic conditions for millimeter- to centimeter-scale layers in banded mafic eclogites from the Austrian Tauern Window, whereas CO_2 activities were almost constant between the same layers (Fig. 9).

The banding is displayed by alternations of omphacite-, garnet-, clinozoisite-, zoisite-, dolomite-, and phengite-rich assemblages. Their model concerning the H_2O-CO_2-NaCl-system is consistent with the presence of different saturated saline brines, carbonic fluids, or immiscible water-rich and CO_2- ± N_2-rich fluid phases. Fluid inclusion investigations in quartz, omphacite, kyanite, apatite, epidote and magnesite (see summary in Selverstone et al. 1992) revealed the presence of highly saline brine inclusions (salinity of up to 39 wt. % NaCl eq.) with up to six daughter minerals, and thus supported their model calculations. Low initial melting temperature indicated—besides NaCl and KCl—the presence of $CaCl_2$ and $MgCl_2$. X_{CO2} varied from between 0–0.18 in the brines and between 0.2–1 in the $CO_2 \pm N_2$ fluid. The density of all inclusions was modified due to re-crystallization and partial decrepitation during unroofing (Selverstone et al. 1992).

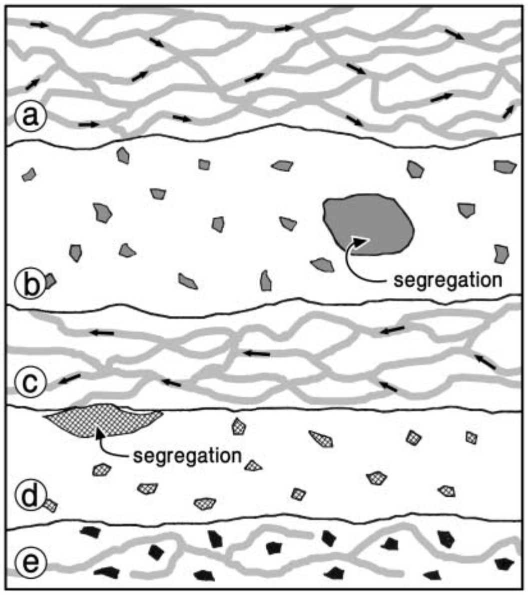

Figure 9. Schematic diagram of a model for the fluid distribution in banded eclogites. Layer (a) and (c) have an interconnected fluid flow (fluid phase has a dihedral angle of <60° in the polycrystalline eclogite layers); arrows indicate direction of fluid flow. Layers (b) and (d) show isolated fluid pockets (fluid has a dihedral angle of >60° in the polycrystalline eclogite layers). Layer (e) contains immiscible fluids, one with a low and one with a high dihedral angle in the polycrystalline eclogite layer (modified after Selverstone et al. 1992).

