Aragonite-calcite-dolomite relationships in UHPM polycrystalline carbonate inclusions from the Kokchetav Massif, northern Kazakhstan

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Abstract: The presence of aragonite in polycrystalline carbonate inclusions in garnet in diamond-grade metamorphic rocks from the Kokchetav Massif, N. Kazakhstan was identified for the first time by means of Raman analyses and mapping, cathodoluminescence images and optical and scanning electron microscopy. Aragonite appears within the inclusions as dirty, chaotically oriented materials surrounded by a clean monocrystalline calcite shell; the grain boundary between the host-garnet and the aragonite-bearing inclusions is often characterized by a wavy or amoeboid shape; no cracks occur around the aragonite-bearing inclusions; no significant shift in the main aragonite Raman band was measured. These observations indicate that residual pressure within the inclusion is minor. These features are inconsistent with an origin of aragonite at peak metamorphic conditions (6 GPa) by decomposition of dolomite.

Key-words: aragonite, calcite, diamond, UHPM petrology, Raman spectroscopy, SEM, cathodoluminescence.

1. Introduction

The upper limit of peak metamorphic conditions (especially the maximum pressure $P_{\max}$) has been increased constantly since ultrahigh pressure metamorphism (UHPM) was first defined (Chopin, 1984; Smith, 1984; Sobolev & Shatsky, 1990). To date the $P_{\max}$ for subducted continental crusts has been estimated at approximately 8–9 GPa (Dobrzhinetskaya *et al.*, 2006; Massonne, 2003; Zhu & Ogasawara, 2002). Most difficulties in the reconstruction of $P_{\max}$ conditions for metapelites and metacarbonates are mainly related to the lack of reliable geobarometers in the 2.0–8.0 GPa interval (Hermann, 2002, 2003b; Hermann & Green, 2001; Lappin & Smith, 1981), although significant progress has been made lately (Thomsen & Schmidt, 2008, and references therein). Inclusions in robust minerals that point to UHPM comprise diamond (C), coesite (SiO₂), TiO₂ polymorph with α -PbO₂ structure. Because of the generally very small size of the UHPM inclusions, which are close to the optical limit, analytical techniques for the accurate investigation of

these inclusions are largely confined to transmission electron microscopy (TEM) (Dobrzhinetskaya *et al.*, 2006; Hwang *et al.*, 2001, 2004, 2005; Langenhorst, 2003) and Raman spectroscopic point analysis and mapping (Korsakov *et al.*, 2007; O'Brien & Ziemann, 2008; Ogasawara *et al.*, 2002; Perraki *et al.*, 2006, 2007).

TEM techniques enabled the identification of inclusions of TiO₂ polymorphs with α -PbO₂ structure in garnet from the UHP Erzgebirge, Germany (Hwang *et al.*, 2001), pointing to a maximum pressure above 4–6 GPa. In addition, inclusions of aragonite and magnesite in diamonds from the UHP Kokchetav Massif, Northern Kazakhstan, identified by TEM with focused ion beam, indicate even higher pressures of approximately 6–9 GPa (Dobrzhinetskaya *et al.*, 2006), on the basis of earlier experimental studies (Buob *et al.*, 2006; Goldsmith & Newton, 1969; Hermann, 2003a; Irving & Wyllie, 1975; Luth, 2001; Sato & Katsura, 2001).

Inclusions of aragonite and pseudomorphs after magnesite were first published by Zhu & Ogasawara (2002). However, this observation was disputed by Hermann (2003a) who claimed that it is inconsistent with other

petrological data (for discussion see Hermann *et al.*, 2001; Katayama *et al.*, 2001; Korsakov & Hermann, 2006; Korsakov *et al.*, 2002, 2004, 2006; Shatsky *et al.*, 1995).

Aragonite inclusions in diamond have recently been interpreted as evidence of very deep subductions of roughly 280 km (Dobrzhinetskaya *et al.*, 2006) although *P-T* conditions for the main eclogite stage in the eclogites from the relevant Jæren nappe in the Norwegian Caledonian orogenic belt, have been estimated at 2.3–2.8 GPa and 585–655 °C (Smit *et al.*, 2008). Aragonite and magnesite present clear disequilibrium textures, indicating the replacement of magnesite by aragonite (Smit *et al.*, 2008). They are inferred to have occurred via a coupled dissolution/precipitation reaction not related to the breakdown of dolomite.

