# CERITE-(Ce) AND THORIAN SYNCHYSITE-(Ce) FROM THE NIEDERBOBRITZSCH GRANITE, ERZGEBIRGE, GERMANY: IMPLICATIONS FOR THE DIFFERENTIAL MOBILITY OF THE *LREE* AND Th DURING ALTERATION

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## ABSTRACT

A detailed survey of accessory minerals in the poorly to moderately differentiated F-poor biotite granites from Niederbobritzsch, Erzgebirge, Germany, reveals the presence of various, late magmatic to postmagmatic secondary rare-earth (*REE*) minerals, including cerite-(Ce), thorian synchysite-(Ce), synchysite-(Ce), and an unidentified Th-rich *REE* fluorocarbonate(?). Cerite-(Ce) is a *REE* silicate that, to date, has been found in only half a dozen occurrences worldwide. It had not previously been described from a granite. The composition of cerite-(Ce) from Niederbobritzsch is characterized by lower bulk *REE* contents but higher abundances of Si, Al, Ca, and F than that from other occurrences. Dissolution of thorian monazite-(Ce) during interaction with a F-, $CO_2$- and Ca-bearing fluid gave rise to the formation of thorian synchysite-(Ce) containing up to 18.1 wt% $ThO_2$. Previously reported contents of Th in synchysite-(Ce) did not exceed 1.6 wt% $ThO_2$. The spatial relations between the secondary *REE* minerals and their precursor attest to a differential mobility of the *LREE* and Th during fluid–rock interaction. Under the prevailing *PTX*-conditions, the *LREE* were more soluble and, thus, mobilized further away from their site of removal relative to Th, which tended to be reprecipitated next to its precursor. Virtually unchanged whole-rock *REE* budgets and continuous, unfractionated chondrite-normalized *LREE* patterns of the secondary *REE* minerals, however, imply that the lanthanides were transported over distances of millimeters or centimeters only.

*Keywords*: cerite-(Ce), synchysite-(Ce), rare-earth elements, thorium, accessory minerals, lanthanide tetrad effect, electron-microprobe analysis, biotite granite, Niederbobritzsch pluton, Erzgebirge, Germany.

## SOMMAIRE

Un examen détaillé des minéraux accessoires des granites à biotite faiblement ou modérément évolués et à faible teneur en fluor à Niederbobritzsch, Erzgebirge, en Allemagne, révèle la présence d'une variété de minéraux secondaires à terres rares tardimagmatiques ou bien postmagmatiques, par exemple cérite-(Ce), synchysite-(Ce) thorifère, synchysite-(Ce), et un fluorocarbonate(?) non identifié contenant Th et terres rares. La cérite-(Ce) est un silicate de terres rares signalé jusqu'ici à six endroits au monde, et dans des roches autres qu'un granite. Sa composition à Niederbobritzsch se distingue par une teneur plus faible en terres rares, et plus forte en Si, Al, Ca, et F. La dissolution de la monazite-(Ce) thorifère au cours d'une interaction avec une phase fluide contenant F, $CO_2$ et Ca a mené à la formation de la synchysite-(Ce) pouvant contenir jusqu'à 18.1% (poids) de $ThO_2$. On ne connaissait pas cette espèce avec plus de 1.6% de $ThO_2$. Les relations spatiales entre les minéraux secondaires à terres rares et leurs précurseurs témoignent d'une mobilité differentielle des terres rares légères et du thorium au cours de l'interaction de roche et $H_2O$. Dans les conditions ambiantes de température et de pression dans ce contexte, les terres rares légères étaient davantage solubles et, ainsi, ont été mobilisées sur une plus grande échelle que le thorium, qui a été reprécipité tout près de son précurseur. En revanche, le profil des terres rares des roches entières est resté inchangé. Les spectres continus et non évolués des terres rares légères dans ces minéraux secondaires, par rapport aux teneurs chondritiques, laissent supposer que les terres rares ont été transportées sur une échelle millimétrique ou tout au plus centimétrique.

(Traduit par la Rédaction)

*Mots-clés*: cérite-(Ce), synchysite-(Ce), terres rares, thorium, minéraux accessoires, effet de tétrade, analyse à la microsonde électronique, granite à biotite, pluton de Niederbobritzsch, Erzgebirge, Allemagne.

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## Introduction

Mass-balance calculations and direct observations have demonstrated that the major proportion of the rare-earth elements (*REE*, with the exception of Eu), as well as Y, Th, U, and other high-field-strength elements (Zr, Hf, Nb, Ta, W) in most crustal rocks is accommodated in accessory minerals (*e.g*., Bea 1996). Allanite, monazite and apatite constitute the primary hosts for the light rare-earth elements (*LREE*) in peraluminous granites of I- and S-type affinity (Jefferies 1985, Ward *et al*. 1992, Bea 1996, Förster 1998c). Allanite and thorite are the main contributors to the bulk-rock Th content of allanite-bearing, weakly peraluminous granites, whereas monazite accounts for most of the Th in strongly peraluminous granites, which characteristically lack allanite (*e.g*., Förster 1999).

In this fourth paper in a series on *REE*–Y–Th–U-rich accessory minerals in peraluminous granites, I report the occurrence and chemical composition, and discuss the genesis, of two rare secondary *LREE* minerals, cerite-(Ce) and thorian synchysite-(Ce), from the Niederbobritzsch granite, eastern Erzgebirge, Germany. I report the first electron-microprobe data on cerite-(Ce), which has not yet been observed in a granitic rock. Breakdown of Th-rich monazite-(Ce) resulted in the formation of thorian synchysite-(Ce), which shows the highest concentration of Th known to date for this mineral. Furthermore, the textural and paragenetic relations between the primary and secondary *REE* minerals allow conclusions on the differential mobility of the *REE* and Th during granite alteration. Moreover, the relative distance of migration of the lanthanides and Th between source mineral and site of reprecipitation can be estimated from their whole-rock budgets and the shape of chondrite-normalized *LREE* patterns of the secondary accessory minerals.

## Background Information

Magmatically crystallized accessory minerals display different stabilities during fluid-induced, pervasive late-magmatic to hydrothermal alteration that normally affect peraluminous granites. Whereas monazite is commonly relatively immune to hydrothermal decomposition, unaltered and non-metamict allanite and thorite are only rarely recorded in such granites. However, even monazite is locally reported to become severely altered and to have dissolved during albitization, sericitization, chloritization, or greisenization of granites, although the driving forces for that instability are not yet completely understood (Cathelineau 1987, Poitrasson *et al*. 1996, 2000).

Alteration of primary accessory minerals and subsequent remobilization and redeposition of the *LREE* in peraluminous granites may result in crystallization of newly formed allanite, monazite, apatite and thorite or other secondary minerals. The latter include phosphates (brockite), silicates (titanite, epidote), *LREE* fluorocarbonates (bastnäsite, synchysite, parisite), fluorides (fluocerite), oxides (cerianite) and, very rarely, oxyfluorides (*e.g*., Johan & Johan 1993).

The chemical composition of primary *REE*–Y–Th–U-rich accessory minerals in the Variscan granites from the German part of the Erzgebirge, including monazite (Förster 1998a), xenotime (Förster 1998b), thorite and zircon (Förster 1998c), and uraninite (Förster 1999), has been intensively studied. However, there is no adequate investigation of secondary *REE* minerals. The presence of compositional extremes such as cheralite-(Ce), monazite-(Ce) rich in the huttonite component, brabantite, xenotime extremely rich in heavy rare-earth elements (*HREE*), thorite with a significant concentration of U, Y, *HREE*, and Zr, *etc.*, among the magmatic accessory minerals gave rise to the expectation that their alteration minerals may also include phases of "atypical" composition.

