Thermobarometric methodologies applicable to eclogites and garnet ultrabasites

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Introduction

Thermobarometry of HP/UHP rocks is of vital importance for the understanding of tectonic and rock forming processes and large-scale vertical transport of matter at great depths within the Earth. In recent years new sets of experiments, the extraction of internally consistent thermodynamic data set, together with elaborated composition–activity models for critical minerals have taken the art of estimation of metamorphic conditions several important steps forward. In this contribution we would like to present methods we regard as important for basic and ultrabasic compositions, and address problems of vital interest in modern geothermobarometric evaluations of HP/UHP rocks.

Carswell & Harley (1990) gave a comprehensive review on this task, and some of their fundamentals will not be reproduced here. For a more general review of geothermobarometry, the reader is recommended Chapter 15 of Spear (1993).

Mineral assemblages of interest

The essential mineral assemblage of eclogites (\textit{s. s.}) is garnet + omphacite + quartz. Additional phases may be many, and the silicates phengite, amphibole, kyanite and zoisite/clinozoisite are fairly common. Rutile is apparently present in most eclogites, while Al- and F-rich titanite has been described from rather few localities. Dolomite and calcite (after primary aragonite) are not uncommon. The high-$P$ SiO$_2$ polymorph coesite has been found as preserved relics or as distinctive polycrystalline quartz polymorphs included in primary phases as garnet, omphacite or zircon.

The principal mineral assemblage of \textit{UHP ultrabasites} consists of garnet, diopside, enstatite and forsterite. Depending on both the $P$–$T$ conditions and the presence of minor chemical components such as K, Ti, F and Cl additional phases like phlogopite, K-richerite, Ti-clinohumite, Mg-chlorite and antigorite are stable under HP/UHP conditions. In most cases these accessory phases are not of great interest for common geothermobarometric calculations. We will therefore not discuss the occurrence and implications of these minerals with respect to $P$–$T$ determinations. The interested reader is referred to Poli & Schmidt (2002) and references therein.
Practical geothermometers and geobarometers for HP/UHP rocks

Practical geothermometers are based on chemical reactions with low $\Delta V$ and high $\Delta S$ and $\Delta H$. Such reactions are strongly temperature dependent, and have steep slopes in a $P–T$ diagram. Likewise, good geobarometers can be found among mineral reactions with high $\Delta V$ and low to moderate $\Delta S$ and $\Delta H$. Such reactions are highly dependent on variations in pressure and less dependent on temperature, and thus have very gentle slopes in a $P–T$ diagram (Fig. 1). However, as most available geothermometers are, to a certain degree, dependent on pressures, and geobarometers dependent on temperatures, we commonly need a combination of at least one geothermometer and one geobarometer to constrain metamorphic conditions properly.

The most frequently used thermometers for garnet-bearing basic and ultrabasic rocks can be subdivided into three categories:

- Fe$^{2+}$–Mg exchange thermometers between garnet and either clinopyroxene, orthopyroxene, olivine or phengite,
- two-pyroxene thermometers based on the pyroxene solvus,
- trace element thermometers.

Practical geobarometers for HP/UHP rocks are all based on net transfer reactions between complex solid solutions. A key point is the distribution of Al between VI and IV coordination, the former being favoured by increasing pressure.

Only simple equations for the most widely used thermometers and barometers will be given. For the more complicated expressions the reader is recommended to consult the original papers. Furthermore, we have not discussed the use of more elaborated thermodynamics-based methods as exemplified by THERMOCALC (Powell & Holland, 1988, 1994) or TWQ (Berman, 1991).

Some cautionary notes before proceeding

In calculating temperature and pressure for HP/UHP rocks such as eclogites and garnet peridotites, the careful study of the textural relationships is inevitable. At temperatures around 650–700 °C the intracrystalline diffusion of Fe$^{2+}$ and Mg in most minerals except garnet is fast enough for homogenisation. Above this temperature garnet will also homogenise. One relevant assumption for calculation of peak metamorphic pressures and temperatures in many HP/UHP rocks is then that core compositions of coexisting minerals reflect the metastable peak metamorphic conditions and therefore indicate equilibrium. This presumption is valid for many orogenic UHP eclogites and garnet peridotites, and xenoliths, whose minerals show evidence for a rapid exhumation history, which is visible only in narrow zoning at the outermost rims combined with extensive homogeneous plateaus in the core region of the minerals. Most HP/UHP rocks also show intensive retrograde overprinting combined with deformation as well as generation of new minerals, which, in the case of garnet ultrabasites often are of the same phases as the primary minerals. Therefore it is important for calculating peak metamorphic pressures and temperatures in UHP rocks only to use the first generations of minerals, which in most cases occur as porphyroclasts that are in contact with each other. The timing of maximum pressure and maximum temperature in HP/UHP terranes may also
greatly diverge, and this can easily result in wrong combinations of mineral analyses when different thermometers and barometers are combined. This problem has also been addressed by e.g. Carswell et al. (1997, 2000).

HP and UHP metamorphic rocks commonly have a complex history, often including rapid subduction followed by accelerated exhumation. Therefore it is important to be aware the problems that can arise in disequilibrium, as well as equilibrium partitioning among different elements in minerals due to significantly different diffusivities (e.g. Paquin & Altherr, 2001a). To detect such disequilibrium partitioning, detailed microanalytical (EPMA) profiling across mineral grains is needed to evaluate both inter- and intraphase partitioning. Also the fact that $P$–$T$ determinations are mostly related to cation exchange equilibria, continued cation diffusion among coexisting minerals during the retrograde history must be taken into account. The degree of thermal resetting is commonly not readily identified. Moreover the different sizes of the relevant mineral grains and cutting effects of grains can also significantly influence the $P$–$T$ results.

In the following paragraphs we want to present the most important geothermobarometers, discuss some pitfalls in calculating metamorphic pressures and temperatures, and in addition discuss some new aspects, offering the best possible results.
Geothermometers

The most frequently used thermometers for garnet-bearing basic and ultrabasic rocks can be subdivided into three categories:

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- trace element thermometers.

Geothermometers based on Fe$^{2+}$–Mg exchange between garnet and other Fe–Mg minerals

The following mineral pairs have been subject to special interest as potent geothermometers based on the strongly temperature dependent exchange of Fe$^{2+}$ and Mg between garnet and common coexisting phases in HP/UHP rocks:

- garnet–clinopyroxene,
- garnet–orthopyroxene,
- garnet–olivine,
- garnet–hornblende,
- garnet–phengite,
- garnet–biotite.

Garnet–biotite

Biotite is a fairly uncommon phase in HP and UHP rocks, but has been described from low-$T$ eclogites from e.g. the Western Gneiss Region (WGR) of Norway (Krogh, 1980), and from several Fe-Ti garnet peridotites and “orthopyroxene eclogites” from the WGR (Carswell et al., 1983, 1995). The status of biotite in the latter rocks has, however, been disputed. In pelitic systems, biotite is apparently unstable at high pressures, phengite being the stable mica. Thus, the garnet–biotite system has no important relevance to HP/UHP metamorphism.

Garnet–hornblende

The garnet–hornblende Fe–Mg system has been empirically calibrated (Graham & Powell, 1984; Perchuk et al., 1985; Powell, 1985; Ravna, 2000b). None of these calibrations have, however, proved to be successful for amphibole-bearing eclogites, and will not be discussed further here.

Garnet–phengite

The garnet–phengite Fe–Mg geothermometer was first proposed by Krogh & Råheim (1978), based on a minimum of experimental data from Råheim & Green (1974). Green & Hellman (1982) presented experimental results for this reaction for different bulk compositions, showing the dependence of this equilibrium on $P$, $T$ and $X$. For basaltic systems with mg# $\approx 67$ their expression is
where $K_D = \frac{(\text{Fe/Mg})^{\text{grt}}}{(\text{Fe/Mg})^{\text{pht}}}$ (CD Image 1). This thermometer has been used with generally not some success, but is recommended due to serious uncertainties linked to the possible presence of Fe$^{3+}$ in phengite, which is not readily detected by routine analyses. Recently Coggon & Holland (2002) presented a new linearised expression for this reaction, but this method is not evaluated here.

**Garnet–clinopyroxene**

This is one of the most widely used geothermometers for high-grade metamorphic basites and ultrabasites, due to the common appearance of garnet and clinopyroxene in such rocks.