Münchberg Gneiss Complex, Germany

The Münchberg Gneiss Complex, which contains eclogites and eclogite-facies rocks in the its upper parts, is believed to be an inverted nappe in the Central European Variscides. The eclogite-facies conditions are estimated at pressures of >24 kbar and temperatures of between 600 and 700°C (Klemd 1989; Klemd et al. 1991, 1994; O'Brien 1993). The eclogite-facies stage was followed by an amphibolite-facies overprint of between 10 to 14 kbar at the same temperature range, thereby suggesting an almost isothermal exhumation to higher crustal levels (Franz et al. 1986; Klemd 1989; Klemd et al. 1994; O'Brien 1993). Pegmatitic segregations from the contact zone to garnet-amphibolites (retrograded eclogites) have been the subject of a detailed field and laboratory study by Franz and Smelik (1995). These authors interpreted the pegmatites, which have a leuco-tonalitic composition, to be the product of partial melting of the surrounding eclogites during the isothermal decompression in the presence of a free H_2O-rich fluid phase. In order to prove the formation of a water-saturated melt a mass balance calculation for H_2O production was undertaken by Franz and Smelik (1995). They estimated that a partial melting of about 2.5 vol. % could generate enough melt to produce the volume of the pegmatites observed in the Münchberg Gneiss Complex. The matrix of the pegmatites mainly consist of graphic intergrowth of quartz and albite, which are associated with zoisite and minor clinozoisite, phengite, Ca-amphibole and biotite. The occurrence of such water-saturated partial melts within subduction zones is of considerable importance with regards to element transport in this environment (see above). In order to verify the presence of a former water-saturated melt, a fluid inclusion study on zoisite, which contains abundant fluid inclusions, was conducted (Klemd unpub. data). The size of the fluid inclusions range from <3 to 280 μm. Most fluid inclusions are primary and are normally two-phase (liquid and vapor) aqueous inclusions, which are aligned parallel to the b-axis of the zoisite or occur as large isolated single inclusions (Fig. 10). However secondary fluid inclusions occurring along healed microfactures were also observed. Some primary and secondary fluid inclusions contain—apart from liquid and vapor—up to two daughter minerals, which did not dissolve during heating (Fig. 10). The liquid/solid ratios are strongly variable, whereas the liquid/vapor ratio of most of the inclusions is relatively constant between 0.75−0.90. According to the criteria of Roedder (1984) this suggests the accidental trapping of the daughter minerals. Primary and secondary fluid inclusions behaved identical during the microthermometric study. Final melting temperatures range between –4.0 and –0.1°C (103 measurements), thereby indicating a low salinity of <6 wt. % NaCl. The apparent initial melting was observed between –28 and –10°C, implying a NaCl and KCl dominated aqueous fluid. Yet rare clathrate melting at between 10 and 20°C indicates the presence of minor amounts of other gases such as CO_2 and/or CH_4. T_h values range from 155 to 280°C and thus, densities of <1 g/cm^3. The presence of low-salinity and -density aqueous fluid inclusions is typical for late-stage fluids in pegmatites (e.g., London 1986). The presence of such fluid inclusions furthermore provide unambiguous evidence for the exsolution of a low-density fluid from the water-saturated

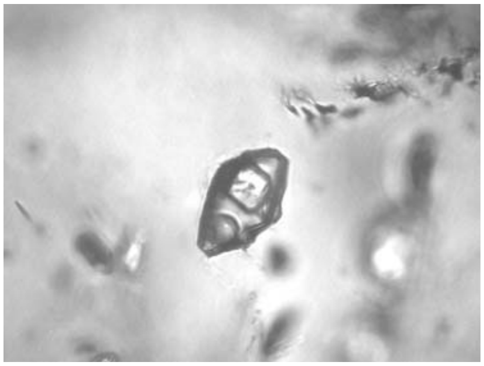

Figure 10. Photomicrograph showing a large isolated primary three-phase fluid inclusion (inclusion diameter = 25 μm) in a pegmatitic segregation from the contact zone to garnet-amphibolites (retrograded eclogites) from the Münchberg Gneiss Complex in Germany. The inclusion contains—besides a liquid and a vapor-bubble—one unidentified solid phase, which did not dissolve during heating (for further explanation see text).

leuco-tonalitic melt during zoisite crystallization and consequently confirm the hypothesis of Franz and Smelik (1995).

