

# Pohorje eclogites revisited: Evidence for ultrahigh-pressure metamorphic conditions

## Ultravisokotlačni metamorfizem pohorskega eklogita

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### Abstract

Kyanite eclogites from the Pohorje Mountains, Slovenia, are providing the first evidence of ultrahigh-pressure Eo-Alpine metamorphism in the Eastern Alps. Polycrystalline quartz inclusions in garnet, omphacite and kyanite are surrounded by radial fractures and exhibit microtextures diagnostic for the recovery after coesite breakdown. The non-stoichiometric supersilicic omphacites found in Pohorje eclogites contain up to 5 mol % of Ca-Eskola molecule. Such clinopyroxenes are known to be stable exclusively at high-pressure conditions exceeding 3 GPa. Their breakdown during decompression resulted in exsolution of quartz rods and needles that are oriented parallel to omphacite c-axis. The absence of coesite is a consequence of near-isothermal decompression during the first stages of exhumation.

Pressure and temperature conditions for the formation of the peak metamorphic mineral assemblages have been assessed through a consideration of a) Fe<sup>2+</sup>-Mg partitioning between garnet and omphacite pairs, based on different calibrations; b) the equilibrium between garnet + clinopyroxene + phengite ± kyanite ± quartz/coesite assemblage. Estimated peak pressure and temperature conditions of 3.0-3.1 GPa and 750-783 °C are well within the coesite, i.e. the ultrahigh-pressure stability field.

### Izvleček

Pohorski kyanitovi eklogiti predstavljajo prvi dokaz za obstoj eo-alpinske ultravisokotlačne metamorfoze v Vzhodnih Alpah. Radialne razpoke okoli polikristalnih kremenovih vključkov v granatu, omfacitu in kyanitu ter njihove specifične mikrostrukture pričajo o obstoju coesita, ki je med ekshumacijo zaradi dekompresije prešel v kremen. Popolna odsotnost coesita je posledica izotermne dekompresije v začetni stopnji ekshumacije pohorskih eklogitov. Nestehiometrični omfaciti z visoko vsebnostjo SiO<sub>2</sub>, ki vsebujejo do 5 mol % Ca-Eskola molekule in so obstojni izključno pri tlakih večjih od 3 GPa, potrjujejo izpostavljenost pohorskih eklogitov ultravisokotlačnim metamorfnim pogojem. Zaradi dekompresije so se v njih izločile kremenove iglice in paličice, ki so orientirane vzporedno z omfacitovo c-osjo.

Tlačni in temperaturni pogoji nastanka pohorskih eklogitov so bili določeni s pomočjo različnih geotermometrov, ki temeljijo na izmenjavi Fe<sup>2+</sup> in Mg ionov med granatom in omfacitom, kot tudi na osnovi ravnotežja med mineralnimi fazami: granat + monoklinski piroksen + fengit ± kyanit ± kremen/coesit. Izračunane tlačne in temperaturne vrednosti se gibljejo v razponu od 3.0-3.1 GPa in 750-783 °C ter odговarjajo ultravisokotlačnemu (coesitovemu) stabilnostnemu območju.

### Introduction

Ultrahigh-pressure (UHP) metamorphism is an important type of orogenic metamorphism that has been recognized in many Phanerozoic collision belts (e.g. LIOU et al., 1998; CHOPIN, 2003, and references therein). Well investigated intracratonic collisional orogens that exhibit scattered effects of subsolidus UHP recrystallization include the Quinling-Dabie-Sulu belt of east-central China, the Kokchetav Complex of northern Kazah-

stan, the Dora Maira massif of the Western Alps, and the Western Gneiss Region (WGR) of Norway (LIOU et al., 1994; COLEMAN & WANG, 1995; ERNST et al., 1995). This four classic and several other UHP terranes (Figure 1) share common structural and lithological characteristics (LIOU, 2000). Supracrustal rocks of these UHP regions experienced subduction-zone metamorphism at mantle depths, followed by a retrograde amphibolite-granulite facies overprint during exhumation, and finally thermal recrystallization and defor-

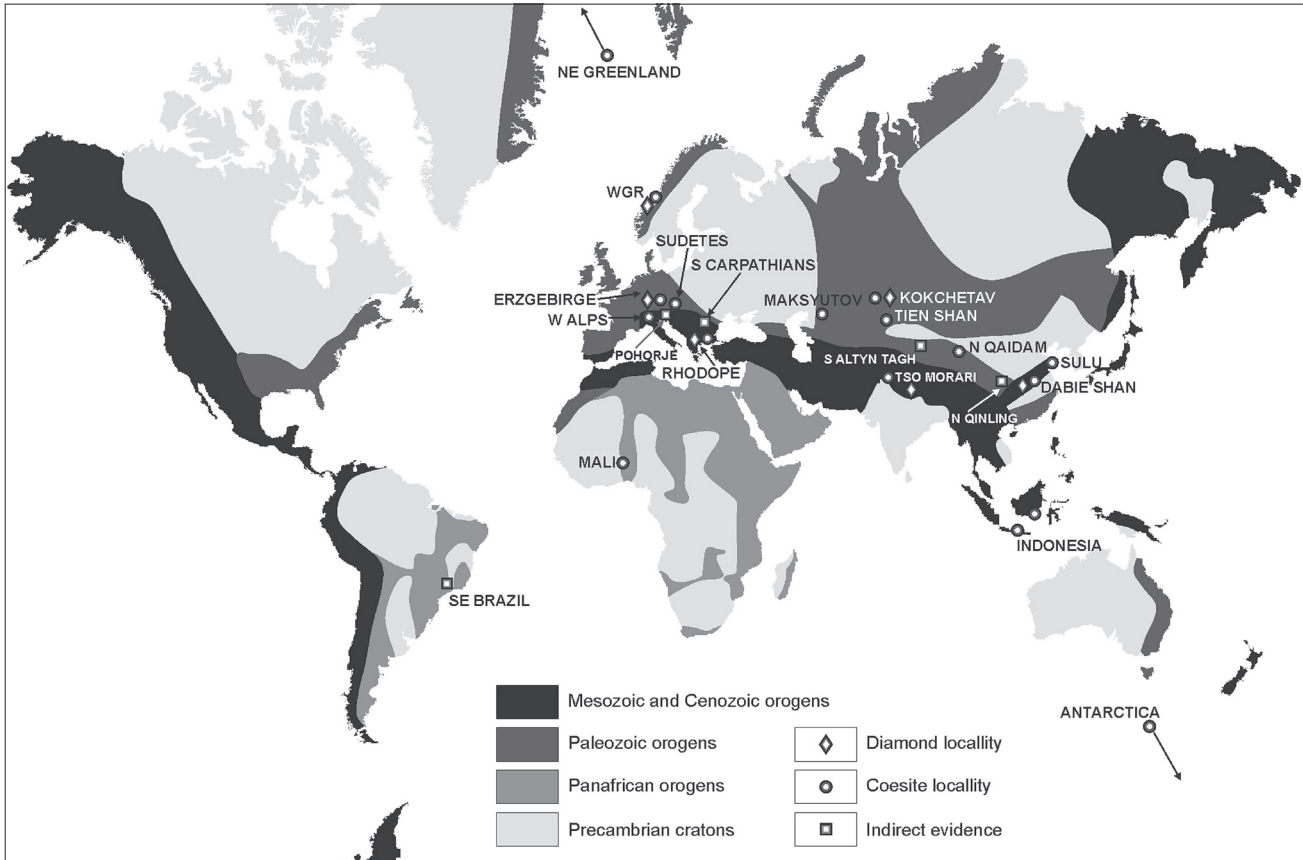


Figure 1. Distribution of recognized UHP metamorphic terranes in the world through time and space. So far, evidence of UHP metamorphism was not found only in Australia and North America (modified from LIU et al., 1998; CHOPIN, 2003).

mation during postcollisional granitic intrusions and orogeny.

With the discovery of UHP metamorphism geologists realized that, contrary to general belief, continental crust in convergent settings may be subducted to enormous depths, and that the most formidable geodynamic problems concerning UHP metamorphic rocks are not the mechanisms of their deep burial, but the mechanisms which facilitated their subsequent exhumation to the Earth's surface without a complete breakdown of the UHP mineral assemblages. From the recurrent occurrences both in time and space, since late Proterozoic, it is clear that UHP metamorphism is a common process, inherent to continental collision.

Ultrahigh-pressure metamorphism is synonymous with eclogite-facies metamorphism that has occurred within the stability field of coesite (Figure 2). Unequivocal identification of UHP conditions depends on the presence of relict coesite or diamond, high-pressure polymorphs of silica and carbon, as direct indicators of metamorphic pressures of at least 3 GPa (coesite) or 4 GPa (diamond). But since the metastable preservation of relict UHP phases during exhumation and decompression is now known to be very rare, a simple microscopic identification of UHP metamorphic rocks is normally not possible, and the evidence for UHP conditions must be deduced from indirect petrographic and microtextural observations. In absence of an actual coesite relict, polycrystalline quartz aggregates are strongly indicative tex-

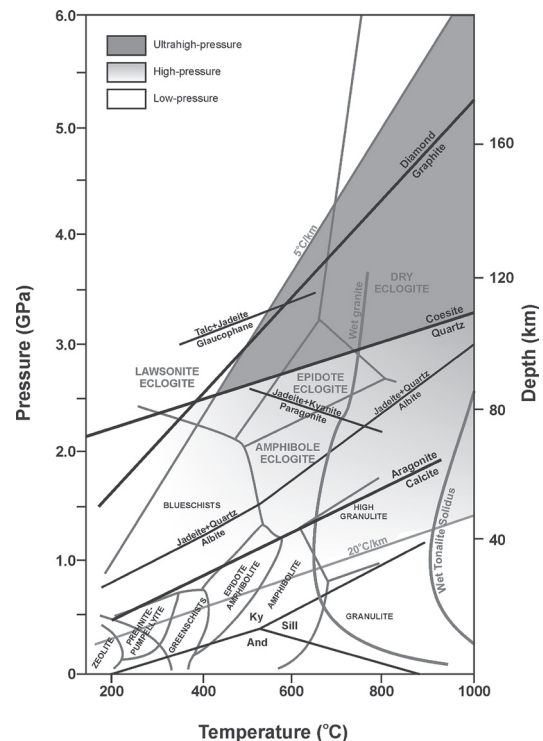


Figure 2. Simplified P-T facies diagram. UHP eclogites are defined as metabasic rocks with a dominant plagioclase-free, eclogite-facies mineral paragenesis of garnet and omphacitic clinopyroxene, but with additional petrographic or mineral-chemistry features that indicate equilibration at pressures within the coesite P-T stability field. Subdivision of the eclogite facies field is based on OKAMOTO & MARUYAMA (1999). Also shown are the stability fields for diamond and coesite according to HOLLAND & POWELL (1998).