The rhombohedral *LREE* silicate cerite-(Ce), ideally $(Ce,La,Nd,Ca)(Fe^{3+},Mg,Al)(SiO_4)_6(SiO_3OH)(OH,F)$ (*e.g.,* Moore & Shen 1983), is known from only about half a dozen occurrences worldwide. It was first described by J.J. Berzelius from the Bastnäs *REE* deposit in Sweden, and provided the source for the discovery of cerium (Hisinger & Berzelius 1804). Other occurrences comprise: Precambrian pegmatites near Jamestown, Colorado (Goddard & Glass 1936), *REE*-bearing hydrothermal veins from the Mountain Pass carbonatite, California (Glass *et al*. 1958), metasomatized metamorphic rocks from the Ural Mountains (Silberminz 1929; cited in Glass *et al*. 1958) and the Ukrainian Shield (Marchenko 1989) in Russia, a skarn deposit in the People's Republic of Korea (Marchenko 1989), syenite pegmatites in the Oslo region, Norway (Larsen 1996), carbonatites from the Kola Peninsula, Russia (Belolipetskii & Voloshin 1996), and metamorphosed carbonatites within the Central Metasedimentary Belt boundary zone in the Grenville Province, Ontario (Moecher *et al*. 1997).

Synchysite, theoretically $(Ce,La,Y,Nd,Ca,Th)(CO_3)_2F$, may be extremely variable with respect to predominant elements of the *REE* plus Y (Ce, Nd, or Y). Synchysite-(Ce) was first discovered in syenitic pegmatites from Narssarssuk, Greenland (Flink 1901). The Grebnik bauxite deposit in former Yugoslavia constitutes the first site from which synchysite-(Nd) was described (Maksimović & Pantó 1978). The first record of synchysite-(Y), formerly named "doverite", is from the Scrubs Oaks iron mine, New Jersey (Smith *et al*. 1955). Synchysite-group minerals are known from a variety of geological environments. They occur in (1) carbonatites and associated mineralization (Hogarth *et al*. 1985, Andersen 1986, Wall & Mariano 1996), (2) granitic rocks with related pegmatites and metasomatic rocks (Johan & Johan 1993), (3) hydrothermal ore deposits (Lottermoser 1995), (4) sedimentary rocks (Maksimović & Pantó 1978), (5) as fissure minerals in

Alpine metamorphic rocks (Huen & Gramaccioli 1969), and (6) even in dinosaur bones (Lozinski 1971). A more complete list of references to occurrences of synchysite is provided by Förster (in prep.).

## GEOLOGICAL CONTEXT

The Variscan Erzgebirge is situated in the border region between Germany (Saxony) and the Czech Republic, at the northwestern margin of the Bohemian Massif, which constitutes the largest area of exposure of Variscan metamorphic basement rocks in central Europe. It represents a NE–SW-trending antiformal structure in the Saxothuringian Zone of the Variscan orogen, which exposes crystalline rocks metamorphosed in the early Carboniferous (*e.g.*, Kröner & Willner 1998). In the late Carboniferous and early Permian, the Erzgebirge basement was invaded by rhyodacitic to rhyolitic lava flows and lamprophyric dikes and, volumetrically more importantly, by numerous granite plutons of various sizes and compositions (Fig. 1). These granites of late- and post-collisional structural position are sub-

divided into five major groups according to mineralogical, geochemical and isotopic criteria (Förster *et al.* 1998): low-F biotite granites, low-F two-mica granites, high-F, high-P Li-mica granites, high-F, low-P Li-mica granites, and moderate-F, low-P biotite granites. A great number of these granites have directly (tin and tungsten) or indirectly (uranium) contributed to the formation of extensive and highly varied metallic ore deposits, for which the Erzgebirge is famous among economic geologists (*e.g.*, Tischendorf & Förster 1994).

The Niederbobritzsch massif in the eastern Erzgebirge, Carboniferous in age according to Pb–Pb zircon evaporation dating (320 ± 6 Ma; Tichomirova 1997), belongs to the group of late-collisional low-F biotite monzogranites that possess transitional I- to S-type affiliation (Förster *et al.* 1999). It forms a multiphase pluton that consists of four mappable, texturally and compositionally distinct intrusive units genetically related by magma differentiation *via* fractional crystallization (*e.g.*, Rösler & Budzinski 1994). The samples that contain the *LREE* minerals discussed herein represent granites of the first and third stages of intrusion, respec-
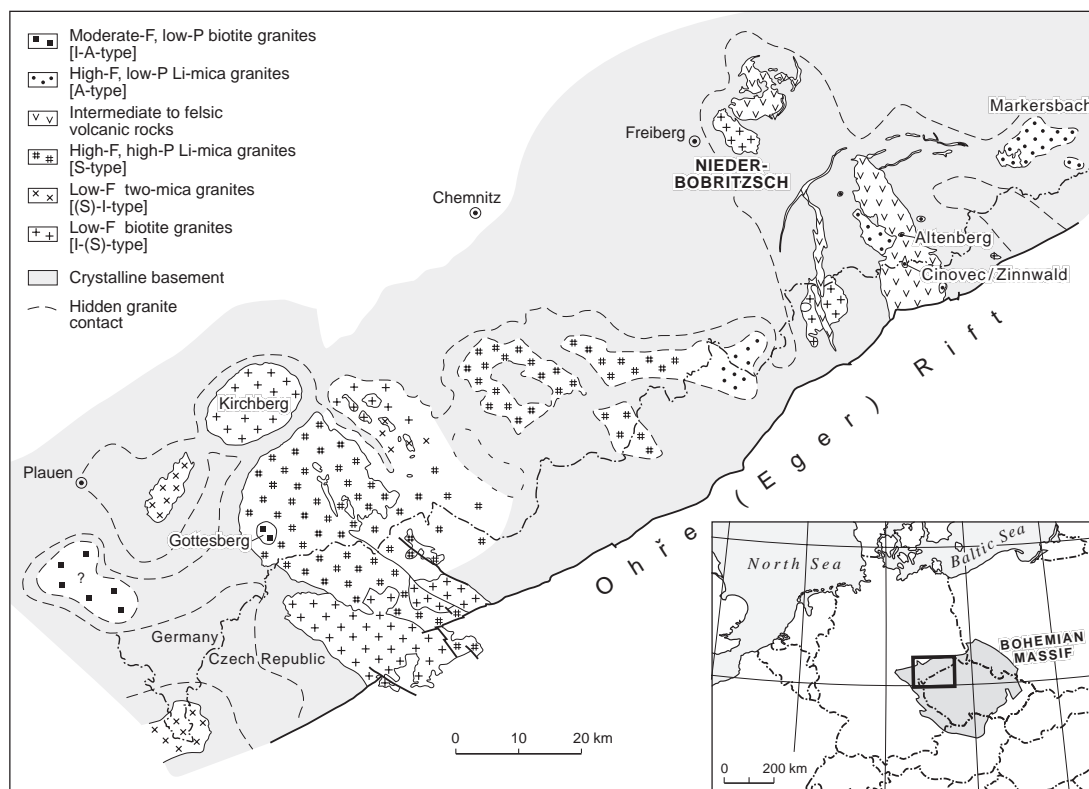


FIG. 1. Geological sketch-map showing the distribution of the various groups of Variscan granites in the Erzgebirge (slightly modified from Förster *et al.* 1999) and the positions of granites in which secondary fluorocarbonates or fluorides of the *REE* have been identified. See text for further explanations.

tively. Their compositions in terms of major and trace elements are given in Table 1.

