Genesis of chromium-rich kyanite in eclogite-facies Cr-spinel-bearing gabbroic cumulates, Pohorje Massif, Eastern Alps

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ABSTRACT

Natural kyanites with Cr$_2$O$_3$ contents >1 wt% are very rare and known only from high-P environments. One example are eclogite-facies gabbroic cumulates containing Cr-spinel from the Pohorje Massif, Eastern Alps, Slovenia. In these rocks turquoise coloured Cr-rich kyanites are present in two different textural types: A first type has formed as blocky crystals of several hundred µm in size around clusters of small drop-like Cr-spinels. This kyanite shows a highly irregular Cr distribution and may contain up to 15.6 wt% Cr$_2$O$_3$ which is one of the highest Cr$_2$O$_3$ contents reported so far. A second type is present as part of reaction coronas around large red-brownish Cr-spinel and forms deep-blue needle-like crystals which rarely exceed 100 µm in size. This kyanite contains up to 8.2 wt% Cr$_2$O$_3$ and is associated with Cr-rich corundum (≤ 9.1 wt% Cr$_2$O$_3$) and Cr-Al-rich pargasite (≤3.9 wt% Cr$_2$O$_3$). The formation of kyanite around Cr-spinel droplets is interpreted to be the result of increasing PT conditions during prograde metamorphism where Cr-spinel and plagioclase or quartz react to Cr-kyanite, ±garnet, ±omphacite. In contrast, the formation of kyanite associated with Cr-rich corundum and Cr-rich pargasite within coronas around Cr-spinel occurred in an early stage of the retrogressive evolution of the gabbroic cumulates at eclogite-facies conditions of ~2.5 GPa and 750 – 800°C triggered by the influx of H$_2$O-rich fluids. The driving force for developing these coronas was an increase in the chemical potential of silica caused by the infiltrating hydrous fluid phase. PT estimates using matrix mineral assemblage place the peak metamorphic conditions close to the quartz/coesite transition with temperatures in the range of 750–810°C and pressures of ~2.9 GPa.

Keywords: Cr-rich kyanite, Cr-rich corundum, eclogite facies cumulates, Pohorje Massif,
INTRODUCTION

Kyanite is a common metamorphic mineral in metapelites and Al-rich metabasites at medium to high pressures and can accommodate substantial amounts of manganese, iron (e.g. Chinner et al. 1969; Grambling and Williams 1984) and especially chromium in its crystal structure. Cr–Al substitution results in a spectacular turquoise-blue color and strong pleochroism as reported by Sobolev (1968), Cooper (1980), and Gil-Ibarguchi (1991). Cr–Al substitution in synthetic kyanite, on the other hand, produces a deep emerald green color (Langer and Seifert 1974). This suggests that the blue color of natural Cr-bearing kyanite results from a combination of Cr and additional minor substituents such as Fe and/or Ti (White and White 1967; Rost and Simon 1972). Natural kyanite with Cr$_2$O$_3$ contents >1 wt% have been known so far only from high-P environments. The highest Cr$_2$O$_3$ content documented in the literature so far is 15.7 wt% which corresponds to ~18 mol% Cr$_2$SiO$_5$ component and was reported by Negulescu and Sabau (2012) from chromite-bearing meta-gabbroic eclogites. Kyanite with up to 12.7 and 11.8 wt% Cr$_2$O$_3$ were reported by by Sobolev et al. (1968) and Pivin et al. (2011) from kimberlite-derived grosspydite and clinopyroxenite nodules. Kyanite with up to 25 mol% Cr$_2$SiO$_5$ was synthesized by Langer and Seifert (1974) at 3 GPa and 1300-1500°C. These authors suggested that significant amounts of Cr can enter the kyanite structure only at P ≥1.8 GPa and T ≥900°C and that the amount of Cr incorporated is positively correlated with both P and T. A comparison with PT conditions of equilibration estimated for Cr-kyanite-bearing eclogite from the South Carpathians by Negulescu and Sabau 2012 shows that whereas high pressures are indeed essential, temperatures as low as 600°C are sufficient to allow substantial Al–Cr substitution. Hence, high pressures in excess of ~2GPa and a suitable source of Cr which is usually Cr-spinel are essential pre-requisites for the formation of Cr-rich kyanite.
Eclogites within the Eastern alpine crystalline basement typically appear as lenses and small bodies of up to several hundred meters in size within a narrow E-W trending zone, ~400 km in length, immediately north of the Periadriatic Lineament which is termed Eo-alpine high pressure belt (EHB) (Hoinkes et al. 1991; Thöni and Jagoutz 1993; Exner et al. 2001; Sölva et al. 2005 a,b). The southeasternmost part of the EHB is represented by eclogites of the Pohorje massif (e.g. Ippen 1892; Hinterlechner-Ravnik and Moine 1977; Hinterlechner-Ravnik et al. 1991a,b; Janak et al. 2004; Miller et al. 2005a; Vrabec et al. 2012) and of the Koralpe and Sauwalpe basement complexes (Miller 1990; Miller and Thöni 1997; Miller et al. 2005b) (Fig. 1a). Most Eoalpine eclogites including those from the Pohorje massif are derived from MORB-type precursors (Miller et al. 1988; Miller and Thöni 1997; Miller et al. 2005b) and only a minor part has intra-plate characteristics (Hoinkes et al. 1991; Konzett et al. 2011). Major and trace element systematics of the Koralpe-Sauwalpe-Pohorje eclogites indicate two different modes of formation of the precursors: (1) low-Mg gabbros derived from evolved tholeiitic magmas not significantly influenced by cumulate formation and (2) high-Mg–Al–Ca gabbros depleted in alkalis and with pronounced positive Eu-anomalies which are thought to represent plagioclase-rich cumulates (Miller 1990; Sassi et al. 2004). A significant portion of these meta-cumulates contains kyanite as a major constituent of the eclogite-facies assemblage (Sassi et al. 2004; Miller et al. 2005b, 2007).