tural feature of former coesite existence (SMITH, 1984; GILLET et al., 1984) but tend to disappear due to recrystallization during prolonged thermal annealing. A further distinctive petrographic feature of partly or completely replaced coesite inclusions is the development of radial expansion cracks, extending from the inclusion boundary into the enclosing mineral. This reflects the roughly 10 % volume increase on transition from coesite to  $\alpha$ -quartz. Several other uncommon petrological features and assemblages that have been reported from various UHP metamorphic rocks provide additional evidence for UHP metamorphism. Quartz rods have been observed in omphacite from eclogites of several UHP terranes. In all cases,  $\text{SiO}_2$  needles and rods in omphacite have been interpreted as exsolution products from a preexisting super-silicic clinopyroxene that contained excess silica at peak metamorphic conditions (e.g. SMITH, 1984; LIOU et al., 1998; KATAYAMA et al., 2000; SCHMÄDICKE AND MÜLLER, 2000; ZHANG & LIOU, 2000; DOBRZHNETSKAYA et al., 2002). Potassium-bearing clinopyroxene with extremely high potassium content (up to 1.5 wt%  $\text{K}_2\text{O}$ ) is stable at pressures of 4–10 GPa. During decompression, potassic clinopyroxene develops characteristic textures with oriented precipitates of K-feldspar (SOBOLEV & SHATSKY, 1990). Orthopyroxene exsolutions in garnet require formation pressures in excess of 6 GPa and hence over 200 km of depth. Exsolutions suggest the existence of a super-silicic precursor garnet with several mol % of majorite component (VAN ROERMUND et al., 2001).  $\alpha$ - $\text{PbO}_2$ -type  $\text{TiO}_2$  inclusions in garnet indicate achieved pressures in the range from 4.5 to 6.5 GPa at a temperature of 1000 °C (HUANG et al., 2000). Although the indirect indicators of UHP metamorphism are very useful since the preservation of metastable coesite and diamond is very rare, they cannot be used alone as a proof that UHP metamorphism was achieved.

When direct mineral indicators are absent, converging indirect pieces of evidence, together with reliable geothermobarometrical calculations, are needed to verify the existence of UHP metamorphism.

Pohorje in north-eastern Slovenia (Figure 3) is the south-easternmost prolongation of the Eastern Alps. It is a part of the extensive Alpine orogen where UHP metamorphism was documented in the Western Alps (e.g. CHOPIN, 1984) and was shown to be related to the Tertiary orogeny (e.g. TILTON et al., 1991). Metamorphic processes related to the older, Cretaceous Alpine orogeny are mainly recognized in the Austroalpine units of the Eastern Alps (e.g. THÖNI & JAGOUTZ, 1992). So far, up to high-pressure (HP) eclogite facies metamorphic conditions were recognized in the Koralpe and Saualpe areas situated just north of Pohorje (MILLER, 1990). The Pohorje Mountains consist of a stack of Cretaceous Austroalpine nappes, predominately composed of micashists, gneisses and amphibolites, but also include several lenses of eclogitic rocks that are of special interest since they have high preservation potential for ultrahigh-pressure metamorphic indicators. Eclogites were previously investigated by HINTERLECHNER-RAVNIK (1982), HINTERLECHNER-RAVNIK et al. (1991) and KOCH (1999). Geothermobarometric estimations from the first two works are rather broad, with estimated pressure ranging from 1.2–1.8 GPa at temperature from 460–900 °C. Pressure and temperature estimates by KOCH (1999) fall into the same (high-pressure) range, but are more narrowly constrained to 1.5 GPa at 760 °C.

First two samples of eclogites from Pohorje indicating possible UHP conditions were investigated by JANÁK et al. (2004). This work presents new samples from several new localities bringing undisputed mineralogical, petrological, microtextural and microchemical evidence for ultra-

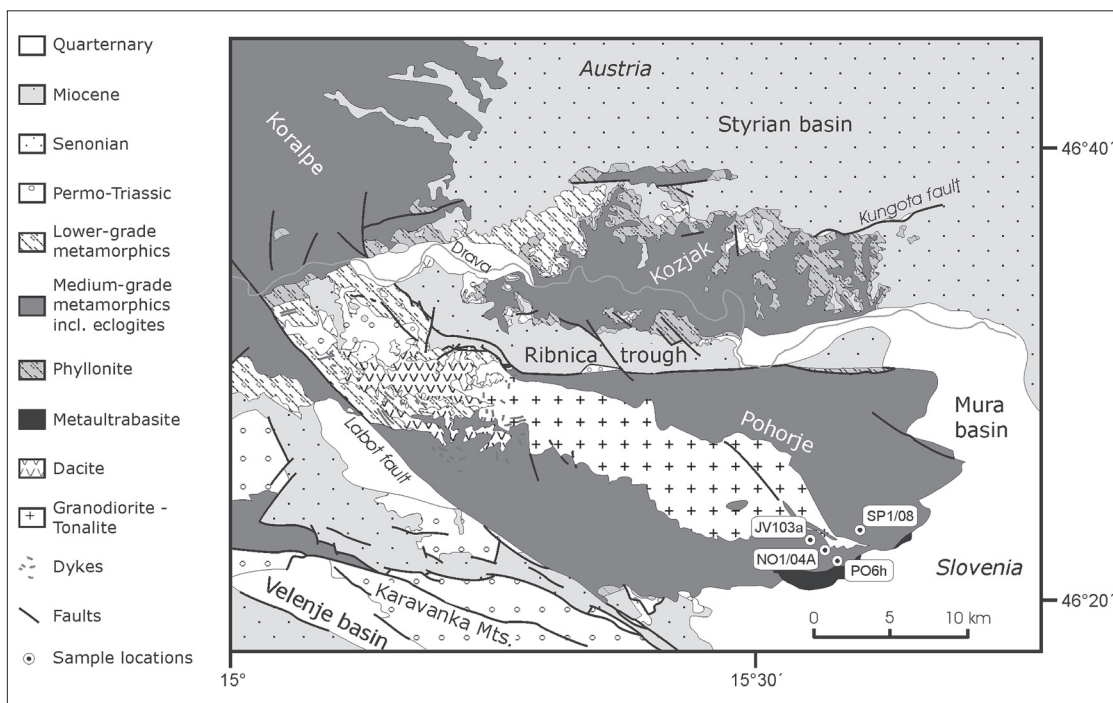


Figure 3. Simplified geologic map of Pohorje and adjacent areas (modified from Mioč & Žnidarčič, 1977) showing locations of the investigated eclogite samples.



high-pressure metamorphism of eclogites in the Austroalpine units of the Eastern Alps, exposed in the Pohorje Mountains of Slovenia. The evidence for ultrahigh-pressure conditions is strongly supported by extensive and precise geothermobarometric calculations based on different widely accepted calibrations.

## Methods

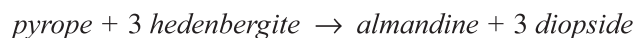
### Electron Probe Micro-Analysis

Representative microchemical analyses of the main constituent minerals were determined by EPMA technique using a CAMECA SX-100 electron microprobe at Dionýz Štúr Institute of Geology in Bratislava. Bombarding of micro-volumes of sample with a focused electron beam (5–30 keV) induced emission of X-ray photons. The wavelengths of collected X-rays were identified by recording their WDS spectra (Wavelength Dispersive Spectroscopy). Analytical conditions were 15 keV accelerating voltage and 20 nA beam current, with a peak counting time of 20 s and a beam diameter of 2–10  $\mu\text{m}$ . Raw counts were corrected using a PAP routine.

### Garnet-clinopyroxene $\text{Fe}^{2+}$ -Mg exchange geothermometry

Temperature conditions of metamorphism were obtained using the partitioning of  $\text{Fe}^{2+}$  and Mg between co-existing garnet and clinopyroxene (omphacite). Due to the common appearance of clinopyroxene and garnet in a mineral assemblage of high-grade metamorphic rocks of basic and ultrabasic composition this is one of the most widely used methods in geothermometry of such rocks. When these two minerals are contiguous phases, they effectively exchange the two elements and the exchange balance is a function of temperature.