### PETROGRAPHY AND MINERALOGY OF THE GRANITES

The cerite-(Ce)-bearing sample, TB–334–FT, is a medium- to coarse-grained, porphyritic granodiorite to monzogranite (hybrid granite), which characteristically hosts abundant fine- to medium-grained, dark enclaves of syenodioritic composition. These enclaves are interpreted to represent the unmelted granite protolith (Rösler & Budzinski 1994). Grains of synchysite-(Ce) are found in a more evolved unit, a fine- to medium-grained, equigranular monzogranite (TB–336–FT) almost devoid of enclaves.

The intrusive units of the Niederbobritzsch massif show correspondence in terms of major minerals (quartz, K-feldspar, plagioclase, albite, biotite), but differ strongly with respect to the occurrence and composition of primary accessory phases (Table 2). Allanite-(Ce) constitutes the principal host of the *LREE* in the hybrid granite, in which it typically forms large (up to 2 mm size), compositionally zoned, euhedral to subhedral solitary grains that are heavily altered and hydrated, and isotropic to weakly anisotropic (see also Rösler & Bothe 1990). Electron-microprobe analyses (Table 2, anal. 1) indicate moderately high concentra-

TABLE 1. MAJOR- AND TRACE-ELEMENT COMPOSITION OF GRANITES FROM THE NIEDERBOBRITZSCH MASSIF, GERMANY

| Sample No. Sub-intrusion No. | TB-334-FT 1 | TB-372-FT 2 | TB-336-FT 3 | TB-343-F aplite |
|---|---|---|---|---|
| $SiO_2$ (wt%) | 66.8 | 70.0 | 74.2 | 76.2 |
| $TiO_2$ | 0.59 | 0.36 | 0.25 | 0.12 |
| $Al_2O_3$ | 15.6 | 14.7 | 13.1 | 12.7 |
| $Fe_2O_3^a$ | 3.54 | 2.55 | 1.64 | 0.61 |
| MnO | 0.059 | 0.047 | 0.026 | 0.011 |
| MgO | 1.40 | 0.65 | 0.45 | 0.15 |
| CaO | 2.46 | 1.46 | 0.65 | 0.51 |
| $Na_2O$ | 3.80 | 3.86 | 3.22 | 3.28 |
| $K_2O$ | 4.39 | 4.82 | 5.07 | 5.17 |
| $P_2O_5$ | 0.23 | 0.21 | 0.11 | 0.03 |
| $H_2O$ | 0.93 | 0.91 | 0.99 | 0.93 |
| $CO_2$ | 0.09 | 0.08 | 0.13 | 0.13 |
| F | 0.079 | 0.085 | 0.043 | 0.025 |
| O=F | 0.033 | 0.036 | 0.018 | 0.011 |
| Total | 99.9 | 99.7 | 99.8 | 99.9 |
| Li (ppm) | 58 | 54 | 60 | 18 |
| Sc | 6.7 | 4.6 | 3.7 | 2.4 |
| V | 57 | 24 | 19 | <3 |
| Cr | 10.3 | 5 | 3.8 | <3 |
| Co | 6.4 | 1.9 | 1.4 | 0.36 |
| Zn | 69 | 37 | 38 | 13 |
| Ga | 21 | 25 | 18 | 15 |
| Rb | 167 | 262 | 257 | 258 |
| Sr | 390 | 196 | 87 | 45 |
| Y | 16 | 21 | 20 | 20 |
| Zr | 203 | 182 | 115 | 92 |
| Nb | 13 | 11 | 13 | 16 |
| Cs | 6.3 | 13.4 | 13.5 | 13.4 |
| Ba | 878 | 667 | 455 | 152 |
| La | 47 | 40 | 26 | 16 |
| Ce | 89 | 76 | 53 | 34 |
| Pr | 10.5 | 9.0 | 6.5 | 4.4 |
| Nd | 35 | 30 | 22 | 16 |
| Sm | 5.8 | 5.8 | 4.5 | 3.7 |
| Eu | 1.4 | 0.86 | 0.57 | 0.26 |
| Gd | 4.5 | 5.0 | 3.9 | 3.4 |
| Tb | 0.61 | 0.76 | 0.63 | 0.58 |
| Dy | 3.2 | 4.1 | 3.6 | 3.4 |
| Ho | 0.60 | 0.75 | 0.70 | 0.66 |
| Er | 1.6 | 2.1 | 2.0 | 2.1 |
| Tm | 0.24 | 0.31 | 0.33 | 0.35 |
| Yb | 1.5 | 2.1 | 2.1 | 2.4 |
| Lu | 0.24 | 0.34 | 0.33 | 0.38 |
| Hf | 6.1 | 6.0 | 4.2 | 3.9 |
| Ta | 1.0 | 2.6 | 2.6 | 3.1 |
| Pb | 21 | 37 | 38 | 41 |
| Th | 15 | 20 | 25 | 31 |
| U | 3.4 | 17 | 16 | 12 |
| A/CNK | 1.01 | 1.04 | 1.10 | 1.07 |
| Y/Ho | 27.2 | 28.0 | 27.9 | 30.2 |
| Zr/Hf | 33.1 | 30.5 | 27.3 | 23.4 |
| $La_N/Lu_N$ | 19.9 | 11.9 | 8.31 | 4.31 |
| Eu/Eu* | 0.778 | 0.471 | 0.398 | 0.217 |

[a] total iron as $Fe_2O_3$, A/CNK = molar $Al_2O_3/(CaO + Na_2O + K_2O)$.

TABLE 2. CHEMICAL COMPOSITION OF PRIMARY ACCESSORY MINERALS FROM NIEDERBOBRITZSCH, GERMANY

| Sample | TB-334-FT | | | | | | | | TB-336-FT | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Mineral | Aln | Thr | Thr | Zrn | Zrn | Mnz | Mnz | Xnt | Urn | Zrn | Zrn |
| Anal. No. | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 |
| $P_2O_5$ wt% | 0.05 | 0.50 | 0.68 | 0.00 | 0.12 | 25.1 | 29.9 | 34.2 | 0.00 | 0.85 | 0.00 |
| $SiO_2$ | 29.2 | 19.7 | 19.8 | 32.4 | 25.8 | 3.38 | 0.41 | 0.40 | 0.00 | 23.5 | 31.9 |
| $TiO_2$ | 2.92 | 0.05 | 1.53 | | | | | | | | |
| $ZrO_2$ | | 0.08 | 9.65 | 65.5 | 53.1 | | | | | 54.9 | 66.2 |
| $HfO_2$ | | | | 1.78 | 1.07 | | | | | 1.80 | 1.72 |
| $ThO_2$ | 1.55 | 61.5 | 52.6 | 0.00 | 2.05 | 15.4 | 12.4 | 0.27 | 6.07 | 0.18 | 0.02 |
| $UO_2$ | 0.05 | 8.02 | 1.43 | 0.16 | 0.80 | 0.57 | 0.97 | 2.29 | 86.3 | 1.52 | 0.15 |
| $Al_2O_3$ | 10.8 | 0.52 | 0.53 | 0.00 | 1.34 | 0.00 | 0.00 | 0.00 | 0.00 | 0.73 | 0.00 |
| $Sc_2O_3$ | | | | 0.00 | 0.07 | | | | | 0.14 | 0.01 |
| $Y_2O_3$ | 0.28 | 0.60 | 0.25 | 0.00 | 1.21 | 1.08 | 1.70 | 41.5 | 0.80 | 2.82 | 0.00 |
| $La_2O_3$ | 4.81 | 0.02 | 0.18 | | | 13.1 | 12.4 | 0.00 | | | |
| $Ce_2O_3$ | 10.4 | 0.06 | 1.25 | 0.00 | 0.83 | 26.1 | 24.5 | 0.12 | 0.04 | 0.11 | 0.00 |
| $Pr_2O_3$ | 1.06 | 0.00 | 0.26 | | | 2.58 | 2.56 | 0.05 | | | |
| $Nd_2O_3$ | 3.44 | 0.06 | 1.05 | 0.02 | 0.77 | 9.29 | 8.86 | 0.28 | 0.12 | 0.12 | 0.00 |
| $Sm_2O_3$ | 0.45 | 0.08 | 0.23 | 0.00 | 0.23 | 1.46 | 1.49 | 0.20 | 0.05 | 0.12 | 0.00 |
| $Gd_2O_3$ | 0.17 | 0.11 | 0.07 | 0.00 | 0.23 | 0.88 | 1.03 | 2.72 | 0.19 | 0.15 | 0.00 |
| $Tb_2O_3$ | | | | | | 0.09 | 0.13 | 0.56 | 0.09 | | |
| $Dy_2O_3$ | 0.06 | 0.12 | 0.04 | 0.00 | 0.18 | 0.14 | 0.47 | 4.09 | 0.12 | 0.30 | 0.07 |
| $Ho_2O_3$ | | | | | | 0.08 | 0.07 | 1.02 | | | |
| $Er_2O_3$ | | 0.09 | 0.00 | | | 0.08 | 0.18 | 4.07 | 0.19 | | |
| $Tm_2O_3^a$ | | | | | | | | 0.67 | | | |
| $Yb_2O_3$ | | 0.02 | 0.00 | 0.00 | 0.24 | 0.00 | 0.05 | 4.88 | 0.05 | 0.58 | 0.04 |
| $Lu_2O_3$ | | | | | | 0.00 | 0.00 | 0.74 | | | |
| CaO | 9.18 | 4.32 | 1.36 | 0.03 | 2.83 | 0.74 | 2.67 | 0.22 | 0.00 | | 0.00 |
| FeO | 12.9 | 0.16 | 2.76 | 0.00 | 2.27 | 0.00 | 0.00 | 0.00 | | 2.06 | 0.00 |
| MgO | 0.81 | | | | | | | | | | |
| MnO | 0.71 | | | | | | | | | | |
| PbO | 0.00 | 0.26 | 0.03 | 0.00 | 0.03 | 0.22 | 0.21 | 0.08 | 3.92 | 0.01 | 0.00 |
| F | 0.00 | 0.00 | 0.00 | | | | | | | | |
| Total | 88.8 | 96.2 | 93.7 | 99.9 | 93.2 | 100.2 | 100.0 | 98.4 | 97.9 | 89.8 | 100.2 |

