Short Communication

# Extreme Enrichment of Cs during the Crystallization of the Ehrenfriedersdorf Pegmatite Melt Related to the Variscan Tin Mineralization

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## Abstract

This short paper shows the excessive enrichment of Cs in a volatile-rich evolved pegmatitic silicate melt. This water-rich melt (plus B and F) with about 30% bulk water was, with high probability, created by an input of a supercritical fluid from the earth's mantle. The water content of a granitic melt is at ~900°C, and crustal pressures (<5 kbar) are too low to create such a volatile-rich evolved melt. Furthermore, the quartz contains nanodiamonds and graphite. These are strong hints to the participation of supercritical fluids.

*Keywords:* $H_2O$-$B_2O_3$-F-rich melt, Cs-rich melt inclusions, Multistage liquid-liquid immiscibility, Supercritical fluids

## Introduction

During the study of melt inclusions in quartz of a pegmatite body related to the Variscan Ehrenfriedersdorf tin deposit in the Central Erzgebirge/Germany, we often found high concentrations of Cs in different inclusion types: water-poor melt inclusions rich in Cs, water-rich melt inclusions with a moderate Cs content, and extreme Cs-pentaborate rich inclusions trapped near the crest of the main solvus. The primary solvus curve (B vs. $H_2O$) results from the simultaneous enrichment of water, boron, and fluorine and forms a pseudo-binary solvus ($H_2O$ + $B_2O_3$ + F + Silicate melt) versus temperature (Figure 1a and 1b).



**Figure 1b:** Fluorine versus water ($H_2O$) concentration obtained from melt inclusions from the same Ehrenfriedersdorf pegmatite quartz.

From these curves (Figures 1a and 1b), we see that at the critical point (solvus crest), a high concentration of $H_2O$, $B_2O_3$, and F are present: about 27.5, 4.2, and 9.0%, respectively. The data are from published and unpublished data from Veksler and Thomas (2002) [1-4].

From unpublished hydrothermal diamond anvil cell (HDAC) experiments performed in 2002 together with Ilya Veksler and Christian Schmidt, we know that using synthetic pegmatite melts similar to the Ehrenfriedersdorf pegmatite with about 50 [% (vol/vol)] water in the temperature range from 840 down to 300°C multistage liquid-liquid immiscibility processes happens. Each main phase ever formed tends to liquid immiscibility. Such compartments are
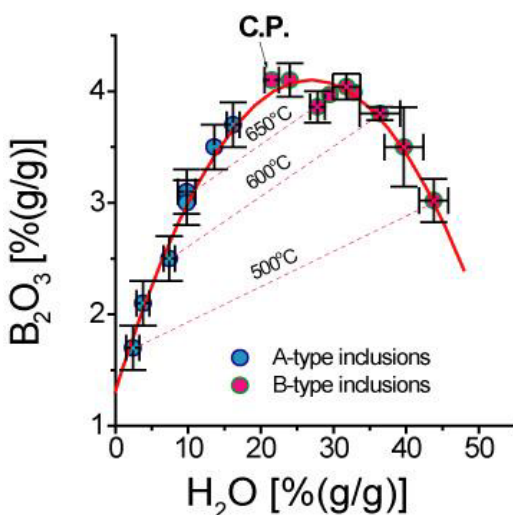


