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Emerald from the Habachtal: New observations

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Abstract

The emerald mineralization in the Habachtal (Austria) is geologically and tectonically complex, and previous investigators have identified fluid inclusion evidence for a hydrothermal/metamorphic origin for the emeralds. In this paper we report the discovery of emeralds with a distinctly different inclusion population including melt inclusions, which demonstrates that at least some and probably most of the emerald mineralization in the Habachtal occurred from an extremely fluid-rich pegmatite-like aluminosilicate melt under supercritical conditions, at high temperatures and moderate pressures (~700°C, 5 kbar). This conclusion is based on presence of very highly-ordered graphite, and extremely water-rich melt inclusions in emerald. The Lorentz distribution of MgCO₃ against the water concentration is a very robust proof for the supercritical state. We suggest that the purely metamorphic model, based on the extrapolation of fluid inclusion data to the regional metamorphic conditions (550 °C and 5 kbar) by some previous investigators are inconsistent with our finding of high-temperature indications (well-ordered graphite, high-temperature fluid inclusions and melt inclusions). This apparent conflict suggests a more complex situation and requires a re-investigation of the emerald genesis in the Habachtal deposit.

Key words

Melt inclusion, Fluid inclusion, Well-ordered graphite, Supercritical state, Emerald

Introduction

In the 1980's the genesis of the emeralds from the Habachtal (Austria) was generally discussed on the basis of fluid inclusions and mineral equilibria (e.g. Grundmann 1983, Grundmann and Morteani 1989, Nwe and Grundmann 1990). At that time the study of melt inclusions was not a conventional technique and was used only by some specialists. Indeed, melt inclusions were often not recognized as such. On that basis we suggest that some conclusions are now questionable in light of the new information acquired from new techniques. The work on the genesis of emerald by Franz and Morteani (2002) has to be mentioned here, in particular the temperature and pressure estimates, the transport properties and the complexation behavior of beryllium.

In this contribution we will concentrate on our own observations, hoping that they can be integrated into other studies and a more in-depth interpretation, especially on a more regional scale. The essential points from our study are the identification of well-crystallized high-temperature graphite, and the discovery of melt inclusions, both of which provide a basis for a recalculation of temperatures and pressures of formation, and evidence of the action of supercritical melt/fluids during the emerald crystallization.

In this study we use the term “supercritical melt/fluid” in the sense of Hack et al., (2007) to indicate a combination of aluminosilicates and H₂O (typically with numerous other elements) that above certain conditions is completely miscible in all proportions. That is, it exists as a single-phase fluid, but which must disassociate into melt + aqueous fluid at temperatures and pressures below a critical point. This is analogous to gasses (e.g. CO₂) that at various temperatures and pressures can be solid, liquids or gasses, but become a single phase with properties similar to both, as well as some unique to that phase, above a critical point. Likewise, melt inclusions trapping such a phase will homogenize by critical behavior, homogenizing to a single phase at or near the critical temperatures of a pseudobinary solvus (see Thomas et al. 2000). For these reasons we also use the term “melt/fluid” to indicate a phase that shows both melt and fluid properties, but which is strictly neither. In the view of

(Thomas et al. 2019) pegmatite-forming melts are the most common form of supercritical melt/fluids.

Samples and methods

In early summer 2000, the first author visited the emerald deposit below the Leckbachscharte in the Habachtal/Austria. We thank Lois and Andreas Steiner from Bramberg who provided the emerald samples used in this study. All samples are from the Habachtal emerald deposit, and this is confirmed by the type and arrangement of the mineral inclusions (e.g., biotite, actinolite and/or tremolite), and the fluid and mineral inclusions, which are well characterized for Habachtal emeralds (see Gübelin and Koivula 1986). From four loose emerald crystals (about 6 x 10 mm) double polished thick sections about 500 μm thick were made: three parallel to the c-axis and one perpendicular to the c-axis. Ten smaller emerald crystal samples (about 5 x 4 mm in diameter), about 300 μm thick, generally cut perpendicular to the c-axis, were also used. All loose emerald crystals are from a narrow stratigraphic horizon within the Habach Formation (see here also Nwe and Grundman 1990). Additionally, from an emerald crystal (about 15 x 4 mm) on biotite schist (Fig. 1) from the gallery D of the Habachtal mine we prepared two 350 and 450 μm thick double-polished thick sections. From the biotite schist we also prepared two microprobe samples for the study of the carbonaceous material. During preparation, we discovered small microcrystals of emerald (1 x 0.2 mm) distributed in the biotite schist. For comparison beryl samples from Orlovka, Transbaikalia/Russia and Ehrenfriedersdorf, Erzgebirge/Germany, as well as emerald samples from the Lened prospect, NW Territories/Canada and the Vasquez-Yacopí emerald district/Colombia were used.

Microscopy

The samples were studied with non-destructive methods to preserve the material for future, more sophisticated techniques. Most studies were performed with a polarized light microscope Jenalab Pol for reflected and transmitted light, equipped with a ProgRes C10 camera, and a stereomicroscope ZEISS “Stemi 305 trino” with the same camera, or with an Olympus OM-DE-M10 II camera.

