

Short Communication

To the Geochemistry of Beryllium: The Other Side of the Coin

Rainer Thomas*

Im Waldwinkel 8, D-14662 Friesack, Germany

*Corresponding author: Rainer Thomas, Im Waldwinkel 8, D-14662 Friesack, Germany

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Abstract

Two very different examples of Be mineralizations show that Be can be enriched to very high values. This short paper tries to find the origin of such unusual behavior. Possibilities are discussed.

Keywords: Water-rich melt inclusions, Be-enrichment, Gaussian and Lorentzian element distribution, Supercritical phases, Mantle-crust connection

Introduction

There are a couple of comprehensive contributions to the chemistry, mineralogy, petrology, and geochemistry of beryllium: Gmelin [1] and the following issues up to 1997, Beus [2], Everest [3], Grew ES and coauthors (2002) [4], London D [5]. Considering such substantial work, it should be said all essential facts. However, careful microscopical and Raman spectroscopic studies of beryl mineralization tell us a different, maybe second, story. That is related to the supercritical melt and fluid state. While studying minerals from pegmatites related to the Variscan tin mineralization of Ehrenfriedersdorf in central Erzgebirge/Germany, we often found high concentrations of beryllium, which does not fit the expected ideas. In one melt inclusion (No. 61), Webster et al. [6] determined 1130 ppm Be with ion microprobe. This runaway value was the start-point for an intense search for higher Be values. And we were successful. In 2011 Thomas et al. [7] could, for the first time, present a more significant number of Be data for the Ehrenfriedersdorf pegmatite. Conspicuously, the data showed a strong dependence on the melt inclusions' homogenization temperature and water concentration. As daughter minerals, we found in Ehrenfriedersdorf pegmatite beryllonite [NaBePO₄] and hambergite [Be₂BO₃(OH, F)]. Beryllonite is related chiefly to water-rich melt inclusions in beryl of the beryl-quartz veins. In other beryl mineralizations, for example, Orlovka, Eastern Transbaikalia/Russia (Thomas et al. 2009 and unpublished data together with Badanina [8], and the Habachtal emerald deposit Thomas et al. 2020) [9], we found Be-carbonates as the main Be daughter phase. Many data and thoughts are presented in the concise papers by Thomas et al. [10,11]. Taleb's book, "The Black Swan. The Impact of the Highly Improbable" [12], significantly influenced our thinking. Particularly the finding of water-rich melt inclusions, which depict a pseudobinary melt-water solvus in emerald, has stimulated our understanding of processes that are not so obvious. In this short contribution, we want to show that beryllium can enrich to very high concentrations – far away from all expectations. The first indications

came from melt and fluid inclusions produced synthetically in morganite crystals from the Muiane pegmatite (Thomas et al., 2010) [13] during heating at 700°C, 1.0 kbar for 20 hours.

Samples

For this study, we used two different samples: well-transparent morganite crystals from the Muiane pegmatite [13] and beryl from a small beryl-quartz vein related to the Variscan tin deposit Ehrenfriedersdorf in the central Erzgebirge, Germany [14] – see Figure 1.

Other photos of such beryl-quartz samples from the Sauberg mine are in Thomas et al. [15,16].

Methods

Samples used in this study have been prepared over a long time, starting in 1996. For this, we used different high-pressure devices and analytical methods. A concise description of the methods used is summarized in Thomas et al. [17,18] and the ESMs. This study used a petrographic polarization microscope with a rotating stage coupled with the RamMics R532 Raman spectrometer working in the spectral range of 0-4000 cm⁻¹ using a 60mW single mode 532nm laser. For Raman spectroscopic routine measurements, we used an Olympus long-distance LMPLN100x objective. Details are given in Thomas et al. [15,16]. In a paper published last year [19] used for the homogenization of melt inclusions the HDAC (Hydrothermal Diamond Anvil Cell) technique because water-rich melt inclusions show the tendency to leak or decrepitate during heating on the microscopic heating stage due to the growing pressure inside the inclusions. However, the HDAC method has the disadvantage that only a single or only a small couple of inclusions can be studied. Therefore we used different high-pressure devices coupled with rapid quenching because the obtained samples are larger and contain many inclusions which can be analyzed with other methods over the years. Of course, we also used the HDAC technique to see that our interpretations obtained from rapid quench experiments were realistic.



Figure 1: Specimen from a beryl-rich quartz (Qtz) vein from the Sauberg mine near Ehrenfriedersdorf. The sample is from a vertically directed vein - is rotated by 90°. The dark minerals on the roof and the bottom are cassiterite, molybdenite, and other minor ore minerals.

