

Relict Unusually Low Iron Pyrope-Grossular Garnets in UHPM Calc-silicate Rocks of the Kokchetav Massif, Kazakhstan

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Abstract

Knowledge of the compositional ranges of rock-forming minerals in ultrahigh-pressure (UHP) rocks occurring both as deep mantle xenoliths in kimberlites and subducted crustal metasediments is critical for estimating the conditions of their formation. Garnet is one of the most important minerals of UHP rocks. This study deals with unusually low iron (less than 2 wt% FeO) pyrope-grossular garnets with Mg# more than 90 and Ca# of ~60–65, which have been detected for the first time in nature as relics within some garnet grains of layered calc-silicate rocks from the Kokchetav massif. These relics represent the earliest generation of garnet formed under peak metamorphic conditions. Using a cathodoluminescence (CL) method, relics are visible in a number of samples as irregular, light, luminescent portions occurring unevenly distributed within garnet grains. Similar features are revealed by electron microprobe X-ray elemental maps of single mineral grains within a thin section, but not as fast as the CL method that takes only seconds.

New results on calc-silicate rocks demonstrate that fluids must have penetrated carbonate-rich layers, whereas adjacent garnet-pyroxene rocks acted as impermeable barriers protected against retrograde attack. Oriented arrays of exsolution-like needles (rutile?, ilmenite?) were found for the first time within Ti-clinohumite, possibly formed during pressure release after peak metamorphic conditions.

Introduction

PYROPE-GROSSULAR (Mg-Ca) garnets with Mg# [100Mg/(Mg+Fe)] between 70 and 85 and Ca# [100Ca/(Mg+Ca+Fe+Mn)] between 40 and 80 are extremely rare in natural rocks. They are restricted to inclusions in diamond, xenoliths of corundum-kyanite eclogites, and grosspydites from kimberlites, in part diamondiferous. All these rock types contain jadeitic pyroxene, kyanite, corundum, and sometimes coesite (Sobolev et al., 1968, 1999; Ponomarenko et al., 1976; Sobolev, 1977, 2006). Diamondiferous calc-silicate rocks from the Kokchetav massif, Kazakhstan also contain garnets of such unusual composition (Sobolev et al., 2001, 2006; Shatsky, Sobolev, 2003; Shatsky et al., 2006a, 2006b). These calc-silicate rocks have been termed dolomite (dolomitic) marbles by Ogasawara et al.,

(2000), Ogasawara (2005), Yoshioka and Ogasawara (2005), and Zhang et al. (1997). Calc-silicate rock compositions stand in sharp contrast to the unique coesite-bearing pyrope quartzites first described by Chopin (1984), which contain pure pyrope of nearly end-member composition. Ultrahigh-pressure dolomite marbles are also known in the Dabie Shan, China with coesite present as inclusions in dolomite (Schertl and Okay, 1994).

The investigated rock samples display a layered structure, possibly recording relict sedimentary bedding. The occurrence of forsterite (96–97% of end-member composition) with Ni contents below the detection limit along with high MnO contents (~0.3 wt%) (Schertl et al., 2004; Sobolev et al., 2006) further demonstrates a metasedimentary origin. Other Ca-Mg and Mg minerals associated with garnets are diopside, phlogopite, Mg-calcite, dolomite, and Ti-clinohumite. Magnesite (Shatsky et al., 1995) and coesite (Katayama et al., 2002) were

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detected only as inclusions in garnet, zircons, and microdiamonds (Sobolev et al., 1994; Dobrzhietskaya et al., 2006). Potassium-rich fluids played an important role in diamond formation in these rocks (Hwang et al., 2005).

The closest analogues to minerals from the Kokchetav calc-silicate rocks are deep mantle samples, such as inclusions in diamonds from New South Wales, Australia, alluvial deposits, and some rare xenoliths in kimberlites. These samples contain grossularitic garnets, diopsidic pyroxenes with very low iron contents (as low as 0.52 wt% FeO), coesite, and carbonates (Sobolev et al., 1984; Meyer et al., 1997; Davies et al., 2003). Stoichiometric diopside with Ca# close to 50 is a specific feature of these pyroxenes. Calc-silicate assemblages (Sobolev et al., 1984) are the third of the three most general categories of diamond inclusions, including ultramafic and eclogitic inclusion assemblages in diamonds (Meyer, 1987).

First results on the luminescent, low-iron garnet relics from layered Kokchetav calc-silicate rocks recently were presented by Schertl et al. (2004) and Sobolev et al. (2001, 2006). A cathodoluminescence microscopy (CL) study of pyrope-grossular garnet grains containing inhomogeneously distributed luminescent relics showed that garnet compositions within these relics vary in narrow ranges, both in Mg# from 92–95 and Ca# from 60–65. Such a high Mg# implies very low amounts of FeO ranging between 1 and 2 wt%. Dark, non-luminescent parts of the same grains contain more than ~2 wt% FeO and are more inhomogeneous in composition, especially regarding their Mg# from 76–90 and Ca# from 41–56. The non-luminescent, host garnets cover most of the whole compositional range of typical garnets described elsewhere from Kokchetav calc-silicate rocks (e.g., Sobolev et al., 2006). Such formerly unknown relict garnet compositions were discovered for the first time by careful application of the CL technique (for details see the section on Methods). Routine investigation of a multitude of thin sections using the CL microscope revealed the occurrence of such “patchy” garnets to be by no means rare. It is important to note, however, that garnets from different calc-silicate layers within the same thin section may show or completely lack luminescence due to their different chemical compositions. Similarly, the distribution of microdiamonds, whether present or absent, varies from layer to layer within a single thin section.

Since more samples and thin sections have become available, we are able to present new results together with already existing data, and to offer a much more comprehensive picture of UHP calc-silicate rocks from the Kokchetav massif. All samples selected for this study contain interlayered examples of (1) typical dolomite (dolomitic) marbles; (2) Mg-calcite-bearing rocks enriched in garnet and pyroxene; and (3) garnet-pyroxene rocks. The interlayering of all three rock types in the same hand specimens on a centimeter scale confirms the close relationship of all these rock types.