**Figure 1a:** Boron versus water concentration in conjugate type-A (blue) and type-B melt inclusions (red) in the Ehrenfriedersdorf pegmatite quartz. Both compounds portray a solvus curve (melt-water). Included are the corresponding isotherms (500, 600, and 650°C) - see Thomas et al. (2003) [1].
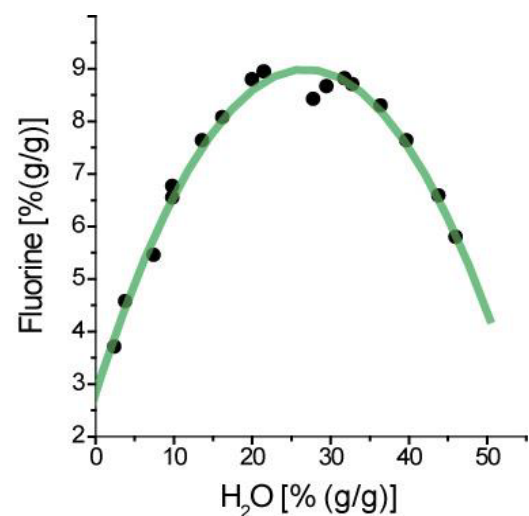
very contrasting and show extreme enrichment of rare elements like boron, fluorine, cesium, beryl, tin, and others (e.g., Thomas et al. 2019 and 2022) [5,6]. This specific experiment, unfortunately, ended short before the total homogenization at about 900°C by the crash of a diamond of the HDAC. This experiment shows, however, clearly that the formation of such water-rich melt is only possible at very high temperatures, and consistently, with cooling, multi-phase separation happens steadily down to low temperatures around 160°C (Figures 2 and 3). If we look at Figure D at Schröcke's contribution (1954) [7], it follows that primary forming this pegmatite type is impossible in situ. We need high water and energy to develop a mass of pegmatite bodies shown there (see also Johannes and Holtz, 1996) [8]. In a couple of publications, Thomas [9-14] and Thomas et al. [15,16] have shown that by the finding of typical mantle minerals in granites and pegmatites, the supplier of the necessary water (energy and other components) can be supercritical fluids coming directly from the mantle region. From the unfinished HDAC experiment (see above), we have learned that during heating and cooling, many phase changes happen, primarily by liquid-liquid immiscibility (see exemplary Figures 2 and 3).
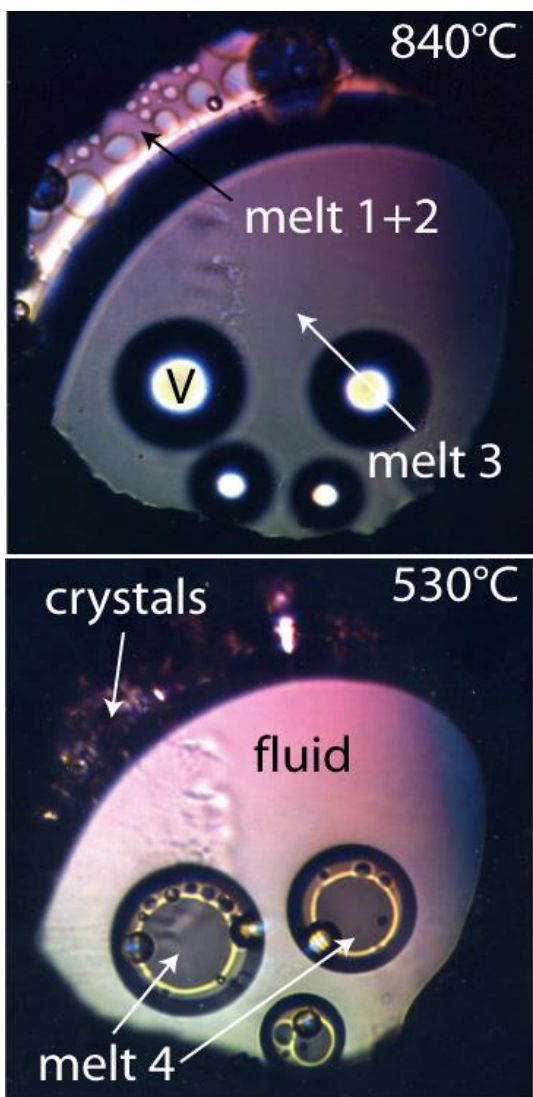


**Figure 2:** Look through the microscope at the sample chamber formed by an Ir-gasket with a hole of 300 μm between two diamonds of the HDAC at two different temperatures. Conspicuous are the different phases formed by liquid-liquid immiscibility.
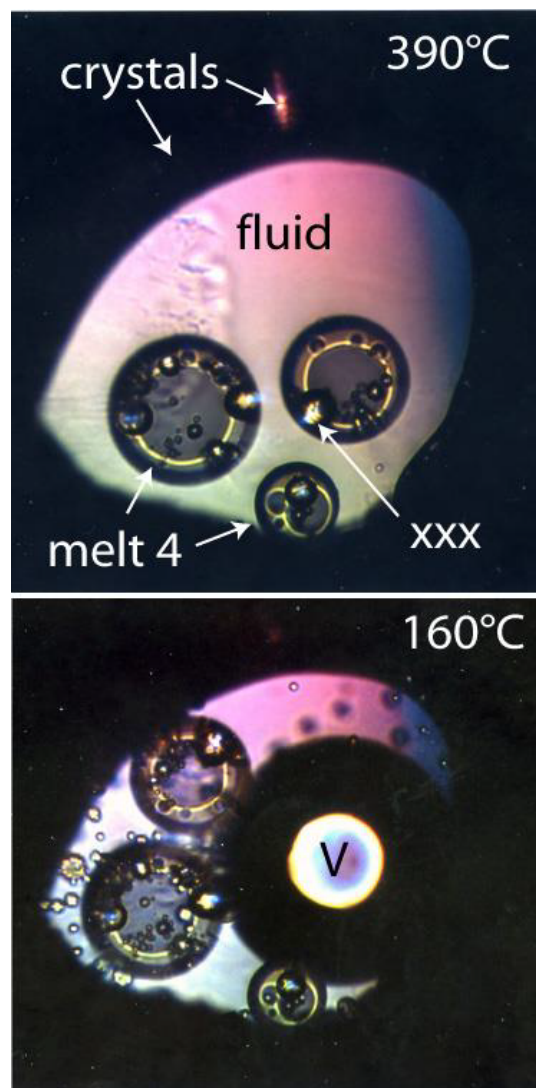
**Figure 3:** The same HDAC experiment at lower temperatures (390 and 160°C). V: Vapor, XXX: late-formed crystal. The "crystals" marked area stands for the melt 1+2, now wholly solidified.