Here we report the occurrence of high-Mg cumulate-type eclogites from the Pohorje Massif that are unique amongst all eastern Alpine eclogites known so far in that their precursors contain Cr-spinel as cumulate phase. These Cr-spinels create a geochemical micro-environment in which unusually Cr-rich kyanite is present together with Cr-rich omphacite, pargasite and corundum. The Cr-contents of kyanite are amongst the highest found so far in a natural environment. We present (1) mineral chemical data for the Cr-rich high pressure assemblage along with bulk rock compositions of the host rocks, (2)
results of phase equilibrium calculations to determine $PT$ conditions of formation of the Cr-rich phase assemblage, and (3) a model for the formation of the Cr-rich phase assemblage.

**GEOLOGICAL SETTING**

Eclogites and associated high-pressure metapelites form an important albeit small portion of the Eastern alpine crystalline basement and testify to intracontinental subduction during Jurassic to Cretaceous collision of the African and Eurasian lithospheres (Thöni 1999). Peak $PT$-conditions for the Eoalpine eclogite-facies metamorphism increase from ~1.2 GPa and 550°C in the westernmost portions of the Eastern Alps to ~3.0 GPa and 800°C in the Pohorje Massif (Hoinkes et al. 1991; Janak et al. 2004; Miller and Konzett 2005; Vrabec et al. 2012; this study). A multitude of geochronological methods applied to the eclogite facies assemblages yields consistent ages of 85–115 Ma (Thöni 2006 and references; Konzett et al. 2011). For the Pohorje Massif the age of high-$P$ metamorphism is tightly constrained by U-Pb zircon and whole rock-garnet Sm-Nd ages for eclogites and their host metapelites with 90.7±1.0 and 92.0±0.5 Ma, respectively (Miller et al. 2007; Janak et al. 2009). For the mainly gabbroic eclogite precursors, Permian emplacement ages in the range 247–275 Ma were determined (Thöni and Jagoutz 1993; Miller and Thöni 1997). In terms of large-scale tectonics the Pohorje Massif is a nappe stack which consists of three tectonic units (Mioč and Žnidarčič 1977; Fodor et al. 2003) (Fig. 1b). The lowermost unit is termed Pohorje nappe (Janák et al. 2006) and consists of medium to high-grade micaschist, gneiss and amphibolite with lenses of marble, quartzite, eclogite and ultrabasic rocks. This unit is folded into an ESE–WNW-striking antiform containing the Pohorje tonalite-granodiorite in its core which was emplaced during the Oligocene to Miocene (Altherr et al. 1995; Fodor et al. 2008). The Pohorje nappe is overlain by low-grade metamorphic Paleozoic slate and phyllite and the uppermost nappe on top of these rocks consists of Permo-Triassic sandstone and conglomerate. This nappe stack is covered by early Miocene sediments of the Pannonian Basin.
The eclogite samples investigated in this study were collected from poorly exposed outcrops along a road situated at N 46° 24’ 14.3” and E 015° 29’ 25.7” close to Slovenska Bistrica (Fig. 1b).

**ANALYTICAL METHODS**

Mineral compositions were determined with a scanning electron microprobe JEOL JSM-6310 at the University of Graz, Austria, using an energy and wavelength dispersive spectrometer (15 kV acceleration voltage and 6 nA beam current) with 30 seconds on peak and 15 seconds on background for elements determined by WDX. The following standards were used: Na (WDX), jadeite; Fe, Mg (EDX), garnet and kaersutite; K, Al, Si (EDX), adularia; Ca, Ti (EDX), titanite; Cr (EDX), chromite; Mn (EDX), rhodonite; Zn (EDX), gahnite; F (WDX), synthetic F-phlogopite. Since Si content in phengite is crucial for pressure determination, a muscovite standard was used instead of adularia for Si in order to ensure a similar matrix for analyses of unknowns and standard. Additional electron microprobe analyses were obtained using a JEOL Superprobe JXA 8200, Universitaetszentrum für Angewandte Geowissenschaften (UZAG) at the University of Leoben (Austria). Analytical conditions were 15 kV accelerating voltage and 10 nA beam current with 30 seconds on peaks and 15 seconds on backgrounds of the X-ray lines. Zirconium in rutile was analyzed using a JEOL JXA-8100 Superprobe at the University of Innsbruck with analytical conditions of 15 kV and 150 nA. Counting times were set to 300 sec on the peak and 150 sec on the backgrounds of the ZrLa line using a PETH-crystal. This yields a 2-sigma count statistical error of 9% for a Zr concentration of 300 ppm. The accuracy of Zr measurements was checked intermittently with a rutile standard kindly supplied by T. Zack. Mineral formulae and single geothermobarometer reactions were calculated with the Mathematica package PET (Dachs 2004).

Whole rock major and trace element compositions were determined by X-ray fluorescence spectroscopy using a Bruker Pioneer S4 XRF at the Institute of Earth Sciences, University of Graz. The samples were prepared as fused pellets using 7 gram of Li2B4O7 and 1 gram of finely powdered and dried sample. The loss on ignition (LOI) was determined from the total weight change after heating to 1030°C for 1 hour.

Unpolarized spectra of kyanites were measured on a HORIBA Labram HR-800 confocal Raman-spectrometer, using the 514 nm excitation wavelength of a 30 mW Nd-YAG laser, through a 100x objective with a numerical aperture of 0.9. Standard optical and electron microprobe backscattered electron images were used to target areas that are homogeneous in composition and free of visible inclusions. Size and power of the laser spot on the surface was approximately 1 μm and 5
mW, respectively. Confocal pinhole and entrance slit were set to 1000 and 100 µm. The scattered Raman light was dispersed by a grating with 1800 lines/mm and detected by an open-electrode CCD with 1024 x 256 pixels, each sizing 43 µm. The spectral resolution, determined by measuring the Rayleigh line, was 1.4 cm⁻¹. Background and Raman bands were fitted by the built-in spectrometer software LabSpec to first or second order polynomials and convoluted Gauss-Lorentz functions. The accuracy of Raman line shifts was checked by regular measurements of the emission lines of a Ne spectral calibration lamp and is on the order of 0.5 wavenumbers.

