

Zeitschrift: Schweizerische mineralogische und petrographische Mitteilungen = Bulletin suisse de minéralogie et pétrographie
Band: 70 (1990)
Heft: 3

Artikel: Brannerite from Lengenbach, Binntal (Switzerland)
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DOI: <https://doi.org/10.5169/seals-53623>

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Brannerite from Lengenbach, Binntal (Switzerland)

by Stefan Graeser¹ and Richard Guggenheim²

Abstract

A small idiomorphic crystal of brannerite (UTi_2O_6) included in and completely overgrown by the sulphosalt mineral sartorite (PbAs_2S_4) was found at the famous sulphosalt locality Lengenbach in Binntal (Switzerland). It is a strange fact that this crystal, in contrast to normal brannerite, is not completely metamict but could be X-rayed using Gandolfi, Weissenberg, and Precession techniques without preceding heat treatment. The study gave the following data: space group $I2/m$, $a = 8.87$ (1), $b = 3.703$ (2), $c = 6.797$ (4) Å, $\beta = 104.07^\circ$. A goniometrical investigation of the ideally shaped crystal yielded a remarkable number of face forms: (001), (101), ($\bar{1}01$), (401), (110), ($\bar{2}11$), (211), (411), ($\bar{4}11$), (023)? The comparison of axial ratios calculated from the X-ray study, and goniometrical measurements, respectively, suggests that by the beginning metamictization process the volume did not increase but, unexpectedly, seemed to decrease. Likewise, the cell volume of the natural mineral ($V = 217 \text{ Å}^3$) is slightly smaller than that of the fresh, synthesized crystals ($V = 224 \text{ Å}^3$). The peculiar fact that brannerite from Lengenbach is only slightly metamict may be due to the comparatively young age of the mineral (about 11 m.y.) and its hydrothermal origin.

Keywords: Brannerite, metamict state, X-ray diffraction, optical goniometry, SEM, Lengenbach, Binntal, Switzerland.

1. Introduction

The mineral quarry Lengenbach in Binntal (Ct. Valais, Switzerland) has become famous for its large number of very special sulphosalt minerals found over a period of more than 200 years. These sulphosalts are mainly composed of elements like Pb, Cu, Tl, Ag, As, and sulphur; they occur in a series of a white, sugary dolomite of Triassic age. For the last 30 years, the minerals have been exploited by a syndicate of Swiss museums, university institutes and private persons for purely scientific interest. When looking through the great number of mineral samples that have been collected each year by the syndicate, we found a very uncommon mineral intimately intergrown with the more familiar sulphosalt minerals. The consequent investigation of this mineral led to the result that it was no sulphide but a U-Ti-oxide in the form of brannerite. The occurrence of brannerite in Lengenbach, its remarkable shape, and very special properties gave rise to this description. Perhaps it should be mentioned that the find of this tiny brannerite crystal remained unique: no second specimen was found within the subsequent 10 years. The reason

for the long delay in this study was caused by the difficulty to interpret correctly the crystal faces found by the use of optical goniometry. It was the latest version of the crystal drawing program SHAPE (DOWTY, 1989) that enabled this project.

It was on specimen L 14213 of the official Lengenbach exploitation which contained a sartorite crystal (PbAs_2S_4) of about 8 mm length that we detected the point of a minute crystal which was almost completely covered by the surrounding sartorite material. As this overgrown mineral looked very uncommon we decided to destroy the surrounding sartorite and were extremely surprised to dig out a nearly perfect crystal of prismatic habit of 0.6 mm length (Fig. 1). It was this sole crystal which served as object for all the investigations described in this work. Though we waited for years to find additional material, this crystal remains the only sample of brannerite in Lengenbach up to this day.