### Sample Material

The sample material (Qu8) comes from a miarolitic pegmatite body in the Sauberg tin mine near Ehrenfriederesdorf, Germany. A description of the locality is in Webster et al., 1997 [4]. The quartz sample was as big as your fist. Many 500 μm thick on both sides polished slices are produced from this sample. The vapor phase of some melt inclusions in this quartz contains high hydrogen, methane, and $CO_2$ concentrations: $X_{H2}=0.58$, $X_{CH4}=0.26$, $X_{CO2}=0.16$ (Thomas and Webster, 2000) [17]. In a quartz crystal (Qu8-45) from the same pegmatite, here not studied, we have found large aggregates of graphite and nanodiamond.

### Methodology

The general used methods are described in Webster et al. 1997 [4] and Thomas [13] and references in there). For the microprobe study (main and trace elements), we mainly used the CAMECA SX50 microprobe. We used Raman spectroscopy (see Thomas 2023e and references) [13] to determine the water as the basis component for constructing the pseudo-binary solvus curves (see also Thomas and Davidson, 2016) [18].

## Results

This contribution is only restricted to cesium (Cs) results. Cesium, with a Clarke value of about 5.0 ppm in granitic rocks (Rösler and Lange, 1975) [19], is enriched to extremely high values of about 160000 ppm. That corresponds to an enrichment of 32000 fold, an incredible value. Further, we see relationships between Cs and $H_2O$, Cs and $B_2O_3$, and $B_2O_3$ with $H_2O$. Figure 4a demonstrates the enrichment of Cs (as $Cs_2O$) with water. The Cs shows here a good Lorentzian distribution. The data come from typical melt inclusion in the pegmatite quartz from the Sauberg mine. The same distribution type results for Cs and B in Figure 4b. This figure shows strong enrichment of Cs at a more or less constant $B_2O_3$ concentration of about 2.3% $B_2O_3$. According to He et al. (2020) [20], $B_2O_3$ reduces pollucite's [(Cs, Na)(AlSi$_2$)O$_6$ • nH$_2$O] crystallization temperature (maybe under 700-600°C) and improves immobilization through an encapsulation effect here by Al-silicates.

The melt inclusions are relatively water-poor (~5%) and represent the heavy residue. Figure 4c shows the simplified solvus curve for the system melt-$H_2O$ versus $B_2O_3$ (Figure 1a). Figure 4d displays the extreme Cs enrichment near the solvus crest of the Melt-$H_2O$ – $B_2O_3$ system as Cs-pentaborate (Ramanite-(Cs). At first, this Cs-pentaborate was found in pegmatite material from the Isle of Elba (see Thomas et al., 2008) [21] – later also in Malkhan (Thomas et al., 2012) [22] and Ehrenfriedersdorf (Sauberg mine). The Lorentzian distribution of Cs vs. B is untypical, and Cs vs. $H_2O$ is typical for some elements (Be, Sn, and others [5,6]. Table 1 gives the fit data for the three Cs distributions.