Microthermometry

Microthermometric measurements were performed using a calibrated LINKAM THMS 600 heating and freezing stage, together with a TMS92 temperature programmer and a LNP2 cooling system mounted on an Olympus microscope. The stage was calibrated with synthetic fluid inclusions (SYNFLING) and melting points of different standards. All measurements were performed under argon. The standard deviation depends on absolute temperature and is always less than $\pm 2.5^{\circ}\text{C}$ for temperatures greater 100°C , and is $\leq 0.2^{\circ}\text{C}$ for cryometric measurements lower than 20°C .

Raman spectroscopy

Raman spectra were recorded with a JobinYvon LabRamHR800 spectrometer (grating 1800g/mm), equipped with an Olympus optical microscope and a long-working-distance LMPlanFI 100x/0.80 objective. The 514 and 488nm excitation of a coherent Ar^+ laser, Model Innova 70C, with a power of 45 mW on the sample, at a resolution $\leq 0.6\text{ cm}^{-1}$ were used. The spectra were collected at a constant laboratory temperature (20°C) with a Peltier-cooled CCD detector and the position of the Raman bands were controlled and eventually corrected using the principal plasma lines in the Argon laser. For water determination in the inclusion glass we used the method presented by Thomas et al. (2009). As a reference we used a synthetic glass with 5.21% (g/g) water, cross-checked with 30 different glasses of well-characterized water concentration (Thomas 2000, Thomas et al. 2006, and Thomas et al. 2009).

For the identification of minerals and daughter mineral phases in the inclusions we used the RRUFF-database (Lafuente et al., 2015), as well as our own reference materials (well-characterized minerals and reagent-grade chemicals).

From the Raman spectra of carbonaceous material (see Beyssac et al. (2002)) in the range between 1000 and 2000 cm^{-1} we estimated the temperature using the techniques of Hurai et al. (2015), as well as Beyssac et al. (2002).

Results

This study is focused on emerald samples taken from the Habachtal and we confine ourselves to the new discovery of melt inclusions and graphite in emerald and its melt inclusions, as well as in the biotite schist host, which were previously not described. For confirmation and comparison with the graphite data from the Habachtal emerald, we studied the graphite in

several samples of beryl and emerald from other deposits and used well-ordered graphite from Sri Lanka as a reference.

Carbonaceous material

The most often described and abundant minerals enclosed in Habachtal beryl crystals are biotite, phlogopite, muscovite, chlorite, actinolite, talc, plagioclase, epidote, and clinozoisite (Grundmann 1983). In addition, quartz, K-feldspar, calcite, phenakite, apatite, tourmaline, sphene, rutile, zircon, magnetite, pyrite, pyrrhotite, chromite, ilmenite, chalcopyrite and scheelite are found in varying, but generally small amounts (Grundmann 1983, see also Leitmeier 1937). Graphite in emerald from the Habachtal has not previously been described in the literature. Graphite in the surrounding rocks was mentioned but not studied, by, for example, Grundmann and Morteani (1982), Grundmann (1983) and Trumbull et al. (2009). During our Raman study of the emerald samples small (up to $2 \times 10 \mu\text{m}$) well-ordered graphite crystals were found. It is worth noting that most graphite crystals appear in growth zones characterized by numerous and very large inclusions, by implication these are zones of extremely rapid crystal growth.

The graphite in emerald is characterized by a strong and symmetric G band at about 1580 cm^{-1} with a FWHM (full-width at half maximum) of about 16.6 cm^{-1} , similar to the well-crystallized high-temperature graphite from Sri Lanka (see also Wopenka and Pasteris (1993) – see Figures 2 and 3a, and Thomas et al. (2018).

Generally, graphite crystals were found in the root zone of the Habachtal emerald crystals, however, we also found well-ordered graphite crystals in the outer growth zones, and in the centers of the crystals, arranged as intermittent central strings of graphite crystals parallel to the c-axis. Tables 1a and 1b give the results of the Raman study on graphite from Habachtal, and for comparison the brief data for graphite from Sri Lanka and Orlovka, Ehrenfriedersdorf, Lened, and Yacopi. In the Orlovka sample the graphite comes from colorless beryl crystals with a diameter of about 25 mm. The Raman bands (S1 bands) at about 2700 cm^{-1} in the second order Raman spectra are characteristic of well-ordered graphite. This band splits into two band at about 2710 and 2740 cm^{-1} , respectively, also typical for well-ordered graphite.

Using the techniques of Hurai et al. (2015) on 10 well-formed graphite flakes in Habachtal emeralds we calculated temperatures between 744 and 671°C . This

geothermometer is based on metamorphic, hydrothermal, pegmatitic and magmatic formed carbonaceous substances and graphite. Because the D1 band is missing or only weakly present, the D2, and D3 bands are completely missing, and the R2-coefficient is zero, this gives a calculated temperature of 641°C according to Beyssac et al. (2002). Note that the geothermometer presented by Beyssac et al. (2002) is based on the transformation of organic matter into graphite by metamorphic processes. Using Aoya et al. (2010) this gives a slightly higher temperature of 655°C (maximal value of the valid range). In contrast, the graphite in the Habachtal emeralds were probably produced through reactions such as $\text{CO}_2 \rightarrow \text{C} + \text{O}_2$ or $\text{CH}_4 + \text{O}_2 \rightarrow \text{C} + 2\text{H}_2\text{O}$, perhaps under supercritical conditions, and not by simple transformation of preexisting organic material. It is important to note that the stability of fully ordered graphite + fluid is greater than for poorly ordered graphite (Barrenechea et al. 2009).