The first attempt to calibrate this system quantitatively was empirically done by Mysen & Heier (1972). However, Råheim & Green (1974) did the first experimental calibration of the system, expressing the relationship between temperature, pressure and the distribution coefficient $K_{D}^{\text{grt-cpx}} = \frac{(\text{Fe/Mg})^{\text{grt}}}{(\text{Fe/Mg})^{\text{cpx}}}$. Later on, many different versions of this geothermometer have been proposed (e.g. Ellis & Green, 1979; Powell, 1985; Krogh, 1988; Pattison & Newton, 1989; Ai, 1994; Ravna, 2000a). All of these contain corrections for $X_{\text{Ca}}^{\text{grt}}$ and the last three also include correction factors for $X_{\text{Mg}}^{\text{grt}}$. Most of these versions apparently give reliable and comparable results, at least for systems containing garnet with intermediate Ca contents. For rocks with low-Ca garnets (e.g. garnet ultrabasites) or high-Ca garnets the deviation between the different calibrations are greater due to different correction factors for the non-ideality of Ca in garnet solid solution (see e.g. Carswell *et al.*, 1997). While the expressions of Ellis & Green (1979) and Powell (1985) have rectilinear corrections for $X_{\text{Ca}}^{\text{grt}}$, Krogh (1988) demonstrated a curvilinear relationship between ln$K_D$ and $X_{\text{Ca}}^{\text{grt}}$, at least in the compositional range $X_{\text{Ca}}^{\text{grt}} = 0.10–0.50$. Based on a variety of experimental data, Krogh (1988) derived the following geothermometric expression

$$T K_{100} \ [^\circ C] = \frac{1879 + 6731X_{\text{Ca}}^{\text{grt}} - 6173(X_{\text{Ca}}^{\text{grt}})^2 + 100P [\text{GPa}]}{\ln K_D + 1.393} - 273.$$  

Pattison & Newton (1989) presented a large set of self-consistent data on the Fe–Mg equilibria between garnet and clinopyroxene. Multiple regression of their data yield the geothermometric expression
This expression reproduces the experimental data of Pattison & Newton (1989) well within ± 40 °C, but commonly yields unrealistic low temperatures on natural rocks. Berman et al. (1995) used the Pattison & Newton (1989) dataset to refine the thermometer through thermodynamic analysis, and application of this reformulation to a number of amphibolite to granulite facies terrains returned temperatures between 70 to 200 °C above those obtained with the original Pattison & Newton (1989) geothermometer, and compatible with independent temperature estimates.

Ai (1994) combined new experimental data on Mg-rich systems with the Pattison & Newton (1989) data set, as well as with data from 15 other sources, altogether 271 pairs of garnet–clinopyroxene. Multiple regression of the data returned the expression

\[
T_{\text{PN89}} [°C] = \frac{561 + 3395X_{\text{Ca}}^{\text{grt}} - 2388(X_{\text{Ca}}^{\text{grt}})^2 + 9781X_{\text{Mg}}^{\text{grt}} - 31026(X_{\text{Mg}}^{\text{grt}})^2}{\ln K_D + 0.512} + \\
+ \frac{26217(X_{\text{Mg}}^{\text{grt}})^3 + 103.7P[\text{GPa}]}{\ln K_D + 0.512} - 273.
\]

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\[
T_{\text{Ai94}} [°C] = \frac{1987 + 3648.55X_{\text{Ca}}^{\text{grt}} - 1629(X_{\text{Ca}}^{\text{grt}})^2 - 659X_{\text{Mg}}^{\text{grt}} + 176.6P[\text{GPa}]}{\ln K_D + 0.512} - 273.
\]

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Ravna (2000a) used an extended database of 311 garnet–clinopyroxene pairs from 27 experimental sources, excluding the large self-consistent data set of Pattison & Newton (1989). He also included 49 garnet–clinopyroxene pairs from natural Mn-rich samples to retrieve empirical correction factors for \(X_{\text{Mn}}^{\text{grt}}\), and gave the expression

\[
T_{\text{R00}} [°C] = \frac{1939 + 3270X_{\text{Ca}}^{\text{grt}} - 1396(X_{\text{Ca}}^{\text{grt}})^2 + 3319X_{\text{Mn}}^{\text{grt}} - 3535(X_{\text{Mn}}^{\text{grt}})^2}{\ln K_D + 1.223} + \\
+ \frac{1105X_{\text{Mg}}^{\text{grt}} - 3561(X_{\text{Mg}}^{\text{grt}})^2 + 2324(X_{\text{Mg}}^{\text{grt}})^3 + 169.4P[\text{GPa}]}{\ln K_D + 1.223} - 273.
\]

This calibration (CD Image 2) includes a very wide range of compositions of both garnet and clinopyroxene, and it is expected to work for most compositional ranges covered by natural rocks. A comparison between different calibrations of the thermometer as functions of chemical variations of garnet was also shown (Ravna, 2000a).

The effect of additional components. Commonly, uncertainties related to the garnet–clinopyroxene geothermometer are cited as ± 30 to 50 °C. The use of most of the above-cited expressions will for most samples produce temperatures within these limits, and they are all subject to the crucial limitation due to the ferric–ferrous iron problem (see discussion below). Moreover, none of the calibrations contain any correction for \(X_{\text{Jd}}^{\text{px}}\). Koons (1984) proposed that for more Jd-rich clinopyroxenes \((X_{\text{Jd}}^{\text{px}} > 0.7)\) e.g. in metagranitoids, \(K_D\) appears to vary inversely with jadeite content. Koons (1984)
attributed this to non-ideality in Fe\textsuperscript{2+}MgNa\textsubscript{1}Al\textsubscript{1} substitution resulting in preferential ordering of Fe\textsuperscript{2+} into M\textsubscript{2} sites in the clinopyroxene. In a geothermometric study of UHP eclogites from the Su-Lu terrane, Hirajima (1996) showed a distinct negative correlation between lnK\textsubscript{D} and X\textsubscript{Jd} in the range 0.45 < X\textsubscript{Jd} < 0.75, resulting in a corresponding positive correlation between calculated T and X\textsubscript{Jd}. In this study calculated T shows a scatter of ca. 300 °C at one outcrop. This could apparently not be ascribed to estimation error of Fe\textsuperscript{3+}/Fe\textsuperscript{tot} alone. He concluded that we cannot estimate the equilibrated T of UHP rocks using the common garnet–clinopyroxene geothermometers without the introduction of a new correction factor for X\textsubscript{Jd} in clinopyroxene. An independent indication can be extracted from the experimental data of Schmidt (1993). At 650 °C and pressures of 20–26 kbar two pyroxenes – omphacite with about Jd\textsubscript{50}Aug\textsubscript{50} and jadeitic pyroxene ranging from Jd\textsubscript{65}Aug\textsubscript{35} to Jd\textsubscript{78}Aug\textsubscript{22} – coexisted with garnet in tonalitic compositions. There is a tendency of positive correlation between X\textsubscript{Na} and Fe/(Fe + Mg) in clinopyroxene from these experiments, but not as pronounced as that shown by Hirajima (1996). Ravna (2000a) showed that for 0 < X\textsubscript{Jd} < 0.50 there was no obvious influence of X\textsubscript{Jd} on the K\textsubscript{D} values. All these evidence points toward a certain influence of X\textsubscript{Jd} on the K\textsubscript{D} value at higher (> Jd\textsubscript{55}? ) X\textsubscript{Jd} values, and thus on calculated temperatures.

**Garnet–olivine**

The advantage of this extensively used experimental calibration (O’Neill & Wood, 1979, corrected by O’Neill, 1980) (T\textsubscript{OW79}), which has an intrinsic calibration uncertainty of approximately ± 60 °C, lies in the simple solid solution model of olivine. The thermometric expression (CD Image 3) can be retrieved from the original papers of O’Neill & Wood (1979) and O’Neill (1980). However, although only garnet incorporates significant amounts of Fe\textsuperscript{3+}, an enormous discrepancy of up to 200 °C (Canil & O’Neill, 1996) can result in calculated temperature estimates depending on whether the Fe\textsuperscript{3+} content in garnet is considered or disregarded. When Fe\textsuperscript{3+} content in garnets is ignored, the TOW\textsubscript{79} is in best agreement with the results of the widely used two-pyroxene thermometer calibration of Brey & Köhler (1990) (T\textsubscript{BK290}), therefore Canil & O’Neill (1996) recommend ignoring possible Fe\textsuperscript{3+} contents in garnets.

