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7 **Genesis of chromium-rich kyanite in eclogite-facies Cr-spinel-bearing gabbroic**

8 **cumulates, Pohorje Massif, Eastern Alps**

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18   **ABSTRACT**

19   Natural kyanites with Cr_2O_3 contents >1 wt% are very rare and known only from high-P environments.

20   One example are eclogite-facies gabbroic cumulates containing Cr-spinel from the Pohorje Massif,

21   Eastern Alps, Slovenia. In these rocks turquoise coloured Cr-rich kyanites are present in two different

22   textural types: A first type has formed as blocky crystals of several hundred μm in size around clusters

23   of small drop-like Cr-spinels. This kyanite shows a highly irregular Cr distribution and may contain up

24   to 15.6 wt% Cr_2O_3 which is one of the highest Cr_2O_3 contents reported so far. A second type is present

25   as part of reaction coronas around large red-brownish Cr-spinel and forms deep-blue needle-like

26   crystals which rarely exceed 100 μm in size. This kyanite contains up to 8.2 wt% Cr_2O_3 and is

27   associated with Cr-rich corundum ($\leq$ 9.1 wt% Cr_2O_3) and Cr-Al-rich pargasite ($\leq$3.9 wt% Cr_2O_3). The

28   formation of kyanite around Cr-spinel droplets is interpreted to be the result of increasing *PT*

29   conditions during prograde metamorphism where Cr-spinel and plagioclase or quartz react to Cr-

30   kyanite, ±garnet, ±omphacite. In contrast, the formation of kyanite associated with Cr-rich corundum

31   and Cr-rich pargasite within coronas around Cr-spinel occurred in an early stage of the retrogressive

32   evolution of the gabbroic cumulates at eclogite-facies conditions of ~2.5 GPa and 750 – 800°C

33   triggered by the influx of H_2O-rich fluids. The driving force for developing these coronas was an

34   increase in the chemical potential of silica caused by the infiltrating hydrous fluid phase. *PT* estimates

35   using matrix mineral assemblage place the peak metamorphic conditions close to the quartz/coesite

36   transition with temperatures in the range of 750–810°C and pressures of ~2.9 GPa.

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38   **Keywords:** Cr-rich kyanite, Cr-rich corundum, eclogite facies cummulates, Pohorje Massif,

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41 **INTRODUCTION**

42   Kyanite is a common metamorphic mineral in metapelites and Al-rich metabasites at medium to

43   high pressures and can accomodate substantial amounts of manganese, iron (e.g. Chinner et al. 1969;

44   Grambling and Williams 1984) and especially chromium in its crystal structure. Cr–Al substitution

45   results in a spectacular turquoise-blue color and strong pleochroism as reported by Sobolev (1968),

46   Cooper (1980), and Gil-Ibarguchi (1991). Cr–Al substitution in synthetic kyanite, on the other hand,

47   produces a deep emerald green color (Langer and Seifert 1974). This suggestes that the blue color of

48   natural Cr-bearing kyanite results from a combination of Cr and additional minor substituents such as

49   Fe and/or Ti (White and White 1967; Rost and Simon 1972). Natural kyanite with Cr_2O_3 contents >1

50   wt% have been known so far only from high-P environments. The highest Cr_2O_3 content documented

51   in the literature so far is 15.7 wt% which corresponds to ~18 mol% Cr_2SiO_5 component and was

52   reported by Negulescu and Sabau (2012) from chromite-bearing meta-gabbroic eclogites. Kyanite with

53   up to 12.7 and 11.8 wt% Cr_2O_3 were reported by by Sobolev et al. (1968) and Pivin et al. (2011) from

54   kimberlite-derived grosspydite and clinopyroxenite nodules. Kyanite with up to 25 mol% Cr_2SiO_5 was

55   synthesized by Langer and Seifert (1974) at 3 GPa and 1300-1500°C. These authors suggested that

56   significant amounts of Cr can enter the kyanite structure only at P $\geq$1.8 GPa and T $\geq$900°C and that the

57   amount of Cr incorporated is positively correlated with both *P* and *T*. A comparison with *PT* conditions

58   of equilibration estimated for Cr-kyanite-bearing eclogite from the South Carpathians by Negulescu

59   and Sabau 2012 shows that whereas high pressures are indeed essential, temperatures as low as 600°C

60   are sufficient to allow substantial Al–Cr substitution Hence, high pressures in excess of ~2GPa and a

61   suitable source of Cr which is usually Cr-spinel are essential pre-requisites for the formation of Cr-rich

62   kyanite.

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64   Eclogites within the Eastern alpine crystalline basement typically appear as lenses and small

65   bodies of up to several hundred meters in size within a narrow E-W trending zone, ~400 km in length,

66   immediately north of the Periadriatic Lineament which is termed Eo-alpine high pressure belt (EHB)

67   (Hoinkes et. al. 1991; Thöni and Jagoutz 1993; Exner et al. 2001; Sölva et al. 2005 a,b). The south-

68   easternmost part of the EHB is represented by eclogites of the Pohorje massif (e.g. Ippen 1892;

69   Hinterlechner-Ravnik and Moine 1977; Hinterlechner-Ravnik et al. 1991a,b; Janak et al. 2004; Miller

70   et al. 2005a; Vrabec et al. 2012) and of the Koralpe and Saualpe basement complexes (Miller 1990;

71   Miller and Thöni 1997; Miller et al. 2005b) (Fig. 1a). Most Eoalpine eclogites including those from the

72   Pohorje massif are derived from MORB-type precursors (Miller et al. 1988; Miller and Thöni 1997;

73   Miller et al. 2005b) and only a minor part has intra-plate characteristics (Hoinkes et al. 1991; Konzett

74   et al. 2011). Major and trace element systematics of the Koralpe-Saualpe-Pohorje eclogites indicate

75   two different modes of formation of the precursors: (1) low-Mg gabbros derived from evolved tholeiitic

76   magmas not significantly influenced by cumulate formation and (2) high-Mg–Al–Ca gabbros depleted

77   in alkalis and with pronounced positive Eu-anomalies which are thought to represent plagioclase-rich

78   cumulates (Miller 1990; Sassi et al. 2004). A significant portion of these meta-cumulates contains

79   kyanite as a major constituent of the eclogite-facies assemblage (Sassi et al. 2004; Miller et al. 2005b,

80   2007).

81   Here we report the occurrence of high-Mg cumulate-type eclogites from the Pohorje Massif that

82   are unique amongst all eastern Alpine eclogites known so far in that their precursors contain Cr-spinel

83   as cumulate phase. These Cr-spinels create a geochemical micro-environment in which unusually Cr-

84   rich kyanite is present together with Cr-rich omphacite, pargasite and corundum. The Cr-contents of

85   kyanite are amongst the highest found so far in a natural environment. We present (1) mineral chemical

86   data for the Cr-rich high pressure assemblage along with bulk rock compositions of the host rocks, (2)

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87   results of phase equilibrium calculations to determine *PT* conditions of formation of the Cr-rich phase

88   assemblage, and (3) a model for the formation of the Cr-rich phase assemblage

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90   **GEOLOGICAL SETTING**

91   Eclogites and associated high-pressure metapelites form an important albeit small portion of the

92   Eastern alpine crystalline basement and testify to intracontinental subduction during Jurassic to

93   Cretaceous collision of the African and Eurasian lithospheres (Thöni 1999). Peak *PT*-conditions for the

94   Eoalpine eclogite-facies metamorphism increase from ~1.2 GPa and 550°C in the westernmost portions

95   of the Eastern Alps to ~3.0 GPa and 800°C in the Pohorje Massif (Hoinkes et al. 1991; Janak et al.

96   2004; Miller and Konzett 2005; Vrabec et al. 2012; this study). A multitude of geochronological

97   methods applied to the eclogite facies assemblages yields consistent ages of 85–115 Ma (Thöni 2006

98   and references; Konzett et al. 2011). For the Pohorje Massif the age of high-*P* metamorphism is tightly

99   constrained by U-Pb zircon and whole rock-garnet Sm-Nd ages for eclogites and their host metapelites

100 with 90.7±1.0 and 92.0±0.5 Ma, respectively (Miller et al. 2007; Janak et al. 2009). For the mainly

101 gabbroic eclogite precursors, Permian emplacement ages in the range 247–275 Ma were determined

102 (Thöni and Jagoutz 1993; Miller and Thöni 1997). In terms of large-scale tectonics the Pohorje Massif

103 is a nappe stack which consists of three tectonic units (Mioč and Žnidarčič 1977; Fodor et al. 2003)

104 (Fig. 1b). The lowermost unit is termed Pohorje nappe (Janák et al. 2006) and consists of medium to

105 high-grade micaschist, gneiss and amphibolite with lenses of marble, quartzite, eclogite and ultrabasic

106 rocks. This unit is folded into an ESE–WNW-striking antiform containing the Pohorje tonalite-

107 granodiorite in its core which was emplaced during the Oligocene to Miocene (Altherr et al. 1995;

108 Fodor et al. 2008). The Pohorje nappe is overlain by low-grade metamorphic Paleozoic slate and

109 phyllite and the uppermost nappe on top of these rocks consists of Permo-Triassic sandstone and

110 conglomerate. This nappe stack is covered by early Miocene sediments of the Pannonian Basin.