The exchange of iron and magnesium between clinopyroxene and garnet is represented by exchange reaction:



The equilibrium constant for the considered equilibrium is expressed by the following function:

$$K_{eq} = \frac{a_{\text{Fe}}^{\text{grt}}}{a_{\text{Mg}}^{\text{grt}}} \cdot \left[ \frac{a_{\text{Mg}}^{\text{cpx}}}{a_{\text{Fe}}^{\text{cpx}}} \right]^3$$

where  $a_i^j$  is the activity of component  $i$  in phase  $j$ . If the minerals are ideal solid solutions, activities are equivalent to concentrations and

$$K_{eq} = \frac{X_{\text{Fe}}^{\text{grt}}}{X_{\text{Mg}}^{\text{grt}}} \cdot \frac{X_{\text{Mg}}^{\text{cpx}}}{X_{\text{Fe}}^{\text{cpx}}} = \frac{(X_{\text{Fe}}^{2+}/X_{\text{Mg}})^{\text{grt}}}{(X_{\text{Fe}}^{2+}/X_{\text{Mg}})^{\text{cpx}}} = K_D$$

where  $K_D$  is the distribution coefficient,  $X_{\text{Fe}}^{\text{grt}}$  is the mole fraction of  $\text{Fe}^{2+}$  in the three equivalent divalent sites in garnet structure,  $X_{\text{Fe}}^{\text{cpx}}$  is the mole

fraction of  $\text{Fe}^{2+}$  in the clinopyroxene, etc. If the minerals are not ideal (i.e. their compositions differ from those of pure ideal end-members used in experiments) compositional differences are corrected by the introduction of activities, which express the thermodynamically effective concentrations of components. Then

$$a = X \cdot \gamma$$

where  $\gamma$  is defined as the activity coefficient and thus

$$K_{eq} = \frac{X_{\text{Fe}}^{\text{grt}}}{X_{\text{Mg}}^{\text{grt}}} \cdot \frac{X_{\text{Mg}}^{\text{cpx}}}{X_{\text{Fe}}^{\text{cpx}}} \cdot \frac{\gamma_{\text{Fe}}^{\text{grt}}}{\gamma_{\text{Mg}}^{\text{grt}}} \cdot \frac{\gamma_{\text{Mg}}^{\text{cpx}}}{\gamma_{\text{Fe}}^{\text{cpx}}} = K_D \cdot K_\gamma$$

Temperatures have been estimated using six different quantitative calibrations of the garnet-clinopyroxene system revealing garnet-clinopyroxene  $\text{Fe}^{2+}$ -Mg exchange geothermometers of ELLIS & GREEN (1979), POWELL (1985), KROGH (1988), PATTISON & NEWTON (1989), AI (1994) and KROGH RAVNA (2000).

ELLIS & GREEN (1979) determined the distribution coefficient as a function of P, T and Ca-content in garnet ( $X_{\text{Ca}}^{\text{grt}}$ ) and derived the empirical relation:

$$T_{EG-79} (^{\circ}\text{C}) = \frac{3104 \cdot X_{\text{Ca}}^{\text{grt}} + 3030 + 10.86 \cdot P(\text{kb})}{\ln K_D + 1.9034} - 273$$

where  $X_{\text{Ca}}^{\text{grt}}$  is defined as

$$X_{\text{Ca}}^{\text{grt}} = \frac{\text{Ca}}{\text{Ca} + \text{Mg} + \text{Fe}^{2+}}$$

They have shown that  $K_D$  is apparently independent of the  $\text{Mg}/(\text{Mg} + \text{Fe}^{2+})$  content in clinopyroxene and garnet, but that there is a marked dependence of  $K_D$  upon the Ca-content of garnet. This Ca-effect is believed to be caused by a combination of non-ideal Ca-Mg substitutions in garnet and clinopyroxene. Consequently, a rectilinear correction for  $X_{\text{Ca}}^{\text{grt}}$  in garnet was proposed.

POWELL (1985) made an upgrade to ELLIS & GREEN (1979) geothermometer defining:

$$T_{P-85} (^{\circ}\text{C}) = \frac{2790 + 10 \cdot P(\text{kb}) + 3140 \cdot X_{\text{Ca}}^{\text{grt}}}{\ln K_D + 1.735} - 273$$

which gives slightly lower temperatures than calibration of ELLIS & GREEN (1979).

KROGH (1988) suggested a curvilinear relationship between  $\ln K_D$  and  $X_{\text{Ca}}^{\text{grt}}$  in garnet:

$$T_{K-88} (^{\circ}\text{C}) = \frac{1879 + 6731 \cdot X_{\text{Ca}}^{\text{grt}} - 6173 \cdot (X_{\text{Ca}}^{\text{grt}})^2 + 100 \cdot P(\text{GPa})}{\ln K_D + 1.393} - 273$$

at least for the compositional range  $X_{\text{Ca}}^{\text{grt}} = 0.10$ – $0.50$ . The Ca-content in garnet was calculated as:

$$X_{\text{Ca}}^{\text{grt}} = \frac{\text{Ca}}{\text{Ca} + \text{Mn} + \text{Fe}^{2+} + \text{Mg}}$$

Calculated temperatures do not vary with the  $\text{Mg}/(\text{Mg} + \text{Fe}^{2+})$  content in garnet and Na-content in the clinopyroxene. Temperatures below  $900^{\circ}\text{C}$  are a bit lower than those obtained by the method

of POWELL (1985), and the difference is larger for lower temperatures and lower values of  $X_{Ca}^{grt}$ .

PATTISON & NEWTON (1989) performed multiple regression of a large set of data on the  $Fe^{2+}$ -Mg equilibrium between garnet and clinopyroxene resulting in the following relationship:

$$T_{PN-89} (^{\circ}C) = \frac{561 + 3395 \cdot X_{Ca}^{grt} - 2388 \cdot (X_{Ca}^{grt})^2 + 9781 \cdot X_{Mg}^{grt} - 31026 \cdot (X_{Mg}^{grt})^2}{\ln K_D + 0.512} + \frac{26217 \cdot (X_{Mg}^{grt})^3 + 103.7 \cdot P(GPa)}{\ln K_D + 0.512} - 273$$

which includes the curvilinear corrections for  $X_{Ca}^{grt}$  and also for Mg-number ( $Mg_{\#}$ ) in garnet:

$$Mg_{\#} = 100 \cdot X_{Mg}^{grt} = 100 \cdot \frac{Mg}{Mg + Fe^{2+}}$$

This thermometer works well with experimental data of PATTISON & NEWTON (1989) but commonly yields unrealistically low temperatures for natural rocks. An important feature discovered by PATTISON & NEWTON (1989) and later supported by other researchers (e.g. AI, 1994; BERMAN et al., 1995) is that  $K_D$  decreases with decreasing  $X_{Mg}^{grt}$  at all temperatures.

AI (1994) investigated about 300 garnet-clinopyroxene pairs and by multiple regression arrived to the expression:

$$T_{A-94} (^{\circ}C) = \frac{1987 + 3648.55 \cdot X_{Ca}^{grt} - 1629 \cdot (X_{Ca}^{grt})^2 - 659 \cdot X_{Mg}^{grt}}{\ln K_D + 1.076} + \frac{176.6 \cdot P(GPa)}{\ln K_D + 1.076} - 273$$

with curvilinear correction for  $X_{Ca}^{grt}$  and rectilinear correction for  $X_{Mg}^{grt}$  in garnet. Ai's thermometer is suitable especially for the systems with low-Ca and high-Mg garnets.

In addition to significant dependence between the distribution coefficient  $K_D$  and  $X_{Ca}^{grt}$  and  $X_{Mg}^{grt}$ , KROGH RAVNA (2000) incorporated the effect of Mn content in garnet  $X_{Mn}^{grt}$ :

$$X_{Mn}^{grt} = \frac{Mn}{Ca + Mn + Fe^{2+} + Mg}$$

and proposed the following P-T-compositional relationship:

$$T_{KR-00} (^{\circ}C) = \frac{1939 + 3270 \cdot X_{Ca}^{grt} - 1396 \cdot (X_{Ca}^{grt})^2 + 3319 \cdot X_{Mn}^{grt} - 3535 \cdot (X_{Mn}^{grt})^2}{\ln K_D + 1.223} + \frac{1105 \cdot X_{Mg}^{grt} - 3561 \cdot (X_{Mg}^{grt})^2 + 2324 \cdot (X_{Mg}^{grt})^3 + 169.4 \cdot P(GPa)}{\ln K_D + 1.223} - 273$$

which confirmed his conclusion from 1988 that the  $Fe^{2+}$ -Mg equilibrium between co-existing garnet and clinopyroxene is independent of the variations in the Na-content of the clinopyroxene, at least in the  $X_{Na}^{cpx}$  range from 0 to 0.51. This means

that the jadeite content in clinopyroxene has a certain influence on calculated temperatures only at higher  $X_{Na}^{cpx}$  values. Since the natural jadeite content of eclogites is commonly lower than the recommended value, Na is not a problematic additional component in the garnet-clinopyroxene exchange thermometer for eclogites. Application of this thermometer gives reasonable results for most compositional ranges covered by garnet-clinopyroxene pairs from natural rocks.

The uncertainty of the garnet-clinopyroxene geothermometer is usually estimated to  $\pm 30$  to  $50$   $^{\circ}C$  and in most cases almost all of the above-mentioned geothermometers, give temperatures within this interval. However, there is one important drawback that should always be considered when using  $Fe^{2+}$ -Mg exchange geothermometers. The problem is that generally the data is only available for total iron content ( $Fe^{tot}$ ), therefore it is not known how much garnet and clinopyroxene iron is present in the exchanging ferrous ( $Fe^{2+}$ ) and non-exchanging ferric ( $Fe^{3+}$ ) states. There are several methods to calculate the  $Fe^{3+}/Fe^{2+}$  ratio in garnet and clinopyroxene (charge balance criteria, equalizing the amount of  $Fe^{3+}$  with the Na excess over ( $Al^{tot}+Cr$ ), standard titration method, etc.) but they are unfortunately very sensitive to analytical errors and not always reliable.

Garnets are less of a problem than clinopyroxenes because of their customary higher  $Fe^{tot}$  contents and much lower  $Fe^{3+}/Fe^{2+}$  ratios (CARSWELL et al., 1997). In Fe-rich garnets all iron can be treated as ferrous without affecting the calculated temperatures significantly. But in Fe-poor garnets the underestimation of  $Fe^{3+}$  will result in higher  $K_D$  value, and consequently, in underestimated temperatures (KROGH RAVNA, 2000). In common eclogites the  $Fe^{3+}/Fe^{tot}$  ratio is reported to be low, in the range of 0.0–0.06 (CARSWELL et al., 2000; SCHMID et al., 2003) and can be therefore calculated by using stoichiometric charge balance.