Methods

CL-measurements were performed using a “hot cathode” microscope (type HCl-LM) at the Ruhr-University Bochum (Neuser, 1995; Schertl et al. 2004, 2005). With a vacuum chamber adapted for use with a polarizing microscope, normal thin sections polished and covered by a carbon coating can be studied under an electron beam. The operating conditions used for CL examination were: 14 keV beam energy and ~9 $\mu\text{A}/\text{mm}^2$ current beam density. A digital camera with high sensitivity under weak lighting conditions was used to record the CL-images presented here. The CL technique was especially advantageous to the present study because an entire thin section can be studied within minutes: the exposure time for a single CL-photo is only a few seconds. It is possible to study the same thin section under plane-polarized light, under crossed polars, and under cathodoluminescence, and, in addition, to use the same section for later electron microprobe (EMP) measurements, thus achieving a mutually complementary, in-depth validation of petrographic results. The concomitant EMP studies were carried out using the JEOL-8100 microprobe (Novosibirsk) with an accelerating voltage of 15 kV and current intensity of 15 nA.

Results: Sample Description

The Kokchetav massif is well known as the type locality of diamondiferous metamorphic rocks (e.g., Sobolev and Shatsky, 1990; Shatsky et al., 1995). Detailed descriptions of UHP-metamorphic (UHPM) rocks of the Kokchetav massif and discussion of their conditions of formation are summarized by Coleman and Wang (1995) and Parkinson et al. (2002). Although calc-silicate rocks are relatively scarce within the UHPM diamondiferous rock

sequences of the Kokchetav massif considered in its entirety, they represent, along with garnet-pyroxene rocks, about 15% of the diamondiferous rock volume of the Kundy Kol diamond deposit. The remaining 85% of the deposit consists of garnet-biotite gneisses and retrograded varieties. The mapping of Kundy Kol was conducted by careful evaluation of underground mining galleries and core-logging of shallow drilling. However, this deposit covers only a small part of an area of more the 200 km² within the Kokchetav massif, where diamond-bearing UHP rocks are found.

Calc-silicate rocks are very important because of their unusual mineralogy, but also have been a principal focus of study since it was recognized that they contain up to 3000 carats of microdiamonds per metric ton, with an average of 20 carats per metric ton for the whole Kundy Kol diamond deposit. The calc-silicates form layers and lens-like bodies with thicknesses up to few meters within garnet-biotite gneissic country rocks. Recent studies within the underground mining gallery showed that these rocks may extend up to 30 m, exhibiting steeply dipping folds (Sobolev et al., 2003; Shatsky et al., 2006b). However, due to a more detailed enquiry in the underground gallery it turned out that within this 30 m thick layer calc-silicate rocks are intercalated with garnet-biotite gneisses that are present as a number of 1–2 meter thick layers (Shatsky et al., 2006b). Most samples of calc-silicates studied by several authors were collected both in the underground mining gallery and in the waste deposit outside. Only a few of these samples are layered, demonstrating different lithologies, and thus also different mineral compositions. We consider such samples as extremely valuable, inasmuch as they contain the features of micro-outcrops in one hand specimen.

One very fresh calc-silicate rock sample (K98-11a) with remarkable CL-features (Schertl et al., 2004) has been restudied to clarify relationships between the different diamond-bearing vs. diamond-free layers, and the Mg-calcite vs. dolomite matrix. The aim of the present paper is to document different garnet grains within each compositional layer, their abundance, location, and specific alteration zones. Of special interest are the relict garnets characterized by their yellowish-brown luminescence color. For this reason three new thin sections were investigated, cut perpendicular to the sections of the prior study (Schertl et al., 2004, their Fig 2 and Table 1). A further detailed paper will focus on

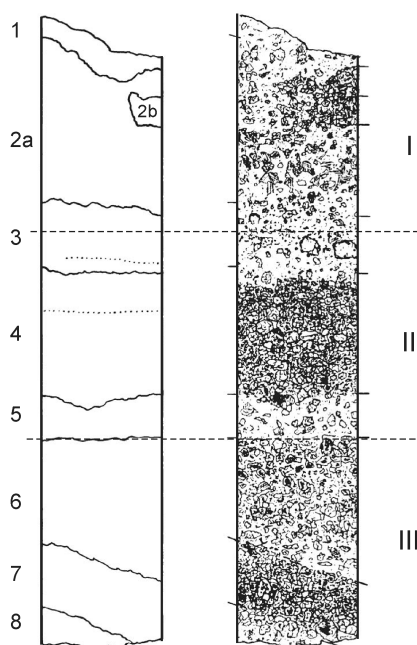


FIG. 1. Schematic cross-section of the diamondiferous calc-silicate rock (sample K-98-11a) investigated. Numbers 1–8 refer to the different layers observed; I, II, and III refer to the different thin sections (see Schertl et al., 2004; their Fig. 2).

the mineral chemistry, phase relationships, and formation conditions derived from this particular sample and in addition on other similar layered/banded composite calc-silicate rocks from Kokchetav.

The study of the new set of thin sections confirmed the presence of diamonds occurring as inclusions both in garnets and pyroxenes within the entire dark lower part of the rock sample (Schertl et al., 2004, their Fig. 2). Thus, in addition to the observations made previously (occurrence of diamonds in layers 2a, 5, and 8; Fig. 1), diamonds were also discovered within layers 4, 6, and 7 (see Fig. 1), leaving only one layer, 3, where diamonds have not been detected. One spectacular example of a diamond-bearing garnet is shown in Figures 2 and 4 (O), where the grain size of several diamond inclusions reaches about 100 µm, a diameter that is normally typical of garnet-pyroxene rocks only (Shatsky et al., 1998). Very close to the garnet grain presented here, more diamond inclusions were observed in another garnet host (see Fig. 2). The occurrence of unusually large diamonds as observed

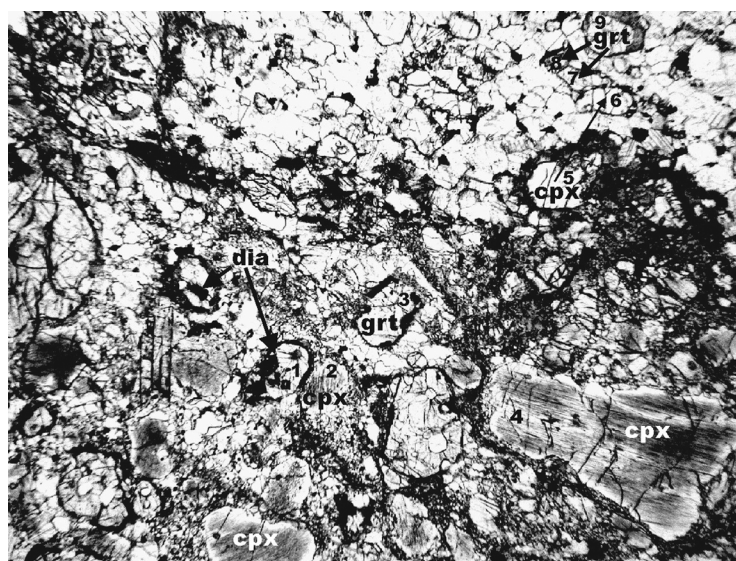


FIG. 2. Photomicrograph of a contact zone between dolomite-bearing (upper right) and Mg-calcite-bearing (lower left) portions of a composite sample of calc-silicate rock K98-11a (plane-polarized light). This part is equivalent to contact between zones 3 and 4 of the same sample from Schertl et al.(2004); see Figure 1. Large diamond inclusions (up to 100 μm) are present in two garnet grains. See Figure 4(0) for detailed image of grt1. All analyzed garnet and pyroxene grains are numbered (1–9) and analyses are presented in Table 1. The closest distance between analyzed garnet (3) and pyroxene (5) from different zones is about 2 mm. The field of view is about 11 mm in longest dimension. Here and in the following figures mineral symbols are after Kretz (1983).