Our graphite temperature data in emeralds are significantly higher than the estimations using the fluid inclusions by different authors (Grundmann 1983, Nwe and Grundmann 1990, Franz and Morteani 2002). These authors interpreted the entire emerald-bearing sequence as a tectonic *mélange*, produced mainly by alpine tectonism. The PT conditions for the pre-Alpine event and the Alpine event were <3 kbars and <450°C and 4.5 to 6 kbars and 500 to 550°C, respectively.

In addition, a small number of other grains are characterized by the typical D1, G, and D2 Raman bands giving lower calculated temperatures of about 593°C (Beyssac et al. 2002). However, we note that these grains show clear indications of weak to strong damage to the graphite crystals, as noted by a typical mosaic structure, possibly produced by some cataclastic processes (see Figure 3b).

According to Wopenka and Pasteris (1993) the very low R2 values for the intact graphite crystals indicate a high degree of crystalline perfection along the basal plane of the graphite structure. The R2 data give L_a values (in-plane crystallite size) between 1000 and larger than 8000 Å. The data given in Table 1a and 1b demonstrates a good correlation between L_a and temperatures.

The graphite temperature and structural data shows clearly that the formation temperatures of the Habachtal emerald is significantly higher than the estimated temperatures based on fluid inclusions given by Grundmann 1983, Nwe and Grundmann 1990, and others. Because the Raman spectrum of carbonaceous material (CM) shows the maximum temperature conditions reached during regional metamorphism (Beyssac et al., 2002), we have also studied CM in the biotite schist, the data are given in Tab. 1. Calculations from the

Raman spectra the CM of biotite schist gives a maximum temperature of 559°C, corresponding very well with the peak of the Alpine metamorphism (500-550°C) in the region. The CM in biotite schist shows a significantly lower degree of order compared to the well-ordered graphite in the Habachtal emerald. Therefore, a simple incorporation of the CM from the matrix into the emerald is not feasible, the differences are too great.

Fluid inclusions

A detailed description of the common fluid inclusions in emeralds of the Habachtal is given in Nwe and Grundmann (1990). The same fluid inclusions have been found by us in all the Habachtal emerald samples we studied, including the different types of H₂O-CO₂ inclusions. However, all these inclusions are, according to our studies, of secondary origin, since they show homogenization temperatures that are too low in relationship to the adjacent melt inclusions. Additionally, some appear to have formed by separation of the fluid part from the melt inclusions by a splitting process. The coplanar appearance of fluid inclusions to the c-axis is not an adequate criterion for their primary origin (see Luckscheider and Morteani 1989; Schenk et al. 1990), although it may previously have been seen as such. Moreover, the strong zonation, to be discussed latter, suggests that the dense arrangement of primary melt inclusions parallel to the c-axis is a zone of weakness, which provided excellent opportunities for the trapping of pseudo-secondary and secondary inclusions under a later, lower temperature overgrowth of late-stage emerald-III. Such secondary inclusions will not be treated further in this study.

Relatively large, rare, fluid inclusions, with magnesite [MgCO₃] daughter crystals in one of our sample are given in Figure 4a and 4b. These inclusions generally contain daughter crystals of MgCO₃, sometimes together with quartz and trilithionite [KLi_{1.5}Al_{1.5}AlSi₃O₁₀F₂]. The presence of MgCO₃ implies that these inclusions are related directly to the primary crystallization process and are possibly pseudo-secondary in origin or are cogenetic in the sense of Thomas et al. (2019) and represent their Type-C inclusions (primary magmatic fluid-rich inclusions) according to the A-B-C nomenclature of Thomas and Davidson (2012) and Thomas et al. (2019), which are directly linked to one united process of immiscibility. There are also rare small two-phase fluid inclusions (aqueous fluid + vapor bubble), which cut the growth zones at an acute angle, which are probably secondary.

Additionally, tabular fluid inclusions (Fig. 4c), as well as the more equant melt inclusions (Fig. 5b and 5c) occur parallel to the c-axis. Most of these inclusions show a more or less sharp shadow (left side of the inclusion in Fig. 4c) in the emerald. We interpret this shadow as a migration track in the emerald, a product of dissolution at one end of the inclusion and epitaxial growth of new emerald at the other end of the inclusion, in response to the thermal and diffusion gradients, resulting in a visually distinct second growth phase within the emerald. Thus, at trapping conditions density gradients, together with high diffusion rates lead to partial separation of inclusion phases and migration of the inclusion (a type of splitting – see Akizuki, 1965).

The primary magmatic type-C fluid inclusions, containing MgCO_3 , trilitionite, SiO_2 , traces of apatite, and sometime also graphite as daughter phases (see Fig 4a and 4b), homogenize at $297 \pm 9^\circ\text{C}$ into the liquid phase (15 different inclusions) and the smaller two-phase fluid inclusions homogenize at $300 \pm 8^\circ\text{C}$ (13 inclusions). The ice melting temperature is for both inclusion types -14.4°C and -4.3°C , respectively. These values correspond to 15.4 and 6.9 equivalent % NaCl. According Raman spectroscopy this inclusion type contains 1.1 ± 0.3 % (g/g) Na_2CO_3 (11 determinations), as well as 0.02 % (g/g) H_3BO_3 equivalents. The vapor phase is composed from CO_2 , N_2 , and CH_4 ($X_{\text{CO}_2} = 0.907$, $X_{\text{N}_2} = 0.09$, $X_{\text{CH}_4} = 0.003$). The aqueous liquid phase contains extremely high D_2O concentrations (~ 10 % (g/g)). Such high values are only possible at very high temperatures under supercritical conditions.