Clinopyroxenes are more problematic, especially because they tend to be non-stoichiometric under HP/UHP conditions due to the presence of the Ca-Eskola molecule. The most problematic are Fe-poor clinopyroxenes which show a large spread in calculated  $Fe^{3+}/Fe^{tot}$  ratios. The charge balance calculations are unsuitable in this case. The published  $Fe^{3+}/Fe^{tot}$  ratios from omphacites vary between 0.0 and 0.5 (CARSWELL et al., 1997) and were proven by Mössbauer studies (CARSWELL et al., 2000) and micro-XANES (SCHMID et al., 2003).

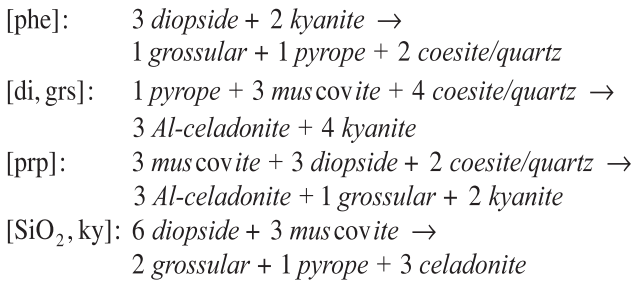
For eclogitic rocks from Pohorje, the  $Fe^{3+}/Fe^{tot}$  ratio directly determined by Mössbauer spectroscopy is reported to vary between 0.15 to 0.41 in omphacite, with a mean of 0.30, and tends to be low and constant in garnets, with the value of 0.02–0.03 (KOCH, 1999).

#### *Geobarometry based on garnet-clinopyroxene-phengite-kyanite-quartz/coesite assemblage*

Reliable geobarometers applicable to HP and UHP metamorphic rocks are rather scarce. In eclogites containing an assemblage of garnet +

clinopyroxene + phengite ± kyanite ± quartz/coesite, an equilibrium between these phases may be used for thermobarometric estimations. Such geobarometer is based on net-transfer reactions representing a balanced reactions among phases (or components of phases) in which progress of the reactions result in a change in the modal amounts of the phases. This means that net-transfer reactions cause the production and consumption of phases and therefore result in large volume changes making the equilibrium constants pressure sensitive.

Possible net-transfer reactions defining this equilibrium are given as follows (KROGH RAVNA & TERRY, 2001; KROGH RAVNA & PAQUIN, 2003):



These reactions define an invariant point in both the coesite and quartz stability field, depending on which SiO<sub>2</sub> polymorph is stable. Phases in square brackets are absent in the reactions.

For pressure calculations the calibrations of WATERS & MARTIN (1996), KROGH RAVNA & TERRY (2001) and KROGH RAVNA & TERRY (2004) have been applied.

WATERS & MARTIN (1996) calibrated geobarometer applicable to HP and UHP eclogites with the garnet + clinopyroxene + phengite assemblage, using the reaction [SiO<sub>2</sub>, ky] and thermodynamic data set of HOLLAND & POWELL (1990):

$$P_{WM-96} (kbar) = 28.5 + 0.02044 \cdot T - 0.003539 \cdot T \cdot \ln K$$

where  $\ln K$  term is calculated as follows:

$$\ln K = 6 \ln a_{di} - \ln a_{prp} - 2 \ln a_{grs} + 3 \ln a_{invphe}$$

The phengite activity may be calculated from:

$$a_{invphe} = \frac{a_{ideal ms}}{a_{ideal cel}} = \frac{X_{Al M_1} \cdot X_{Al T_1}}{X_{Mg M_1} \cdot X_{Si T_1}}$$

with  $X_{Al T_1} = 4 - Si$ ,  $X_{Si T_1} = Si - 2$  and  $M_1$  the octahedral cation sites. Activity model for diopside was taken from HOLLAND (1990) and for garnet from NEWTON & HASELTON (1981).

KROGH RAVNA & TERRY (2001, 2004) used all four above reactions and constructed geobarometric expressions for UHP (with coesite) and HP (with quartz) assemblages. The corresponding equilibrium constants are:

$$K^{[phe, coe/qtz]} = \frac{a_{prp}^{grt} \cdot a_{grs}^{grt} \cdot (a_{SiO_2}^{coe/qtz})^2}{(a_{di}^{cpx})^3 \cdot (a_{ms}^{phe})^3 \cdot (a_{Al_2SiO_5}^{ky})^2} \quad K^{[di, grs, coe/qtz]} = \frac{(a_{cel}^{phe})^3 \cdot (a_{Al_2SiO_5}^{ky})^4}{a_{prp}^{grt} \cdot (a_{ms}^{phe})^3 \cdot (a_{SiO_2}^{coe/qtz})^4}$$

$$K^{[prp, coe/qtz]} = \frac{a_{grs}^{grt} \cdot (a_{cel}^{phe})^3 \cdot (a_{Al_2SiO_5}^{ky})^2}{(a_{di}^{cpx})^3 \cdot (a_{ms}^{phe})^3 \cdot (a_{SiO_2}^{coe/qtz})^2} \quad K^{[SiO_2, ky]} = \frac{a_{prp}^{grt} \cdot (a_{grs}^{grt})^2 \cdot (a_{cel}^{phe})^3}{(a_{di}^{cpx})^6 \cdot (a_{ms}^{phe})^3}$$

For the above reactions they formulated linearized barometric expressions, which are:

$$\begin{aligned} P_{KRT-04}^{[phe, qtz]} (GPa) &= 7.235 - 0.000659 \cdot T + 0.001162 \cdot T \cdot \ln K^{[phe, qtz]} \\ P_{KRT-04}^{[phe, coe]} (GPa) &= 11.422 - 0.001676 \cdot T + 0.002157 \cdot T \cdot \ln K^{[phe, coe]} \\ P_{KRT-04}^{[di, grs, qtz]} (GPa) &= -2.624 + 0.005741 \cdot T + 0.0004549 \cdot T \cdot \ln K^{[di, grs, qtz]} \\ P_{KRT-04}^{[di, grs, coe]} (GPa) &= -0.899 + 0.003929 \cdot T + 0.0002962 \cdot T \cdot \ln K^{[di, grs, coe]} \\ P_{KRT-04}^{[prp, qtz]} (GPa) &= 0.355 + 0.003695 \cdot T + 0.0003059 \cdot T \cdot \ln K^{[prp, qtz]} \\ P_{KRT-04}^{[prp, coe]} (GPa) &= 0.568 + 0.003345 \cdot T + 0.0002705 \cdot T \cdot \ln K^{[prp, coe]} \\ P_{KRT-04}^{[SiO_2, ky]} (GPa) &= 1.801 + 0.002781 \cdot T + 0.0002425 \cdot T \cdot \ln K^{[SiO_2, ky]} \end{aligned}$$

The intersection of “quartz absent” lines defines a single point within the coesite (UHP) stability field, and analogously, the intersection of “coesite absent” lines defines another single point within the quartz (HP) stability field (Figure 4). Therefore the intersection of any two of these sets of lines uniquely defines P and T for a single sample.

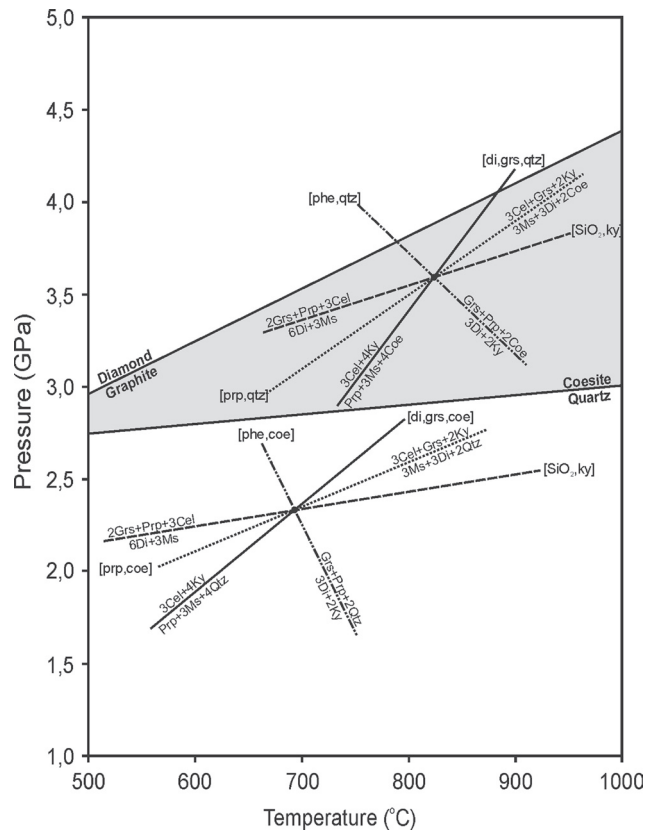


Figure 4. The intersection of reaction lines in the quartz and coesite stability fields (after KROGH RAVNA & TERRY, 2004). Phases in square brackets are absent in the reactions.

The content of ferric iron was calculated as:

$$Fe^{3+} = 2 - (Al + Cr + Ti)$$

The uncertainty limits for this thermobarometer are  $\pm 65^\circ C$  and  $\pm 0.32$  GPa. These geothermobarometric methods are supposedly less affected by subsequent thermal re-equilibration than common cation exchange thermometers, and the methods

also diminish the problems related to estimation of  $\text{Fe}^{3+}$  in omphacite (KROGH RAVNA & PAQUIN, 2003). Activity models for phengite, clinopyroxene and garnet were taken from HOLLAND & POWELL (1998), HOLLAND (1990) and GANGULY et al. (1996), respectively.

For calculating peak metamorphic conditions for a specific eclogite sample, garnet with maximum  $a_{\text{py}}^{\text{grt}} \cdot (a_{\text{grs}}^{\text{grt}})^2$ , omphacite with minimum  $a_{\text{di}}^{\text{cpx}}$  (and thus maximum jadeite content) and phengite with maximum  $a_{\text{cel}}^{\text{phe}}$  (maximum Si content) are required. Analyses of phases used for geothermobarometry are given in Table 1.

matrix often accompanied with elongated grains of blue kyanite.