in garnets very close to the contact of a garnet-pyroxene-Mg-calcite rock with dolomite marble is drastically different from those documented in dolomite marble itself (Ogasawara et al., 2000; Ogasawara, 2005). Because of the presence in one thin section of a contact zone between dolomite marble (calc-silicate rock) and a Mg-calcite-bearing zone containing a series of large (100 μm) diamonds included within garnet, we found it necessary to present garnet and diopside compositional data in Table 1 with specific numbers (1–9) of analyzed grains indexed to Figure 2. The contact itself is marked by deformed mineral grains and an enrichment of mica flakes that may reflect the penetration channel along which fluids infiltrated.

A multitude of diamond inclusions within pyroxene were observed in one layer corresponding to layer 2a of Schertl et al. (2004, their Fig. 2 and Table 1). This new set of thin sections also revealed the presence of a 2 mm thick dolomitic layer within the upper right part of sample K98-11a composed of Mg-calcite matrix (corresponding to layer 2a of Fig. 2 in Schertl et al., 2004). Garnets with luminescent relics occur even within this tiny layer.

Other new samples investigated (K-204, K-604) give examples of the occurrence of diamond-free Ti-clinohumite + forsterite-bearing calc-silicates in direct contact with diamond-bearing calc-silicates in one thin section. The well-pronounced contact between a garnet-pyroxene zone and a Mg-calcite-rich zone in sample K204 is nicely marked by the presence of well-developed, clinopyroxene-rich, reaction rims around garnets (Fig. 3). Most interestingly, garnets belonging to the garnet-pyroxene rock exhibit a very distinctive reaction rim, but only at contacts with Mg-calcite of the carbonate-rich layer. Garnets touching carbonates within the garnet-pyroxene rock, however, do not show a reaction rim. In the Mg-calcite-rich zone, conversely, all garnets are characterized by pronounced reaction rims. Thus in all probability, fluids must have penetrated the carbonate-rich rocks whereas the adjacent garnet pyroxene rock was impermeable to retrograde reactions driven by fluid infiltration. Careful CL investigations of garnets belonging to layers with Mg-calcite matrices of all our composite calc-silicate rocks available (samples K98-11a, K-204, K-604) do not show any luminescent relics.

TABLE 1. Representative Analyses of Garnets (grt) and Pyroxenes (cpx) from the Contact Zone between Dolomite and Mg-Calcite Layers, Sample K98-11a¹

Name	1		2	3	4		5	6	7	8	9
	grt-C	grt-R	cpx	grt	cpx-C	cpx-R	cpx	cpx	grt	grt	grt
SiO ₂	40.1	40.1	53.9	40.3	54.0	53.9	54.9	54.9	41.5	42.1	41.6
TiO ₂	0.33	0.30	0.04	0.35	0.03	0.04	0.04	0.08	0.60	0.55	0.80
Al ₂ O ₃	21.5	21.7	1.00	21.7	1.65	1.56	0.55	0.31	22.1	22.4	21.9
FeO _{tot}	12.7	12.00	2.96	11.4	3.19	2.73	0.82	0.58	2.85	3.23	3.01
MnO	0.82	0.83	0.07	0.78	0.08	0.07	0.04	0.06	0.64	0.66	0.58
MgO	8.11	7.41	16.1	7.39	15.7	15.8	17.8	17.9	12.3	15.3	13.6
CaO	16.8	17.9	24.5	18.4	23.4	24.2	24.6	25.2	19.2	15.1	17.8
Na ₂ O	bdl	bdl	0.31	bdl	0.46	0.49	0.10	0.04	bdl	bdl	bdl
K ₂ O	bdl	bdl	0.03	bdl	0.44	0.02	0.12	0.02	bdl	bdl	bdl
Total	100.4	100.2	99.0	100.4	99.0	98.6	98.9	99.0	99.3	99.3	99.3
Number of ions on the basis of 12 O for garnets and for 6 O for pyroxene											
Si	3.004	3.009	1.987	3.012	1.990	1.984	2.002	2.000	3.018	3.025	3.017
Ti	0.019	0.017	0.001	0.020	0.001	0.001	0.001	0.002	0.033	0.030	0.043
Al	1.896	1.918	0.043	1.911	0.071	0.068	0.024	0.013	1.898	1.902	1.872
Fe _{tot}	0.797	0.751	0.091	0.712	0.098	0.084	0.025	0.018	0.173	0.194	0.182
Mn	0.052	0.053	0.002	0.049	0.002	0.002	0.001	0.002	0.040	0.040	0.036
Mg	0.905	0.828	0.887	0.824	0.860	0.868	0.966	0.971	1.334	1.642	1.472
Ca	1.352	1.436	0.967	1.478	0.922	0.956	0.961	0.983	1.501	1.161	1.379
Na	bdl	bdl	0.022	bdl	0.033	0.035	0.007	0.003	bdl	bdl	bdl
K	bdl	bdl	0.001	bdl	0.021	0.001	0.006	0.001	bdl	bdl	bdl
Total	8.030	8.015	4.005	8.016	3.999	3.999	3.974	3.993	8.000	7.994	8.002
Mg#	53.2	52.5	90.7	53.6	89.7	91.2	97.5	98.2	88.5	89.4	89.0
CA#			49.7	49.5	49.1	50.1	49.2	49.9	50.4	39.1	46.2

¹Numbers in Table 1 correspond to grain numbers in Fig. 1; bdl = below detection limit; C = core; R = rim of the same grain. See Figure 1 for location of analyzed grains.

Garnet

The application of CL microscopy offers the possibility to identify many more garnet grains containing luminescent, light relics in different composite samples of calc-silicate rocks compared to previous studies (Sobolev et al., 2001, 2006; Schertl et al., 2004) and to follow-up with EMP analyses.

