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An unusual titanium-rich oxide mineral from Oslo, Norway

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Abstract

An unusual Ti-rich oxide mineral of composition $Sr_{0.21}REE_{0.26}Si_{0.43}Ti_{14.00}Fe_{3.50}V_{1.28}Cr_{1.58}O_{38}$ has been found in an anatase-albitite dike at Oslo, Norway. The mineral is metamict because of a small Th content, and contains abundant water (12.14 wt.%). It is black with a metallic to adamantine luster and gives a black-brown streak. The Mohs hardness is 6. The reflectivity is 17.0-17.4% (546 nm) in air, weakly anisotropic. Heating in air or nitrogen gives X-ray powder lines of rutile (700, 800, and 900°C) or brannerite (1000 and 1200°C). The chemistry of the mineral resembles that of crichtonite.

Occurrence

Three samples containing small, black, shiny crystals surrounded by reaction halos and occurring in a 20-cm wide dike were sampled by the author during 1965 in a quarry for road-material (Huken Quarry) near the abandoned Aanerud copper mine near Grorud in Oslo. The material has subsequently been removed by quarrying operations and spread over the streets of Oslo. The mineral occurs as pseudocubes up to 2 mm in size. Microscopic investigation of polished sections revealed some scattered inclusions of galena, and the mineral is often rimmed by pyrrhotite. Thin sections and powder X-ray photographs of the extremely fine-grained dike matrix showed the presence of quartz, albite and anatase, making it an anatase albitite dike.

Chemical analysis

Electron probe microanalyses of polished sections were made on an ARL-EMX microprobe at the Central Institute of Industrial Research, Oslo, using a series of natural and synthetic standards (Åmli and Griffin, 1975; Segalstad and Larsen, 1978). Matrix corrections were made according to Bence and Albee (1968), using correction factors from Albee and Ray (1970), Åmli and Griffin (1975), and Albee (pers. comm., 1977). The rare-earth elements (REE) were analyzed by the procedure described by Åmli and Griffin (1975), using the same standards with the same accuracy as in their work. The analytical results, which represent the mean of four analyzed points, are presented in Table 1. No compositional zoning was observed.

The mineral was heated from 20°C to 1200°C in a nitrogen gas atmosphere in a "derivatograph" (combined DTA + DTGA + TGA instrument) at the Department of Chemistry, University of Oslo. A weight loss of 12.14% was experienced up to 470°C, associated with a broad endothermic peak. This is believed to represent metamict water loss. The microprobe analysis, including 12.14 wt.% water, totals 100.78%, assuming all iron to be Fe^{3+}. Traces of Y, Pr, Eu, Tb, and Ho were also found. All other elements were below their limits of detection as seen by spectrometer scanning.

Table 1 shows the unit cell contents normalized to 6 and 38 oxygens, assuming all water as metamict water (see above). The formula can be written as $(Fe^{3+},Cr^{3+},V^{5+})Ti_2O_6$ or as $Sr_{0.21}REE_{0.26}Si_{0.43}Ti_{14.00}Fe_{3.50}V_{1.28}Cr_{1.58}O_{38}$, assuming iron and vanadium in their highest oxidation states.

X-ray crystallography

Unheated mineral material gave no X-ray diffraction pattern, due to its metamict state. To achieve X-ray data the mineral was first recrystallized in two ways: in air at 1000°C for 12 hours, and in nitrogen at 1000°C for 2 hours (Table 2). The X-ray data were identical for these two runs, showing the X-ray pattern of brannerite. Heating in nitrogen at 1200°C for 2 hours also gave brannerite X-ray patterns. Heating in air at temperatures lower than 1000°C , for duratiuons up to 8 days, produced rutile X-ray patterns (Table 2).

Physical properties

The mineral occurs as 1–2 mm black pseudocubes, showing a metallic to adamantine luster. Cross-like development is also found. It gives a black-brown streak with a reddish tint and is brittle with a conchoidal fracture. The Mohs hardness is 6. The Vickers microhardness was not measured due to the small amount of material and the brittle nature of the mineral. It is weakly anisotropic in reflected light. The reflectivity is 17.0–17.4% at 546 nm in air, measured with a Zeiss reflectometer calibrated against Zeiss standards and corrected for secondary

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Table 1. Chemical composition (wt.% oxides) and unit cell contents (number of atoms assuming 6 and 38 oxygens) of the Ti-rich oxide mineral from Oslo, Norway.

		O = 6	O = 38
TiO_2	55.93	2.0398	12.9187
SiO_2	1.28	.0619	.3920
Al_2O_3	.45	.0257	.1628
Fe_2O_3	13.99	.5107	3.2344
MnO	.08	.0031	.0196
MgO	.12	.0089	.0564
CaO	.25	.0129	.0817
SrO	1.11	.0313	.1982
Cr_2O_3	6.01	.2305	1.4598
V_2O_5	5.84	.1872	1.1856
Sc_2O_3	.55	.0231	.1463
ZrO_2	.21	.0025	.0158
Na_2O	.13	.0129	.0817
K_2O	.22	.0134	.0849
ThO_2	.38	.0042	.0266
La_2O_3	1.22	.0218	.1381
Ce_2O_3	.87	.0155	.0982
H_2O	12.14		
	100.78		

Table 2. Heating experiments of the Ti-rich oxide mineral from Oslo, Norway.

temperature	duration	atmosphere	pattern
1200°C	2 h	N_2	brannerite
1000°C	12 h	air	brannerite
1000°C	2 h	N_2	brannerite
900°C	24 h	air	rutile
800°C	67 h	air	rutile
700°C	8 d	air	rutile

glare. The specific gravity, determined using pycnometers filled with toluene at 20°C, is 4.02 for the unheated mineral.