The eclogites consist of garnet, omphacite, kyanite, and zoisite as major primary mineral phases. In some samples crystals of phengitic mica, quartz (after coesite?), rutile and rarely zircon are also present. Among the secondary mineral phases are mainly amphibole, diopside, plagioclase, biotite, sapphirine, corundum and spinel. They occur in the coronas, symplectites and fractures of the primary minerals. Secondary minerals developed after peak metamorphic conditions and are related to the exhumation of these rocks.

Table 1. Representative microprobe analyses of mineral compositions used for thermobarometry.

Sample	JV103a	NO1/04A	PO6h	SP1/08	JV103a	NO1/04A	PO6h	SP1/08	JV103a	NO1/04A	PO6h	SP1/08
Mineral	Grt	Grt	Grt	Grt	Cpx	Cpx	Cpx	Cpx	Phe	Phe	Phe	Phe
SiO <sub>2</sub>	40.99	40.80	40.83	40.35	55.02	5.5	55.28	54.92	53.36	51.53	51.00	52.66
TiO <sub>2</sub>	0.01	0.02	0.02	0.00	0.11	0.12	0.14	0.10	0.02	0.00	0.74	0.02
Al <sub>2</sub> O <sub>3</sub>	23.16	22.99	23.06	22.58	8.34	8.03	8.04	7.95	26.87	26.84	27.59	27.05
Cr <sub>2</sub> O <sub>3</sub>	0.00	0.14	0.04	0.27	0.02	0.19	0.18	0.06	0.30	0.37	0.08	0.05
FeO	15.77	13.92	13.91	14.88	2.55	2.45	2.48	2.28	1.48	1.71	1.03	1.20
MnO	0.38	0.26	0.28	0.34	0.02	0.02	0.00	0.06	0.00	0.01	0.00	0.00
MgO	13.37	15.02	14.22	12.91	12.30	12.43	12.71	12.08	3.62	4.00	4.22	3.90
CaO	7.81	7.42	7.76	7.60	18.19	18.83	18.80	18.22	0.11	0.08	0.00	0.16
Na <sub>2</sub> O	0.01	0.02	0.00	0.03	3.73	3.69	3.75	3.75	0.06	0.08	0.32	0.06
K <sub>2</sub> O	nd	nd	nd	nd	bd	bd	bd	bd	9.11	10.06	10.46	9.50
Total	101.50	100.59	100.12	98.97	100.28	100.81	101.38	99.42	94.93	94.68	95.44	94.60
Si	2.978	2.960	2.984	3.005	1.958	1.954	1.949	1.970	3.510	3.431	3.377	3.482
Ti	0.001	0.001	0.001	0.000	0.003	0.003	0.004	0.003	0.001	0.000	0.037	0.001
Al	1.983	1.966	1.987	1.983	0.350	0.336	0.334	0.336	2.083	2.107	2.154	2.108
Cr	0.000	0.008	0.002	0.016	0.001	0.005	0.005	0.002	0.016	0.019	0.004	0.003
Fe <sup>3+</sup>	0.061	0.106	0.039	0.000	0.000	0.000	0.011	0.000	0.000	0.035	0.000	0.000
Fe <sup>2+</sup>	0.897	0.739	0.811	0.931	0.076	0.073	0.062	0.068	0.081	0.060	0.057	0.066
Mn	0.023	0.016	0.017	0.021	0.001	0.001	0.000	0.002	0.000	0.001	0.000	0.000
Mg	1.447	1.624	1.549	1.433	0.652	0.657	0.668	0.646	0.355	0.397	0.416	0.385
Ca	0.608	0.577	0.608	0.607	0.694	0.716	0.710	0.700	0.008	0.006	0.000	0.011
Na	0.001	0.003	0.000	0.005	0.258	0.254	0.257	0.261	0.008	0.010	0.041	0.008
K	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.765	0.855	0.884	0.801
Total	7.999	8.000	7.998	8.001	3.993	3.999	4.000	3.988	6.827	6.921	6.970	6.866

Analyses (in wt%) of garnet (Grt), clinopyroxene (Cpx) and phengite (Phe). Garnet is normalized to 12, clinopyroxene to 6 and phengite to 11 oxygens. Abbreviations are as follows: bd - below detection; nd - not determined.

## Results

### *Petrography and mineral chemistry*

Eclogites from four localities in the Pohorje Mountains have been investigated (Figure 3). The dominant rock type is weakly retrograded eclogite, which occurs in bands, lenses and boudins within the surrounding continental crustal rocks (orthogneisses, paragneisses and micaschists). In macroscopic scale, eclogites contain big distinctive grains of garnet surrounded by omphacite

Garnets form euhedral to subhedral crystals with size ranging from large porphyroblasts up to several mm in diameter, to very tiny inclusions of few microns, which are found within kyanite and omphacite crystals. Garnets are texturally uniform, unzoned (Figure 5a), and nearly homogeneous in composition, as major element zoning is absent in all observed grains. Garnets with 27–55 mol% of pyrope, 25–48 mol% of almandine and spessartine, and 18–27 mol% of grossular and andradite content belong to the almandine-pyrope-grossular series with high pyrope content, as



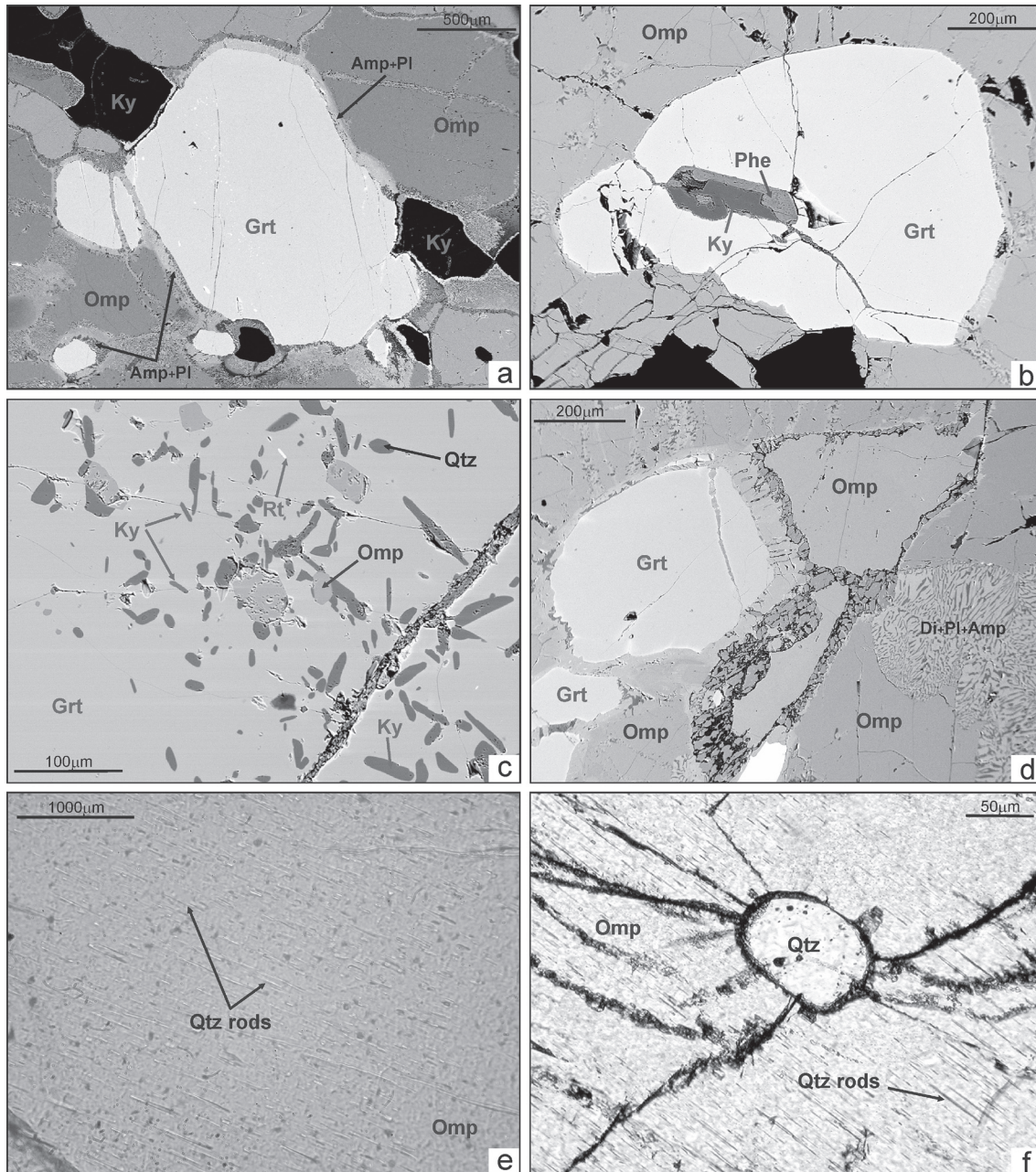


Figure 5. Primary and secondary mineral phases in eclogites.

(a) Photomicrograph – backscattered electron image (BSE) of unzoned homogeneous garnet grains lacking any inclusions. Symplectitic rims of amphibole + plagioclase are replacing garnet rims in contact with omphacite.

(b, c) Typical inclusions in garnet belong to phengite, kyanite, omphacite, quartz and rutile (BSE).

(d) Homogeneous omphacites are replaced by symplectites of diopside + plagioclase + amphibole.

(e) Quartz rods and needles in matrix omphacite shown in plane-polarized light. Quartz rods are distinctly oriented and parallel to omphacite c-axis.

(f) Omphacite with tiny quartz exolutions is hosting quartz inclusion surrounded by radial fractures (BSE). Abbreviations after KRETZ (1983).

it is common for UHP metamorphic rocks (CHOPIN, 1984). Inclusions in garnet are relatively rare; these are typically omphacite, rutile, kyanite, quartz and phengite (Figure 5b, c). Garnet rims are commonly resorbed by amphibole + plagioclase symplectite (Figure 5a).