Inclusions of single dolomite crystals in garnets from UHP metamorphic rocks from the Kokchetav Massif, N. Kazakhstan frequently contain diamonds (Korsakov *et al.*, 2005; Ogasawara *et al.*, 2000; Perraki *et al.*, 2009), although they bear no indicator of the existence of aragonite and magnesite. This observation implies that dolomite was stable over the entire pressure-temperature-time path of the diamond-bearing rocks of Kokchetav (Hermann, 2003a).

Information on aragonite coexisting in equilibrium with magnesite as inclusion in garnet or clinopyroxene is lacking. Dolomite inclusions in garnet from diamond-bearing marbles from the Kokchetav Massif contain multiphase inclusions. They are composed of calcite, magnesite, and amorphous SiO₂ with high H₂O content (Shatsky *et al.*, 2006). The origin of this type of inclusions is related to the crystallization of silicate-carbonate melts (Korsakov & Hermann, 2006; Korsakov *et al.*, 2006; Shatsky *et al.*, 2006). So far, diamonds were not recognized inside or in association with aragonite or magnesite, although polycrystalline calcite inclusions in garnet and clinopyroxene may contain diamond or graphite inclusions (Korsakov & Hermann, 2006). Sometimes, polycrystalline calcite inclusions bear cavities or holes indicating that some H₂O-soluble components of carbonate inclusions could have been lost during sample preparation. The lack of a systematic study of the carbonate inclusions by Raman spectroscopy makes it a high possibility that aragonite or other exotic minerals (*e.g.*, H₂O-soluble alkaline carbonates, sulphates) were overlooked (*cf.* Chopin *et al.*, 2008).

We investigated several polycrystalline carbonate inclusions of the diamond-grade metamorphic rocks from the Kokchetav Massif. The unexposed carbonate inclusions at the thin-section surface were first studied by Raman mapping (RM). The samples were then polished until the inclusions were exposed at the thin-section surface. Subsequently the inclusions were studied by cathodoluminescence (CL), reflected-light optical microscopy (ROM) and scanning electron microscopy (SEM). The aim of this study is to (i) identify phase compositions and spatial distribution of H₂O-soluble components in polycrystalline carbonate inclusions and (ii) study the aragonite–calcite dolomite relationships and (iii) discuss the possible origin of aragonite in the polycrystalline carbonate inclusions.

2. Materials and methods

2.1. Experimental techniques

Raman mapping was performed with a Kaiser System Hololab 5000R modular Raman microspectrometer (*f*/1.8). The microscope was fitted with a 100× objective (N.A. 0.75, W.D. 4.7 mm). The samples were excited with approximately 45 to 50 mW net power on the sample of a 785 nm laser light from a diode laser. The scattered light was guided to the spectrograph through a confocal collection fibre with a numerical aperture of 0.15. A back-illuminated deep depletion Pelletier cooled CCD detector operating at –70 °C was used for the detection of the scattered light. The Raman signal was collected in the spectral interval 100–1800 cm^{–1} with a spectral resolution of 4 cm^{–1}. Further details of the calibration procedure can be found elsewhere (Hutsebaut *et al.*, 2005). The laser spot size was ~1 µm. The spectra were recorded with a 15 s accumulation time. After collection, the Raman spectra were processed in matlab with the Biodata toolbox (De Gussem *et al.*, 2009). The Raman spectra were background-subtracted with the iterative polynomial fitting procedure described by Lieber & Mahadevan-Jansen (2003) (200 iterations, fifth-order polynomial).

Cathodoluminescence (CL) microscopy study was carried out at University of Leuven, Belgium. The internal structures of polycrystalline carbonate inclusions were investigated under accelerating conditions of 18 kV and 900 mA.

Textural relations were examined in polished thin sections by reflected-light optical microscopy and back-scattered electron images on a Camebax electron microprobe (Electron Microscopy Unit, Université Catholique de Louvain-la-Neuve) and a JEOL 6380LA (Institute of Geology and Mineralogy SB RAS, Novosibirsk). The phase compositions were determined on a JEOL JXA-8100 using an acceleration voltage of 15 kV and a beam current of 1 nA and on a Camebax electron microprobe using an acceleration voltage of 15 kV and a beam current of 6 nA.