In general, garnet grains containing luminescent relics are of irregular shape and normally have a size from 0.5 to 0.8 mm in longest dimension. Some grains are as large as 5–7 mm. Irregularly distributed reaction rims envelop some garnet grains but their presence is irregular and randomly scattered rather than systematic. In some cases, only small

fragments of such rims are present, which was probably caused by fluids heterogeneously penetrating the calc-silicate rocks during retrograde metamorphism. Earlier studies (Sobolev et al., 2001; Schertl et al., 2004) showed that clinopyroxene and spinel are major constituents of these rims, with scarce sapphirine and corundum. Examples of contrasting shapes of studied garnet grains are presented in Figures 4A, 4C, 4E, 4G, 4I, and 4K. A very rare occurrence of a fully preserved, thick reaction rim is presented in Figure 4C, where the major part of a whole grain has been replaced by a clinopyroxene-rich rim.

On the one hand, garnet grains may contain only one (or a few) luminescent spot(s) distributed irreg-

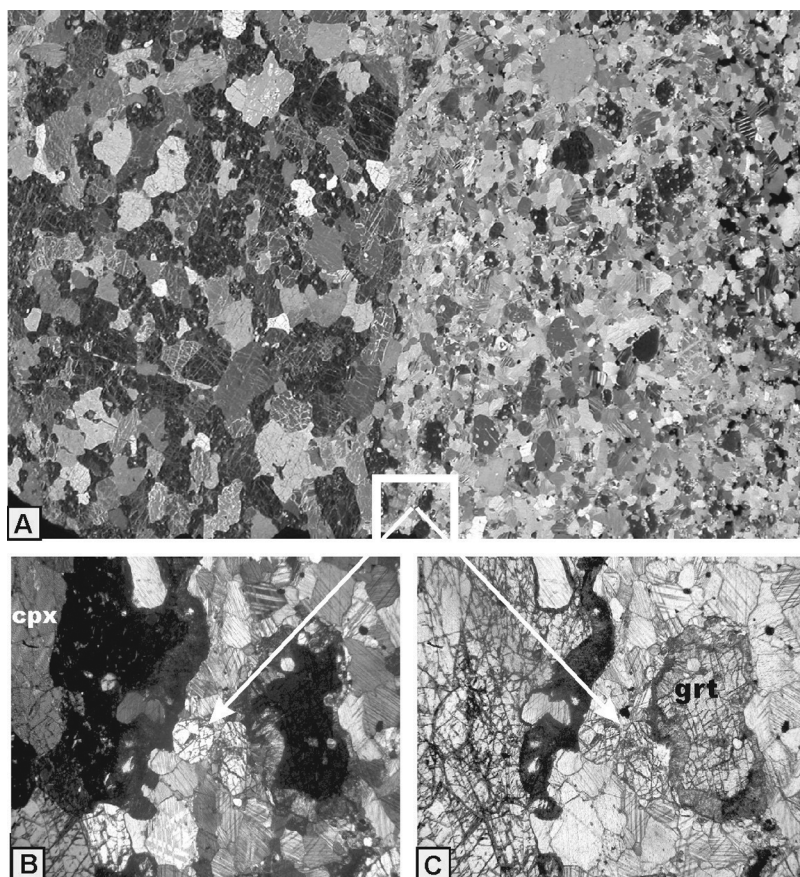


FIG. 3. Photomicrograph of a contact between garnet-pyroxene rock (left) with minor dolomite and calc-silicate rock (right) rich in matrix-dolomite (A, crossed polars). Note the presence of reaction rims around garnets only at the contact with the carbonate-rich part and around the garnet grain embedded in dolomite as presented in B (crossed polars) and C (plane-polarized light). B and C are enlargements of the box marked in (A). The field of view of (A) is about 25 mm and of (B, C) 1 mm.

ularly throughout the whole grain. Generally, they are located in the inner parts of garnet, and rarely, however, also near the rim. Some of them are large enough (up to 100–150 μm) to check their chemical composition by the EMP technique. Analysis of 11 luminescent spots in garnets from sample K98-8 confirms a very homogeneous composition for all the luminescent parts (Sobolev et al., 2001). On the other hand, patchy grains are observed which fade into net-like structures (Fig. 4A). Whereas the luminescent cores of garnet clearly represent an early generation (possibly formed under UHP metamorphic conditions), the net-like structures in all probability are attributable to deformational processes leading to cracks within the yellowish-brown lumi-

nescent older garnet in which a younger, non-luminescent garnet filled the cracks during annealing (Scherl et al., 2004).

Compositions of luminescent portions of grains as well as dark, non-luminescent portions vary essentially in FeO, MnO, MgO, TiO_2 , and CaO contents; the younger (darker but luminescent) garnets typically are lower in Ca and Mn and higher in Ti, Fe, and Mg (for details see Scherl et al., 2004). FeO contents of bright luminescent spots are within 1.01–1.90 wt%, whereas higher amounts of FeO (1.90 wt%) were detected in darker but still luminescent relics (Fig. 4K). The bright luminescent spots contain the lowest amounts of FeO (about 1.01 wt%), see Fig. 4A and Table 2. Analyzed garnet

TABLE 2. Representative Analyses of Garnet Grains Mainly Containing Luminescent Relics¹