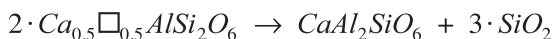
Omphacite occurs in large anhedral grains in the matrix (Figure 5d) or as inclusions in garnet (Figure 5c) and kyanite. Similarly to garnets, omphacites also show uniform grains and almost homogeneous composition for all major oxides. The jadeite component of omphacites, calculated from KATAYAMA et al. (2000):

$$Jd = Na - Fe^{3+} - 2 \cdot Ti$$

varies between 18–37 mol%. The total cation deficiency (omphacite cation totals are less than 4.00 per six oxygen atoms) and excess Al on the octahedral site suggest the existence of non-stoichiometric pyroxenes or pyroxenes with octahedral vacancies. Ca and Al combine and form the Ca-Eskola molecule ( $CaEs - Ca_{0.5}\square_{0.5}AlSi_2O_6$ ; empty rectangle  $\square$  represents a vacancy on the M2 site). The cation sum of natural clinopyroxenes, calculated on the basis of six oxygens, decreases progressively from the theoretical value of 4.00 as the



<sup>VI</sup>Al content increases (CAWTHORNE & COLLERSON, 1974). The Ca-Eskola clinopyroxene, which is stable at peak metamorphic conditions, is highly unstable at lower pressure (SMYTH, 1980). It rapidly breaks down to Ca-Tschermak component (CaTs – CaAl<sub>2</sub>SiO<sub>6</sub>) and quartz, following the retrograde reaction:



which can be simplified to:



The Ca-Tschermak component is assigned to be equivalent to the <sup>IV</sup>Al content (KATAYAMA et al., 2000), and may be calculated from:

$$CaTs = 2 - Si = {}^{IV}Al$$

The decompressional breakdown of Ca-Eskola molecule results in the exsolution of tiny needles and rods of quartz that are the most striking feature of matrix omphacites from Pohorje eclogites (Figure 5e, f). They display an orientation parallel to the c-axis of omphacite. Microprobe analysis of quartz needles show essentially pure SiO<sub>2</sub>. The amount of the Ca-Eskola component in omphaci-

tes from Pohorje samples, calculated from KATAYAMA et al. (2000):

$$CaEs = {}^{TOT}Al - 2 \cdot {}^{IV}Al - K - (Na - Fe^{3+} - 2 \cdot Ti)$$

is reaching 5 mol%. Integral analysis of omphacite, together with SiO<sub>2</sub> precipitates, under defocused electron beam (25–30 μm) yields even higher values, up to 9 mol%. Omphacite is very sensitive to retrogression. During decompression, omphacitic clinopyroxene must reduce its jadeite content, which results in the production of plagioclase. The typical product of omphacite retrogression is the formation of symplectites of fine-grained diopside + plagioclase + amphibole (Figure 5d).

Phengite occurs sporadically in the matrix (Figure 6a) and as minor inclusions in garnet (Figure 5b) and omphacite. Measured phengite grains were nearly homogenous in composition since the content of major cations is close to constant. Phengite belongs to white micas which result from solid solution between muscovite and celadonite and is formed by an inverse Tschermak substitution starting from muscovite. The amount of celadonite component present is evident from the Si content of phengite, which rapidly increases with

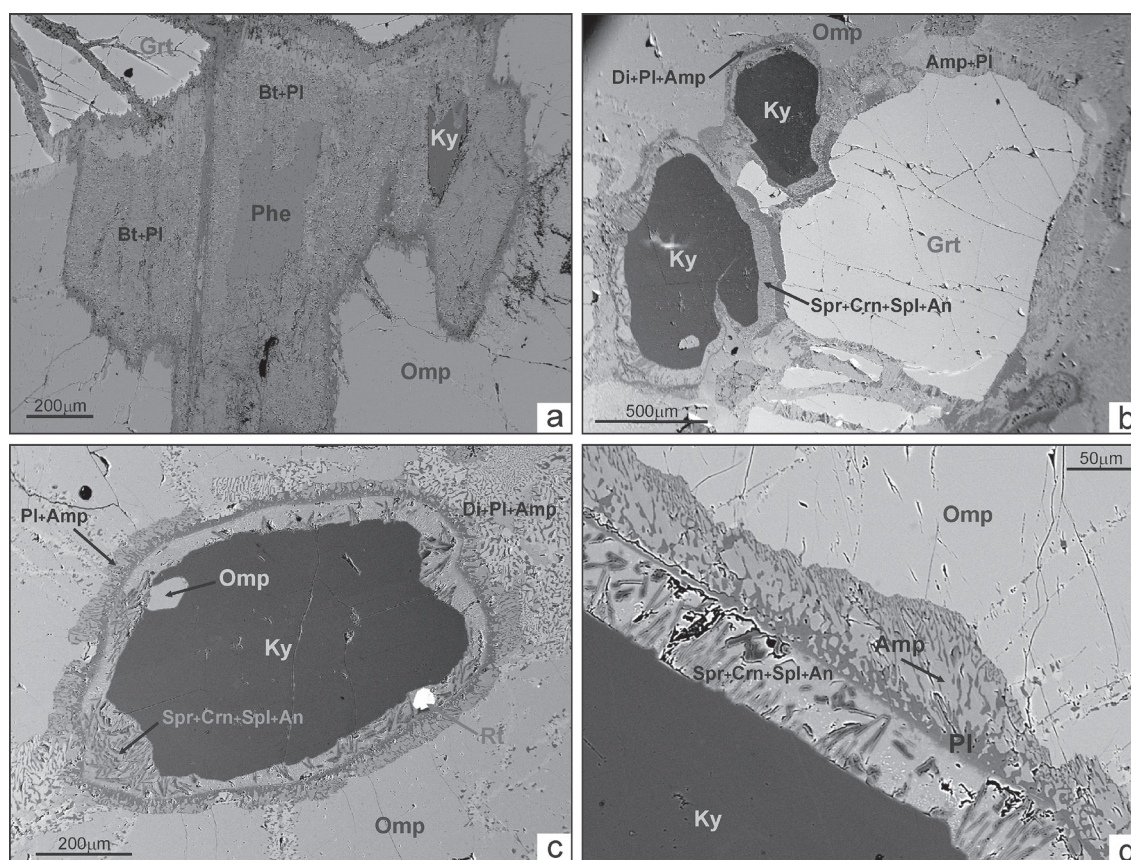


Figure 6. Primary and secondary mineral phases in eclogites (photomicrographs – backscattered electron images).

(a) Preserved remnant of phengite with clearly visible cleavage is surrounded by symplectitic intergrowth of biotite and plagioclase.

(b) Dark-gray kyanite grains in comparison with garnet and omphacite. All minerals shown are surrounded by symplectites of secondary mineral phases. The most typical are amphibole + plagioclase after garnet, diopside + plagioclase + amphibole after omphacite and sapphirine + corundum + spinel + anorthite after kyanite.

(c) Kyanite with omphacite inclusion is surrounded by coronas of secondary minerals. Two distinct symplectitic belts are present. Inner corona, next to kyanite, consists of sapphirine + corundum + spinel + anorthite. Outer corona, next to omphacite, is made of plagioclase + amphibole ± diopside.

(d) Detail of kyanite corona in which separate symplectitic constituents are clearly visible. Abbreviations after KRETZ (1983).

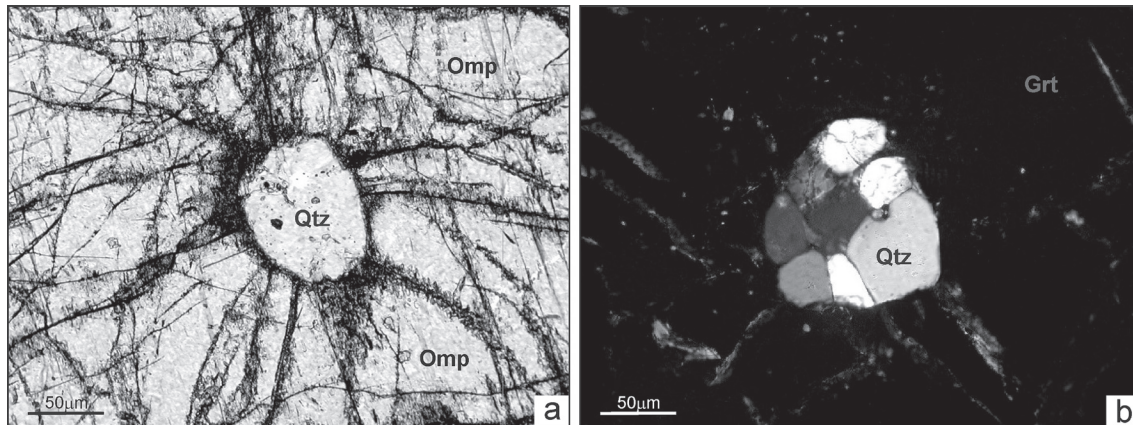


Figure 7. Quartz (former coesite?) inclusions in eclogites.

(a) Radial fractures surrounding quartz inclusion in omphacite under plane-polarized light.

(b) Polycrystalline polygonal quartz inclusion (PPQ) surrounded by tiny radial fractures within garnet host under crossed polars. Abbreviations after KRETZ (1983).

increasing pressure (HERMANN, 2002). The strong variation of phengite composition as a function of pressure makes phengite a crucial mineral component for determination of UHP metamorphism (MASSONE & SZPURZKA, 1997). Investigated phengite grains from Pohorje eclogites contain up to 3.5 Si per formula unit (pfu). The biotite + plagioclase intergrowths are typical replacements of phengite (Figure 6a).