WHOLE ROCK GEOCHEMISTRY AND SAMPLE PETROGRAPHY

The samples contain 43.3–49.9 wt% SiO₂ along with 13.6–22.9 wt% Al₂O₃, 11.8–18.5 wt% CaO and 9.1–14.7 wt% MgO. Mg-numbers [100*Mg/(Mg+Fe)] are between 75 and 91. Na₂O shows a variation of 1.4–3.1 wt%, Cr and Ni contents are 476–4908 ppm and 166–469 ppm, respectively, with the Cr-spinel bearing samples PM22 and PM26 showing the highest Cr and Ni contents of any eclogites reported so far from the Pohorje Massif (Sassi et al. 2004; Miller et al. 2007). In the Al₂O₃–TiO₂ diagram devised by Pearce (1983) all but two samples plot into the field for plagioclase-rich cumulates (Fig. 2a) which is consistent with high Mg-numbers and CaO contents and with the extremely low K₂O and P₂O₅ contents. The positive correlation trends in Xₘg versus Cr, Ni, Al₂O₃, CaO are similar albeit with a larger scatter compared to those reported by Sassi et al. (2004) and Miller et al. (2007) for cumulate-type (high-Mg) eclogites (Figs. 2b-e) from other localities of the Pohorje Massif.

All investigated eclogites show either equigranular, or in rare instances, corona textures with a mm-scale grain size and characterized by the assemblage omphacite+garnet+rutile. Kyanite, calcic amphibole, zoisite, quartz and accessory phase zircon are common in most samples while phengite and corundum are rarely present. The Cr-spinel bearing samples PM22 and PM26 contain omphacite+garnet+kyanite+calcic amphibole+phengite+quartz+rutile+zircon and
omphacite+garnet+calcic amphibole+kyanite+zoisite+corundum, respectively (Figs. 3a,b). Both, PM22 and PM26, show variable degrees of retrogression evidenced by extremely fine-grained symplectites around omphacite, garnet, kyanite, phengite, and calcic amphibole.

Matrix omphacite forms anhedral to subhedral grains which appear unaffected by retrogression or, more commonly, are mantled by plagioclase±calcic amphibole±clinopyroxene symplectites (symp I) (Fig. 4a). The textures of the omphacite-symplectites indicate a two stage growth commencing with the formation of clinopyroxene+plagioclase followed by calcic amphibole growth at the expense of the former two phases. Omphacite is also present as well preserved inclusions in large matrix kyanite even when matrix omphacite was completely retrogressed and as rare constituent of reaction coronas around Cr-spinel.

Garnet forms rounded grains with inclusions of kyanite and/or omphacite and are often partially replaced by calcic amphibole±plagioclase symplectites (symp II) (Fig. 4a,b). Sometimes chlorite is part of the garnet-symplectites and partially replaces calcic amphibole.

Kyanite is present as large euhedral crystals up to several hundred µm in size either as a matrix phase or as tiny (≤10 µm) needles included in garnet. In sample PM22 matrix kyanite sometimes contains clusters of small (<50-100 µm) drop-like Cr-spinel inclusions in part intergrown with rutile and omphacite (Fig. 3a). Around these spinel inclusions the kyanite shows a strikingly blue to turquoise color and an intense deep-blue–light blue pleochroism. A second textural type of kyanite only occurs as part of Al-rich reaction coronas around large (≤1 mm) Cr-spinel matrix grains in sample PM26 (Fig. 3b). The kyanite, too, shows deep blue color and forms needle-like crystals intergrown with chromian Al-rich pargasite and Cr-rich corundum. Matrix kyanite often displays variable degrees of retrogressive replacement by extremely fine-grained symplectite rims (symp III). BSE-imaging reveals a two layer structure with an inner layer immediately adjacent to kyanite consisting of intermediate plagioclase (An₅₀)+corundum+spinel±sapphirine and an outer layer of calcium-richer plagioclase (An₉₀)±calcic
amphibole directed towards the eclogite matrix phases (Fig. 4c). Both corundum and spinel are close to endmember Al$_2$O$_3$ and MgAl$_2$O$_4$, respectively and sapphirine is strongly peraluminous.

Phengite was only found in PM22 as rare lath-shaped crystals of up to 300 µm in length which are partially replaced by biotite+plagioclase symplecites (symp IV) (Figs. 4d,e).

Two textural types of amphibole are present in the samples investigated. Texturally primary amphibole forms large subhedral and almost colorless grains scattered in the matrix which are in textural equilibrium with omphacite, garnet and kyanite. This amphibole develops, in some instances, thin symplectitic rims (symp V) (Fig. 4d). Texturally secondary amphibole is present as reaction rims around garnet and as part of Al-rich reaction coronas around Cr-spinel matrix grains as found in sample PM26 (Fig. 4f). Secondary amphibole which is part of the Al-rich reaction coronas do not exceed ~300 µm in size and, if sufficiently rich in Cr, may show a pronounced lime green color and green-to-colorless pleochroism (Fig. 3b).

Corundum is present in three textural types: corundum-I is a matrix phase and forms euhedral colorless crystals of up to 300 µm in size in textural equilibrium with garnet, omphacite and calcic amphibole. It often contains inclusions of kyanite and omphacite (Fig. 4f). Corundum-II forms vermicular grains as part of symplectites around kyanite (Fig. 4c) and corundum-III is exclusively present in Cr-spinel reaction coronas intergrown with chromian Al-rich pargasite and Cr-kyanite and shows an intensely red to pink color and strong pleochroism (Fig. 4f).