2. X-ray diffraction study

As there existed just this unique specimen of 0.6 mm length of the completely unknown mineral,

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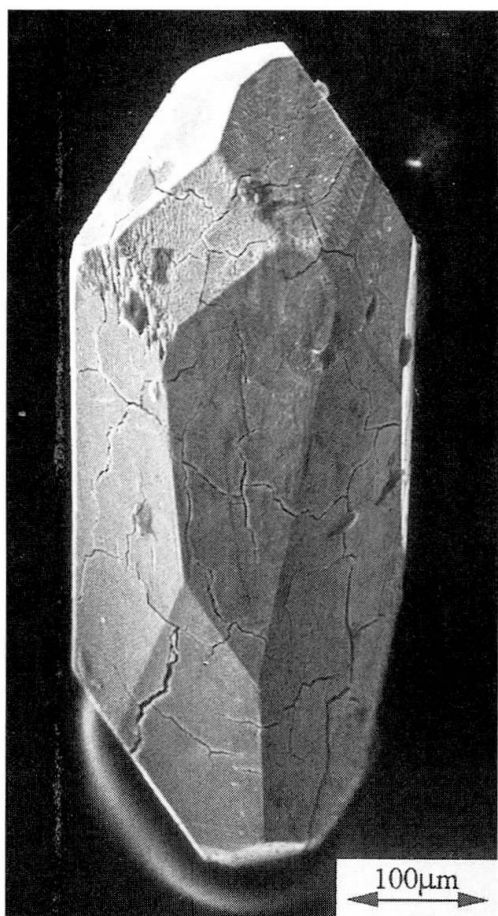


Fig. 1 Brannerite, Lengenbach: SEM photograph at low magnification.

we had to choose special methods of investigation. The first step was to X-ray the mineral by Gandolfi techniques. The result was a powder diagram with about twenty weak and partly broadened diffraction lines. The relatively poor quality of the film was attributed primarily to the size of the crystal, too large for the Gandolfi device. From the d-val-

ues, however, a straightforward determination of the mineral was not possible. In comparing the powder diagrams of ignited brannerite (PDF card 8-002), synthetic brannerite (PDF card 12-477), and the Gandolfi film of our untreated brannerite it becomes obvious that an identification by this procedure could not be attained: the d-values as well as the intensity data for the three samples show remarkable differences (see Fig. 2, Tab. 1). In the case of the Lengenbach brannerite this might be partly caused by the Gandolfi technique, as any orientation effect during the exposure is excluded. Anyway, the differences between synthetic material and ignited brannerite are remarkable, and even between crystals that were recrystallised at varying heating conditions there exist essential differences in the powder diagrams (cf. BIANCONI and SIMONETTI, 1967).

The next step to arrive at an identification was the single crystal method by Weissenberg and Precession techniques. In this case, too, the quality of the diffraction patterns was quite poor – yet, the single crystal data unambiguously pointed towards the uranium-mineral brannerite and thus the bad quality of the reflections became obvious: it was caused by the beginning of metamictization of a uranium bearing mineral.

From the diffraction patterns the following extinction rules could be derived: for hkl : $h + k + l = 2n$, for $0kl$: $k + l = 2n$, for $h0l$: $h + l = 2n$, and for $hk0$: $h + k = 2n$. As the crystal symmetry was found to be monoclinic, the space group was determined as $I2/m$. It is generally known that in the monoclinic system the body-centered cell may be described by a C-centered cell as is usually done. For morphological reasons (see below) we prefer the body-centered cell in this special case for brannerite from Lengenbach.