blank: not analyzed, a: interpolated (straight line between nearest adjoining *REE*s).
Symbols: Aln allanite, Thr thorite, Zrn zircon, Mnz monazite, Xnt xenotime, Urn uraninite.

tions of Th and low contents of U, Y, and the *HREE*. Metamict thorite–coffinite (Table 2, anal. 2) and thorite–zircon (Table 2, anal. 3) solid solutions account for the major proportion of the bulk-rock Th and U contents. Zircon is commonly fresh and poor in the lanthanides and actinides (Table 2, anal. 4). However, metamictization locally gives rise to zircon compositions characterized by strongly enhanced levels of Y, Th, U, Al, Ca, Fe, and the *REE*, and a concurrent depletion in Zr and Si (Table 2, anal. 5). Other accessory minerals that crystallized from the granitic melt are apatite and magnetite. In contrast, pyrite, garnet, hornblende, titanite, and sillimanite, which occur in variable proportions throughout the granite, probably represent minerals from the metamorphosed protolith that were incorporated into the granitic melt as result of resorption of the mafic enclaves (Rösler & Budzinski 1994).

In the less Ca-rich sample TB–336–FT, allanite-(Ce) is absent, and monazite-(Ce) both rich in the huttonite (Table 2, anal. 6) and brabantite components (Table 2, anal. 7) are the principal hosts of the *LREE* and Th. The presence of U-rich xenotime-(Y) (Table 2, anal. 8) and Th-rich uraninite (Table 2, anal. 9) is an indication of the more evolved nature of the granite. Grains of metamict zircon enriched in U, Y, and the *HREE* (Table 2, anal. 10) become increasingly more important in modal abundance relative to grains of unaltered zircon (Table 2, anal. 11). Xenocrystic accessory minerals from the granite protolith are subordinate in abundance compared to sample TB–334–FT.

Despite the presence of altered allanite, thorite, and zircon grains, the biotite granites generally belong to the least intensively overprinted granites among the five groups of Variscan Erzgebirge granites. With respect to the major minerals, late-magmatic and postmagmatic effects in the Niederbobritzsch granite are minor, and confined to partial replacement of pre-existing phases (chlorite ± titanite ± epidote ± rutile in biotite, albite ± white mica ± clinozoisite ± fluorite ± carbonate in plagioclase).

### ANALYTICAL CONDITIONS

Mineral compositions were obtained using a CAMEBAX SX–50 electron microprobe, employing a PAP correction procedure (Pouchou & Pichoir 1985). The operating conditions were: accelerating potential 20 kV, beam current 40–60 nA (measured on the Faraday cup), and beam diameter 3 $\mu$m. The counting times on the peak are 300 s for Pb and 200 s for Th and U, and in each case, half that time for background counts on both sides of the peak. For the *REE* and other elements, counting times were 60 s and 40 s on the peak, respectively.

X-ray lines and background offsets were selected to minimize interferences and their correction (Exley 1980, Roeder 1985). Wavelength-dispersion spectral scans done on complex natural *REE* phosphates (monazite and xenotime) were used to determine the peak and background positions of each element and to identify overlapping peaks. $K\alpha$ lines were used for P, Si, Fe, Ca, and F, $L\alpha$ lines for Y, La, Ce, Yb and Lu, and $L\beta$ lines for Pr, Nd, Sm, Gd, Tb, Dy, Ho and Er. Problems due to interferences of Th$M\beta$ with U$M\alpha$, and of Y$L\alpha$ with Pb$M\alpha$, were eliminated by using the Th$M\alpha$, U$M\beta$ and Pb$M\beta$ lines. Minor interferences of Th$M\gamma$ with U$M\beta$ were corrected using the procedure of Åmli & Griffin (1975). The concentration of F was calculated by empirical correction for the major interference of Ce$L\alpha$ with F$K\alpha$. The following analyzing crystals were used: LIF for the *REE* and Fe, TAP for Si, Al and Y, PET for P, Th, U, Ca and Pb, and PC1 for F.

Primary standards included pure metals for Th and U, vanadinite and a synthetic glass (0.79 wt% PbO) for Pb, synthetic phosphates prepared by Jarosewich & Boatner (1991) for the *REE*, and natural minerals and synthetic oxides for other elements. Accuracy of the calibration was checked routinely using synthetic ThO$_2$ and UO$_{2.15}$, synthetic glass SRM 610, which contains some hundred ppm of Th, U, and Pb, and the *REE* glasses prepared by Drake & Weill (1972). Reproducibility of the stated compositions in the SRM 610 glass was better than 15%, that in the *REE* glasses, better than 5–10%. A further check on calibration was made for reproduction of the stoichiometry and composition of an in-house monazite standard analyzed in various laboratories.

The analytical errors (precision) for the *REE* depend on the absolute abundance of each element. Relative errors are estimated to be <1% at the >10 wt% level, 5–10% at the 1 wt% level, 10–20% at the 0.2 to 1 wt% level, and 20–40% at the <0.1 wt% level. The analytical uncertainties for the actinides and for lead are more uniform and amount to about 10%, even for concentrations below 0.1 wt%. Detection limits were approximately 200–300 ppm for all elements monitored, except lead (≈ 100 ppm).

