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Prismatine granulite from Waldheim/Saxony: Zircon-Reidite

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Abstract

According to microscopic and Raman spectroscopic-based studies of prismatine rock from Waldheim/Saxony, we observed spherical zircon crystals with remnants of reidite and monoclinic ZrO2. The proof of reidite in a metamorphic rock is the first one because up to now, reidite was found only in impact structures. These observations throw new light on the genesis of the HP-HT prismatine rock from Waldheim. We interpret the spherical crystals as hints of a supercritical phase coming from very great depths, very rapidly (possibly together with boron) into the crystallization level of prismatine.

Introduction

During examination of thick sections of prismatine rock from Waldheim/Saxony (see Grew 1986) [1] we often observed spherical crystals of zircon [ZrSiO4] in addition to very rare coesite and stishovite crystals (Thomas and Grew, 2021) [2]. According to Raman spectroscopic studies these zircons often contain remnants of the reidite. Reidite is the high-pressure scheelite-type polymorph of zircon [3-5]. According to Smirnov et al. (2010) [3] the zircon to reidite transformation is not reversible and the reidite structure persist upon the pressure release. However, at temperatures of 1500 K reidite reverts to the zircon structure. At lower temperature samples consist of a mixture of reidite and zircon. At high temperatures of 1000-1500 K the pressure-induced zircon-to-reidite phase transition occurs near 8 GPa (Stangarone et al. 2019) [4]. The transformation of zircon to reidite is reconstructive in nature and is connected with a density change of about 9%) [4]. Thus, reidite or reidite-rich inclusion in quartz can be recognized by radial cracks around such "zircon" grains due to volume expansion of reidite to zircon transition (see Figure 1). Currently, reidite has only been identified in terrestrial and Martian impacts [4,6].

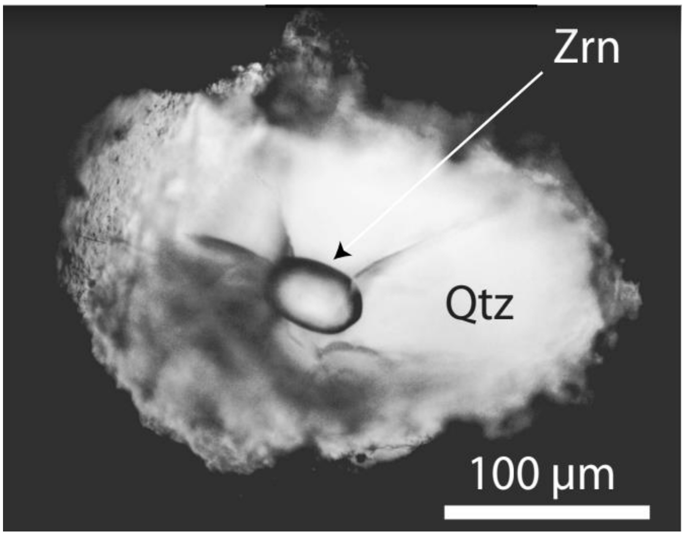

Figure 1: Zircon after reidite inclusion in the center of an elliptical high-quartz crystal. The quartz host displays radial fractures due to the volume expansion of the primary reidite to zircon transition.

Samples and methods

The rock and crystal samples were collected by the first author in 1967 from the exposure near the Waldheim railway station. Kalkowsky (1907) [8] described in his article on the Waldheim granulite rock small drop-shaped zircon grains like oil-droplets in the granulite rock.

Samples

Nearly all minerals (garnet, corundum, quartz, prismatine, feldspar, sillimanite) of the prismatine rock contain randomly distributed spherical zircon crystals with a very smoothed surface and with dimensions between 10 to 50 µm. The frequency of these grains is with about 180 spheres/cm3 not high. We have taken Raman spectra from a large number of such spherical crystals. In addition to spherical zircon crystals there are also present similar small globules of corundum, anorthoclase, rutile, and others minerals.

