

Ianthinite: A rare hydrous uranium oxide mineral from Akkavaram, Andhra Pradesh, India

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Ianthinite is the only known uranyl oxide hydrate mineral that contains both U^{6+} and U^{4+} . For the first time, we report ianthinite from India (at Akkavaram, Andhra Pradesh), which is hosted in basement granitoids. The mineral occurs in the form of tiny grains, encrustations and coatings in intimate association with uraninite and uranophane. X-ray diffraction (XRD) data reveals that d-spacings of the investigated ianthinite are in close agreement with the corresponding values given for ianthinite standard in International Centre for Diffraction Data (ICDD) card no. 12-272. The crystallographic parameters of the studied ianthinite are: $a_o = 11.3$ (1) Å, $b_o = 7.19$ (3) Å and $c_o = 30.46$ (8) Å, with a unit cell volume of 2474 (27) Å³. The association of investigated ianthinite with uraninite suggests that the former has formed due to oxidation of the latter. Since a major part of the uraninite was exposed to oxidizing meteoric water, much of it has been transformed into hydrous uranium oxide (ianthinite) and very little part remained unaltered as uranium oxide (uraninite). Absence of schoepite in the investigated ianthinite suggests that after its formation it (ianthinite) was not exposed to oxygen/oxidizing meteoric water. As the oxidation was partial and short lived, some amount of primary uraninite is also preserved.

1. Introduction

The ianthinite was named so in 1926 from Greek ianthinos, 'violet', in allusion to its colour (Schoep 1926; Gaines *et al.* 1997, p. 261). Ianthinite was first described by Schoep (1926) from the Shinkolobwe (Kasolo) uranium mine in Shaba, Congo. Ianthinite is the only known uranyl oxide hydrate mineral that contains both U^{6+} and U^{4+} (Schoep 1926; Burns *et al.* 1997). The crystal system of ianthinite is orthorhombic, with space group $P2_1cn$. The structure of ianthinite was reported by Burns *et al.* (1997), and the formula differs slightly from that was originally reported (Bignand 1955; Guillemin and Protas 1959) by being more reduced ($U^{4+}:U^{6+} = 2:4$ rather than $U^{4+}:U^{6+} = 1:5$). It is

reported from quite a few uranium deposits (Fron del 1958; Heinrich 1958, p. 67). For the first time, we report ianthinite, including its x-ray crystallographic characteristics, from India (at Akkavaram, Andhra Pradesh), and evaluate paragenetic implications of the same. The reported ianthinite, at Akkavaram, is hosted in basement granitoids.

2. Brief geology of uranium mineralisation

In the area of ianthinite occurrence (figure 1), the basement granitoids, locally called Mahboobnagar granites, and associated rocks constitute part of the Eastern Dharwar Craton (EDC). The basement granitoids comprise Peninsular Gneisses and

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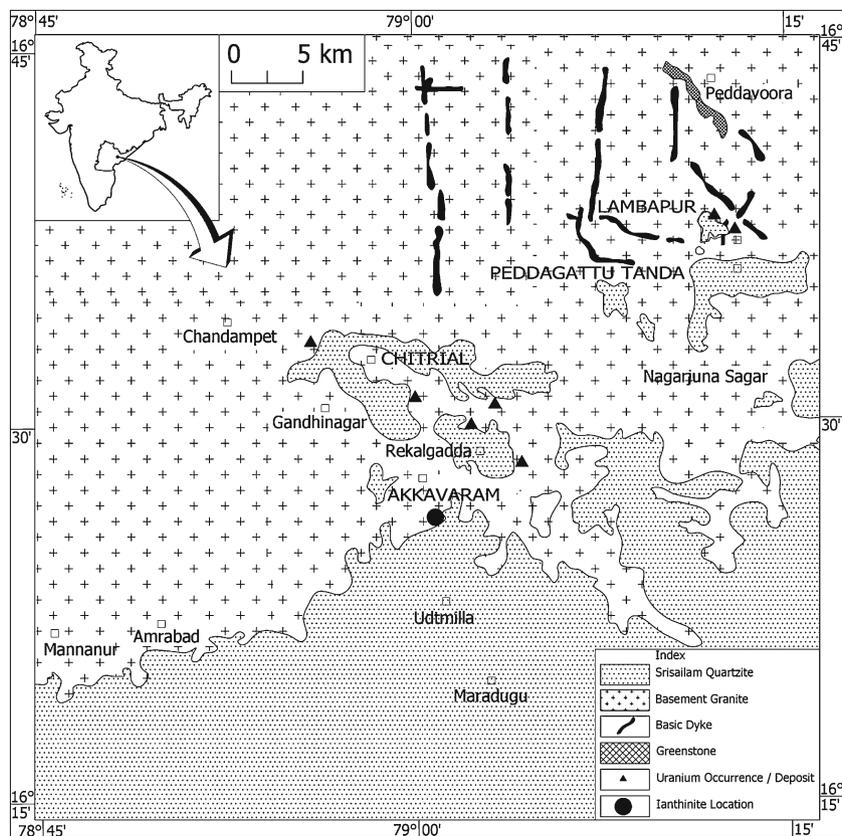


