Crystallochemical studies on davidite from Bichun, Jaipur District, Rajasthan, India

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Crystallochemical data on metamict davidite from albitites and albitised rocks from the Bichun area (Jaipur district, Rajasthan, India) of Banded Gneissic Complex (BGC) are provided. Davidite occurs as euhedral, subhedral to anhedral crystals in the form of disseminated grains and also as fracture filled veins. The crystals of davidite are up to 8 cm in length and 6 cm in width. The powder X-ray diffraction (XRD) pattern of the heat-treated davidite (at 900°C) reveals well-defined reflections of crystallographic planes. The calculated unit-cell parameters of the heat treated davidite are: $a_0 = b_0 = 10.3556 \text{ \AA}$ and $c_0 = 20.9067 \text{ \AA}$, with unit-cell volume (V) = $1941.6385 \text{ \AA}^3$; and $\alpha = \beta = 90^\circ$ and $\gamma = 120^\circ$, which are in agreement with the values of davidite standard. Geochemical data reveals that the investigated davidite contains 51.5–52.6% TiO_2 , 14.8–15.1% Fe_2O_3 , 9.8–10.2% FeO , 6.97–7.12% U_3O_8 , 6.72–6.92% RE_2O_3 , 3.85–3.61% K_2O , 0.9–1.4% Al_2O_3 , and 0.8–1.2% SiO_2 . The calculated structural formulae of the two davidite crystals are: D-1: $\text{K}_{0.0044/0.004}\text{Ba}_{0.0044/0.005}\text{Ca}_{0.20/0.20}\text{Na}_{0.012/0.012}\text{Mn}_{0.053/0.053}\text{Mg}_{0.14/0.14}\text{Pb}_{0.0076/0.008}\text{Fe}_{2.675/2.675}\text{Fe}_{1.59/1.59}\text{Y}_{0.1175/0.118}\text{P}_{0.053/0.053}\text{Nb}_{0.008/0.008}\text{Sn}_{0.001/0.001}\text{Zr}_{0.033/0.033}\text{U}_{0.468/0.468}\text{Th}_{0.009/0.009}\text{REE}_{0.6829/0.683}6.05/6.05(\text{Ti}_{12.15/12.15}\text{Fe}_{1.9022/1.903}\text{Si}_{0.372/0.372}\text{Al}_{0.517/0.517}\text{Cr}_{0.018/0.018}\text{Co}_{0.009/0.009}\text{Ni}_{0.027/0.027})_{15/15}\text{O}_{36/36}(\text{OH}_{0.319/0.319}[1.681/1.681])_{2/2}$ and D-2: $(\text{K}_{0.004/0.004}\text{Ba}_{0.005/0.005}\text{Ca}_{0.20/0.20}\text{Na}_{0.012/0.012}\text{Mn}_{0.05/0.05}\text{Mg}_{0.094/0.094}\text{Pb}_{0.007/0.007}\text{Fe}_{2.58/2.58}\text{Fe}_{1.71/1.71}\text{Y}_{0.112/0.112}\text{P}_{0.106/0.106}\text{Nb}_{0.006/0.006}\text{Sn}_{0.001/0.001}\text{Zr}_{0.03/0.03}\text{U}_{0.48/0.48}\text{Th}_{0.009/0.009}\text{REE}_{0.665/0.665}6.088/6.088(\text{Ti}_{12.48/12.48}\text{Fe}_{1.87/1.87}\text{Si}_{0.249/0.249}\text{Al}_{0.334/0.334}\text{Cr}_{0.019/0.019}\text{Co}_{0.008/0.008}\text{Ni}_{0.04/0.04})_{15/15}\text{O}_{36/36}(\text{OH}_{0.098/0.098}[1.90/1.90])_{2/2}$. The calculated structural formulae are not fully stoichiometric, which could be due to metamict nature of davidite. The characteristic feature of distribution pattern of REE in davidite is unusually high concentration of LREE and HREE and substantially low content of MREE. It may be due to the occupation of REEs in two distinct crystallographic sites in davidite structure, i.e., M(1) and M(O) sites. Chondrite-normalised plot of davidite reveals a pronounced negative Eu-anomaly ($\text{Eu}/\text{Eu}^* = 0.30\text{--}0.39$), which suggests extremely fractionated nature of the metasomatising fluids from which davidite had crystallized. Metamict davidite-bearing U ores not only from Rajasthan, but also from other parts of India are likely to yield very high U leachability, thereby making them attractive sources of U, which otherwise are ignored by mineral engineers as uneconomic U ores.

Keywords. Mineralogy; mineral chemistry; XRD pattern; metamict davidite; Bichun; Jaipur; Rajasthan; India.

1. Introduction

The davidite was named in 1906 in honour of Tenatt William Edgeworth David, an Australian geologist (Gaines *et al.* 1997). Davidite is rhombohedral, with space group of $HEX-R$ $R\bar{3}$ and $Z = 3$, $D = 4.72$ (Gaines *et al.* 1997). Its crystals are tabular {0001}, or pyramidal with dominant ditrigonal pyramids, or cuboidal or generally massive (Gaines *et al.* 1997). The structure of davidite is $Y_6Z_{15}O_{36}$ or $3(Y_2Z_5O_{12})$, where Y represents larger cations, mainly Fe^{2+} , with some Ce, U, etc., whereas, Z represents the smaller cations, mostly Ti with some Fe^{3+} , V, Cr, etc. (Pabst 1961).

