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Cathodoluminescence microscopy of the Kokchetav ultrahigh-pressure calcsilicate rocks: What can we learn from silicates, carbon-hosting minerals, and diamond?

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Abstract

A comprehensive study of a key calc-silicate rock of complex composition, an ultrahigh-pressure metamorphic rock of the Kokchetav massif, has been performed. New thin sections were examined by cathodoluminescence microscopy, electron probe microanalysis, and transmission/analytical electron microscopy. The obtained results confirmed the presence of microdiamonds and indicative signs of ultrahigh pressures (K in clinopyroxene) for seven of the eight previously recognized layers of the sample. Only one layer (3) containing paragenesis forsterite + Ti-clinohumite + dolomite + luminescent garnet (Mg# = 86–95) + clinopyroxene free of potassium and perovskite lacks diamonds. Symplectitic rims replacing garnet in this layer are formed by spinel growing into augite clinopyroxene with a scarce impurity of sapphirine and corundum and lack hydrous minerals. Garnets (Mg# = 81–83) of the diamond-containing layers (1 and 2a) and (4–8), having Mg# = 38–53, do not exhibit luminescence. They are present, together with K-clinopyroxenes, in the Mg-calcite matrix. A distinctive feature of the symplectitic rims is abundant segregations of corundum, often needle-like, and sapphirine in the augite clinopyroxene matrix with a minor spinel impurity. The symplectitic rims contain high-Mg phlogopite and K-amphibole; the latter was found in the metamorphic rocks for the first time. The different roles of hydrous minerals at the early stages of retrograde metamorphism for different layers reflect different fluid mobilities even within a sample.

Keywords: diamond; garnet; pyroxene; K-amphibole; sapphirine; corundum; ultrahigh-pressure metamorphism; cathodoluminescence; Kokchetav massif

Introduction

During the last 50 years cathodoluminescence (CL) microscopy has become a standard tool in geoscience. While early studies mainly focused on sedimentary rocks, within the last 2 decades this technique has also been applied to various metamorphic and magmatic rocks (Götze et al., 2013; Schertl et al., 2004). In addition, CL is indispensable as a scientific tool for the identification of different zircon domains, which need to be characterized prior to ion probe dating (SHRIMP; e.g., Gebauer et al., 1997).

Here, we would like to show results on UHP-metamorphic rocks from the Kokchetav Massif/Kazakhstan using a “hot cathode” CL microscope. It is important to note, that the investigations presented were entirely made just using normal polished thin sections. This makes CL-microscopy an important petrological tool to contribute to other techniques like e.g. electron microprobe and oxygen isotope analysis. Particularly layered calcsilicate rocks from the Kokchetav massif offer a huge potential by applying CL-microscopy. Different carbonates show different luminescent colors (calcite—yellow, aragonite—green, Mg-calcite—orange, dolomite—red). Thus different lithologies like dolomite- and Mg-calcite-enriched layers (even if they are very thin) can instantly be distinguished. Further petrographical observations reveal dolomite exsolution patterns within Mg-bearing calcite, concentric zonations of dolomite and Mg-calcite, and rare occurrences of calcite (yellow luminescence) in talc-bearing pseudomorphs after forsterite. Diamond can be easily identified by its

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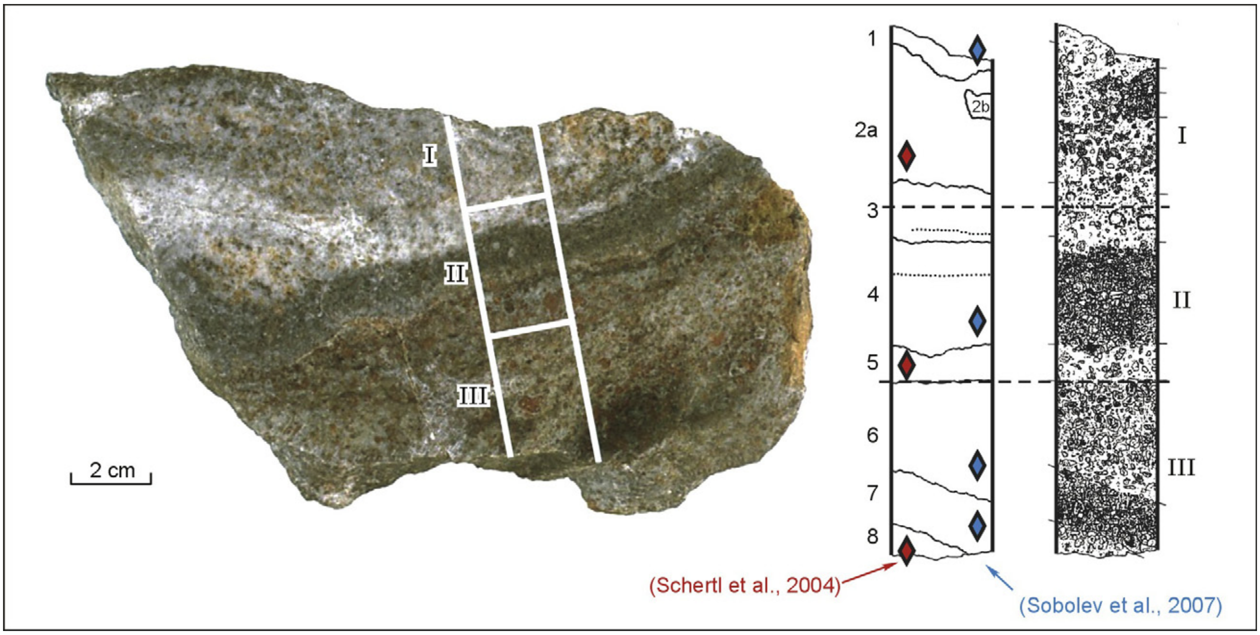

