

A new barium uranyl oxide hydrate mineral, protasite

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ABSTRACT. Protasite, a new barium-containing member of the uranyl oxide hydrate group, occurs as bright orange pseudo-hexagonal platelets associated with uraninite and uranophane on unidentified rock matrix from Shinkolobwe mine, Zaïre. Protasite is monoclinic, *Pn* with *a* 12.295(2), *b* 7.221(1), *c* 6.9558(8) Å, β 90.40(2)°, and *V* 617.50(11) Å³. The tabular pseudo-hexagonal crystals are flattened on {010}, 0.1 mm to 0.5 mm wide and up to 0.1 mm thick. They are biaxial negative, $2V = 60-65^\circ$, β and γ 1.79-1.83, and *X* = *b*. Sector twinning is common. Microprobe analysis shows BaO 15.0, UO₃ 78.0, H₂O(diff.) 7.0%. The structural formula is Ba[(UO₂)₃O₃(OH)₂]·3H₂O, *Z* = 2, and density(calc.) = 5.827(3) g cm⁻³. Complete crystal-structure analysis shows protasite to be the simplest model structure of the uranyl oxide hydrate group.

KEYWORDS: protasite, new mineral, uranyl oxide, Shinkolobwe mine, Zaïre.

DURING the course of a study of secondary uranium minerals, a specimen from the Shinkolobwe mine, Shaba province, Zaïre, was found to contain crystals of an unidentified phase. Electron microprobe and X-ray diffraction investigations show that this mineral is a new barium-containing member of the uranyl oxide hydrate group (Protas, 1959; Christ and Clark, 1960; Evans, 1963). Type material is preserved as specimen NMNH 150832 in the Department of Mineral Sciences, National Museum of Natural History, Smithsonian Institution, Washington, DC. The specimen was originally obtained from M. Gilbert Gauthier, who was formerly associated with the Shinkolobwe mine. Protasite has not as yet been found on any other specimens.

Both the new mineral and the name have been approved by the Commission on New Minerals and New Mineral Names of the International Mineralogical Association.

Occurrence and appearance. Protasite occurs as bright orange pseudo-hexagonal platelets, associated with uraninite and uranophane, on a single specimen of unidentified fine-grained rock matrix from the Shinkolobwe mine. The platelets are transparent but very intensely coloured. The colour of protasite

is the same in transmitted and reflected light. Single platelets, flattened on {010}, range from 0.1 mm to 0.5 mm wide and are up to 0.1 mm thick. Luster is subadamantine. Protasite is brittle with a hackly fracture. Cleavage is good parallel to {010}.

Of the other secondary uranium minerals which occur at Shinkolobwe, fourmarierite most closely resembles protasite in colour and habit. However, the two minerals may be distinguished by the more blocky habit of fourmarierite and its tendency to form parallel aggregates, whereas protasite occurs as separate thinner platelets with striations due to twinning. Fourmarierite is not present on the specimen which contains protasite.

Physical and optical properties. Measurement of the optical properties of protasite proved to be extremely difficult due to the high indices of refraction and the extremely intense colour, coupled with the thin tabular habit. Protasite is biaxial negative. Both β and γ are in the range 1.79-1.83 (589 nm) and the acute bisectrix is parallel to the *b*-axis (normal to the plates). The third index, α , could not be measured accurately. The value of $2V$ measured by Kamb's method is 60-65°. Birefringence is high. Dispersion was not determined. No pleochroism was observed for *Y* or *Z*.

Because of the extreme scarcity and high specific gravity of protasite, the density could not be measured directly. There is insufficient material to perform pycnometric measurements, and the density range is too high for determination by flotation in heavy liquids. The density calculated from the cell dimensions (from single-crystal data) and ideal chemical composition is 5.827(3) g cm⁻³. From the actual chemical analysis (water by difference) the density is 5.88 g cm⁻³. When 5.827 g cm⁻³ is used in a Gladstone-Dale calculation (Mandarino, 1979) a mean refractive index of 1.78 is obtained, which is compatible with the partial determination of the refractive indices, given the biaxial negative sign and the high birefringence.