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111   The eclogite samples investigated in this study were collected from poorly exposed outcrops

112   along a road situated at N 46° 24' 14.3" and E 015° 29' 25.7" close to Slovenska Bistrica (Fig. 1b).

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114   **ANALYTICAL METHODS**

115   Mineral compositions were determined with a scanning electron microprobe JEOL JSM-6310 at the University of

116   Graz, Austria, using an energy and wavelength dispersive spectrometer (15 kV acceleration voltage and 6 nA beam current)

117   with 30 seconds on peak and 15 seconds on background for elements determined by WDX. The following standards were

118   used: Na (WDX), jadeite; Fe, Mg (EDX), garnet and kaersutite; K, Al, Si (EDX), adularia; Ca, Ti (EDX), titanite; Cr

119   (EDX), chromite; Mn (EDX), rhodonite; Zn (EDX), gahnite; F (WDX), synthetic F-phlogopite. Since Si content in phengite

120   is crucial for pressure determination, a muscovite standard was used instead of adularia for Si in order to ensure a similar

121   matrix for analyses of unknowns and standard. Additional electron microprobe analyses were obtained using a JEOL

122   Superprobe JXA 8200, Universitaetszentrum für Angewandte Geowissenschaften (UZAG) at the University of Leoben

123   (Austria). Analytical conditions were 15 kV accelerating voltage and 10 nA beam current with 30 seconds on peaks and 15

124   seconds on backgrounds of the X-ray lines. Zirconium in rutile was analyzed using a JEOL JXA-8100 Superprobe at the

125   University of Innsbruck with analytical conditions of 15 kV and 150 nA. Counting times were set to 300 sec on the peak

126   and 150 sec on the backgrounds of the $ZrL\alpha$ line using a PETH-crystal. This yields a 2-sigma count statistical error of 9%

127   for a Zr concentration of 300 ppm. The accuracy of Zr measurements was checked intermittently with a rutile standard

128   kindly supplied by T. Zack. Mineral formulae and single geothermobarometer reactions were calculated with the

129   Mathematica package PET (Dachs 2004).

130   Whole rock major and trace element compositions were determined by X-ray fluorescence spectroscopy using a

131   Bruker Pioneer S4 XRF at the Institute of Earth Sciences, University of Graz. The samples were prepared as fused pellets

132   using 7 gram of Li_2B4O_7 and 1 gram of finely powdered and dried sample. The loss on ignition (LOI) was determined from

133   the total weight change after heating to $1030^{\circ}C$ for 1 hour.

134   Unpolarized spectra of kyanites were measured on a HORIBA Labram HR-800 confocal Raman-spectrometer,

135   using the 514 nm excitation wavelength of a 30 mW Nd-YAG laser, through a 100x objective with a numerical aperture of

136   0.9. Standard optical and electron microprobe backscattered electron images were used to target areas that are homogeneous

137   in composition and free of visible inclusions. Size and power of the laser spot on the surface was approximately 1 μm and 5

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138   mW, respectively. Confocal pinhole and entrance slit were set to 1000 and 100 μm. The scattered Raman light was

139   dispersed by a grating with 1800 lines/mm and detected by an open-electrode CCD with 1024 x 256 pixels, each sizing 43

140   μm. The spectral resolution, determined by measuring the Rayleigh line, was 1.4 cm^{-1}. Background and Raman bands were

141   fitted by the built-in spectrometer software LabSpec to first or second order polynomials and convoluted Gauss-Lorentz

142   functions. The accuracy of Raman line shifts was checked by regular measurements of the emission lines of a Ne spectral

143   calibration lamp and is on the order of 0.5 wavenumbers.

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145   **WHOLE ROCK GEOCHEMISTRY AND SAMPLE PETROGRAPHY**

146   The samples contain 43.3–49.9 wt% SiO_2 along with 13.6–22.9 wt% Al_2O_3, 11.8–18.5 wt%

147   CaO and 9.1–14.7 wt% MgO. Mg-numbers [100*Mg/(Mg+Fe)] are between 75 and 91. Na_2O shows a

148   variation of 1.4–3.1 wt%, Cr and Ni contents are 476–4908 ppm and 166–469 ppm, respectively, with

149   the Cr-spinel bearing samples PM22 and PM26 showing the highest Cr and Ni contents of any

150   eclogites reported so far from the Pohorje Massif (Sassi et al. 2004; Miller et al. 2007). In the Al_2O_3–

151   TiO_2 diagram devised by Pearce (1983) all but two samples plot into the field for plagioclase-rich

152   cumulates (Fig. 2a) which is consistent with high Mg-numbers and CaO contents and with the

153   extremely low K_2O and P_2O_5 contents. The positive correlation trends in X_{mg} versus Cr, Ni, Al_2O_3 ,

154   CaO are similar albeit with a larger scatter compared to those reported by Sassi et al. (2004) and Miller

155   et al. (2007) for cumulate-type (high-Mg) eclogites (Figs. 2b-e) from other localities of the Pohorje

156   Massif.

157   All investigated eclogites show either equigranular, or in rare instances, corona textures with a

158   mm-scale grain size and characterized by the assemblage omphacite+garnet+rutile. Kyanite, calcic

159   amphibole, zoisite, quartz and accessory phase zircon are common in most samples while phengite and

160   corundum   are   rarely   present.   The   Cr-spinel   bearing   samples   PM22   and   PM26   contain

161   omphacite+garnet+kyanite+calcic   amphibole+phengite+quartz+rutile+zircon   and

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162   omphacite+garnet+calcic amphibole+kyanite+zoisite+corundum, respectively (Figs. 3a,b). Both, PM22

163   and PM26, show variable degrees of retrogression evidenced by extremely fine-grained symplectites

164   around omphacite, garnet, kyanite, phengite, and calcic amphibole.

165   Matrix omphacite forms anhedral to subhedral grains which appear unaffected by retrogression

166   or, more commonly, are mantled by plagioclase±calcic amphibole±clinopyroxene symplectites (symp

167   I) (Fig. 4a). The textures of the omphacite-symplectites indicate a two stage growth commencing with

168   the formation of clinopyroxene+plagioclase followed by calcic amphibole growth at the expense of the

169   former two phases. Omphacite is also present as well preserved inclusions in large matrix kyanite even

170   when matrix omphacite was completely retrogressed and as rare constituent of reaction coronas around

171   Cr-spinel.

172   Garnet forms rounded grains with inclusions of kyanite and/or omphacite and are often partially

173   replaced by calcic amphibole±plagioclase symplectites (symp II) (Fig. 4a,b). Sometimes chlorite is part

174   of the garnet-symplectites and partially replaces calcic amphible.

175   Kyanite is present as large euhedral crystals up to several hundred μm in size either as a matrix

176   phase or as tiny (≤10 μm) needles included in garnet. In sample PM22 matrix kyanite sometimes

177   contains clusters of small (<50-100 μm) drop-like Cr-spinel inclusions in part intergrown with rutile

178   and omphacite (Fig. 3a). Around these spinel inclusions the kyanite shows a strikingly blue to turquoise

179   color and an intense deep-blue–light blue pleochroism. A second textural type of kyanite only occurs as

180   part of Al-rich reaction coronas around large (≤1 mm) Cr-spinel matrix grains in sample PM26 (Fig.

181   3b). The kyanite, too, shows deep blue color and forms needle-like crystals intergrown with chromian

182   Al-rich pargasite and Cr-rich corundum. Matrix kyanite often displays variable degrees of retrogressive

183   replacement by extremely fine-grained symplectite rims (symp III). BSE-imaging reveals a two layer

184   structure with an inner layer immediately adjacent to kyanite consisting of intermediate plagioclase

185   (An_{50})+corundum+spinel±sapphirine and an outer layer of calcium-richer plagioclase (An_{90})±calcic

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186   amphibole directed towards the eclogite matrix phases (Fig. 4c). Both corundum and spinel are close to

187   endmember Al$_2$O$_3$ and MgAl$_2$O$_4$, respectively and sapphirine is strongly peraluminous.

188   Phengite was only found in PM22 as rare lath-shaped crystals of up to 300 μm in length which

189   are partially replaced by biotite+plagioclase symplecites (symp IV) (Figs. 4d,e).

190   Two textural types of amphibole are present in the samples investigated. Texturally primary

191   amphibole forms large subhedral and almost colorless grains scattered in the matrix which are in

192   textural equilibrium with omphacite, garnet and kyanite. This amphibole develops, in some instances,

193   thin symplectitic rims (symp V) (Fig. 4d). Texturally secondary amphibole is present as reaction rims

194   around garnet and as part of Al-rich reaction coronas around Cr-spinel matrix grains as found in sample

195   PM26 (Fig. 4f). Secondary amphibole which is part of the Al-rich reaction coronas do not exceed ~300

196   μm in size and, if sufficiently rich in Cr, may show a pronounced lime green color and green-to-

197   colorless pleochroism (Fig. 3b).