Figure 1. Geological map of a portion of northern part of the Cuddapah basin with location of the Akkavaram. Filled circle shows location of ianthinite.

granitoids with remnants of greenstone belts. The granitoids form a part of the early Proterozoic mobile belt, where occurrences of several K-rich younger granitic bodies, with notable concentrations of uranium, thorium and rare-earths, have been reported (Padma Kumari *et al.* 1977; Shrivastava *et al.* 1992; Singh 2001, 2004). Salient features of the basement granitoids are their fertile, highly-fractured, and deformed nature. Also, dolerite dykes and quartz veins/reefs traverse basement granitoids, with or without shows of uranium mineralisation. In the environs of the northern parts of the Meso- to Neo-Proterozoic Cuddapah sedimentary basin (figure 1), unconformity-related-type uranium deposits, at the contact of basement Mahboobnagar granite and overlying Srisaillam/Banganapalle Formation, in the Srisaillam-Palnad and Kurnool sub-basins of the Cuddapah basin have been identified (Sinha *et al.* 1995). The Akkavaram area, from where ianthinite is reported (figure 1), falls in the Srisaillam sub-basin of the Cuddapah basin, and records significant U-mineralisation both in the basement granitoids and the overlying sedimentary arenaceous (sandstone/grit) unit. The mineralised basement granitoid is weathered and shows uranyl mineral encrustations. The granitoids recorded up to 0.25% U_3O_8 ,

whereas, the overlying arenaceous (sandstone/grit) unit analysed up to 0.031% U_3O_8 . The N-S trending dolerite dykes assayed up to 0.25% U_3O_8 .

3. Ianthinite

3.1 Mode of occurrence

Ianthinite is hosted in basement Mahboobnagar granitoids at Akkavaram, part of Andhra Pradesh (figure 1). It occurs on surface outcrops in the form of (megascopically visible) tiny grains of about 1 to 2 mm size and encrustations and coatings of about 1 to 2 mm thickness in intimate association with uraninite and uranophane. Other minerals in granitoid hosting ianthinite include anatase and rutile, besides microcline, biotite and quartz. According to Schoep and Stradiot (1947), ianthinite is always implanted directly upon uraninite and fills its cracks. Also, they noted that acicular crystals are of prismatic habit, black with a brownish violet tinge in reflected but violet in transmitted light. Spots comprising studied co-existing ianthinite, uraninite and uranophane display fluorescence (F) under ultraviolet light, which (F) may be due to the presence of uranophane. Distribution of

ianthinite-bearing individual clots/patches of about 1 to 2 cm² each in host granitoid surface outcrop is very limited (over about 5 m² area; marked with a filled circle in figure 1), although uranophane-bearing patches are rather widespread. In the overlying sedimentary quartzite unit, uranium minerals present are only uranophane and beta-uranophane. Other phases are anatase, monazite, rutile and zircon, including biotite, microcline and quartz.

3.2 Methodology

Radioactive outcrop samples were first examined megascopically with the help of magnifying lenses. Subsequently, visible yellowish tiny grains and encrustations/coatings were isolated from the host granitoid substrate under ultraviolet light with the help of blade and fine needle. Visible quartz and feldspar grains from separated yellowish material were removed under binocular microscope. The purified fraction was ground to ~300# size in a small agate pestle and mortar. The fine powder (~300#) was slowly poured with the help of a small brush and filled in the groove of sample holder and then pressed with a glass slide to make diffracting surface of smooth powdered material. Three such purified samples were investigated separately by XRD technique. Attempts to petrographically characterize ianthinite proved unrewarding as during thin section preparation of ianthinite-bearing host granitoid, involving wet cutting, grinding and polishing, mineral of interest got washed away from its substrate because of its soft and flaky nature and also its mode of occurrence as soft flaky coatings/encrustations.