2.2. Petrography

The samples in this study belong to the carbonate-bearing garnet-pyroxene rocks of the diamondiferous Unit 1 of the Kokchetav Massif (Dobretsov *et al.*, 1995; Korsakov & Hermann, 2006; Ogasawara *et al.*, 2000; Pechnikov & Kaminsky, 2008; Shatsky *et al.*, 1995; Schertl *et al.*, 2004). Some diamondiferous garnet-pyroxene rocks have been considered to be isolated bodies within pelitic gneisses (Shatsky *et al.*, 1995; Sobolev & Shatsky, 1990). These rocks are closely associated with mainly diamond-free metacarbonate rocks. Although in some cases there is a contact between the diamond-free and the diamond-bearing samples, in general diamond spatial distribution is highly heterogeneous and diamond-bearing and diamond-free UHPM rocks may occur together. This study has

focused mainly on an unusual composite sample (GAK101) containing variable proportions of carbonate and silicate minerals in different layers (Fig. 1).

Sample GAK101 consists of four different layers ranging from almost white (layer 1) over grey (layer 2 and 3) to green (layer 4) with variable amounts of carbonate minerals, garnet and clinopyroxene (Fig. 1a and Table 1). Grey layers are rich in sulphides (*e.g.*, pyrite and pyrrhotite), Ti-clinohumite and serpentine pseudomorphs after forsterite. Dolomite was identified exclusively in layer 2

(Fig. 1). Only the light-coloured, almost white, layer 1 contains accessory microdiamonds. The mineral assemblages from different layers and their specific features are presented in Table 1.

Polycrystalline carbonate inclusions up to 400 μm in size predominantly appear within layer 3 (Fig. 1). They occur mainly in garnet and clinopyroxene porphyroblasts and have been found in zircon, as well (Korsakov *et al.*, 2002). These carbonate inclusions closely resemble the polycrystalline carbonate inclusions that were interpreted to be crystallization products of UHPM carbonate melts (Korsakov & Hermann, 2006). However, there exist significant differences between these two types of carbonate inclusions. Almost all magnesian-calcite polycrystalline inclusions display rounded shapes and sharp carbonate-garnet interface. Contrary to the polycrystalline carbonate melt inclusions described by Korsakov & Hermann (2006) neither diamond nor other phases (*e.g.*, silicates) were identified within the aragonite-bearing polycrystalline carbonate inclusions studied here. The lack of dense radial crack patterns around the aragonite-bearing inclusions is another typical feature of this type of inclusions. The number of the subgrains within each polycrystalline inclusion varies significantly from inclusion to inclusion. Monocrystalline carbonate inclusions from diamond-bearing marbles and diamond-free garnet-clinopyroxene rock are abundant in garnet and clinopyroxene. There is no systematic spatial distribution of poly- and monocrystalline carbonate inclusions within the garnet-host.

Diamond and graphite exclusively occur in diamond-bearing marbles, mainly as inclusions in K-bearing clinopyroxene and garnet porphyroblasts. Graphite was found (i) as inclusion in garnet and clinopyroxene (often together with diamond) and (ii) in the sample matrix itself. No graphite was found in the diamond-free part of the sample, despite thorough checking. This is consistent with the previously reported observation that sulphide-rich zones are diamond-free (Korsakov & Hermann, 2006; Schertl *et al.*, 2004).

3. Results

3.1. Raman spectroscopic analysis

Carbonates are distinguishable by their diagnostic Raman spectra (Bischoff *et al.*, 1985; Burke, 2001; Gillet *et al.*, 1993; Frost & Dickfos, 2007; Liu & Mernagh, 1990; Perraki *et al.*, 2006; Scheetz & White, 1977; Williams *et al.*, 1992 and references therein). However, the pressure dependence of the vibration frequencies is well known only in the case of particular carbonates (Gillet *et al.*, 1993). Because of the small sample volumes and the possibility to analyse unexposed inclusions, non-destructive Raman mapping is a very promising tool for the identification and study of the spatial distribution of carbonates (*e.g.*, calcite, aragonite, dolomite, and magnesite) and H_2O -soluble minerals within inclusions.