Results

Morganite from the Muiane Pegmatite, Mozambique

Morganite is the pale pink variety of beryl colored by Mn^{2+} . Crystals from the Muiane pegmatite contain a lot of melt and daughter mineral-rich fluid inclusions. From first homogenizations at 700°C and 1.0 kbar for 20 hours, some melt inclusions homogenized totally, and during fast cooling, these inclusions heterogenized into a silicate melt and a fluid subphase containing hambergite $[Be_2BO_3(OH,F)]$ and small bromelite $[BeO]$ daughter crystals. According to Raman measurements, the silicate glass phase beside the water-rich phase has $7.0 \pm 0.2\%$ ($n=36$) H_2O . After heating and quenching, a microscopic study of the morganite ships showed newly formed, very plane melt and fluid inclusions in newly formed halos around large melt inclusions produced during partial decrepitation under pressure. And to our surprise, these inclusions are rich in bromelite (Figure 2). These inclusions were not present before the heating procedure under constant CO_2 pressure.

That means that bromelite in water or water-rich melts are at 700°C highly mobile. This test tube-type experiment under pressure showed us Be's high solubility and mobility. We obtained 14 to 17% Be in the H_2O solution from well-formed inclusions. That is far from

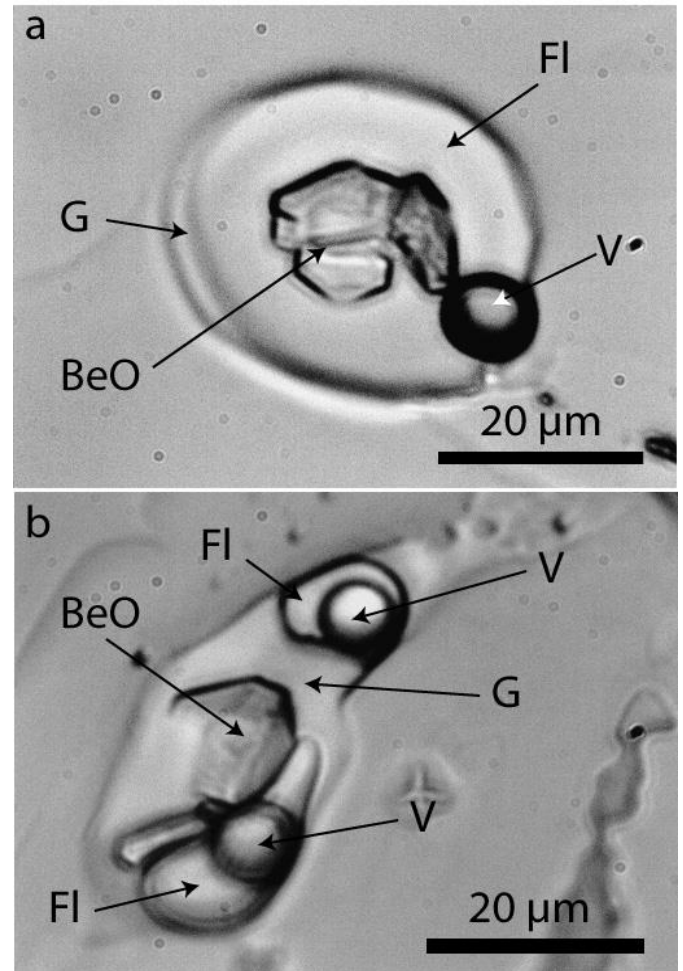


Figure 2: Bromelite $[BeO]$ -rich inclusions in morganite, produced by heating to 700°C at a constant pressure of 1.0 kbar (20 hours) and fast quenching after the run.

all ideas, for the natural examples given in Grew [4]. Another point is essential. There are two newly formed inclusion types: Melt- or glass-rich inclusions (Type-A melt inclusions) and water-rich inclusions with only a tiny part of the glass or melt (Type-B melt inclusions). Both inclusion types formed at the same time at 700°C. Furthermore, the observations show that the Be-content in the silicate glass with 7% water is very low and in the water-rich glass very high, higher than in the extreme water-rich inclusions.

Beryl-quartz Vein from the Sauberg Mine Near Ehrenfriedersdorf, Erzgebirge, Germany

This beryl contains a lot of fluid and melt inclusions. Many melt inclusions have beryllonite daughter crystals, which can be used to estimate the inclusions' natural Be content [7]. Note here the inclusions are samples of the specific mineral-forming phases [20]. New studies [14] show that the beryl-quartz vein has a complicated history. This mineralization shows clear hints of the participation of supercritical melts or fluids – showing an interaction between mantle and crust [21]. The beryllium distribution of water-rich melt inclusions (Figure 3) around the solvus crest of a pseudobinary melt-water solvus shows this exceptionally well.