From the corresponding isochores for the type-C fluid inclusions we obtain a pressure of about 5 kbar at 690°C (minimum of the graphite temperature) and the smaller two-phase fluid inclusion gives a pressure of about 4.4 kbar, which underlines their secondary character. In addition to melt inclusions, the existence of type-C fluid inclusions with high NaCl and other components (Figures 4 d,e, and f), which homogenize according to the scheme :

(Roedder 1984, Figure 9-13 on page 287)

demonstrate clearly that the temperature data given by previous authors are too low to be primary fluid inclusions. Unfortunately, homogenization of these type-C inclusions is generally not possible with conventional heating stages due to the inclusions strong tendency to decrepitate, starting at 400°C , only homogenization under high pressure can resist this tendency.

To resolve these apparent dilemmas, we have prepared and studied an emerald crystal embedded in biotite schist from the gallery D of the emerald deposit Habachtal (Fig. 1). In this crystal we see clearly that the high-temperature fluid and melt inclusions are related to old cores arranged around two biotite crystals inside of the emerald. The emerald in this zone is light green against the emerald-colored rim zone. This observation suggested a two- or three-stage formation process at least. With this in mind, we can differentiate between the high-temperature emerald-I (with melt inclusions) and the medium-temperature emerald-II (fluid inclusions only). In emerald-II there are no melt inclusions, however there are some small high-temperature fluid inclusions present. The outer rim (emerald-III) is melt inclusion-free, only very small high-temperature fluid inclusions can be seen.

Melt inclusions

All the studied samples contain elongated melt inclusions parallel to the c-axis, containing silicate glass, a fluid phase and a vapor bubble. Small daughter crystals of MgCO_3 are often present. Daughter crystals of quartz are occasionally present, and daughter crystals of halite are extremely rare. Fluid and CO_2 -rich inclusions, described by previous authors, are rarely observed in our samples. If present, the fluid inclusions are relatively large and may be pseudo-secondary or secondary in relationship to the melt inclusions.

Most melt inclusions have a well-formed elongate cylindrical habit, aligned parallel to the c-axis, described as “tube-type inclusions” in Nwe and Grundmann (1990). The shape allows a good visual estimation of the volume proportions of the components (silicate glass, aqueous fluid, CO_2 , and occasional daughter crystals). However, there are also some more isometric inclusions present, which are generally somewhat larger. Figure 5 shows typical tubular melt inclusions in emerald of the Habachtal, and Figure 6 shows the more isometric melt inclusions, which are generally crystallized and contain several different mineral phases (mostly silicates), an aqueous fluid phase and a vapor bubble. With Raman spectroscopy we have identified actinolite, beryl, fluorophlogopite, graphite, magnesite (among other carbonates), quartz, calcite and tremolite. According to their general appearance, the crystallized melt inclusions in emerald from the Habachtal visually resemble the inclusions in beryl from the Orlovka pegmatite, East Transbaikalia, Russia (Thomas et al. 2009), however, the daughter phases inside the melt inclusions are different. These are determined mainly by the interaction of the beryl-(emerald)-forming media with the metamorphic paragenesis. A

first estimation of the chemistry of the beryl-(emerald)-forming media for Orlovka are given in Thomas et al. 2009.

In addition to the intact melt inclusions, containing silicate glass, aqueous fluid and a vapor bubble, former melt inclusions are also present, in which the fluid sub-phase has separated from the glass portion of the same originally multiphase inclusion by splitting (see Akizuki 1965) as a result of density contrast immediate after trapping. As noted, there is strong evidence of selective migration of some melt inclusions, and it is possible for the melt (now glass) and the aqueous fluid components to migrate at different rates causing physical separation of the melt and fluid portions. At supercritical conditions the solubility of beryl is large and splitting of inclusions is rapid. In addition, there are also tube-type pure MgCO_3 inclusions, suggesting that a significant percentage of the inclusions identified as fluid inclusions are actually formed by splitting of melt inclusions. We suggest that the separation of the fluid phase from the glass phase by splitting (a type of phase separation) produces the illusion of the dominance of fluid inclusions and has helped mask the existence of melt inclusions.

Water concentration of the inclusion glass

The very strong Raman band of beryl at 3595 and 3608 cm^{-1} in the second-order range makes the determination of water difficult, as it overlaps with the water bands. Therefore, we used the relatively weak band near 1630 cm^{-1} corresponding to the bending vibration of molecular water dissolved in the inclusion glass. From 18 determinations on nine inclusions we obtained a water concentration of $4.45 \pm 0.52\%$ (g/g) in the inclusion glass.

Bulk water concentration

The bulk water concentration was determined by volumetric estimation of the glass and fluid phases plus the water concentration in the glass calculated from Raman spectroscopy.