The uranium mineralization due to davidite, brannerite and uraninite in Bichun (Survey of India Toposheet No. 64J/7: $26^\circ 49' 41''N$, $75^\circ 20' 42''E$) and Nayagaon ($26^\circ 47' 40''N$, $75^\circ 19' 12''E$) areas in Jaipur district, Rajasthan (figure 1) is known (Shaji *et al.* 2011; Latha *et al.* 2015). Although preliminary petrographic aspect of uranium mineralization has been described in earlier publications (Shaji *et al.* 2011; Latha *et al.* 2015), crystallochemical aspects of uranium phases have not yet been investigated. In this, we provide comprehensive petrographic account and crystallochemical data on davidite from Bichun area, and evaluate their implications in context with the regional albitisation and associated uranium mineralization in this part of western India.

2. Geology

The regional geological setting of the area is shown in figure 1. The Bichun area, from where davidite has been investigated, falls in the Banded Gneissic Complex (BGC) terrain. The various constituent lithounits of the BGC are granite gneiss, migmatite, quartzite, schists and phyllites. These lithounits of the BGC are intruded by amphibolite (metamorphosed basic rocks), quartzo-feldspathic rock, granite, albitite, pegmatitic veins and vein quartz. The BGC commonly shows N–S to NNE–SSW trending foliation, with 60° – 70° westerly dips. The albitite, which occurs as linear bodies, follows the trends of foliation of the BGC.

The albitites are light pink to aventurine red in colour, and fine to coarse grained with or without saccharoidal texture. They comprise almost fully of anhedral albite with minor microcline and quartz. The albitites ($n = 6$) are reported to contain 3.85–6.71% Na_2O and 0.23–1.07% K_2O (Shaji *et al.* 2011). They also contain 0.008–0.024% total U, out of which 0.006–0.020% is leachable U (Shaji *et al.* 2011). In an experimental work, metamict davidite of Bichun has yielded 85–96% U leachability, under the conditions of about $150^\circ C$ temperature, concentrated H_2SO_4 (~ 0.3 Molar) acid and MnO_2 (as oxidant) for about 16–17 hr duration (Singh *et al.* 2012). Except for the presence of radioactive phases, there is no difference between the radioactive albitite and nonradioactive albitite.

3. Methods of investigation

Petrographic study was done using a Nikon optical microscope. Davidite crystals visible to the naked eye (larger ones) were separated from host rocks with the help of a knife followed by sequential heavy media liquid separation. Separated methylene iodide heavy (MIH) fractions were diffracted to check for the presence of impurity of other minerals. In initial MIH fractions, impurities of quartz, albite and microcline were noted. Hence, they were once again subjected to heavy media liquid separation. Rediffraction of these fractions did not show any impurity. These purified materials were then ground to -200μ to get homogenous mineral powders. Such powders of each sample were then divided into two halves. One portion of each sample was taken up for X-ray diffraction (XRD) study, whereas, the other portion was used for geochemical study. Though the other types of davidite described under the microscope were confirmed by XRD study, they were not taken up for further work due to recovery of inadequate quantity of pure material needed for crystallochemical study. The XRD study was carried out in a GE XRD-3003 TT XRD System. The accelerating voltage was maintained at 40 kV and the tube current at 20 mA. The $CuK\alpha$ radiation ($1.5418 \text{ \AA}$), monochromatised

Figure 1. Regional geological map of the Rajasthan showing location of the Bichun area (after Heron 1953; Sinha-Roy *et al.* 1998).

using curved graphite monochromator, was used for diffraction. For identification, a fast-scanning speed of 0.03 degrees 2θ /sec, over a long angular range (4–70 degrees 2θ), with a sampling time of 2 seconds, was adopted. For obtaining high 2θ precision data on the unit-cell parameter, powdered davidite samples were slow-scanned with a speed of 0.01 degrees 2θ /sec and a sampling time of 2 seconds. The respective 2θ values of all the reflections and values of their corresponding interplanar spacings (d-spacings) and integrated intensities (I/I_0) were obtained directly by ANALYSE software. The unit-cell dimension was determined from the powder diffraction data, so obtained using ANALYSE software. Geochemical analyses of davidite samples ($n = 2$) were done by titrimetry (Fe^{+3}), fluorimetry (U), gravimetry (LOI), and rest of the elements by inductively coupled plasma-optical emission spectrometry (ICP-OES).