Mt. Emilius, Italy

Eclogite-facies metabasites of the Mt. Emilius continental unit (western Italian Alps) were the subject of a more recent study by Scambelluri et al. (1998). The Alpine eclogite-facies metamorphism occurred at a temperature between 450 and 550°C and pressure of 11 to 13 kbar as was derived from conventional geothermobarometry (Dal Piaz et al. 1983). Scambelluri et al. (1998) investigated two rock types, namely eclogites with the mineral assemblage omphacite-garnet-glaucophane-epidote-phengite/paragonite and eclogitized granulites with the mineral assemblage omphacite-garnet-epidote-amphibole-chlorite. Epidote was considered to have formed prograde by reaction (21) and to have been stable under peak eclogite-facies conditions (Dal Piaz et al. 1983). The high-pressure foliation of both rock types is crosscut by eclogite-facies garnet-omphacite-epidote veins, which were all the subject of fluid inclusion studies. In some cases Scambelluri et al. (1998) also investigated fluid inclusions in garnet and omphacite from the eclogitized granulite domains surrounding the high-pressure veins. All vein minerals contain texturally primary to pseudosecondary high-salinity inclusions with up to 50 wt. % NaCl eq. No compositional difference or varying density was found for fluid inclusions in different minerals of the same vein, thereby excluding a possible H-diffusion exclusively in epidote (cf. Giaramita and Sorensen 1994). The high-salinity aqueous fluids were either two-phase (liquid + vapor) or multiphase (liquid + vapor + salt + quartz). Initial melting temperature between −50 to −34°C was interpreted to indicate the presence of $NaCl\text{-}CaCl_2\text{-}MgCl_2$ as the main chloride components. In the eclogitized granulites primary inclusions in garnet and omphacite however displayed much lower salinity between 9 and 23 wt. % NaCl eq. Estimated inclusion density varies between 0.8 and 1.1 g/cm^3. The isochores for all inclusions pass below peak metamorphic conditions. The highest-density isochore falls at least 5 kbar short of the estimated *P-T* conditions for the eclogite-facies metamorphism. This indicates that the fluid density must have been modified (see above Selverstone et al. 1992) during the post-peak metamorphic evolution. However, textural evidence indicates that the inclusion fluid must have been trapped under eclogite-facies conditions (Scambelluri et al. 1998). Despite these density modifications Scambelluri et al. (1998) excluded a compositional change of the inclusion fluid during post-peak metamorphic conditions. They considered the distinct fluid salinity difference in omphacite, garnet and epidote of the high-pressure veins as well as in omphacite and garnet of the eclogitized granulite to be the result of progressive hydration during the eclogitization of the granulites. Thus the increasing salinity resulted from extensive fluid-rock interaction during eclogitization of the granulites, i.e., the water gets incorporated into the hydrous eclogite-facies minerals, thereby causing an increasing salinity in the residual inclusion fluid (Scambelluri et al. 1998).

Dabie-Sulu terrane, China

The first fluid inclusion study on coesite-bearing UHP-eclogites from the Central Dabie Shan involving several eclogite-facies minerals such as kyanite, omphacite and clinozoisite revealed the presence of $NaCl \pm CaCl_2 \pm MgCl_2$-rich brines without significant CO_2-contents in texturally primary and secondary aqueous as well as $CH_4\text{-}N_2$-rich inclusions (Cong and Touret 1993). Since then several fluid inclusion studies, which were often combined with oxygen-isotope studies, have been carried out on the HP and UHP rocks of the Dabie Shan and Sulu terranes (e.g., You et al. 1996; Xiao et al. 2000, 2001; Franz et al. 2001; Fu et al. 2001, 2002, 2003; Schmid et al. 2003).

The Dabie-Sulu terranes constitute the eastern part of a Triassic suture between the Sino-Korean and Yangtse cratons. The eastern part of this metamorphic terrane was displaced more than 500 km by the NNE-SSW trending sinistral strike-slip Tan-Lu fault (Xu et al. 1992).