MgCO_3 concentration

The water-rich melt inclusions generally contain small daughter crystals, which according to the Raman spectroscopy is MgCO_3 (magnesite) indicated by the very strong Raman band at 1093 cm^{-1} and weaker bands at 205 , 318 , and 737 cm^{-1} [RRUFF-reference: R050676, 96%

match, magnesite from Tyrol, Austria]. The MgCO_3 concentration in the inclusions is strongly correlated with bulk water concentration of the melt inclusions, and shows a Lorentz distribution (see Thomas et al. 2019), which according to those authors is consistent with the formation of the melt inclusions forming at near-critical conditions, used here in the sense of the lowest temperatures at which H_2O and silicate melt are completely miscible in all proportions. Note, the melt inclusions trapped near the solvus crest and the Gaussian or Lorentzian distribution of some trace elements (in this case Be and CO_3^{2-}) and main elements versus the water concentration are the most direct and reliable robust record of samples of supercritical fluids.

The H_2O - MgCO_3 -data are given in Table 2 and the Lorentz distribution is plotted in Figure 7. The following fitting parameter for MgCO_3 and water were obtained:

Center [% (g/g) H_2O]: 27.5

Width [% (g/g) H_2O]: 5.3

Offset [% (g/g) MgCO_3]: 1.6

Height [% (g/g) MgCO_3]: 6.9

In our view, MgCO_3 was formed by a secondary reaction from the originally present alkali carbonates by reaction with the Mg ions ubiquitous in this system. At high carbonate concentration Be forms the readily room temperature soluble complex compound $\text{K}_2[\text{Be}(\text{CO}_3)_2]$. The high MgCO_3 concentration is a direct indication of the high alkali carbonate concentration near the supercritical temperature range.

Pseudo-binary solvus

Because the calculated water and MgCO_3 -concentration are well correlated it seems reasonable to assume that the water content also correlates with the temperature forming a pseudobinary solvus (see Thomas et al. 2000). However, because we have not determined the homogenization temperatures of the melt inclusions, we can use the model of by Thomas and Davidson (2016) and Thomas et al. (2019) for an estimate of these temperatures. Table. 2 also gives the calculated solvus data based on the fluid inclusion and graphite temperature data, respectively.

Implications of these results

The presence of previously undetected melt inclusions, some of which have separated post-trapping into glass and a fluid sub-phase (vapor and solution) may shed light on the apparently low temperatures calculated from fluid inclusions alone. In our view previous measurements were performed only on a part of the melt inclusions, or on secondary fluid inclusions. The arrangement of the fluid inclusions parallel to the c-axis is not a straightforward proof of their primary origin (e.g., Luckscheider and Morteani 1989; Schenk et al. 1990), as is sometimes assumed. Thus, giving only a partial homogenization temperature. If we extrapolate the isochors from Luckscheider and Morteani (1989) and Schenk et al. (1990) to a solvus, we necessarily obtain higher temperatures. In effect the highest fluid inclusion temperatures represent the lowest range for the trapping of melt inclusions. As support for our suggestion is the important observation that all the graphite temperature data is significantly higher than all the fluid inclusion temperatures. Moreover, all the graphite data demonstrates high-grade metamorphic conditions from upper amphibolite to granulite facies rocks (Wopenka and Pasteris 1993, Grew 1974), inconsistent with the regional geology. Together with the existence of melt inclusions, this implies a significant discrepancy in metamorphic conditions described for the Habachtal. Our solution to this dilemma is to invoke a separate supercritical fluid from another, most probably pegmatitic source.

Discussion

Grundmann (1983) and Nwe and Grundmann (1990) derived values for the conditions of the emerald mineralization as 530°C and 5-6 kbar, using fluid inclusions and mineral equilibria. However, we have demonstrated that the emerald samples from the Habachtal used in this study contain melt inclusions. This strongly implies that the previous temperature estimates (550°C as maximum) are significantly too low and gives incorrect parameters for the genesis of the Habachtal emerald.

The demonstration of well-ordered graphite inside the emeralds is also crucial in the interpretation of the genesis. According to Grew (1974) the formation of highly-ordered graphite requires a temperature of 660-700°C at a pressure of 4.5 to 5 kbar. Similar results presented by Shengelia et al. (1979) using X-ray diffraction studies of graphite, demonstrated that the graphite lattice parameter *c* reflects the highest temperatures (up to 800°C) reached and which is stable against regressive metamorphism. The Raman spectrum of graphite in the

emeralds is consistent with the graphite from Sri Lanka, which is generally accepted as a standard of well-ordered graphite (Dissanayake 1981) and were formed under granulite facies conditions ($T > 700^{\circ}\text{C}$). Because the graphitization processes are irreversible, the temperature data are indicative of the peak temperature of the metamorphic history (Beyssac and Lazzeri 2012). Therefore, our results are in sharp contrast to the general accepted results obtained by authors previously working on the Habachtal emerald genesis using fluid inclusion data alone.

In the Habachtal the P-T conditions of the pre-Alpine event (<3 kbars and $<450^{\circ}\text{C}$) and 4.5 to 6 kbars and 500 to 550°C for the Alpine event (see Franz et al. 1986, Grundmann and Morteani 1989, Luckscheiter and Morteani 1980), have been derived from mineral equilibria. As we have no reason to query the estimated regional PTX conditions we must infer an overlaying, more localized process, which has led to the emerald mineralization, but has not significantly changed the bulk, regional mineralization. That means, however, that the conventional genetic interpretation of the Habachtal emerald mineralization are incomplete, and that the origin of the Habachtal emerald deposits is separate from, but may be related to, the regional metamorphic context as a general framework. We would suggest that our study returns to the early genetic interpretation by Leitmeier (1937), who assumed, in analogy to Fersmann (1929) an injection of Be-rich pegmatitic solutions from a granitic magma. Given our result, however, these solutions are mostly probably supercritical in nature, rather than conventional hydrothermal fluids.