Fig. 1. Cross section of a diamondiferous calcsilicate (sample K-98-11a) from the Kokchetav massif. Numbers I, II, and III refer to different thin sections; numbers 1–8 refer to the different layers; their variable mineral assemblages and specific features are presented in Table 1. Red and blue diamonds refer to diamondiferous layers (for further explanations see text).

greenish-blue luminescence colors, even zonation of diamond easily becomes visible (Schertl et al., 2004: their Fig. 3*n*). Very interesting results were derived from garnet. Although the calcsilicates generally contain garnets lacking luminescence, through very careful CL-studies about 10% of these garnets were disclosed to show complex growth structures. Typically, yellowish-brown luminescent garnet of an earlier generation may contain some "veining" of a second garnet generation lacking luminescence (see Schertl and Sobolev, 2013: their Fig. 8).

Garnet and clinopyroxene play a dominant role as an important rock forming minerals in calcsilicate including marble and garnet-pyroxene rocks. They form inclusions within zircon; clinopyroxene represents parts of the matrix, and it additionally occurs as important breakdown product and, for instance, formed from garnet and olivine. Especially pyroxene inclusions within zircons are of big value in that the rock matrix occasionally does not contain clinopyroxene which reacted out during the long metamorphic history. Clinopyroxene however survived inside zircon where it was protected from alteration.

Our focus of the current paper is on different types of clinopyroxene, garnet, carbonates, and diamond from calcsilicate rocks, sometimes also called impure or dolomitic marbles and garnet pyroxene rocks with different proportions of carbonates. Schertl and Sobolev (2013) and Shirey et al. (2013) have pointed out that these rocks are characterized by very variable proportions of carbonate and silicate minerals—sometimes even in hand specimen layered rock types were found, which are composed of alternated carbonate rich and garnet-pyroxene rich layers (Fig. 1). In the calcsilicate rocks diopsidic clinopyroxene forms inclusions in garnet and zircon, it makes up considerable parts of the matrix and, important for the evolution of the early retrograde history, it is part of several breakdown products, e.g., of garnet and forsterite. Especially the clinopyroxene-rich symplectites around the most Mg-rich garnets are quite complex. Clinopyroxene is extremely variable in composition; the symplectites contain additional spinel, rarely sapphirine and corundum (Sobolev et al., 2001). In their key paper on the diamondiferous rocks from Kokchetav massif, Sobolev and Shatsky (1990) already pointed to the very unusual chemistry of some clinopyroxenes, which may contain appreciable amounts of K_2O, similarly to the most potassic clinopyroxenes from inclusions in kimberlitic diamonds (e.g., Sobolev et al., 1972, 1991). This observation is very important since it documents that at very high pressures the "big" potassium cation is able to occupy parts of the M1-position in the clinopyroxene structure (Harlow, 1997).

An extremely valuable tool in distinguishing different fine-scale growth zones, inhomogeneities, intergrowth textures, etc. is the method of cathodoluminescence (CL) microscopy (e.g., Götze et al., 2013). With this method it is possible to study such textures using "normal" polished thin section covered with carbon, which, later on in a second step, can be used for electron microprobe (EMP) studies. As an enormous advantage, an entire thin section can be examined within a few minutes. The Kokchetav calcsilicate rocks turned out to be a perfect candidate for such kind of studies since nearly all rock forming minerals (Mg-calcite, dolomite, clinopyroxene, garnet, K-feldspar) are luminescent. In particular, the CL-method is very promising for garnets and clinopyroxenes which contain less than roughly 2–3 wt.% FeO_{tot} (too high amounts of iron suppresses or even erases luminescence). In regard to the different carbonate minerals (calcite, Mg-calcite, dolomite, magnesite, aragonite), it is possible to find out within seconds as to whether e.g. the matrix is dominated by