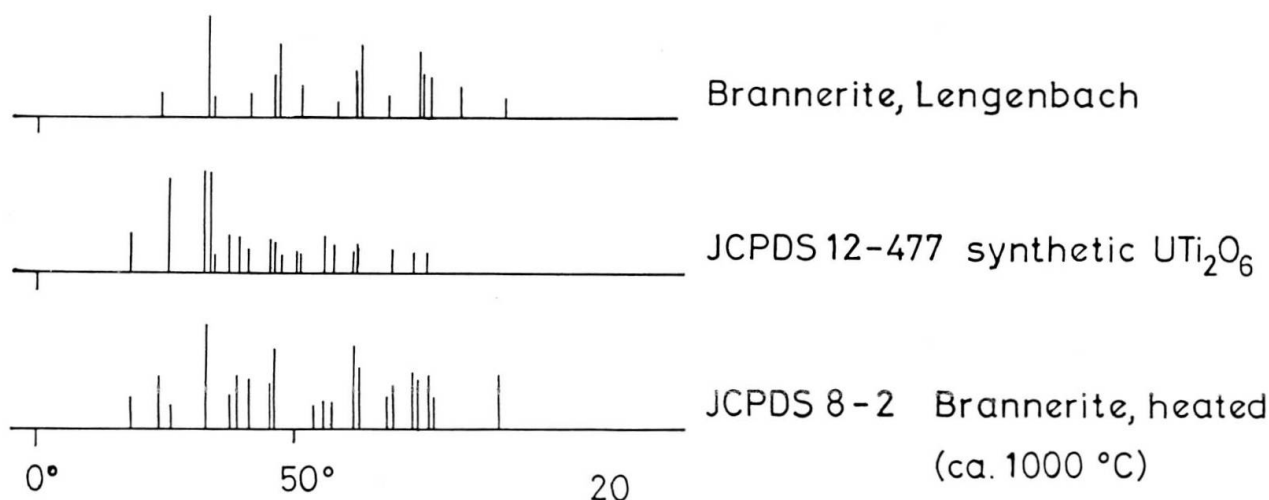


Fig. 2 Powder diagrams of brannerite: untreated, synthetic material, and natural brannerite (ignited at ca. 1000 °C).

Tab. 1 d-values of untreated brannerite (Gandolfi camera).

GANDOLFI DATA		(I2/m)		(C2/m)	
I/I ₁	d _{obs} (Å)	d _{calc}	hkl	d _{calc}	hkl
20	4.690	4.709	101	4.704	-201
100	3.402	3.401	110	3.412	110
30	3.282	3.297	002	3.284	-202
30	2.752	2.743	-211	2.754	111
40	2.491	2.490	-112	2.490	-112
80	2.446	2.446	211	2.451	-311
30	2.260	2.261	112	2.260	-312
10	2.008	2.015	103	2.009	-403
50	1.891	1.890	013	1.886	-313
70	1.860	1.852	020	1.857	020
20	1.729	1.723	121	1.727	-221
60	1.615	1.614	022	1.616	-222
40	1.598	1.594	-413	1.599	113
40	1.570	1.570	303	1.568	510
30	1.475	1.475	-314	1.475	-421
10	1.363	1.363	123	1.363	-423

Gandolfi camera, 114.7 mm FeK α -radiation

3. Electron microscopical investigation (SEM)

Even by inspection under small magnification with a binocular microscope it became obvious that the tiny crystal is perfectly shaped and displays no sign of any damage. In order to get high quality pictures of this very uncommon mineral we decided to study the crystal by SEM techniques, too, especially because this kind of study offered the possibility to check the chemical composition of the mineral. This additional investigation appeared even more important as the identification of the mineral using only single crystal X-ray diffraction was not conclusive. The occurrence of one single U-Ti-oxide mineral among and intimately intergrown with the typical Lengenbach sulphosalts represented indeed a highly unexpected fact!

The electron microscopical studies were carried out on the scanning electron microscope at the Geological Institute (Cambridge Stereoscan Mark 2A, equipped with EDAX-System model 707). The pictures in small scale magnification show the perfectly shaped crystal of columnar habit and a remarkable number of different crystal faces (Fig. 1). For the discussion of the additional pictures at higher magnifications, see below under "Metamict State".

For the SEM study, the crystal was mounted on a carbon plate of spectral pure quality and covered

with carbon. The EDS analyses, performed on various spots of the crystal, yielded always identical data (mainly uranium and titanium, with traces of calcium and silicon as impurities, see Fig. 3) thus confirming unambiguously the results of the X-ray study: the crystal dealt with represents indeed the U-Ti-mineral brannerite!