Cr-spinel was found in PM22 as clusters of honey yellow droplets <50-100 µm in size included in matrix kyanite (Fig. 3a) and in PM26 as reddish-brown euhedral and often strongly poikilitic crystals of up to 1 mm in size. Cr-spinel in PM26 always possesses a spectacular two-layer reaction corona which consists of an inner layer of blue kyanite needles intergrown with pink corundum-III and an outer layer of light green pargasite (Fig. 3b).

Additional minor to accessory constituents of the eclogite-facies assemblages from sample
PM26 is zoisite and pentlandite. PM22 contains zircon and rutile with rutile forming small drop-like inclusions in kyanite associated with Cr-spinel or occurring as matrix phase. Zoisite is present in sample PM26 only as small matrix grains intergrown with omphacite, garnet and/or kyanite.

MINERAL CHEMISTRY

Garnet is pyrope-rich with an observed compositional range pyrope$_{49-53}$grossular$_{19-21}$almandine$_{27-31}$spessartite$_{0.5-2}$ in PM22 and pyrope$_{60-68}$grossular$_{21-25}$almandine$_{11-14}$spessartite$_{<1}$ in PM26, respectively (Figs. 4a,b; Tables 1, 2). No significant compositional zoning could be observed in any of the garnets analyzed. The garnet composition mainly reflects differences in the whole rock composition of the two samples as evidenced by garnet X$_{Mg}$ [=Mg/(Mg+Fe$^{2+}$)] of 0.61-0.66 in PM22 and of 0.81-0.86 in the unusually Mg-rich cumulate PM26. (Table 2).

Matrix omphacite and omphacite inclusions in kyanite are typically unzoned with an observed compositional range diopside$_{56-59}$jadeite$_{31-34}$calcium Tschermak’s pyroxene$_{0.03-0.04}$acmite$_{0.00-0.03}$ in PM22 and diopside$_{57-63}$jadeite$_{27-29}$calcium Tschermak’s pyroxene$_{0.05-0.08}$acmite$_{<0.01}$ in PM26, respectively (Tables 1, 2). Aside from large Cr-poor matrix omphacite, Cr-rich omphacite is present in sample PM26 as part of a reaction corona around large Cr-spinel grains and in sample PM22 associated with Cr-spinel droplets as inclusions in kyanite. This omphacite contains as much as 5.3 wt% Cr$_2$O$_3$, equivalent to 14.8 mol% NaCrSi$_2$O$_6$ (kosmochlor) component (Table 3).

Large matrix kyanite crystals devoid of Cr-spinel inclusions are homogeneous and show a close-to-endmember composition. Kyanite with clusters of drop-like Cr-spinel inclusions from sample PM22 shows a strong and complex discontinuous Cr-zoning in the vicinity of Cr-spinel (Fig. 5) with highly variable Cr$_2$O$_3$ contents reaching 15.6 wt% which is equivalent to 17.6 mol% X$_{Cr-Ky}$ (Table 4; Fig. 6). Fe$_2$O$_3$ contents of the Cr-rich zones reach 0.6 wt% and are positively correlated with Cr$_2$O$_3$ contents. Cr-rich kyanite in reaction coronas around Cr-spinels from sample PM26 does not display
any Cr-zoning and shows lower Cr$_2$O$_3$ contents not exceeding 8.2 wt%. In order to test the effect of Cr–Al exchange on the Raman spectra of kyanite, five compositionally homogeneous areas of sufficient size within zoned Cr-bearing kyanites containing 0.6, 2.1, 6.1, 8.9, and 10.7 wt% Cr$_2$O$_3$ were selected and Raman spectra recorded. Increasing Cr contents result in a systematic and linear shift of the major bands towards lower wave numbers accompanied by a broadening of the bands (Fig. 7a). For example the band at 487 cm$^{-1}$ in the spectrum of kyanite with 0.6 wt% Cr$_2$O$_3$ is shifted to 481 cm$^{-1}$ in the spectrum of kyanite with 10.7 wt% Cr$_2$O$_3$. The corresponding increase in band width at half height is from 4.4 to 12.2 cm$^{-1}$ (Fig. 7b).

Matrix corundum-I only shows very minor Al substitution by Cr and Fe$^{3+}$ (Table 2) whereas corundum-II within symplectites around kyanite is pure Al$_2$O$_3$. By contrast, corundum-III is characterized by variable and in part extremely high Cr$_2$O$_3$ contents of up to 9.1 wt% which corresponds to an eskolaite component of up to 6.3 mol.% (Table 4).

Spinel from sample PM22 is Cr-Fe-dominated and contains minor Al, Mg and Zn (Table 4). In terms of endmembers, the observed range in composition is chromite$^{55-56}$magnesio-chromite$^{22-24}$magnetite$^{01-04}$hercynite$^{14-15}$gahnite$^{03-04}$. In sample PM26 spinel shows significantly lower Fe and Cr combined with higher Al and Mg contents. The observed range in composition is chromite$^{00-05}$magnesiochromite$^{51-56}$magnetite$^{01-02}$hercynite$^{14-15}$gahnite$^{01-02}$spinel$^{00-14}$. (Fig. 8).

Texturally primary amphibole is barroisite to magnesio-hornblende (Leake et al. 2004) (Fig. 9) which contains minor K, Ti and Cr (Tables 1, 2). The texturally secondary amphibole present in the Al-rich spinel reaction coronas in sample PM26 is pargasite, alumino-pargasite or chromian pargasite (Table 3). Cr$_2$O$_3$ contents are highly variable with 0.1-3.9 wt% and decrease with increasing distance from Cr-spinel. The positive Cr–$^{[IV]}$Al and negative Cr–$^{[VI]}$Al correlations are consistent with a combined Tschermaks and $^{[VI]}$Al=$^{[VI]}$Cr exchange.