A variety of analytical techniques were used to obtain high-precision whole-rock geochemical data (*e.g.*, Förster *et al*. 1999). The concentrations of the major elements, V, and Cr were established by wavelength-dispersion X-ray-fluorescence spectrometry. Analysis for fluorine was performed using ion-selective electrodes. The amount of total water and CO$_2$ were determined by combustion – infrared detection. Concentrations of the rare-earth elements plus Rb, Sr, Y, Zr, Cs, Ba, Hf, Pb, Th, and U were established by inductively coupled plasma – mass spectrometry (ICP–MS; Perkin–Elmer/Sciex Elan Model 500 ICP – mass spectrometer). Analysis for Li, Sc, Co, Zn, Ga, Nb, and Ta was also performed by ICP–MS (Fisons/VG Plasma Quad PQ 2+). The concentration of Be was determined by inductively coupled plasma atomic emission spectrometry on a Varian Liberty 200 ICP – emission spectrometer.

RESULTS

*Petrographic description of the REE minerals*

Owing to their small grain-size and surface deterioration by the electron beam, the *REE* minerals do not show up well in optical and back-scattered electron (BSE) images. Therefore, it is preferable to describe the minerals and their textural relationships in the text rather than to show them in microphotographs.

*Cerite-*(*Ce*) fills a small euhedral fracture in albite, about 50 µm in length and 5–15 µm in width. An *unidentified REE mineral* occurs as two tiny, bright (in the BSE image) elongate grains within a patchily zoned, strongly hydrothermally altered euhedral crystal of allanite, which also contains inclusions of thorite too small to be analyzed (1–3 µm across). It is located along the internal growth-zones of the host allanite. *Th-poor synchysite-*(*Ce*) is hosted in biotite and constitutes an anhedral grain of about 50 µm in length and 20 µm in width, which shows an amoeboid texture and evidence of considerable corrosion. It contains many vacuoles that are irregular in shape and typically less than 5 µm long. They likely represent more soluble areas within the mineral, and are not the result of plucking during thin-section preparation. *Thorian synchysite-*(*Ce*) displays the same texture as the Th-poor synchysite-(Ce). Textural relationships indicate that thorian synchysite-(Ce) forms the breakdown product of thorian monazite-(Ce), with which it is intimately intergrown.

*Chemical composition of the REE minerals*

*Cerite-*(*Ce*) in sample TB–334–F is strongly enriched in the *LREE* and contains Y and the *HREE* in concentrations below their detection limits (Table 3, analyses 1–3). The sum of the oxides of La, Ce, Pr, Nd, Sm, and Gd in cerite-(Ce) ranges from 60.3 to 63.4 wt%. Chondrite-normalized *REE* patterns of cerite-(Ce) are steep and free of anomalies (Fig. 2a). Cerite-(Ce) contains between 22.5 and 23.1 wt% $SiO_2$, appreciable contents of Ca (6.9–8.2 wt% CaO) and Al (2.4–3.4 wt% $Al_2O_3$), and minor amounts of Fe (0.1–0.6 wt% FeO). Fluorine is invariably present in concentrations ranging from 1.3 to 2.5 wt%. Analytical totals between 94.6 and 96.8 wt% suggest the presence of some wt% $H_2O$. Ti, Th, U, Mg, Mn, and Pb were sought but not found.

The *unidentified REE mineral* in allanite is F-bearing (3.4 wt%) and contains 55 wt. % $LREE_2O_3$ (Table 3, anal. 4). It is distinguished by high concentrations of Ca (8.2 wt% CaO) and, particularly, Th approaching 16.3 wt% $ThO_2$. P, Si, Ti, U, Al, and Fe occur in concentrations of less than 1 wt%.

*Thorian synchysite-*(*Ce*) associated with monazite (Table 3, anal. 4–8) in sample TB–336–FT contains between 4.8 and 18.1 wt% $ThO_2$. Thorium occupies up to 11.5 at.% of the cations (the minimum content of cerium amounts to 14 at.%), which justifies use of the name thorian synchysite-(Ce) according to the recommendations of the IMA. The *LREE* are present in concentrations between 28.9 and 45.4 wt% $LREE_2O_3$. The concentrations of Y plus *HREE* vary between 2.0 and 5.7 wt% of the oxides. The *LREE:HREE* ratio is high (8–15). Ca constitutes the dominant divalent cation (16.8–18.3 wt% CaO). Fluorine concentration ranges from 4.9 to 6.4 wt%. Systematically detected elements, which occur in concentrations less than 1 wt%, comprise P, Si, U, and Al.

The amount of thorium is positively correlated with that of Si (correlation coefficient $R = 0.930$), Ca
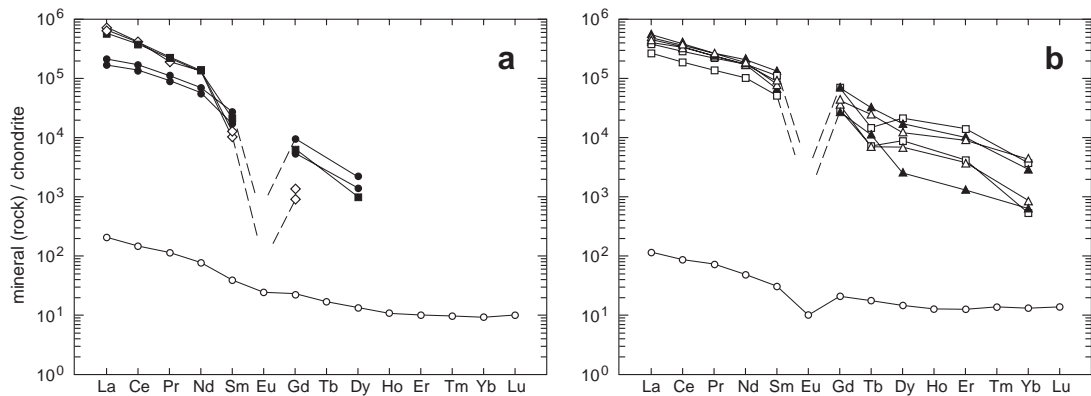


Concentration ranges of REE in: ◇ cerite-(Ce), □ thorian synchysite-(Ce), △ synchysite-(Ce), ● allanite-(Ce), ▲ monazite-(Ce). ■ unidentified REE mineral; ○ whole-rock.

FIG. 2.    Chondrite-normalized *REE* patterns of primary and secondary *REE* minerals in granite samples FT–334–FT (a) and FT–336–F (b) from Niederbobritzsch. Chondrite data were taken from Anders & Grevesse (1989).