198   Corundum is present in three textural types: corundum-I is a matrix phase and forms euhedral

199   colorless crystals of up to 300 μm in size in textural equilibrium with garnet, omphacite and calcic

200   amphibole. It often contains inclusions of kyanite and omphacite (Fig. 4f). Corundum-II forms

201   vermicular grains as part of symplectites around kyanite (Fig. 4c) and corundum-III is exclusively

202   present in Cr-spinel reaction coronas intergrown with chromian Al-rich pargasite and Cr-kyanite and

203   shows an intensely red to pink color and strong pleochroism (Fig. 4f).

204   Cr-spinel was found in PM22 as clusters of honey yellow droplets <50-100 μm in size included

205   in matrix kyanite (Fig. 3a) and in PM26 as reddish-brown euhedral and often strongly poikilitic crystals

206   of up to 1 mm in size. Cr-spinel in PM26 always possesses a spectacular two-layer reaction corona

207   which consists of an inner layer of blue kyanite needles intergrown with pink corundum-III and an

208   outer layer of light green pargasite (Fig. 3b).

209   Additional minor to accessory constituents of the eclogite-facies assemblages from sample

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210 PM26 is zoisite and pentlandite. PM22 contains zircon and rutile with rutile forming small drop-like

211 inclusions in kyanite associated with Cr-spinel or occuring as matrix phase. Zoisite is present in sample

212 PM26 only as small matrix grains intergrown with omphacite, garnet and/or kyanite.

213

214 **MINERAL CHEMISTRY**

215 Garnet is pyrope-rich with an observed compositional range $pyrope_{49-53}grossular_{19-}$

216 $_{20}almandine_{27-31}spessartite_{0.5-2}$ in PM22 and $pyrope_{60-68}grossular_{21-25}almandine_{11-14}spessartine_{<1}$ in

217 PM26, respectively (Figs. 4a,b; Tables 1, 2). No significant compositional zoning could be observed in

218 any of the garnets analyzed. The garnet composition mainly reflects differences in the whole rock

219 composition of the two samples as evidenced by garnet X_{Mg} [$=Mg/(Mg+Fe^{2+})$] of 0.61-0.66 in PM22

220 and of 0.81-0.86 in the unusually Mg-rich cumulate PM26. (Table 2).

221 Matrix omphacite and omphacite inclusions in kyanite are typically unzoned with an observed

222 compositional range $diopside_{56-59}jadeite_{31-34}$calcium Tschermak's $pyroxene_{0.03-0.04}acmite_{0.00-0.03}$ in

223 PM22 and $diopside_{57-63}jadeite_{27-29}$calcium Tschermak's $pyroxene_{0.05-0.08}acmite_{<0.01}$ in PM26,

224 respectively (Tables 1, 2). Aside from large Cr-poor matrix omphacite, Cr-rich omphacite is present in

225 sample PM26 as part of a reaction corona around large Cr-spinel grains and in sample PM22 associated

226 with Cr-spinel droplets as inclusions in kyanite. This omphacite contains as much as 5.3 wt% Cr_2O_3,

227 equivalent to 14.8 mol% $NaCrSi_2O_6$ (kosmochlor) component (Table 3).

228 Large matrix kyanite crystals devoid of Cr-spinel inclusions are homogeneous and show a

229 close-to-endmember composition. Kyanite with clusters of drop-like Cr-spinel inclusions from sample

230 PM22 shows a strong and complex discontinuous Cr-zoning in the vicinity of Cr-spinel (Fig. 5) with

231 highly variable Cr_2O_3 contents reaching 15.6 wt% which is equivalent to 17.6 mol% X_{Cr-Ky} (Table 4;

232 Fig. 6). Fe_2O_3 contents of the Cr-rich zones reach 0.6 wt% and are positively correlated with Cr_2O_3

233 contents. Cr-rich kyanite in reaction coronas around Cr-spinels from sample PM26 does not display

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234   any Cr-zoning and shows lower Cr_2O_3 contents not exceeding 8.2 wt%. In order to test the effect of Cr–

235   Al exchange on the Raman spectra of kyanite, five compositionally homogeneous areas of sufficient

236   size within zoned Cr-bearing kyanites containing 0.6, 2.1, 6.1, 8.9, and 10.7 wt% Cr_2O_3 were selected

237   and Raman spectra recorded. Increasing Cr contents result in a systematic and linear shift of the major

238   bands towards lower wave numbers accompanied by a broadening of the bands (Fig. 7a). For example

239   the band at 487 cm^{-1} in the spectrum of kyanite with 0.6 wt% Cr_2O_3 is shifted to 481 cm^{-1} in the

240   spectrum of kyanite with 10.7 wt% Cr_2O_3. The corresponding increase in band width at half height is

241   from 4.4 to 12.2 cm^{-1} (Fig. 7b).

242   Matrix corundum-I only shows very minor Al substitution by Cr and Fe^{3+} (Table 2) whereas

243   corundum-II within symplectites around kyanite is pure Al_2O_3. By contrast, corundum-III is

244   characterized by variable and in part extremely high Cr_2O_3 contents of up to 9.1 wt% which

245   corresponds to an eskolaite component of up to 6.3 mol.% (Table 4).

246   Spinel from sample PM22 is Cr-Fe-dominated and contains minor Al, Mg and Zn (Table 4). In

247   terms of endmembers, the observed range in composition is chromite$_{55-56}$magnesio-chromite$_{22-}$

248    $_{24}$magnetite$_{01-04}$hercynite$_{14-15}$gahnite$_{03-04}$. In sample PM26 spinel shows significantly lower Fe and Cr

249   combined with higher Al and Mg contents. The observed range in composition is chromite$_{00-}$

250    $_{05}$magnesiochromite$_{51-56}$magnetite$_{01-02}$hercynite$_{14-15}$gahnite$_{01-02}$spinel$_{00-14}$. (Fig. 8).

251   Texturally primary amphibole is barroisite to magnesio-hornblende (Leake et al. 2004) (Fig. 9)

252   which contains minor K, Ti and Cr (Tables 1, 2). The texturally secondary amphibole present in the Al-

253   rich spinel reaction coronas in sample PM26 is pargasite, alumino-pargasite or chromian pargasite

254   (Table 3). Cr_2O_3 contents are highly variable with 0.1-3.9 wt% and decrease with increasing distance

255   from Cr-spinel. The positive Cr-[IV]Al and negative Cr-[VI]Al correlations are consistent with a

256   combined Tschermaks and [VI]Al=[VI]Cr exchange.

257   Phengite from sample PM22 shows 3.25-3.35 Si a.p.f.u. along with minor paragonite solid-

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258   solution [(Na/(K+Na+Ca)= 0.04-0.07] (Table 1).

259   Matrix rutile contains 0.2-0.8 wt% Cr_2O_3 and 0.3-0.4 wt% Fe_2O_3 along with 302-403 ppm Zr

260   and <65 ppm Nb (n=9). The rutile inclusions in kyanite associated with Cr-spinel-I show significantly

261   higher Cr_2O_3 (1.5-1.9 wt%) and Nb (206-289 ppm) combined with lower Fe_2O_3 (0.05-0.13 wt%) and
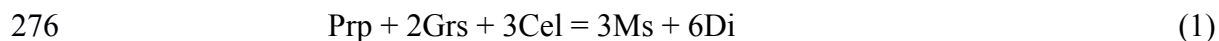
262   Zr (194-330 ppm) (Table 5).

263

264   *PT* **CONDITIONS OF ECLOGITE FACIES METAMORPHISM**

265   **Phase equilibrium calculations**

266   Estimates of *PT* conditions of eclogite-facies metamorphism in the Pohorje eclogites are

267   controversial. Janak et al. (2004) and Vrabec et al. (2012) reported conditions of ~820°C and 3 GPa

268   based on the garnet-omphacite-phengite thermobarometer from Krogh-Ravna and Terry (2004).

269   Results of Sassi et al. (2004), Miller et al. (2005a) and Miller and Konzett (2005) yield consistently

270   lower *PT* estimates of 650–720°C and 2.1–2.6 GPa. Sample PM22 contains the assemblage

271   garnet+omphacite+phengite which allows the application of various geothermobarometers. Using

272   different thermodynamic datasets and activity models but the same mineral compositions, *PT*

273   conditions in the range 640-810°C and 2.0–2.9 GPa were obtained using reactions (1) – (3) or reactions

274   (1) and (4) (Table 1, Fig. 10).

275

276   Prp + 2Grs + 3Cel = 3Ms + 6Di   (1)

277   3Di + 2Ky = Prp + Grs + 2Qtz/Coe   (2)

278   3Cel + 4Ky = Prp + 3Ms + 4Qtz/Coe   (3)

279   1/3 Prp + Hed = 1/3 Alm + Di   (4)

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281   The highest *PT* values of 780–810°C at 2.7-2.9 GPa were calculated using the net transfer reactions

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282   (1)–(3) which are considered robust because they are independent of ferric/ferrous iron consideration

283   using the calibration of Krogh-Ravna and Terry (2004). Using the thermodynamic database from

284   Holland   and   Powell   (1998)   and   calculating   activities   with   AX_2

285   (http://www.esc.cam.ac.uk/research/research-groups/research-projects/tim-hollands-software-pages/ax)

286   reactions (1)–(3) yield significantly lower P conditions of 2.0–2.1 GPa at a similar T of 770-780°C.