Name	K98-11a (layer 3)*										K-204-II									
	(grt3)		(grt1)		D		L		b (grt2)		D		L		grt6		D		grt5	
	L	D	L	D	D	D	L	L	L	L	D	D	L	L	L	L	D	D	C	R
SiO ₂	41.4	41.3	41.2	41.1	41.1	41.1	41.2	40.9	41.2	41.2	41.2	41.2	40.9	40.5	40.5	40.5	40.5	40.5	40.5	40.9
TiO ₂	0.24	0.6	0.16	0.81	0.25	0.25	0.24	0.42	0.75	0.75	0.61	0.61	0.14	0.67	0.67	1.26	1.26	1.26	0.98	0.98
Al ₂ O ₃	22.1	21.4	22.6	22	22.6	22.6	22.2	22.1	21.4	21.4	21.5	21.5	22.3	21.6	21.6	20.3	20.3	20.3	21.3	21.3
FeO _{tot}	1.16	2.86	1.01	3.09	2.51	2.51	1.11	1.42	3.38	3.38	2.71	2.71	1.9	4.46	4.46	5.48	5.48	5.48	5.78	5.78
MnO	0.98	0.59	1.14	0.7	0.86	0.86	1.02	0.98	0.51	0.51	0.61	0.61	1.34	0.75	0.75	0.73	0.73	0.73	0.82	0.82
MgO	9.7	9.95	10.2	11.5	10.9	10.9	9.18	9.3	10.1	10.1	10.4	10.4	9.63	10.1	10.1	9.11	9.11	9.11	10.8	10.8
CaO	23.8	22.9	22.9	19.9	20.6	20.6	24	23.7	22.1	22.1	22.1	22.1	23.2	21.3	21.3	22.1	22.1	22.1	19.5	19.5
Na ₂ O	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
K ₂ O	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
Total	99.4	99.6	99.2	99.1	98.8	98.8	99	98.8	99.4	99.4	99.1	99.1	99.4	99.4	99.4	99.5	99.4	99.4	100.1	100.1
Number of ions on the basis of 12 O for garnets																				
Si	3.03	3.03	3.012	3.008	3.013	3.013	3.03	3.015	3.027	3.027	3.028	3.028	3.004	2.992	2.992	3.014	3.014	3.014	3.003	3.003
Ti	0.013	0.033	0.01	0.045	0.014	0.014	0.013	0.023	0.041	0.041	0.034	0.034	0.01	0.037	0.037	0.07	0.07	0.07	0.054	0.054
Al	1.906	1.85	1.947	1.898	1.953	1.953	1.924	1.92	1.853	1.853	1.862	1.862	1.93	1.881	1.881	1.78	1.78	1.78	1.843	1.843
Fe _{tot}	0.071	0.175	0.062	0.189	0.154	0.154	0.068	0.088	0.208	0.208	0.167	0.167	0.117	0.276	0.276	0.341	0.341	0.341	0.355	0.355
Mn	0.061	0.037	0.071	0.043	0.053	0.053	0.064	0.061	0.032	0.032	0.038	0.038	0.083	0.047	0.047	0.046	0.046	0.046	0.051	0.051
Mg	1.058	1.088	1.111	1.254	1.191	1.191	1.006	1.022	1.106	1.106	1.139	1.139	1.054	1.112	1.112	1.01	1.01	1.01	1.182	1.182
Ca	1.866	1.8	1.794	1.56	1.618	1.618	1.891	1.872	1.739	1.739	1.74	1.74	1.826	1.686	1.686	1.762	1.762	1.762	1.534	1.534
Na	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
K	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
Total	8.004	8.012	8.005	7.998	7.996	7.996	7.995	8.001	8.005	8.005	8.007	8.007	8.022	8.03	8.03	8.025	8.025	8.025	8.021	8.021
Mg#	93.7	86.1	94.7	86.9	88.6	88.6	93.6	92.1	84.2	84.2	87.2	87.2	90	80.1	80.1	74.8	74.8	74.8	76.9	76.9
Ca#	62.7	60.3	59.9	52.2	54.2	54.2	63.8	62.7	58.4	58.4	58.4	58.4	60.5	55.5	55.5	58.5	58.5	58.5	50.8	50.8

¹L = light luminescent portions of garnet grains; D = dark portions of the same grain; bdl = below detection limit; C = core of grain; R = rim of the same grain; layer 3 after Schertl et al. (2004).

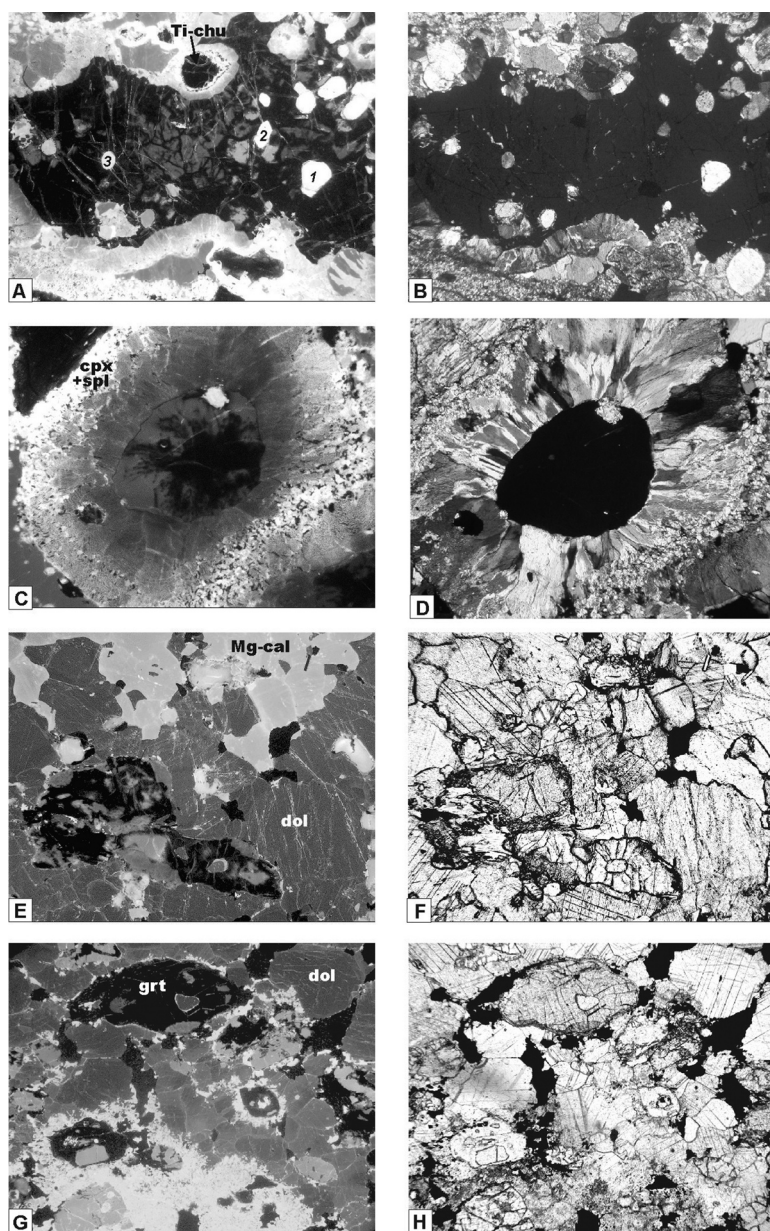
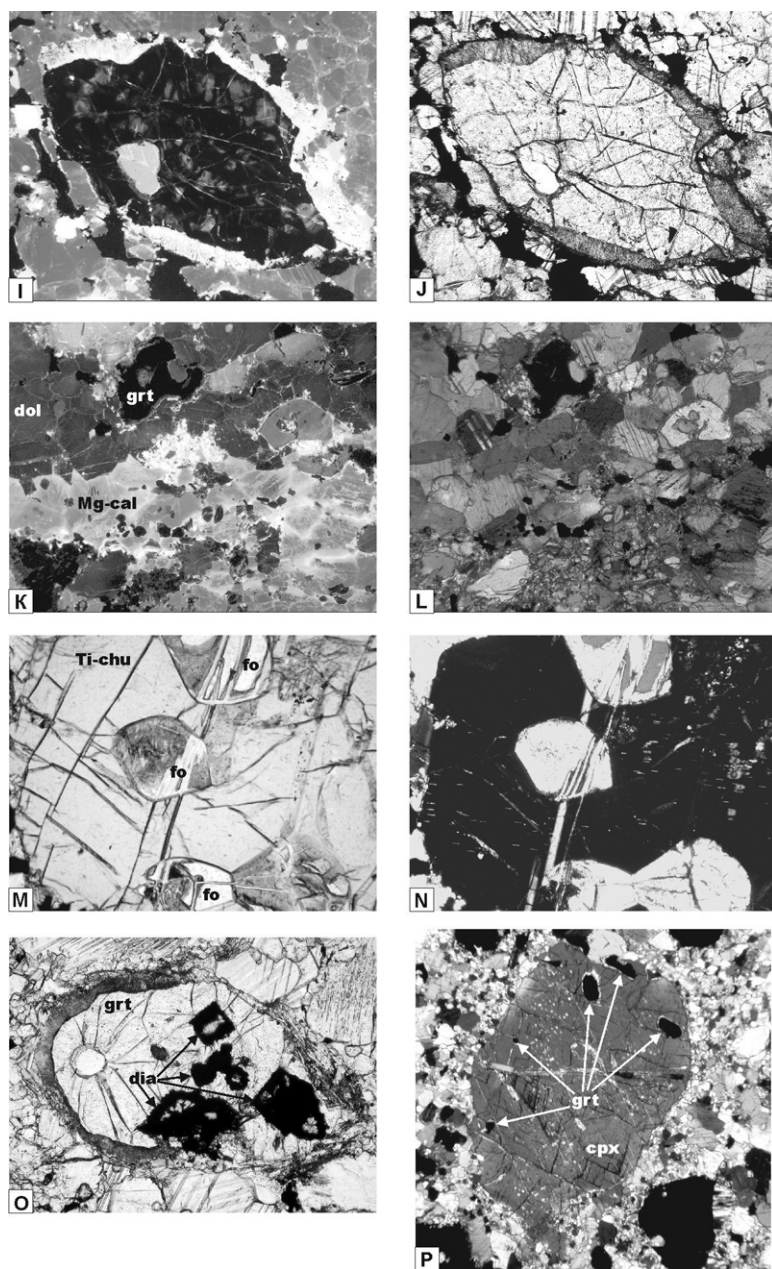