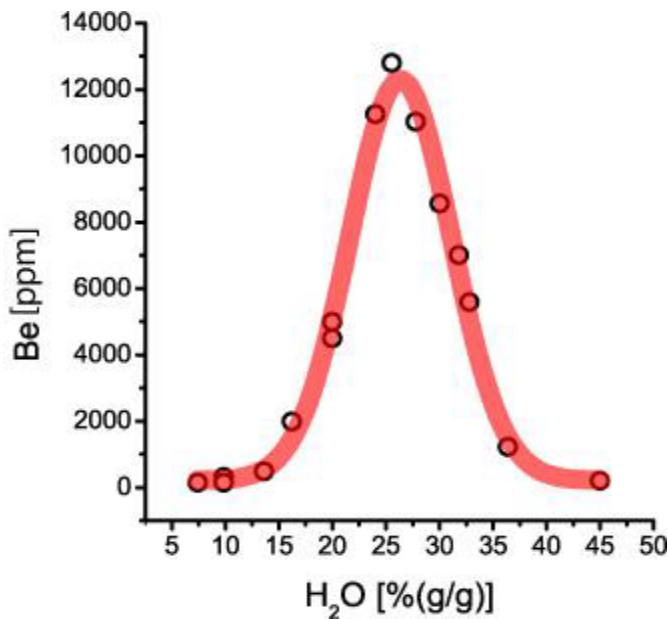


Figure 3: Gaussian distribution of Be (in ppm) in water-rich melt inclusions in beryl from the Sauberg mine near Ehrenfriedersdorf. The abscissa represents the measured inclusions' determined bulk water content (H₂O). All points are the mean of at least five determinations. The center of the peak is at 26.4% H₂O, the width is 9.5% H₂O, the height is 12075 ppm Be, and the offset is 214 ppm Be. The offset represents the general enrichment level of the mineralization in question.

Note, however, that the shown Gaussian curve represents average values produced by the limited number of analyses. The highest up-to-now measured Be value is 71500 ppm (from the volume of a well-formed beryllonite daughter crystal in a melt inclusion). By such values, the Gaussian curve degenerates to a Lorentzian curve type – typical for supercritical conditions. In normal beryl mineralization [5], such extreme enrichment is entirely out of the question. We must find an acceptable answer because the measured data are correct and always checked (starting with Webster et al.) – [6]. In the case of the beryl-quartz veins from the Sauberg mine near Ehrenfriedersdorf, enrichment in a miarolitic cavity is here not in question. The steady presence of HP and HT minerals (nanodiamond, moissanite, beryl-II, kumdykolite, and others) in the beryl-quartz mineralization makes it probable that supercritical phases from mantle depths participate in this mineralization. The finding of high-pressure and high-temperature minerals related to the Variscan granites and mineralizations supported this idea. To such phases belong spherical nanodiamond crystals, moissanite, stishovite, coesite, cristobalite-X-I, and beryl-II intergrown with moissanite and kumdykolite [15,16,21]. These minerals are all foreign crystals not in natural equilibrium with present surrounding mineralizations and rocks. Fundamental questions arise from the direct paragenetic relationship of beryl and moissanite at around 700°C and a pressure ≤ 2 kbar: (i) is the supercritical phase (melt, fluid?) primarily rich in beryllium? (ii) which role acts the spherical beryl-moissanite intergrow? (iii) what is the mechanism for the simultaneous growth of beryl and moissanite? (iv) Can such a mechanism be used for the technological crystallization of moissanite at significantly lower temperatures?.

Discussion

In cooperation with my coauthors, I found many element

distributions showing such extreme enrichment, and such enrichment shows precise Gaussian or Lorentzian distribution curves [10,11]. For the Ehrenfriedersdorf deposit, we found Gaussian or Lorentzian distributed plots for the elements Li, Be, B, P, Cl, Zn, As, Sn, Cs, Ta, and W. A prerequisite for this analytical approach was developing a simple, destructions-free and fast analytical method for determining water in homogenized melt inclusions [22] on the base of the Raman spectroscopy. Different techniques were developed and used to determine the elements in question. Noteworthy was the Raman spectroscopic and electron microscopic determination of B, Be, and other elements [23,24], as well as the synchrotron radiation XRF (SXRF) method [25,26], the femtosecond LA-ICP-QMS microanalysis [27]. Why would up to now not similar distribution found? Is it a question of the direct availability of necessary experimental and analytical techniques? Or are such distributions related to the supercritical phases? Further studies on melt inclusions, for example, performed on mineralizations related to the Lusatian Block, made the last possibility highly plausible. More work is necessary!

Acknowledgment

I have written these lines in “we-form” because progress in the inclusion research would not be possible without the advisors and coauthors. I thank many colleagues who accompanied me for over 50 years in my research. Thanks go to Edwin (Ed) W. Roedder (1919-2006), which brought me on the right path. Furthermore, I think here first to Jim D. Webster (1955-2019), who was very interested in my work on melt inclusions in granites and pegmatites of the Variscan Erzgebirge, and I-Ming Chou and William (Bill) A. Bassett, who introduced me to work with the HDAC device and enabled me to judge this technique. Unforgotten is also the longstanding cooperation with Paul Davidson.

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