

THE ORIGIN AND ZONING OF HYPOGENE AND SUPERGENE Fe–Mn–Mg–Sc–U–REE PHOSPHATE MINERALIZATION FROM THE NEWLY DISCOVERED TRUTZHOFFMÜHLE APLITE, HAGENDORF PEGMATITE PROVINCE, GERMANY

HARALD G. DILL[§] AND FRANK MELCHER

Federal Institute for Geosciences and Natural Resources, P.O. Box 510163, D-30631 Hannover, Germany

AXEL GERDES

*Frankfurt University, Institute of Geosciences, Petrology and Geochemistry, Altenhöferallee 1,
D-60438 Frankfurt am Main, Germany*

BERTHOLD WEBER

Bürgermeister-Knorr Str. 8, D-92637 Weiden i.d.OPf., Germany

ABSTRACT

An apelite containing Fe–Mn–Mg–Sc–U–REE phosphates, some Cu–Pb–Zn sulfides, barite, and U–Nb–Ta–Ti–Fe–Mn oxides was recently discovered near Trutzhofmühle (THM) at the western border of the Hagendorf Pegmatite Province, Germany. We describe the sequence of phosphate crystallization in six stages of mineralization (I to VI) covering the time span from the Late Carboniferous through the Recent supergene alteration, and six sequences (1a/1b to 5) reflecting the reaction of phosphate-bearing solutions with the gneissic country-rocks (exo-aplitic) and with intra-aplitic rock-forming minerals that formed during crystallization. Age dating was carried out on columbite-(Fe) and torbernite using laser-ablation techniques. Precipitation of columbite-(Fe) and early magmatic phosphates (Mn-rich apatite, monazite) in the THM apelite is correlated with a thermal event around 302 Ma postdating the intrusion of the post-kinematic Flossenbürg granite. The sequences 1a and 1b, containing the lazulite solid-solution series, gordonite and childrenite–eosphorite series, reflect late magmatic and early hydrothermal exo-aplitic processes. The late magmatic and early hydrothermal stages of the intra-aplitic sequences 2 to 5 are characterized by triplite, wolfeite, triploidite, an unnamed K–Ba–Sc–Zr phosphate, an unnamed Zr–Sc phosphate–silicate, phosphoferrite, Mn-rich vivianite, and lermontovite–vyacheslavite (?). Complexing agents such as fluorine and phosphate control the formation of Sc phosphates and silicates. In contrast with the neighboring Hagendorf pegmatite, the magmatic and hydrothermal phosphate mineralization of the THM apelite does not contain any Li-bearing phosphates and is very low in F. Rockbridgeite, whitmoreite, “ferrolaueite”, Al-bearing rockbridgeite, mitridatite, “metamitridatite”, kolbeckite and strunzite appear during late hydrothermal processes and weathering. Kolbeckite formed at the transition from hypogene to supergene processes. Its morphology varies from a rather simple combination of faces (platy kolbeckite I) under hydrothermal conditions to complex mineral aggregates (stubby kolbeckite II) produced under weathering conditions. The latest supergene alteration consists of wavellite, beraunite, cacoxenite, strengite, P- and Mn-bearing “limonite”, autunite, Sc-bearing vochtenite, Sc-bearing churchite-(Y) and diadochite. The latter phosphates with predominantly Fe, Al and U in close association with kaolinite are the representatives of supergene alteration, which is related in time and space to the Miocene penneplanation between 4.8 and 6.9 Ma. The boron- and phosphate-bearing THM apelite is not directly linked to any of the granitic plutons nearby, and is not easily classified within the scheme of rare-element pegmatites.

Keywords: apelite, Permo-Carboniferous, Fe–Mn–Mg–Sc–U–REE phosphates, columbite-(Fe), U–Pb radiometric dating, laser ablation, Trutzhofmühle, Hagendorf Pegmatitic Province, Germany.

SOMMAIRE

Une venue aplitique contenant des phosphates de Fe–Mn–Mg–Sc–U–REE, des sulfures de Cu–Pb–Zn, barite, et des oxydes de U–Nb–Ta–Ti–Fe–Mn a récemment été découverte près de Trutzhofmühle (THM), à la limite occidentale de la province pegmatitique de Hagendorf, en Allemagne. Nous subdivisons la séquence de cristallisation des phosphates en six stades (I à VI) développés sur l'intervalle du Carbonifère tardif jusqu'à l'altération supergène Récente, et en six séquences (1a/1b à 5) pour souligner les réactions des solutions phosphatées avec l'encaissant gneissique (associations exo-aplitiques) et avec les miné-

[§] E-mail address: harald.dill@bgr.de

raux primaires formés dans l'aplite même. Nous avons daté la columbite-(Fe) et la torbernite avec une technique d'ablation au laser. La cristallisation de la columbite-(Fe) et des phosphates primaires (apatite manganifère, monazite) dans l'aplite THM est contemporaine d'un événement thermique à environ 302 Ma suivant la mise en place du granite post-kinématique de Flossenbürg. Les séquences 1a et 1b, contenant les solutions solides lazulite et childrenite-éosphorite et la gordonite, sont développées aux stades tardi-magmatique et hydrothermal précoce dans un milieu exo-aplitique. Les mêmes stades au sein de l'aplite ont donné les séquences 2 à 5, contenant triplite, wolfeite, triploïdite, un phosphate de K-Ba-Sc-Zr sans nom, un phosphate-silicate de Zr-Sc sans nom, phosphoferrite, vivianite manganifère, et lemontovite-vyacheslavite (?). Les complexes contenant le fluor et le phosphate ont régi la formation des phosphates et des silicates de Sc. Contrairement au cas de la pegmatite de Hagendorf voisine, les assemblages magmatiques et hydrothermaux dans l'aplite THM ne contiennent pas de phosphates porteurs de Li, ni enrichis en F. Rockbridgeite, whitmoreite, "ferrolauéite", rockbridgeite riche en Al, mitridatite, "métamitridatite", kolbeckite et strunzite apparaissent lors des processus hydrothermaux tardifs et de la météorisation. La kolbeckite s'est formée au passage des processus hypogènes aux processus supergènes. Sa morphologie varie d'une combinaison plutôt simple de faces (kolbeckite I, en plaquettes), formée en conditions hydrothermales, à des agrégats complexes (kolbeckite II, trappue), formée en milieu de météorisation. Les altérations les plus tardives ont produit wavellite, béraunite, cacoenite, strengite, "limonite" porteuse de P et de Mn, autunite, vochtenite et churchite-(Y) scandifères, et diadochite. Ces derniers phosphates, avec une prédominance de Fe, Al et U, étroitement associés à la kaolinite, sont représentatifs de l'altération supergène, qui est liée dans le temps et l'espace à la pénélration au Miocène entre 4.8 et 6.9 Ma. La venue d'aplite THM, enrichie en bore et en phosphate, ne semble pas apparentée à aucun des plutons granitiques dans la région, et n'est pas facilement classifiée dans le schéma proposé pour les pegmatites à éléments rares.

(Traduit par la Rédaction)

Mots-clés: aplite, Permo-Carbonifère, phosphates de Fe-Mn-Mg-Sc-U-REE, columbite-(Fe), datation radiométrique U-Pb, ablation au laser, Trutzhofmühle, province pegmatitique de Hagendorf, Allemagne.

INTRODUCTION

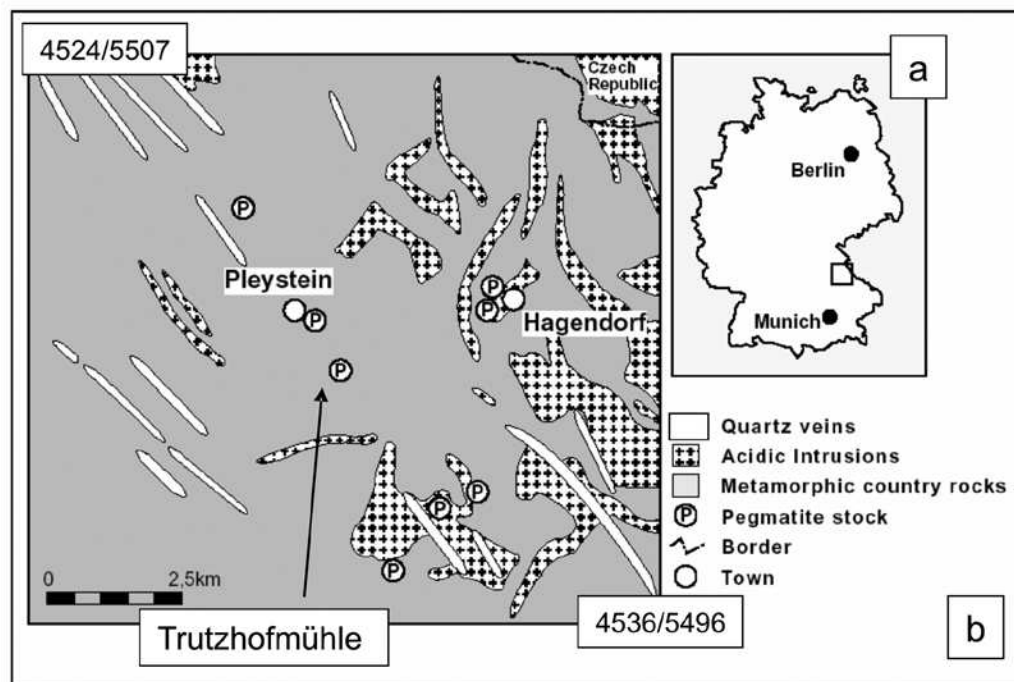
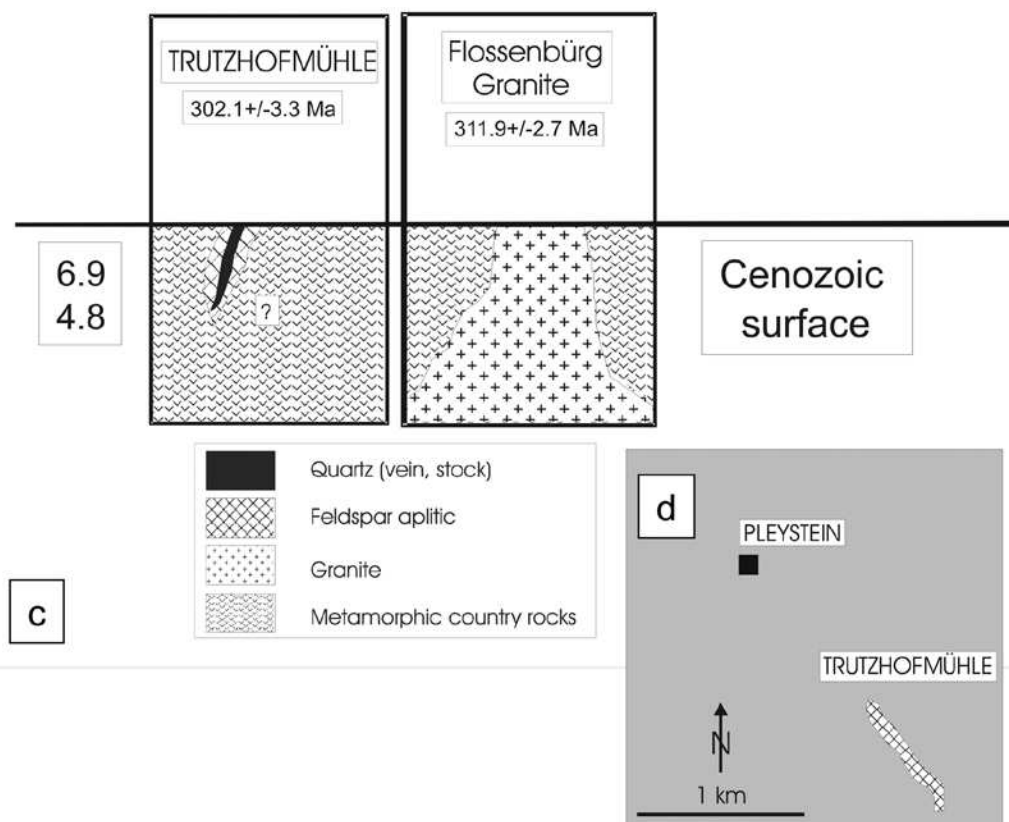
Phosphate minerals in granitic pegmatites are of interest to the economic geologist, especially where they are enriched in Li, U, Sc and the rare-earth elements (REE). An aplite hosting a suite of Fe-Mn-Mg-Sc-U-REE phosphates has been discovered recently near Trutzhofmühle, at the western border of the Hagendorf Pegmatite Province, Germany, renowned for its mineral wealth. We discuss the origin of its complex phosphate mineralization in a wider context with the neighboring pegmatite bodies and correlate these findings with the entire geological history of the Bohemian Massif from the Late Variscan to the Recent. Emphasis is placed on U/Pb age dating of columbite and uranyl phosphates to constrain the age of formation and of alteration of the phosphates within the aplite body.

GEOLOGICAL SETTING

The study area, which is part of the northeastern Bavarian Basement, is mainly underlain by Moldanubian paragneisses composed of variable amounts of biotite, sillimanite, cordierite, quartz, garnet and feldspar (Forster 1965) (Figs. 1a, b). Structural adjustments of the Moldanubian crystalline rocks in the Oberpfalz are constrained to the period 450 to 330 Ma (Weber & Vollbrecht 1989). Late Carboniferous felsic intrusive rocks are second in order of abundance, the most important of which is the Flossenbürg granite (Fig. 1b), which has been dated by the Rb/Sr whole-rock method at 311.9 ± 2.7 Ma (Wendt *et al.* 1994). The K-Ar ages of muscovite and biotite, 300 and 292 Ma, respectively,

record the cooling history of the granite. The fine- to medium-grained Flossenbürg granite, petrographically classified as a monzogranite, is located mainly in the center and at the eastern edge of the study area, near the Czech-German border (Fig. 1b). Toward the west, several dikes of aplite and pegmatite were exposed by denudation. The pegmatites of Hagendorf North and South and the quartz pegmatite near Pleystein are the best-known and carry abundant Li, Fe, Mn and Zn phosphates (Forster *et al.* 1967, Forster & Kummer 1974, Wilk 1967, Uebel 1975, Mücke 1981, 1987, 2000). The felsic intrusive bodies are surrounded by swarms of quartz veins (Fig. 1b). The Trutzhofmühle (THM) aplite dike strikes NW-SE subparallel to a swarm of quartz veins (Figs. 1b, c). The THM aplite carries black tourmaline (schorl-dravite) in a matrix of albite-oligoclase ($<An_{25}$), K-feldspar, quartz and muscovite (Table 1). Dodecahedra of garnet with a spessartine-grossular

FIG. 1. Position and geological setting of the Trutzhofmühle aplite. a) Position of the study area in Germany. b) Regional geology in the area around Pleystein-Hagendorf, northeastern Bavaria, Germany (modified after Forster 1965). c, d) Position and orientation of the Trutzhofmühle aplite in relation to the neighboring Flossenbürg granite. Ages for the intrusion of the THM Aplite and Flossenbürg granite obtained from radiometric dating are given in boxes. The Cenozoic erosion surface and peneplain capping the THM aplite and Flossenbürg granite around 6.9 to 4.8 Ma is marked with a horizontal line in the center of the boxes. The various sections are not to scale.



core zone and pyrope–almandine rim are abundant in the THM aplite. The country rocks of the THM aplite may be subdivided into two different groups, the flaser biotite and cordierite–sillimanite gneisses, and the calc-silicate series with labradorite–amphibole calc-silicate fels, diopside – plagioclase – zoisite – calc-silicate fels and garnet – zoisite – clinozoisite – calc-silicate fels (Fig. 2). A low-relief landscape of Tertiary age developed on the northeastern Bavarian basement analogous to the landforms still developing in the present-day savannah in central Africa under subtropical climates (Louis 1984).