Recent chronological studies on the HP and UHP rocks give ages of between 240 and 220 Ma for the peak metamorphic event (e.g., Hacker et al. 2000). The UHP unit mainly consists of gneisses, marble, jadeite quartzite, minor eclogite and garnet clinopyroxenite layers and lenses as well as associated ultramafic rocks. The extremely low-$\delta^{18}O$ whole-rock signature in some of the HP and UHP eclogites and garnet clinopyroxenites from the Dabie-Sulu terrains—which is interpreted to be due to interaction of the meteoric fluids with the pre-metamorphic protolith of the eclogites and garnet clinopyroxenites before subduction (for discussion and extensive reference list see Zheng et al. 2003)—encouraged Fu et al. (2001, 2002, 2003) to undertake fluid inclusion studies on these rocks. Their aim was to search for possible relics of such a pre-metamorphic fluid in eclogite-facies minerals such as garnet, omphacite and epidote. The UHP eclogites have the following peak-metamorphic mineral assemblage: garnet-omphacite-coesite/quartz-phengite±rutile±epidote±kyanite±amphibole-apatite-ilmenite-magnetite. Some garnet porphyroblasts contain epidote, dolomite, kyanite, K-feldspar and apatite, which are interpreted to have been trapped under prograde (pre-peak) metamorphic conditions (see reactions (17) to (21)). Therefore the fluid inclusions, which were found in epidote and kyanite, may contain relics of a very early fluid phase (Fu et al. 2003). The peak metamorphic assemblage of the HP-eclogites is garnet-omphacite-epidote-quartz-rutile±amphibole-apatite while the garnet clinopyroxenites reveal the assemblage garnet-diopside-calcite/dolomite-ilmenite/magnetite-apatite. The HP and UHP eclogites and garnet clinopyroxenites display a wide range of whole-rock $\delta^{18}O$ values, from –10 to 11‰, whereby no differences were reported either for the HP- or the UHP rocks. Fu et al. (2001, 2003) established two generations of primary fluid inclusions, early pre-peak metamorphic low-salinity inclusions (<14 wt. % NaCl eq.; $T_h = 95–340°C$), which occur in quartz inclusions in epidote and in epidote cores, and syn-peak metamorphic, texturally primary inclusions in garnet, omphacite and epidote (Fig. 3), which mainly revealed aqueous inclusions with a wide variety of salinity (>14 wt. % NaCl eq. to halite saturation) and homogenization temperature (110 to 390°C) as well as $N_2 \pm CO_2 \pm CH_4$-rich inclusions. No difference in composition or density was reported for individual samples concerning the inclusion fluids among the investigated peak-metamorphic minerals. In order to assign primary inclusion fluids to certain rock types, Fu et al. (2002, 2003) reported that high-$\delta^{18}O$ HP/UHP eclogites and clinopyroxenites have primary fluid inclusions with high-salinity brines. Low initial melting temperature <–35.5°C indicate the presence of divalent ions such as Ca^{2+}, Mg^{2+} and Fe^{2+} besides Na. Furthermore N_2-rich inclusions are associated with the high-salinity brines. In contrast low-$\delta^{18}O$ HP/UHP eclogites have low-salinity inclusions with up to two accidentally trapped solid inclusions in quartz inclusions in epidote and in cores of epidote porphyroblasts. These low-salinity inclusions reveal high initial melting temperature >–20°C, thereby indicating a NaCl and KCl dominant system. Consequently the authors assumed a correlation between $\delta^{18}O$ values and fluid salinity. They concluded that peak metamorphic fluids in high-$\delta^{18}O$ HP/UHP eclogites would be $CaCl_2$-$MgCl_2$-dominated high-salinity brines, while NaCl-dominated low-salinity brines would occur in low-$\delta^{18}O$ HP/UHP rocks. Due to the extremely low-$\delta^{18}O$ values of some of these rocks Fu et al. (2003) suggested that the low-salinity fluids in epidote could be remnants of meteoric water, which had interacted with the protoliths of the high-pressure rocks prior to plate subduction, and which were subsequently modified during peak metamorphic conditions. Nonetheless I want to point out that the correlation between fluid salinity and oxygen-isotope composition is ambiguous, since some low-$\delta^{18}O$ eclogites from the Central Dabie Shan have syn-peak omphacite and epidote, which contain texturally primary inclusions with high-salinity brines (Fu et al. 2002). It should furthermore be noted that all primary inclusion fluids underwent a density modification, since none of the calculated fluid isochores correlate with peak metamorphic conditions. Furthermore, some of the “accidentally trapped” solids in epidote (as described above) may have been formed by back reactions with the inclusion fluid (cf. Heinrich and Gottschalk 1995).