TABLE 3. CHEMICAL COMPOSITION OF SECONDARY *REE* MINERALS FROM NIEDERBOBRITZSCH, GERMANY

| Sample | TB–334–FT | | | | TB–336–FT | | | | | | | | | | | |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Mineral | cerite-(Ce) | | | unident. | thorian synchysite-(Ce) | | | | | | | | synchysite-(Ce) | | | |
| Anal. No. | 1 | 2 | 3 | 4 | 5 | 5a | 6 | 6a | 7 | 7a | 8 | 8a | 9 | 9a | 10 | 10a |
| P$_2$O$_5$ (wt%) | 0.01 | 0.00 | 0.02 | 0.21 | 0.06 | *0.1* | 0.24 | *0.5* | 0.28 | *0.7* | 0.25 | *0.6* | 0.05 | *0.1* | 0.00 | |
| SiO$_2$ | 23.0 | 22.9 | 22.5 | 1.37 | 0.42 | *1.0* | 0.48 | *1.2* | 0.82 | *2.3* | 0.95 | *2.6* | | | | |
| TiO$_2$ | 0.00 | 0.00 | 0.00 | 0.86 | | | | | | | | | | | | |
| ThO$_2$ | 0.00 | 0.00 | 0.00 | 16.3 | 4.76 | *2.7* | 12.0 | *7.1* | 17.9 | *11.5* | 18.1 | *11.2* | 0.79 | *0.5* | 0.00 | |
| UO$_2$ | 0.00 | 0.00 | 0.00 | 0.3 | 0.02 | | 0.13 | *0.1* | 0.24 | *0.1* | 0.21 | *0.1* | 0.00 | | 0.03 | |
| Al$_2$O$_3$ | 2.75 | 2.98 | 2.40 | 0.6 | 0.22 | *0.7* | 0.29 | *0.9* | 0.16 | *0.5* | 0.15 | *0.5* | | | | |
| Y$_2$O$_3$ | 0.00 | 0.00 | 0.00 | 0.03 | 3.25 | *4.3* | 1.91 | *2.6* | 1.11 | *1.7* | 1.10 | *1.6* | 2.04 | *2.7* | 1.13 | *1.5* |
| La$_2$O$_3$ | 21.0 | 21.6 | 22.4 | 16.9 | 10.6 | *9.7* | 9.57 | *9.1* | 7.72 | *8.0* | 7.66 | *7.7* | 12.5 | *11.6* | 13.1 | *12.3* |
| Ce$_2$O$_3$ | 31.0 | 30.2 | 31.6 | 27.9 | 21.5 | *19.5* | 18.2 | *17.2* | 14.1 | *14.5* | 14.1 | *14.0* | 24.5 | *22.6* | 24.7 | *23.1* |
| Pr$_2$O$_3$ | 2.26 | 2.05 | 2.33 | 2.42 | 2.34 | *2.1* | 1.97 | *1.9* | 1.69 | *1.7* | 1.55 | *1.5* | 2.49 | *2.3* | 2.71 | *2.5* |
| Nd$_2$O$_3$ | 6.87 | 6.96 | 6.96 | 7.27 | 9.13 | *8.1* | 7.65 | *7.1* | 5.93 | *6.0* | 5.87 | *5.7* | 9.67 | *8.7* | 9.53 | *8.7* |
| Sm$_2$O$_3$ | 0.22 | 0.23 | 0.18 | 0.36 | 1.88 | *1.6* | 1.36 | *1.2* | 0.87 | *0.8* | 0.95 | *0.9* | 1.54 | *1.3* | 1.52 | *1.3* |
| Gd$_2$O$_3$ | 0.02 | 0.03 | 0.03 | 0.15 | 1.48 | *1.2* | 0.91 | *0.8* | 0.70 | *0.7* | 0.65 | *0.6* | 1.05 | *0.9* | 0.84 | *0.7* |
| Tb$_2$O$_3$ | 0.00 | 0.00 | 0.00 | 0.00 | 0.04 | | 0.05 | | 0.03 | | 0.04 | | 0.05 | | 0.04 | |
| Dy$_2$O$_3$ | 0.00 | 0.00 | 0.00 | 0.03 | 0.58 | *0.5* | 0.24 | *0.2* | 0.25 | *0.1* | 0.09 | *0.1* | 0.32 | *0.3* | 0.26 | *0.2* |
| Ho$_2$O$_3$ | 0.00 | 0.00 | 0.00 | 0.03 | | | 0.00 | | 0.00 | | 0.00 | | 0.03 | | 0.00 | |
| Er$_2$O$_3$ | 0.00 | 0.00 | 0.00 | 0.00 | 0.23 | *0.2* | 0.08 | *0.1* | 0.07 | *0.1* | 0.09 | *0.1* | 0.16 | *0.1* | 0.07 | *0.1* |
| Yb$_2$O$_3$ | 0.00 | 0.00 | 0.00 | 0.00 | 0.07 | *0.1* | 0.02 | | 0.01 | | 0.02 | | 0.08 | *0.1* | 0.02 | |
| Lu$_2$O$_3$ | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | | 0.00 | | 0.00 | | 0.00 | | 0.00 | | 0.00 | |
| CaO | 7.78 | 7.65 | 6.91 | 8.23 | 18.2 | *48.2* | 18.0 | *50.0* | 16.9 | *51.1* | 19.0 | *52.7* | 18.1 | *48.9* | 18.1 | *49.5* |
| FeO | 0.28 | 0.63 | 0.14 | 1.38 | | | | | | | | | | | | |
| MgO | 0.00 | 0.00 | 0.00 | | | | | | | | | | | | | |
| MnO | 0.00 | 0.00 | 0.00 | | | | | | | | | | | | | |
| PbO | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | | 0.01 | | 0.04 | | 0.07 | *0.1* | 0.00 | | 0.00 | |
| F | 1.45 | 1.29 | 2.47 | 3.39 | 5.62 | | 5.46 | | 5.81 | | 5.53 | | 5.31 | | 4.66 | |
| Total | 96.0 | 96.1 | 96.8 | 86.2 | 78.0 | | 76.3 | | 72.2 | | 73.1 | | 76.4 | | 74.6 | |

blank: not analyzed. The proportion of cations (in atom percent) is given in italics in columns 5a, 6a, 7a, *etc.*

($R = 0.878$), and P ($R = 0.971$), and shows negative correlations with the *LREE* ($R = –0.980$), Y plus *HREE* ($R = –0.971$), and Y plus *REE* ($R = –0.988$). These correlations preclude a substitution of Th for the lanthanides according to the common mechanism, $Th^{4+} + Si^{4+} \leftrightarrow REE^{3+} + P^{5+}$ (huttonite substitution) and argue instead for the other mechanism $Th^{4+} + Ca^{2+} \leftrightarrow 2\ REE^{3+}$ (brabantite substitution). Charge balance can also be maintained by the reactions $Th^{4+} + P^{5+} \leftrightarrow 3\ REE^{3+}$ and $2\ Th^{4+} + Si^{4+} \leftrightarrow 4\ REE^{3+}$.

*Synchysite-(Ce)* is poor in Th (0–0.8 wt% ThO$_2$) and contains between 49.5 and 53.2 wt% *LREE*$_2$O$_3$, and between 2.3 and 3.7 wt% (Y$_2$O$_3$ + *HREE*$_2$O$_3$) (Table 3, anal. 9–10). The *LREE:HREE* ratio is higher (14–22) than in the Th-rich variety of the mineral. Other components, in addition to Ca (17.9–19.8 wt% CaO) and F (3.3–5.3 wt%), are present in subordinate quantities. In all analyses of synchysite, the ratio of Ca *versus* the other detected cations (in atom %) is close to 1:1, as predicted from its ideal stoichiometry (see Table 3).

## DISCUSSION

### Occurrence of secondary REE minerals in the Erzgebirge granites

The presence of cerite-(Ce) and synchysite-(Ce) in the granite from Niederbobritzsch supports the idea that secondary *REE* minerals are more widespread in the Variscan Erzgebirge granites than previously considered, and that a careful search in other granites of the region is warranted. Moreover, abundance of secondary *REE*-bearing phases demonstrates that, in part of the granites, primary accessory phases such as monazite and xenotime became unstable during fluid–rock interaction and underwent decomposition, with remobilization of the lanthanides and actinides into newly formed alteration minerals.

In addition to Niederbobritzsch, fluorocarbonates and fluorides of the *REE* were recently noted from the following granites in the Erzgebirge (see Fig. 1):

bastnäsite-(Ce) as an alteration product of allanite-(Ce) in the Kirchberg granite (Förster *et al*. 1998), fluocerite-(Ce) and bastnäsite-(Ce) in fluorite from the Altenberg granite (Förster *et al.* 1987), bastnäsite-(Ce), synchysite-(Ce), and synchysite-(Y) in the granites from Cinovec/ Zinnwald (Johan & Johan 1993, Förster, in prep.), synchysite-(Ce) in microgranites from Gottesberg (Förster 1999), synchysite-(Ce) – synchysite-(Y) solid solutions in the Markersbach granite (Förster, in prep.). Moreover, the extremely rare *REE* arsenate chernovite-(Y) presently was discovered in the granites from Altenberg (unpubl. data of the author) and Zinnwald (Kempe *et al*. 1999, unpubl. data of the author).