4. Davidite

4.1 Host rock and mode of occurrence

The mineral davidite is hosted in variously albitised lithounits of the BGC in the Bichun area. Apart from albitites, the most prominently albitised rocks are albitised biotite granites, albitised hornblende-biotite granite and leucocratic alkali feldspar granite. The albitite is aventurine- (figure 2a), buff to light pink coloured (figure 2b) and, in places, contains quartz veins which are light grey, milky white to opalescent (figure 2c, d). The albitite is massive and fractured. In albitite, davidite occurs in various forms, e.g., euhedral, subhedral to anhedral crystals. Davidite crystals occur in the form of disseminated aggregates (figure 2a) and fracture-fills as thick veins and stringers (figure 2c, d). At places, they encircle albite crystal boundary (figure 2b). Some of

Figure 2. Field photographs of albitites hosting davidite (D): (a) Disseminated crystals of euhedral davidite within aventurine-red coloured albitite. Length of pen lid = 6.5 cm. (b) Light pinkish coloured albitite with davidite crystals along fractures. Note a few disseminated tiny davidite grains. (c) Fractured albitite and associated quartz vein. Note black-coloured davidite crystals filling fractures. Length of pen = 15 cm. (d) Black-coloured aggregates of davidite crystals at the contact of albitite and quartz vein. Length of pen lid = 6.5 cm. (e) A large crystal of davidite.

the bigger crystals of davidite are up to 8 cm in length and 5–6 cm in width (figure 2e). In addition, fine-size davidite grains are also present within the U-mineralised albitites.

4.2 Petrography

Megascopically, davidite crystals are black, brownish-black, with dull lustre. Its surface

shows conchoidal fractures on freshly broken surfaces. It is massive and compact. Fresh davidite is pitch-black in colour and shows typical vitreous lustre (figure 2a–d). Under transmitted light, davidite is opaque to translucent (reddish-brown). Under reflected light, it is grey with slightly brownish tint and has higher reflectance than that of uraninite. It generally shows isotropic nature. In general, davidite yields

medium density alpha tracks over CN-film (figure 3e).

Davidite hosted in albitised biotite granite, albitised hornblende-biotite granite and leucocratic

alkali feldspar granite generally occurs as: (1) dispersed grains along interstitial spaces (figure 3a–b) and fractures as rounded, globular and euhedral–subhedral crystals in different sizes, e.g., 0.14–0.20,

Figure 3. Microphotographs of crystals of davidite (D) hosted in various albitised lithounits of the BGC: (a) Fine- to medium-grained davidite. RL, 1N. (b) Low- to medium-density discrete alpha tracks on CN film. (c) Davidite showing symplectic intergrowth sphene. TL, 1N. (d) Davidite-sphene intergrowth as seen under reflected light. RL, 1N, air. (e) Low- to medium-density alpha tracks on CN film corresponding to davidite shown in (c) and (d). (f) Type-I, fine-sized radioactive inclusion of pseudomorphic davidite within albite. Development of expansion cracks (yellow arrow) are seen in host crystal. Note hematitic outer rim and amorphous core. RL, 1N. (g) Dispersed, globular (and fractured) type-II davidite crystal (D) in interstitial spaces of albitite. Note alteration rim of Fe–Ti oxide around davidite crystal. Very low density alpha tracks corresponding to davidite crystal are shown in inset. RL, 1N. (h) Globular davidite crystal in interstitial spaces of albitite with thin alteration rim around it. RL, 1N. (i) Davidite (D) with rutile (R) in vein form hosted in albitite. Note fine white-coloured specks in davidite in upper left corner of photo. RL, 1N. (j) Medium density alpha tracks corresponding to davidite shown in (i). Note absence of tracks over rutile.

Figure 3. (Continued.)

0.3–0.4 and 0.5 to ≥ 1 mm. Ilmenite and sphene are closely associated with davidite that are present around its grain margins and as very fine-sized unevenly dispersed specks within it, indicating inhomogeneity of davidite. (2) Symplectic intergrowth of davidite with sphene (figure 3c–e) generally as dispersed globular masses of 0.75–1.25 mm. Veins of davidite–sphene–ilmenite occur along the fractures. These veins are composed of symplectic intergrowth of davidite and sphene, with the sphene forming a rim around davidite in association with ilmenite.

In albitite, davidite occurs as veins, anhedral dispersed grains and inclusions within albite. Three types of davidites are identified. They are fine-sized, rounded inclusions within albite (type-I), intergranular anhedral dispersed grains (type-II) and vein-form (type-III). Fine sized (<0.1 mm) rounded inclusions are pseudomorphic davidite (figure 3f) that have yielded only a few alpha tracks over CN-film and expansion cracks in host crystals. Type-I, pseudomorphic davidite represents primary ore. Type-II, dispersed davidite grains are globular, of 0.2–0.6 mm sizes, and occur either in intergranular spaces or along fractures. They

show variable alterations with the formation of complex Fe–Ti oxides (figure 3g–h). At times, davidite is only seen as specks within reddish-yellowish altered mass. Variable, feeble low density alpha tracks were recorded over altered davidite. Opaque-translucent brown veins comprise interwoven davidite (type-III) and rutile (figure 3i–f), where davidite registers low density alpha tracks on CN-film, whereas, no track is registered by rutile (figure 3i–f).

