FIRST REPORT OF DOMEYKITE AND KOUTEKITE (COPPER ARSENIDES) IN SIWALIK SANDSTONES OF ROMEHRA, HAMIRPUR DISTRICT, HIMACHAL PRADESH

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Koutekite and two polymorphs (i.e., alpha and beta) of domeykite (rare copper arsenide minerals) are reported for the first time from the uraniferous Lower Siwalik sandstones of the Romehra area, Hamirpur district, Himachal Pradesh. The calculated cell size of alpha-domeykite (Cubic) is $a_0 = 9.646$ Å and that of beta-domeykite (Hexagonal) is $a_0 = 7.151$ Å and $c_0 = 7.304$ Å. Koutekite (Hexagonal) has measured cell parameters of $a_0 = 11.58$ Å and $c_0 = 14.55$ Å. However, in koutekite of Romehra area an important interplanar spacing (d) at 2.081Å is merging with 'd' of beta domeykite at 2.061Å and another interplanar spacing at 2.47Å exhibits comparatively higher intensity than the one published in JCPDS Data Card No.13-581. Association of domeykite with uraniferous sandstones points out that uranium mineralisation in Lower Siwaliks of the Romehra took place possibly below 90°C temperature.

Introduction

The conglomerate, sandstone and shale sequence of Siwalik Supergroup is about 6000 m thick, and is of Middle Miocene to Pleistocene age. The sequence is represented mostly by fluviatile, freshwater, molasse type of sediments, derived largely from the fertile granitic and metamorphic rocks of Lesser Himalayan Crystalline zones (Verma, 1993; Singh et al. 1993). This sequence is known to be a favourable host for sedimentary type of uranium mineralisation (Singh, 1993; Kaul et al. 1993). During the course of mineralogical studies on uranium-rich Lower Siwalik sandstone of Romehra area (Fig.1), copper arsenides, namely, domeykite (Cu_3As) and koutekite (Cu_5As_2) have been identified. This paper provides XRD results, besides some data on microscopic examination, on these minerals from Romehra and evaluates their implications for uranium mineralisation in Lower Siwaliks of the area. Domeykite and koutekite are being reported for the first time from India.

Regional Geology

The Cenozoic sedimentary sequence comprising the Siwalik Supergroup of rocks (Table 1) provides an excellent setting for uranium mineralisation (Singh, 1993). Promising shows of uranium mineralisation are generally present in two typical lithological settings, namely, (1) the transition zone between Middle and Upper Siwaliks and (2) the Lower and Middle Siwalik contact, as well as the Lower Siwalik sediments.

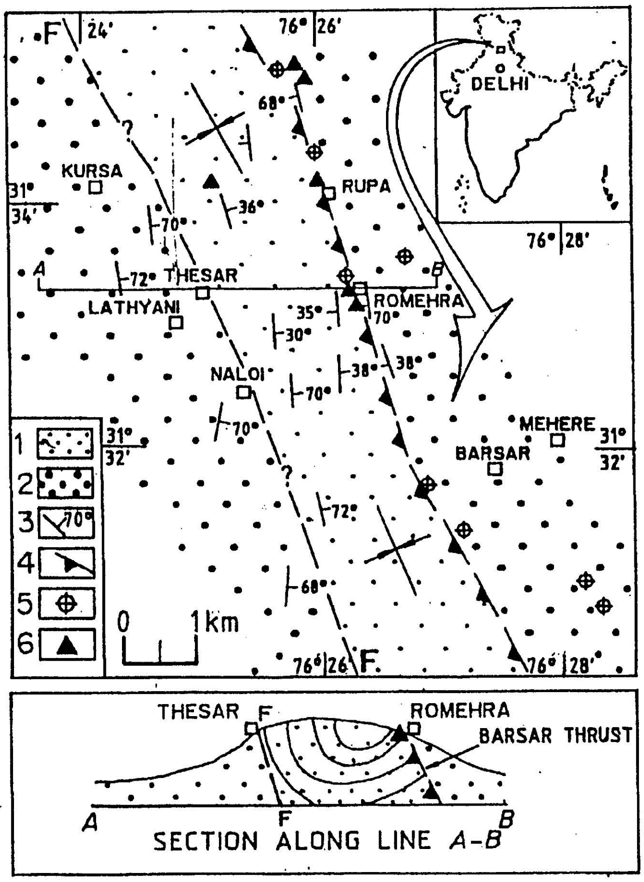

Fig.1. Geological map of Romehra area. 1 - Lower Siwalik, 2 - Middle Siwalik, 3 - Bedding trend, 4 - Thrust, 5 - Spring and 6 - Radioactivity anomaly. Line along F—F could be either a fault or a thrust counterpart of Barsar thrust.