287   The calibration of Brandelik and Massonne (2004) for reactions (1)–(3) yields 710–760°C at 2.4-2.5

288   GPa. The lowest temperatures of 640-680°C and intermediate pressures of 2.2-2.3 GPa are obtained

289   using clinopyoxene-garnet Fe^{2+}–Mg exchange thermometry (reaction 4, Krogh, 2000) together with an

290   updated version of the Waters and Martin (1993) garnet-clinopyroxene-phengite barometer (reaction

291   1).

292   To provide additional constraints on temperatures of equilibration for the Cr-kyanite bearing

293   assemblages, Zr-in-rutile thermometry was applied to sample PM22 in which rutile is present as small

294   (≤40x70 μm) inclusions in Cr-kyanite associated with Cr-spinel and also as larger (≤350x450 μm)

295   grains scattered in the matrix. Although individual rutile grains are compositionally unzoned within the

296   analytical error of an individual analysis, there is some inter-grain variation (Table 5). Using a pressure

297   of 2.5 GPa, averaged temperatures derived from 14 rutile analyses are 721±25°C and 717±17°C based

298   on the calibrations devised by Zack et al. (2004) and Thomkins et al. (2007), respectively. Averaged

299   temperatures for rutile inclusions in Cr-kyanite and for matrix grains do not yield statistically different

300   values.

301

302   **DISCUSSION**

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

304   In samples PM22 and PM26 Cr-kyanite occurs in two different textures, namely (1) as matrix

13

305   kyanite with ±irregularly shaped Cr-rich segments around Cr-spinel inclusions and (2) as part of

306   reaction coronas around large Cr-spinel grains.

307   In case of PM22 it is obvious that Cr-spinel was consumed while matrix kyanite formed (Figs.

308   3,5). Because the Cr-rich kyanite portions are part of the large matrix kyanites we suggest that this

309   reaction took place during prograde metamorphism. Omphacite and rutile inclusions are also found

310   together with Cr-spinel in the Cr-rich kyanites. Possible simplified endmember reactions involving

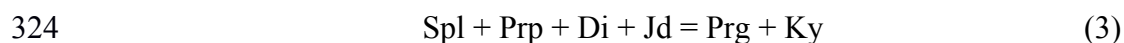311   spinel as a reactant phase are:

312

313                    $Spl + Pl = Ky + Omp \pm Grt$ (1)

314                    $Spl + Qtz = Ky + Grt$ (2)
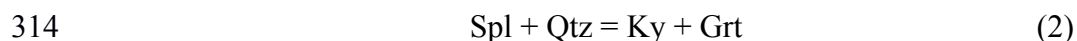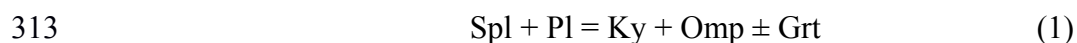
315

316   Unlike in sample PM22, the large Cr-spinels in sample PM26 did not break down during a

317   significant portion of the prograde metamorphic *PT* path. Textures clearly indicate that Cr-spinel reacts

318   with omphacite and garnet to produce a spherical corona consisting of an inner portion that contains

319   Cr-rich kyanite and an outer portion mainly consisting of chromian pargasite (Fig. 3b). Cr-rich

320   corundum as well as omphacite occur in subordinate amounts mainly in the inner portions of the

321   coronas. Based on the observed mineral assemblages in PM26, potential kyanite and corundum

322   producing reactions are

323

324                    $Spl + Prp + Di + Jd = Prg + Ky$ (3)

325                    $Spl + Prp + Grs + Jd = Prg + Ky$ (4)

326                    $Spl + Grs + Jd + Ky = Prg + Crn$ (5)
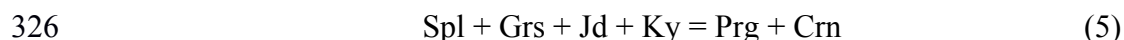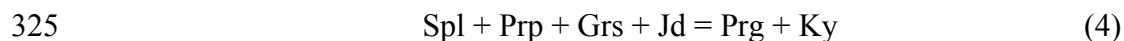
327

328   Their location in PT space was calculated in NCMASH system using appropriate activity models (Fig.

14

329   11a). Following a decompression *PT* path, crystallization of Cr-rich kyanite occurs at significantly

330   higher pressures than formation of Cr-rich corundum. However, a change in water activity may shift

331   reactions to lower *T* and *P*. Nevertheless, textural evidence does not support this conclusion that these

332   minerals formed at different stages along the retrograde path.

333   In general, corona textures indicate that a mineral reaction did not proceed to completion and

334   are a sign of disequilbrium. In case of samples PM22 and PM26, Cr-spinel is a magmatic relic inherited

335   from the eclogite precursor rock and started to react with the eclogite facies minerals garnet and

336   omphacite during progressive metamorphism. As evidenced by the presence of abundant pargasite

337   within the reaction coronas, hydrous fluids must have been involved in the corona formation. These

338   fluids are rarely pure H_2O but usually contain variable amounts of CO_2 along with various dissolved

339   species amongst which $SiO_{2,aq}$ and $NaCl_{aq}$ are often dominant (e.g. Hauzenberger et al., 2001;

340   Manning, 2004). An influx of hydrous fluid associated with a change in the chemical potential of SiO_2

341   and/or Na_2O at the interface between Cr-spinel and the matrix phases provides a potential explanation

342   for corona formation as outlined in Fig. 11b which shows a SiO_2 versus Na_2O chemical potential

343   diagram for 800°C and 2.5 GPa that was calculated using the activity models as for Fig. 11a. Figure

344   11b shows that at pressures and temperatures close to the peak of Eoalpine eclogite-facies

345   metamorphism and in a chemical system characterized by $a_{SiO2}<1$, an increase in μSiO_2 resulting from

346   an influx of fluid may trigger pargasite and/or kyanite-formation through the following reactions (Fig.

347   11b):

348

349   Sp + Di + Prp = Prg   (6)

350   Di + Sp = Prg + Ky   (7)

351   Grs + Sp = Prg + Ky   (8)

352

15

353   The chemical potential of Na_2O probably did not change significantly during reaction progress because

354   of abundant omphacite present in the matrix that buffers this component.

355

356   **The timing of Cr-kyanite formation**

357   Green and Ringwood (1967) showed that phases with aluminium-rich compositions   form

358   kyanite in eclogites with the breakdown of plagioclase occurring at approximately 1.5 GPa and 700°C.

359   Cr-spinel overgrown by and eventually enclosed in newly formed but still Cr-poor kyanite is thought to

360   represent the first step in the formation of Cr-kyanites in sample PM22 that took place at pressures

361   above approximately 1.5 GPa. In a second step rising P and T caused increasing Cr_2SiO_5-solubility in

362   kyanite resulting in an exchange reaction $Al_2SiO_5 + FeCr_2O_4 = Cr_2SiO_5 + FeAl_2O_4$ involving newly

363   formed kyanite and Cr-spinel inherited from the magmatic precursor (cf. Gil-Ibarguchi et al. 1991).

364   Thus, Cr-kyanite from sample PM22 predates the formation of Cr-rich corona kyanite from sample

365   PM26 whose formation requires the breakdown of eclogite-facies phases during the retrograde portion

366   of the PT-path.

367   Retrogression of eclogite to amphibolite is widespread in the Saualpe, Koralpe and Pohorje area

368   of the Eastern Alpine basement and is attributed to a pervasive fluid influx during uplift. Based on the

369   fluid-influx model as outlined in Fig. 11b the formation of Cr-rich kyanites within the spinel coronas

370   from sample PM26 is not a prograde but a retrograde phenomenon associated with the earliest stage of

371   the exhumation path but under still high pressures. This is supported by small inclusions of Cr-rich

372   omphacite found within the coronas which are a clear indication for eclogite facies conditions. Hence,

373   mineral textures and phase equilibrium calculations would be consistent with the following scenario

374   (Fig. 12): during prograde metamorphism large magmatic Cr-spinel grains initially remained

375   unaffected by rising PT conditions due to sluggish reaction kinetics. Influx of a hydrous fluid during

376   the initial stage of decompression increased the chemical potential of SiO_2 and strongly accelerated

16

377   reaction kinetics, allowing various kyanite-, amphibole-, and corundum-forming reactions to proceed.