We note that Zwaan (2006) was critical of the interpretation by Grundmann and Morteani (1989) and others, and suggested that in cases where pegmatitic sources of Be are not apparent one must proceed with caution since fluids can travel great distances from pegmatites, especially in intensely sheared rocks, without leaving any strong evidence. Zwaan (2006) also pointed out that pegmatites do occur in the Zentral gneiss. The Habachtal emeralds contain up to 760 ppm Cs (Calligaro et al., 2000), which suggests a pegmatitic source, and sulfide deposits related to submarine volcanic exhalation are not generally enriched in Be (Zwaan, 2006). Thomas et al. 2019 and reference therein have shown that at supercritical conditions several rare elements (Be, Cs, Rb and others) can be enriched to very high concentrations.

The estimates of temperatures by Nwe and Grundmann (1990) were derived from fluid inclusion studies. However, the existence of very water-rich melt inclusions and the Lorentz distribution of MgCO_3 (probably primarily alkali carbonates) which is correlated with water are strong indications of the involvement of a supercritical phase during the beryl-

forming processes. We have demonstrated previously (Thomas and Davidson 2016, Thomas et al. 2012 and 2019) that above the solvus crest the fluids/melts are characterized by extraordinary physicochemical properties such as extremely high diffusion rates and element fluxes, low dynamic viscosity and extremely low surface tension values, among other properties. Thus, supercritical fluids can diffuse through solids almost like a gas. There are two very different stages: equilibrium conditions at and below the critical point, and above the critical point, where conditions are far from equilibrium. Under supercritical conditions, most processes are very different from common equilibrium conditions. A typical element is Be - we have already shown, that Be is highly mobile under supercritical conditions (Thomas and Davidson 2010).

The demonstration of highly crystalline graphite in emerald, as well as the action of alkali carbonate-rich supercritical fluids at high temperature and pressure also throw light on the speciation and transport of chromium (vanadium) as the principle coloring agents for emerald. Because Cr(III) is nearly insoluble in water, we can assume that the transport of chromium occurs mainly as Cr(II) complex $\text{CrCl}(\text{OH})^0$ (Huang et al. 2019). Similar results were already obtained by Watenphul et al. (2014). According to Holleman and Wiberg (2007), the conversion of water-insoluble chromium into hydrosoluble chromium happens at high temperatures and in the presence of Na_2CO_3 via the formation of sodium chromate $[\text{Na}_2\text{CrO}_4]$. According to our findings on supercritical fluid/melt systems (e.g., Thomas et al. 2019), we can postulate that at cooling near the solvus crest we have a sharp change in the speciation of the solved complexes: in the type-A melt a dominance of the more oxidized species and in the water-rich type-B melt a dominance of the more reduced species. The Cr incorporation into the emerald lattice is then connected with a change in the speciation, as a redox reaction.

The surprising point regarding the supercritical system is that there must be an active, ordering principle and mechanism to bring specific, mostly scarce elements, distributed randomly in a large volume of magma, to a point where the concentration reaches the extremely high values needed for the crystallization of various otherwise rare minerals. Currently, classical chemistry struggles to explain this in terms of solubility in hydrothermal fluids *sensu stricto*. The strong Gaussian or Lorentzian correlation of some elements with water or another volatile element is unusual and needs explanation. We suggest that the unique properties of supercritical fluids provide such a mechanism for such surprising observations.

Previously, the significance of Mg in the emeralds has not been completely recognized. We suggest that the initially present alkali carbonates in the supercritical fluid/melt react during cooling directly with the omnipresent Mg^{2+} ions (see also Grundmann and Morteani 1989) to form MgCO_3 which is very stable at low temperatures. In a similar, but very clearly pegmatitic mineralization of beryl in the Orlovka deposit the alkali carbonates have significance for the generation of supercritical fluid/melt phases (Badanina et al. – in preparation). After rapid quench experiments between 650 and 750°C and 1 to 3 kbar on beryl samples from Orlovka a Lorentzian-distribution of carbonate versus water was:

Center:	29.6 % H_2O
Width:	6.6 % H_2O
Offset:	0.34 [% (mol/mol)] CO_3^{2-}
Height:	5.7 [% (mol/mol)] CO_3^{2-} .

Mobilization of beryllium

At high temperatures around 700 – 600°C beryllium is extreme mobile, as we demonstrated experimentally, and by Raman-spectroscopy with the formation of bromellite (BeO) in and around melt inclusions (Thomas and Davidson, 2010).

The following simplified reaction according to Newkirk and Smith (1965a) and Thomas and Davidson (2010):

provides a means by which beryllium can be transported very easily, since the hydroxide Be(OH)_2 is strongly soluble in aqueous vapor. According to Newkirk and Smith (1965b) the high alkali carbonate concentration near the critical temperature suggests that beryllate anions are important species in supercritical solutions:

Furthermore, CO_2 is extremely soluble in beryllium hydroxide (Gmelin 1930, p. 94). During cooling and crystallization, the CO_2 is rereleased and can be found in the melt and fluid inclusions. The following simplified reaction equations show beryl formation at cooling from albite:

Among other things Grew (1974) explained the formation of well-ordered graphite by the catalytic effect of the silicate minerals on the reacting fluid phase. Thus, we would explain the generation of the well-ordered graphite in the emerald crystals as such a process, at or near supercritical conditions, here at about 650-700°C and approximately 5 kbar.