Fig. 1. (a) Photograph of the sample GAK101 showing four different layers. Layers 1, 2, and 3 consist of diamond-bearing Mg-bearing calcite and dolomite marble layers. Layer 4 is composed of diamond-free garnet-clinopyroxene rocks (detailed description of the different layers is presented in Table 1). I and II are the numbers of thin sections used in this study; the boxes indicate the position of the CL images of (b) and (c); dashed lines indicate boundaries between layers. (b–c) Representative CL images of matrix carbonates and carbonate-inclusions from calcite and dolomite marble, respectively. Arabic numbers and arrows mark the location of microprobe point analyses. Analyses are presented in Table 3.

Table 1. Mineral assemblages and specific features of different layers of sample GAK101.

Layers	Mineral assemblage	Specific features
1 (light-coloured)	Mg-Cal, Grt, K-Cpx, Phl, Cpx-II, Spl, Dia, Gr	Mg-Cal (orange to yellow CL) as matrix and as inclusions in Grt and K-Cpx, K-Cpx with abundant exsolution lamellae of Phl, Kfs
2 (grey-coloured)	Mg-cal, Dol, Grt, Cpx, Ti-Chu, Py, Po, Fo-pseud	Dol-matrix (dark red CL), Mg-cal-matrix (orange CL) with Dol-exsolution lamellae (dark red CL), K-Cpx with few exsolution lamellae of Phl, Kfs
3 (grey-coloured)	Mg-cal, Grt, K-Cpx, Py, Po	Mg-cal-matrix (orange CL) rarely with Dol-exsolution lamellae (dark red CL), Mg-cal inclusions in Grt and K-Cpx (orange to yellow, rare dark red CL), rare Ar inclusions in Grt (no CL or very weak greenish CL, can be easily overlooked), K-Cpx with few exsolution lamellae of Phl, Kfs
4 (green-coloured)	Grt, Cpx, Mg-Cal, Py, Ilm	Mg-cal (orange CL), Cpx with very weak or no CL

Mineral abbreviations according to Kretz (1983).

The two polymorphs of CaCO_3 , calcite and aragonite, were distinguished in the samples studied by their diagnostic Raman spectra (Fig. 2 and Table 2). Calcite is characterized by a strong band at 1086 cm^{-1} , along with other weaker bands at 156 , 283 , and 713 cm^{-1} (Edwards *et al.*, 2005). The main band of aragonite is also located at 1086 cm^{-1} with subsidiary bands at 154 , 181 , 191 , 208 , 249 , 261 , 273 , 283 , and 704 cm^{-1} (Edwards *et al.*, 2005). Only the bands marked in *italics* were documented in this study. The host garnet is characterized by a strong band at

896 cm^{-1} , along with other weaker bands at 367 , 547 , 835 and 1022 cm^{-1} (Fig. 2). A slight downshift of roughly 1 cm^{-1} in the 283 cm^{-1} calcite band was observed. A weak band at 282 cm^{-1} in the aragonite spectrum appears. Most likely this band is caused by very fine-grained calcite-aragonite intergrowth, because the band at around 283 cm^{-1} in the Raman spectrum of aragonite is generally very weak (Edwards *et al.*, 2005). Several additional very intense and rather narrow bands appear around 1325 , 1347 , and 1452 cm^{-1} in the aragonite spectrum (Fig. 2a). When excited with a different laser source (Ar^+ , 514.5 nm) the aragonite exhibited no band at these positions. Thus, these bands are considered to be luminescent bands. Calcite also has several luminescent bands, but these are generally broader and less intense (Fig. 2b).

Raman mapping of a polycrystalline carbonate inclusion revealed mainly calcite and an area with bands typically assigned to aragonite (Fig. 3). The band position of aragonite and calcite corresponds to literature spectra obtained at ambient conditions (Fig. 2 and Table 2). The measured Raman band positions might also be slightly affected by the analytical conditions and exhibit slight differences compared to the literature ones (different calibration standards, slit width, gratings, etc.). It can thus be misleading to check whether minor Raman band shifts indicate residual overpressure inside the inclusion. When a subsurface inclusion is exposed at the surface through polishing, its residual pressure disappears. Hence, one inclusion was exposed at the thin section surface and reanalysed to detect residual pressures. The band positions of calcite and aragonite are equal to the positions of the intact inclusion. This observation implies that no measurable shifts of the main Raman band of calcite and aragonite in the polycrystalline inclusion were overlooked.