X-ray diffraction (XRD) study was carried out in Siemens D 500 diffractometer in XRD Laboratory, AMD, Hyderabad. The accelerating voltage was maintained at 35 kV and the tube current at 22 mA. CuK α radiation (1.5418 Å), monochromatised using curved graphite monochromator, was

used for diffraction. For identification, a scanning speed of 0.03 degrees 2 θ /s, over a long angular range (4–90 degrees 2 θ), with a sampling time of 2 s, was selected. Mineral identification was done from the powder diffraction data so obtained by comparing the same with the relevant International Centre for Diffraction Data (ICDD) card.

For obtaining high 2 θ precision data on the crystallographic parameters, the powdered sample was slow-scanned with a speed of 0.01 degrees 2 θ /s and a sampling time of 2 s. The respective 2 θ values of the various hkl reflections (table 1) and the values of their corresponding interplanar spacings (d-spacings) were obtained directly by using Wassermann ADM software. From the powder diffraction data so obtained, the crystallographic parameters, viz., unit cell dimension (a₀) and unit cell volume (V), of ianthinite were determined.

3.3 X-ray crystallographic characteristics

The XRD pattern of the co-existing ianthinite, uraninite and uranophane is shown in figure 2. From the peak intensity ratios (figure 2), it is apparent that modal abundance of uraninite is very less compared to ianthinite and uranophane. Interplanar spacings (d-spacings) and their respective relative intensities (I/I₀), with corresponding data given for ianthinite in International Centre for Diffraction Data (ICDD) card are presented in table 1.

Critical examination of X-ray powder diffraction data reveals that d-spacings of reflections of investigated ianthinite are in close agreement with the corresponding values given for ianthinite standard in ICDD card no. 12-272. However, relative intensities (I/I₀) of the investigated ianthinite are perceptibly less compared to I/I₀ given in the relevant card. It may be related with preferred orientation along certain crystallographic (hkl) planes leading to development of flaky/acicular/needle-like

Table 1. Interplanar spacings (d-spacings) and relative intensities (I/I₀) of the lines observed in the investigated ianthinite from the basement granites of Akkavaram, AP, with published corresponding values given in ICDD card.

Data on ianthinite from Akkavaram, AP			Data on ianthinite given in ICDD card no.12-272		
Sl. no.	d (Å)	Intensity (I/I ₀)	d (Å)	Intensity (I/I ₀)	hkl
1	7.6681	100	7.63	100	004, 103
2	3.8049	23	3.81	80	008, 206
3	3.5934	11	3.59	60	020
4	3.3435	5	3.35	60	122, 216
5	3.2283	13	3.24	80	109, 305
6	2.9655	6	2.95	20	119, 315
	a ₀ = 11.3 (1) Å			a ₀ = 11.52 Å	
	b ₀ = 7.19 (3) Å			b ₀ = 7.15 Å	
	c ₀ = 30.46 (8) Å			c ₀ = 30.305 Å	
	V = 2474 (27) Å ³			V = 2496.16 Å ³	