378   The spatial distribution of phases within the coronas is consistent with increasing chemical potential of

379   SiO_2 and decreasing chemical potentials of Al_2O_3 and Cr_2O_3 from spinel towards the matrix (Fig. 12).

380

IMPLICATIONS

382   Within the two investigated samples PM22 and PM26, Cr-spinel-bearing gabbroic cumulates

383   from the Pohorje Massif, blue Cr-kyanite formed in two different textural micro-environments. A first

384   type present in sample PM22 encloses clusters of small drop-like Cr-spinel inclusions and contains up

385   to 15.6 wt% Cr_2O_3. The most intense blue color occurs in the immediate vicinity to the Cr-spinel. A

386   second type is present in sample PM26 as part of Al-rich reaction coronas developed around large red-

387   brownish Cr-spinel magmatic relics. Within these coronas Cr-kyanite appears as deep blue needle-like

388   crystals that contain up to 8.2 wt% Cr_2O_3 and is associated with red-pink Cr-rich corundum containing

389   up to 9.1 wt% Cr_2O_3 and Cr-Al-rich pargasite with up to 3.9 wt% Cr_2O_3. The blue color of kyanite and

390   the red-pink color of corundum are a result of Cr-Al substitution in octahedral sites during high

391   pressure/ultra-high pressure metamorphism. Whereas Cr-kyanite in sample PM22 formed under

392   increasing *PT* conditions during prograde metamorphism, Cr-kyanite and the associated Cr-rich

393   corona-assemblage in sample PM26 were generated during the earliest stage of retrogressive evolution

394   of these rocks still at eclogite-facies PT conditions of ~2.5 GPa and 750-800°C.

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543 **LIST OF FIGURE CAPTIONS**

544

545 **Figure 1. (a)** Schematic map of the Saualpe-Koralpe-Pohorje domain (modified from Miller et al.,

546 2007) showing the distribution of regions overprinted by greenschist, amphiboite and eclogite facies

547 metamorphic conditions; major eclogite bodies are displayed by filled ellipses; **(b)** Simplified

548 geological map of the Pohorje Mountains and adjacent areas (modified after Mioč and Žnidarčič, 1977

549 and Janák et al., 2004); the sampling area is indicated by the dashed rectangle in the southeastern part

550 of the Pohorje Massif. Major fault systems are represented by bold lines.

551

552 **Figure 2. (a)-(e)** Correlation plots of selected major and trace elements for Cr-spinel-bearing (PM22:

553 black star; PM26: open star) and Cr-spinel-free (black dots) eclogites from the Slovenska Bistrica area

554 compared to Mg-rich and Mg-poor eclogite bulk compositions from the Koralpe, Saualpe and Pohorje

555 Mountains reported by Miller et al. (2007) (M07) and Sassi et al. (2004) (S04); field boundaries in **(a)**

556 according to Pearce (1983); $Mg\# = [100*Mg/(Mg+Fe_{tot}^{2+})]$

557

558 **Figure 3.** Optical photomicrographs of Cr-rich assemblages; (a) cluster of turquoise-colored Cr-bearing

559 kyanites enclosing vermicular Cr-spinel grains from sample PM22; note the zonal coloring which is

560 most intense in the immediate vicinity of the Cr-spinel inclusions where Cr contents of kyanite are

561 highest; (b) turquoise-colored Cr-bearing kyanites and pink Cr-bearing corundum forming the inner

562 portion of a reaction corona around a large Cr-spinel grain from sample PM26; the outer portion of the

563 corona consists of pale-geen Cr-pargasite which may contain relics of omphacite and garnet indicating

564 a reaction Cr-spinel + omphacite + garnet + H_2O = kyanite + corundum + pargasite.

565

566 **Figure 4.** back-scattered electron (BSE) images showing selected microtextures of eclogite-facies

25

567 assemblages affected by subsequent retrograde overprint; **(a)** weakly retrogressed domain of Cr-

568 kyanite-bearing sample PM22 with omphacite and garnet mantled by narrow symplectitic rims of

569 Amp+Di+Plag (symp I) and of Amp+Plag (symp II), respectively. Symplectites around kyanite consist

570 of Crn+Spl+Pl (symp III). **(b)** High-Mg coronitic eclogite PM26 containing abundant garnet with

571 kyanite and omphacite inclusions. Incipient retrogressive breakdown of omphacite to form symp I

572 assemblages can be observed in the upper center. **(c)** complex symplectite corona around kyanite: 1)

573 the main part contains $Crn+An_{90}$, $Spr+An_{90}$ and $Spl+An_{90}$ symplectites which are surrounded by a thin

574 An_{50} rim. **(d)** texturally primary amphibole from sample PM22 with a thin symplectitic reaction rim

575 towards coexising omphacite (symp V); **(e)** Phengite surrounded by a symplectite Pl+Bt rim (symp

576 IV); **(f)** two textural types of corundum from sample PM26; Crn-I forms lath-shaped poikilitic matrix

577 grains up to 300 μm in size whereas Crn-III is found as part of reaction coronas around Cr-spinel grains

578 associated with Cr-rich kyanite and Cr-rich pargasite; a third textural type of Crn (Crn-II) forms tiny

579 needles which are part of symplectite rims around kyanite (see Fig. 3c).

580

581 **Figure 5.** BSE image and Al, Cr, and Fe X-ray maps of Cr-rich kyanite from samples PM22. Droplets

582 of Cr-spinels are enclosed in kyanite, which is surrounded by a plagioclase–corundum–Mg-Al-spinel

583 symplectite (symp III). The higher Cr content in kyanite is seen as lighter gray areas around the white

584 spinels in the BSE image and as light bluish to greenish colour in the Cr X-ray map. Dark color (black–

585 blue) indicate low concentrations while green–yellow–red colors indicate higher concentrations.

586

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

588 from the literature.

589

590 **Figure 7. (a)** Raman spectra for kyanites with 0.6 and 10.7 wt%. With increasing Cr content the bands

26

591   show both a broadening and a systematic shift towards lower wave numbers; **(b)** band shift and

592   broadening of three Raman bands as a function of Cr content for kyanites with 0.6, 2.1, 8.9, and 10.7

593   wt% Cr_2O_3.

594

595   **Figure 8.** Composiional variation of spinel from samples PM22 and PM26 in terms of molar Al–Mg–

596   Fe^{3+}

597

598   **Figure 9.** Compositional variation of textrually primary and secondary calcic amphiboles from samples

599   PM22 and PM26; primary amphiboles contain low and constant Cr_2O_3 contents in the range 0.10-0.15

600   wt% without any significant Al–Cr variation.

601

602   **Figure 10.** Peak metamorphic *PT* conditions of kyanite eclogite sample PM22 using various mineral

603   equilibria or calibrations (Krogh-Ravna and Terry 2004; Holland and Powell 1998; Brandelik and