METHODS

Examination of thin sections was supplemented by XRD analysis using a Philips PW 3710 with Cu radiation, a fixed primary slit system, and a secondary monochromator, and by X-ray-fluorescence analysis of powdered samples by means of a PANalytical Axios and a PW 2400 spectrometer. Electron-microprobe analyses were carried out using a CAMECA SX100 equipped with five wavelength-dispersive spectrometers and a Princeton Gamma Tech energy-dispersive system. Oxide, phosphate and silicate phases were analyzed at an acceleration voltage of 20 kV and a sample current (on brass) of 20 nA. The minerals albite, chromite, kaersutite, almandine, apatite, magnetite, pentlandite, biotite, rutile, rhodonite and galena and pure metals were used as standards.

Columbite-group minerals and torbernite were analyzed *in situ* in polished thick sections for U, Th and Pb isotopes by a laser-ablation – inductive coupled plasma – mass spectrometry (LA–ICP–MS) technique using a Thermo-Scientific Element II sector-field ICP–MS coupled to a New Wave UP213 ultraviolet laser system at Johann Wolfgang Goethe University in Frankfurt (JWGU) (Gerdes & Zeh 2006, 2008). Laser spot-sizes varied from 12 to 30 μm for torbernite and 20

to 80 μm in the case of columbite. Data were acquired in peak-jumping mode over 800 mass scans during 20 s measurement of background followed by a 30-s ablation of the sample. A teardrop-shaped, low-volume laser cell was used to enable sequential sampling of heterogeneous grains (*e.g.*, growth zones) during time-resolved acquisition of data (*cf.* Janousek *et al.* 2006). The signal was tuned for maximum sensitivity for Pb and U while keeping oxide production monitored as $^{254}\text{UO}/^{238}\text{U}$ well below 1%. Raw data were corrected offline for background signal, common Pb based on the interference- and background-corrected ^{204}Pb signal, laser-induced elemental fractionation, instrumental mass-discrimination, and time-dependent elemental fractionation of Pb/U. The interference of ^{204}Hg (mean = 97 ± 17 cps, counts per second) on the mass 204 was estimated using a $^{204}\text{Hg}/^{202}\text{Hg}$ of 0.2299 and the measured ^{202}Hg . In about one third of the analyses, the interference- and background-corrected ^{204}Pb was below the estimated limit of detection (~ 10 cps). In general, the $^{206}\text{Pb}/^{204}\text{Pb}$ was greater than 4000, a level where the common Pb correction has a negligible effect on the $^{206}\text{Pb}/^{238}\text{U}$ age. Zircon crystals GJ–1 (Jackson *et al.* 2004) and Plešovice (Sláma *et al.* 2008) were used for external standardization. Previous studies have shown the possibility to use non-matrix-matched standardization for LA–ICP–MS U–Pb dating (*e.g.*, Meier *et al.* 2006, Horstwood *et al.* 2003, Frei *et al.* 2008, Melcher *et al.* 2008).

Late Proterozoic monazite dated by the same method as used in this study yielded concordant results; the $^{207}\text{Pb}/^{206}\text{Pb}$ and the $^{206}\text{Pb}/^{238}\text{U}$ ages agreed to better than 1% (Meier *et al.* 2006). This indicates, in accordance with our concordant results on torbernite, a negligible difference in the U–Pb fraction between phosphates and zircon after correction of the time-dependent element fractionation. In the present study, the latter was rather low owing to the low density of energy (< 0.5 J/cm ^{2}) and repetition rate (5 Hz) used. The $^{206}\text{Pb}/^{238}\text{U}$

TABLE 1. WHOLE-ROCK CHEMICAL COMPOSITIONS OF PORTIONS OF THE TRUTZHOFFMÜHLE APLITE

SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	B	Nb	Ta	Ba	Ce	Co	Sc	Th	U	Li	Nb/Ta
Marginal zone of the THM aplite bearing tourmaline and garnet																				
77.81	0.03	13.01	0.76	0.03	0.17	0.36	3.38	2.90	0.60	1348	9	5	28	23	3	6	3	3	3	1.93
Feldspar zone of the THM aplite																				
74.24	0.04	13.85	1.04	0.25	0.11	0.97	1.60	4.40	1.52	90	18	5	31	30	3	87	3	23	14	3.60
Quartz zone of the THM aplite																				
95.83	0.02	1.57	0.85	0.00	0.01	0.03	0.03	1.15	0.03	39	4	5	120	27	3	1	3	3	2	0.80

Compositions are reported in wt.% and ppm. Fluorine contents are less than 0.5 wt.%, whereas Cl contents are below 0.01 wt.%.

Stage	Stage I		Stage II	Stage III	Stage IV			Stage V	Stage VI
Sequence	Early magmatic		Late magmatic	Early hydrothermal	Late hydrothermal			Early weathering (with hiatuses marked by pronounced "limonitization")	Late weathering
Physico-chemical Conditions "Iron color stratigraphy"	Eh<0 T: 400 to 500 °C < 3 kbar		Eh<0 T medium {1} 475_°C /3.8_kbar reducing	Eh ≤ 0 ("Blue - green Fe facies") T medium to low < 200 °C hydration reducing pH > 5	Eh ≤ 0 ≤ Eh ("Green - purple Fe facies") T low dependant on the alkalinity of the solution reducing to slightly oxidizing pH > 5			Eh> 0.4 mV ("Yellow - brown Fe facies") T low oxidizing pH < 5	Eh>>0.4 mV ("Brown - red Fe facies") T low oxidizing pH ≤ 4
Country rocks	GARNET-ZOISITE CALCSILICATE FELS LABRADORITE-AMPHIBOLE CALCSILICATE FELS DIOPSIDE-PLAGIOCLASE-ZOISITE CALCSILICATE FELS								
1a Mg-Al-P (exo-aplitic)			Lazulite s.s.s.	Gordonite					Wavellite
2 Ca-Fe-Mn-P (intra-aplitic)	Uraninite Ferrocolumbite Barite	Mn-rich Apatite	Triplite Wolfeite Tripliodite	Phosphoferrite Mn-rich Vivianite Metavivianite	Rockbridgeite- frondelite Whitmoreite "Ferrolaueite" "Al- Rockbridgeite"	Strengite	Fe >>Ca	Strunzite P-, Mn-bearing "limonite"	Beraunite Caoxenite P-,Mn-bearing "limonite" Kaolinite
3 Ba-Sc-Zr-P (intra-aplitic)		Zr-Sc - phosphate- silicate (unnamed)	K- Sc-Zr-Ba phosphate (unnamed) Zr-Sc-phosphate- silicate (unnamed)		Mitridatite > "Metamitridatite"		Ca>> Fe		
4 U-REE-P (intra-aplitic)		Nd-Sm Monazite		Lermontovite- vyacheslavite (?)	Kolbeckite I			Kolbeckite II	Autunite Sc-bearing vochtenite (?) Sc-bearing Churchite-(Y) Torbernite
5 S-Zn-P (intra-aplitic)				Chalcopyrite Pyrite Sphalerite	Keckite I			Keckite II	
1b Fe-Al-P (exo-aplitic)				Childrenite s.s.s.					
Country rocks	BIOTITE GNEISS								

FIG. 2. Zonation (sequences 1 to 5) and evolution (stages I to VI) of phosphate mineralization of the THM apelite. Line 1 : stage I through stage VI. Line 2 : mineralizing processes (from early magmatic to weathering). Line 3: physicochemical conditions described in terms of temperature (T), pressure, redox conditions (Eh), fluid composition (pH and composition). Color facies refers to the various Fe phosphates in each stage. Line 4: country rocks and wallrocks (calc-silicate rocks). Line 5: exo-aplitic phosphate mineralization of sequence 1a. Lines 6 to 9: intra-aplitic phosphate mineralization of sequences 2 to 5. Line 10: exo-aplitic phosphate mineralization of sequence 1b. Line 11: country rocks and wallrocks (gneisses).

increases during the ablation by about 10% in case of zircon GJ-1 (60 μm spot) and <16% in case of the torbernite. Thus the difference between corrected and the uncorrected ratio is relatively small. Reported uncertainties (2σ) were propagated by quadratic addition of the external reproducibility (2 s.d.) obtained from the reference zircon ($n = 12$) during the analytical session and the within-run precision of each analyses (2 s.e.). Concordia diagrams (2σ error ellipses) and concordia ages with two-sigma uncertainty were produced using Isoplot/Ex 2.49 (Ludwig 2001). For further details on analytical protocol and data processing, see Gerdes & Zeh (2006, 2008).

RESULTS

The phosphate contents of the THM aplite

The highest phosphate contents were analyzed in the feldspar zone of the THM aplite (Table 1). Electron-microprobe analyses of rock-forming minerals from this zone yielded the following mean values: muscovite (0.07 wt.% P_2O_5), albite (0.25 wt.% P_2O_5), K-feldspar (0.70 wt.% P_2O_5). Not surprisingly, the alkali feldspars are most strongly enriched in P (London 1992). The low phosphate contents determined in the quartz zone may be accounted for by sporadic phosphate minerals

disseminated in the quartz matrix (Table 1). Almandine–spessartine in the tourmaline and garnet zones of the THM aplite show a rather homogeneous distribution of P (up to 0.25 wt.% P_2O_5), with a weak tendency to decrease toward the rim (Fig. 3).

The phosphates of the THM aplite are dealt with in detail in the succeeding paragraphs and are listed in Table 2.

The Ca–Mg–(Al) phosphates

Fluorine- and chlorine-free apatite-(CaOH) occurs as anhedral grains developing into radiating aggregates of slender prisms, which amalgamate to globular crusts lining the walls of druses and vugs in the THM aplite. The apatite has an Mn content in the range 2.4–3.4 wt.% MnO (Table 3, Figs. 4a, b). Manganese-rich apatite is not uncommon in granitic pegmatites (Cruft 1966, Keller & von Knorring 1989, Pieczka 2007). Aggregates of deep blue lazulite occur in contact with apatite near the edge of the dike (Table 3). Another phosphate closely resembling lazulite with respect to its bluish tint, yet free of Fe, turned out to be gordonite, as documented by XRD.

Mn²⁺–Fe²⁺ phosphates

Wolfeite, the major representative of Fe–Mn phosphates in the aplite dike, replaces apatite (Table 3, Fig. 4c). During phosphate mineralization, the Fe/Mn value gradually decreases, and the triploidite (Mn) component becomes more prominent. The rare presence of triplite, the fluorine-bearing end member, was also determined by means of XRD.

Hydrated Fe²⁺–Mn²⁺ phosphates

The wolfeite–triploidite solid-solution series and Mn-rich apatite are both replaced by Mn-rich vivianite via phosphoferrite (Table 3, Fig. 4d). This hydration is observed even under the petrographic microscope or on a macroscopic scale by the stepwise change in color, from dark brown into bluish tints.

Hydrated Mn²⁺–Fe²⁺–Fe³⁺ phosphates

Minerals of the rockbridgeite–frondelite solid-solution series are the most widespread phosphate minerals in the aplite (Fig. 5a). They mostly appear as colloform crusts and fill interstices among aggregates of mitridatite (Table 3, Fig. 4f). Rarely, they occur in aggregates between plates of muscovite. Apart from Fe-rich rockbridgeite described by Roberts *et al.* (1974), there are rhythmites that reveal a gradual change from Fe-rich rockbridgeite through Al-bearing rockbridgeite into hydrated Al-bearing rockbridgeite varieties (Fig. 6). In the latter zone, obviously a mixture with other strongly

TABLE 2. PHOSPHATE MINERALS MENTIONED IN THE TEXT, THEIR CHEMICAL FORMULA, AND THE SEQUENCE AND STAGE AT WHICH THEY APPEARED*

Apatite (Mn-bearing)	(Ca,Mn) ₅ (PO ₄ CO ₃) ₃ (F,Cl,OH)	2	I
Autunite	Ca(VO ₄) ₂ (PO ₄) ₂ ·10–12H ₂ O	3–4	VI
Beraunite	Fe ²⁺ (Fe ³⁺) ₂ (PO ₄) ₂ (OH) ₂ ·4H ₂ O	2	VI
Cacoxenite	Al(Fe ³⁺) ₂ (PO ₄) ₂ (OH) ₂ ·75H ₂ O	2	VI
Chilidrenite s.s.	(Fe ²⁺ ,Mn)AlPO ₄ (OH) ₂ ·H ₂ O	1b	III–IV
Churchite-(Y)	(Y,Er)PO ₄ ·2H ₂ O	3–4	VI
Diadochite	(Fe ²⁺) ₂ (PO ₄) ₂ (SO ₄)(OH)·6H ₂ O	5	VI
"Ferrolaueite"	Fe ²⁺ Fe ³⁺ 2(PO ₄)2(OH)2·8(H ₂ O)	2	IV
Frondelite	(Mn,Fe ²⁺)(Fe ³⁺) ₂ (PO ₄) ₂ (OH) ₂	2	IV
Gordonite	MgAl ₂ (PO ₄) ₂ (OH) ₂ ·8H ₂ O	1a	III–IV
Kekchite	Ca(Mn,Zn) ₂ (Fe ³⁺) ₂ (PO ₄) ₂ (OH) ₂ ·2H ₂ O	5	IV–V
Kolbeckite	ScPO ₄ ·2H ₂ O	3	IV–V
Lauite	Mn ²⁺ (Fe ³⁺) ₂ (PO ₄) ₂ (OH) ₂ ·8H ₂ O	2	IV
Lazulite s.s.	(Mg,Fe)Al ₂ (PO ₄) ₂ (OH) ₂	1a	II
Lermontovite ?	U ⁴⁺ (PO ₄) ₂ (OH) ₂ ·H ₂ O	4	III
"Metamitridatite"	(Fe ²⁺ ,Fe ³⁺) ₂ (PO ₄) ₂ ·8H ₂ O	2	IV
Metavivianite	Ca ₂ (Fe ³⁺) ₂ (PO ₄) ₂ O ₂ ·3H ₂ O	2	IV
Mitridatite	CePO ₄	4	I
Monazite-(Ce)	(Fe ²⁺ ,Mn)(Fe ³⁺) ₂ (PO ₄) ₂ ·3H ₂ O	2	III
Phosphoferrite	(Fe ²⁺ ,Mn)Fe ³⁺ (PO ₄) ₂ (OH) ₂	2	IV
Rockbridgeite	(Fe ²⁺ ,Mn)(Al,Fe ³⁺) ₂ (PO ₄) ₂ (OH) ₂	2	IV
"Rockbridgeite-(Al)"	Fe ²⁺ PO ₄ ·2H ₂ O	2	IV
Strengite	Mn ²⁺ (Fe ³⁺) ₂ (PO ₄) ₂ (OH) ₂ ·6H ₂ O	2	VI
Strunzite	Cu ²⁺ (VO ₄) ₂ (PO ₄) ₂ ·8–12(H ₂ O)	3–4	VI
Torbernite	(Mn ²⁺ ,Fe ²⁺ ,Mg,Ca) ₂ (PO ₄) ₂ (F,OH)	2	II
Triplite	(Mn ²⁺ ,Fe ²⁺) ₂ (PO ₄) ₂ (OH)	2	II
Triploidite	(Fe ²⁺ ,Mn) ₂ (PO ₄) ₂ (OH)	2	II
Vivianite (Mn-bearing)	(Fe ²⁺ ,Mn) ₂ (PO ₄) ₂ ·8H ₂ O	2	III
Vochtenite ?	(Fe ²⁺ ,Mn)Fe ³⁺ [(VO ₄)(PO ₄) ₂](OH) ₂ ·12–13(H ₂ O)	3–4	VI
Vyacheslavite ?	U ⁴⁺ (PO ₄) ₂ (OH) ₂ ·nH ₂ O	4	III
Wavellite	Al ₂ (PO ₄) ₂ (OH,F) ₂ ·5H ₂ O	1a	VI
Whitmoreite	Fe ²⁺ Fe ³⁺ 2(PO ₄) ₂ (OH) ₂ ·4H ₂ O	2	IV
Wolfeite	(Fe ²⁺ ,Mn) ₂ (PO ₄) ₂ (OH)	2	II
K-Ba-Sr-Zr phosphate	(K,Ba)(Sc,Zr) ₂ (PO ₄) ₂	3	II
Zr-Sc phosphate-silicate	ZrSc(SiO ₄)(PO ₄) ₂ ·H ₂ O	3	I–II

* Sequences and stages correspond to the subdivision of mineralization in Figure 2. Species shown in quotation marks are not IMA-approved. s.s.: solid-solution series.