4. Goniometrical measurements

The ideal shape of the crystal was a challenge to undertake a crystal measurement on the goniometer though it was obvious that the extremely small size would be a real handicap. The tentative measurements were carried out on an optical goniometer (type NEDINSCO/TERPSTRA). The crystal was mounted on the Weissenberg Goniometer head with the same adjustment that was used for the X-ray work. The first results were very encouraging as the reflex signals turned out to be clearly recognisable. Yet, the great difficulty arose from the fact that the goniometer's telescope was too weak to recognise which reflex belonged to which face. We could quite easily compute axial ratios and the Miller indices but it became very problematic to attribute the indices to the right faces. From the goniometrical measurements resulted about 10 different forms for which indices could be calculated (see Tab. 2, Fig. 4).

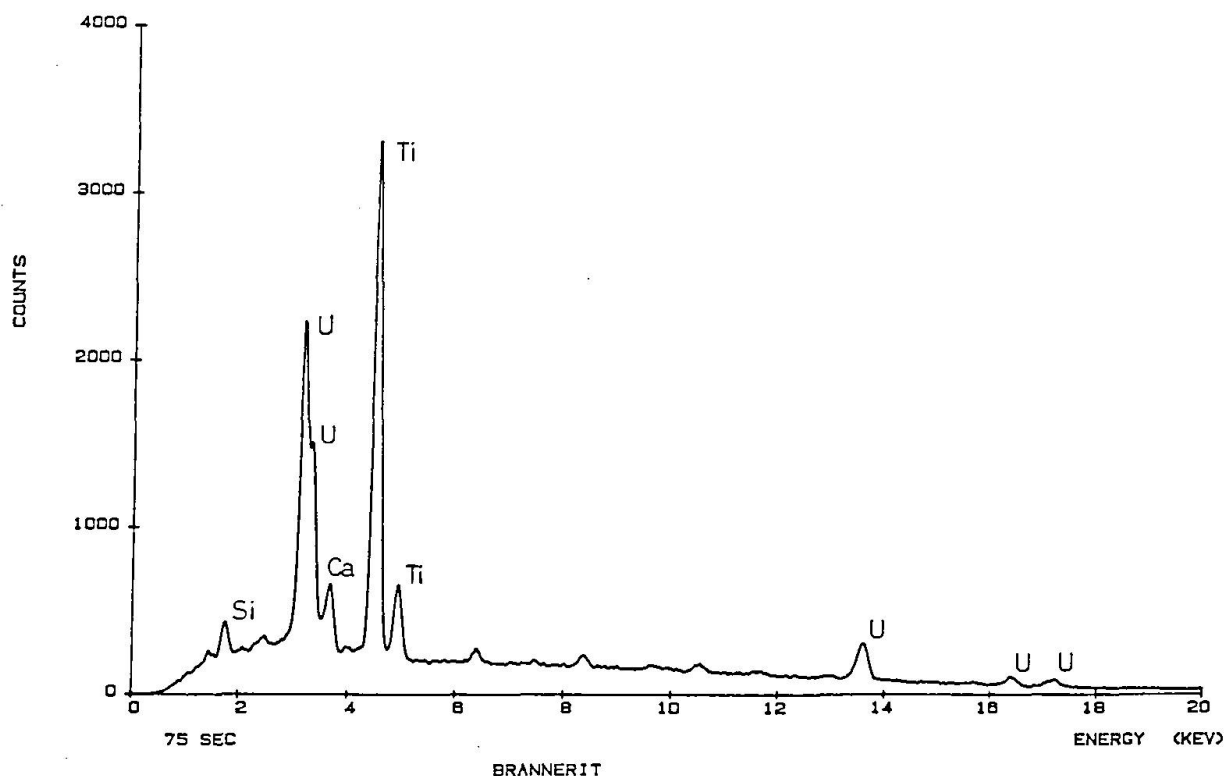


Fig. 3 Qualitative EDS-analysis of Lengenbach brannerite.