4.3 X-ray crystallography

Initial diffraction of davidite, occurring in natural state, did not yield any XRD pattern (figure 4a) suggesting that it is metamict in natural state. Its successively heat-treated product at 900°C yielded a well-defined XRD pattern (figure 4b–e). From the data (table 1), it is apparent that the observed values of d-spacings and I/I_0 are in close agreement with the values given in the relevant data card. It may be noted that six reflections, 3.8100, 2.0720, 2.0290, 1.9820, 1.7800, and 1.7410 Å, of minor I/I_0 of <5 to 12 given in the relevant data card are absent in the studied

Figure 4. Successively heat-treated XRD patterns of davidite. Note bottom most pattern (a) lacks in reflections due to metamict nature of davidite (natural state). XRD patterns (b), (c), (d) and (e) are of successively heat-treated davidite (a) at 750°C, 800°C, 850°C and 900°C, respectively, for 3-hr duration on each occasion in a muffle furnace.

davidite. Similarly, four reflections, 6.8600, 2.4800, 2.4290, and 1.9190 Å of moderate I/I_0 of 18–40 are also not recorded in the studied davidite. Interestingly, the investigated davidite shows development of four additional reflections, 4.1209 Å (33), 2.4689 Å (25), 2.4201 Å (20), and 1.9569 Å (11) of moderate I/I_0 of 11 to 33 that are not given in its data card. The calculated unit-cell parameters of the studied davidite are: $a_0 = b_0 = 10.3556$ Å and $c_0 = 20.9067$ Å, with unit-cell volume (V) = 1941.6385 Å³; and $\alpha = \beta = 90^\circ$ and $\gamma = 120^\circ$. The data shows that despite the absence, and development of additional reflections of minor to moderate I/I_0 , there is no deviation in unit-cell parameters of the studied davidite when compared with that of the values of davidite standard ($a_0 = b_0 = 10.3700$ Å and $c_0 = 20.8700$ Å, with unit-cell volume (V) = 1943.62 Å³; and $\alpha = \beta = 90^\circ$ and $\gamma = 120^\circ$).

4.4 Mineral chemistry

Geochemical data (table 2) reveals that the investigated davidite ($n = 2$) contains 51.5–52.6% TiO₂, 14.8–15.1% Fe₂O₃, 9.8–10.2% FeO,

6.97–7.12% U₃O₈, 6.72–6.92% RE₂O₃, 3.85–3.61% K₂O, 0.9–1.4% Al₂O₃, and 0.8–1.2% SiO₂. Further, contents of ThO₂ (0.13–0.14%), MgO (0.2–0.3%), MnO (0.2%), CaO (0.6), Na₂O (0.02%), and water of hydration (0.07–0.27%, LOI) are low (table 2). It is highly radioactive due to high U and subordinate amount of Th contents. Among various trace elements, Zr (1403–1592 ppm) content is the highest followed by Sr (917–1100 ppm). Appreciable amounts of Pb (826–851 ppm), Ba (322–367 ppm), Zn (170–180 ppm), and Cu (25–27 ppm) are also present. Chemical analysis (major/minor oxides and trace elements) of davidites (D-1 and D-2) and their structural formulae, calculated on the basis of 36(O), are given.

D-1: K_{0.0044/0.004}Ba_{0.0044/0.005}Ca_{0.20/0.20}
Na_{0.012/0.012}Mn_{0.053/0.053}Mg_{0.14/0.14}
Pb_{0.0076/0.008}Fe_{2.675/2.675}Fe_{1.59/1.59}
Y_{0.1175/0.118}P_{0.053/0.053}Nb_{0.008/0.008}
Sn_{0.001/0.001}Zr_{0.033/0.033}U_{0.468/0.468}
Th_{0.009/0.009}REE_{0.6829/0.683}6.05/6.05
(Ti_{12.15/12.15}Fe_{1.9022/1.903}Si_{0.372/0.372}
Al_{0.517/0.517}Cr_{0.018/0.018}Co_{0.009/0.009}
Ni_{0.027/0.027})_{15/15}O_{36/36}
(OH_{0.319/0.319}1.681/1.681)_{2/2} and

Table 1. *X-ray diffraction data of investigated davidite from Bichun area, Ajmer district, Rajasthan, vis-à-vis corresponding data given in relevant data card.*

Davidite heated at 800°C from Bichun			Davidite from ICDD Data Card No: 13-0505		
Sl. no.	d in Å	Intensity	d in Å	Intensity	h k l
1	—	—	6.8600	18	0 1 2
2	5.1857	13	5.2100	16	1 1 0
3	—	—	4.1800	25	1 1 3
4	4.1209	33	—	—	2 0 2
5	—	—	3.8100	8	0 1 5
6	3.3970	71	3.4200	70	0 2 4
7	3.3386	18	3.3600	8	2 1 1
8	3.2300	15	3.2100	20	1 2 2
9	3.0504	55	3.0650	50	2 0 5
10	2.9891	32	3.00	40	3 0 0
11	2.8826	100	2.8950	100	1 1 6
12	2.8393	65	2.8500	60	2 1 4
13	2.7472	19	2.755	20	3 0 3
14	2.6292	29	2.6400	35	1 2 5
15	2.5910	8	2.5950	18	2 2 0
16	—	—	2.4800	40	0 2 7
17	2.4689	25	—	—	1 3 1
18	—	—	2.4290	25	2 2 3
19	2.4201	20	—	—	3 1 2
20	2.2446	56	2.2480	50	1 3 4
21	2.1362	35	2.1390	40	3 1 5
22	—	—	2.0720	6	1 2 8
23	—	—	2.0290	6	1 0 10
24	—	—	1.9820	12	0 4 5
25	1.9569	11	—	—	4 1 0
26	—	—	1.9190	25	3 2 4
27	1.9116	32	—	—	1 3 7
28	—	—	1.8970	6	0 2 10
29	1.8474	15	1.8490	10	2 3 5
30	1.7994	35	1.8030	40	3 1 8
31	—	—	1.7800	12	2 1 10
32	—	—	1.7410	< 5	0 0 12
33	1.7058	40	1.7080	20	4 1 6
34	1.6461	11	1.6520	12	5 0 5
35	1.5976	56	1.6010	40	1 3 10
Space group R-3 (148)			Space group R-3 (148)		
$a_0 = b_0 = 10.3556 \pm 0.006 \text{ Å}$			$a_0 = b_0 = 10.3700 \text{ Å}$		
$c_0 = 20.9067 \pm 0.025 \text{ Å}$			$a_0 = 20.8700 \text{ Å}$		
$\alpha = \beta = 90^\circ, \gamma = 120^\circ$			$\alpha = \beta = 90^\circ, \gamma = 120^\circ$		
$V = 1941.6385 \pm 2.25 \text{ Å}^3$			$V = 1943.62 \text{ Å}^3$		