FIG. 4. Photomicrographs of key petrographic features of UHP calc-silicate rocks containing relics of unusual low iron Mg-Ca garnets. Cathodoluminescence (CL) images (A, C, E, G, I, K) of garnet grains containing light luminescent and dark nonluminescent portions. Cross-polarized light images (B, D, L, P) and plane-polarized light images (F, H, J) of the same portions of thin sections (garnet also in O) are presented in the right column. M. Ca. 1 mm big portion of a large Ti-clinohumite grain containing forsterite inclusions (sample K-204, plane-polarized light). N. Same image like in (M), crossed polars; the white oriented needles possibly represent exsolution lamellae of rutile? or ilmenite? O. Garnet grain (about 900 μm in diameter, see also Fig. 2, grain # 1) containing abundant relatively large diamond inclusions (plane-polarized light). P. Clinopyroxene with garnet inclusions in a Mg-calcite matrix (crossed polars). The field of view is about 20 mm.

FIG. 4. *Continued.*

compositions are presented in Figure 5 using a Mg-Ca-Fe-projection. Garnet compositions from some unusual, rare mantle xenoliths from kimberlites as well as Ca-rich garnets from calc-silicate parageneses of diamond inclusions (grossular, coesite, diop-

side, carbonates) are presented for comparison. The remarkable compositions of luminescent garnets from the studied samples plot outside the general compositional field of garnets from calc-silicate rocks. Luminescent garnets form a dense cluster on

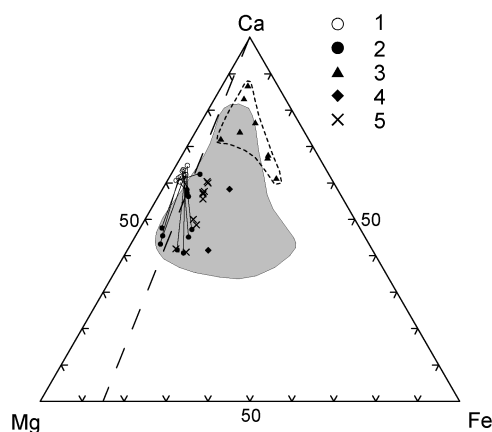


FIG. 5. Composition of Mg-Ca garnets from UHPM calc-silicate rocks of Kokchetav massif (1, 2, and shaded area) projected into a Ca-Mg-Fe diagram (in atom proportions). Numbers indicated are: Luminescent (1) and nonluminescent (2) portions of garnet grains; Ca-Mg rich garnet inclusions in diamonds from New South Wales alluvial deposits, Australia (3); selected garnet compositions from grosspyrite xenoliths, Zagadochnaya pipe, Yakutia (4); and from composite sample of corundum eclogite, Obnazhennaya pipe, Yakutia (5). Broken line represents garnet compositions with Mg# 85. Data source: Sobolev et al., 1968, 1984, 2006; this paper; Davies et al., 2003; Meyer et al., 1997; Qi et al., 1997.

the plot with very limited variations in Ca# from 60 up to 64.6 and Mg# from 90 up to 94.7 (Fig. 5 and Table 1). Non-luminescent portions of the same grains demonstrate a considerably wider range in Ca# (41.9–62.7) but a narrow range in Mg# (79.7–85.9; see Table 1), which is, however, low compared with the Mg# of luminescent relics. Non-luminescent parts of some garnet grains of the layered rock sample studied are very similar to typical garnets of calc-silicate rocks from the Kokchetav massif located outside the mining gallery (see shaded field of Fig. 5).

In very rare cases, homogeneous luminescent relics comprise up to 70% of a garnet grain in thin section (e.g. Figs. 4C and 4I), in agreement with earlier studies (Sobolev et al., 2001, 2006; Schertl et al., 2004). In general, however, luminescent portions make up 5 to 50 vol% of garnet grain surfaces. It is important to note that only about 10–20 vol% of all garnet grains from the dolomite-rich layers associated with forsterite and Ti-clinohumite show luminescent portions. A comparison of CL vs. crossed polar or plane light images of the same garnet grains demonstrates that mineral inclusions

are not responsible for the luminescent relics (see Fig. 4).