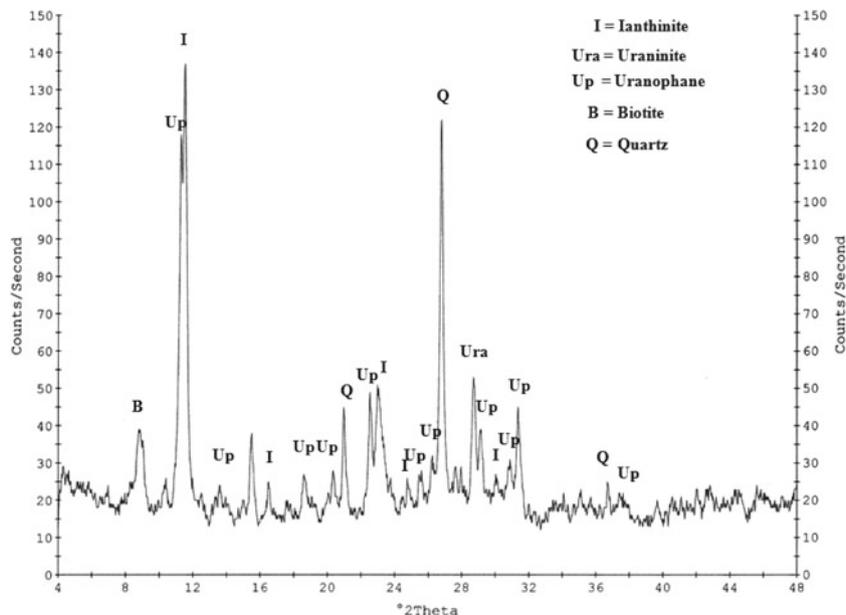


Figure 2. X-ray powder diffraction pattern of co-existing ianthinite, uraninite and uranophane from Akkavaram.

crystal habits of the ianthinite. The crystallographic parameters of the studied ianthinite are: $a_o = 11.3$ (1) Å, $b_o = 7.19$ (3) Å and $c_o = 30.46$ (8) Å, with a unit cell volume of 2474 (27) Å³. Interestingly, values of d-spacings and I/I_o of co-existing uranophane (figure 2) also match well with the corresponding values given for uranophane in its ICDD card no. 8-442. Crystallographic constants of associated uranophane are: $a_o = 15.87$ Å, $b_o = 7.20$ Å, $c_o = 6.66$ Å, $\beta = 97^{\circ}51'$ and unit cell volume = 760 Å³.

4. Discussion

Ianthinite plays a key role in understanding paragenesis of the complex assemblage of uranyl minerals, although its occurrence in nature is very rare. Its rarity in nature is mainly due to its instability in the presence of oxygen. It oxidizes readily in air to schoepite and, accordingly, ianthinite is also considered a common precursor to schoepite and metaschoepite (Deliens *et al.* 1984; Finch and Ewing 1991, 1992, 1994; Percy *et al.* 1994). The absence of schoepite in the investigated ianthinite therefore, suggests that after its formation it (ianthinite) was not exposed to oxygen/oxidizing meteoric water as a result of which it (ianthinite) remained intact in the host granitoids. As the rigour of oxidation was partial and short lived, some amount of primary uraninite is also preserved (figure 2). In the presence of uraninite (figure 2), existence of epiianthinite (an yellow alteration product which appears just before schoepite formation, with crystallographic

continuity with that of ianthinite) is ruled out, as in such a material (epiianthinite) even traces of primary uraninite (present in material investigated by us) are not perceived (Schoep and Stradiot 1947; George 1949; Urbanec and Cejka 1979; Finch and Murakami 1999), and, generally, only traces of ianthinite occur as elongated patches of violet brown. Percy *et al.* (1994) also identified ianthinite as an early oxidation product of uraninite at the Nopal I Mine near Pefia Blanca, Mexico. The already known range of stability for ianthinite in natural waters is limited (Taylor *et al.* 1992), and in an aqueous solution we assume activity of H₂O to be ~ 1 . Also, with increasing temperature, the stability field of ianthinite decreases and vanishes near 100°C, where it is replaced by α -U₃O₈ and β -UO₂(OH)₂ (Finch and Murakami 1999).

Ianthinite is structurally similar in its layers to schoepite (Finch and Ewing 1994; Burns *et al.* 1997). Some uranium, however, is present as U⁴⁺, which is absent in schoepite, i.e., entirely of U⁶⁺. A new crystal chemical formula for ianthinite, inferred from a single-crystal structure study (Burns *et al.* 1997) is: [U²⁺(UO₂)₄O₆(OH)₄(H₂O)₄](H₂O)₅. Differential thermal analysis (DTA) studies of ianthinite revealed endotherms at 110°C (dehydration), 630°C (UO₃ to UO_{2.67}), exotherms at 320°C (U⁴⁺ oxidation) (Guillemin and Protas 1959). The first and second endotherms are always associated with release of H₂O groups from inter-layer sites and complete dehydration, respectively, whereas, the formation of new crystalline phase is characterized by the first exotherm (Sidorenko *et al.* 1986).

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