D-2: $(\text{K}_{0.004/0.004}\text{Ba}_{0.005/0.005}\text{Ca}_{0.20/0.20}\text{Na}_{0.012/0.012}\text{Mn}_{0.05/0.05}\text{Mg}_{0.094/0.094}\text{Pb}_{0.007/0.007}\text{Fe}_{2.58/2.58}\text{Fe}_{1.71/1.71}\text{Y}_{0.112/0.112}\text{P}_{0.106/0.106}\text{Nb}_{0.006/0.006}\text{Sn}_{0.001/0.001}\text{Zr}_{0.03/0.03}\text{U}_{0.48/0.48}\text{Th}_{0.009/0.009}\text{REE}_{0.665/0.665})_{6.088/6.088}(\text{Ti}_{12.48/12.48}\text{Fe}_{1.87/1.87}\text{Si}_{0.249/0.249}\text{Al}_{0.334/0.334}\text{Cr}_{0.019/0.019}\text{Co}_{0.008/0.008}\text{Ni}_{0.04/0.04})_{15/15}\text{O}_{36/36}(\text{OH}_{0.098/0.098})_{1.90/1.90}/2/2$.

The calculated structural formulae are not fully stoichiometric.

It may be noted that the total rare earth element (REE) content in the davidite samples is extremely high (49,101–50,705 ppm). Compared to light REE (LREE) content (43,885–45,446 ppm), heavy REE (HREE) content (5216–5258 ppm) is substantially low, leading to very high LREE/HREE

Table 2. Chemical analysis (Oxides and LOI in Wt.% and elements in ppm) of davidite (D-1 and D-2) from the Bichun area, Jaipur district, Rajasthan, India.

Sl. no.	Oxide/element/ratio	D-1	D-2	Sl. no.	Oxide/element/ratio	D-1	D-2
1	SiO ₂	1.2	0.8	29	Nd	634	532
2	TiO ₂	51.5	52.6	30	Sm	121	164
3	Al ₂ O ₃	1.4	0.9	31	Eu	26	35
4	Fe ₂ O ₃	14.8	15.1	32	Gd	286	252
5	FeO	10.2	9.8	33	Tb	68	60
6	MnO	0.2	0.2	34	Dy	941	924
7	MgO	0.3	0.2	35	Ho	244	236
8	CaO	0.60	0.6	36	Er	1032	997
9	Na ₂ O	0.02	0.02	37	Tm	201	219
10	K ₂ O	3.85	3.61	38	Yb	2134	2169
11	P ₂ O ₅	0.20	0.4	39	Lu	352	361
12	U ₃ O ₈	6.97	7.12	40	Y	5544	5284
13	ThO ₂	0.14	0.13	41	∑REE	50704	49101
14	∑RE ₂ O ₃	6.72	6.92	42	∑LREE	45446	43885
15	H ₂ O ⁻ (at 110°C)	0.02	0.02	43	∑HREE	5258	5216
16	LOI	0.25	0.05	44	∑MREE	1565	1507
17	Total	98.37	98.47	45	∑LREE/∑HREE	8.64	8.41
18	Li	<10	<10	46	(LREE) _N	118508	114157
19	Cu	25	27	47	(HREE) _N	41131	41458
20	Cr	521	543	48	(MREE) _N	9220	8848
21	Pb	826	851	49	(LREE) _N /(HREE) _N	2.88	2.75
22	Zr	1592	1403	50	(La/Lu) _N	8.64	8.11
23	Zn	170	180	51	(La/Yb) _N	9.24	8.75
24	Ba	322	367	52	(Ce/Yb) _N	1.82	1.75
25	Sr	917	1100	53	(La/Sm) _N	152.38	128.28
26	La	29247	28138	54	(Gd/Lu) _N	0.10	0.09
27	Ce	14979	14654	55	(Gd/Yb) _N	0.11	0.09
28	Pr	439	389	56	(Eu/Eu) [*]	0.30	0.39

Mode/nature of occurrence and locality of D-1 and D-2: As vein material in the Bichun area.