604   Massonne 2004;.Waters and Martin 1993 in combination with Cpx–Grt exchange thermometer after

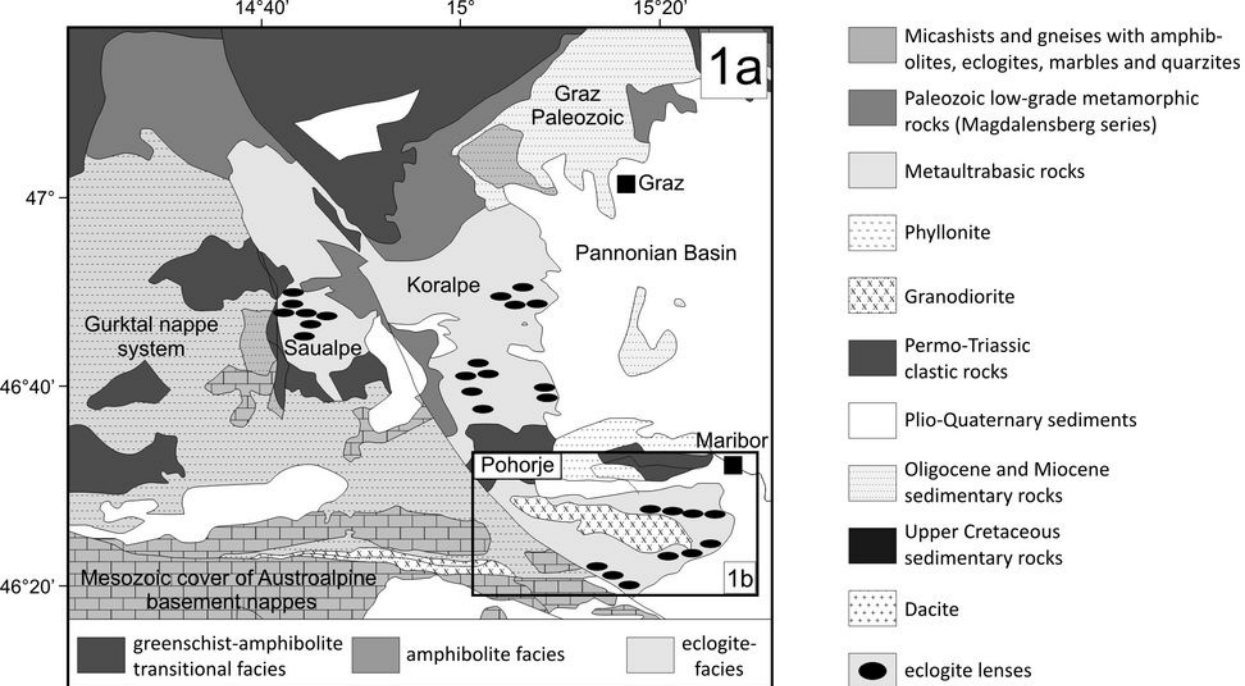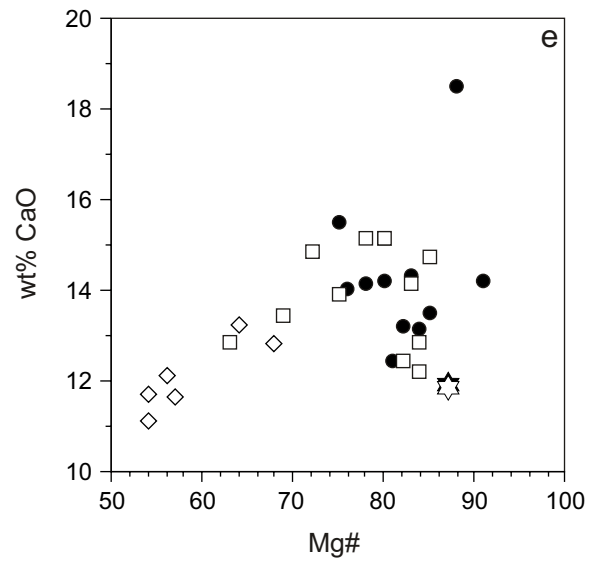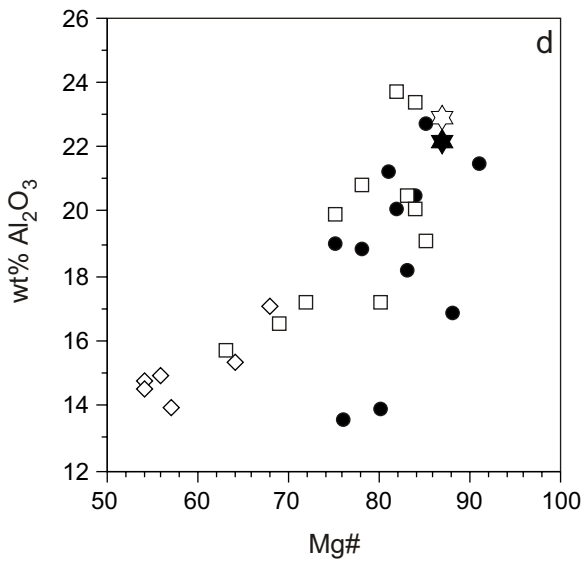605   Krogh 2000). The numbers on reaction curves correspond to reaction number in the text.
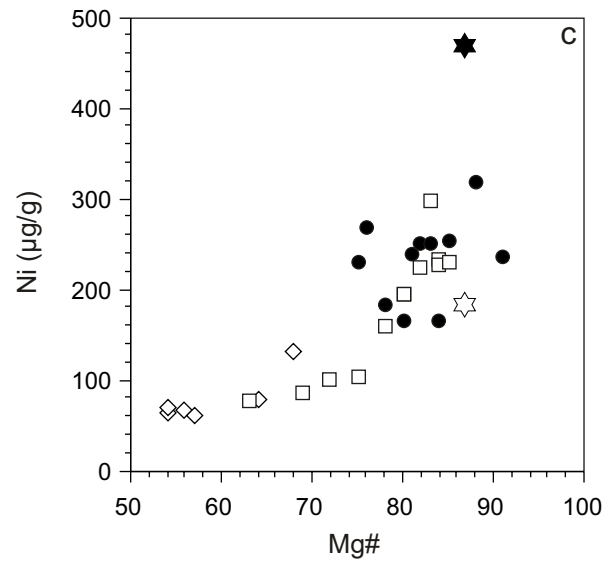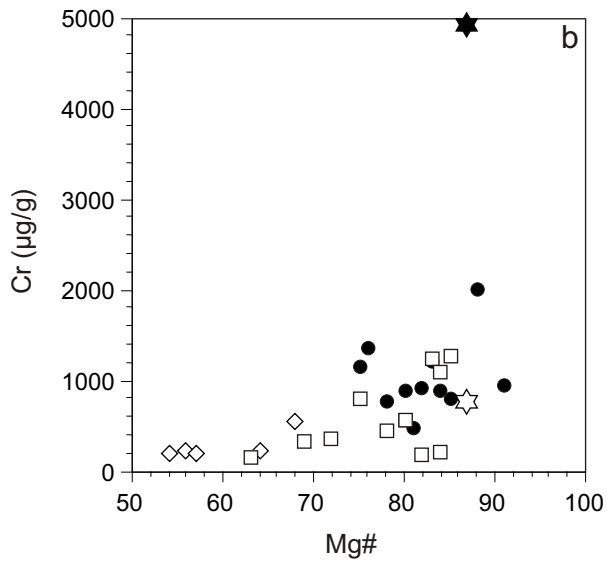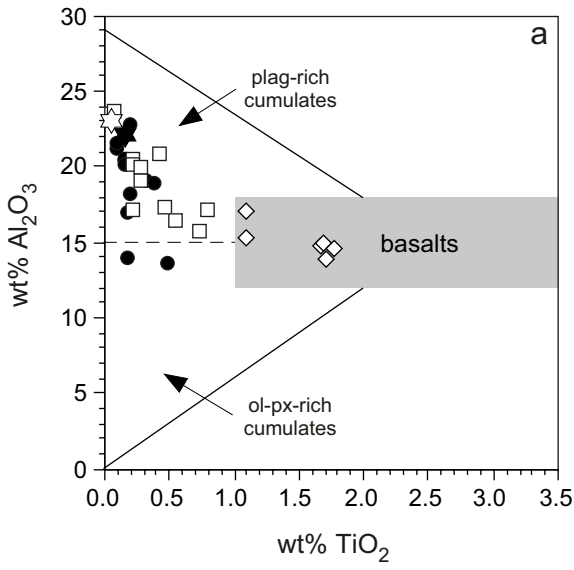
606

607   **Figure 11.** Calculated Cr-kyanite and Cr-corundum-forming reactions for sample PM26 expressed in

608   terms of endmembers using Perple_X (Connolly, 1990) with the thermodynamic dataset of Holland and

609   Powell (1998 and updates). Endmember activity corrections were performed using the program AX_2

610   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)**

611   *PT* diagram with Cr-kyanite and Cr-corundum-forming reactions. Reactions 2 and 4 produce kyanite

612   and pargasite at or close to peak *PT* conditions. Along an assumed exhumation path corundum forms at

613   lower PT conditions. Stippled lines are calculated with lower X_{H2O}. **(b)** Simplified isothermal and

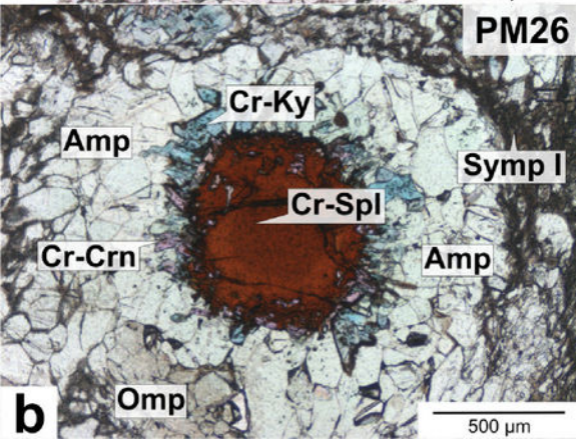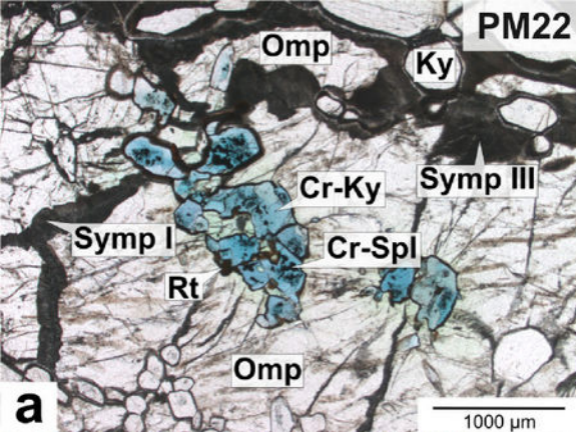614   isobaric $\mu SiO_2 - \mu\ Na_2O$ diagram reproducing the observed formation of Ky, Prg, and Cor. Locally

27

615   reduced SiO_2 activity was responsible for Cor formation (Ky = Cor).

616

617   **Figure 12.** Sketch explaining the formation of observed spherical coronas around Cr-spinel: (a)

618   Crystallization of eclogite facies assemblage where Cr-spinel remained as magmatic cummulate phase

619   unaffected. (b) Infiltration of H_2O-rich fluids (+$SiO_{2,aq}$, +$NaCl_{aq}$) during onset of exhumation

620   increasing chemical potential of SiO_2 which facilitates the breakdown of Cr-spinel. (c) Observed

621   corona in sample PM26 (Fig. 3).