### Overall chemical composition of cerite-(Ce) and synchysite-(Ce)

Present knowledge on the compositional variability of cerite-(Ce) is limited and confronted with serious analytical difficulties. Its compositions were previously determined by wet-chemical analysis or spectrographic methods on impure samples consisting of two ore more complexly intergrown and finely disseminated mineral phases (*e.g*., Goddard & Glass 1940, Hanson & Pearce 1940, Moore & Shen 1983). From these analytical results, chemical compositions of cerite-(Ce) were obtained by subtraction of impurities and recalculation to 100%. Thus the mineral from Niederbobritzsch probably is the first grain of cerite-(Ce) analyzed by electron microprobe.

Compared to previous compositions of cerite-(Ce) (given in parentheses) compiled by Glass *et al.* (1958) and given by Marchenko (1989), the mineral from Niederbobritzsch (see Table 3) is slightly poorer in *REE* (*ca*. 65–71 wt% $REE_2O_3$), but richer in Ca (3.0–5.8% CaO), Al (0.3–1.3% $Al_2O_3$) and F (0.9–1.7%). With respect to the concentration of $SiO_2$, it is at the high end of the known range of compositions (17.2–22.8 wt%).

Although synchysite-(Ce) has been described from several occurrences, compositional data for that mineral, surprisingly, are uncommon and incomplete. Complete electron-microprobe analyses of synchysite-(Ce) are almost non-existent (*e.g*., Ngwenya 1994). Identification of that mineral is commonly based on optical, physical, and crystallographic properties or on semiquantitative chemical analyses. The vast majority of previously examined examples of synchysite-(Ce) contain Th in concentrations below 1 wt%. To my knowledge, the highest Th content known to date (1.6 wt% $ThO_2$) was determined in a synchysite-(Ce) grain in a calcite carbonatite from Tundulu, Malawi (Ngwenya 1994).

Chemically, the unidentified *REE* mineral in allanite-(Ce) does not resemble any known mineral. An analytical total of 86 wt% suggests that it is probably a fluorocarbonate or a F-bearing hydroxide. Because it is likely that the chemical data given in Table 3 refer to a fine-scale intergrowth or mixture of more than one min-

eral (see below) rather than a single mineral species, this material will not be discussed further in this paper. However, it appears worth tabulating the compositional data, for the sake of future studies.

In defining compositional ranges of the minerals studied, one has to make sure that the measured concentrations refer to components of the structure and not to analytical artefacts. The degree to which potential analytical problems might have influenced the compositional data presented herein will be discussed in the following section.

### Potential analytical problems

Small grain-size, narrow zones of homogeneous composition, and a great number of holes [particularly in the synchysite-(Ce) grains] pose a series of potential problems to the electron-microprobe analyst. These textural features only allowed a maximum beam-size of 3 μm. A more defocused beam, however, would be required to minimize decomposition of the minerals, which was a problem particularly for the synchysite-(Ce) minerals and cerite-(Ce). Mineral degradation is one potential reason for the low totals and high apparent $H_2O$ concentration in cerite-(Ce) compared to its theoretical composition. Furthermore, differential volatility of elements under the electron beam may have caused slight disturbances in the relative proportions among the elements. The petrographic features described pose another problem in that elements from adjacent minerals may have been in the excitation volume of the electron beam. This circumstance can potentially lead to compositions that represent a mixture of two (or more) phases. External compositional influences from the neighboring major silicates also may account for the Si and Al contents measured in thorian synchysite-(Ce). High contents of Si, Ti, Al, and Fe in the "unidentified" *REE* mineral in allanite-(Ce) are likely analytical artefacts from the host mineral. Also, part of the Ca and the *REE* may relate to the allanite host. Finally, although the homogeneity of the phases studied was routinely checked by thorough BSE imaging, the presence of mineral inclusions on the submicrometer scale cannot be totally excluded. Contamination by a small percentage of a *REE* fluorocarbonate (? synchysite) also could explain the slightly higher contents of Ca and F, the lower contents of the *REE* and the lower analytical total in the cerite-(Ce) relative to results of wet-chemical analyses for this mineral. Intimate admixtures of *REE*-bearing phases (bastnäsite, allanite, monazite, törnebohmite) and other minerals (fluorite, quartz) with cerite-(Ce) are almost universal (*e.g*., Goddard & Glass 1940, Hanson & Pearce 1940, Glass *et al*. 1958, Marchenko 1989). All previously described examples of cerite-(Ce) are fine-grained intergrowths or aggregates of several minerals, and pure samples for chemical analyses have not yet been isolated. A better understanding of compositional variations in this *LREE*

silicate mineral must await additional electron-microprobe work involving grains of larger size within a matrix that minimizes potential analytical problems.

*Conditions of mineral formation*

Textural relationships suggest that both cerite-(Ce), synchysite-(Ce), and the unidentified *REE* phase are secondary minerals and of postmagmatic origin.

The F-rich nature and the high content of Ca in *cerite-(Ce)* in sample TB–334–F imply that the mineral crystallized from a F⁻- and Ca$^{2+}$-bearing aqueous solution under conditions of low activity of $CO_3^{2-}$. Given the apparent lack of $CaF_2$ in the vicinity of the *REE* mineral, the concentrations of F and Ca, however, were apparently below the saturation levels for fluorite. The presence of fluorine in the fluid may be attributed to the replacement of biotite by chlorite. The absence of other primary or secondary *REE* minerals in the neighborhood of cerite-(Ce) limits identification of the sources of the *LREE*. Nevertheless, the *LREE* and Ca in cerite-(Ce) may be liberated either during alteration of allanite-(Ce) (*e.g.*, Table 2, anal. 1) or breakdown of earlier-formed *LREE*-fluorocarbonates. The albitization of plagioclase may have further contributed to the Ca budget of the fluid. If allanite is considered as the source of the *LREE* and Ca, which may also explain the Al enrichment in cerite-(Ce), strong fractionation of the *LREE* and *HREE* during alteration must have occurred, as implied by the contrasting *REE* patterns of both minerals (Fig. 2a). Late-stage thorite (*e.g.,* Table 3, anal. 2) and zircon (Table 3, anal. 5) constitute potential hosts of the *HREE*, Y, and Th released during alteration of allanite-(Ce) but not fixed in cerite-(Ce) because of its affinity to the *LREE*.

The crystallization sequence of cerite-(Ce) and the secondary *REE* fluorocarbonate(?) in allanite cannot be established from paragenetic relationships. However, the occurrence of cerite-(Ce) as a fracture-controlled mineral may suggest that it postdates the formation of the other phase. In this situation, unknown fluorocarbonates [? synchysite-(Ce)] with *LREE* abundances similar to the *REE* phase in allanite (Fig. 2a) would be another favorable precursor mineral for cerite-(Ce).

Formation of the *unidentified Th-rich REE fluorocarbonate*(?) is undoubtedly related to the destabilization of allanite-(Ce) during interaction with a fluid phase, which added F and $CO_2$ and removed the *LREE*, Th, and probably also Ca from the allanite structure. Relative to the abundances in the precursor allanite, the newly formed alteration mineral has concentrated the *LREE*, whereas the original *HREE* concentrations remained nearly unchanged (see Fig. 2a). This hypothesis suggests that the *LREE* were mobilized more effectively than the *HREE*.