The faster diffusion of Fe and Mg in olivine implies rapid adjustment to changing P–T conditions compared to the Fe-Mg diffusion garnet (Ganguly & Tazzoli, 1994; Dimanov & Sautter, 2000). This implies that the Fe-Mg core compositions of olivine are in most cases not in equilibrium with the Fe-Mg core compositions in garnet. The question remains how it is possible to retain reliable T estimates. Brenker & Brey (1997) found that for olivine-rich bulk compositions (> 75 modal %) changing P–T conditions result in large changes in the Fe/Mg ratio in garnet, but only in negligible changes in the Fe/Mg ratio in olivine. This is caused by the fact that the Fe/Mg ratio in olivine reflects the Fe/Mg ratio of the bulk composition as olivine is the dominant mineral phase in the peridotitic systems and therefore acts as a buffer.

Taylor (1998) found highly variable T estimates for his experimental series at T > 1150 °C with T\textsubscript{calc}–T\textsubscript{expt} ≈ 200–300 °C. Moreover, Nimis & Trommsdorff (2001) suggested that the small ΔG\textsubscript{0} of the Fe–Mg reaction between garnet and olivine (Ganguly...
& Saxena, 1987) result in large uncertainties of the \( TOW_{79} \) formulation. However, Brey & Köhler (1990) found that the combination of \( TOW_{79} \) and the Al-in-orthopyroxene barometer (Brey & Köhler, 1990) \( (PBK_{90}) \) demonstrates good reproducibility of their experiments and that the thermometer can be applied to natural peridotitic rocks in its present form.

**Garnet–orthopyroxene**

The first formulation of Mori & Green (1978) is based on their experimental phase equilibria for natural garnet lherzolites. But this thermometer version did not include a pressure correction term and hence is not of great importance. Harley (1984a) has experimentally investigated the partitioning of Fe and Mg in both the FMAS and CFMAS systems between garnet and aluminous orthopyroxene. The thermometric calibration \( (TH_{84}) \) is expressed as

\[
TH_{84} \, [^\circ C] = \frac{3740 + 1400 X_{grt}^{grt} + 22.86P}{RT \ln K_D + 1.96} - 273,
\]

with \( K_D = (\text{Fe/Mg})_{grt}/(\text{Fe/Mg})_{opx}, X_{grs}^{grt} = \text{Ca}/(\text{Ca} + \text{Mg} + \text{Fe}) \) and \( P \) in kbar.

Brey & Köhler (1990) noted that the \( TH_{84} \) slightly overestimates at low and underestimates at high temperatures, whereby the best agreement is at \( \sim 1000 \, ^\circ C \) for his CFMAS experiments. A new version of this thermometer (Lee & Ganguly, 1988) based on new experiments in the FMAS system yields overestimates of more than 125 \(^\circ C\) compared to the experimental temperatures by Brey & Köhler (1990). Better results of the Lee & Ganguly (1988) thermometer version will be achieved when the correction term for Ca and Mn in garnet is neglected (Brey & Köhler, 1990). Brey & Köhler (1990) also formulated a thermometer expression based on Fe–Mg exchange equilibria for six different mineral pairs in their experiments. Their garnet–orthopyroxene thermometer is expressed as

\[
TH_{84} \, [^\circ C] = \frac{1456 + 9.86P}{\ln K_D + 0.55} - 273,
\]

with \( K_D = (\text{Fe/Mg})_{grt}/(\text{Fe/Mg})_{opx} \) and \( P \) in kbar.

This thermometer version gives, compared to the Harley (1984a) version, slightly higher temperatures at high \( T \) and slightly lower temperatures at low \( T \). A general problem is that the slope of the \( K_D \) lines in a \( P–T \) diagram are quite flat, resulting in a relative large error if combined with the Al-in-orthopyroxene barometer of Brey & Köhler (1990) (Fig. 1, CD Image 4).

**Fe-Mg geothermometry and the problem of Fe\(^3+\)**

The \( T \) estimates based on Fe–Mg exchange thermometry between garnet, olivine, orthopyroxene and clinopyroxene are generally not entirely reliable due to uncertainties in the \( \text{Fe}^{3+}/\text{Fe}^{tot} \) ratios of both natural phases and the phases in the original laboratory experiments from which the thermobarometers were calibrated (Canil & O’Neill, 1996).
It is now well known that the experiments used to calibrate these Fe–Mg exchange thermometers produced garnet, orthopyroxene and clinopyroxene with substantial Fe$^{3+}$ contents, similar to that of natural samples (e.g. Brey & Köhler, 1990; Canil & O’Neill, 1996; Smith, 1999). In natural garnet peridotites the Fe$^{3+}$/Fe$^{tot}$ ratios increase in the order olivine (~ 0.00), garnet (~ 0.03), orthopyroxene (~ 0.03–0.10) and clinopyroxene (~ 0.2–0.4), and the Fe$^{3+}$ content in garnet increases significantly with increasing $P$ and $T$. In common eclogites the Fe$^{3+}$/Fe$^{tot}$ ratio in garnet is expected to be low, as shown by Mössbauer studies of garnet from UHP eclogites from Dabie Shan showing a Fe$^{3+}$/Fe$^{tot}$ ratio of only 0.06 (reported by Carswell et al., 2000). This is also supported by micro-XANES studies (Schmid et al., 2003), where Fe$^{3+}$/Fe$^{tot}$ ratios of garnets from the same area were in the range 0.0–0.03.

The inaccuracy of the Fe–Mg exchange geothermometry cannot, however, be quantified as the exact redox conditions of the original experiments are not well known (Luth & Canil, 1993). For ultrabasic systems it is recommended to treat all Fe as Fe$^{2+}$ as this approximation has shown to yield the best agreement between $T_{BK290}$ (as a Fe$^{3+}$ independent thermometer) and various Fe–Mg thermometers. However, it is highly desirable to measure the Fe$^{3+}$ contents in the mineral phases to be aware of the problems of Fe$^{3+}$ in applying Fe–Mg exchange thermometry and to test to what extent the calculated temperatures are shifted towards higher or lower temperatures. Various methods have been proposed to treat this problem.

A common method is to use charge balance criteria to calculate the Fe$^{3+}$/Fe$^{tot}$ ratio of minerals. For clinopyroxene 4 cations and 6 oxygens may be used. Charge balance can then be obtained by oxidising an adequate portion of Fe$^{2+}$ to Fe$^{3+}$ (Ryburn et al., 1976; Neumann, 1976; Droop, 1987). However, we now know that under HP/UHP conditions clinopyroxene appear to be non-stoichiometric due to the presence of the Ca-Eskola molecule Ca$_{0.5}$AlSi$_2$O$_6$. Other attempts include calculation of Fe$^{3+}$ equal Na excess over Al + Cr. Similar calculations have been proposed for amphiboles (e.g. Schuhmacher, 1991) and phengite (e.g. Schliestedt, 1980). All such calculations are, however, very sensitive to the quality of the chemical analyses of the mineral, even in the case of high-quality WDS electron microprobe analyses (Carswell & Zhang, 1999). For relatively Fe-rich clinopyroxenes this does not appear to be a very serious problem, but for Fe-poor systems an unreliable spread in calculated Fe$^{3+}$/Fe$^{tot}$ ratios is obtained. In the case of non-stoichiometry, such calculations may even appear meaningless. Sobolev et al. (1999) concluded in a detailed Mössbauer study of Fe$^{3+}$ in coexisting garnet and clinopyroxene from diamondiferous eclogite from the Udachnaya kimberlite and garnet peridotite from the Mir kimberlite that values of Fe$^{3+}$/Fe$^{tot}$ calculated from EMP analyses generally are inaccurate, although they do not greatly affect temperature estimates in eclogites due to compensation effects between garnet and clinopyroxene. According to Sobolev et al. (1999), the precision in determination of SiO$_2$ largely controls the Fe$^{3+}$/Fe$^{tot}$ values based on stoichiometry due to its abundance and high ionic charge. In addition, high-Na clinopyroxenes (> 4–5 wt% Na$_2$O) are even more sensitive to EMP errors, and therefore can produce larger uncertainties in temperature estimates. This lead the authors to question the correctness of previously published $K_p$ values and temperatures based on any geothermometers involving Fe$^{2+}$–Mg distribution.
Calculated the Fe\(^{3+}/\)Fe\(^{tot}\) ratios for omphacites in 12 UHP samples from Dabie Shan varied between 0 and 0.5 Carswell et al. (1997), while Tabata et al. (1998) gave a range of 0.16–0.82 for omphacites from the same region. Mössbauer studies of the Fe\(^{3+}/\)Fe\(^{tot}\) ratio in omphacite separates from two Dabie Shan UHP eclogite samples indicated that roughly 50% of the Fe is present as Fe\(^{3+}\) (reported by Carswell et al., 2000).