Discussion

The crichtonite group contains a number of related mineral species of the type $AB_{21}O_{38}$, which are characterized by their predominant large cations, *i.e.*, crichtonite (Sr), senaite (Pb), davidite (REE + U), landauite (Na), loveringite (Ca), lindsleyite (Ba), and mathiasite (K) (Gatehouse *et al.*, 1978; Haggerty *et al.*, 1983). A rhenium-rich titanium and iron oxide of the crichtonite series was reported by Sarp *et al.* (1981). A large number of AB_2O_6 minerals containing Ca, REE, U, Th, Nb, Ta, Ti, *etc.* belong to the euxenite, aeschynite, and brannerite groups. Moreover, Povilatis (1963) considered that brannerite (ideally UTi_2O_6) and thorutite (ideally $ThTi_2O_6$) form a complete series of solid solutions. However, Fleischer (1963) pointed out that the chemical analyses presented by Povilatis show a gap from $Th_{0.21}$ to $Th_{0.87}$. Due to the ionic radii of the elements involved it may be difficult for other cations to substitute for U and Th in the brannerite-thorutite structure to any large extent.

A vanadium-dominated titanium oxide, $V_2Ti_3O_9$, called schreyerite by Medenbach and Schmetzer (1978), has also been reported, and synthetic compounds similar to schreyerite have been described (Grey and Reid, 1972); Grey *et al.*, 1973). A polymorph of schreyerite, called kyzulkumite, was reported by Smyslova *et al.* (1981).

Some unnamed titanium-rich oxide minerals have been found, containing fairly large amounts of Cr, V, Zr, Ca, Fe, *etc.* (Cameron, 1978, 1979; Mathiesen, 1970). Although Cameron's mineral description is not accompanied by X-ray data, he believed his minerals to belong to the pseudobrookite or the crichtonite groups. Mathiesen's mineral description is accompanied by incomplete chemical analyses and some X-ray powder data, but it is difficult to determine from the data which mineral he analyzed. The X-ray pattern of his "anisotropic phase" resembles somewhat that of the Oslo mineral heated to 1000°C. and the occurrence is similar, in that the albititic host rocks, habit and physical properties are common to both. The chemistry of Mathiesen's mineral from Bidjovagge resembles that of davidite.

The work by Patchett and Nuffield (1960) on the synthesis of brannerite suggests that brannerite regains its original structure on ignition. Although there is no difference between the X-ray data of brannerite and the Oslo mineral when heated to 1000°C in air and in nitrogen, and the derivatograph runs showed no peaks other than the one DTA peak assumed to be associated with the release of metamict water, it is not believed that the Oslo mineral is isostructural with brannerite. The fairly large amount of transition metals is believed to make the rutile structure also unsuitable for this mineral. Rather, it is reasonable to believe on the basis of the chemistry that this unusual titanium-rich oxide mineral belongs to the crichtonite group (Hey *et al.*, 1969; Grey *et al.*, 1976). The high amount of metamict water probably makes it difficult to reconstitute the metamict mineral to its original structure.

Grey *et al.* (1976) found that in crichtonite and related minerals Sr, Pb, and REE occupy only one of the available 39 anion sites in the unit cell. The formula can be expressed as $A_{1-x}B_{21}O_{38}$, where *B* is largely Ti, Mn, Fe, and the variable x indicates that full occupation of the anion site by large cations is not always achieved, *A* being REE, Pb, Sr, Ca, Th, K, Na, *etc.* Among the large cations, Sr is predominant in the Oslo mineral, as in the crichtonite sample from Dauphiné, France (Grey *et al.*, 1976). The amount of Sr is, however, only one fourth of that in the French crichtonite. The largest difference is in the large amount of chromium and vanadium replacing iron in the Oslo mineral. The Oslo mineral would have the structural formula $A_{0.71}B_{19.59}O_{38}$, while the French mineral has $A_{0.9}B_{21}O_{38}$.

Haggerty *et al.* (1983) point out that the $A_{1-x}B_{21}O_{38}$ minerals have TiO_2 contents lying in a "window" between ilmenite at lower TiO_2 contents, and rutile at higher values. The TiO_2 content of the Oslo mineral (56 wt.%) is more like the value for davidite (~55 wt.%) than for crichtonite (~60.5 wt.%).

Total content of REE is higher than the content of Sr, a fact also characteristic of davidite, however, the Oslo mineral lacks U, which is a specific constituent of davidite. Hence the chemistry of the mineral resembles more that of crichtonite, although REE + Th really are the predominant large cations.

Further finds of crichtonite group minerals may reveal if REE + Th is characteristic of a separate mineral species within the crichtonite group, amongst the Oslo mineral may be included.

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