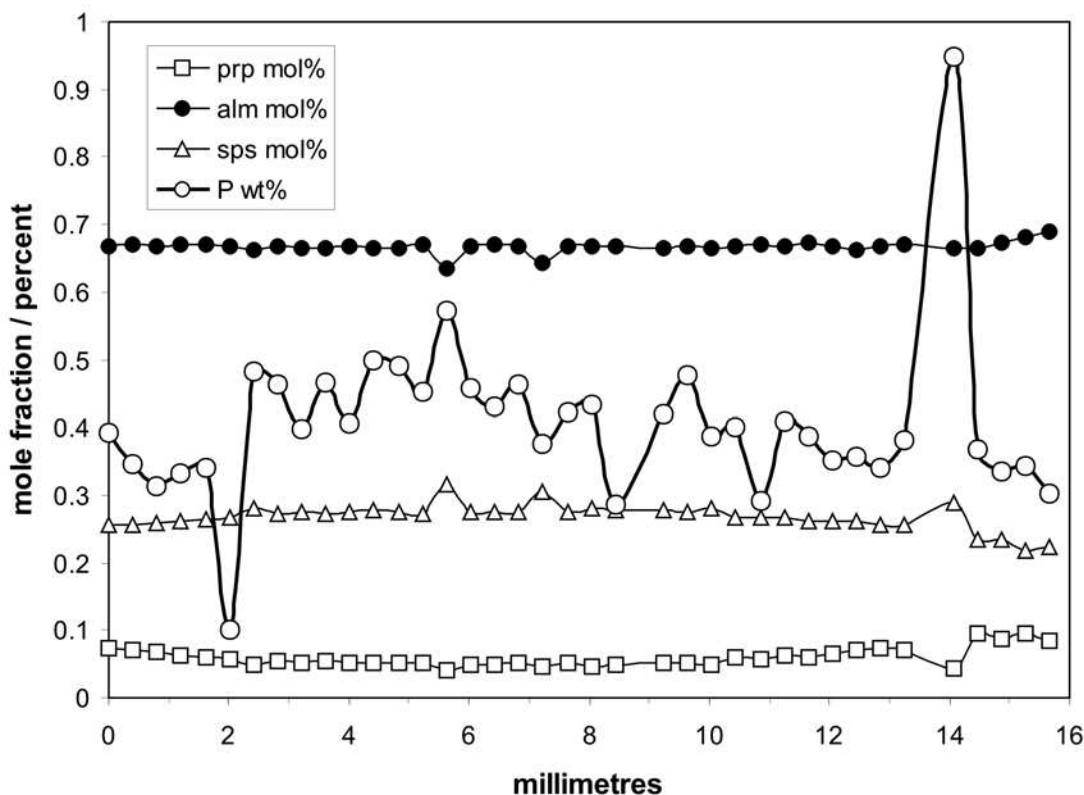


FIG. 3. Line scan displaying the phosphate contents of garnet phenocrysts in the Trutzhofmühle aplite using the electron microprobe (EMP). Data along the traverse are given in wt.% for phosphorus (P) and in mol.% for pyrope (prp), almandine (alm) and spessartine (sps) components.

hydrated Fe phosphates such as laueite (?) and Fe–Al phosphates such as childrenite (?) occur. Strunzite is a rare hydrated Mn–Fe³⁺ phosphate growing into the open space of vugs and cavities or developing radiating aggregates (Fig. 7a). In a few samples, “ferrolaueite” was spotted (Fig. 7b). Despite its lack of Mn, the Fe²⁺–Fe³⁺ phosphate beraunite is also mentioned in this section (Figs. 5c, 7c); it is present as massive phosphate ore and occurs in aggregates of acicular crystals.

Hydrated Fe³⁺ phosphate

Strengite replaces aggregates of rockbridgeite and whitmoreite (Fig. 7d), or it occurs as an open-space filling in druses with strunzite (Fig. 7e). Cacoxenite is the latest phosphate in the mineral succession containing trivalent iron. Although its Al content is below the detection limit, its morphology and the XRD data support our identification. It coats muscovite and replaces rockbridgeite (Fig. 7f).

Hydrated Fe³⁺–Ca–Zn phosphates

Mitridatite and its hydrated meta-phases (“meta-mitridatite”) are the most common Ca–Fe phosphates (Fig. 4f). Orange to reddish brown aggregates found in a rhythmic intergrowth with rockbridgeite were identified as keckite. Whereas keckite I occurs in massive aggregates intergrown with rockbridgeite, keckite II grows into vugs of rockbridgeite lined with “limonite” (Figs. 5b, c). The grain size of keckite is very small so that it is difficult to determine its morphology. It seems to be elongate along [001] and intergrown parallel to {100}.

Hydrated Al–Fe–Mg phosphates with unfamiliar anions

Some Al-rich phosphates have been determined by their chemical composition as belonging to the childrenite–eosporite solid-solution series (Table 3).

TABLE 3. REPRESENTATIVE COMPOSITIONS OF SOME PHOSPHATE-BEARING MINERALS FROM THE THM SUITE

Section	AS 7699	AS 7700	AS 7699	AS 7848	AS 7848	AS 7699	AS 7700	AS 7848	AS 7848	AS 7703	AS 7703	AS 7703	AS 7703	AS 7703	AS 7703
Anal. Sequence /stage	3 I/2	12 I/2	1 II/2	24b II/3	35b II/3	11 III/2	5 III/2	3 III-IV/1b	20 III-IV/1b	12 IV/2	9 IV/2	10 IV/2	6 IV/2	22 VI/2	13
Mineral	1*	1*	2	3	4	5	5	6	7	8	9	10	11	12	13
SiO ₂ wt. %	b.d.l.	b.d.l.	b.d.l.	b.d.l.	15.37	b.d.l.	0.80	b.d.l.	b.d.l.	0.05	0.21	0.26	b.d.l.	b.d.l.	0.80
P ₂ O ₅	42.99	42.26	32.34	41.60	17.01	30.11	32.89	31.31	32.09	33.47	23.94	29.98	31.30	38.29	7.86
SO ₃	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	0.22
Cl	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	0.23	0.10	b.d.l.	b.d.l.	0.02
Na ₂ O	0.12	b.d.l.	b.d.l.	0.14	b.d.l.	0.06	b.d.l.	b.d.l.	b.d.l.	0.21	0.07	0.13	b.d.l.	b.d.l.	b.d.l.
MgO	b.d.l.	0.10	b.d.l.	b.d.l.	b.d.l.	0.20	0.05	0.28	0.43	b.d.l.	b.d.l.	b.d.l.	0.07	b.d.l.	b.d.l.
Al ₂ O ₃	b.d.l.	b.d.l.	b.d.l.	b.d.l.	2.33	b.d.l.	1.14	21.72	21.42	1.66	0.99	1.22	1.69	1.07	2.69
K ₂ O	b.d.l.	0.07	b.d.l.	5.77	b.d.l.	b.d.l.	0.10	b.d.l.	b.d.l.	b.d.l.	0.13	0.17	b.d.l.	b.d.l.	b.d.l.
CaO	53.08	50.64	1.08	0.57	1.65	b.d.l.	0.36	0.34	0.67	0.48	10.00	13.58	b.d.l.	b.d.l.	0.07
Sc ₂ O ₃	b.d.l.	b.d.l.	b.d.l.	26.46	13.61	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	0.04	b.d.l.	b.d.l.	b.d.l.
TiO ₂	b.d.l.	b.d.l.	0.16	b.d.l.	0.25	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.
MnO	2.38	5.45	24.43	2.13	b.d.l.	7.95	6.27	17.09	14.66	3.44	0.77	0.99	0.45	b.d.l.	b.d.l.
FeO	0.59	0.63	37.83	3.03	3.51	34.70	44.71	13.10	14.47						
Fe ₂ O ₃										51.72	26.27	35.34	47.48	39.83	73.31
As ₂ O ₃	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.
Y ₂ O ₃	n.a.	n.a.	n.a.	n.a.	2.17	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
ZrO ₂	n.a.	n.a.	n.a.	5.90	33.70	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
BaO	b.d.l.	b.d.l.	b.d.l.	14.42	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	0.18	0.18	b.d.l.	b.d.l.	b.d.l.
PbO	b.d.l.	b.d.l.	b.d.l.	0.15	0.27	0.14	0.08	0.19	0.14	0.12	b.d.l.	b.d.l.	0.18	0.35	0.20
UO ₂	n.a.	n.a.	n.a.	n.a.	4.65	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Total	99.16	99.14	95.84	100.16	94.52	73.16	86.40	84.03	83.88	91.16	62.79	82.00	81.17	79.53	85.17
Oxygen	12.5	12.5	4.5	12	15	8	8	5	5	14.5	14	14	9	4	2
Si <i>apfu</i>					2.022		0.049			0.005	0.031	0.030			0.015
P	3.020	2.997	0.925	3.020	1.895	1.854	1.720	1.012	1.031	3.023	3.004	2.914	1.934	1.013	0.125
S															0.003
Cl											0.057	0.019			0.001
Na	0.019			0.024		0.008				0.044	0.019	0.029			
Mg		0.012				0.022	0.005	0.016	0.024				0.007		
Al					0.361		0.083	0.978	0.958	0.209	0.173	0.165	0.145	0.039	0.065
K		0.008		0.631			0.008				0.025	0.024			
Ca	4.719	4.545	0.039	0.052	0.233		0.024	0.014	0.027	0.055	1.587	1.671			0.001
Sc				1.977	1.560							0.004			
Ti			0.004		0.024										
Mn	0.167	0.386	0.699	0.154		0.490	0.328	0.553	0.471	0.311	0.097	0.097	0.028		
Fe ²⁺	0.037	0.040	0.961	0.218	0.386	1.899	2.077	0.418	0.459						
Fe ³⁺										4.152	2.930	3.053	2.606	0.937	1.037
As															
Y					0.151										
Zr				0.247	2.162										
Ba				0.485							0.010	0.008			
Pb				0.003	0.010	0.003	0.001	0.002	0.001	0.003			0.003	0.003	0.001
U					0.136										
Total	7.962	7.988	2.628	6.810	8.939	4.274	4.295	2.993	2.974	7.802	7.934	8.014	4.724	1.992	1.248

* The concentration of F was measured, but values are below detection limit (<0.1 wt%). ** All Fe calculated as Fe³⁺. Sequence/stage according to Table 1. Minerals: 1: Mn-rich apatite, 2: wolfeite, 3: K-Ba-Sc-Zr phosphate, 4: Zr-Sc phosphate-silicate, 5: Mn-rich vivianite, 6: eosphorite–childrenite solid solution, 7: childrenite–eosphorite solid solution, 8: rockbridgeite**, 9: “metamitridatite”?, 10: mitridatite, 11: whitmoreite, 12: strengite, 13: phosphorus-bearing goethite.

Compositions and analytical totals (65–90 wt.%) are, locally, strongly variable, and high metal : phosphorus ratios (>4) in some cases suggest an intergrowth of

childrenite–eosphorite (Fig. 8a) with more Al-rich material, identified by XRD as wavellite (Fig. 8b). A few aggregates of Al-rich hydrated phosphates were

determined to have 8–18 wt.% Al_2O_3 , 30–56 wt.% Fe_2O_3 (total Fe), 12–33 wt.% P_2O_5 , and <4.5 wt.% CaO, <1.5 wt.% K_2O and 0.4–2.7 wt.% SO_3 , <5.7 wt.% MnO. No known mineral fits this bulk composition. Even if hydrated phosphate minerals with a high metal : phosphate ratio such as childrenite–eosphorite solid-solution series or oxy-phosphates such as grattarolaite are considered, an intergrowth of a phosphate with a sulfate-bearing phase is most likely.

Hydrated and non-hydrated Sc–REE–U–(Zr–K) phosphates and phosphate-silicates

The newly discovered THM apatite is unusual among the pegmatites in central Europe because it carries various Sc minerals. Four different mineral phases bearing Sc have been spotted in the THM apatite; two of them are new Sc minerals and, after complete characterization, must be added to the group of ten Sc minerals so far accepted by the IMA.

Deep blue kolbeckite is the most widespread Sc phosphate in the THM apatite and was spotted only in a quartz matrix as euhedral crystals isolated from the remaining Fe–Mn phosphates, or growing in solution cavities with associated goethite (Dill *et al.* 2006b) (Fig. 8c). Kolbeckite contains up to 2.66 wt.% Fe and 2.27 wt.% Ca, respectively. Owing to the crystal habit, three subtypes can be established. Type-I kolbeckite developed tabular crystals with the basal pinacoid {001} prevailing in size over {110} faces (Fig. 5d). No pronounced “limonitization” has been recognized around these crystals.

Stubby kolbeckite (type IIa) displays complex aggregates of crystals with the faces {001}, {110}, {041}, {011} and {010} (Fig. 5e). The {001} faces display a conspicuous lineation toward [100]. The habit of type-IIb kolbeckite crystals closely resembles that of type-IIa crystals, but its faces {041} and {011} are downsized to almost nil and beyond recognition under the stereomicroscope (Fig. 5f).

Kolbeckite is replaced along cracks by scandian churchite-(Y) containing variable contents of Ca (2.3–4.2 wt.%), Sc (2.5–3.3 wt.%) and Yb (3.2–4.7 wt.%) (Fig. 8d). In one aggregate, 2.6 wt.% U was established in scandian churchite-(Y). Churchite and kolbeckite are isotypic, and trivalent scandium and yttrium show a similar chemical behavior not very different from that of the REE. Hence, scandium contents in churchite-(Y) are not surprising.