Raman spectroscopy

Raman spectra were recorded with the EnSpectr Raman microscope RamMics M532 in the spectral range of 80 - 4000 cm-1 using a 50-mW single mode 532 nm laser (however, only 5 mW on sample), an entrance aperture of 20 µm, a holographic grating of 1800 g/mm, and a spectral resolution of 4 - 6 cm-1. Depending on the grain size we used microscope objectives with magnifications between 3.2x and 100x. The position of the Raman bands was controlled before and the end of each series of measurements of the Si band using a single crystal chip of semiconductor-grade silicon. The run-to-run repeatability of the line position (from 20 measurements each) was ± 0.3 cm-1 for Si (520.4 ± 0.3 cm-1) and 0.5 cm-1 for diamond (1332.3 ± 0.5 cm-1 over the range 80 – 2000 cm-1), respectively. As diamond-reference we used a water-clear natural diamond crystal.

For the identification of the different mineral phases using Raman micro-spectroscopy, we used the RRUFF database [9].

Results

According to the supplementary material for Stangarone et al. (2019) [4] given in their Table S2 and S3 there are clear differences in the Raman spectra of zircon and reidite. In the Raman spectra of the spherical zircon crystals in the prismatine rock from Waldheim we often see bands characteristic of reidite (see table 1).

Table 1: Calculated wavenumbers (w), symmetry and relative intensity of zircon and reidite (in rising order) beside the main Raman bands of the reidite-rich zircon in the prismatine-granulite rock from Waldheim/Saxony (Germany).

Zircon			Reidite			Reidite-rich zircon	
w (cm^{-1})	symmetry	rel. intensity	w (cm^{-1})	symmetry	rel. intensity	w (cm^{-1})	rel. intensity
197	E_g (1)	30	209	E_g (1)	79	**205**	284
216	B_{1g} (1)	22				215	469
225	E_g (2)	120				225	449
250	B_{2g} (1)	21	242	B_g (1)	16		
			300	E_g (2)	152		
			326	A_g (1)	193	**325**	59
341	E_g (3)	552	350	B_g (2)	435	**350**	1000
387	B_{1g} (2)	49					
			409	A_g (2)	1000	**408**	32
439	A_{1g} (1)	1000				435	161
			458	E_g (3)	327		
			465	B_g (3)	328	**466**	139
542	E_g (4)	24	558	E_g (4)	457		
636	B_{1g} (3)	4				630	11
			852	B_g (5)	427		
			861	A_g (3)	27	**867**	43
			891	E_g (5)	426		
922	E_g (5)	2					
970	A_{1g} (2)	234				969	47
1015	B_{1g} (4)	959				1001	362

Remark: The bold numbers in the reidite-rich zircon column are the most intense peaks corresponding to reidite found in the Waldheim zircons.

Sometimes these reidite bands are relatively strong especially the 350 cm-1 band. Among them the reidite 350 cm-1 band is generally the strongest. The proof of a reidite component in zircon indicate a minimum pressure of about 8 GPa at about 1300 K (highest temperature found for the prismatine parageneses of Waldheim).

Furthermore, in the Raman spectra of the spherical zircon-reidite crystals there are some bands which give clear hints to the existence of monoclinic ZrO2 (see Bauer 2018) [7]: 187, 222, 330, 473, and 633 cm-1. According to Tschauner (2019) [6] at very high pressures zircon break down into oxides. Therefore, the pressure should be higher than 8 to 12 GPa [3], corresponding to a deep of 240 to 360 km.

Short discussion

Together with the finding of coesite and stishovite [2], [9]: in preparation), reidite and monocline ZrO2 in zircon give clear hints that such phases arrived very rapidly from very great depths into the higher crustal level (90 km) via supercritical fluid/melt in analogy to Arndt et al. 2010 [10]. It maybe such supercritical phase brought the spherical crystals along with boron from the great deep into the level where the prismatine crystallized (together with coesite). Such finding sheet new light to the origin of boron in the Bohemian Massif. Other spherical crystal which was found in this parageneses are nano-diamond, and moissanite.

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