In summation, with these new results the previously accepted metasomatic/metamorphic genesis of the Habachtal emerald (see also Giuliani et al. 2019) cannot be maintained in its original form. Groat et al. (2008) wrote “that in the most cases a combination of mechanisms (magmatic, hydrothermal, and metamorphic) were needed to bring Be into contact with the chromophores.” So, with our short contribution we hope expand the mechanisms by adding a new possibility: the working of supercritical melts and/or fluids. We suggest that the earlier ideas that the Habachtal emeralds are related to long-distance effects of granite pegmatites (see Fersmann 1929, Leitmeier 1937, Schneiderhöhn 1961) warrants active reconsideration.

The significantly higher temperatures for the beryl- and emerald-formation together with the evidence for the involvement of supercritical processes suggests a mechanism beginning with the Be-enrichment of all rocks in question by an initial high-temperature process forming emerald-I and -II. In a later re-crystallization process, possibly during the Alpine metamorphism, in a now Be-rich surrounding, at least some emerald crystals were formed using the old beryl as seeds. The timing of these events, which event generated the supercritical fluid and delivered most of the beryllium needs to be cleared up by careful age datings. We note here, that supercritical fluids are not connected exclusively to magmatic processes. In Thomas et al. (2018) it was demonstrated that supercritical melt/fluids can be generated at peak metamorphic conditions around 700°C in non-magmatic facies. Therefore, we would suggest that the classification of the Habachtal emerald by Giuliani et al. (2019) needs to be modified slightly by allowing for processes related to supercritical high-temperature fluids. We suggest that the term “metasomatic fluid” needs to be used with caution as it usually interpreted to mean a hot aqueous solution. However, our work suggests a continuum from hydrothermal fluids through to pegmatite-forming supercritical melt/fluids with many intermediate phases, not all of which show clear magmatic sources.

Conclusions

In this contribution we have demonstrated the existence of well-ordered graphite as well as melt inclusions and high-temperature fluid inclusions in emeralds from the Habachtal. These

are in addition to the low-temperature fluid inclusions detailed by previous authors. A careful analysis of these new melt, fluid, and graphite inclusions present in these emeralds strongly suggests that the data obtained previously were from secondary or pseudo-secondary fluid inclusions, rather than being primary. Thus, the temperature and pressure data derived from them is too low, at least for the initial emerald formation.

Our work strongly suggests that the formation of the Habachtal emerald deposit, and quite possibly other gem and mineral deposits in that region, requires a rethink. New techniques and ideas provide a starting point, which we hope will be taken up with renewed vigor.

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Figure Captions

Fig. 1 a) An emerald crystal in biotite schist from gallery D of the Habachtal emerald deposit. b) two polished thick section from this crystal, the upper section is cut from outer growth zone, the lower one is cut from the center of the crystal. The largest inclusions, including the melt inclusions, are concentrated in elliptical core zones marked by large and small biotite flakes. This core zone is white to pale green, in contrast to the emerald green outer growth zones.

Fig. 2 a) Raman spectrum of carbonaceous material (CM) in emerald-bearing biotite schist from the Habachtal, and spectra of graphite (Gr) in the emerald-I and emerald-II of this rock.

The position of the Raman bands D1, G, and D2 of the first-order region are given for orientation as per Beyssac et al. (2002). b) Raman spectra of graphite in the Habachtal emerald. Spectrum a) represent the well-ordered graphite, and b) graphite, which was influenced by a cataclastic process (see fig. 3). According to Hurai et al. (2015) 2 b) gives a calculated temperature of 595°C, and according to Beyssac et al. (2002) a calculated temperature of 562°C. The spectrum of the Sri Lanka graphite is given for comparison.

Fig. 3 Graphite aggregates in the Habachtal emerald. a) Gr 1: well-ordered graphite; b) cataclastic influenced graphite

Fig. 4 Fluid inclusions in the Habachtal emerald. a) large inclusion with magnesite (Mgs) and graphite (Gr) daughter phases; L – aqueous solution, V – vapor bubble; b) large fluid inclusion with quartz (Qtz), trillithionite (Tri), and graphite (Gr); c) fluid inclusion parallel to the c-axis, formed by splitting. The shadow on the left side is interpreted as a migration track, and thus is a later, post-trapping emerald recrystallization; d, e) high-temperature fluid inclusions in emerald of the biotite schist from the gallery D; f) high-temperature fluid inclusions in the outermost growth zone of same crystal, where the inclusion d) and e) are located

Fig. 5 Melt inclusions in Habachtal emerald. a) a melt inclusion with typical phase assembly, containing glass (G), an aqueous solution (L), a vapor bubble (V), and a solid phase S, in this case MgCO_3 . Melt inclusions b), c), and d) have the typical tubular form arranged parallel to the c-axis

Fig. 6 a), b), c), and d) Melt inclusions in Habachtal emerald. The glass (G) is here recrystallized or partly recrystallized into different silicates (S) and carbonates and contain an aqueous fluid phase (L) and a vapor bubble (V) between the mineral phases. Mgs – magnesite

Fig. 7 Distribution of MgCO_3 in Habachtal melt inclusions in relation to the water concentration. The distribution shows a strong Lorentz distribution