Two new Sc phosphates have been encountered in a sample rich in manganese-rich apatite. Mineral (1) comprises perfectly euhedral crystals, ca. 50 μm in size, of a complex K–Ba–Zr–Sc phosphate (Fig. 8e). Smaller (<20 μm) euhedral crystals are identified as being a Zr–Sc phosphate-silicate. Both minerals are further associated with chlorite, quartz, and a hydrous Fe–Al silicate. In back-scattered electron images, the K–Ba–Zr–Sc phosphate displays both sector zoning

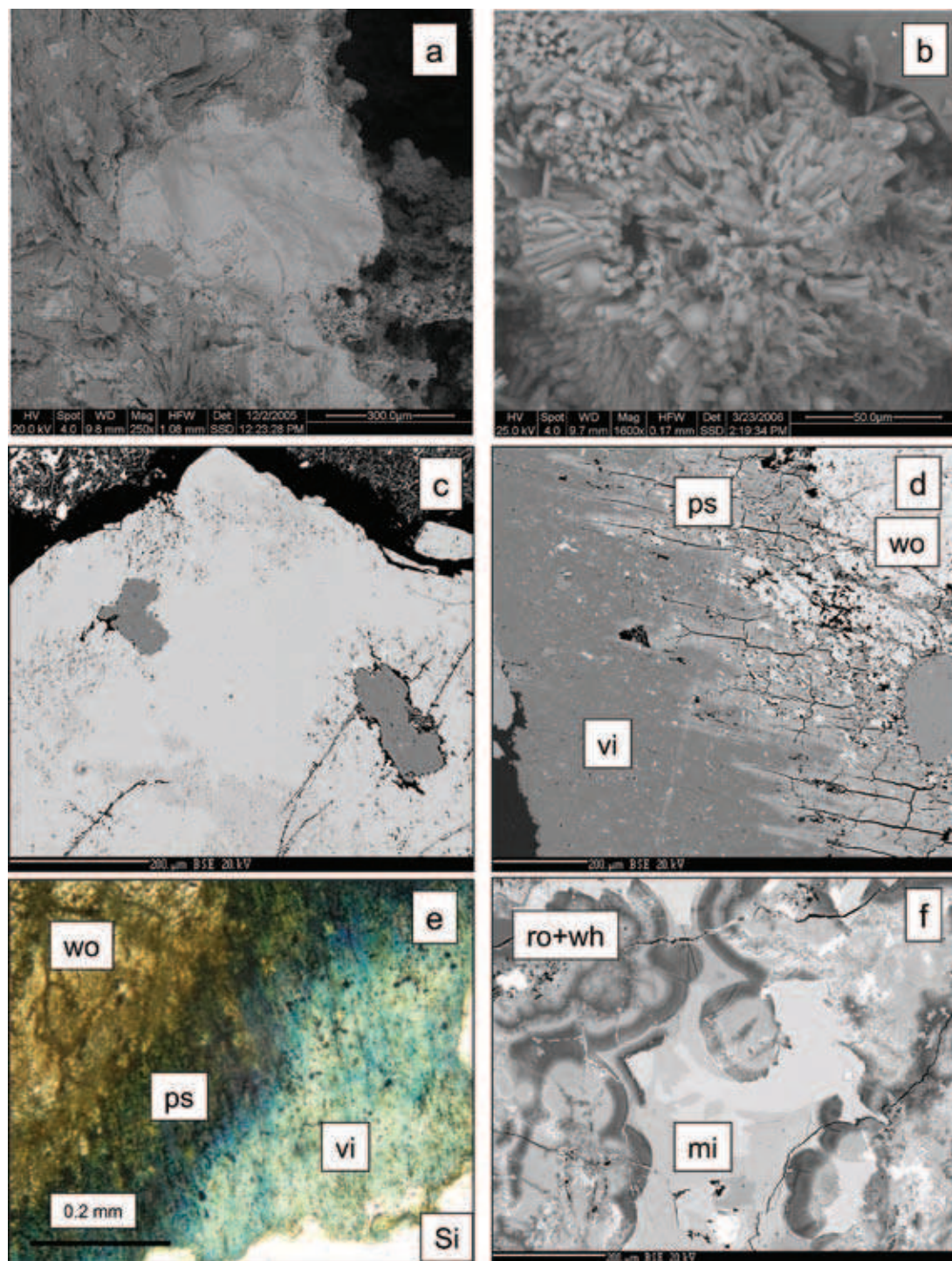
and discontinuous growth zonation that is caused by variable Ba concentrations compensated by K, Zr, Mn and Fe. Compositional variations detected by electron microprobe are: 5.7–8.8 wt.% K_2O , 7.9–14.4 wt.% BaO, 5.9–9.1 wt.% ZrO_2 , 24.2–26.7 wt.% Sc_2O_3 and 41.6–43.6 wt.% P_2O_5 . In contrast, FeO (2.6–3.7 wt.%), MnO (1.0–2.1 wt.%) and CaO (0.2–0.6 wt.%) are present in minor concentrations.

The Zr–Sc phosphate-silicate has a more variable composition: 12.5–34.7 wt.% ZrO_2 , 13.4–37.1 wt.% Sc_2O_3 , 17.0–33.3 wt.% P_2O_5 and 6.5–15.4 wt.% SiO_2 . Minor elements include CaO (1.6–1.9 wt.%), FeO (1.1–3.5 wt.%), Y_2O_3 (2.2–2.7 wt.%) and UO_2 (1.3–4.6 wt.%). The phase is unstable under the electron beam and, in view of the high U contents, tends to metamictization.

The only hydrated uranyl phosphates known to occur in the apatite are autunite and torbernite. Another U mineral, vochtenite, could not be identified with certainty.

Anhydrous grains of a green mineral 1 mm in size were found disseminated within a siliceous matrix or concentrated along fissures in quartz and identified as U-bearing monazite (Fig. 8f). A similar greenish phosphate was described by Gramaccioli & Segalstad (1978) from the Piona pegmatite in northern Italy. Unlike the phosphate reported from the apatite dike, the Italian counterpart is rich in Th (11% ThO_2), and it was suspected to be uranium-rich cheralite. The ratio $(\text{Ca} + \text{U} + \text{Th})/(\text{Ce} + \text{La} + \text{Pr} + \text{Nd})$ of the THM monazite was calculated to 0.99, and that in the Piona monazite, 0.91, versus 1.47 for type cheralite. Some of these green grains are replaced by minerals almost identical in their outward appearance with the U-bearing monazite, but much higher in U contents than the host mineral, reaching 75 wt.% U, and much lower in Ce, La, Ca and P contents. With respect to the chemical composition and color, this replacing mineral resembles the hydrous tetravalent U phosphates leermontovite and vyacheslavite, both of which differ only in the state of hydration (Brandel & Dacheux 2004).

FIG. 4. Phosphate minerals from the Trutzhofmühle apatite. a) Early anhydrous manganese-rich apatite in muscovite in a quartz-feldspar matrix of stage I (SEM). b) Radiating aggregates of slender crystals of Mn-rich apatite, which formed during the waning phases of stage I (SEM). c) Massive wolfeite (1 + 2) of stage II with relict Mn-rich apatite (3) of stage III marking the transition from the early magmatic to the late magmatic stage (EMPA–BSE). d) Massive wolfeite (wo, stage II) with relict Mn-rich apatite of stage I are both hydrated and converted into Mn-rich vivianite (vi) via phosphoferrite (ps) marking the transition from the magmatic to the early hydrothermal stage III (EMPA–BSE). e) Massive wolfeite (wo) is gradually converted into Mn-rich vivianite (vi) via phosphoferrite (ps) at the grain boundary to quartz (Si). The dark flakes along the contact



consist of chloritized biotite marking the transition from the magmatic to the early hydrothermal stage; thin section, plane-polarized light. f) Colloform crusts of rockbridgeite (ro) and whitmoreite (wh), with mitridatite (mi) marking the transition from the Ca-poor into the Ca-rich late hydrothermal stage IV.

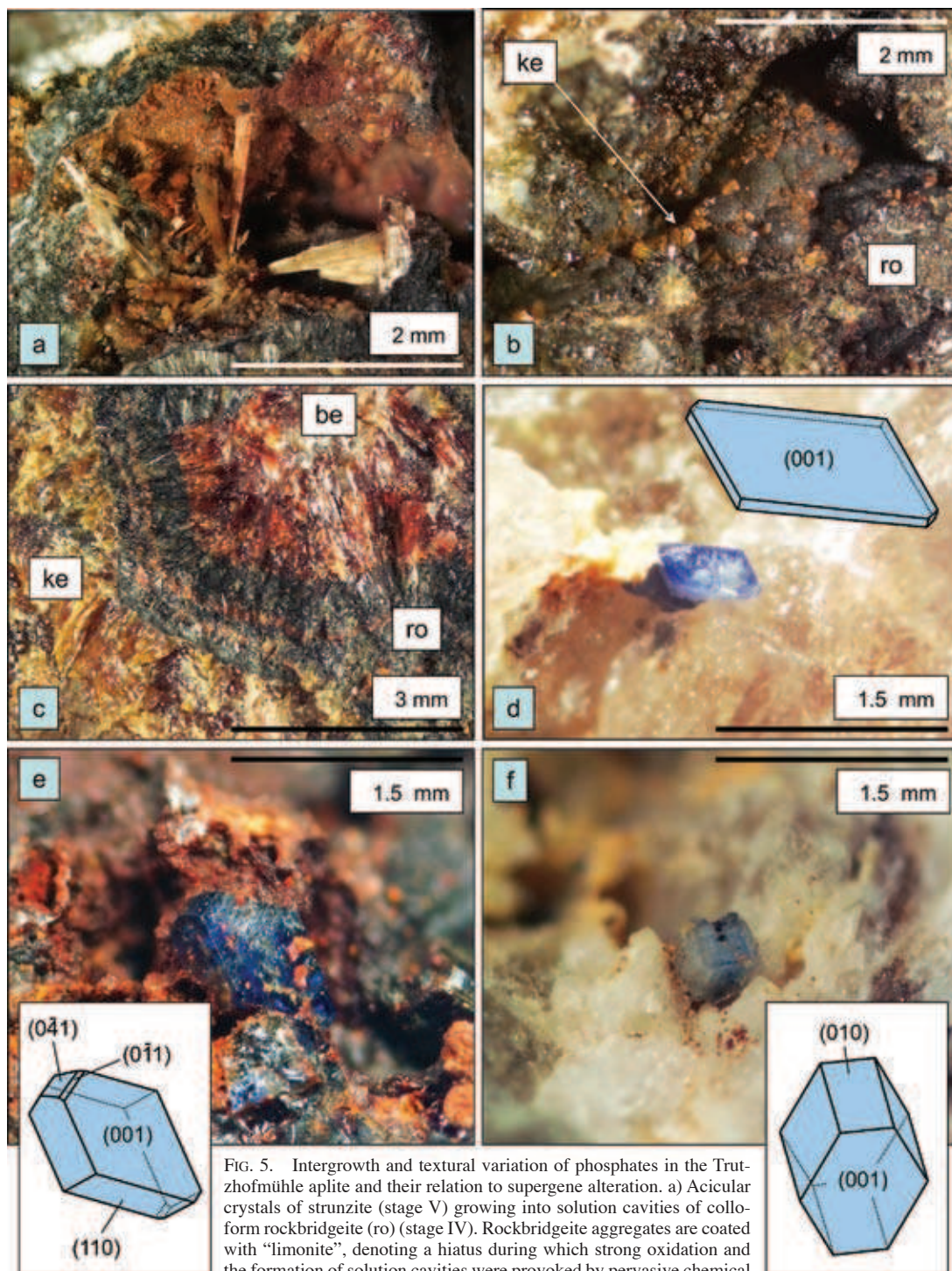


FIG. 5. Intergrowth and textural variation of phosphates in the Trutzhoffmühle aplite and their relation to supergene alteration. a) Acicular crystals of strunzite (stage V) growing into solution cavities of colloform rockbridgeite (ro) (stage IV). Rockbridgeite aggregates are coated with "limonite", denoting a hiatus during which strong oxidation and the formation of solution cavities were provoked by pervasive chemical weathering. b) Rockbridgeite (ro) of stage IV overgrown with crystal aggregates of keckite II of stage V. c) Rockbridgeite (ro) of stage IV intergrown with keckite I of stage IV, both replaced by beraunite (be) (stage VI). In this zone of the THM aplite, no dissolution of pre-existing phosphates occurred, and at stage V, strunzite did not evolve. It reflects a gradual replacement of Fe^{2+} by Fe^{3+} in these complex phosphates (solid-state

transformation). d) Tabular crystals of kolbeckite (type I) in quartz, with the basal pinacoid {001} terminating the crystal and the {110} face poorly represented. Kolbeckite I forms isolated single crystals in the quartz of stage IV. No pronounced "limonitization" has been recognized around these crystals. e) Stubby crystal of kolbeckite (type IIa) in quartz showing complex crystal aggregates with the faces {001}, {110}, {041}, {011} and {010}. Kolbeckite II follows an episode of strong "limonitization" prior to the onset of stage-V mineralization. f) Stubby crystal of kolbeckite (type IIb) in quartz corroded by dissolution and "limonitization". This crystal habit is characterized by a downsizing of the faces {041} and {011} to almost nil.

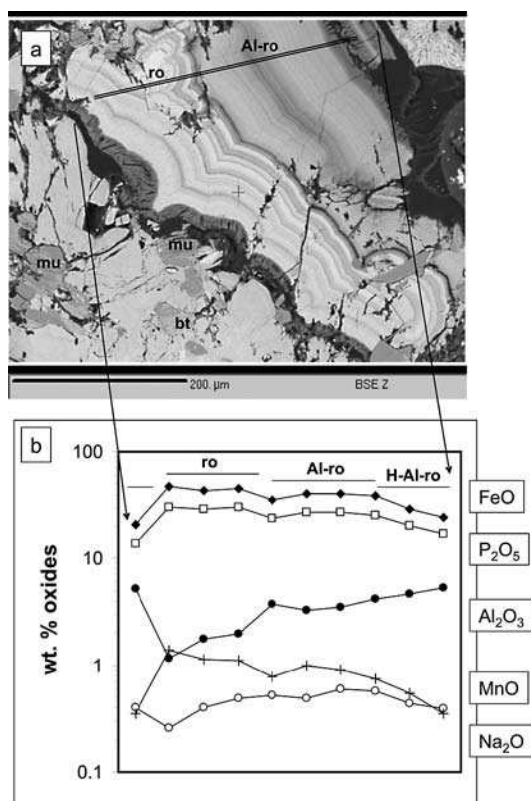


FIG. 6. Micromorphological changes and chemical variation of rockbridgeite. a) Colloform rhythmites in quartz – muscovite (mu) – biotite (bt) matrix. The transect of the line scan is shown by a double line (BSE image). b) Variation of FeO, P_2O_5 , Al_2O_3 , MnO and Na_2O along a transect through phosphate crusts revealing gradual changes from rockbridgeite, through Al-bearing rockbridgeite into a hydrated form of Fe–Al phosphate (most likely an intergrowth of rockbridgeite or “ferrolaueite” or both and childrenite). This zonal arrangement of mineralization shows how exo-aplitic (childrenite) and intra-aplitic sequences (rockbridgeite) correspond with each other.