The crystal is elongated along the roentgenographic a-axis, but for morphological considerations we preferred to take the elongated axis as the c-axis; the face indices are computed taking c as the elongation axis. Compared with the single crystal data, a- and c-axes are interchanged.

BIANCONI and SIMONETTI (1967) described the first Swiss occurrence of brannerite in the form of well developed crystals from pegmatites in the Le-

ventina gneisses (Ct. Ticino). These crystals show a completely different morphology compared to our Binntal brannerite: according to the crystal drawings in the publication they are platy along the (102) face, elongated in the direction of the b-axis and show a much smaller variability of crystal faces. Unfortunately, from the description it becomes not obvious how the crystals were orientated nor what kind of axial ratios were computed. Moreover, be-

Tab. 2 Ψ - and ρ -angles from optical goniometry.

Indices h k l	F_{obs}	R_{obs}	F_{calc}	R_{calc}
001	90°	15.75°	90°	15.75°
-101	-90	48.2	-90	49.4
101	90	58.4	90	59.9
401	90	80.4	90	80.6
110	29.7	90	29.7	90
-211	-45.1	74.2	-45.8	74.6
211			51.4	76.2
-411	-65.3	80.7	-65.3	80.6
411	66.1	80.9	67.3	81.4
?? 023	11.5	57.8	9.5	59.8

$$\beta = 105.75^\circ$$

$$a : 1 : c = 1.821 : 1 : 2.538$$

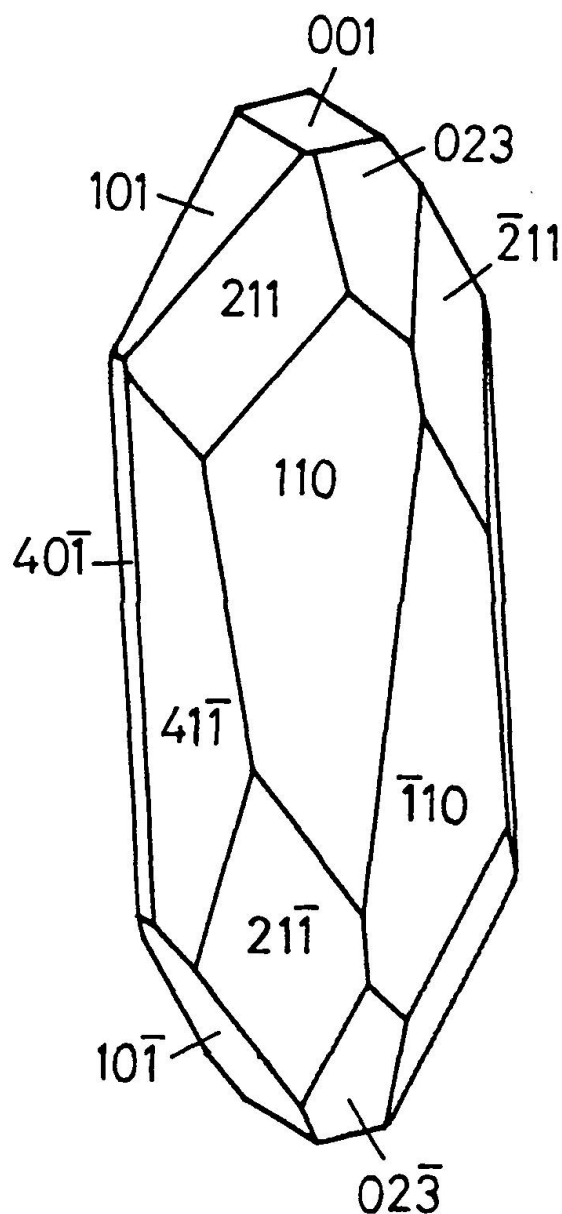


Fig. 4 Idealized crystal drawing according to the goniometrical measurement.

cause of some obscurities, it is not possible to calculate axial ratios from the published data of measured face angles.