3.2. Optical microscopy, cathodoluminescence and SEM-EDS studies

Over 100 polycrystalline carbonate inclusions were analysed by CL and SEM. Polycrystalline carbonate inclusions (calcite or calcite and dolomite), exhibit a wide variety of textures observable either with the reflected-light microscope or in cathodoluminescence images (Fig. 1, 4 and 5).

Fig. 2. Representative Raman spectra of (a) aragonite (blue spectrum) and (b) calcite (red spectrum), and garnet (black spectrum).

Table 2. Wavenumbers (cm^{-1}) of aragonite and calcite Raman bands in spectra of a representative unexposed polycrystalline inclusion.

Calcite				Aragonite			
ν^* (cm^{-1})	$(d\nu/dP)_T$ ($\text{cm}^{-1}/\text{GPa}$)	ν (cm^{-1})	P (GPa)	ν^* (cm^{-1})	$(d\nu/dP)_T$ ($\text{cm}^{-1}/\text{GPa}$)	ν (cm^{-1})	P (GPa)
156	2.47 ± 0.3	156	10^{-4}	152	2.7 ± 0.2	154	0.7
				180	3.4 ± 0.6	180	10^{-4}
				206	3.3 ± 0.5	207	0.3
283	5.27 ± 0.4	282	-0.19	704	1.5 ± 0.1	704	10^{-4}
713	2.22 ± 0.2	713	10^{-4}	1086	2.3 ± 0.2	1086	10^{-4}
1086	5.87 ± 0.4	1086	10^{-4}				

Pressure shifts of the Raman modes of aragonite and calcite after Gillet *et al.* (1993). ν^* = theoretical, ν = measured in this study.

Fig. 3. BSE image and Raman maps of the polycrystalline carbonate inclusion presented in Fig. 4g–i.

Figure 4 shows that carbonate textures are variable and that blocky textures dominate. Monocrystalline magnesian-calcite inclusions occur intimately close to polycrystalline carbonate inclusions within a garnet porphyroblast. Many polycrystalline inclusions commonly show intricate compositional zoning as indicated by CL study (Fig. 1b). Brighter zones within polycrystalline inclusions contain higher Sr content up to 0.5 wt%, whereas darker zones are richer in Fe, Mn and Mg. In calcites, Mn is generally considered to be the main CL activator (Marshall, 1988) although electron microprobe analyses indicate that many other elements are also present and a simple relationship between CL intensity and Mn concentration is therefore lacking. All investigated aragonite-bearing inclusions are characterised by an extremely weak CL pattern. A very weak greenish colour of CL was documented in only one case (Fig. 5c). Interestingly, the calcite coexisting with aragonite within the same inclusion shows also very weak luminescence. Some polycrystalline carbonate inclusions contain fine-grained dirty aggregates with high interference colours (Fig. 5a, b). Calcite coexisting with aragonite, at least on an optical basis, behaves as a monocrystal, although the orientation of aragonite is often different from the orientation of calcite. Furthermore, no crack patterns associated with these inclusions were found. Cracks only appeared during the final polishing of the sample to expose the inclusion at the thin-section surface. SEM study of the polycrystalline carbonate inclusions revealed that they are rather heterogeneous (Fig. 3), confirming the results of CL imaging. In back-scattered electron (BSE) images, calcite exhibits different shades of grey with brighter parts rich in Mg, Mn and Fe and darker areas rich in Sr (Table 3).

Three different carbonates can be distinguished on the basis of their CL images: calcite, dolomite, and aragonite. Calcite can be further distinguished into different generations: orange Mg-bearing calcite, bright-yellow secondary pure calcite (Fig. 1c), dark-yellow calcite enriched in Sr (Fig. 1b) and dark-orange to red calcite enriched in Fe, Mn, and Mg (Fig. 5). Dolomite appears dark red. Dolomite and Mg-bearing calcite form distinct layers (Fig. 1) and are the dominant carbonate minerals. Aragonite does not produce CL or only very weak greenish CL. The garnet and pyroxene crystals contain rare carbonate inclusions exhibiting yellow to orange luminescence. Microprobe analyses