In comparison to Figure 4a, the distribution of $Cs_2O$ vs. $H_2O$ shown in Figure 4d is a little bit shifted to higher water concentrations (maybe the real critical point of the system) or by the crystal water in the formula of Ramanite-(Cs) [CsB$_5$O$_8$ • 4H$_2$O] – see Thomas et al. 2008) [21].
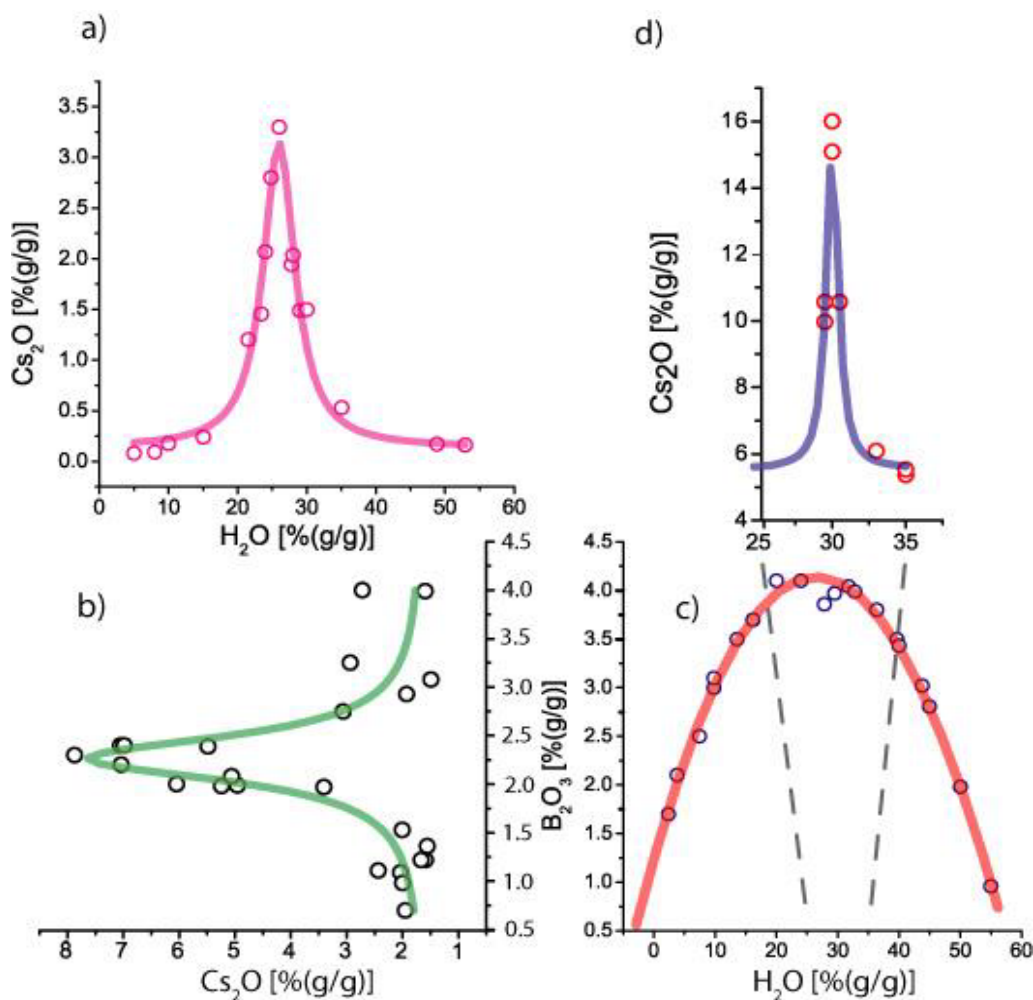


**Figure 4:** (a) Distribution of Cs with $H_2O$, (b) Cs with B, (c) $H_2O$ and B, (d) Cs as Ramanit-(Cs) with $H_2O$. The microprobe data for (b) are from Thomas et al. 2019 [5].

**Table 1:** Lorentzian fit data.

| Distribution | Area | Center (%) | Width (%) | Offset (%) | Height (%) | R² |
|---|---|---|---|---|---|---|
| $Cs_2O$-$B_2O_3$ | 5.226 | 2.264 | 0.553 | 1.621 | 6.012 | 0.90983 |
| $Cs_2O$-$H_2O$ | 26.592 | 25.991 | 5.631 | 0.134 | 3.006 | 0.96752 |
| Ramanite-(Cs) | 13.309 | 29.992 | 0.900 | 5.676 | 9.419 | 0.99436 |

## Discussion

The here-shown enrichment of Cs during the crystallization of a pegmatite-forming melt related to the Variscan tin deposit Ehrenfriedersdorf is unexpectedly high. The origin of such distributions is, at the moment, not clear. More research is indispensable. Are such Lorentzian-type distributions of elements with water a characteristic feature of the participation of supercritical fluids at the tin mineralization here? Some elements (Be) are Gaussian distributed (see Thomas 2023d) [12]. What are the reasons for the different distribution types? Which physicochemical processes are the determining steps? Figure 4 shows that the behavior of Cs in water-rich high-temperature melt-water systems is very complicated. Therefore, is storing the radioactive $^{137}$Cs as boron-stabilized pollucite doubtful (see Yokomori et al., 2014) [23,24]. Because each element in the supercritical state can enriched to high values, we assume, in principle, that universal cooperative interactions between the particles under these conditions will work. The opposite is, up to now, not proved.

## Acknowledgment

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