Phengite from sample PM22 shows 3.25-3.35 Si a.p.f.u. along with minor paragonite solid-
solution \[\{(\text{Na}/(\text{K+Na+Ca}))= 0.04-0.07\]\ (Table 1).

Matrix rutile contains 0.2-0.8 wt% \(\text{Cr}_2\text{O}_3\) and 0.3-0.4 wt% \(\text{Fe}_2\text{O}_3\) along with 302-403 ppm Zr and <65 ppm Nb \((n=9)\). The rutile inclusions in kyanite associated with Cr-spinel-I show significantly higher \(\text{Cr}_2\text{O}_3\) (1.5-1.9 wt%) and Nb (206-289 ppm) combined with lower \(\text{Fe}_2\text{O}_3\) (0.05-0.13 wt%) and Zr (194-330 ppm) (Table 5).

**PT CONDITIONS OF ECLOGITE FACIES METAMORPHISM**

**Phase equilibrium calculations**

Estimates of \(PT\) conditions of eclogite-facies metamorphism in the Pohorje eclogites are controversial. Janak et al. (2004) and Vrabec et al. (2012) reported conditions of \(\sim 820^\circ\text{C}\) and 3 GPa based on the garnet-omphacite-phengite thermobarometer from Krogh-Ravna and Terry (2004). Results of Sassi et al. (2004), Miller et al. (2005a) and Miller and Konzett (2005) yield consistently lower \(PT\) estimates of 650–720°C and 2.1–2.6 GPa. Sample PM22 contains the assemblage garnet+omphacite+phengite which allows the application of various geothermobarometers. Using different thermodynamic datasets and activity models but the same mineral compositions, \(PT\) conditions in the range 640-810°C and 2.0–2.9 GPa were obtained using reactions (1) – (3) or reactions (1) and (4) (Table 1, Fig. 10).

\[
\begin{align*}
\text{Prp} + 2\text{Grs} + 3\text{Cel} &= 3\text{Ms} + 6\text{Di} \\
3\text{Di} + 2\text{Ky} &= \text{Prp} + \text{Grs} + 2\text{Qtz}/\text{Coe} \\
3\text{Cel} + 4\text{Ky} &= \text{Prp} + 3\text{Ms} + 4\text{Qtz}/\text{Coe} \\
\frac{1}{3} \text{Prp} + \text{Hed} &= \frac{1}{3} \text{Alm} + \text{Di}
\end{align*}
\]

The highest \(PT\) values of 780–810°C at 2.7-2.9 GPa were calculated using the net transfer reactions...
(1)–(3) which are considered robust because they are independent of ferric/ferrous iron consideration using the calibration of Krogh-Ravna and Terry (2004). Using the thermodynamic database from Holland and Powell (1998) and calculating activities with AX_2 (http://www.esc.cam.ac.uk/research/research-groups/research-projects/tim-hollands-software-pages/ax) reactions (1)–(3) yield significantly lower $P$ conditions of 2.0–2.1 GPa at a similar $T$ of 770-780°C. The calibration of Brandelik and Massonne (2004) for reactions (1)–(3) yields 710–760°C at 2.4-2.5 GPa. The lowest temperatures of 640-680°C and intermediate pressures of 2.2-2.3 GPa are obtained using clinopyroxene-garnet Fe$^{2+}$–Mg exchange thermometry (reaction 4, Krogh, 2000) together with an updated version of the Waters and Martin (1993) garnet-clinopyroxene-phengite barometer (reaction 1).

To provide additional constraints on temperatures of equilibration for the Cr-kyanite bearing assemblages, Zr-in-rutile thermometry was applied to sample PM22 in which rutile is present as small ($\leq$40x70 μm) inclusions in Cr-kyanite associated with Cr-spinel and also as larger ($\leq$350x450 μm) grains scattered in the matrix. Although individual rutile grains are compositionally unzoned within the analytical error of an individual analysis, there is some inter-grain variation (Table 5). Using a pressure of 2.5 GPa, averaged temperatures derived from 14 rutile analyses are 721±25°C and 717±17°C based on the calibrations devised by Zack et al. (2004) and Thomkins et al. (2007), respectively. Averaged temperatures for rutile inclusions in Cr-kyanite and for matrix grains do not yield statistically different values.

DISCUSSION

The formation of Cr-kyanite in the context of high-P metamorphism in the Pohorje Massif

In samples PM22 and PM26 Cr-kyanite occurs in two different textures, namely (1) as matrix
kyanite with ±irregularly shaped Cr-rich segments around Cr-spinel inclusions and (2) as part of reaction coronas around large Cr-spinel grains.

In case of PM22 it is obvious that Cr-spinel was consumed while matrix kyanite formed (Figs. 3, 5). Because the Cr-rich kyanite portions are part of the large matrix kyanites we suggest that this reaction took place during prograde metamorphism. Omphacite and rutile inclusions are also found together with Cr-spinel in the Cr-rich kyanites. Possible simplified endmember reactions involving spinel as a reactant phase are:

\[ \text{Sp} + \text{Pl} = \text{Ky} + \text{Omp} \pm \text{Grt} \]  
\[ \text{Sp} + \text{Qtz} = \text{Ky} + \text{Grt} \]  