Sector twinning is present in all crystals of protasite which were examined. The probable twin law is a rotation of 60° around [010]. Protasite is

data are corrected for film shrinkage and have been indexed using the program of Appleman and Evans (1973). The wavelength used was 1.5405 Å (Cu-K α_1). The unit cell derived from refinement of the powder diffraction data is $a = 12.345(8)$, $b = 7.181(4)$, $c = 6.936(2)$ Å, and $\beta = 90.57(4)^\circ$. These errors, obtained from the refinement calculations, are much too low and do not reflect the true precision of the measurements, which are subject to numerous experimental errors due to the generally poor quality of the patterns, line overlap, and the lack of an internal standard. The experimental errors undoubtedly explain the differences between the powder-refinement cell and the much more accurate cell obtained from the single-crystal measurements.

Crystal-structure analysis. A complete three-dimensional crystal-structure determination was carried out for protasite, based on 2913 reflections (2505 observed greater than background) measured on an automated four-circle single-crystal diffractometer with Mo-K α radiation (Zr filter). A linear absorption coefficient of 404 cm $^{-1}$ was calculated. Absorption corrections by Gaussian quadrature were applied. The structure was determined by Patterson and difference Fourier techniques and refined by full-matrix least-squares to a final R value of 0.073. This rather high value is typical of structure refinements of minerals in the uranyl oxide hydrate group (Pagoaga, 1983; Piret-Meunier and Piret, 1982). It is probably due to the poor crystallinity and high absorption in these minerals. Assignment of oxo and hydroxyl oxygen atoms is based on bond-length and bond-strength calculations (Brown and Wu, 1976). The computer programs of Stewart *et al.* (1976, 1983) were used throughout the single-crystal structure determination. Details of the structure refinement (Pagoaga, 1983) will be published elsewhere (Pagoaga *et al.*, in preparation).

Crystal chemistry. Protasite is crystallographically the least complicated member of the uranyl oxidized hydrate mineral group. In this group the essential cation is hexavalent uranium in the form of the uranyl ion (UO $_2$) $^{2+}$. The only anionic species present are O $^{2-}$ and (OH) $^-$. Other large cations including K $^+$, Ca $^{2+}$, Sr $^{2+}$, Ba $^{2+}$, Pb $^{2+}$, and possibly Bi $^{3+}$ may be present. In protasite the uranyl ions, coordinated by three O $^{2-}$ and two (OH) $^-$ anions form infinite sheets of composition [(UO $_2$) $_3$ O $_3$ (OH) $_2$] $_n^{2n-}$ which, in projection, resemble those found in α -U $_3$ O $_8$ (Loopstra, 1964 and 1970). The near-linear uranyl ions are roughly perpendicular to the sheets which are bonded together by interlayer Ba $^{2+}$ ions and water molecules.

The structure of protasite is the simplest of those so far determined in the uranyl oxide hydrate

group, and as such represents a model structure for the group. Each protasite sheet contains only three independent uranium atoms, and there is only one independent sheet in the structure. There is one independent interlayer Ba $^{2+}$, giving a Ba:U ratio of 1:3, and there are three independent interlayer water molecules. Other members of the group have lower cation:uranium ratios and more independent sheets. A detailed comparison of their crystal chemistry is in preparation.

Two other uranyl oxide minerals, bilietite and bauranoite, are similar to the new mineral protasite in that they contain Ba $^{2+}$ as the only additional cation. However, bilietite and bauranoite have BaO:UO $_3$ ratios of 1:6 and 1:2, respectively, while protasite has a ratio of 1:3. The crystal structure of bilietite (Pagoaga, 1983) shows it to have the same general layer structure as protasite. Because of the lower Ba:U ratio, a smaller number of interlayer sites are occupied by Ba atoms leading to two independent types of sheets with six independent U atoms.

No single-crystal data are available for bauranoite. The reported powder-diffraction data (Rogova *et al.*, 1974) are quite different from those of protasite. We have examined a specimen, in the collection of the Smithsonian Institution's National Museum of Natural History, labelled 'Bauranoite, Burpala deposit, Transbaikalia, USSR', NMNH 133493, acquired from Prof. A. S. Povarennykh. The powder-diffraction pattern of this sample shows that it probably belongs to the uranyl oxide hydrate group, but the pattern is significantly different from that of protasite. The material also differs from protasite in habit, being massive rather than in tabular crystals, and is browner in colour.

Mineral name. The name protasite was chosen for this new mineral to honour Prof. Jean Protas (1931–) of the University of Nancy, who has contributed a great deal to our understanding of the uranyl oxide hydrates through his excellent analytical and crystallographic investigations of these minerals.

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