Kyanite forms frequently twinned subhedral grains (Figure 6b) and small rod-like inclusions within garnet (Figure 5c) and omphacite minerals. Rare inclusions found in kyanite belong to garnet, omphacite (Figure 6c) and quartz. Microprobe analysis of all measured kyanite grains revealed almost pure  $\text{Al}_2\text{SiO}_5$ . Retrogression of kyanite is expressed by development of complex coronas consisting of sapphirine + corundum + spinel + anorthite (Figure 6b, c, d). The width of the corona is progressively increasing with the increasing degree of retrogression. Spinel belongs to Fe-Mg

spinel. Sapphirines contain up to 1.4 Si pfu and are clearly peraluminous. Growth of corundum and tiny lamellar grains of sapphirine is restricted only to domains formerly occupied by kyanite.

Zoisite mainly forms individual elongated grains but may also be found as minor inclusions in garnet and omphacite. It contains rare inclusions of rutile.

Quartz inclusions are present in garnet (Figure 5c), omphacite (Figure 5f, 7a) and kyanite. They are frequently surrounded by radial fractures (Figure 7a) which may imply the possibility for the existence of former coesite. Some of the quartz inclusions surrounded by radial fractures, are aggregates of several polycrystalline quartz grains (Figure 7b). They strongly resemble the PPQ (polycrystalline polygonal quartz) and MPQ (multicrystalline polygonal quartz) textures described by WAIN et al. (2000). Those quartz inclusions are interpreted as possible pseudomorphs after coesite.

Table 2. Calculated temperatures and pressures.

Sample	Temperature (°C)							Minimum	Maximum	Average
	EG-79	P-85	K-88	PN-89	A-94	KR-00				
JV103a	843	822	802	573	741	748	741	843	791	
NO1/04A	921	903	888	777	817	820	817	921	870	
PO6h	824	803	781	588	710	717	710	824	767	
SP1/08	801	779	755	516	694	702	694	801	746	

Temperatures calculated at 3 GPa.

Geothermometers: EG-79: ELLIS & GREEN (1979), P-85: POWEL (1985), K-88: KROGH (1988), PN-89: PATTISON & NEWTON (1989), A-94: AI (1994), KR-00: KROGH RAVNA (2000). PN-89 calibration is excluded from minimum and average temperature calculations.

Sample	Pressure (GPa)					Minimum	Maximum	Average
	KRT-04 <sup>[phe, qtz]</sup>	KRT-04 <sup>[di, grs, qtz]</sup>	KRT-04 <sup>[prp, qtz]</sup>	KRT-04 <sup>[SiO<sub>2</sub>, kyl]</sup>	WM-96			
JV103a	2.9	3.2	3.1	3.1	3.0	2.9	3.2	3.1
NO1/04A	2.9	3.2	3.1	3.1	2.9	2.9	3.2	3.1
PO6h	2.9	3.2	3.1	3.1	2.8	2.8	3.2	3.0
SP1/08	2.9	3.2	3.1	3.1	3.0	2.9	3.2	3.1

Pressures calculated at 800 °C.

Geobarometers: WM-96: WATERS & MARTIN (1996), KRT-04: KROGH RAVNA & TERRY (2001, 2004).



*Geothermobarometry*

Calculated temperatures from different calibrations of the garnet-clinopyroxene system (ELLIS & GREEN, 1979; POWELL, 1985; KROGH, 1988; PATTISON & NEWTON, 1989; AI, 1994; KROGH RAVNA, 2000)

differ substantially (Table 2, Figure 8). The unrealistically low temperatures were obtained by PATTISON & NEWTON's (1989) geothermometer, while the highest temperatures were calculated from the calibration of ELLIS & GREEN (1979). POWEL (1985) and KROGH (1988) calibrations give reasonable

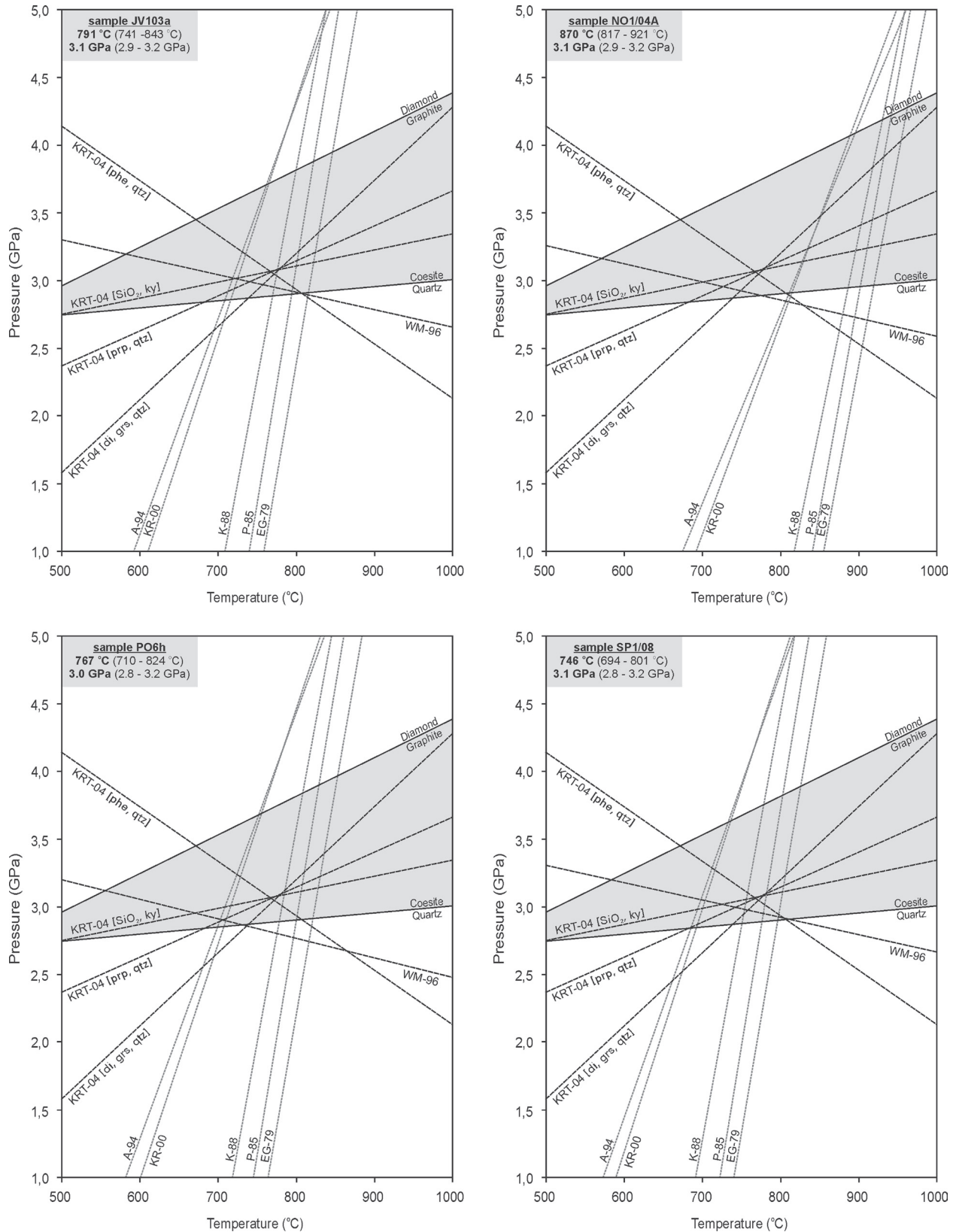


Figure 8. Comparison of geothermobarometric results calculated with different geothermometers and geobarometers. Geothermometers: EG-79: ELLIS & GREEN (1979), P-85: POWEL (1985), K-88: KROGH (1988), A-94: AI (1994), KR-00: KROGH RAVNA (2000). Geobarometers: WM-96: WATERS & MARTIN (1996), KRT-04: KROGH RAVNA & TERRY (2001, 2004). Abbreviations after KRETZ (1983).



results but obtained temperatures are still very high. The most reliable are temperatures obtained by geothermometers of AI (1994) and KROGH RAVNA (2000). With the exception of PATTISON & NEWTON'S (1989) calibration which obviously underestimates peak temperature conditions in mafic and ultramafic lithologies, the temperature intervals calculated at 3.0 GPa pressure range from 741 to 843 °C for JV103a sample, from 817 to 921 °C for NO1/04A sample, from 710 to 824 °C for PO6h sample, and from 694 to 801 °C for SP1/08 sample. Average peak temperatures obtained are 791 °C (JV103a sample), 870 °C (NO1/04A sample), 767 °C (PO6h sample), and 746 °C (SP1/08 sample).

Peak pressure estimations of WATERS & MARTIN (1996) and KROGH RAVNA & TERRY (2001, 2004) calibrations yielded consistent results (Table 2, Figure 8). The intersections between these two geobarometers and the geothermometers of AI (1994) and KROGH RAVNA (2000) define average peak pressures of 3.0 GPa for PO6h sample and 3.1 GPa for JV103a, NO1/04A and SP1/08 samples, calculated at 800 °C. Excellent fitting is obtained mostly between WATERS & MARTIN (1996) geothermobarometer, the pyrope absent reaction with coesite and the SiO<sub>2</sub>-kyanite absent reaction from KROGH RAVNA & TERRY (2001, 2004) calibration system.

The combination of garnet-clinopyroxene Fe<sup>2+</sup>-Mg exchange geothermometer (KROGH RAVNA, 2000) with the geobarometric calibrations based on the net-transfer reactions in the garnet-clinopyroxene-phengite-kyanite-quartz/coesite system (KROGH RAVNA & TERRY, 2004), resulted in similar but more precise estimations of peak metamorphic conditions. The intersections between the used geothermometer and geobarometers define optimized maximum pressure of 3.0 GPa for samples JV103a, PO6h and SP1/08 at temperature range from 750 to 782 °C; and pressure of 3.1 GPa at temperature 783 °C for NO1/04A sample (Figure 9).

All estimated peak pressure and temperature values consistently plot above the quartz-coesite transformation curve and thus correspond well to the ultrahigh-pressure stability field of coesite (Figure 8, 9). The quartz-coesite and graphite-diamond transformation boundaries were calculated from thermodynamic data of HOLLAND & POWELL (1998).