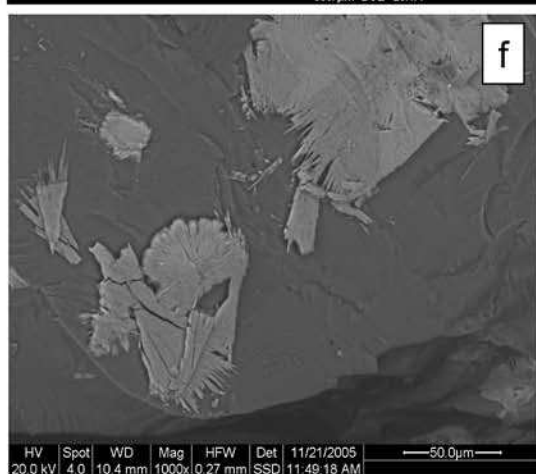
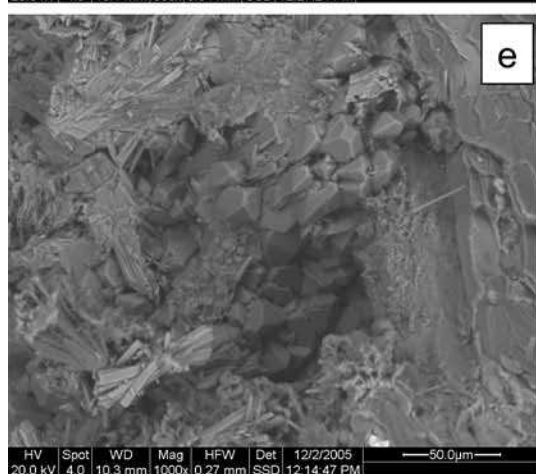
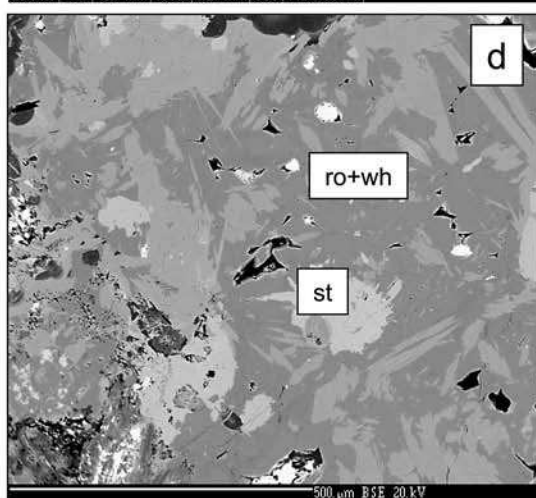
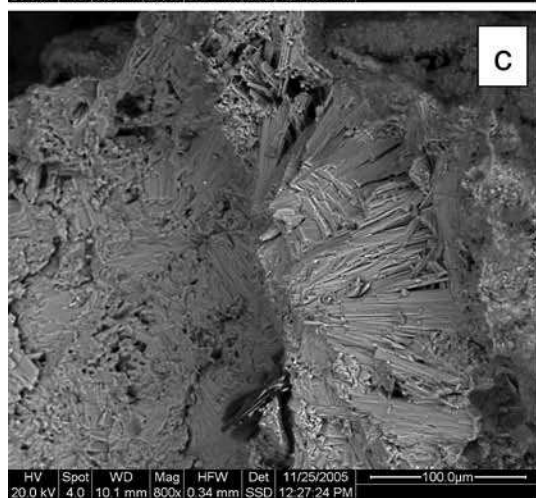
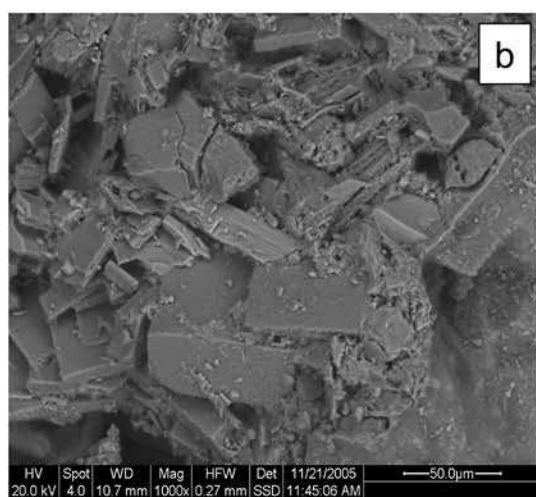
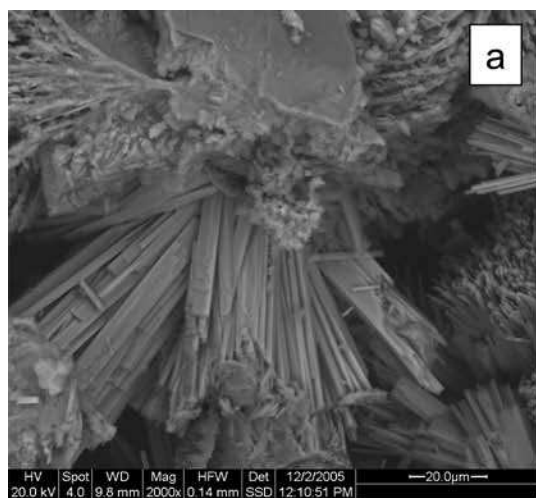
Phosphate-bearing oxy-hydroxides

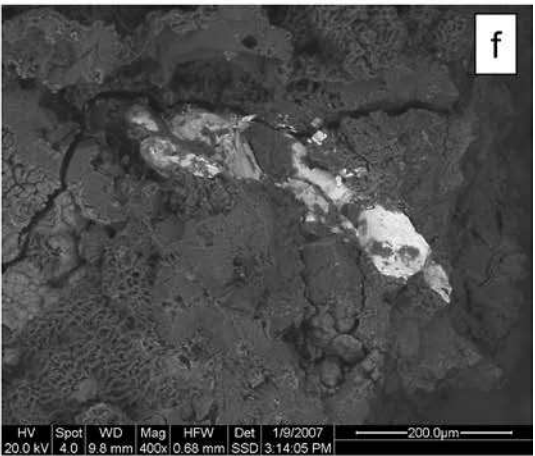
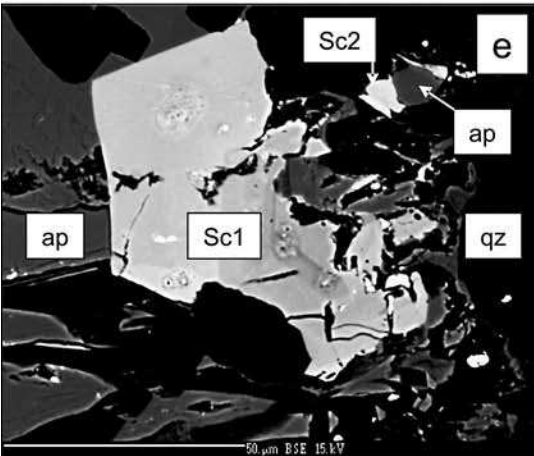
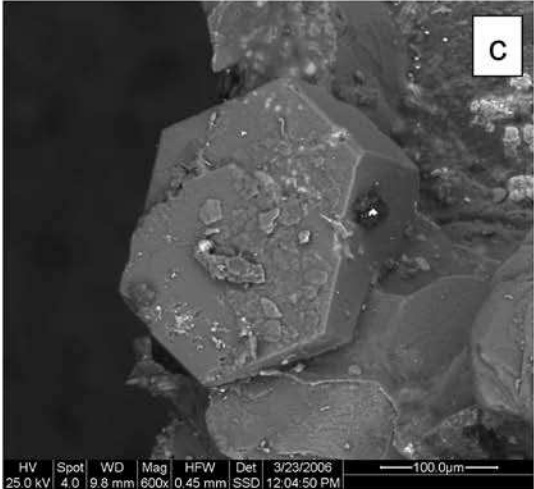
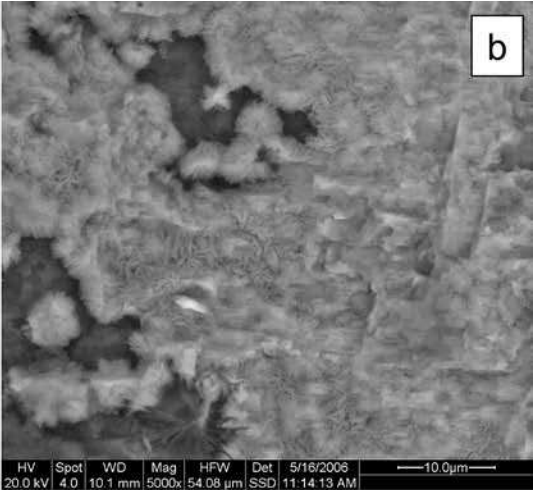
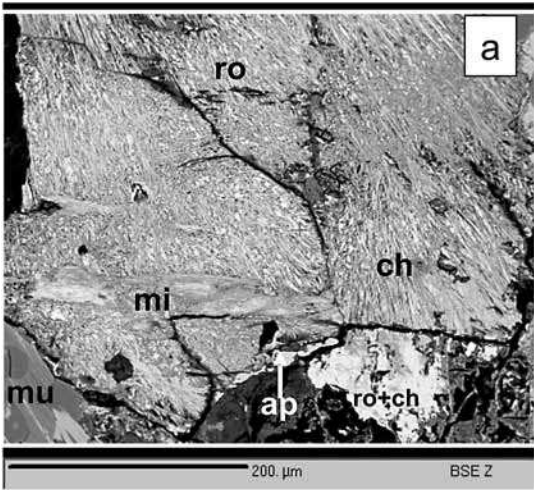
Goethite occurs as a late-stage mineral in the aplite dike (Fig. 2). It is almost pure $FeOOH$, with traces of SiO_2 (Table 3). In addition to pure goethite, another Fe oxide hydrate was identified bearing significant amounts of phosphate and aluminum. The reactions of phosphate with natural samples of ferrihydrite, hematite and goethite were investigated by Parfitt (1989). In this case, Al phosphates have been taken up by “Fe limonite” and incorporated into the goethite structure. An alteration phase similar in texture but different in composition was encountered in the surroundings of the THM aplite during the study of aggregates of a ilmenite–rutile intergrowth informally called “nigrine” (Dill *et al.* 2007a). The chemical composition points to a Ti-rich precursor phase (76 wt.% TiO_2) with appreciable concentrations of impurities, *e.g.*, 2.0 to 2.5 wt.% FeO, 6.1 to 8.5 wt.% Al_2O_3 , 3.5 to 4.1 wt.% P_2O_5 , and subordinate amounts of V, Si and Ca. Totals in the range 90 to 95 wt.% suggest considerable incorporation of H_2O or the $(OH)^-$ complex. The phase may be considered a special type of “leucoxene”, *i.e.*, submicroscopic intergrowths of TiO_2 , Al-rich phosphates and silicates.

Sulfides and sulfates

The only sulfate mineral encountered, barite, occurs as inclusions in columbite-(Fe), and associated with uraninite. In comparison with neighboring pegmatites, sulfur-bearing minerals are very rare in the THM aplite.

FIG. 7. Phosphate minerals from the Trutzhofmühle aplite. a) Typical vuggy mineralization of stage V with radiating aggregates of strunzite in a quartz druse. It is typical of the advanced weathering characterized by intensive limonitization and dissolution (SEM, BSE image). b) “Ferrolaueite” plates at stage IV between muscovite are corroded by supergene fluids (SEM, BSE image). c) Beraunite crust of stage VI marking another period of dissolution and redistribution of Fe during Neogene weathering (SEM, BSE image). d) Strengite (st, stage IV) replaces aggregates of rockbridgeite (ro) and whitmoreite (wh) (stage IV). It illustrates the decomposition of hydrothermal Mn^{2+} -bearing Fe^{2+} – Fe^{3+} phosphates into Fe^{3+} phosphates without hiatus or limonitization (EMPA, BSE image). e) Strengite (stage IV) infilling druses, together with radiating aggregates of strunzite (stage V). Late hydrothermal phosphates of stage IV and phosphates of stage V (early weathering) occupy the same open space left after a hiatus and dissolution of older phosphates (SEM, BSE image). f) Rosettes of cacoxenite coating muscovite. This example shows a simple, nonreactive overgrowth of the most recent supergene phosphates of stage VI on non-phosphates. See also reaction in Figure 8a (SEM, BSE image).





Sphalerite (up to 7.7 wt.% Fe) forms larger aggregates along the grain boundaries between quartz and phosphates. Thus, the iron contents are lower than at the Hagendorf-South (12.4 to 16.8 wt.% Fe) and Püllersreuth (11.4 wt.% Fe) pegmatites (Forster *et al.* 1967). Locally, chalcopyrite and pyrite were spotted as isolated mineral grains within the quartz–feldspar matrix.

Oxides

Oxides are also associated with the phosphates, but in minor quantities compared to the pegmatites around Hagendorf. Uraninite formed during the emplacement of the aplite together with columbite-(Fe). Columbite-(Fe) was also found in aggregates of ilmenite intergrown with rutile in the immediate surroundings of the THM aplite around Pleystein (Dill *et al.* 2007a), and recorded from the 109 m and 76 m levels of the Hagendorf South pegmatite mine (Forster *et al.* 1967). Columbite-(Fe) from the THM aplite contains moderately lower Ti and Sc and higher Ta contents than columbite-(Fe) included in ilmenite–rutile aggregates. The columbite-(Fe) is markedly enriched in W and Sn relative to the niobian rutile and columbite-(Fe) found in ilmenite–rutile aggregates, but contains only a moderate amount of Sc.

U–Pb dating of columbite-(Fe) and torbernite

Fifteen LA–ICP–MS U–Pb analyses on a 20 by 5 mm section of a crystal of columbite-(Fe) from Hagendorf are presented in Table 4a and Figure 9a. Spots are located along a profile through the entire grain. The U concentrations are high (1094–1546 ppm), and the Th:U ratio generally is <0.003. Only six analyses

show $^{206}\text{Pb}/^{204}\text{Pb}$ below 10000 (2759 to 6666), making moderate common Pb corrections necessary. The $^{207}\text{Pb}/^{206}\text{Pb}$ ages vary from 284 ± 21 to 448 ± 27 Ma ($\pm 2\sigma$), whereas $^{206}\text{Pb}/^{238}\text{U}$ ages are very homogeneous, with a weighted mean age of 300 ± 2 ($\pm 2\sigma$, MSWD of 1.15). The mean squared weighted deviates (MSWD) of about 1 indicate adequate propagation of errors and a uniform $^{206}\text{Pb}/^{238}\text{U}$ age population. The heterogeneity of the $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{207}\text{Pb}/^{235}\text{U}$ could be attributed to insufficient correction for the contribution of common Pb in about half of the datasets. A possible explanation would be also a molecular (or polyatomic) interference on mass 207. These can be formed by the recombination of ions from the sample with Ar and other ions such as O and H (coming from impurities in the Ar gas or from the sample itself) in the cooler regions of the plasma. Such interferences are, however, not very common and pronounced at the higher mass-range during laser-ablation analyses with double focusing ICP–MS. As ^{207}Pb is about 19 times less abundant than ^{206}Pb , it is more prone to common Pb correction and molecular interferences. A lack of correlation between the $^{206}\text{Pb}/^{204}\text{Pb}$ and the $^{207}\text{Pb}/^{206}\text{Pb}$ age, and high values of $^{206}\text{Pb}/^{204}\text{Pb}$, argue against a common Pb correction problem. The relatively high ^{207}Pb signal strengths and lack of correlation with the $^{207}\text{Pb}/^{206}\text{Pb}$ age make a molecular interference less likely. From about 500 LA–ICP–MS U–Pb spot analyses on columbite at JWG (e.g., Melcher *et al.* 2007, 2008; A. Gerdes, unpubl. data), the Hagendorf columbite-(Fe) is the first to show this variable $^{207}\text{Pb}/^{206}\text{Pb}$ at rather homogeneous $^{206}\text{Pb}/^{238}\text{U}$. Although we have no further evidence, a possible interference on mass 207 seems at the moment the most likely explanation for the observed higher $^{207}\text{Pb}/^{206}\text{Pb}$ of some analyses. The weighted mean $^{206}\text{Pb}/^{238}\text{U}$ age of 300 ± 2 Ma is, nevertheless, the best estimate for crystallization of columbite-(Fe) at Hagendorf.