Legend (panel 1a):

- Micashists and gneises with amphibolites, eclogites, marbles and quarzites
- Paleozoic low-grade metamorphic rocks (Magdalensberg series)
- Metaultrabasic rocks
- Phyllonite
- Granodiorite
- Permo-Triassic clastic rocks
- Plio-Quaternary sediments
- Oligocene and Miocene sedimentary rocks
- Upper Cretaceous sedimentary rocks
- Dacite
- eclogite lenses

greenschist-amphibolite transitional facies | amphibolite facies | eclogite-facies

Panel 1a labels: Graz Paleozoic, Graz, Pannonian Basin, Koralpe, Gurktal nappe system, Saualpe, Pohorje, Maribor, Mesozoic cover of Austroalpine basement nappes, 1b

Panel 1b labels: Labot fault, Ribnica trough, Lovrenc fault, Drava, Maribor, Slovenj Gradec, Valenje Basin, Periadriatic Fault, Sampling Area, Slovenska Bistrica, 10km

Legend:
- □ high-Mg (M07, S04)
- ◇ low-Mg (M07)
- ● Cr-spinel-free (this study)
- ★ PM22
- ☆ PM26

a — PM22

Labels: Omp, Ky, Symp III, Cr-Ky, Cr-Spl, Symp I, Rt, Omp

Scale bar: 1000 μm

b — PM26

Labels: Cr-Ky, Cr-Spl, Amp, Symp I, Cr-Crn, Amp, Omp

Scale bar: 500 μm

00005755 ———— 50 μm   JEOL

Al

Cr

Fe

a

P [GPa] (vertical axis, from 0.5 to 3.0)

T [°C] (horizontal axis, from 600 to 1000)

Prp + Grs

Sp + Di + Ky

Sp + Grs + Jd + Ky

Prg + Crn

1
2
3
4
5

1 Prg+Grs+Jd = Di+Prg+Ky
2 Sp+Prp+Grs+Jd = Prg+Ky
3 Sp+Di+Jd = Prp+Grs+Prg
4 Sp+Prp+Di+Jd = Prg+Ky
5 Sp+Di+Jd = Prg+Ky+Grs

$X_{H_2O} = 1$
$X_{H_2O} = 0.5$
$X_{H_2O} = 0.25$

b

μ_{Na_2O} [kJ] (vertical axis, from -770 to -740)

μ_{SiO_2} [kJ] (horizontal axis, from -872 to -868)

T = 800°C
P = 2.5 GPa

Crn
Jd
Sp+Grs
Prg+Jd
Sp
Prp+Jd
Di+Jd
Prg+Grs
Prp+Jd+Ky
Prg
Sp+Grs
Ky+Prg
Di+Ky
Jd
Prg+Grs
Ky
Di+Sp
Prg+Grs
Prg
Crn
Ky
Prp+Di+Sp
Prp+Di+Ky
Prg
Sp
Prp+Ky
Di+Sp=
Prg+Ky

a Crystallization of eclogite Facies mineral assemblage

b H_2O-rich fluid Infiltration $+SiO_{2,aq}$ ($+NaCl_{,aq}$)

c Formation of Cr-rich Ky + Crn + Prg

Labels in a: Grt, Sp, Omp, Ky
Labels in b: Omp, Grt, Sp, Ky
Labels in c: Grt, Cr-Ky, Prg, Sp, Omp, Cr-Crn, Ky

Tabelle1

Table 1. Represantative analyses of minerals stable at peak metamorphic conditions from sample PM22

	Omphacite		Garnet				Amphibole		Kyanite	Phengite
			Grt core	Grt rim	Grt core	Grt rim				
	PM22o3	PM22o4	PM22g94	PM22g180	PM22G109	PM22g14	PM22a7	PM22a10	PM22ky20	PM22ph20
SiO_2	55.00	55.79	39.63	39.90	40.77	39.77	51.40	51.18	38.12	52.04
TiO_2	0.14	0.14	<0.1	<0.1	<0.1	<0.1	0.37	0.35	<0.02	0.72
Al_2O_3	9.24	9.41	22.76	22.69	23.19	22.94	11.62	11.60	61.19	29.78
$Cr2O_3$	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.10	0.11	0.03	0.37
FeO^{tot}	2.51	2.61	15.66	15.91	14.87	16.07	4.19	4.22	0.37	0.58
MnO	<0.1	<0.1	0.68	0.44	0.53	0.47	<0.01	<0.01	<0.01	<0.1
MgO	11.74	12.25	13.26	13.47	14.06	13.20	16.95	16.94	-	4.04
CaO	16.27	16.11	7.41	7.30	7.31	7.32	9.75	9.76	-	0.11
K2O	<0.1	<0.1	-	-	-	-	0.60	0.61	-	9.21
Na2O	4.74	4.79	-	-	-	-	2.73	2.86	-	0.29
Sum	99.64	101.10	99.40	99.71	100.73	99.77	97.71	97.63	99.71	97.14
Si	1.960	1.958	2.940	2.949	2.971	2.942	7.074	7.060	1.035	3.347
Ti	0.004	0.004	-	-	-	-	0.038	0.036	-	0.035
Al	0.388	0.389	1.990	1.977	1.992	2.000	1.885	1.886	1.957	2.257
Cr	-	-	-	-	-	-	0.011	0.012	0.001	0.019
Fe^{3+}	0.011	0.013	0.130	0.124	0.066	0.117	0.237	0.226	0.008	-
Fe^{2+}	0.064	0.063	0.842	0.859	0.840	0.877	0.245	0.261	-	0.031
Mn	-	-	0.043	0.028	0.033	0.029	-	-	-	-
Mg	0.624	0.641	1.466	1.484	1.527	1.455	3.477	3.483	-	0.387
Ca	0.621	0.606	0.589	0.578	0.571	0.580	1.438	1.442	-	0.008
K	-	-	-	-	-	-	0.105	0.107	-	0.756
Na	0.328	0.326	-	-	-	-	0.728	0.765	-	0.036
Sum	4.000	4.000	8.000	7.999	8.000	8.000	15.238	15.278	3.001	6.876

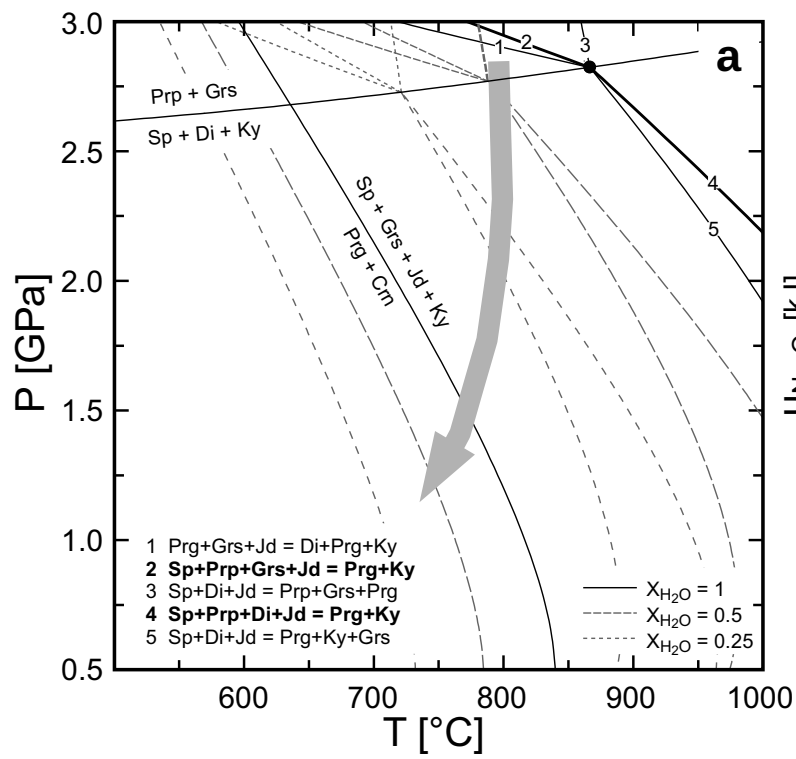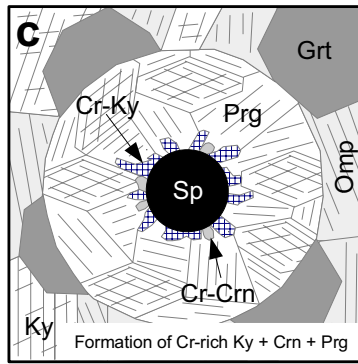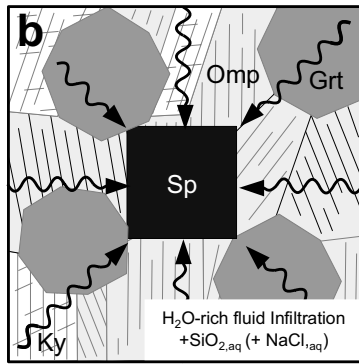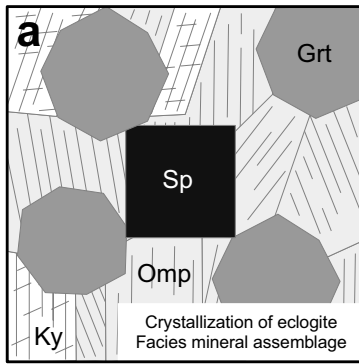|		Omphacite			Garnet				Amphibole	
	X_{Jd}	0.346	0.350	X_{Prp}	0.499	0.503	0.514	0.495	X_{Mg}	0.934	0.930
	X_{Mg}	0.907	0.911	X_{Grs}	0.200	0.196	0.192	0.197		
				X_{Alm}	0.286	0.291	0.283	0.298		
				X_{Sps}	0.015	0.009	0.011	0.010		
				X_{Mg}	0.635	0.633	0.645	0.624		