## Discussion

UHP metamorphism in eclogites from Pohorje is evident both from microtextural observations and from the results of geothermobarometric calculations of peak metamorphic conditions, which revealed very high pressures and temperatures of 3.0–3.1 GPa and 750–783 °C. These values correspond well to the coesite, i.e. ultrahigh-pressure, stability field. Pressures calculated in this work are much higher than the former estimates of 1.8 GPa by HINTERLECHNER-RAVNIK et al. (1991) or 1.5 GPa by KOCH (1999).

Remnants of coesite, a direct mineral indicator of UHP conditions, were not found but its exi-

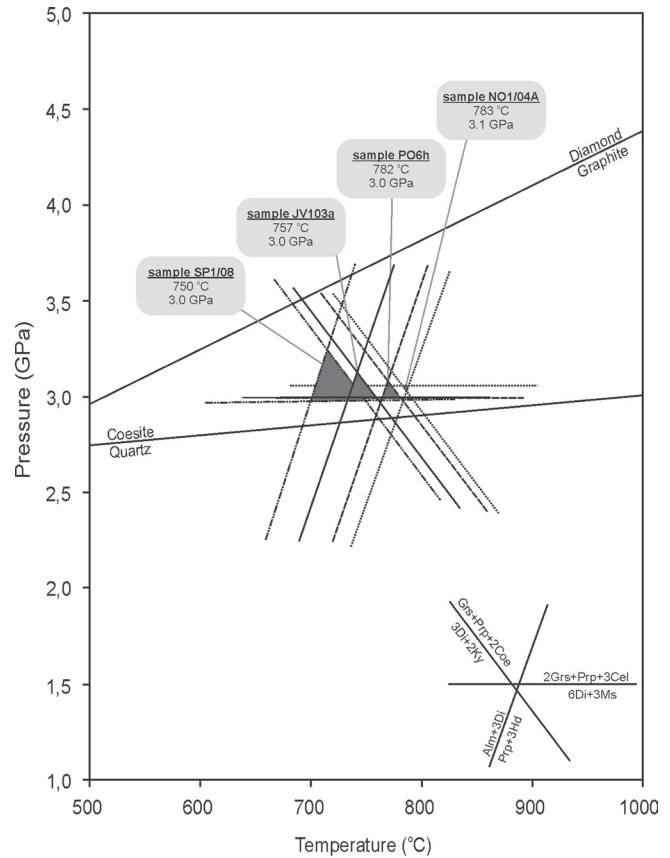


Figure 9. Results from geothermobarometry. Combination of garnet + omphacite + phengite + kyanite + quartz/coesite assemblage (KROGH RAVNA & TERRY, 2004) with garnet-clinopyroxene Fe<sup>2+</sup>-Mg exchange thermometer (KROGH RAVNA, 2000). The quartz-coesite and graphite-diamond curves are calculated from thermodynamic data of HOLLAND & POWELL (1998). Abbreviations after KRETZ (1983).

istence is clearly revealed from: (1) radial fractures around quartz inclusions within robust host minerals (garnet, kyanite and omphacite) that were caused by expansion ensuing the transformation of high-pressure coesite to its low-pressure polymorph; and (2) polycrystalline appearance of these inclusions interpreted as a pseudomorphs after former coesite due to their distinctive PPQ and MPQ microtextures (WAIN et al., 2000).

Radial fractures around quartz inclusions may imply the possibility for the existence of former coesite and are therefore an indicator of possible UHP conditions. The roughly 10% of volume increase in coesite-quartz transformation process produces considerable overpressure (more than three times the lithostatic pressure), which buffers the inclusion at the coesite-quartz transformation boundary (GILLET et al., 1984).

The multistage transformation of coesite to strain-free quartz was described from experimental studies (MOSENFELDER & BOHLEN, 1997) and also observed in UHP rocks from many well-established UHP localities (e.g. WAIN et al., 2000). Transformation begins with the growth of quartz on the coesite-host contact, which is followed by the development of shear cracks with no open volume (HIRTH & TULLIS, 1994), providing new sites for quartz growth. With progressing transformation, quartz rim around coesite inclusion succes-

sively changes from textureless to fibrous radial texture and to more irregular, feather-like texture. In the final stage of transformation, quartz inclusions exhibit typical radial palisade texture; if any relic coesite is present, palisades of quartz radiate from it. When absolutely no coesite is preserved, its former existence may be deduced from the three different sequential textural types of quartz inclusions: PRQ, PPQ and MPQ (WAIN et al., 2000). Polycrystalline radial-texture quartz (PRQ) inclusions develop prior to radial fracturing in the host mineral and result from stress release. They consist of individual strain-free palisades, which often radiate from a core zone. The core zone is made of quartz which has irregular mosaic texture, sutured boundaries and undulatory extinction. Polycrystalline quartz inclusions with mosaic texture and sutured contacts containing 30–100 grains also belong to the PRQ group. With proceeding recovery, the number of grains per inclusion is continuously reduced. Polycrystalline polygonal quartz (PPQ) inclusions consist of 10–50 polygonal strain-free quartz grains. Their formation post-dates radial fracturing. The next step of recovery is represented by multicrystalline polygonal quartz (MPQ) inclusions with 2–10 monocrystalline quartz grains per inclusion. Eventually, the recovery is completed when the whole inclusion recrystallizes to a single unstrained monocrystalline quartz surrounded by radial fractures.

Additional evidence for UHP metamorphism is coming from the presence of highly pressure-sensitive non-stoichiometric supersilicic clinopyroxenes that directly indicate high pressure and temperature conditions (GASPARIK & LINDSLEY, 1980; FOCKENBERG & SCHREYER, 1997). They were reported as a typical constituent of eclogites from various UHP terranes (summarized by BRUNO et al., 2002). Such clinopyroxenes containing Ca-Eskola molecule in solid solution favourably form at high pressures exceeding 3 GPa (SCHMÄDICKE & MÜLLER, 2000). Due to the pressure decrease quartz needles and rods form as an exsolution product from supersilicic clinopyroxene. They are oriented along the *c*-axis of omphacite and are resulting from the omphacitic clinopyroxene that contained excess silica at peak metamorphic conditions (ZHANG & LIOU, 2000). The occurrence of oriented quartz needles and rods in matrix omphacites is typical feature of many UHP eclogites (e.g. LIOU et al., 1998). The eclogites from Pohorje show both, direct and indirect, evidence for pyroxene containing the Ca-Eskola component: the presence of clinopyroxene with Ca-Eskola molecule in solid solution, and quartz rods and needles as an exsolution product.

The survival of coesite relics depends on many factors, like the presence of sufficiently rigid host mineral, the extent of metamorphic re-equilibration of a mineral assemblage during exhumation, the trend of exhumation P-T path, the rate of exhumation, the presence of fluid phase on the reactant side of retrograde reactions (e.g. MOSENFELDER & BOHLEN, 1997; HERMANN, 2002). Continental crustal rocks entering the UHP realm are not completely

dry, as one would expect. The majority of UHP assemblages contains hydrous minerals, like phengitic mica and epidote, that are stable under UHP conditions and may evolve small amounts of fluids by dehydration reactions (CHOPIN, 2003). Therefore, UHP parageneses may only be preserved if the entire exhumation path is situated within the stability field of phengite. This can happen either when continuous cooling is accompanying exhumation or when the entire exhumation process occurred at  $T < 700^\circ\text{C}$  (HERMANN, 2002). In contrast, in terranes that show isothermal decompression, breakdown of phengite and concomitant partial melting may cause a complete recrystallization of the subducted crustal rocks during exhumation, and thus destruction of all UHP mineral assemblages.

Granulite facies metamorphism is usually required for sapphirine formation (ACKERMAN et al., 1975). Composition of sapphirines from Pohorje eclogites is clearly peraluminous and is significantly different from the composition of sapphirines that are stable within granulite facies conditions (HIGGINS et al., 1979). Furthermore, the formation of sapphirine is very dependent on  $\text{H}_2\text{O}$  activity, and for this reason is by itself not an indication that typical granulite facies conditions were reached (SIMON & CHOPIN, 2001). Therefore it is proposed that sapphirine in Pohorje eclogites formed during decompression at lower-temperature conditions than those common for granulite-facies. Presence of sapphirine in coronas around kyanite in eclogites from Pohorje clearly indicates that during the early stages of decompression high temperature conditions persisted. Due to this near-isothermal decompression, fracturing and introduction of fluids was possible already at high temperatures. Because the Pohorje eclogites crossed the transformation border between coesite and quartz at such high temperatures, there was no possibility for the survival of coesite.

The only known UHP metamorphism of Alpine eclogites so far was documented in the Western Alps, e.g. Dora Maira Massif (CHOPIN, 1984), Zermatt-Saas Zone (REINECKE, 1991), and is of Tertiary age (TILTON et al., 1991; RUBATTO et al., 1998). The determined P-T conditions of Eo-Alpine metamorphism in Pohorje are the highest reported within the Austroalpine units of the Eastern Alps. Thus, the Pohorje eclogites are the first evidence of UHP metamorphism in Eastern Alps, and also the first evidence that UHP metamorphic conditions were also reached during the Cretaceous orogeny.

## Conclusions

Kyanite eclogites from Pohorje experienced UHP metamorphic conditions of 3.0–3.1 GPa at temperature range from 750 to 783 °C.

Radial fractures around polycrystalline quartz inclusions with microtextures diagnostic for recovery after coesite, together with oriented quartz exolutions in clinopyroxene, and omphacites with Ca-Eskola molecule are the microtextural evidence for UHP metamorphism.

During the first stages of exhumation, eclogites were exposed to near-isothermal decompression that lead to complete breakdown of coesite.

Pohorje eclogites record the highest pressure conditions of Eo-Alpine metamorphism in the Alps and thus provide the first evidence that UHP metamorphism in the Alps occurred already during the Cretaceous orogeny.

UHP eclogites from Pohorje represent the first occurrence of UHP metamorphic rocks within the Eastern Alps.

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