The intimate association of *thorian synchysite-(Ce)* with thorian monazite-(Ce) supports the proposal that the former is a replacement product of the latter. During interaction of a F–$CO_2$–Ca-bearing fluid, the Th-rich monazite-(Ce) grain was completely dissolved, and the mobilized elements were trapped in thorian synchysite-(Ce) immediately at the site of their release. Strong similarities in the Th concentration and the *REE* patterns (Fig. 2b) between the primary and secondary *REE* minerals suggest alteration under nearly closed-system conditions, as also does the presence of Si and P in thorian synchysite-(Ce). Additional phosphorus, not incorporated into the structure of thorian synchysite-(Ce), is likely consumed in the formation of secondary apatite, which is observed in the vicinity of the alteration assemblage.

*Th-poor synchysite-(Ce)* is not associated with any potential precursor mineral. It may have originated from breakdown of Th-poor monazite which, however, is rare in the granite. Incomplete dissolution of Th-rich monazite, resulting in preferential loss of the *LREE* to a F–$CO_2$–Ca-bearing solution, is another plausible mechanism that may account for the Th-poor secondary *REE* mineral.

The crystallization of synchysite-(Ce), Ca-rich cerite-(Ce), and the unidentified Ca-bearing *REE* mineral suggests that the fluids from which they precipitated were enriched in Ca$^{2+}$. Depletion of Ca from the parent fluid would have resulted in the formation of parisite and, finally, bastnäsite, which are poorer in Ca but apparently absent at Niederbobritzsch. The formation of fluorocarbonates and F-bearing cerite-(Ce) also attests to an overall F-rich composition of the solutions. Thermodynamic calculations have demonstrated that fluoride or mixed carbonate–fluoride complexes can dominate *REE* speciation (*e.g.*, Wood 1990a, b). The scarcity of the secondary F-bearing *REE* minerals in the Niederbobritzsch granites, however, implies that a high concentration of fluorine was probably achieved only locally (close to zones of chloritization of biotite) and is not necessarily a component of the composite fluid percolating through the granitic rock. The occurrence of *REE* fluorocarbonates in the F-poor Niederbobritzsch and Kirchberg biotite granites indicates that their formation was not restricted to F-rich granites, such as those from Altenberg, Zinnwald, Markersbach, and Gottesberg in the Erzgebirge.

*Mobility of the REE and Th during fluid–rock interaction*

The occurrence of secondary *REE* minerals in the Niederbobritzsch granite is consistent with evidence indicating that the *REE* and Th can be mobile during alteration of granitic rocks (*e.g.*, Exley 1980, Cathelineau 1987, Ward *et al*. 1992, Irber 1999). The apparent close spatial association of thorian synchysite-(Ce) with its source phase, thorian monazite-(Ce), however, suggests that Th was less mobile than the *LREE*, which may be transported away over longer distances. The limited solubility of Th relative to the *LREE* is apparently

not a special feature of the Niederbobritzsch granite and is more the rule, in general, given the widespread occurrence of secondary thorite in altered allanite (*e.g.*, Littlejohn 1981, Buda & Nagy 1995) and thorite inclusions in altered zircon (Rubin *et al.* 1989). Insignificant mobility of Th also is demonstrated by the presence, in the same monazite crystal, of altered parts richer in Th than unaltered parts, indicating that the newly formed monazite can effectively take up Th removed during fluid–rock interaction (Poitrasson *et al.* 1996). Although Th-rich monazite generally appears to be more stable than Th-poor monazite, it also may be the subject of dissolution, as demonstrated in this paper.

The chondrite-normalized *REE* patterns of the Niederbobritzsch granites, which contain the secondary *LREE* minerals, are regular (see Fig. 2). Furthermore, no visible disturbances (enrichment or depletion) in the bulk-rock *REE*, Y, and Th budgets could be recognized (see Table 1). Consequently, these elements were not mobilized over distances exceeding several decimeters or meters, but likely over distances of a few millimeters or centimeters only (less than the size of the samples crushed for bulk-rock analysis). This is in agreement with previous observations indicating that the whole-rock abundances of the *REE* (except of Eu), Y, and Th in metaluminous and peraluminous I- and S-type granitic rocks are barely affected, even under the conditions of strong, fluid-induced alteration (*e.g.*, Ball *et al.* 1985, Ward *et al.* 1992, Poitrasson *et al.* 1996). Mobilization and transport of the *LREE* over only a few μm during alteration of britholite-(Ce) and redeposition into bastnäsite-(Ce) also have been recognized in volcanic rocks from the Vico volcanic center, Latium, Italy (Della Ventura *et al.* 1999).

Similarities among the secondary *REE* phases and their precursor minerals with respect to the shape of chondrite-normalized *LREE* patterns and the absence of any discontinuities at La and Nd may also suggest that the *LREE* in the granites studied did not migrate over great distances. It is commonly expected that an aqueous fluid that mobilizes the rare earths from a parent mineral will initially display *REE* patterns similar to those of the source, as will a secondary mineral precipitated from that fluid. However, with increasing distance from the source, the *REE* in the fluid will progressively fractionate, primarily because the solubilities of the lanthanide species are unlikely to all be the same. Fractionated *REE* patterns are attributed to chemical complexation in aqueous fluids rich in potential ligands such as F and $CO_2$ (Bau 1996). Irregular, curved *REE* patterns known as the lanthanide tetrad effect (see Masuda & Agaki 1989) are not observed in the secondary *LREE* minerals from Niederbobritzsch.

## Final Remarks

The chemical data for the secondary *REE* minerals from Niederbobritzsch offer new insight into their over-all compositional variability. The relatively high concentrations of Al in cerite-(Ce) may indicate solid solution toward törnebohmite, ideally $REE_2Al(OH)[SiO_4]_2$ (Shen & Moore 1982). Enrichment of fluorine is compatible with suggestions of Moore & Shen (1983) on the occurrence of an F-analogue of cerite-(Ce). The demonstrated ability of synchysite-(Ce) to incorporate high concentrations of Th supports the suggestion that in the case of an even higher activity of Th in the fluid, a fluorocarbonate of the composition synchysite-(Th) may potentially be formed. Within the bastnäsite-group minerals, the existence of thorian bastnäsite as a replacement product of ferrian thorite has already been documented (Pavlenko *et al.* 1965).

Synchysite has been demonstrated previously to represent a breakdown product of allanite (Littlejohn 1981) and apatite (Hogarth *et al.* 1985). However, the occurrence of thorian synchysite-(Ce) in the Niederbobritzsch granite implies that synchysite also can be formed as a replacement mineral of monazite. Alteration of monazite into parisite, $REE_2Ca(CO_3)_3F_2$, and secondary apatite is known from the granites of Xihuashan, China (Maruéjol *et al.* 1990). Replacement of monazite by bastnäsite has been described in "amazonite"-bearing granitic pegmatites of the Kola Peninsula, Russia (Belolipetskii & Voloshin 1996).

Although well demonstrated in laboratory experiments (*e.g.*, Litvina *et al.* 1996, Yaita & Tachimori 1996), the significance of the lanthanide tetrad effect in geochemistry is not universally accepted (*e.g.*, McLennan 1994, Pan 1997). Therefore, it remains questionable whether the mere absence of a tetrad effect necessarily indicates the absence of significant *REE* transport. The lanthanide tetrad effect is a characteristic feature of many Erzgebirge granite intrusions (*e.g.,* Cocherie *et al.* 1991, Bau 1996, Irber 1999, Förster *et al.* 1999), but these are more highly evolved, richer in fluorine, and more intensively altered than the granite from Niederbobritzsch. In these more highly evolved rocks, fractionated *REE* patterns are confined to late-crystallized primary and secondary accessory minerals, including monazite (Förster 1998a), xenotime (Förster 1998b), and thorite (Förster 1998c).

Finally, the lack of significant transport of the *REE*, Y, and Th indicates that these elements can be used with some confidence in modeling the magmatic evolution of the Niederbobritzsch granite and probably many compositionally similar igneous rocks elsewhere.

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