Fig. 4. Plane-polarized (a, d, g), cross-polarized (b, e, h), and reflected light (c, f, i) photomicrographs of a polycrystalline carbonate inclusions in garnet with representative textures of polycrystalline carbonate inclusions with blocky – granular (a, b, c) and fibrous-like (d, e, f) textures. Arrows in reflected-light photographs indicate cavities and holes. Numbered blue and red points correspond to the microprobe analyses given in Table 3.

proved that the yellow inclusions are nearly Mg-free CaCO_3 ($\text{Ca}_{0.98}\text{Mg}_{0.02}\text{CO}_3$), whereas (i) the Mg-bearing calcite (orange luminescent) is $\text{Ca}_{0.95}\text{Mg}_{0.04}\text{Fe}_{0.01}\text{CO}_3$ and (ii) dolomite (dark red luminescent) is $\text{Ca}_{0.50}\text{Mg}_{0.49}\text{Fe}_{0.01}\text{CO}_3$. Sometimes dolomite exsolution patterns were identified within Mg-bearing calcite (Fig. 1c). Similar features were observed by Ogasawara *et al.* (2000) and Schertl *et al.* (2004).

4. Discussion

4.1. Origin of aragonite in UHPM rocks

Aragonite in the polycrystalline carbonate inclusions occurs as fine-grained “dirty” aggregates, whereas calcite tends to form clean coarser-grained aggregates (Fig. 4 and 5). In the aragonite-bearing inclusion of Fig. 4, the clean shell, consisting of calcite, optically appears as a

monocrystal. In the case of an UHPM origin of aragonite and later calcite formation by partial replacement of aragonite during retrograde metamorphism, the opposite would have been expected, *i.e.* monocrystalline aragonite surrounded by polycrystalline fine-grained calcite. It has been reported that newly formed minerals, replacing other minerals or forming pseudomorphs after them, are generally more fine-grained compared to the reactant minerals. In the coesite-to-quartz transformation in metamorphic rocks (Chopin, 1984; Smith, 1984) rather large relics of coesite are preserved within fine-grained quartz aggregates. In general, relics of coesite partly transformed to quartz are characterized by radial growth of polycrystalline quartz around a coesite core and radial fractures in the surrounding host mineral. These cracks result from the different elastic properties of the inclusion and the host mineral and the significant volume change related to the coesite-to-quartz transformation (Chopin, 1984; Gillet *et al.*, 1984; Smith, 1984; Van der Molen & van Roermund, 1986).

Fig. 5. Photomicrographs of (a–b) aragonite-bearing sample GAK101 and (c–d) polycrystalline carbonate melt inclusions in garnet sample G0. (a) and (c) are plane-polarized light, (b) cross-polarized, and (d) CL photographs. The CL colour and intensity of calcite varies from orange to dark red (enriched in Fe, Mn, Mg), and the yellow zones are enriched in Sr.

The lack of magnesite in the polycrystalline carbonate inclusions studied here and the coexistence of fine-grained aragonite aggregates with coarse-grained calcite aggregates indicate that aragonite could not be formed by the breakdown of dolomite to magnesite and aragonite.

Alternatively, aragonite may be formed by recrystallization of a highly strained calcite grain. Such mechanism was proposed for aragonitic marbles (Vance, 1968) and documented in experiments (Newton *et al.*, 1969). The

transformation of calcite to aragonite would also reduce the residual pressure.

Raman spectra of both calcite and aragonite correspond well with Raman spectra obtained at ambient conditions. This indicates that there is no overpressure inside the inclusions: their residual pressure can be estimated as high as one atmosphere. Pressure and temperature dependence of the main calcite and aragonite bands is rather well established (Gillet *et al.*, 1993) and can be used for the

Table 3. Representative electron-microprobe analyses (wt%) of the polycrystalline aragonite and calcite inclusions presented in Fig. 1 and 4 (sample GAK101).