5. Metamict state

From all that we could learn about the mineral brannerite, this unique crystal from Lengenbach seems to represent the first natural brannerite so far that was not completely metamict and therefore could be X-rayed without preceding ignition. Obviously, as stated in the work by BIANCONI and SIMONETTI (1967), the recrystallization process by ignition produces differing d -values depending on the degree and duration of the heating treatment. Additionally, the d -spacings of synthetic brannerite

are not fully compatible with values obtained from any ignited natural brannerite. This is the reason why our Lengenbach brannerite could not be identified by only the Gandolfi diagram.

However, our X-ray study by Gandolfi, Weissenberg and Precession techniques clearly proved that the structure of the mineral had suffered from the radioactive decay of the uranium. The weak and diffuse lines of the Gandolfi diagram and the broad reflections on the single crystal films provide unambiguous evidence for this beginning metamictization.

Further impressive indications were gained from the SEM pictures. If the crystal is studied with higher magnifications, the quality of the faces becomes more and more rough and strange cracks cutting through the surface could be observed (Figs. 5 and 6). The first and presumably the correct impression of these features was that they represent expansion cracks caused by an increase in the volume. As is well known, the transition from crystalline state to the amorphous state generally is coupled with a remarkable increase in volume. Therefore, the metamictization process that finally changes the crystal into a glassy mass will cause a change of the crystal volume, too. A result that is documented in this case by the characteristic expansion cracks.

The crystallographical study of the mineral, especially the fact that on the same crystal structural phenomena could be studied by X-rays and morphological properties by goniometrical measurements enabled a very special investigation: while the morphology and axial ratios calculated from crystal faces are assumed to act as indicators for the original unmetamict state of the mineral, structural properties like lattice parameters, etc. undoubtedly will characterize the actual partially metamict state of our brannerite. It is this point that yields a strange inconsistency: with the axial ratios determined by optical goniometry, and single crystal X-ray diffraction, respectively, we have a means of directly comparing the two states in the mineral's history. As is well known from the mineral zircon, the increase of the c -parameter by progressive metamictization was occasionally used to determine the age of the mineral. Yet, in the case of the described brannerite the data are puzzling.

Axial ratios of brannerite from Lengenbach:

X-ray diffraction: $a : 1 : c = 2.395 : 1 : 1.835$
 optical goniometer: $a : 1 : c = 2.538 : 1 : 1.821$
 (a/c exchanged)

Provided that the lattice parameters for b_0 and c_0 were not essentially changed by the metamictiza-

Tab. 3 Cell parameters of brannerite from Lengenbach (refined from Gandolfi film), and for synthetic material.

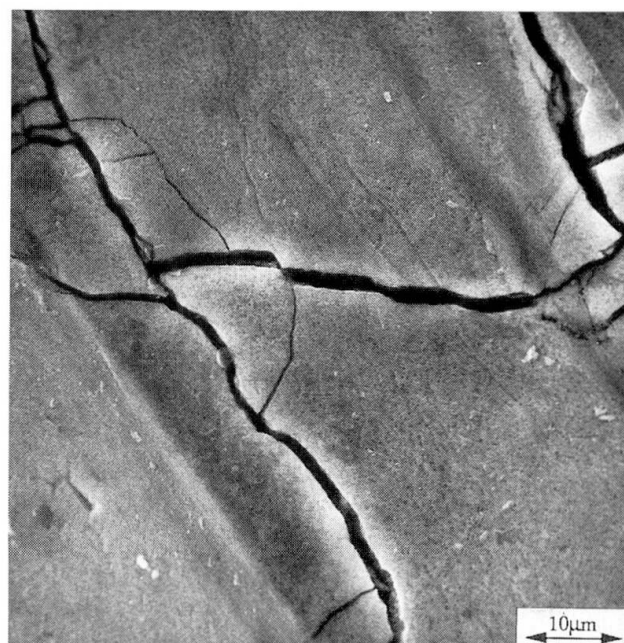
		I2/m ¹⁾		C2/m ¹⁾		synthetic ²⁾
a	=	8.87	(1) Å	9.79	(1) Å	9.87
A b	=	3.703	(2)	3.714	(3)	3.76
c	=	6.797	(4)	6.776	(7)	6.95
beta	=	104.07°	(3)	117.92°	(8)	119.5°
V	=	217 Å ³		217 Å ³		224 Å ³
a : 1 : c	=	2.395 : 1 : 1.835		2.636 : 1 : 1.824		2.625 : 1 : 1.848