Schmid et al. (2003) determined ferric iron in the UHP minerals garnet, omphacite and phengite by micro-XANES. Using samples of eclogites from Dabie Shan they showed that omphacite and phengite both have elevated Fe\(^{3+}/\)Fe\(^{tot}\) ratios, while coexisting garnet had a low Fe\(^{3+}/\)Fe\(^{tot}\) ratio. Charge balance calculations showed no Fe\(^{3+}\) in omphacite, while the Fe\(^{3+}/\)Fe\(^{tot}\) ratio detected by micro-XANES was 0.25–0.30. In garnet, on the other hand, no Fe\(^{3+}\) was detected, while charge balance calculations gave Fe\(^{3+}/\)Fe\(^{tot}\) = 0.027–0.054. Schmid et al. (2003) concluded that the contents of ferric iron calculated by charge balance – at least in the case of low-Fe omphacite and phengite – obviously have little bearing for P–T estimates. To retrieve confident results, one needs to determine the Fe\(^{3+}\) content for every specific mineral assemblage used in thermobarometry.

Carswell & Zhang (1999) have highlighted the seriousness of this problem, showing a strong negative correlation between calculated Fe\(^{3+}/\)Fe\(^{tot}\) ratios in omphacite and temperatures calculated from Fe\(^{2+}\)–Mg partitioning between garnet and omphacite (see Fig. 2). A possible regional T gradient across the Dabie Shan UHP terrane (Wang et al., 1992) will thus be masked by the uncertainties introduced by calculation of the Fe\(^{3+}/\)Fe\(^{tot}\) ratio in clinopyroxene. Carswell & Zhang (1999) suggested that error brackets of at least ± 100 °C should be attached to individual garnet–clinopyroxene Fe\(^{2+}\)–Mg estimates simply because of uncertainties regarding the proportions of Fe\(^{3+}\) and Fe\(^{2+}\) present in the omphacites. As an independent test, a series of omphacite analyses (n = 39) from a single thin section from sample DAB 9872 from Dabie Shan (from the database of Schmid, 2001) was combined with a garnet containing the highest Mg/Fe ratio. Based on charge balance calculations the Fe\(^{3+}/\)Fe\(^{tot}\) ratio in the omphacite vary from 0–0.546 (mean value 0.064), and the corresponding temperatures vary from 914–646 °C (calculated at 4.0 GPa), with a mean of 867 ± 58 °C. If Fe\(^{3+}\) is assumed to equal Na – (Al\(^{tot}\) + Cr), the Fe\(^{3+}/\)Fe\(^{tot}\) ratio lies in the range 0–0.489 (mean value 0.178) and the corresponding temperatures between 914–673 °C, with a mean of 824 ± 65 °C. The negative correlation between estimated Fe\(^{3+}/\)Fe\(^{tot}\) and calculated T (Fig. 1) fall in the middle of the apparent “regional” trend for Dabie Shan UHP eclogites, supporting the conclusions of Carswell & Zhang (1999). Schmid (2001) analysed the Fe\(^{2+}\) content of omphacite in the same sample by standard titration methods, and calculated a Fe\(^{3+}/\)Fe\(^{tot}\) ratio of 0.35. Using this ratio, average temperature calculated for this sample using the same garnet composition and all 39 omphacite analyses as above, results in 758 ± 12 °C. Carswell et al. (1997) adopted a Fe\(^{3+}/\)Fe\(^{tot}\) ratio of 0.5 for omphacites from UHP eclogites in Dabie Shan, which in this case results in 690 ± 10 °C. The results from another sample of Schmid by using micro-XANES yielded a Fe\(^{3+}/\)Fe\(^{tot}\) ratio for omphacite of 0.25–0.30. Choosing the lower of these limits results in temperature estimates of 798 ± 13 °C. An independent estimate of 794 ± 65 °C at 3.70 ± 0.32 GPa (Ravna & Terry, 2003) for a garnet-clinopyroxene-phengite-kyanite-coesite eclogite from the same area is obtained from sample DB48 of Carswell et al. (1997). These highly diverging results should
remind us about extreme caution when applying the garnet–clinopyroxene Fe−Mg thermometer without separate estimations of Fe$^{2+}$ and Fe$^{3+}$ in clinopyroxene. All the problems discussed above for clinopyroxene can be addressed to amphibole and phengite as well. The estimation of Fe$^{3+}$/Fe$_{total}$ in these minerals would face similar uncertainties, and temperature estimates obtained with these methods should thus be treated as highly uncertain.

Solvus thermometry

**Two-pyroxene thermometers**

Studies of the mutual solubility of clinopyroxene coexisting with orthopyroxene have shown that the transfer of enstatite and diopside components between coexisting pyroxenes are strongly temperature controlled and hence provide the basis of a thermometer (e.g. Davis & Boyd, 1966; Boyd, 1973; Wood & Banno, 1973; Wells, 1977; Bertrand & Mercier, 1985; Brey & Köhler, 1990; Nimis & Taylor, 2000). The two-pyroxene solvus in a simple CMS system is controlled by a single reaction that expresses the Ca–Mg exchange in the M2 sites between the two pyroxenes, and is written as

$$\text{CaMgSi}_2\text{O}_6 + \text{Mg}_2\text{Si}_2\text{O}_6 \leftrightarrow \text{Mg}_2\text{Si}_2\text{O}_6 + \text{CaMgSi}_2\text{O}_6$$

At least 13 different calibrations of this thermometer exist, of which we only present the most widely used versions. The Wells (1977) formulation, which is expressed as

$$TW_{77}[^{\circ}\text{C}] = \frac{7341}{3.355 + 2.44X_{Fe^{2+}}^{\text{opx}} − \ln K} − 273,$$
with $K = a(Mg_2Si_2O_6)^{cpx} / a(Mg_2Si_2O_6)^{opx}$ and $X_{Fe}^{opx} = Fe^{2+}/(Fe^{2+} + Mg^{2+})$, reproduces the experiments of Brey et al. (1990) very well, but there is an increasing underestimation at higher temperatures presumably as no pressure term is incorporated in the equation. The thermometer version of Bertrand & Mercier (1985) generally underestimates temperatures although these authors include a correction term for the minor chemical components Na and Fe in their equation (Brey & Köhler, 1990). The thermometer is expressed as

$$TBM_{90}[^\circ C] = \frac{36273 + 399P}{(19.31 - 8.314 \ln K - 12.15 Ca_{cpx}^{*})^2} - 273,$$

where $K = (1 - Ca_{cpx}^{*} / (1 - Ca_{opx}^{*})$; $Ca_{cpx}^{*} = X_{Ca}^{Mg} / (1 - X_{Na}^{Mg})_{opx}$, $Ca_{opx}^{*} = X_{Ca}^{Mg} / (1 - X_{Na}^{Mg})_{cpx} + (-0.77 + 10^{-3} T)[Fe / (Fe + Mg)]$ and $P$ is in kbar.

Brey & Köhler (1990) attribute the underestimation of the Bertrand & Mercier (1985) calibration to the Fe correction of Ca in clinopyroxene, which is mainly based on experiments that were carried out in a temperature range too narrow to yield a universally applicable correction factor. The Brey & Köhler (1990) experiments are best reproduced by the Bertrand & Mercier (1985) thermometer if a correction factor of –0.97 is used instead of –0.77.

Brey & Köhler (1990) calibrated a new version of this two-pyroxene thermometer ($TBK_{290}$) based on reversed experiments and modified the correction term for Fe. Their equation is written as

$$TBK_{290}[^\circ C] = \frac{23664 + (24.9 + aX_{Fe}^{cpx}) P}{13.38 + (\ln K)^2 + bX_{Fe}^{opx}} - 273,$$

with $K = (1 - Ca_{cpx}^{*}) / (1 - Ca_{opx}^{*})$; $Ca_{cpx}^{*} = Ca_{cpx}^{Mg} / (1 - Na_{cpx}^{Mg})$, $X_{Fe}^{cpx} = Fe / (Fe + Mg)$ and $P$ in kbar.

An evaluation of older versions of the two-pyroxene thermometer is given by Carswell & Gibb (1987). However, it is important to note that pyroxene solvus relationships at low temperatures are not well constrained due to the steepening of the solvus limbs at successively lower temperatures. Therefore it is not recommended to use the two-pyroxene thermometers for equilibration temperatures $\leq 900$ °C to yield the best possible results. The recent two-pyroxene calibration of Taylor (1998) for lherzolites and websterites has so far not been tested on many natural peridotites and will therefore not be considered in this review.