Unlike in sample PM22, the large Cr-spinels in sample PM26 did not break down during a significant portion of the prograde metamorphic PT path. Textures clearly indicate that Cr-spinel reacts with omphacite and garnet to produce a spherical corona consisting of an inner portion that contains Cr-rich kyanite and an outer portion mainly consisting of chromian pargasite (Fig. 3b). Cr-rich corundum as well as omphacite occur in subordinate amounts mainly in the inner portions of the coronas. Based on the observed mineral assemblages in PM26, potential kyanite and corundum producing reactions are

\[ \text{Sp} + \text{Prp} + \text{Di} + \text{Jd} = \text{Prg} + \text{Ky} \]  
\[ \text{Sp} + \text{Prp} + \text{Grs} + \text{Jd} = \text{Prg} + \text{Ky} \]  
\[ \text{Sp} + \text{Grs} + \text{Jd} + \text{Ky} = \text{Prg} + \text{Crn} \]  

Their location in PT space was calculated in NCMASH system using appropriate activity models (Fig. 3d, 3e).
Following a decompression $PT$ path, crystallization of Cr-rich kyanite occurs at significantly higher pressures than formation of Cr-rich corundum. However, a change in water activity may shift reactions to lower $T$ and $P$. Nevertheless, textural evidence does not support this conclusion that these minerals formed at different stages along the retrograde path. In general, corona textures indicate that a mineral reaction did not proceed to completion and are a sign of disequilibrium. In case of samples PM22 and PM26, Cr-spinel is a magmatic relic inherited from the eclogite precursor rock and started to react with the eclogite facies minerals garnet and omphacite during progressive metamorphism. As evidenced by the presence of abundant pargasite within the reaction coronas, hydrous fluids must have been involved in the corona formation. These fluids are rarely pure H$_2$O but usually contain variable amounts of CO$_2$ along with various dissolved species amongst which SiO$_2,aq$ and NaCl$_{aq}$ are often dominant (e.g. Hauzenberger et al., 2001; Manning, 2004). An influx of hydrous fluid associated with a change in the chemical potential of SiO$_2$ and/or Na$_2$O at the interface between Cr-spinel and the matrix phases provides a potential explanation for corona formation as outlined in Fig. 11b which shows a SiO$_2$ versus Na$_2$O chemical potential diagram for 800°C and 2.5 GPa that was calculated using the activity models as for Fig. 11a. Figure 11b shows that at pressures and temperatures close to the peak of Eoalpine eclogite-facies metamorphism and in a chemical system characterized by $a_{SiO2}$<1, an increase in $\mu$SiO$_2$ resulting from an influx of fluid may trigger pargasite and/or kyanite-formation through the following reactions (Fig. 11b):

$$\text{Sp + Di + Prp} = \text{Prg} \quad (6)$$

$$\text{Di + Sp} = \text{Prg + Ky} \quad (7)$$

$$\text{Grs + Sp} = \text{Prg + Ky} \quad (8)$$
The chemical potential of $\text{Na}_2\text{O}$ probably did not change significantly during reaction progress because of abundant omphacite present in the matrix that buffers this component.

The timing of Cr-kyanite formation

Green and Ringwood (1967) showed that phases with aluminium-rich compositions form kyanite in eclogites with the breakdown of plagioclase occurring at approximately 1.5 GPa and 700°C. Cr-spinel overgrown by and eventually enclosed in newly formed but still Cr-poor kyanite is thought to represent the first step in the formation of Cr-kyanites in sample PM22 that took place at pressures above approximately 1.5 GPa. In a second step rising $P$ and $T$ caused increasing $\text{Cr}_2\text{SiO}_5$-solubility in kyanite resulting in an exchange reaction $\text{Al}_2\text{SiO}_5 + \text{FeCr}_2\text{O}_4 = \text{Cr}_2\text{SiO}_5 + \text{FeAl}_2\text{O}_4$ involving newly formed kyanite and Cr-spinel inherited from the magmatic precursor (cf. Gil-Ibarguchi et al. 1991). Thus, Cr-kyanite from sample PM22 predates the formation of Cr-rich corona kyanite from sample PM26 whose formation requires the breakdown of eclogite-facies phases during the retrograde portion of the $PT$-path.

Retrogression of eclogite to amphibolite is widespread in the Saualpe, Koralpe and Pohorje area of the Eastern Alpine basement and is attributed to a pervasive fluid influx during uplift. Based on the fluid-influx model as outlined in Fig. 11b the formation of Cr-rich kyanites within the spinel coronas from sample PM26 is not a prograde but a retrograde phenomenon associated with the earliest stage of the exhumation path but under still high pressures. This is supported by small inclusions of Cr-rich omphacite found within the coronas which are a clear indication for eclogite facies conditions. Hence, mineral textures and phase equilibrium calculations would be consistent with the following scenario (Fig. 12): during prograde metamorphism large magmatic Cr-spinel grains initially remained unaffected by rising $PT$ conditions due to sluggish reaction kinetics. Influx of a hydrous fluid during the initial stage of decompression increased the chemical potential of $\text{SiO}_2$ and strongly accelerated
reaction kinetics, allowing various kyanite-, amphibole-, and corundum-forming reactions to proceed. The spatial distribution of phases within the coronas is consistent with increasing chemical potential of SiO₂ and decreasing chemical potentials of Al₂O₃ and Cr₂O₃ from spinel towards the matrix (Fig. 12).

**IMPLICATIONS**

Within the two investigated samples PM22 and PM26, Cr-spinel-bearing gabbroic cumulates from the Pohorje Massif, blue Cr-kyanite formed in two different textural micro-environments. A first type present in sample PM22 encloses clusters of small drop-like Cr-spinel inclusions and contains up to 15.6 wt% Cr₂O₃. The most intense blue color occurs in the immediate vicinity to the Cr-spinel. A second type is present in sample PM26 as part of Al-rich reaction coronas developed around large red-brownish Cr-spinel magmatic relics. Within these coronas Cr-kyanite appears as deep blue needle-like crystals that contain up to 8.2 wt% Cr₂O₃ and is associated with red-pink Cr-rich corundum containing up to 9.1 wt% Cr₂O₃ and Cr-Al-rich pargasite with up to 3.9 wt% Cr₂O₃. The blue color of kyanite and the red-pink color of corundum are a result of Cr-Al substitution in octahedral sites during high pressure/ultra-high pressure metamorphism. Whereas Cr-kyanite in sample PM22 formed under increasing PT conditions during prograde metamorphism, Cr-kyanite and the associated Cr-rich corona-assemblage in sample PM26 were generated during the earliest stage of retrogressive evolution of these rocks still at eclogite-facies PT conditions of ~2.5 GPa and 750-800°C.