¹⁾ natural brannerite (this work)
²⁾ synthetic UTi₂O₆ (PATCHETT AND NUFFIELD, 1960)

tion process (as suggested by the closely related values for these two axial ratios), then the crystal lattice would not have been enlarged but, on the contrary, would have shrunk by a considerable amount: from the goniometrical ratios a fictitious «a₀-value» could be calculated of about 9.4 Å for the unmetamict mineral! This speculation would suggest that the a₀-parameter decreased from a primary value of about 9.4 Å to the actual value of 8.87 Å for the slightly metamict mineral. Of course, we are aware of the absurdity of such considerations but, at the moment, we are unable to offer a more reasonable explanation for the phenomenon.

At all events, this inconsistency cannot be explained by inaccuracy of the goniometer measurements, the discrepancy lying far off the error limit. The same mystery, besides, becomes apparent if we compare the lattice data of the natural mineral with synthetic brannerite (see Tab. 3): cell parameters and cell volume seem to be smaller for the natural slightly metamict brannerite than for the fresh synthetic UTi₂O₆.

There remains another problem for which we cannot provide a fully satisfying answer at this time: the obviously non-metamict state of the mineral. Any studies on X-ray diffraction of brannerite that we could find in literature were carried out on ignited or synthetic material. The Lengenbach brannerite, though clearly showing the traces of



Figs 5 and 6 SEM pictures at higher magnification, showing the influence of beginning metamictization.

advanced metamictization, yielded unambiguous diffraction data for Gandolfi system and single crystal methods as well. In a mineral like brannerite where uranium is an integer constituent of the structure and not just an impurity, the metamictization process is a clear function of time, provided that the composition is stoichiometric as is undoubtedly to be expected. Unfortunately, for most of the brannerite descriptions no explicit age data are communicated but in many cases the crystals dealt with originate from much older rocks than the Swiss occurrences. In their description of Lodrino brannerite (BIANCONI and SIMONETTI, 1967), the authors indicated that a radiometric age determination on the mineral would be carried out but no such data have become available so far (V. KÖPPEL, private communication). Anyway, there exist some radiometric data on pegmatites of the region, and these show clear Alpine ages of about 20–25 m.y. (KÖPPEL, 1990). For the brannerite this age presumably represents a maximum age as its formation occurred subsequent to the pegmatitic stage. Even in this case, the young Alpine formation obviously was not adequate to prevent the brannerite from complete metamictization. For the Lengenbach brannerite, too, no direct age data are available, but there exist K–Ar determinations on accompanying feldspar minerals (hyalophane) from the Lengenbach quarry itself yielding an age of 11.4 m.y. (PURDY and STALDER, 1973). Distinct from the pegmatitic formation of brannerite at Lodrino, all the minerals in the dolomite at Lengenbach are of hydrothermal origin, including the hyalophane, sulphosalts, and brannerite. The age data for hyalophane obviously should agree with that for the mineral brannerite, likewise. By this, our brannerite's age is half of that of the Lodrino

mineral, yet, it remains an open question if only this difference in the age is responsible for the different behaviour of the two occurrences or if perhaps the different origin – pegmatitic versus hydrothermal formation – too, had some influence.

Acknowledgements

The "Arbeitsgemeinschaft Lengenbach", the syndicate exploiting the Lengenbach minerals, kindly provided us with the sample containing the brannerite crystal. We are greatly obliged to Marcel Düggelein (SEM Laboratory) who operated the SEM.

John B. Saunders, Natural History Museum Basel, corrected and commented the English version of the manuscript.

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Manuscript received August 2, 1990; accepted September 20, 1990.