Analyst: Dr. Smeer Durani, Chemistry Laboratory, AMD, Hyderabad.

ratio (8.41–8.64). Significantly, the content of middle REE (MREE) is very low (1507–1565 ppm). Similar trend is also exhibited by the chondrite-normalised (normalising values after Boynton 1984) values. The (LREE)_N is nearly three times higher (114,157–118,508) than (HREE)_N (41,131–41,458), with high (LREE)_N/(HREE)_N ratio (2.75–2.88). The value of (MREE)_N is the lowest than both (LREE)_N and (HREE)_N. In a nutshell, (LREE)_N > (HREE)_N > (MREE)_N. Furthermore, (La/Lu)_N, (La/Yb)_N, and (Ce/Yb)_N ratios are also high, being 8.11–8.64, 8.75–9.24, and 1.75–1.82, respectively. On the other hand, although the investigated davidite is characterized by extremely high (La/Sm)_N ratio (128.3–152.4), its (Gd/Lu)_N and (Gd/Yb)_N ratios, 0.09–0.10 and 0.09–0.11, respectively, are extremely low (table 1). The overall trend of chondrite-normalised values of the REE is: La > Ce > Lu > Yb > Tm > Er > Pr > Ho > Dy > Tb > Gd > Nd > Sm >

Eu. The chondrite-normalised plot exhibits steep slope towards Eu both from La to Sm (LREE) and also once again steep slope from Gd to Lu (HREE) leading to pronounced negative Eu-anomaly (Eu/Eu^{*}=0.30–0.39). Due to the lowest content of the MREE, the chondrite-normalised plot exhibits steeply sloping curve from both the sides towards the MREE simulating rather an asymmetrically-stretched U-shaped slope (figure 5), with its base being V-shaped simulating a pronounced negative Eu-anomaly. Similar unusual REE pattern of davidite has also been reported by Dixon and Wylie (1951).

4.5 Geochemical comparison from global occurrences

The bulk chemical composition of davidite from some of the world localities is given in table 3.

Figure 5. Chondrite-normalised plot of davidite (Chondrite-normalising values after Boynton 1984). Note a rather asymmetrically-stretched U-shape pattern, with its V-shaped bottom simulating a negative Eu-anomaly.

Table 3. Chemical composition of davidite (D-1 and D-2) from Bichun area, Jaipur district, Rajasthan compared with davidite from some of the world localities.

Oxide (wt.%)	1	2	3	4	D – 1	D – 2
Al ₂ O ₃	—	—	0.37	0.39	1.4	0.9
SiO ₂	—	0.06	1.69	0.34	1.2	0.8
TiO ₂	54.3	54.5	54.37	55.20	51.5	52.6
V ₂ O ₅	—	1.40	0.31	0.33	—	—
Cr ₂ O ₃	—	0.17	0.87	0.91	0.076	0.079
Fe ₂ O ₃	13.0	10.2	18.84	19.80	14.8	15.1
MgO	0.6	nil	0.73	0.77	0.3	0.2
CaO	1.5	0.30	1.28	—	0.6	0.6
MnO	—	—	0.21	0.22	0.2	0.2
FeO	16.0	16.5	7.14	7.50	10.2	9.8
SrO	—	—	0.26	0.27	0.108	0.130
PbO	1.5	0.72	—	—	0.089	0.092
ZrO ₂	—	0.40	0.52	0.55	0.215	0.190
(RE) ₂ O ₃	8.3	5.60	8.96	9.42	6.72	6.922
ThO ₂	1.1	0.07	0.43	0.45	0.135	0.128
UO ₂	4.6	9.80	3.56	3.74	6.97	7.12
Na ₂ O	—	0.15	0.03	0.03	0.02	0.02
K ₂ O	—	—	0.08	0.08	3.85	3.61
H ₂ O ⁺	—	0.05	0.17	—	0.25	0.05
H ₂ O [−]	—	—	0.00	—	0.02	0.05
Total	100.9	99.92	99.82	100.0	98.65	98.59

1. Radium Hill, South Australia, 2. Tete district, Mozambique, 3. Pandora prospect, Quijotoa Mountains, Pima County, Arizona (1–4 (4 recalculated from 3) after Pabst 1961, table 2; and D-1 and D-2 present study).

Also, for a comparison at a glance, gross geochemical behaviour of various elements in davidites from different world localities is shown in geochemical plots (figure 6). Critical scrutiny of geochemical data (table 3) reveals that the davidite from Bichun contains low Ti (51.5–52.60% TiO₂) relative to davidite from South Australia (54.3% TiO₂), Mozambique (54.50% TiO₂), and Arizona

(55.20% TiO₂). Although total Fe is more in davidite of the Bichun (~25%), individually, FeO (9.8–10.2%) is significantly low, compared to that from Australia (16.0%) and Mozambique (16.5%); only in the case of Arizona davidite, FeO is less, i.e., 7.5%. In contrast, the content of Fe₂O₃ (14.8–15.1%) in davidite of Bichun is more compared to that of Australia (13.0%) and Mozambique

Figure 6. Geochemical plots of davidites from Bichun and world localities. Index: 1. Radium Hill, South Australia. 2. Tete district, Mozambique. 3. Pandora prospect, Quijotoa Mountains, Pima County, Arizona (1 to 4 after Pabst 1961 and D-1 and D-2 present study).