Tabelle1

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

	Omphacite		Garnet				Amphibole	Kyanite	Corundum	Zoisite
			Grt rim	Grt rim	Grt core	Grt core				
	PM26o3	PM26o14	PM26g7	PM26g142	PM26g7	PM26g14	PM26a1	PM26_ky32	PM26k23	PM26zo1
SiO_2	54.59	54.59	42.07	42.14	42.10	41.78	45.73	38.17	-	41.39
TiO_2	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.13	<0.01	<0.05	<0.1
Al_2O_3	9.46	10.40	23.66	23.92	23.32	23.59	17.33	61.42	99.64	31.82
$Cr2O_3$	0.11	0.11	<0.1	<0.1	<0.1	0.16	0.30	0.28	0.34	<0.1
FeO^{tot}	1.02	1.01	7.10	6.97	7.12	6.72	2.42	0.10	<0.05	0.71
MnO	<0.1	<0.1	0.19	0.07	0.17	0.13	<0.01	<0.05	<0.05	<0.2
MgO	12.28	12.68	17.83	18.04	17.21	18.68	16.99	-	-	0.10
CaO	17.84	17.06	9.04	9.06	9.78	8.45	11.18	-	-	24.70
Na_2O	4.13	4.19	-	-	-	-	3.44	-	-	-
K_2O	<0.2	<0.2	-	-	-	-	0.06	-	-	-
Sum	99.43	100.03	99.89	100.20	99.70	99.51	97.56	99.87	99.98	98.01
Si	1.946	1.929	2.997	2.988	3.012	2.975	6.342	1.033	-	3.108
Ti	-	-	-	-	-	-	0.014	-	-	-
Al	0.397	0.433	1.986	1.999	1.966	1.980	2.832	1.959	2.993	2.816
Cr	0.003	0.003	-	-	-	0.009	0.033	0.006	0.007	-
Fe^{3+}	-	-	0.021	0.024	0.009	0.060	0.140	0.002	-	0.040
Fe^{2+}	0.030	0.030	0.402	0.389	0.417	0.340	0.141	-	-	-
Mn	-	-	0.011	0.004	0.010	0.008	-	-	-	-
Mg	0.653	0.668	1.893	1.907	1.835	1.983	3.512	-	-	0.011
Ca	0.681	0.646	0.690	0.688	0.750	0.645	1.661	-	-	1.987
Na	0.285	0.287	-	-	-	-	0.925	-	-	-
K	-	-	-	-	-	-	0.011	-	-	-
Sum	3.995	3.996	8.000	7.999	7.999	8.000	15.611	3.000	3.000	7.962
X_{Jd}	0.295	0.308	X_{Prp} 0.632	0.638	0.609	0.666	X_{Mg} 0.962		X_{Fe}	0.014
X_{Mg}	0.956	0.957	X_{Grs} 0.230	0.230	0.249	0.217				
			X_{Alm} 0.134	0.130	0.138	0.114				
			X_{Sps} 0.004	0.001	0.003	0.003				
			X_{Mg} 0.825	0.831	0.815	0.854				

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

	Omphacite		Pargasite	Aluminopargasite
	PM22om1	PM26om1	PM26a1	PM26AM8
SiO_2	54.04	54.39	44.07	45.82
TiO_2	0.09	<0.05	0.16	0.09
Al_2O_3	7.75	9.37	16.15	16.83
Cr_2O_3	5.24	3.65	3.94	1.50
FeO^{tot}	2.21	0.77	2.07	2.48
MnO	<0.05	<0.05	0.02	0.02
MgO	10.42	11.06	16.50	16.80
CaO	15.48	16.03	10.65	10.51
Na_2O	5.33	5.43	3.54	3.47
K_2O	<0.05	<0.05	0.09	0.08
Sum	100.56	100.70	97.19	97.62
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^{3+}	0.019	-	0.000	0.000
Fe^{2+}	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_{Mg}	0.922	0.962	0.934	0.923
X_{Na}	0.384	0.380		
X_{Kos}	0.148	0.102		
X_{Jd}	0.203	0.270		
X_{Acm}	0.019	0.000		
X_{Ca-Ts}	0.062	0.060		
X_{Di}	0.532	0.547		
X_{Hd}	0.047	0.023		

TABLE 4. Chemical composition of Cr-rich kyanite, corundum, and spinel from samples PM22 and PM26

	Cr-kyanite						Corundum			Cr-spinel			
	PM22ck1	PM22ck2	Pm22ky2/1	PM26ky1	PM26ky2		PM26k3	PM26k8		PM22sp11	PM22sp12	PM26sp15	PM26sp22
SiO_2	35.63	35.41	35.13	36.16	36.52		-	-		-	-	-	-
TiO_2	0.00	0.10	0.00	0.00	0.00		<0.05	<0.05		<0.05	<0.05	<0.05	<0.05
Al_2O_3	49.90	50.29	49.01	55.33	55.10		90.65	91.06		8.86	9.09	26.89	20.45
Cr_2O_3	14.37	13.99	15.60	7.82	8.18		9.07	9.06		57.14	56.60	43.37	49.46
Fe_2O_3	0.50	0.36	0.43	0.27	0.20		<0.05	<0.05		-	-	-	-
FeO^{tot}	-	-	-	-	-		-	-		27.67	27.44	14.90	17.19
MnO	<0.05	<0.05	<0.05	<0.05	<0.05		-	-		0.14	0.34	0.03	0.09
MgO	-	-	-	-	-		-	-		5.08	4.90	14.56	12.12
ZnO	-	-	-	-	-		-	-		1.40	1.45	0.43	0.43
Sum	100.40	100.15	100.17	99.58	100.00		99.72	100.12		100.28285	99.8199	100.1781	99.7326
Si	1.006	1.001	0.999	1.006	1.012		-	-					
Ti	-	-	-	-	-		-	-					
Al	1.661	1.676	1.642	1.814	1.800		1.874	1.875		0.358	0.369	0.946	0.753
Cr	0.321	0.313	0.351	0.172	0.179		0.126	0.125		1.549	1.542	1.024	1.222
Fe^{3+}	0.011	0.008	0.009	0.006	0.004		-	-		0.093	0.089	0.030	0.025
Fe^{2+}	-	-	-	-	-		-	-		0.701	0.702	0.342	0.424
Mn	-	-	-	-	-		-	-		0.004	0.010	0.001	0.002
Mg	-	-	-	-	-		-	-		0.260	0.251	0.648	0.564
Zn	-	-	-	-	-		-	-		0.035	0.037	0.009	0.010
Sum	2.999	2.998	3.001	2.998	2.995		2.000	2.000		3.000	3.000	3.000	3.000
X_{Cr-Ky}	0.161	0.157	0.175	0.086	0.090	X_{Esk}	0.063		X_{Cr}	0.775	0.771	0.512	0.611
						X_{Cor}	0.937		X_{Mg}	0.271	0.263	0.655	0.571

TABLE 5. Chemical composition of rutile inclusions in kyanite and matrix rutile grains (PM22)

	Inclusion in kyanite				Matrix			
	ru-1	**ru-2**	**ru-9**	**ru-10**	**ru-6/1**	**ru-6/2**	**ru-7/1**	**ru-7/2**
TiO2	97.71	97.06	97.42	97.77	99.54	99.13	98.39	98.16
Cr2O3	1.62	1.90	1.51	1.46	0.18	0.17	0.25	0.28
Fe2O3	0.08	0.04	0.06	0.05	0.31	0.32	0.37	0.38
Sum	99.41	99.00	98.99	99.28	100.03	99.62	99.01	98.82
Ti	0.986	0.984	0.987	0.988	0.996	0.996	0.995	0.995
Cr	0.017	0.020	0.016	0.016	0.002	0.002	0.003	0.003
Fe3+	0.001	0.000	0.001	0.001	0.003	0.003	0.004	0.004
Sum	1.005	1.005	1.004	1.005	1.001	1.001	1.002	1.002
Zr [ppm]	194±34	275±34	236±35	330±34	347±28	403±28	347±28	302±28
Nb [ppm]	289±96	267±96	249±95	206±95	<65	<65	<55	<65