Brey & Köhler (1990) formulated a Ca-in-orthopyroxene thermometer which considers only the Ca content in orthopyroxene. Their equation is as follows:

$$TBK_{390}[^\circ C] = \frac{6425 + 26.4P}{- \ln Ca_{opx}^{cpx} + 1.843} - 273,$$

with $P$ in kbar.

However, caution should be exercised as the Ca content in orthopyroxene is lowered in the presence of Al (Brey & Köhler, 1990), and may also be lowered through
the presence of Na in M2 sites in natural systems to counterbalance the incorporation of Fe. Nevertheless, the Ca-in-orthopyroxene thermometer provides insights into the closure temperature of the Ca–Mg exchange, which rules pyroxene solvus relations and hence can be used to evaluate equilibrium or disequilibrium conditions.

Trace element thermometers

The Ni-in-garnet thermometer

Further information about equilibration temperatures can be obtained by applying the Ni-in-garnet thermometer that considers the Ni partitioning in garnet in equilibrium with olivine. Empirical (Griffin et al., 1989; Ryan et al., 1996) as well as experimental studies (Canil, 1994, 1999) have shown that the Ni content in garnet is strongly temperature dependent with Ni contents increasing with increasing temperature, whereas the Ni content in mantle-derived olivine is more or less constant at 2900 ± 360 ppm (± standard deviation) (Ryan et al., 1996). Griffin et al. (1996) suggested that the diffusion of Ni in garnet is about the same as (or a bit faster than) Fe and Mg, so the Ni thermometer seems to respond very rapidly to temperature changes, especially to heating.

There is a discrepancy between the empirical and experimental calibration of the Ni-in-garnet thermometer (for discussion see Canil, 1994, 1996, 1999; Griffin & Ryan, 1996). We recommend the use of the experimental calibration of Canil (1999). The general problem is that an empirically calibrated thermometer (e.g. Ryan et al., 1996) can only be as precise as the independent P–T estimates of the used samples are. The calibration of Ryan et al. (1996) does not consider the different pressures of their samples. Since higher temperature mantle samples generally are derived from higher pressure regimes in the mantle, the linear regression from Ryan et al. (1996) in an ln\(D_{\text{Ni}}\) \(\text{Grt/Ol}\) versus \(1/T\) diagram (see Canil, 1999, page 245) is characterised by a flatter curve than the regression of Canil (1999). This results in an underestimation at \(T < 900\) °C and overestimation at \(T > 1400\) °C of the calculated temperatures. Canil (1999) has clearly shown that a pressure correction for the samples used by Ryan et al. (1996) yields an almost identical regression line as the one of Canil (1999).

The general advantage of this thermometer is that the calculated temperatures are reliable whether the garnet contains significant amounts of Fe\(^{3+}\) or not. Another advantage is the pressure independence of this thermometer. As Ni contents in peridotitic garnets are quite low, electron microprobe analyses are in most cases not accurate enough. However, numerous other analytical methods such as secondary ion mass spectrometry, laser ablation ICP-MS and proton probe work quite well.

Partitioning of transition elements (Sc, V, Cr, Co and Mn) between orthopyroxene and clinopyroxene in peridotitic and websteritic mantle rocks

It is well known from several studies that the partitioning of selected transition elements such as Sc, V, Cr, Co and Mn between mantle minerals is strongly controlled by temperature (Hervig & Smith, 1982; Hervig et al., 1986; Stosch, 1987; Bodinier et al., 1987). A detailed study, evaluating the partitioning of transition elements between
orthopyroxene and clinopyroxene for geothermobarometry yields the following five empirical equations (Seitz et al., 1999):

\[
T_{\text{Sc}}[^{\circ}\text{C}] = \frac{5663 + 17.64P}{3.25 - \ln D_{\text{Sc}}} - 273,
\]

\[
T_{\text{V}}[^{\circ}\text{C}] = \frac{3975 + 18.06P}{2.27 - \ln D_{\text{V}}} - 273,
\]

\[
T_{\text{Cr}}[^{\circ}\text{C}] = \frac{2829 + 11.00P}{1.56 - \ln D_{\text{Cr}}} - 273,
\]

\[
T_{\text{Mn}}[^{\circ}\text{C}] = \frac{-2229 - 0.20P}{-1.37 - \ln D_{\text{Mn}}} - 273,
\]

\[
T_{\text{Co}}[^{\circ}\text{C}] = \frac{-2358 - 4.31P}{-0.98 - \ln D_{\text{Co}}} - 273,
\]

with \(D_M\) = concentration [cations p.f.u.] of element \(M\) in orthopyroxene/concentration [cations p.f.u.] of element \(M\) in clinopyroxene, \(T\) in K and \(P\) in kbar.

All five empirical thermometer formulations show only minor pressure dependence (CD Image 5). Moreover, compositional influences on these thermometers such as the amount of Na or tetrahedral Al in the pyroxenes have not been found. The potential of these thermometers lies in the different diffusivities of the relevant elements, which can be used to evaluate equilibrium/disequilibrium conditions (Paquin & Altherr, 2001a,b) and/or to model thermal events based on zoning profiles. As the diffusivity of Co and Mn is much faster than that for Sc, V and Cr, different thermal stages can be indicated by these elements. In the case of equilibrium all five independent thermometers should yield concordant values.

At this stage these trace element thermometers have not frequently been used for temperature estimation, most likely due to the large-scale analytical methods such as LA-ICP-MS or SIMS needed for measurement of the transition elements. Therefore comparisons between more widely used thermometers and these new methods are not available. Nevertheless, experimental calibrations of these thermometers are necessary to confirm the empirical calibrations.

**Ca-Cr system in lherzolitic garnets**

Another test for the calculated peak metamorphic condition is provided by the Ca/Cr system in lherzolitic garnet coexisting with clinopyroxene, orthopyroxene and olivine. Concerning the Ca/Cr ratio in garnet, Brenker & Brey (1997) have shown that the abundance of Cr in garnet is a function of the effective bulk composition and does not depend on \(P\) and \(T\). For a given Cr content in garnet, Ca in garnet deceases with increasing pressure and increasing temperature. At constant \(P\) and \(T\), Ca increases linearly with Cr, so that the Ca/Cr ratio in a \(P-T\) diagram is defined by a straight line. This co-variation between Ca and Cr in garnet of lherzolitic samples was first recognised
by Sobolev et al. (1973) and Sobolev (1977). Based on the studies of Brey (1990) and Nickel (1983), Brenker & Brey (1997) formulated an empirical equation between \( P \) and \( T \) and the Ca/Cr ratio in lherzolitic garnets with the assumption that the slope of the Ca-Cr isolines are constant (lherzolite trend) for any \( P-T \) value. Please note that contrary to the original equation of Brenker & Brey (1997) the terms \( X_{Ca}^{Grt} \) and \( X_{Cr}^{Grt} \) stand for cations per formula unit (Brenker, pers. comm.) The equation is written as

\[
X_{Ca}^{Grt} = 0.449 X_{Cr}^{Grt} - 107 \cdot 10^{-6} T - 146 \cdot 10^{-4} P + 0.567,
\]

with \( T \) in K and \( P \) in GPa.

In a detailed study of compositional systematics related to tectonic settings of Cr-pyrope garnets in the lithospheric mantle Griffin et al. (1999) have shown that the slope of the lherzolite trend varies with tectonic setting and therefore with the local geotherm. This suggests that the \( P/T \) ratio exerts a control on the Ca/Cr ratio. As high Ca garnets with high Ca/Cr ratios are not covered by the algorithm of Brenker & Brey (1997), Griffin et al. (1999) suggest not to use the algorithm for high Ca-garnets and, moreover, not to compare samples that may be derived from different tectonic settings. Nimis & Trommsdorff (2001) stated that the uncertainties of the thermobarometric formulation are very large with calculated standard errors of estimate of 1.2 GPa and 159 °C and conclude that the formula is of dubious validity. But Paquin & Altherr (2001b) pointed out that the evaluation of Nimis & Trommsdorff (2001) was misleading as they ignored the variable Cr contents in garnet in their evaluation. However, the Ca-Cr system should be considered as a test for the calculated metamorphic temperatures and pressures and not as a proper geothermobarometer.