No.	Inclusion-I			Inclusion-II				Inclusion-III						
	c1 Ar	c2 Ar	r1 Cal	r2 Cal	2c Cal	2r1 Ar	2r2 Ar	1	2	3	4	5	6	7
SiO ₂	0.02	0.00	0.00	0.03	0.01	0.01	0.00	0.00	0.01	0.01	0.00	0.00	0.01	0.00
TiO ₂	0.01	0.00	0.00	0.01	0.00	0.00	0.01	0.00	0.00	0.00	0.01	0.00	0.00	0.01
Al ₂ O ₃	0.01	0.01	0.01	0.03	0.00	0.01	0.02	0.00	0.00	0.01	0.02	0.00	0.01	0.02
FeO	0.12	0.16	0.25	0.17	0.22	0.06	0.09	0.11	0.11	0.06	0.27	0.34	0.30	0.08
MgO	0.00	0.00	0.00	0.00	0.48	0.00	0.00	0.07	0.00	0.04	0.07	0.08	0.08	0.00
MnO	0.00	0.01	0.00	0.01	0.01	0.00	0.00	0.00	0.02	0.02	0.69	1.23	0.99	0.00
CaO	56.3	56.0	56.5	57.6	55.8	57.5	57.1	56.0	56.8	56.3	56.2	56.2	57.5	56.4
Na ₂ O	0.01	0.00	0.01	0.00	0.03	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.02	0.00
K ₂ O	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.00	0.00	0.00	0.01	0.00
SrO	0.11	0.14	0.10	0.01	0.00	0.08	0.07	0.09	0.30	0.11	0.17	0.14	0.17	0.57
BaO	0.00	0.00	0.02	0.00	0.07	0.00	0.03	0.00	0.00	0.07	0.00	0.00	0.05	0.00
Total	56.60	56.28	56.88	57.83	56.60	57.67	57.32	56.26	60.95	61.11	61.23	59.80	59.09	59.64

estimation of the residual pressure in the carbonate inclusions in the garnet porphyroblast. Residual pressures in other inclusions (e.g., coesite) within host minerals for the similar UHPM lithologies have been estimated as high as 2.2 GPa (Korsakov *et al.*, 2007; Parkinson & Katayama, 1999; Ye *et al.*, 2001).

The lack of significant shifts in the main bands of both aragonite and calcite indicates very low residual pressure in the aragonite-calcite inclusions. Numerical modelling using elastic constants for aragonite and calcite inclusions and the host garnet allows us to estimate the P - T conditions at which aragonite was captured (Fig. 6). Assuming that peak metamorphic conditions were $P = 6$ GPa and $T = 1000$ °C (Korsakov & Hermann, 2006; Shatsky *et al.*, 1995) and that aragonite in inclusions never transformed to calcite, the residual pressure in the inclusions is estimated as high as 1.7 GPa. In the case of aragonite-to-calcite transformation the residual pressure would have been increased to 4.5 GPa ($\alpha = 0.5$). Taking into account the higher peak metamorphic conditions reported by Ota *et al.* (2000) and Massonne (2003), the residual pressure would have been expected even higher (Fig. 6).

Using different hypothetical values for residual pressures (e.g., $P_{in} = 0.001$, 0.01, and 0.1 GPa) we calculated P_0 as function of T_0 (Fig. 6). The results of this modelling reveal that the aragonite inclusions could have been captured only at pressures significantly lower than those of the peak metamorphic conditions, close to the aragonite-calcite equilibrium line. Lack of information on the residual pressure of aragonite inclusions in diamond (Dobrzhinetskaya *et al.*, 2006), does not allow us to check whether aragonite was captured in the dolomite stability field (at P 6 GPa) or not.

This is inconsistent with a model for the origin of polycrystalline calcite inclusions by partial or complete transformation, since in that case significant overpressure should be expected. This was observed in the case of coesite inclusions in different minerals (Korsakov *et al.*, 2007; Parkinson & Katayama, 1999; Ye *et al.*, 2001).

Aragonite-bearing inclusions are characterized by very weak CL patterns (Fig. 5c). Hence, they can be easily overlooked, unless these inclusions are checked with Raman spectroscopy. Contrary to aragonite-bearing inclusions, former melt inclusions described by Korsakov & Hermann (2006) have very strong luminescence (Fig. 5e), which can be used as a diagnostic feature. The absence of any other carbonate (e.g., alkaline carbonates or magnesite) besides calcite and aragonite in the unexposed polycrystalline inclusions indicates that cavities and holes on the polished surface of these inclusions are related with crushing of fine-grained aggregates. CL and SEM studies of the polycrystalline inclusions show that they predominantly consist of coarse-grained aggregates of calcite. The distribution of impurities (e.g., Mg, Sr, Mn, and Fe) within the inclusions is highly heterogeneous.