(10.2%). But, like davidite of Bichun, that of Arizona also contains more Fe_2O_3 (19.80%). Also, the REE content in davidite of Bichun is less (6.72–6.92%) compared to those from Australia (8.3%) and Arizona (9.42%). From the available data (table 3), it is also apparent that among world occurrences, davidite from the Mozambique has the highest UO_2 (9.8%) and the lowest ThO_2 (0.07%) and REE (5.60%) contents. Next to this, UO_2 (6.70–6.85%) in davidite of Bichun is more and ThO_2 (0.13–0.14%) is less relative to U and Th contents in davidite from Australia (4.6% UO_2 ; 1.1% ThO_2) and Arizona (3.74% UO_2 ; 0.45% ThO_2). When compared with davidite of Australia, Mozambique and Arizona, the investigated davidite of Bichun contains more K_2O , Al_2O_3 , SiO_2 and total water of hydration (H_2O); and less Na_2O , ZrO_2 , PbO , Cr_2O_3 and MgO contents (table 3).

5. Discussion and conclusions

Microscopic examination of the investigated davidite reveals that it is isotropic in nature. Such an optical behaviour of davidite is due to its metamict nature in its natural state, a fact further revealed by the lack of XRD pattern in its initial diffraction (figure 4a). The bombardment by alpha particles resulted in collapse of davidite structure leading to its metamictisation. It is only after controlled heating at varying temperatures, *viz.*, 750°, 800°, 850° and 900°C, in a muffle

furnace, for a period of 3 hrs on each occasion, its heat-treated product of 900°C yielded well-defined XRD pattern (figure 4e) due to restoration of its crystallinity. In fact, the non-stoichiometric calculated structural formulae of the davidites are due to their metamict nature. Like other metamict minerals (Ellsworth 1932; Heinrich 1958), the opening of davidite structure on account of development of criss-cross micro-cracks and attendant general expansion is also known (Gatehouse *et al.* 1979). Due to metamictisation, structure of the investigated davidite might have behaved like an open system, thereby facilitating migration of cations and anions ultimately leading to stoichiometric deviation of its formula unit. Further, absence of certain reflections of minor to moderate I/I_0 is also due to metamict nature of davidite, and lack of restoration of these reflections even after heat-treatment.

Available literature reveals that genetically uranium mineralization in the Bichun area is linked with the alkali metasomatism of various lithounits of the BGC (Shaji *et al.* 2011; Latha *et al.* 2015). Significantly, the Bichun area falls in the albitite–pyroxenite–microcline belt of western India (Singh *et al.* 1998) which bears ample evidences of alkali metasomatism, involving introduction of Na, K, Rb, Li, and Cs in varying proportions (Singh *et al.* 1998; Jain *et al.* 1999; Sinha *et al.* 2000; Yadav *et al.* 2002, 2004; Jayalal 2008; Singh *et al.* 2013) which is a regional exogenous event. It has resulted in the formation

of albitite (dominant), microcline (subordinate), etc. (Singh *et al.* 1998). Preliminary petrographic studies of different rocks hosting uranium mineralization also support such observations (Latha *et al.* 2015). Accordingly, tentatively it may be envisaged that the higher K_2O content in the studied davidite may possibly be due to highly alkaline nature of the metasomatising fluids, including geochemical characteristics of enveloping rocks that were responsible for davidite formation. Also, relatively more Al_2O_3 content in davidite is possibly due to the source rock characteristics as rocks with higher Al_2O_3 content are reported to bear signatures of more intense metasomatism/albitisation (Shaji *et al.* 2011), a process that is envisaged to have also been responsible for davidite formation. Metasomatised/albitised/microclinised nature of BGC hosting davidite in the Bichun area also seem to corroborate such an inference.

The two prominent modes of occurrences of davidite, i.e., disseminated and fracture filling, are common (figure 2a–d). These features seem to reveal that davidite mineralization is dominantly of syn-magmatic and epigenetic hydrothermal types, implying thereby that at least two phases of U-mineralization were involved. Commonly, with progressive albitisation, successive melts gradually get depleted in Ca, Mg, Fe, Ti including trace elements, and become enriched not only in Na and/or K, but also in metal complexes-charged volatiles (Yang 2008). Accordingly, it is postulated that such metasomatising fluids would have caused not only albitisation (and microclinisation), but also simultaneous crystallization of disseminated davidite crystals (figure 2a–d) wherever accompanying metal complexes, particularly U, attained saturation consequent to changed physiochemical conditions. Fractured nature of albitites suggests that, after their formation, they have been subjected to deformation and attendant fracturing that induced secondary porosity and permeability. It is a known fact that Na-metasomatising fluids originate from the deeper parts of the crust and ascend through deep-seated fractures (Cuney and Kyser 2008); and formation of albitites along NNE trending albitite belt of Rajasthan, in which Bichun area falls, is not an exception to this (Ray 1990; Sinha *et al.* 2000; Yadav *et al.* 2002, 2004; Singh *et al.* 2013). Such ascending albitising fluids might have further accentuated development of secondary pore system consequent to corrosive and solution activity in the rocks enveloping such fractures. Also, it is postulated that successive

batches of ascending fluids might have scavenged intrinsic U from the enveloping country rocks and precipitated the same as davidite (major phase) crystals, with occasional minor phases as uraninite and U–Ti complexes (Shaji *et al.* 2011; Latha *et al.* 2015), along the fractures and secondary pore systems as veins and stringers (figure 3). Since such fluids were locally unusually enriched in U, thickness of davidite veins, in places, is more. Due to sudden change in physiochemical conditions decoupling of U complexes in secondary pore system would have been more, resulting in sudden saturation of U and formation of davidite crystals depending upon the availability of other required cations and anions.