Fifteen LA–ICP–MS spot analyses were made on columbite-(Fe) from the aplite dike (Table 4a, Fig. 9b). The U content is more variable (697–5395 ppm) than that in crystals of columbite-(Fe) from Hagendorf. The ratio Th/U varies from 0.002 to 0.010, and $^{206}\text{Pb}/^{204}\text{Pb}$, from about 320 to 57900. Thus for most of the analyses, a considerable correction for common Pb had to be applied. This is expressed in larger uncertainties in $^{207}\text{Pb}/^{206}\text{Pb}$ and also $^{206}\text{Pb}/^{238}\text{U}$. The $^{207}\text{Pb}/^{206}\text{Pb}$ uncertainties vary from 20 to 160 Ma and thus are at least two to three times larger than in $^{206}\text{Pb}/^{238}\text{U}$. This is common for Paleozoic grains where, in general, age estimates are based on the more precise $^{206}\text{Pb}/^{238}\text{U}$ ratios. It is worth noting that the $^{206}\text{Pb}/^{238}\text{U}$ uncertainties of the individual analyses are nearly twice those of the Hagendorf columbite-(Fe), suggesting some heterogeneity of the Pb/U due to mobility of Pb at the micrometer scale (cf. Romer 2003). This heterogeneity is also reflected in the RSD (relative standard deviation) of the $^{206}\text{Pb}/^{238}\text{U}$ of all 15 analyses of columbite-(Fe), which is 1.3% for Hagendorf and 2.3% for Trutzhofmühle. For the

FIG. 8. Phosphate minerals from the Trutzhofmühle aplite. a) Acicular rockbridgeite (ro), mitridatite (mi), childrenite (ch) and apatite (ap) replacing a quartz – muscovite (mu) – biotite assemblage of the host aplite. Reaction between phosphates of exo-aplitic stages III–IV and intra-aplitic stage IV and hydrosilicates of the host aplite. See also non-reactive coating in Figure 7f (EMPA, BSE image). b) Radiating aggregates of wavellite forming a coherent coating on the aplitic host rocks. Non-reactive process typical of phosphates of stage VI which precipitated after a long-lasting hiatus during the Neogene (SEM, BSE image). c) Stubby crystal of kolbeckite (type II) growing into a cavity of siliceous gangue (stage V) (SEM, BSE image). d) Rosettes of a Sc–U–Ca-bearing churchite-(Y) coating quartz formed during the Neogene (stage VI) (SEM, BSE image). e) Mn-rich apatite (ap) within (black) a matrix of quartz (qz) replaced by a newly discovered K–Ba–Zr–Sc phosphate (Sc 1) and a Zr–Sc phosphate-silicate (Sc 2). Zonation seen in the K–Ba–Zr–Sc phosphate (Sc 1) is caused by varying Ba contents. f) Platy U-bearing monazite intergrown with quartz of the aplite at stage I (SEM, BSE image).

TABLE 4a. AGE DATING OF COLUMBITE-(Fe) FROM THE HAGENDORF PEGMATITE AND THE TRUTZHOFFMÜHLE APLITE

														Age (Ma)					
spot No.	μm	$^{207}\text{Pb}^a$ cps	U^b ppm	Pb^b ppm	^{206}Pb ^{204}Pb	Th^b U	$^{206}\text{Pb}^c$ ^{238}U	$\pm 2\sigma$ %	$^{207}\text{Pb}^c$ ^{235}U	$\pm 2\sigma$ %	Rho^d	$^{207}\text{Pb}^c$ ^{206}Pb	$\pm 2\sigma$ %	^{207}Pb ^{235}U	$\pm 2\sigma$	^{206}Pb ^{238}U	$\pm 2\sigma$	^{207}Pb ^{206}Pb	$\pm 2\sigma$
Hagendorf Pegmatite (Stage I)																			
Ch2	60	55691	1346	59	104500	0.002	0.04762	2.4	0.3536	2.6	0.95	0.05385	0.8	307	7	300	7	365	19
Ch3	60	67248	1355	62	102213	0.003	0.04825	2.0	0.3647	2.2	0.92	0.05482	0.9	316	6	304	6	405	20
Ch4	60	71629	1305	60	20171	0.002	0.04760	2.4	0.3613	2.6	0.92	0.05505	1.0	313	7	300	7	414	23
Ch5	60	67946	1275	57	6666	0.002	0.04683	2.4	0.3405	2.6	0.90	0.05275	1.1	298	7	295	7	318	26
Ch6	60	63771	1276	57	3449	0.003	0.04727	3.1	0.3561	3.3	0.95	0.05463	1.1	309	9	298	9	397	24
Ch7	60	50019	1186	51	88477	0.002	0.04658	2.2	0.3410	2.5	0.89	0.05310	1.1	298	6	293	6	333	25
Ch8	60	65200	1546	697	6851	0.003	0.04849	2.7	0.3531	2.8	0.94	0.05281	0.9	307	8	305	8	321	22
Ch9	60	48634	1094	47	5644	0.002	0.04664	2.3	0.3454	2.6	0.87	0.05372	1.3	301	7	294	7	359	30
Ch10	60	85010	1321	63	2759	0.005	0.04811	3.0	0.3529	3.1	0.96	0.05320	0.9	307	8	303	9	337	20
Ch11	30	7671	1358	60	16347	0.003	0.04750	3.0	0.3479	3.6	0.83	0.05265	2.0	303	10	299	9	314	46
Ch12	80	66504	1331	60	135899	0.003	0.04737	2.6	0.3653	2.9	0.92	0.05471	1.1	316	8	298	8	400	26
Ch13	80	152436	1536	99	3959	0.002	0.04793	2.6	0.3434	2.7	0.94	0.05196	0.9	300	7	302	8	284	21
Ch14	80	45275	1299	58	85934	0.003	0.04833	2.5	0.3732	2.9	0.86	0.05533	1.5	322	8	304	7	426	32
Ch15	80	45145	1297	57	87552	0.003	0.04760	2.4	0.3699	2.7	0.89	0.05590	1.2	320	7	300	7	448	27
Ch16	80	56473	1449	66	3867	0.003	0.04809	2.5	0.3945	15	0.17	0.05429	3.9	338	44	303	8	383	89
Trutzhofmühle (THM) Aplite (Stage I)																			
PI2	60	190906	2569	123	1154	0.008	0.04834	4.7	0.3517	4.9	0.96	0.05277	1.4	306	13	304	14	319	32
PI3	30	22564	1483	66	2652	0.005	0.04675	3.3	0.3406	3.8	0.87	0.05284	1.8	298	10	295	9	322	42
PI4	20	24314	1476	77	323	0.006	0.04576	7.5	0.3232	8.6	0.87	0.05122	4.2	284	22	288	21	251	98
PI5	20	9415	1345	59	1859	0.005	0.04719	4.4	0.3369	5.6	0.80	0.05178	3.4	295	14	297	13	276	77
PI7	20	9005	1024	49	1009	0.005	0.04897	4.7	0.3506	5.5	0.85	0.05193	2.9	305	15	308	14	282	67
PI8	20	2436	298	14	1473	0.002	0.04752	5.2	0.3283	8.6	0.60	0.05010	6.9	288	22	299	15	200	160
PI11	30	15591	1225	55	28264	0.004	0.04858	4.0	0.3571	4.2	0.94	0.05332	1.5	310	11	306	12	342	33
PI12	30	46689	3418	151	1348	0.006	0.04690	2.8	0.3422	3.2	0.87	0.05292	1.6	299	8	295	8	325	36
PI13	40	66019	1860	88	698	0.008	0.04742	4.8	0.3449	5.0	0.97	0.05275	1.1	301	13	299	14	318	26
PI14	40	140222	5395	246	596	0.009	0.04666	3.9	0.3360	4.2	0.94	0.05222	1.4	294	11	294	11	295	33
PI15	40	31006	1554	69	57894	0.005	0.04861	2.5	0.3534	2.8	0.90	0.05273	1.2	307	7	306	8	317	27
PI16	40	48492	1831	86	1608	0.006	0.04953	3.0	0.3596	3.2	0.95	0.05266	1.0	312	9	312	9	314	23
PI17	40	55772	2696	119	1746	0.008	0.04793	3.9	0.3490	4.0	0.97	0.05282	0.9	304	11	302	12	321	20
PI18	60	209117	3514	158	888	0.009	0.04667	3.1	0.3414	3.6	0.87	0.05306	1.8	298	9	294	9	331	41
PI20	60	54222	697	34	447	0.004	0.04885	2.5	0.3588	3.7	0.67	0.05327	2.7	311	10	307	7	340	62
Reference zircon *																			
PI	60	28528	551	28	19017	0.11	0.05401	1.1	0.3962	1.2	0.72	0.0532	0.7	339	4	339	3	337	16
GJ-1	60	27266	296	26	57443	0.032	0.09764	1.5	0.8070	2.0	0.00	0.05994	0.8	601	9	601	9	601	17

* Within-run background-corrected mean ^{207}Pb signal in counts per second. ^b The U and Pb content and the Th/U ratio were calculated relative to GJ-1 reference (LA-ICP-MS values, A. Gerdes, unpubl. data). ^c Corrected for background, within-run Pb/U fractionation and common Pb using Stacey & Kramers (1975) model Pb composition and subsequently normalized to GJ-1 reference (ID-TIMS value/measured value); the ratio $^{207}\text{Pb}/^{235}\text{U}$ is calculated using $^{207}\text{Pb}/^{206}\text{Pb} / (^{238}\text{U}/^{206}\text{Pb} \cdot 1/137.88)$. ^d Rho is the error correlation defined as $\text{err}^{206}\text{Pb}/^{238}\text{U} / \text{err}^{207}\text{Pb}/^{235}\text{U}$. * Mean and standard deviation (2σ) of reference zircon GJ-1 and Plešovice. For standard GJ-1, $n = 7$.

latter, all fifteen spots gave equivalent and concordant results, with a $^{206}\text{Pb}/^{238}\text{U}$ weighted mean age of 301 ± 4 Ma (MSWD = 1.5) and a concordia age of 302 ± 3 Ma (MSWD of concordance and equivalence = 1.5). The slightly elevated MSWD indicates some excess scatter of the data, which could be related to insufficient propagation of errors in the correction for common Pb, heterogeneity in Pb/U, as discussed before, or a combi-

nation of both. However, the concordia age, which is controlled by the more robust $^{206}\text{Pb}/^{238}\text{U}$ age, represents the best estimate of crystallization of columbite-(Fe) and thus the aplite dike.

Thirty-three LA-ICP-MS U-Pb spot analyses on a polished section of torbernite crystals are presented in Table 4b, and the data are plotted in Figure 9c. The U-Pb values display a large scatter, with $^{206}\text{Pb}/^{238}\text{U}$

TABLE 4b. AGE DATING OF TORBERNITE FROM THE NEIGHBORHOOD OF TRUTZHOFFMÜHLE (STAGE VI)

spot No.	μm	$^{207}\text{Pb}^a$ cps	U^b ppm	Pb^b ppm	^{206}Pb ^{204}Pb	$^{206}\text{Pb}^c$ ^{238}U	$\pm 2\sigma$ %	$^{207}\text{Pb}^c$ ^{235}U	$\pm 2\sigma$ %	Rho^d	$^{207}\text{Pb}^c$ ^{206}Pb	$\pm 2\sigma$ %	Age (Ma)			
													^{206}Pb ^{238}U	$\pm 2\sigma$	^{207}Pb ^{235}U	$\pm 2\sigma$
B1	12	19283	42	258	41067	0.0006620	1.9	0.004223	2.2	0.84	0.04627	1.2	4.27	0.08	4.28	0.09
B4	12	18594	40	253	39320	0.0007042	2.1	0.004479	2.9	0.75	0.04613	1.9	4.54	0.10	4.54	0.13
B5	12	19068	42	255	40529	0.0007023	1.9	0.004501	2.3	0.84	0.04648	1.3	4.53	0.09	4.56	0.10
B6	12	18607	40	252	39139	0.0006958	2.0	0.004415	2.4	0.85	0.04602	1.3	4.48	0.09	4.47	0.11
B7	12	18641	39	247	14114	0.0007023	2.2	0.004414	3.0	0.73	0.04558	2.1	4.53	0.10	4.47	0.14
B8	16	36997	51	323	78911	0.0007095	1.5	0.004559	1.9	0.81	0.04661	1.1	4.57	0.07	4.62	0.09
B18	12	10687	35	227	16410	0.0007172	2.9	0.004609	4.1	0.73	0.04661	2.8	4.62	0.14	4.67	0.19
B19	12	14020	44	279	29962	0.0007070	2.0	0.004525	2.8	0.71	0.04641	2.0	4.56	0.09	4.58	0.13
B20	12	15665	34	214	33332	0.0006981	2.4	0.004482	2.9	0.81	0.04657	1.7	4.50	0.11	4.54	0.13
B21	12	14418	35	218	40566	0.0006956	1.8	0.004449	2.5	0.71	0.04639	1.8	4.48	0.08	4.51	0.11
B22	12	15537	32	205	8726	0.0007043	1.9	0.004521	2.8	0.66	0.04656	2.1	4.54	0.08	4.58	0.13
B23	12	16007	35	222	34007	0.0007025	1.7	0.004455	2.5	0.69	0.04600	1.8	4.53	0.08	4.51	0.11
B24	12	15686	34	210	49441	0.0006929	1.5	0.004431	2.1	0.73	0.04638	1.4	4.46	0.07	4.49	0.09
A7	20	39722	37	241	85100	0.0007130	1.6	0.004534	1.7	0.96	0.04613	0.5	4.59	0.08	4.59	0.08
A8	20	37827	35	230	13087	0.0007183	1.8	0.004565	2.1	0.89	0.04609	1.0	4.63	0.09	4.62	0.10
A9	20	38373	43	276	81261	0.0007126	1.9	0.004532	2.1	0.89	0.04613	1.0	4.59	0.09	4.59	0.10
A12	20	32568	41	252	72148	0.0006745	1.9	0.004190	2.5	0.77	0.04505	1.6	4.35	0.08	4.25	0.10
A13	20	34695	43	257	73989	0.0006630	1.8	0.004233	2.0	0.89	0.04630	0.9	4.27	0.07	4.29	0.08
A14	20	29910	55	301	63935	0.0006085	2.3	0.003897	2.4	0.94	0.04645	0.8	3.92	0.09	3.95	0.09
A10	20	41170	47	322	88111	0.0007523	1.7	0.004787	1.9	0.91	0.04615	0.8	4.85	0.08	4.85	0.09
A6	20	39186	48	390	15118	0.0008853	7.9	0.005580	7.9	0.99	0.04571	1.1	5.70	0.45	5.65	0.45
B28	12	19197	51	426	57040	0.0009321	1.8	0.005942	1.9	0.92	0.04624	0.8	6.01	0.11	6.02	0.12
B29	12	17204	53	431	19075	0.0009135	1.5	0.005859	2.0	0.75	0.04652	1.3	5.89	0.09	5.93	0.12
B30	12	16412	44	299	11352	0.0007588	2.6	0.004884	2.9	0.90	0.04668	1.3	4.89	0.13	4.95	0.14
B31	12	17967	48	429	7232	0.0009987	2.1	0.006390	2.7	0.79	0.04641	1.7	6.43	0.14	6.47	0.17
B32	12	31404	52	516	2543	0.001030	1.9	0.006603	2.6	0.71	0.04648	1.8	6.64	0.12	6.68	0.17
B33	12	17560	49	439	11575	0.001014	1.7	0.006339	2.8	0.60	0.04536	2.3	6.53	0.11	6.42	0.18
A1	30	102554	34	324	27452	0.001052	2.0	0.006595	2.1	0.96	0.04548	0.6	6.78	0.14	6.67	0.14
A2	20	54215	46	443	129079	0.001071	2.3	0.006743	2.5	0.91	0.04565	1.0	6.90	0.16	6.82	0.17
A3	20	49867	45	412	38487	0.001018	2.2	0.006431	2.4	0.92	0.04581	1.0	6.56	0.15	6.51	0.16
A4	16	40212	35	329	50084	0.001046	1.8	0.006736	2.7	0.69	0.04672	1.9	6.74	0.12	6.82	0.18
A5	20	51019	42	427	44416	0.001111	1.9	0.006986	2.1	0.89	0.04558	1.0	7.16	0.13	7.07	0.15
A11	20	43843	36	350	58453	0.001068	1.9	0.006791	2.2	0.88	0.04612	1.0	6.88	0.13	6.87	0.15
PI*	80	15255	628	32	20120	0.05392	1.3	0.39411	1.5	0.72	0.05307	0.7	338.5	4.8	337.4	4.1

^a Within-run background-corrected mean ^{207}Pb signal in counts per second. ^b The U and Pb content and the Th/U ratio were calculated relative to GJ-1 reference (LA-ICP-MS values, A. Gerdes, unpubl. data). ^c Corrected for background, within-run Pb/U fractionation and common Pb using Stacey & Kramers (1975) model Pb composition and subsequently normalized to GJ-1 reference (ID-TIMS value/measured value); the ratio $^{207}\text{Pb}/^{235}\text{U}$ is calculated using $^{207}\text{Pb}/^{206}\text{Pb} / (^{238}\text{U}/^{206}\text{Pb} * 1/137.88)$. ^d Rho is the error correlation defined as $\text{err}^{206}\text{Pb}/^{238}\text{U} / \text{err}^{207}\text{Pb}/^{235}\text{U}$. ^e Mean ($n = 12$) and standard deviation (2σ) of the Plešovice (PI) reference zircon.

ages ranging from 3.9 to 7.2 Ma. Fifteen spots on the outer domain of torbernite yielded equivalent and concordant results with a concordia age of 4.55 ± 0.02 Ma ($\text{MSWD}_{\text{C+E}} = 0.94$), which we interpret as the age of torbernite crystallization. Four spots gave slightly lower ages, which are best explained by Pb loss. The remaining 14 spots have $^{206}\text{Pb}/^{238}\text{U}$ ages that scatter between 4.9 and 7.2 Ma, which point either to incorporation of old inherited Pb or to an earlier event of torbernite crystallization.