The clinopyroxene/plagioclase symplectite geothermometer

According to metallurgical concepts the phase transition omphacite \( \rightarrow \) clinopyroxene + plagioclase is classified as a discontinuous precipitation reaction (Joanny et al., 1991). Thus the lamellar spacing \( (L) \) depends on temperature \( (T) \) according to the growth law

\[
\log L = A - B/T,
\]

where \( A \) and \( B \) are constants. Therefore thin symplectites characterise lower, while coarse symplectites higher temperatures. The Jd content of the symplectic clinopyroxene formed together with plagioclase in the presence of quartz will act as a monitor of pressure. Thus the evolution of symplectites after omphacite can be used to evaluate parts of the decompression postdating maximum \( P \) conditions of eclogites. Joanny et al. (1991) presented empirical thermometric expressions as functions of the spacing of symplectic lamellae. This method has a potential that has not been widely used, but recently Ravna & Roux (2002) on the basis of three separate symplectite stages deducted a detailed uplift path for eclogites within the uppermost allochthon of the Scandinavian Caledonides.
Geobarometers

As geothermometers appear to be abundant, reliable geobarometers for HP/UHP rocks are scarce. Most of them are based on reactions involving transfer of Al from tetrahedral to octahedral coordination sites. In the following we will present the more common geobarometers, and discuss some additional approaches that may be useful if they are experimentally calibrated.

The Al-in-orthopyroxene barometer

The octahedral Al$^{3+}$ content in orthopyroxene coexisting with garnet in peridotites is known as a suitable indicator of the pressure conditions at which the rocks equilibrated. In a simple MAS system the Mg-Tschermaks net transfer reaction with Al$_2$Mg$_{-1}$Si$_{-1}$ exchange between orthopyroxene in equilibrium with garnet is written as

$$\text{Mg}_5\text{Si}_2\text{O}_6 + \text{MgAl}_2\text{SiO}_6 = \text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}.$$ ...

Several studies have been carried out to calibrate various versions of this barometer (e.g. Harley, 1984b; Nickel & Green, 1985; Gasparik, 1987; Brey & Köhler, 1990; Taylor, 1998). Here we only present the most widely used calibrations. The exact barometer equations should be looked up in the original papers, as the equations are too large to be shown here.

Harley (1984b) investigated experimentally the pressure–temperature–compositional dependence of the Al$^{3+}$ content in orthopyroxene coexisting with garnet in both the FMAS and CFMAS systems (PH$_{84}$). He has taken $X_{\text{Al}}^\text{Mg}$ as $^{3+}\text{Al}/2$. His calibration does not consider the effect of minor components such as Cr, Mn, Na, Ti and in particular Fe$^{3+}$ that can influence the pressure results significantly. Moreover, Carson & Powell (1997) addressed problems such as analytical uncertainties, the estimation of Fe$^{3+}$, effects of retrograde diffusion and off-centre sectioning of garnet on $P$–$T$ estimates by using both the $T\text{H}_{84}$ and $P\text{H}_{84}$. An evaluation of 13 different Al-in-orthopyroxene calibrations has been carried out by Carswell & Gibb (1987). These authors found out that only the calibration of Nickel & Green (1985) yielded satisfactory results. The Nickel & Green (1985) barometer version, which is based on experiments in the CMAS and Cr-bearing SMACCR systems, is using a modified $X_{\text{Al}}^\text{Mg}$ term that allows the presence of Cr, Ti and Fe$^{3+}$ in M1 and Na in M2 sites. However, Brey & Köhler (1990) found that the Nickel & Green (1985) version works well only in the pressure range of their experiments and that extrapolation to higher pressures result in a strong inaccuracy. Brey & Köhler (1990) formulated a new version of this barometer (PBK$_{90}$) which is capable of reproducing the experimental conditions for all available systems over a wide pressure range. Their barometer expression is based on thermodynamic evaluation in the MAS system by Gasparik & Newton (1984) and reproduces their own experiments within ± 0.22 GPa without any systematic dependence on either $T$ or $P$.

Recently Taylor (1998) calibrated a new version based on non-reversed experiments with $P \leq 3.5$ GPa in which a Ti correction was applied to the activity term...
Effect of Fe$^{3+}$ on the Al-in-orthopyroxene barometer

The effect of the oxidation state of iron on the Al-in-orthopyroxene barometry is not directly evident as it is in the Fe-Mg thermometry. The significant influence arises from the effect which Fe$^{3+}$ may have on the determination of the activity of the MgAl$_2$SiO$_6$ component in orthopyroxene. Several studies have shown that the content of Al$^{3+}$ in the octahedral sites (M1) in orthopyroxene coexisting with garnet is particularly pressure dependent and hence serve as a geobarometer for garnet-bearing peridotites (e.g. MacGregor, 1974; Harley & Green, 1982; Harley, 1984b; Finnerty & Boyd, 1984; Nickel & Green, 1985; Brey & Köhler, 1990). But in more chemically complex orthopyroxenes not only Fe$^{3+}$ but also Cr$^{3+}$ and Ti$^{4+}$ are commonly restricted to the M1 sites, which would require equal amounts of Al in the tetrahedral sites to retain charge balance. This kind of substitution clearly has the potential to limit the amount of Al$^{3+}$ available for substitution into the octahedral site M1, resulting in a considerable reduction of the calculated activity of the MgAl$_2$SiO$_6$ component in orthopyroxene (Canil & O’Neill, 1996). Up to date, the extent of the error produced by ignoring Fe$^{3+}$ (and also Cr$^{3+}$ and Ti$^{4+}$) in calculating metamorphic pressures using the Al-in-orthopyroxene barometer remains completely unknown (Canil & O’Neill, 1996).

The Cr-in-clinopyroxene barometer

Recently a new single clinopyroxene barometer ($P_{NT00}$) was calibrated based on experimental clinopyroxenes synthesised at 850–1500 °C and 0.0–6.0 GPa in the CMS, CMAS–Cr and more complex lherzolitic systems, including previously published data (Nickel, 1989; Brey et al., 1990; Taylor, 1998). This calibration thus covers a wide range of natural peridotitic compositions from fertile pyrolite to refractory, high-Cr lherzolite (Nimis & Taylor, 2000). For geobarometric evaluation they considered the Cr exchange between clinopyroxene and coexisting garnet. In their barometric equation, pressure is formulated as a function of temperature and clinopyroxene composition, expressed as

$$P_{NT00} [\text{kbar}] = - \frac{T}{126.9} \ln a_{\text{CacTs}}^{\text{cpx}} + 15.483 \ln \left( \frac{\text{Cr#}\text{cpx}}{T} \right) + \frac{T}{71.38} + 107.8,$$

with $a_{\text{CacTs}}^{\text{cpx}} = \text{Cr} - 0.81 \cdot \text{Cr#} \cdot (\text{Na+K})$, $\text{Cr#} = \frac{\text{Cr}}{\text{Cr} + \text{Al}}$, with elements in atoms per 6 oxygens and $T$ in K.

This formulation has a temperature dependence of around 0.12–0.24 GPa/50 °C which is less that that of the widely used Al-in-orthopyroxene barometer. However, a careful evaluation of the database for their calibration reveals a severe problem. There is a systematic divergence between experimental pressures of the reversed experiments
carried out by Brey et al. (1990) and calculated pressures using \( P_{\text{NT0}} \). The \( P_{\text{NT0}} \) tends to overestimate at low pressures and increasingly underestimates at high pressures (Paquin & Altherr, 2001b). One might speculate that this observation is due to incomplete equilibration in the experiments of Nickel (1989) and Taylor (1998). Therefore more independent reversed experiments over a wide pressure range are highly desirable to verify this barometer version.

Geothermobarometry based on the assemblage garnet–clinopyroxene–phengite–kyanite–quartz/coesite

The assemblage garnet + clinopyroxene + phengite ± kyanite ± quartz/coesite is not uncommon in some Al-rich eclogites, and equilibria between these phases have successfully been used for estimation of \( P \) and \( T \) of HP and UHP rocks. The following net transfer reactions between these phases in the KCMASH system can be written as:

- The phengite absent reaction [phe]
  
  \[ 3 \text{diopside} + 2 \text{kyanite} = 1 \text{grossular} + 1 \text{pyrope} + 2 \text{coesite/quartz}, \]  
  (1a,1b)

- The clinopyroxene absent reactions [di, gr]
  
  \[ 1 \text{pyrope} + 3 \text{muscovite} + 4 \text{coesite/quartz} = 3 \text{celadonite} + 4 \text{kyanite}, \]  
  (2a, 2b)

and the \( \text{SiO}_2\)-kyanite absent reaction [SiO\(_2\), ky]

\[ 6 \text{diopside} + 3 \text{muscovite} = 2 \text{grossular} + 1 \text{pyrope} + 3 \text{celadonite}. \]  
(3)

In the KCMASH system these reactions define an invariant point in both the coesite and quartz stability field, depending on which \( \text{SiO}_2 \) polymorph is stable (Fig. 3). The geothermobarometric methods based on the net transfer reactions in this system are suggested to be less affected by later thermal re-equilibration than common cation exchange thermometers, and the methods also diminish the problems related to estimation of \( \text{Fe}^{3+}/\text{Fe}^{2+} \) in omphacite.