Non-luminescent garnets themselves exhibit local chemical heterogeneity within a single calc-silicate layer within a Mg-calcite matrix. At least two types of garnet compositions differing in their FeO contents (and Mg#) are found in layer 2 of sample K98-11a (Schertl et al., 2004). One group of relatively homogeneous garnets contain 3–3.5 wt% FeO and another contains 5.5–6.5 wt% FeO. The garnets occur both as separate, isolated grains partly surrounded by a clinopyroxene-bearing reaction rim, and as a series of inclusions within large pyroxene grains (e.g. Fig. 4P). Four of these inclusions presented in Figure 4P contain 3.2–3.5 wt% FeO but one inclusion contains 6.7 wt%.

Summarizing the data on garnet compositions in Figures 5 and 6, it is necessary to stress again the very unusual compositional features of luminescent garnets. They differ systematically from other garnets from calc-silicate rocks not only in their uniquely high Mg# but also in their considerably lower TiO_2 (0.14–0.24 wt%) and higher MnO contents (0.98–1.34 wt%) compared to non-luminescent, dark portions of the same grains. The Ca#s of bright, luminescent garnet enclaves are significantly higher compared to dark, non-luminescent portions.

Associated minerals

Pyroxene is the most important mineral associated with garnet, both in dolomite- and Mg-calcite-bearing calc-silicate rocks. It occurs in the rock matrix and as inclusions in garnet. For the present study we sought to identify pyroxenes that may have been part of an equilibrium assemblage with bright, luminescent garnet relics. We studied pyroxene inclusions in the largest garnet grain from sample K98-11a, which contains garnet relics with different intensities of luminescence (Fig. 4A). The triangular pyroxene inclusion with smooth corners (marked 1 in Fig. 4A) is the best candidate in our opinion for equilibrium with luminescent garnet relics because of its uniquely low core and rim FeO contents (0.28 and 0.46 wt%, respectively; Table 3). The core pyroxene is completely white in luminescence and its rim is slightly yellowish. Another inclusion (also white in luminescence) contains 0.37 wt% FeO. These three pyroxenes have practically pure diopside compositions with very low amounts of Al_2O_3 (0.33 wt%), TiO_2 (0.03–0.07 wt%), and a complete absence of Na_2O and K_2O (Table 3). The pyroxene

TABLE 3. Representative Analyses of Clinopyroxenes, Forsterites, and Ti-Clinochumites¹

Name	K98-11a (inclusion in big. grt)				K98-11a		K-604		
	C	R		Ti-chu	C	R	fo*	fo	Ti-chu
SiO ₂	54.6	54.7	54.5	37.5	54.8	54.7	41.8	41	37.2
TiO ₂	0.06	0.03	0.07	1.53	0.09	0.07	bdl	bdl	2.1
Al ₂ O ₃	0.66	0.33	0.37	0.02	0.78	0.96	bdl	bdl	bdl
FeO	0.46	0.28	0.37	3.82	0.76	0.8	4	3.98	3.34
MnO	0.04	0.04	0.08	0.32	0.05	0.03	0.32	0.3	0.29
MgO	17.8	18.1	17.9	52	17.6	17.4	53.7	55.1	54.2
CaO	25.3	25.4	25.3	0.03	25.2	24.9	0.02	0.01	0.02
Na ₂ O	0.02	0.01	0.03	bdl	0.17	0.06	bdl	bdl	bdl
K ₂ O	0.03	< 0.01	< 0.01	bdl	0.03	0.16	bdl	bdl	bdl
Total	99	98.9	98.6	95.2	99.5	99.1	99.84	100.5	97.1
Number of ions on the basis of 6 O for clinopyroxenes and of 4 O for forsterites and Ti-clinohumites									
Si	1.991	1.995	1.994	0.947	1.99	1.993	0.999	0.978	0.922
Ti	0.002	0	0.002	0.029	0.002	0	bdl	bdl	0.039
Al	0.028	0.014	0.016	0.001	0.033	0.041	bdl	bdl	bdl
Fe	0.014	0.01	0.011	0.081	0.023	0.024	0.08	0.079	0.069
Mn	0.001	0	0.002	0.007	0.002	0	0.01	0.01	0.01
Mg	0.967	0.984	0.976	1.957	0.952	0.945	1.913	1.958	2.001
Ca	0.988	0.993	0.992	0.001	0.98	0.972	0	0	0
Na	0.001	0	0.002	bdl	0.012	0	bdl	bdl	bdl
K	0.001	0	0	bdl	0.001	0.01	bdl	bdl	bdl
Total	3.994	3.997	3.996	3.022	3.997	3.99	3	3.021	3.038
Mg#	98.6	99.2	98.9	96	97.6	97.5	96	96.1	96.7
Ca#	50.2	50.1	50.2	—	50.1	50.1	—	—	—

¹For forsterites and Ti-clinohumites NiO = bdl.

inclusions have no analogues among pyroxenes from other UHPM rocks that contain more than 1–2 wt% Al₂O₃ and 1–2 wt% FeO (Zhang et al., 1997; Ogasawara et al., 2000; Shatsky and Sobolev, 2003; Shatsky et al., 1995).

Dolomite is closely associated with garnets containing luminescent relics. The maximum FeO content of dolomite inclusions in big garnet is 0.88 wt% (Fig. 4 A, marked 3). Mg-calcite typically forms rims around dolomite inclusions in garnets; in some cases, it contains up to 4.8 wt% MgO, which is, however, considerably lower than published data (Shatsky et al., 1995).

In addition, forsterite and Ti-clinohumite were detected as closely associated with garnets contain-

ing luminescent relics in dolomite-rich zones (Schertl et al., 2004). Earlier we stressed that these forsterites lack NiO but contain high amounts of MnO (Schertl et al., 2004; Sobolev et al., 2006), contradicting a magmatic origin and confirming a metasedimentary one. Fresh grains of forsterite are extremely rare, mostly altered to a talc-bearing assemblage, and in a few instances form inclusions in Ti-clinohumite (see Fig. 4M and 4N). Forsterite contents of olivines vary within a narrow range from 95 to 97.

An interesting discovery, observed for the first time in calc-silicate rocks from the Kokchetav massif, is the presence of small submicrometer thin, oriented arrays of rods within Ti-clinohumite (Fig.