Discussion

As shown above, the presence of a discrete and free fluid phase during HP and UHP metamorphism was substantiated by the finding of syn-peak metamorphic low- to high-salinity aqueous fluid inclusions and or gaseous CO_2-N_2-rich inclusions in eclogite-facies minerals in veins or in the matrix of these rocks. This is in accordance with several other fluid inclusion studies on HP and UHP rocks (e.g., Philippot and Selverstone 1991; Philippot 1993; Giaramita and Sorensen 1994; El-Shazly and Sisson 1999; Franz et al. 2001; Gao and Klemd 2001). Consequently the composition of the eclogite-facies fluid strongly varies between the different eclogite-facies terranes, as is indicated by all the above-mentioned studies. For example, even within single terranes such as the Dabie-Sulu in eastern China, where the timing of peak metamorphism is tightly constrained, fluid inclusion investigation revealed strong fluid activity gradients, which apparently persisted during high-pressure metamorphism. This is in support of other fluid inclusion studies on HP/UHP rocks world-wide (e.g., Philippot and Selverstone 1991; Selverstone et al. 1992; Klemd et al. 1992, 1995; Xiao et al. 2000; Schmid et al. 2003). For example, eclogite-facies mineral assemblages in textural equilibrium with epidote minerals always contain H_2O-salt inclusions, while those without epidote minerals may contain CO_2 (Selverstone et al. 1992). Such fluid gradients suggest local fluid production and/or internal buffering as well as limited fluid flow on a relatively small scale during eclogite-facies metamorphism in subduction zones. This is in agreement with the preservation of small scale isotopic heterogeneities in eclogites as observed by Scambelluri and Philippot (2001), who proposed that fluids mostly remain entrapped in the subducting rocks within subduction zones and are released into the overlying mantle only at depths greater than those revealed by most exposed eclogites (>120 km). The isolation of aqueous and CO_2-rich fluids in pockets in eclogites would—due to their large dihedral angle (>65°)—prevent any large-scale flow along grain boundaries from the slab to the overlying mantle wedge until a depth of about 150 km (e.g., Severstone et al. 1992; Mibe et al. 2003). Therefore the transport of aqueous fluid and thereby trace elements from the subducting oceanic crust into the overlying mantle wedge, which is necessary for the formation of island arc magmas, can be achieved mainly by hydrofracturing, since the influence of shear deformation on aqueous fluid connectivity is rather limited at geological strain rates (Davies 1999). This is supported by the findings of Gao and Klemd (2001). They observed large eclogite veins, which were generated from hydrofracturing related to the dehydration of the surrounding blueschist host (cf. Kirby et al. 1996), thereby implying the possibility of massive fluid transfer in the subduction zone at about 60 km depth.

However, limited fluid flow as well as the local fluid production and/or buffering will prevent petrologists from assuming a distinct fluid composition for eclogite-facies metamorphism in order to calculate *P-T* conditions or quantitative phase diagrams, which demand the input of a certain H_2O and/or CO_2 activities from fluid-phase equilibria. Furthermore differences in fluid regimes between eclogite-facies rocks cannot exclusively be related to different tectonic settings, and thus geodynamic settings—when derived from fluid inclusion studies only—will remain ambiguous (e.g., Andersen et al. 1993; Klemd and Bröcker 1999).

CONCLUDING REMARKS

Fluid inclusion investigations on epidote minerals in combination with other petrological studies such as stable and radiogenic isotope or geothermobarometrical investigations provide important information on geodynamic processes for a range of hydrothermal and metamorphic processes which are related to the formation of epidote mineral-bearing assemblages. Furthermore fluid inclusions in epidote minerals provide direct evidence on the composition of the fluid phase involved in the formation of these minerals and thus on fluid-rock interaction processes. Consequently, microthermometrical and analytical studies of fluid inclusions in epidote minerals should be conducted in regional metamorphic rocks, in skarn and other hydrothermal ore deposits and in metasomatically influenced rocks such as epidosites in order to gain information on fluid related epidote mineral-forming processes. Such data will provide a wealth of information for example on fluid immiscibility and composition during the formation of these minerals in these environments. In addition laboratory-simulated experiments should be conducted in order to quantify possible re-equilibration and/or the role of volatile diffusion behavior of fluid inclusions in epidote minerals during internal over- and underpressure conditions.

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