Lower Siwalik rocks consist of sub-greywackes, with fine- to medium-grained clasts containing calcareous

Table 1. The litho-stratigraphical succession of the Siwalik Supergroup of rocks (*after* Verma, 1993; Raiverman, 1997)

Group	Stage/Rock type	Age
Upper Siwalik	Boulder Conglomerate	Early Pleistocene
(1800 to 2400 m)	Pinjor Stage	Late Pliocene
	Tatrot Stage	Late Pliocene
Middle Siwalik	Dhok Pathan Stage	Early Pliocene
(1800 to 2400 m)	Nagri Stage	Late Miocene
Lower Siwalik	Chinji Stage	Middle Miocene
(1500 m)	Kamlial Stage	Middle Miocene

cement disseminated throughout the rock mass interbedded with well developed sandy clays of chocolate and maroon colours. The clay horizons often pass laterally into clay conglomerates. Coarse sandstone in upper part, near Middle Siwaliks, often becomes conglomeratic. The red clays also change to green mudstone and siltstones. The Lower Siwalik sandstone is hard, compact, jointed and grey/green and maroon in colour. Large and small scale ripple marks, cross-beds, horizontal bedding, flute and load casts are the primary sedimentary structures observed.

Medium to coarse conglomeratic sandstone, alternating with purple clays, characterise the Middle Siwalik rocks. Sub-angular to sub-rounded pebbles and cobbles of quartzite, schist, sandstone and phyllite frequently appear in the sandstone unit alongwith small pockets of underlying clays. Sandstone in Middle Siwalik is generally loose and friable, and light grey to olive green in colour. Carbonaceous (coalified) plant fragments are sparsely distributed in a number of sandstone units. Large and small scale cross-beds, linguoid and lunate ripple marks, mud cracks, horizontal bedding, flute casts and scour- and fill-structures are the primary sedimentary structures in the sandstones.

Generally, the Middle Siwalik sediments are distinguishable into lower and upper units. The lower unit lacks fine clastics, as compared to the upper unit which shows mixed interbedded assemblage of medium to fine sandstone and clay.

Upper Siwalik lithology is marked by the polymictic conglomerates, coarse to medium sandstones and clays. Polymictic conglomerate comprises pebbles, cobbles and boulders of granite, quartzite, schist, sandstone and phyllite. Sediments of Upper Siwaliks are loose and incoherent. Sandstone units are profusely cross-bedded and display scour- and fill-structures.

Local Geology

The Romehra area, with known uranium occurrences, is located in the Solasingidhar ridge in Hamirpur district, Himachal Pradesh, in the Una-Hamirpur section, about 50 km NE of Una. The study area exposes the Lower and Middle Siwalik sediments. The Lower Siwaliks are represented by compact, massive, fine-grained, calcareous/ferruginous sandstones, interbedded with purple to greyish green mudstones, in a sequence becoming finer upwards; while the Middle Siwaliks are made up of coarse, friable, greyish, pepper-salt sandstones. The Lower Siwaliks are thrust over the Middle Siwaliks along a prominent tectonic element, the Barsar thrust. Structurally, the Solasingidhar ridge forms a synformal anticline, with the stratigraphically older Lower Siwalik litho-units occupying the core, underlain by the younger Middle Siwalik rocks. The general trends of the formations are N-S to N10°W-S10°E with moderate dips due west, with a few local reversals. The ferruginous and radioactive sandstones, smeared with secondary copper minerals viz., malachite and azurite, are exposed along the eastern scarp face of the Solasingidhar, and lies within a range of about 180 m from the Barsar thrust. The surface uranium values range from 0.004 to 1.8% U_3O_8 (chem), and that of copper from 0.043 to 1.20%. The radioactive minerals identified include uraninite, pitchblende, uranophane and metazeunerite.