Waters & Martin (1993) presented a new geobarometer based on the thermodynamic data set of Holland & Powell (1990) for the fairly common eclogitic mineral assemblage garnet + clinopyroxene + phengite through Equation 3 with the derived barometric expression

\[
P_{3\text{WM1}} [\text{kbar}] = 26.9 + 0.0159 T [\text{K}] - 0.00249 T \ln K.
\]

This expression was later revised (Waters, 1996) to

\[
P_{3\text{WM2}} [\text{kbar}] = 28.05 + 0.02044 T - 0.003539 T \ln K,
\]

where

\[
\ln K = 6 \ln a_{\text{di}} - \ln a_{\text{py}} - 2 \ln a_{\text{gr}} + 3 \ln a_{\text{invphe}}
\]

and

\[
a_{\text{invphe}} = a_{\text{ideal me}}/a_{\text{ideal cel}} = (X_{\text{Al}})/((X_{\text{Mg}})/(X_{\text{Si}})).
\]

with

\[
X_{\text{Al}} = (4 - \text{Si}) \text{ and } X_{\text{Si}} = (\text{Si} - 2).
\]
Activity models for diopside and garnet were taken from Holland (1990) and Newton & Haselton (1981), respectively. This barometer has shown to be very suitable for phengite-bearing HP and UHP eclogites from Dabie Shan, China (Carswell et al., 1997) and the Western Gneiss Complex of southern Norway (Wain, 1997, 1998; Cuthbert et al., 2000).

The relation between garnet, clinopyroxene and kyanite in coesite-bearing rocks has been proposed as a potential geobarometer by Sharp et al. (1992) and Nakamura & Banno (1997).

Ravna & Terry (2001, 2003) presented geothermobarometric expressions for UHP assemblages among (a) garnet-clinopyroxene-kyanite-phengite-coesite, and for the corresponding HP assemblages among (b) garnet-clinopyroxene-kyanite-phengite-
quartz, using the net transfer reactions 1–3 above with the equilibrium constants expressed as

\[ K_{1a} = \frac{a_{\text{pyr}}^{\text{grt}} a_{\text{grs}}^{\text{grt}} (a_{\text{SiO}_2}^{\text{coes}})^2}{(a_{\text{di}}^{\text{cpx}})^3 (a_{\text{Al}_2\text{SiO}_4}^{\text{ko}})^2} \]

\[ K_{1b} = \frac{a_{\text{pyr}}^{\text{grt}} a_{\text{grs}}^{\text{grt}} (a_{\text{SiO}_2}^{\text{coes}})^2}{(a_{\text{di}}^{\text{cpx}})^3 (a_{\text{Al}_2\text{SiO}_4}^{\text{ko}})^2} \]

\[ K_{2a} = \frac{(a_{\text{cel}}^{\text{phe}})^3 (a_{\text{Al}_2\text{SiO}_4}^{\text{ko}})^4}{(a_{\text{pyr}}^{\text{grt}})(a_{\text{mus}}^{\text{phe}})^3 (a_{\text{SiO}_2}^{\text{coes}})^4} \]

\[ K_{2b} = \frac{(a_{\text{cel}}^{\text{phe}})^3 (a_{\text{Al}_2\text{SiO}_4}^{\text{ko}})^4}{(a_{\text{pyr}}^{\text{grt}})(a_{\text{mus}}^{\text{phe}})^3 (a_{\text{SiO}_2}^{\text{coes}})^4} \]

and

\[ K_3 = \frac{a_{\text{pyr}}^{\text{grt}} (a_{\text{grs}}^{\text{ko}})^2 (a_{\text{cel}}^{\text{phe}})^3}{(a_{\text{di}}^{\text{cpx}})^6 (a_{\text{mus}}^{\text{phe}})^3}. \]

They formulated a set of linearised barometric expressions for each of these reactions, given as

Equation 1a (phe, q)

\[ P_{1a}^{\text{RT}} [\text{GPa}] = 7.235 + 0.000659T + 0.001162T \ln K_{1a}, \]

Equation 1b (phe, coe)

\[ P_{1b}^{\text{RT}} [\text{GPa}] = 11.424 + 0.001676T + 0.002157T \ln K_{1b}, \]

Equation 2a (di, gr, q)

\[ P_{2a}^{\text{RT}} [\text{GPa}] = -2.624 + 0.005741T + 0.000454T \ln K_{2a}, \]

Equation 2b (di, gr, coe)

\[ P_{2b}^{\text{RT}} [\text{GPa}] = -0.899 + 0.003929T + 0.000296T \ln K_{2b}, \]

Equation 3 (ky, coe/q)

\[ P_{3}^{\text{RT}} [\text{GPa}] = 1.801 + 0.002781T + 0.0002425T \ln K_{4}. \]

Additional constraints demanded the iso-lnK curves for the equivalent reactions including SiO₂ to intersect at the quartz–coesite transition. The present expression for reaction 4 deviates from that given by Waters & Martin (1993) and Waters (1996), probably due to a different approach in retrieving the data.

Equations 1a, 2a and 3 all intersect in a single P–T point within the coesite field, while 1b, 2b and 3 intersect within the quartz stability field (Fig. 3). The intersection of any two of these sets of reactions will thus uniquely define P and T for a single sample. Calculations by THERMOCALC (Powell & Holland, 1988) on a variety of samples yield averaged standard deviations for this intersection of ± 65 °C and ± 0.32 GPa in the coesite field and ± 82 °C, ± 0.32 GPa in the quartz stability field. The intersections of the present linear curves deviate less than 10 °C, 0.02 GPa from those obtained by THERMOCALC.
Fig. 4. A plot showing the compositional effect of garnet (a), clinopyroxene (b) and phengite (c) on the intersection of the reactions between the minerals garnet-clinopyroxene-phengite (gentle slope in the $P$–$T$ diagram) and garnet-clinopyroxene-kyanite-$\text{SiO}_2$ (steeper slopes). Note the change in slope of the latter equilibrium as pressures change from the quartz to coesite stability field.
Ravna & Terry (2001, 2003) used a combination of the ideal activity model for the phengite solid solution proposed by Holland & Powell (1998), the clinopyroxene activity model of Holland (1990), and the garnet activity model of Ganguly et al. (1996). Phengite structural formulae has been normalised to $\Sigma \text{Si,Al,Ti,Cr,Fe,Mn,Mg} = 12.000$. Garnet is normalised to $X = 3.000$, $Y = 2.000$, and $\text{Fe}^{3+} = 2 - (\text{Al} + \text{Cr} + \text{Ti})$. Maximum recordable $P$ conditions for a specific eclogite should, according to Equation 3, be represented by garnets with maximum $(a_{\text{grs}}^{\text{grs}})^2 a_{\text{grt}}^{\text{grt}}$, omphacite with minimum $a_{\text{di}}^{\text{omphacite}}$ (and correspondingly maximum $X_{\text{Jd}}$) and phengite with maximum $a_{\text{phe}}^{\text{phengite}}$ (maximum Si content) (Carswell & Zhang, 1999; Carswell et al., 2000). The relationship between pressure, temperature and composition of garnet, clinopyroxene and phengite, respectively, is shown in Figure 4 a–c.

Application of these thermobarometers to relevant eclogites from various worldwide localities shows good consistency with petrographic evidence (Terry et al., 2000; Gilotti & Ravna, 2002; Ravna & Terry, 2003). Ravna & Terry (2003) give several examples of the wide applicability of the methods, ranging from low-$T$ blueschist type eclogites from the Franciscan and WGR, to UHP eclogites from WGR and Dabie Shan and coesite-kyanite eclogite xenoliths from kimberlites.

Equation 1a may serve as a geobarometer in combination with the common garnet–clinopyroxene Fe–Mg geothermometer in phengite absent kyanite-bearing eclogites, while Equation 3 has proven to be a reliable geobarometer in phengite eclogites (Waters & Martin, 1993; Carswell et al., 1997; Wain, 1997, 1998; Cuthbert et al., 2000). Equations 2a and 2b are suggested to be useful pressure indicators for clinopyroxene-free UHP/HP pelitic schists, given that a reliable independent temperature estimate is possible.

