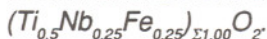


# (Nb,Fe)-substituted anatase from Herrebøkasa, Østfold, Norway

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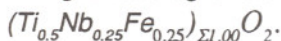
## Abstract

Fine-grained yellow anatase, forming pseudomorphs after euxenite or polycrase, has a larger unit cell than normal anatase and a composition close to



## Sammendrag

Finkornet gul anatas som danner pseudomorfoser etter euxenitt eller polykras, har en større celle enn vanlig anatas og en sammensetning nær



## Introduction

A fine-grained yellow mineral - formed by the alteration of a metamict mineral (euxenite or polycrase) from the Herrebøkasa granite pegmatite in Østfold - gives an X-ray powder pattern of anatase, but with distinctly smaller spacing (larger unit cell). Since we have only a 9 cm Debye-Scherrer film without any internal standard, we see no point in calculating the cell parameters. The aim of the present article is to report and discuss the results of a chemical analysis of this substance.

## The material

The investigated specimen was collected by RK in 1970. It measures 2x4.5 cm, consists mainly of microcline and quartz and has a 1.8 cm long monazite crystal perched on it. A light brown glassy mineral gave an X-ray powder pattern of zircon after heating to 1000°C for 24 hrs. The dull yellow substance (anatase) forms pseudomorphs after prismatic crystals up to 0.5 cm long. Backscatter photomicrographs clearly show the replacement of the original mineral by anatase (Fig. 1). An energy-dispersive spectrum shows Y, Nb, Ti, U, and Th to be the main constituents of the precursor. From this composition and the crystal shape, the original mineral could have been euxenite or polycrase.

Nilssen (1970) described samarskite and a yellow mineral surrounding it and filling cracks in the mineral from Herrebøkasa (called Aspedammen in her paper). The TiO<sub>2</sub> content of this samarskite is only 4.04 wt.%, and it can hardly be regarded as the primary mineral of the pseudomorphs we describe here. The yellow mineral investigated by Nilssen (1970) has a composition similar to that of its associated samarskite, being formed by leaching of Ca and U, some oxidation and a further uptake of water. It is completely metamict but gave a distinct powder pattern after being heated to 1000°C in air. It is quite different from the yellow

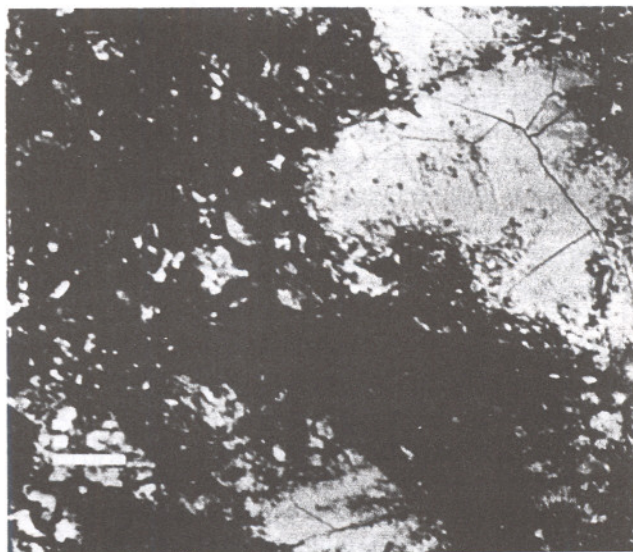


Fig. 1. Remnants of metamict mineral (light areas) partly replaced by (Nb,Fe)-substituted anatase (dark areas). Herrebøkasa granite pegmatite, Østfold, Norway. Backscatter photomicrograph. Scale bar is 100 µm.

mineral we have encountered.

## Chemical data

The anatase was analyzed with a Cameca Camebax electron microprobe operated at 15 kV. Standards were wollastonite (Si), pyrophanite (Ti), hematite (Fe), Nb and Ta metals. The analytical sums are variable due to fluctuating beam currents (17.3-20.5 nA). Two analyses with sums near 100% are:

SiO <sub>2</sub>	0.88	0.80
TiO <sub>2</sub>	44.06	44.46
Fe <sub>2</sub> O <sub>3</sub>	18.96	20.44
Nb <sub>2</sub> O <sub>5</sub>	33.06	31.11
Ta <sub>2</sub> O <sub>5</sub>	1.61	1.61
Sum	98.57	98.42

All the 11 analyses performed show remarkably similar atomic proportions, based on 2 oxygens (standard deviations in parentheses):

Si	0.015	(0.007)
Ti	0.51	(0.02)
Fe <sup>3+</sup>	0.23	(0.01)
Nb	0.24	(0.02)
Ta	0.005	(0.002)
Sum	1.000	

The chemical formula of this anatase is thus very close to (Ti<sub>0.5</sub>Nb<sub>0.25</sub>Fe<sub>0.25</sub>)<sub>Σ1.00</sub>O<sub>2</sub> with about half of the Ti

atoms replaced by Nb and Fe according to the substitution scheme  $2\text{Ti}^{4+} = \text{Nb}^{5+} + \text{Fe}^{3+}$ . This result makes it tempting to postulate that Ti and (Nb,Fe) might be ordered in the structure. A Rietveld refinement of powder data could possibly give some indication, and will be attempted at a later date.

### Discussion

(Nb,Fe)-substitution is well known in the  $\text{TiO}_2$  polymorph rutile. Ilmenorutile with formula  $(\text{Ti,Nb,Fe}^{3+})_3\text{O}_6$  has a rutile structure (but the name has also been used for niobian rutile). However, this substitution is not so well documented in anatase. So-called 'leucoxene' - a yellow alteration product of ilmenite, titanite, perovskite or other Ti-bearing minerals - often consists of anatase; it might be Nb-bearing if formed from a Nb-rich precursor. 'Nioboanatase' is a name given by Semenov to a yellow alteration product of murmanite from Lovozero, Kola Peninsula. A partial analysis (of a mixture of 'nioboanatase' and an amorphous alteration product of murmanite rich in  $\text{SiO}_2$ ) gave  $\text{TiO}_2$  31.11,  $\text{Nb}_2\text{O}_5$  17.80-21.61,  $\text{Ta}_2\text{O}_5$  0.20 wt.%; the unit-cell parameters,  $a = 3.73$ ,  $c = 9.37$  Å, are higher than for normal anatase (Vlasov 1966).

A yellow alteration product of aeschynite from a greisen in central Kazakhstan was described in great detail as a new unnamed mineral by Podolskii *et al.* (1988). Microprobe analysis gave the 'ideal' formula  $\text{K}(\text{Nb,Ti})_3\text{Si}(\text{O,OH})_{10} \cdot 1.5\text{H}_2\text{O}$ . Interestingly, the X-ray study showed the mineral to be tetragonal with cell parameters somewhat larger than those for anatase:  $a = 3.81$ ,  $c = 9.60$  Å. It is, however, difficult to understand how this formula can be reconciled with an anatase structure. We have calculated the Z value from the measured density (2.91-2.97  $\text{g/cm}^3$ ), the cell volume (139.35 Å<sup>3</sup>) and the molecular weight of the empirical formula (933.60), and the result is  $Z = 0.26$ -0.27. This clearly demonstrates the inconsistency of the data set.

### Acknowledgements

Hans-Jørgen Berg did the XRD work. Muriel Erambert assisted with the electron microprobe analyses. Brenda B. Jensen kindly corrected the English text.

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