In davidite, the substitution of U by REE is known (Neumann and Sverdrup 1960). In the investigated davidite, content of U is more and REE is less relative to davidite from the world localities. It would therefore mean that substantial substitution of U by REE has not taken place in davidite of the Bichun leading to low content of REE in it.

The characteristic feature of distribution pattern of REE in davidite is very high content of LREE and relatively low HREE compared to substantially low content of MREE. This unusual feature is again reflected in chondrite-normalised REE pattern of davidite, that is, a rather asymmetrically-stretched U-shaped inward slope (figure 4). Such unusual distribution pattern of REEs may be due to the occupation of REEs in two distinct crystallographic sites in the investigated davidite structure (cf. Dixon and Wylie 1951; Neumann and Sverdrup 1960). Indeed, in the davidite structure, M(1) and M(O) sites are occupied by U and predominant REE, e.g., La^{3+} , Ce^{3+} , respectively, whereas, the REEs with less ionic radii, namely, Er including Y, substitute U in the octahedral site, i.e., M(1), leading to unusually high concentration of LREE and HREE and substantially low content of MREE. Since the substitution of U by REE was limited, U content is high and REE (and Th) content is low in the investigated davidite. In fact, it is substantial substitution of U by REEs (and Th) in davidite from Australia and Arizona that has resulted in low content of U and high content of REEs (and Th) in them. Chondrite-normalised REE plot of davidite (figure 5) reveals a steep slope from Sm to Eu and again from Gd to Lu simulating a pronounced negative Eu-anomaly ($Eu/Eu^* = 0.30–0.39$). Such a high negative

Eu-anomaly suggests extremely fractionated nature of the metasomatising fluids from which davidite of Bichun had crystallized. High $(\text{LREE})_{\text{N}}/(\text{HREE})_{\text{N}}$ ratios reveal higher fractionation of LREE relative to HREE. It is further corroborated by high $(\text{La/Lu})_{\text{N}}$, $(\text{La/Yb})_{\text{N}}$, and $(\text{Ce/Yb})_{\text{N}}$ ratios. The fact that substantial fractionation among LREE has taken place is brought out by high $(\text{La/Sm})_{\text{N}}$ ratio. Contrasting this, low values of $(\text{Gd/Lu})_{\text{N}}$ and $(\text{Gd/Yb})_{\text{N}}$ ratios suggest very less fractionation among HREE.

The high content of Fe_2O_3 in davidite of Bichun is noteworthy, and same may be due to a relative preponderance of oxidizing over reducing conditions during its formation. Significantly, davidite containing more Fe_2O_3 , like davidite of Bichun, from the world localities (e.g., Australia and Arizona) also have relatively more U and less of REE (and Th) implying that possibly a relative dominance of oxidizing condition over reducing condition restricts replacement of U by REE (and Th), leading to low content of the latter in the davidite structure. Oxidising condition is likely to be relatively more under comparatively lower temperature and shallower depth condition. Davidite is a high temperature mineral. Thus, by analogy, davidites of Bichun, Australia and Arizona appear to have formed under relatively lower side ($\sim 400^\circ\text{C}$; cf. Singh *et al.* 2013) of the high temperature regime under comparatively shallower depth condition compared to davidite of Mozambique ($\sim 400\text{--}450^\circ\text{C}$).

Metamict nature of the investigated davidite, as revealed by this study, needs specific mention in view of its implications on U-beneficiation. It is a well-known fact that refractory minerals like davidite pose severe problems in U-beneficiation even under stringent leaching conditions as U is tightly held in their lattice and thus same is not available for reaction with leaching reagent. Due to metamictisation lattice-bound U either gets free from, or gets loosely held in, the lattice (Heinrich 1958) and thus becomes amenable for leaching. Under such a situation, there is enhancement of U leaching from metamict minerals, which makes U beneficiation cost effective and economical. In an experimental work, the investigated metamict davidite of Bichun has yielded 85–96% U leachability (Singh *et al.* 2012), in contrast to very poor leachability of U from non-metamict davidite-bearing U ores. Conditions under which the leachability exercise was carried out include $\sim 150^\circ\text{C}$ temperature, concentrated H_2SO_4 (~ 0.3

Molar) and MnO_2 (as oxidant) for $\sim 16\text{--}17$ hrs duration (Singh *et al.* 2012). By implication, therefore, metamict davidite-bearing U ores not only from Rajasthan, but also from other parts of India and world localities are likely to yield very high U leachability, thereby making them attractive sources of U, which otherwise are ignored by mineral engineers as uneconomic U ores.

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