Tables

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Table 1

Results of the Raman study (488 nm) in the first- and second-order of graphite in emerald from the Habachtal, with some comparison and reference samples. The data with standard deviation from measurements of 10 graphite grains of each sample; others: three measurements

Graphite	Color of the beryl	First-order				Second-order
		G band (cm^{-1})	FWHM of the G band (cm^{-1})	Position of the D1 band (cm^{-1})	Position of the D2 band (cm^{-1})	Position of the S band (cm^{-1})
Brl Habachtal a	emerald	1578.1 ± 2.2	17.5 ± 1.4	-	-	2708/2742
Brl Habachtal b	emerald	1579.2 ± 1.4	15.7 ± 1.3	1352.9 ± 6.9	1601.5 ± 9.0	2712/2740
Brl Habachtal Fluid inclusion	emerald	1577.6	15.1	1355.0	-	2695/2734
Brl in biotite schist, Habachtal - core - rim	pale green	1577.2 ± 1.2	15.1 ± 0.6	1378.8 ± 4.4	-	2715/2735
	emerald	1582	36.7	1352.9	1614.8	n.d.
CM from biotite schist, Habachtal		1589	78.6	1357	1621	2690
Brl Orlovka	colorless	1579.4 ± 0.1	15.8 ± 1.0	-	-	2712/2740
Brl E-Dorf a	green	1580.2	16.1	1353.6	1607.3	2708/2740
Brl E-Dorf b	green	1579.6	16.0	1358.7	-	2698/2735
Brl Lened	emerald	1608 ± 2.4	53.0 ± 5.5	1345 ± 3.4	-	2695/2927
Brl Yacopi	emerald	1602.3	68.6	1339.0	-	Strong fluorescence
Gr Sri Lanka - reference		1578.5 ± 1.1	13.4 ± 0.3	1356.1 ± 3.7	-	2711/2739

Additional samples for comparison and reference from graphite from Sri Lanka, beryl from Orlovka/Transbaikalia, Russia, beryl from the Ehrenfriedersdorf tin-tungsten deposit, from Lened, Canada and Yacopi, Colombia

Brl – beryl, Gr – graphite, CM – carbonaceous material

E-Dorf – Ehrenfriedersdorf tin-tungsten deposit a) hydrothermal formation; b) pegmatitic formation (three grains each)

FWHM – Full width at half maximum

n.d. – not determined

Table 2

Results of the Raman study (488 nm) in the first-order of graphite in emerald from the Habachtal, the R2 ratio, the in-plane crystallite size L_a , the calculated (CM) and the inclusion temperatures. Other beryl samples were used for comparison and the Sri Lanka graphite served as reference

Graphite	Color of the beryl	R2 = D1/(G+D1+D2)	L_a (Å)	Temperature (°C)		
				Hurai et al. (2015)	Beyssac et al. (2002)	Fluid and/or melt inclusions
Brl Habachtal a	emerald	0	8000	744	641	690
Brl Habachtal b	emerald	0.08 ± 0.03	1300	671	605	655
Brl Habachtal Fluid inclusions	emerald	0.04	3175	708	624	297 (700)
Brl in biotite schist, Habachtal - core - rim	pale green	0.02 ± 0.01	5300	724	633	n.d. (700)
	emerald	0.20	220	579	552	n.d.
CM from biotite schist, Habachtal		0.23	165	559	539	(550)
Brl Orlovka	colorless	0	8000	744	641	680
Brl E-Dorf a	green	0.46	40	430	436	429
Brl E-Dorf b	green	0.04	3175	706	623	718
Brl Lened	emerald	0.48 ± 0.06	35	420	427	420
Brl Yacopi	emerald	0.84	<2	287	267	290 - 360
Gr Sri Lanka - reference		0.07 ± 0.02	1600	679	610	(660 – 690)

Brl – beryl, Gr – graphite, E-Dorf – Ehrenfriedersdorf tin-tungsten deposit a) hydrothermal formation; b) pegmatitic formation (three grains each), L_a (Å) - in-plane crystallite size, calculated according to Wopenka and Pasteris (1993). The fluid and/or melt inclusion temperature data for the Habachtal emerald corresponds to this work, data for Sri Lanka are from Dissanayake (1981), Grew (1974), data from Orlovka and Ehrenfriedersdorf are unpublished by Thomas, the data for the Lened emerald are from Marshall et al. (2004), and the data for the Yacopi emerald are from Groat et al. (2008). Temperature data in round brackets are trapping or crystallization temperatures.

Table 3 Melt inclusions in emerald from the Habachtal

H ₂ O [% (g/g)]	MgCO ₃ [% (vol/vol)]	T1 (°C)	T2 (°C)
8.2	1.7	560	605
15.0	2.0	630	669
18.4	2.0	650	687
21.9	2.9	650	698
22.1	2.7	655	698
25.4	6.0	655	700
27.7	8.4	650	698
30.4	4.8	640	691
33.3	2.6	640	679
39.7	2.3	590	638
46.5	1.6	540	575
49.1	1.6	530	546

H₂O and the MgCO₃ concentration were determined using volume estimations and Raman spectroscopy, and the temperature T was estimated according to Thomas and Davidson (2016) and Thomas et al. (2019). T1-lower values, based on the maximal fluid inclusion data; T2 – based on the graphite data. The data in bold type corresponds to the solvus crest.