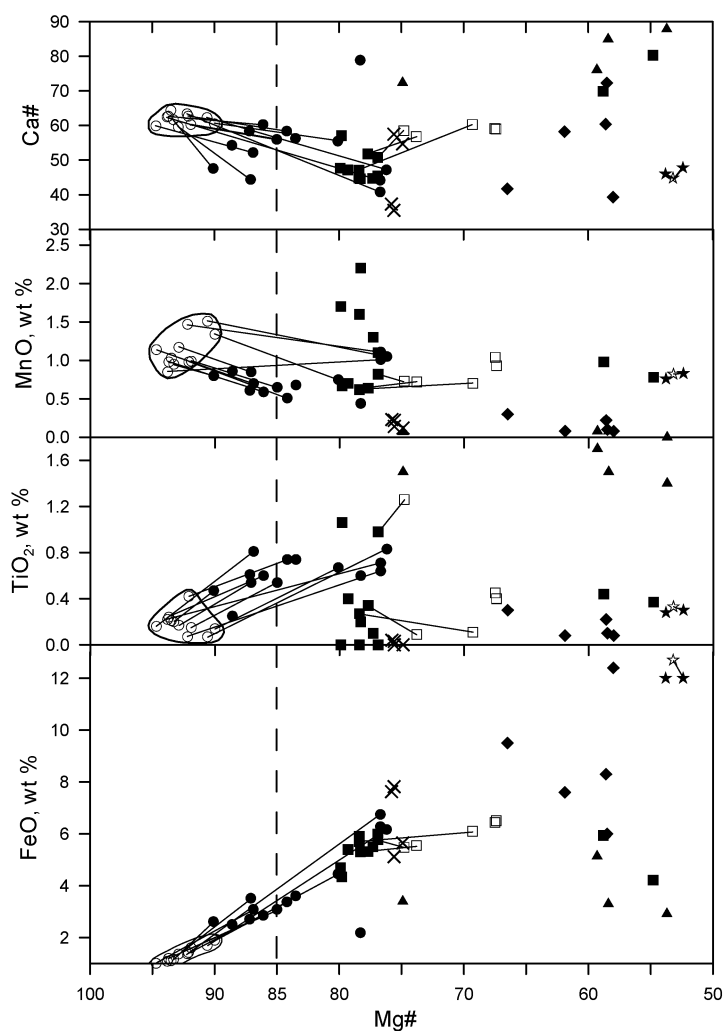


FIG. 6. Mg# vs FeO, TiO_2 , MnO, and Ca# of high Mg-Ca garnets from luminescent and nonluminescent (open and filled circles, respectively) portions of a number of grains from composite samples of layered calc-silicate rocks investigated. Garnets containing large ($\sim 100 \mu\text{m}$) diamond inclusions are shown by stars: core (open star) and rim (black star). Compositions of typical garnet grains from similar rocks of the Kokchetav massif: cores = open squares; and rims = black squares. Triangles, filled diamonds, and crosses, see Figure 4 (nos. 3–5). Positions of plotted analyses relative to luminescent garnet portions are encircled. Broken vertical line indicates the boundary (Mg# 85) of the formerly “forbidden” area for natural garnets.

4M and 4N), possibly representing exsolution-like products (rutile?, ilmenite?) that may have formed during pressure release after peak metamorphic conditions. Future TEM studies will attempt to identify the rods and their structural relationship to the host Ti-clinohumite.

Other minerals occurring in calc-silicate rocks include perovskite (inclusions in forsterite), phlogo-

pite, titanite, spinel, and K-feldspar. These occur both as lamellae in pyroxene and as an interstitial mineral (Scherl et al., 2004).

Discussion

The luminescent garnets described in the present communication, in their extremely low FeO

contents, differ very substantially in composition from typical garnets of UHPM calc-silicate rocks from the Kokchetav massif described in previous studies (e.g. Shatsky et al., 1995; Zhang et al., 1997). The studies of composite, layered rock samples reported herein demonstrate a considerably expanded compositional range of garnets to include Mg# values greater than 90 and Ca#s of 60 to 65. The compositions of luminescent garnet relics plot within a so-called “forbidden” area on a Mg-Ca-Fe diagram for garnets. They represent the purest Mg-Ca-garnet compositions occurring in natural rocks. Experimental data independent of the occurrence of coesite and/or diamond in rocks containing such garnets, testify to UHP conditions, with pressures no less than 3.0 GPa (Boyd, 1970). A distinct trend in TiO₂ content increasing from luminescent toward non-luminescent portions of garnet grains is shown in Figure 6. The increase in TiO₂ correlates with experiments showing that a temperature increase at high pressure results in increased TiO₂ solubility in garnets (Green and Sobolev, 1975; Zhang et al., 2003). The attempts to classify carbonate-bearing (calc-silicate) rocks into dolomite (diamond-bearing) and dolomitic (diamond-free) marbles (Ogasawara et al., 2000; Ogasawara, 2005) did not demonstrate any significant differences in garnet compositions.

The occurrence of garnet grains of different compositions (for example, some containing 3 and others 6 wt% FeO) within the same thin sections and in similar assemblages indicates a failure to achieve chemical equilibrium between relict mineral grains persisting throughout successive retrograde metamorphic events (e.g., see Perchuk et al., 2005). Relict, luminescent garnet grains represent the oldest metamorphic event and have been progressively obliterated during retrograde events.

As noted by Ohta et al. (2003) oxygen-, carbon- and strontium-isotopic heterogeneities and isotopic disequilibrium are widespread on a hand-specimen scale in Kokchetav UHPM rocks. Oxygen isotopic variations are also detected in garnets of variable compositions in dolomite marbles (Rumble, pers. commun.). Oxygen isotopic compositions are also heterogeneous in samples of UHP eclogite from the Kokchetav massif (Masago et al., 2003).

The presence of spectacular “dry” symplectitic rims composed of spinel and pyroxene with traces of sapphirine and corundum preserved occasionally around garnets together with persistent luminescent relict garnets may record rapid, nearly isothermal

exhumation from UHP metamorphic depths (Sobolev et al., 2001; Schertl et al., 2004; Dobretsov and Shatsky, 2004). An early retrograde stage of exhumation at about 18 kbar and 900–950°C (Massonne, 1995) is supported by the observation of increased TiO₂ from luminescent to non-luminescent garnets. Evidence of partial melting of calc-silicate rocks recently observed by Korsakov and Hermann (2006) and Shatsky et al. (2005) along with the discovery of perovskite inclusion in forsterite (Schertl et al., 2004) may argue for the participation of carbonatitic melts and/or fluids under both peak metamorphism and early exhumation conditions (Pal'yanov et al., 1999, 2001, 2005).

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