The formation of aragonite by the breakdown of dolomite is unlikely, because so far polycrystalline carbonate inclusions have been identified in calcite marbles (Korsakov & Hermann, 2006). Low values of residual

Fig. 6. Peak metamorphic conditions for diamondiferous calc-silicate rocks and marbles from the Kokchetav Massif: I-Okamoto *et al.* (2000); Ogasawara *et al.* (2000), II-Zhu & Ogasawara (2002), III-Ogasawara *et al.* (2002), IV-Massonne (2003), V-Dobrzhinetskaya *et al.* (2006). Experimental phase relations for dolomitic carbonates after Goldsmith & Newton (1969), Irving & Wyllie (1975), Luth (2001), Buob *et al.* (2006), and Hermann (2003a). Experimental study (L) of Luth (2001) on the reaction dolomite (dol) = aragonite (ara) + magnesite (mag). Graphite-diamond and coesite-quartz transitions are from Kennedy & Kennedy (1976) and Mirwald & Massonne (1980). The retrograde evolution shown as (A)–(C) is taken from Hermann *et al.* (2001). Aragonite inclusion without phase transformation to calcite: 1–3, dependence of P_0 as function of T_0 for $P_{in} = 0.1$, 0.01 and 0.001 respectively; Calcite inclusion without transformation to aragonite: 4–6, residual pressure (P_{in}) as function of T_0 for $P_0 = 6$, 4 and 3 GPa, respectively.

pressure in aragonite-bearing inclusions are inconsistent with their UHPM origin. This fact can be explained by different models. First of all, aragonite could have been formed during prograde metamorphic events at relatively low P - T parameters. Ogasawara *et al.* (2000) proposed that the subduction path of the Kokchetav Massif should cross the aragonite stability field. Thus, aragonite rather than calcite or magnesian calcite should be the stable CaCO_3 polymorph up to peak metamorphic conditions; protected by the host garnet these inclusions would not react during all subsequent transformations (*cf.* Chopin *et al.*, 2008). The rarity of aragonite in UHPM samples can be associated with very fast transformation (even faster than coesite-to-quartz) to calcite during the retrograde stage. However, the possibility that aragonite has been simply overlooked is high. The same very low residual pressure

would occur if original inclusions were captured as a carbonate melt. Crystallization of aragonite was recently confirmed in HP and HT experiments (Sokol *et al.*, 2001). Aragonite was found to be in equilibrium with diamond and carbonate melts. Fine-grained aggregates of aragonite were also identified in the quenching run products. Therefore, the origin of aragonite by crystallization of UHPM carbonate melts could be an important mechanism in some natural deeply subducted samples. However, the time and the exact *P-T* conditions of the aragonite formation remain poorly defined.

5. Concluding remarks

The Raman spectroscopy study of polycrystalline carbonate inclusions in diamond-grade metamorphic rocks from the Kokchetav Massif, Northern Kazakhstan, revealed the presence of aragonite along with calcite. The aragonite-bearing polycrystalline inclusions exhibit different features compared to other polycrystalline inclusions, interpreted as crystallization products of UHPM carbonate melts. Aragonite appears within the inclusions as “dirty” chaotically oriented materials surrounded by a “clean” and monocrystalline calcite shell. Melt inclusions generally have different shapes of grain boundaries between sub-individuals within the inclusions; boundaries are generally smooth and convex-concave. Grain boundaries between the host-garnet and the aragonite-bearing inclusions also differ from those between the host garnet and the melt inclusions; the former has a smooth garnet-carbonate interface, whereas the latter are often characterized by wavy or amoeboid shape. The melt inclusions are surrounded by rather dense radial crack patterns, whereas no such patterns appear around aragonite-bearing inclusions; tiny cracks that are rarely observed appeared during polishing.

The lack of radial cracks around the polycrystalline carbonate inclusions and the absence of a measurable shift in the main Raman bands clearly indicate that the residual pressure within aragonite-bearing inclusions is minor. These features are inconsistent with an origin of aragonite at peak metamorphic conditions (~6 GPa) by dolomite decomposition. Therefore, the presence of aragonite in diamond-bearing or diamond-grade UHPM rocks cannot be an unequivocal evidence for extremely deep subduction.

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