Coggon & Holland (2002) presented linearised expressions for three fluid-absent reactions, including the Waters & Martin (1993) barometer. They used Equations 2b, 3 and

\[
\text{almandine} + 3 \text{ muscovite} + 4 \text{ quartz} = 3 \text{ Fe-celadonite} + 4 \text{ kyanite},
\]

based on revised mixing properties of phengitic micas. They obtained the following barometric expressions:

\[
P_{3\text{CH}} \ [\text{GPa}] = 1.978 + 0.002726T + 0.0002627T \ln K,
\]

\[
P_{2b\text{CH}} \ [\text{GPa}] = -0.910 + 0.003933T + 0.0003258T \ln K,
\]

\[
P_{4\text{CH}} \ [\text{GPa}] = 1.969 + 0.002597T + 0.0003474T \ln K.
\]

Expressions for Equations 3 and 2b do not deviate much from the corresponding expressions of Ravna & Terry (2001, 2003).

Other, less common geobarometers suitable for HP/UHP rocks

Geobarometers involving plagioclase

Plagioclase is not stable at UHP conditions; thus the various common geobarometers involving this phase (GASP, GAES, GADS, AbJdQ) are of no relevance for such rocks. Nevertheless, minimum pressure estimates based on the jadeite content of omphacite in
HP and UHP rocks devoid of plagioclase are frequently used, even in rocks lacking a SiO₂ phase (quartz or coesite). The presence of coesite or polycrystalline quartz pseudomorphs after coesite adds another, yet higher minimum pressure limit, as does the less common occurrence of diamond.

**Geobarometers involving zoisite/clinozoisite**

Zoisite- and clinozoisite-bearing eclogites provide assemblages suitable for geobarometry. The reactions

\[
6 \text{ zoisite} = 4 \text{ grossular} + 5 \text{ kyanite} + \text{ coesite} + 3 \text{ H}_2\text{O}
\]

and

\[
15 \text{ diopside} + 12 \text{ zoisite} = 13 \text{ grossular} + 5 \text{ pyrope} + 12 \text{ quartz/coesite} + 6\text{H}_2\text{O}
\]

have both been used (e.g. Poli & Schmidt, 1998; Terry et al., 2000).

*The K content of clinopyroxene* has been suggested as a potential geobarometer in UHP rocks, supported by experimental data of e.g. Luth (1995), Harlow (1997, 2002) and Okamoto & Maruyama (1998). Shatsky et al. (1995) have reported K₂O contents in clinopyroxenes up to 1.2 wt% in diamond-bearing metamorphic rocks in the Kokchetav massif, and noted that during exhumation the K₂O was exsolved as K-feldspar lamellae within diopside in carbonate-bearing rocks. There has, however, never been found any exsolved K-feldspar lamellae in omphacite in any UHP terranes, which Shatsky et al. (1995) attributed to the low-K bulk chemistry of ordinary eclogites. However, phengite in eclogites is fairly common, and should provide a K-source for the buffering of K in omphacite. Domanik & Holloway (2000) studied the phase relations of phengitic muscovite in a calcareous metapelite from 6.5–11 GPa. At 9 GPa and 900 °C the K₂O content in omphacite coexisting with phengite was 0.2 wt%, and around 0.1 at \(P < 8\) GPa. Harlow (2002) did multi-anvil experiments on a mixture of natural diopside and F-rich phlogopite in the \(P-T\) interval 3.0 to 11 GPa and 1100–1500 °C. In clinopyroxene the Kcpx (KAlSi₃O₈) content increases with increasing pressure at pressures above 5 GPa without any noticeable temperature effect. These experiments point to the K content of clinopyroxene as a potential geobarometer at higher pressures. The difference in the experiments of Domanik & Holloway (2000) on one side and those of e.g. Harlow (2002) may indicate that K is not as easily partitioned into Na-rich clinopyroxenes as into Ca-rich ones.

If reliable geobarometers involving Kcpx should be formulated, one should look for suitable buffering assemblages as *e.g.*

Muscovite (in phengite) = Kcpx (in clinopyroxene) + kyanite + H₂O

\[
\text{KAI}_2\text{AlSi}_3\text{O}_{10}(\text{OH})_2 = \text{KAI}_2\text{Si}_2\text{O}_6 + \text{Al}_2\text{SiO}_5 + \text{H}_2\text{O}
\]

and

\[
\text{K-feldspar} = \text{Kcpx} + \text{coesite}
\]

\[
\text{KAI}_2\text{Si}_5\text{O}_8 = \text{KAI}_2\text{Si}_2\text{O}_6 + \text{SiO}_2
\]
Ca-Eskola molecule bearing clinopyroxenes at UHP conditions

Eskola (1921) first reported pyroxenes with structural vacancies. These vacancies can be ascribed to the end member Ca\textsubscript{0.5}AlSi\textsubscript{2}O\textsubscript{6}, which was named calcium Eskola pyroxene (CaEs) by Khanukhova et al. (1976). Experimental work on the stability field of CaEs suggests that non-stoichiometric pyroxenes are highly P-sensitive and should be a stable component of natural clinopyroxenes, especially in the presence of excess SiO\textsubscript{2} (Gasparik & Lindsley, 1980). Cation deficiencies in Al-rich (omphacitic) clinopyroxenes have been reported from grospydite xenoliths (Sobolev et al., 1968; Smyth & Hatton, 1977). The appearance of oriented needles of quartz in omphacite seems to be fairly common in UHP eclogites and related rocks (Smith, 1984, 1988; Bakun-Czubarow, 1992; Liou et al., 1998; Zhang & Liou, 1998; Schmädicke & Müller, 2000; Tsai & Liou, 2000; Terry & Robinson, 2001; Dobrzhinetskaya et al., 2002). Katayama et al. (2000) also described matrix clinopyroxenes with quartz rods in eclogite from the Kokchetav massif, Kazakhstan, apparently recrystallised at $P > 6$ GPa, $T > 1000^\circ$C. Inclusions of clinopyroxenes in zircon had calculated cation totals significantly less than 4.0 per six O atoms, and showed no exsolution textures. Bruno et al. (2002) reported jadeite with a high portion (0.08–0.17) of the Ca-Eskola molecule from an UHP meta-granodiorite from the Dora-Maira massif, Western Alps. These observations have been proposed as a result of exsolution of a former non-stoichiometric omphacite through the reaction (Smyth, 1980)

$$2 \text{CaEs} = \text{CaTs} + 3 \text{Qtz.}$$

Katayama et al. (2000) suggested that further experiments on the Ca-Eskola component in clinopyroxene may yield a new geobarometer for UHP metamorphic rocks.

High-Al titanite has been described from a variety of eclogites and associated HP/UHP rocks (Smith, 1977, 1980; Smith & Lappin, 1982; Franz & Spear, 1985; Krogh et al., 1990; Sobolev & Shatsky, 1990; Hirajima et al., 1992; Carswell et al., 1996; Ye & Ye, 1996), and has been taken as evidence of HP/UHP metamorphism. Experimental data (Smith, 1980, 1981; Troitzsch & Ellis, 1999) show that titanite with high Al and F content can be produced at elevated pressures. However, Al- and F-rich titanites have also been reported from low-P metamorphic rocks (Enami et al., 1993; Markl & Piazolo, 1999), indicating that these compositions are not restricted to HP/UHP metamorphism, but are formed in response of the activity of F and bulk compositions (Franz & Spear, 1985; Enami et al., 1993; Carswell et al., 1996; Markl & Piazolo, 1999), as summarised by Castelli & Rubatto (2002). Troitzsch & Ellis (2002) demonstrated that petrogenetic grids based on newly derived thermodynamic properties of Al-rich titanites could explain the predominant occurrence of natural Al-rich titanite at high metamorphic grade such as eclogite facies conditions. Wide spacing of the Al-isopleths for titanite of many high-grade assemblages prevents, however, their use as geobarometers or geothermometers.

Conclusions

The most widely used set of thermobarometers for garnet-bearing ultrabasites is that of Brey & Köhler (1990). The advantage of this set of thermobarometers for lherzolites
based on independent reactions between coexisting minerals is the possibility to evaluate whether equilibrium or disequilibrium exists between the relevant mineral phases. For common (bimineralic) eclogites, we still have to rely on the garnet–clinopyroxene Fe2+-Mg exchange thermometer with all its uncertainties, while reliable pressure estimates are impossible to obtain at present. For phengite- and kyanite-bearing eclogites, pressures and temperatures can uniquely be obtained by either combining the garnet–clinopyroxene Fe2+-Mg exchange thermometer with the garnet–clinopyroxene–phengite barometer, or combining the latter with the garnet–clinopyroxene–kyanite–SiO2 thermobarometer.

References