DISCUSSION

Classification and geodynamic position of the B-bearing THM aplite rich in Fe-Mn-Mg-Sc-U-REE phosphates

The THM aplite intruded into paragneisses and calc-silicates with a mineral assemblage and estimated P-T conditions compatible with those of the “low-pressure facies series” of Miyashiro (1994), the “facies series of type 2a” of Pattison & Tracy (1991), or the “cordierite – K-feldspar zone” described by Vrána *et al.* (1995). The

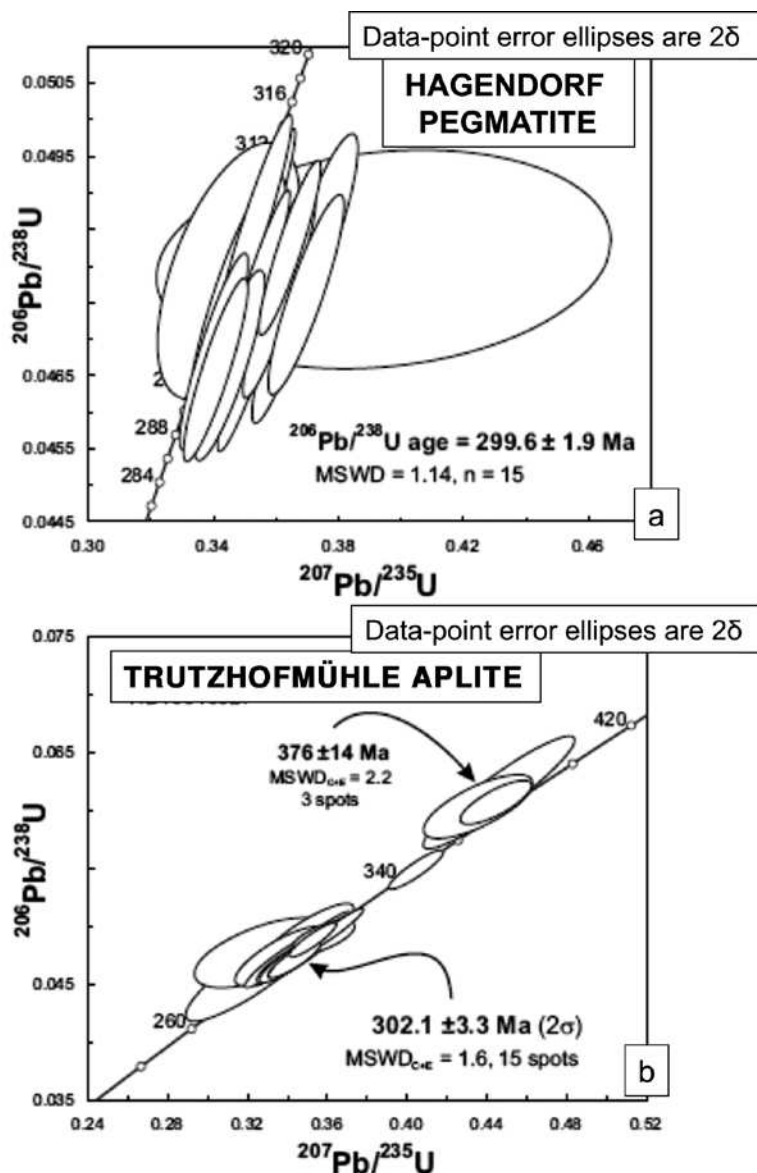
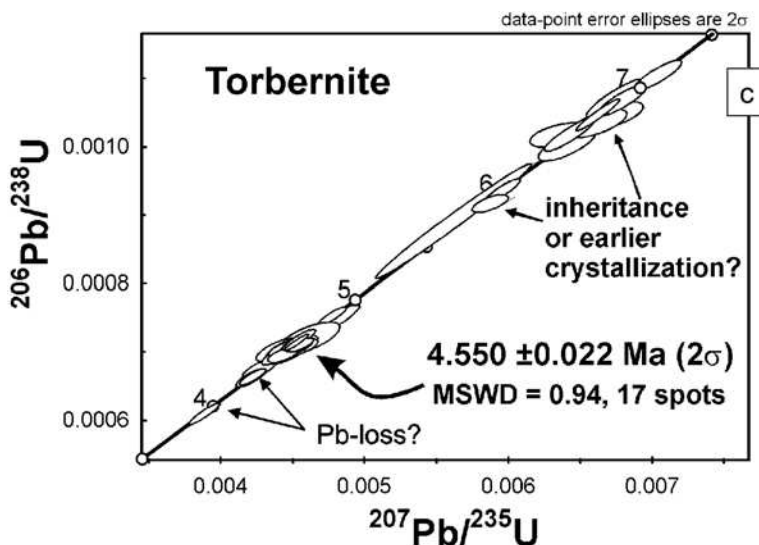


FIG. 9. Age dating of hypogene and supergene minerals from the Hagendorf Pegmatite Province. a) Columbite-(Fe) from the Hagendorf pegmatite. b) Columbite-(Fe) from the Trutzhofmühle aplite. c) Torbernite from the Hagendorf pegmatite.

THM aplite may be classified as a B-bearing phosphate aplite (Table 1). Unlike the neighboring pegmatites of Hagendorf South and North, the THM aplite is poor in Li and does not contain any Li phosphates (Mücke 1987). Similar to the aforementioned pegmatites, the THM aplite is also host to columbite-(Fe). Considering the four classes proposed by Černý (1991) to categorize granitic pegmatites, the THM aplite resembles the LCT

(Li, Cs, Ta) pegmatites with respect to high B and P contents and the low-P Abukuma-type amphibolite-facies conditions preserved in the wallrocks. However, the classification scheme fails to address the conspicuous absence of Li and F in an otherwise Li- and F-enriched environment and the presence of Sc minerals. There are also some chemical features that would place the THM aplite closer to the NYF (Nb, Y, F) pegmatite family,



especially the subclass “REL–REE–MI–REE” (Černý & Ercit 2005). The reference types contain anomalously high values of Sc, Ti, Nb, U, Zr, Y, REE and Th, all of which are present as minerals in the THM aplite. Thus, the family concept of granitic pegmatites does not provide a perfect fit for the THM aplite. Therefore, the similarity between the THM aplite and various reference types may previously be described as follows: $NYF \geq LCT$. The THM boron-bearing phosphate aplite is probably not directly derived from any of the granitic plutons in the vicinity (Fig. 1).

Subdivision of the B-bearing Fe–Mn–Mg–Sc–U–REE phosphate mineralization of the THM aplite

As a rule, phosphate mineralization in pegmatites does not evolve in a unidirectional way, and the overall process of phosphate enrichment involves cross links and a complex evolutionary pathway. Franolet *et al.* (1986), investigating the phosphate mineral associations of the Tsaobismund pegmatite, Namibia, established three associations, each of which, represented schematically in a “genetic spider diagram”, reflects the alteration of phosphate minerals in time and in space. Similar schematic illustrations were presented for the Pleystein quartz pegmatite, Germany, by Wilk (1967), for the pegmatitic bodies around Hagendorf, Germany, by Forster *et al.* (1967), for the Clementine II pegmatite at Okatjimukuju farm, Namibia by Keller & von Knorring (1989) and for the Fermoselle pegmatite, Spain, by Roda Robles *et al.* (1998). However, such a presentation for the THM aplite would suppose an accuracy that is not in accordance with the outcrop situation. Therefore the complex phosphate association of the THM aplite is presented in an easy-to-read x–y plot, where the x-axis

represents the temporal evolution in six stages. The phosphate mineralization is controlled by the temperature of formation, Eh conditions, pH regimes and the state of hydration (Fig. 2).

Along the y-axis, the complex phosphate mineralization is subdivided into six sequences, each controlled by a particular parent material, which is highlighted by diagnostic elements in column one. Two of these phosphate sequences (1a and 1b) resulted from the interaction of phosphate-bearing fluids expelled from the aplite with minerals of the country rocks and, hence, are called as exo-aplitic sequences. Sequences 2 through 5 are termed intra-aplitic because they are independent of the wallrock type and exclusively controlled by the primary phosphates, oxides or sulfides crystallizing from the felsic magma during emplacement. Cross links, such as between manganese-rich apatite and mitridatite or childrenite and rockbridgeite, are not uncommon. One or two stages in a certain sequence may also be absent (Fig. 5a). Leaving these cross links unaddressed does not distort the graphic presentation of the phosphate evolution. In the succeeding paragraphs, the evolution of the phosphate mineralization is discussed sequence by sequence, excluding stage I, which represents the onset of intra-aplitic phosphate mineralization.

Age and the source of phosphate in the THM aplite

Glodny *et al.* (1998) provided a U–Pb age of 482 ± 13 Ma for columbite-group minerals occurring with zircon and monazite in the Domažlice crystalline complex, Czech Republic, and in other aplitic and pegmatitic bodies similar in their structural and textural appearance to the THM aplite. Based upon the intimate intergrowth with rock-forming minerals in the aplite dike,

columbite-(Fe) carrying inclusions of uraninite and barite are assumed to form part of the early magmatic stage-I mineralization (Table 2). The U–Pb age of 302 ± 3 Ma determined for columbite-(Fe) in the THM aplite presumably dates the age of its intrusion and also places an upper limit to the phosphate mineralization discussed in the following sections. The physicochemical conditions under which these minerals formed in the aplite are difficult to constrain. Circumstantial evidence is provided by garnet in the aplite. At relatively low hydrostatic pressures, garnet compositions belong to the pyralospite (pyrope – almandine – spessartine) group (Matthes 1961). For end-member spessartine, the lower reaction limit at pressures between about 200 and 1500 bars occurs at 410°C. For spessartine–almandine solid solution, the limit rises with increasing Alm content from 410°C (Sps₉₀ Alm₁₀) to 500°C (Sps₅₀ Alm₁₀) (Matthes 1961).

Phosphate is concentrated in feldspar and in garnet of the THM aplite, and both may have acted as a source of phosphorus for the secondary phosphates. The question whether garnet may have acted as a source of P to form Li, Fe, Mn and Ca phosphates has been addressed by Breiter *et al.* (2005), but left unanswered since they could not provide clear evidence for any correlation between P in the garnet solid-solution series and the presence of Li, Mn and Fe phosphates. According to their results, there is an effect on the Y and REE distributions in Fe–Mn phosphates. The REE phosphates of stage I are represented by monazite and minor Zr–Sc phosphate-silicate. London *et al.* (1999) found that silicate–phosphate equilibria strongly depend on temperature in granitic bulk-compositions doped with Mn and P. Based upon the weak decrease in the level of P toward the edge of the garnet, we assume an impoverishment in P during crystallization and a transfer of P into the enclosing feldspar matrix, which may have acted as an intermediate repository before P was accommodated into phosphates.

The exo-aplitic Mg–Al phosphate sequence 1a

Magnesium and aluminum are typical of sequence 1a, with lazulite evolving from apatite and being replaced by gordonite during hydrothermal alteration, followed by supergene wavellite. This Mg–Al phosphate assemblage is derived from the decomposition of Al-enriched metapsammopelites. The Al-bearing Mg–Fe phosphate lazulite is the marginal facies of the Mg–Fe–Mn phosphates of the triplite solid-solution series at stage II. The physicochemical conditions of lazulite precipitation have been investigated experimentally by Brunet *et al.* (1998, 2004) and applied in the field among others by Duggan *et al.* (1990) and Morteani & Ackermann (2004). In an environment with abundant borosilicates, as it is the case for the THM aplite, and a pressure of 3.8 kbar, the temperature of formation of the lazulite solid solution is estimated to be

475°C. Such P–T conditions are held to be representative of the stage-II mineral assemblage.

Low-temperature alteration in sequence 1 led to the breakdown of the high-temperature phosphates to wavellite at stage VI. This is a member of the variegated group of Al phosphates that evolve in soils and duricrusts under near-ambient conditions and low concentrations of phosphate (Nriagu 1976, Dill 2001). Generalized stability-relations show that wavellite forms at a pH below 7. Acidic conditions are also indicated by the presence of kaolinite. Variscite or crandallite-group minerals do not exist in this system because increasing acidity of the pore solution and a lowering of the pH value down to 4 causes wavellite precipitation, depending on the activity of H₃PO₄ ($\log a \text{H}_3\text{PO}_4 = -2.75$).

The exo-aplitic Fe–Al phosphates, sequence 1b

This sequence is the Fe-enriched equivalent of sequence 1a, with the childrenite–eosphorite solid-solution series produced by the replacement of Fe-rich chlorite–biotite aggregates and decomposition of Mn-bearing apatite (Fig. 2). Childrenite is the Fe-bearing analogue of gordonite at stages III and IV. A similar scenario has been recorded by Robertson (1982) from the Yukon Territory, Canada, where apatite and lazulite, early epigenetic hydrothermal fracture-fillings, become hydrated during a later stage to childrenite, gordonite, phosphoferrite and vivianite. The phosphate minerals cannot be used to place any constraints on the P–T conditions. The solutions at stage III were slightly acidic, reducing, and apparently carried relatively high concentrations of P, leading to the development of the various Al phosphates as a function of wallrock mineralogy in sequence 1.

The intra-aplitic Ca–Fe–Mn phosphates, sequence 2

Sequence 2 starts with manganiferous apatite, which formed during stage I in the aplite once injected (Fig. 2). The Mn concentrations lie at the lower limit of manganese-rich apatite compiled by Cruft (1966) from various lithologies; the highest Mn concentrations in granitic pegmatites were reported to be in the range 3.0–10.3% MnO. According to Cruft (1966), manganese contents in apatite are explained in part by a replacement of (PO₄)³⁻ by (MnO₄)⁴⁻. Manganese-rich apatite is common in pegmatites, particularly in zoned lithium-rich pegmatites, as at Florence County, Wisconsin, where apatite is rimmed by lithiophyllite and fillowite (Falster *et al.* 1988).