**ACKNOWLEDGMENTS**

We would like to thank Zmargo Zorg, Anton Gutschi and Walter Postl for their support during field work. We are particularly indebted to Zmargo Zorg who has been ranging the Pohorje Massif for eclogite occurrences for many years. Anton Pock, Juergen Neubauer, Karl Ettinger, and Reinhard Kaindl are thanked for thin section preparation, SEM support, performing EPMA analysis, and support.
for Raman analysis, respectively. We thank Håkon Austrheim, Gerhard Franz and an unknown reviewer for their comments and corrections.

REFERENCES CITED


Miller, C. (1990) Petrology of the type locality eclogites from the Koralpe and Saualpe (Eastern Alps), Austria. Schweizerische Mineralogische und Petrographische Mitteilungen, 70, 287-300.


Pivin, M., Berger, J., and Demaiffe, D. (2011) Nature and origin of an exceptionally Cr-rich kyanite-


LIST OF FIGURE CAPTIONS

Figure 1. (a) Schematic map of the Saualpe-Koralpe-Pohorje domain (modified from Miller et al., 2007) showing the distribution of regions overprinted by greenschist, amphibolite and eclogite facies metamorphic conditions; major eclogite bodies are displayed by filled ellipses; (b) Simplified geological map of the Pohorje Mountains and adjacent areas (modified after Mioč and Žnidarčič, 1977 and Janák et al., 2004); the sampling area is indicated by the dashed rectangle in the southeastern part of the Pohorje Massif. Major fault systems are represented by bold lines.

Figure 2. (a)-(e) Correlation plots of selected major and trace elements for Cr-spinel-bearing (PM22: black star; PM26: open star) and Cr-spinel-free (black dots) eclogites from the Slovenska Bistrica area compared to Mg-rich and Mg-poor eclogite bulk compositions from the Koralpe, Saualpe and Pohorje Mountains reported by Miller et al. (2007) (M07) and Sassi et al. (2004) (S04); field boundaries in (a) according to Pearce (1983); Mg# = [100*Mg/(Mg+Fe_{tot}^{2+})]

Figure 3. Optical photomicrographs of Cr-rich assemblages; (a) cluster of turquoise-colored Cr-bearing kyanites enclosing vermicular Cr-spinel grains from sample PM22; note the zonal coloring which is most intense in the immediate vicinity of the Cr-spinel inclusions where Cr contents of kyanite are highest; (b) turquoise-colored Cr-bearing kyanites and pink Cr-bearing corundum forming the inner portion of a reaction corona around a large Cr-spinel grain from sample PM26; the outer portion of the corona consists of pale-green Cr-pargasite which may contain relics of omphacite and garnet indicating a reaction Cr-spinel + omphacite + garnet + H_{2}O = kyanite + corundum + pargasite.

Figure 4. back-scattered electron (BSE) images showing selected microtextures of eclogite-facies
assemblages affected by subsequent retrograde overprint; (a) weakly retrogressed domain of Cr-kyanite-bearing sample PM22 with omphacite and garnet mantled by narrow symplectitic rims of Amp+Di+Plag (symp I) and of Amp+Plag (symp II), respectively. Symplectites around kyanite consist of Crn+Spl+Pl (symp III). (b) High-Mg coronitic eclogite PM26 containing abundant garnet with kyanite and omphacite inclusions. Incipient retrogressive breakdown of omphacite to form symp I assemblages can be observed in the upper center. (c) complex symplectite corona around kyanite: 1) the main part contains Crn+An90, Spr+An90 and Spl+An90 symplectites which are surrounded by a thin An50 rim. (d) texturally primary amphibole from sample PM22 with a thin symplectitic reaction rim towards coexisting omphacite (symp V); (e) Phengite surrounded by a symplectite Pl+Bt rim (symp IV); (f) two textural types of corundum from sample PM26; Crn-I forms lath-shaped poikilitic matrix grains up to 300 µm in size whereas Crn-III is found as part of reaction coronas around Cr-spinel grains associated with Cr-rich kyanite and Cr-rich pargasite; a third textural type of Crn (Crn-II) forms tiny needles which are part of symplectite rims around kyanite (see Fig. 3c).

Figure 5. BSE image and Al, Cr, and Fe X-ray maps of Cr-rich kyanite from samples PM22. Droplets of Cr-spinels are enclosed in kyanite, which is surrounded by a plagioclase–corundum–Mg-Al-spinel symplectite (symp III). The higher Cr content in kyanite is seen as lighter gray areas around the white spinels in the BSE image and as light bluish to greenish colour in the Cr X-ray map. Dark color (black–blue) indicate low concentrations while green–yellow–red colors indicate higher concentrations.

Figure 6. Range of Cr–Al substitution in kyanite from this study compared to data for Cr-rich kyanites from the literature.

Figure 7. (a) Raman spectra for kyanites with 0.6 and 10.7 wt%. With increasing Cr content the bands
show both a broadening and a systematic shift towards lower wave numbers; (b) band shift and
broadening of three Raman bands as a function of Cr content for kyanites with 0.6, 2.1, 8.9, and 10.7
wt% Cr₂O₃.

Figure 8. Compositional variation of spinel from samples PM22 and PM26 in terms of molar Al–Mg–
Fe³⁺.