The mafic non-hydrated phosphates of stage II are typical of pegmatites (Fronzel 1949, Forster *et al.* 1967, Keller 1974, Franolet *et al.* 1980, 1986, Lottermoser & Lu 1997). They were hydrated at a lower temperature, giving rise to phosphoferrite, which subsequently transformed into vivianite. Vivianite was reported as an

important hydrothermal discharge associated with the precipitation of nontronite and limonite in deep-water sediments from SiO₂-rich geothermal fluids by Müller & Förstner (1973), but one may find these Fe²⁺ phosphates also in the bottom sediment of many lakes devoid of hydrothermal activity (Manning *et al.* 1991). Manganiferous vivianite has been recorded from many lakes as well (Friedl *et al.* 1997). According to data published by Nriagu (1972) and Wagman *et al.* (1971), vivianite forms at near-ambient conditions at an Eh < 0.2 and above pH 5 in the system Fe – HPO₄²⁻ – Ca, provided the activity of Ca is low. Raising the temperature above 100°C does not significantly change the stability field. As temperatures exceed 200°C under strongly alkaline conditions, apatite may appear instead. Although no precise range of temperature is known for stage III, a hydrothermal alteration of the primary phosphates of stage II into Mn-bearing hydroxy-phosphates of Fe²⁺ is likely (Fig. 2). The Mn component in vivianite [*i.e.*, the reddingite component, Mn₃(PO₄)₂·3 H₂O] raises the stability field of Fe²⁺-hydroxy-phosphate toward higher Eh values and has an overall stabilizing effect on the Fe²⁺–Mn²⁺ hydroxyphosphate.

From stage III to stage IV, the values of Eh increase slightly. A higher redox potential may be inferred from the partial oxidation of divalent Fe accommodated in the structure of ferrous–ferric hydroxyphosphates such as rockbridgeite, in its Al-enriched modification, whitmoreite and “ferrolaueite” (Fig. 2). However, the state of oxidation was less intense than during succeeding stages, as shown by the overgrowth of rockbridgeite onto the latest stages of manganese-rich apatite (stage I). Tiny crystals of rockbridgeite (stage IV) grew onto the globular aggregates of apatite without any intermediate “limonitization”, which would attest to a hiatus with the strongly oxidizing conditions. Up to the precipitation of rockbridgeite of stage IV, mineralization originated from hydrothermal solutions with redox conditions oscillating around Eh = 0. This agrees well with the results obtained by Leavens (1972), who pointed out that rockbridgeite is a byproduct of vivianite breakdown. Although rockbridgeite may be stable over a wide range of pH, we do not assume any significant lowering of the pH below 6. The amount of sulfides present in the THM aplite is too low to have significantly contributed to a marked acidification of the fluids by their decomposition into sulfates, which could have taken place until the onset of stage V. To date, no independent mineralogical confirmation, such as fluid-inclusion data, can be given for the hydrothermal processes in the THM aplite.

The stability fields of mitridatite and rockbridgeite are almost identical (Nriagu & Dell 1974). Therefore, mitridatite formation is favored by the presence of Ca²⁺. Drastic lowering of the Ca supply triggers the formation of rockbridgeite instead of mitridatite. Mitridatite is known to occur with bone material and Fe-rich carbonate beds (Nriagu & Dell 1974). Neither source

will have contributed to the development of mitridatite in the THM aplite. Only primary apatite or decomposed plagioclase could have acted as sources of Ca²⁺. Apatite is found associated with mitridatite, and both minerals dissolve at lower pH. Indirect evidence for the Eh values is provided by the hydroxyphosphate, which replaces mitridatite in the succeeding stage V. All phosphate minerals of sequence 2, stage IV occur in massive or botryoidal form.

Strunzite is indicative of stage V. According to the stability diagram of Nriagu & Dell (1974), the formation of strunzite is favored by low Fe concentration, low pH (<7), and Eh > 0.4 mV. Taking into account an increase in the redox potential, pH values of less than 5 are more realistic for the meteoric fluids. Between stage IV and V, strong oxidation provoked the formation of “limonite”, coating large parts of crystals of rockbridgeite (Fig. 5a). Prior to the precipitation of acicular crystals of strunzite (stage V), solution cavities evolved in globular rockbridgeite. Mineralogical and structural changes suggest pervasive chemical weathering and a marked hiatus late in (or after) stage IV. There are zones of the THM aplite where no dissolution of pre-existing phosphates occurred and strunzite (*i.e.*, stage V) did not evolve.

Beraunite and cacoenite coexist with phosphate-bearing Fe–Mn oxide-hydroxides and kaolinite in stage VI. Beraunite may directly develop from rockbridgeite of stage IV (Fig. 5c). The intergrowth of rockbridgeite with beraunite reflects a gradual replacement of divalent Fe by trivalent Fe (solid-state transformation). This stage-VI association reflects a further lowering of the pH (pH ≤ 4) and Eh values exceeding 0.4 mV. The final stage of alteration in sequence 2 is conducive to a stage characterized by P-bearing oxyhydroxides and kaolinite, which both suggest strongly oxidizing and acidic conditions. Adsorption of phosphate onto goethite is proven by the high phosphate contents of goethite (Table 2). This has been experimentally studied by Gao & Mucci (2001), who characterized the simultaneous adsorption of phosphate onto limonitic material. Following the pedological studies by Freese *et al.* (1995) and Gustafsson (2001), this type of iron mineralization is part of the formation of acidic soils during the post-glacial period, when the most reactive adsorbents, such as ferrihydrite, Al-humus complexes and phosphate transformed into complex Al-phosphate-bearing goethite in the supergene zone of the THM aplite. Various Fe-bearing phosphates and changing redox conditions observed in the different stages are conducive to a variety of colors of the rocks, which may be applied to the subdivision of the various stages (Fig. 2).

The intra-aplitic Ba–Sc–Zr phosphates, sequence 3

Scandium and zirconium are the most important marker elements of sequence 3 (Fig. 2). To trace this sequence back to rock-forming minerals, all minerals

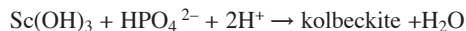
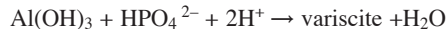
relevant as potential sources of Sc within the THM aplite and its neighboring rocks have been investigated. Columbite-group minerals are potential source-minerals of Sc (Dill *et al.* 2006b). Our results agree with the data published by Kempe & Wolf (2006), who also found considerable Sc in columbite. At 25°C, scandium phosphate is more stable than the corresponding hydroxide, which is most relevant to the transport of Sc in hydrothermal solutions (Wood & Samson 2006). Zirconium is suspected to be liberated from zircon, which is ubiquitous in the paragneisses and also in some of the aplitic bodies.

Scandium minerals appear early in stage II, and are represented by two unnamed new phosphates both intergrown with manganese-rich apatite. Textural observations suggest that both the K–Ba–Zr phosphate and the Sc–Zr phosphate(-silicate) are magmatic high-temperature phases. Their fields of stability presumably overlap with those of Sc silicates (thortveitite, bazzite, cascandite, jervisite, kristiansenite, scandiobabingtonite), which were reported as late-stage phases in cavities of granitic NYF-type pegmatites mainly in Italy and Norway (Mellini *et al.* 1982, Bergstøl & Juve 1988, Foord *et al.* 1993, Orlandi *et al.* 1998, Raade *et al.* 2002). In the THM aplite, scandium was extracted from the silicate liquid and partitioned into fluids owing to the complexing effect of phosphate, which became more and more prominent in the latest stages of the evolution. A comparison of these Sc mineral occurrences reported from Norway and Italy with the Sc mineralization in the THM aplite demonstrates that fluorine and phosphate are crucial as complexing agents triggering which way Sc mineralization evolves during pegmatite–aplite emplacement and their subsequent hypogene and supergene alteration. High fluorine contents as at Baveno, Italy, and Heftetjern, Tørdal, Norway, are responsible for the overall presence of Sc silicates commonly accompanied by fluorite and Li-rich mica, whereas scandium phosphates such as kolbeckite and pretulite are absent at these sites. In contrast, fluorine contents are very low in the THM aplite. Minor amounts of F are recognized only in some minerals of stage II. Not surprisingly, in view of the poor F contents, there is only one mixed-type Sc phosphate(-silicate) out of four Sc minerals determined in the THM aplite, and Sc phosphates are the dominant species.

Kolbeckite is present as two textural types: as tabular crystals (type I) intergrown with quartz, and as stubby crystals (type II) occurring in quartz strongly corroded by dissolution and coated by limonite. Thus, platy type-I kolbeckite presumably formed under reducing conditions, *e.g.*, it is late hydrothermal, formed at stage IV (Fig. 5d), whereas kolbeckite of type II crystallized during strong “limonitization” at stage V.

For the formation of kolbeckite, the exact timing of Sc release from its source minerals during alteration of the primary minerals is most important. Phosphate provided by the decomposition of primary phosphates

reacted with Mn, Fe and Al to form secondary phosphates such as rockbridgeite, mitridatite and members of the series childrenite–eosphorite. The formation of separate Sc phosphates was impeded by the preponderance of Fe and Al and would have led to variscite or Fe³⁺ phosphate according to the reaction below:



During an advanced stage of chemical weathering at stage V, the weathering front was lowered in depth. Pervasive chemical weathering almost completely removed the topmost K-feldspar zone so that only a relict siliceous core and little feldspar remained. Scandium accommodated in the unit cell of columbite together with the trace amounts found in the host rutile and ilmenite in the country rocks were likely released into a weathering zone already strongly depleted in Fe and Al, and Sc could therefore form minerals of its own instead of being captured as a trace element in Fe-rich phosphates (Table 3). This shortage in Fe was attained during sequence 2, just after the formation of mitridatite, which is the only secondary hydroxide phosphate containing notable amounts of Sc, up to 0.13 wt.% Sc (Table 3). On the other hand, the only trace elements detected in kolbeckite are Fe and Ca (Dill *et al.* 2006b). There is little doubt that supergene kolbeckite II formed just after mitridatite, whereas kolbeckite I is a low-temperature hydrothermal mineral accompanying mitridatite at stage IV.

It has been known for decades that single crystals (carbonate minerals, sulfates, quartz, sphalerite) grown under hydrothermal conditions may adopt various morphologies (Kalb 1931, Hartman & Perdok 1955). The analysis of atomic structures of the $\{hkl\}$ faces and the sequence of change in the growth rate have been explained by different chemical compositions, the effect of additives and varying physicochemical conditions (Eh, pH, T, P). It would be premature to draw any definite conclusions from the morphological variations of kolbeckite crystals based on our field studies, but the observations made during other studies can be tested by data from the literature. Hydrothermal or early varieties of a certain mineral species develop rather simple combinations of faces, whereas late-stage or supergene varieties of the same mineral tend to develop complex mineral aggregates (Dowty 1976, Hartman & Strom 1989, Dill & Kemper 1990, Bernstein *et al.* 1992, Kostov & Kostov 1999, Weber 2008). Such crystallographic relations, albeit not ranked as a geothermometer, may be used as a rough tool to constrain the temperature of formation (high *versus* low) and assist in the mineral-based-stratigraphic subdivision of mineralizing processes.

Kolbeckite was subsequently replaced by churchite-(Y) containing some Sc. At stage VI, autunite and the

unknown Sc–Fe-bearing uranyl phosphate are present. Owing to the state of oxidation at stage VI, iron cannot be expected to occur as Fe^{2+} and to form the common uranyl phosphate bassettite. It is likely to be a new Sc-bearing mineral structurally close to what has been described as vochtenite. Because its description is based solely on SEM–EDX analysis, this mineral is listed with question marks in Figure 2.

The intra-aplitic U–REE phosphates, sequence 4

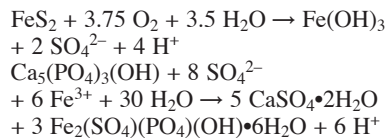
Sequence 4 originated from monazite of stage I, which is replaced by a mineral of the leermontovite – vyacheslavite series during stage III. This hydration took place under reducing conditions in a way quite similar to that described for Fe and Mn in sequence 2. In stage VI, this mineralization was transformed under more oxidizing conditions into churchite-(Y), equivalent to sequence 3 (Fig. 2).

The intra-aplitic S–Zn phosphate, sequence 5

Sequence 5 is made up of two generations of keckite, one occurring as massive (I) aggregates at stage IV, and the other overgrowing rockbridgeite at stage V, and diadochite, all of which have originated from the decomposition of sulfides of stage II – III (Fig. 2). The Cu–Zn sulfides are minor constituents of the mineralized zone and also very different from the sulfide mineralization in Hagendorf South, both in quality and in quantity. The Fe-poor sphalerite from the THM aplite resembles that in the so-called mesothermal Pb–Zn veins found across central Europe, and is different from the marmatitic (Fe-rich) sphalerite at Hagendorf, which is known to have precipitated very early during the emplacement of the pegmatite (Mücke 2000, Dill *et al.* 2008).

Zinc sulfides gradually pass into the Ca-enriched part of the late hydrothermal phosphate mineralization of stage IV and end up as keckite I, forming botryoidal fibrous lamellae (Fig. 5c). After a hiatus, another generation, keckite II, was emplaced by supergene alteration at stage V. Sulfides were exposed to erosion rather late. Otherwise, mixed aluminum phosphates and sulfates of the alunite supergroup would have formed instead of the variegated spectrum of hydroxide phosphates recorded in sequence 2 (Dill 2001, Dill *et al.* 1991).

The Fe sulfide was oxidized, and the resultant sulfate reacted with apatite to form diadochite and gypsum, which were washed out from the soil.



Synopsis and correlation of phosphate mineralization in the Hagendorf pegmatite province

Magmatic and hydrothermal phosphates of stages I to IV: The intrusion of the post-kinematic, S-type, calc-alkaline Flossenbürg granite dated at 312 ± 3 Ma has had a chemical impact on the emplacement of the pegmatitic bodies around Hagendorf and Pleystein, which are enriched in Li, but was only of minor impact on the quartz–feldspar mineralization of the Li-free THM aplite at the edge of the Hagendorf pegmatite field. The concentration of Mn-bearing apatite common to the Hagendorf pegmatite and the THM aplite (early magmatic stage I) may be attributed to the youngest granitic activity in this region (Wendt *et al.* 1994). The early magmatic stage I of the THM aplite took place around 302 ± 3 Ma, but later at 299 ± 2 Ma in the neighboring Hagendorf pegmatite. The late magmatic stage II and early hydrothermal stage III may be encountered in the LCT-type Hagendorf pegmatite (Li–Fe–Mn) and in the NYF $\geq$ LCT THM aplite (Sc–Ba–Zr–Mg–Fe–Mn), although with a different spectrum of cations bound to the phosphates. These phosphates occur as massive aggregates or vein fillings. The presence of Sc-bearing columbite-(Fe), barite, monazite and garnet in the Trutzhofmühle area was responsible for the extraordinary assemblage of phosphates recorded from sequences 2 through 5. Phosphates of sequences 1a and 1b, which were not found at Hagendorf, resulted from reactions between the gneissic country-rocks and phosphate-bearing solutions derived from the THM aplite. Notable differences in the phosphate mineralization between the phosphate THM aplite and Hagendorf pegmatite are caused by different levels of formation, with the THM phosphate-rich aplite being at a deeper level than Hagendorf South.

Early supergene phosphates of stage V: These phosphates may be recognized in several phosphate-bearing pegmatites and aplites in the area and are interpreted as supergene. The age of weathering is assumed to be pre-Tertiary, and its onset is marked by the change in the redox conditions at the boundary between stage IV and V. The supergene stage V is characterized by strong “limonitization” and several hiatuses.

Late supergene phosphates of stage VI: Phosphates of stage VI may be recognized also in the quartz veins adjacent to the THM aplite (Fig. 1). Minerals of the gorcixite – florencite – plumbogummite – crandallite series and variscite intergrown with each other and phosphate-bearing “leucoxene” are representative of this stage VI in the quartz veins (Dill *et al.* 2006a, 2007a). It is related in time and space to the Miocene peneplanation (Fig. 9c).

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