Figure 9. Compositional variation of texturally primary and secondary calcic amphiboles from samples
PM22 and PM26; primary amphiboles contain low and constant Cr₂O₃ contents in the range 0.10-0.15
wt% without any significant Al–Cr variation.

Figure 10. Peak metamorphic $PT$ conditions of kyanite eclogite sample PM22 using various mineral
equilibrum or calibrations (Krogh-Ravna and Terry 2004; Holland and Powell 1998; Brandelik and
Massonne 2004; Waters and Martin 1993 in combination with Cpx–Grt exchange thermometer after
Krogh 2000). The numbers on reaction curves correspond to reaction number in the text.

Figure 11. Calculated Cr-kyanite and Cr-corundum-forming reactions for sample PM26 expressed in
terms of endmembers using Perple_X (Connolly, 1990) with the thermodynamic dataset of Holland and
Powell (1998 and updates). Endmember activity corrections were performed using the program AX_2
provided by Tim Holland ($a_{Sp}$: 0.13; $a_{Ky}$: 0.83; $a_{Grs}$: 0.08; $a_{Prp}$: 0.35; $a_{Cor}$: 0.9; $a_{Prg}$: 0.30; $a_{Jd}$: 0.32). (a) $PT$
diagram with Cr-kyanite and Cr-corundum-forming reactions. Reactions 2 and 4 produce kyanite
and pargasite at or close to peak $PT$ conditions. Along an assumed exhumation path corundum forms at
lower $PT$ conditions. Stippled lines are calculated with lower $X_{H₂O}$. (b) Simplified isothermal and
isobaric $\mu$SiO₂–$\mu$ Na₂O diagram reproducing the observed formation of Ky, Prg, and Cor.
reduced SiO$_2$ activity was responsible for Cor formation ($K_y = \text{Cor}$).

Figure 12. Sketch explaining the formation of observed spherical coronas around Cr-spinel: (a) Crystallization of eclogite facies assemblage where Cr-spinel remained as magmatic cummulate phase unaffected. (b) Infiltration of H$_2$O-rich fluids (+SiO$_2_{aq}$, +NaCl$_{aq}$) during onset of exhumation increasing chemical potential of SiO$_2$ which facilitates the breakdown of Cr-spinel. (c) Observed corona in sample PM26 (Fig. 3).
this study

Pivin et al. (2011)

Delor & Leyreloup (1985)

Gil-Ibarguchi et al. (1991)

Sobolev et al. (1968)

Negulescu & Sabau (2012)
Table 1. Representative analyses of minerals stable at peak metamorphic conditions from sample PM22

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### Table 2. Representative analyses of minerals stable at peak metamorphic conditions from sample PM26

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| X₅ₛ₅ | 0.295      | 0.308      | 0.632      | 0.638      | 0.609      | 0.666      | 0.962      | 0.014      | 0.014      |
| X₆ₛ₅ | 0.956      | 0.957      | 0.230      | 0.230      | 0.249      | 0.217      | 0.134      | 0.130      |
| X₇ₛ₅ | 0.004      | 0.001      | 0.003      | 0.003      | 0.825      | 0.831      | 0.815      | 0.854      | 0.854      |

Seite 1
**TABLE 3.** Chemical composition of Cr-rich omphacite and amphibole from samples PM22 and PM26

<table>
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<tr>
<th></th>
<th>Omphacite PM22om1</th>
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<th>Aluminopargasite PM26a1</th>
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<td>16.83</td>
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<td>97.62</td>
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|                |                |                |                          |                          |
| Si             | 1.936          | 1.923          | 6.208                    | 6.382                    |
| Ti             | 0.002          | -              | 0.017                    | 0.010                    |
| Al             | 0.327          | 0.390          | 2.681                    | 2.762                    |
| Cr             | 0.148          | 0.102          | 0.439                    | 0.166                    |
| Fe<sup>3+</sup>| 0.019          | -              | 0.000                    | 0.000                    |
| Fe<sup>2+</sup>| 0.047          | 0.023          | 0.244                    | 0.289                    |
| Mn             | -              | -              | 0.002                    | 0.002                    |
| Mg             | 0.557          | 0.583          | 3.465                    | 3.488                    |
| Ca             | 0.594          | 0.607          | 1.607                    | 1.569                    |
| Na             | 0.370          | 0.372          | 0.967                    | 0.938                    |
| K              | -              | -              | 0.016                    | 0.014                    |
| Sum            | 4.000          | 4.000          | 15.646                   | 15.620                   |

|                |                |                |                          |                          |
| X<sub>Mg</sub> | 0.922          | 0.962          | 0.934                    | 0.923                    |
| X<sub>Na</sub> | 0.384          | 0.380          |                          |                          |
| X<sub>Ca</sub>| 0.148          | 0.102          |                          |                          |
| X<sub>Fe<sup>3+</sup></sub> | 0.203 | 0.270          |                          |                          |
| X<sub>Al</sub> | 0.019          | 0.000          |                          |                          |
| X<sub>Ca-Ts</sub> | 0.062 | 0.060          |                          |                          |
| X<sub>Si</sub> | 0.532          | 0.547          |                          |                          |
| X<sub>Na</sub> | 0.047          | 0.023          |                          |                          |
TABLE 4. Chemical composition of Cr-rich kyanite, corundum, and spinel from samples PM22 and PM26

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<tr>
<th></th>
<th>PM22ck1</th>
<th>PM22ck2</th>
<th>PM22ky2</th>
<th>PM26ky1</th>
<th>PM26ky2</th>
<th>PM26k3</th>
<th>PM26k8</th>
<th>PM22sp11</th>
<th>PM22sp12</th>
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<td>0.10</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
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<td>&lt;0.05</td>
<td>&lt;0.05</td>
<td>&lt;0.05</td>
<td>&lt;0.05</td>
<td>&lt;0.05</td>
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<td>9.06</td>
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