Methodology

For XRD studies, radioactive rock samples were beneficiated by grinding them to about 100 mesh, followed by heavy liquid separation. Methyline iodide heavy fraction was further subjected to magnetic separation using Frantz isodynamic separator. The XRD study of the isodynamic separates was done on a Siemens Kristalloflex-800 X-ray generator operated at 35 kV and 20 mA, with CuKα (1.5418Å) radiation, monochromatised with a crystal monochromator. The powder patterns were obtained through a DACO-MP microprocessor controlled D-500 diffractometer and LA-100 recording system. The samples were scanned in the two theta range of 4° to 80° with the rate meter fixed at 1x 10 pulses per second, and a time constant of 2 seconds. The minerals were identified by the search-match method, by comparing their interplanar spacings (d) and intensities with those compiled in PDF data cards, published by the Joint Committee on Powder Diffraction Standards (JCPDS). Interpretation of diffractograms of various separates indicated the presence of domeykite and koutekite, mainly in non-magnetic fraction at 1.2 ampere. As domeykite and meta-domeykite are two polymorphs, and have commonly been referred to as alpha-domeykite and beta-domeykite (Berry and Thompson, 1962; Skinner and Luce, 1971), we have also used same terminologies throughout the text, even though in JCPDS data cards merely domeykite and meta-domeykite are mentioned. These minerals have been identified by XRD first, and then optically characterised. However, as both (the polymorphs of) domeykite and koutekite occur in very fine aggregates many of their optical properties could not be studied by petrological microscope.

COPPER ARSENIDES

Alpha- and Beta-Domeykite (Cu_3As)

Domeykite was named in 1845 after Ignacio Domeyko (Gaines et al. 1997, p.39), a Chilean mineralogist. Alpha-domeykite (Cubic; a_0 = 9.62 Å; Z = 16) of Romehra is creamy yellow, isotropic, and occurs as granular aggregates, with 44% reflectivity at 546 nm. Studied beta-domeykite (Hexagonal; a_0 = 7.16 Å, c_0 = 7.33 Å; Z = 6) is bluish, distinctly anisotropic, and occurs as aggregate scattered in the matrix and also along the grain boundaries of the clasts, i.e., quartz, with weak bireflectance, and 46-48% reflectivity at 546 nm. Internal reflections are absent in both the polymorphs. In Romehra area, at places, alpha-domeykite occurs together with beta-domeykite, which has been marked by the difference in the reflectivity. Further, beta-domeykite of Romehra shows relatively higher reflectivity as compared to koutekite.

The interplanar spacings (d) and intensities of the alpha-domeykite and beta-domeykite (Tables 2 and 3), obtained from the X-ray powder patterns, compare very well with the reported corresponding values published for these polymorphs in JCPDS Data Card Nos. 9-333 and 14-454, respectively. However, in studied beta-domeykite one reflection at 3.63 Å from 002, 110 hkl is very poorly developed. The cell sizes, determined for alpha-domeykite (a_0 = 9.646 Å) and beta-domeykite (a_0 = 7.151 Å, c_0 = 7.304 Å), are also in close agreement with their published values of a_0 = 9.62 Å; and a_0 = 7.16 Å, c_0 = 7.33 Å, respectively.

Koutekite (Cu_5As_2)

Koutekite (Hexagonal; a_0 = 11.51 Å; c_0 = 14.54 Å; Z = 18) is a very rare copper arsenide mineral, and was first reported by Johan (1958) from Cerny Dul in Kronose (Giant Mountains), Bohemia; followed by Picot and Vernet (1967), who reported it from Daluis in the high Valley of the Var, France. Johan named it after Jaromir Koutek, a Czech mineralogist. Under the microscope, it appears bluish-grey, violet-grey, weakly bireflecting, strongly anisotropic with 42% reflectivity at 546 nm. It shows a distinct lameller texture. From X-ray powder pattern it is apparent that interplanar spacings (Table 4) and intensities of studied koutekite also match very well with the values published in JCPDS Data Card No.13-581. Likewise, the calculated cell size of koutekite (a_0 = 11.578 Å; c_0 = 14.55 Å) is also very close to its published value (a_0 = 11.51 Å, c_0 = 14.54 Å). However, in koutekite of Romehra an important interplanar spacing at 2.081 Å merges with 'd' spacing of beta-domeykite at 2.061 Å, and another 'd' spacing at 2.482 Å exhibits relatively more intensity compared to the one published in JCPDS Data Card No.13-581. These deviations could be due to impurities.

Table 2. X-ray data of domeykite standard (A) compared with interplanar spacings and cell parameters of alpha-domeykite (B) from Romehra area, Hamirpur district, Himachal Pradesh

Domeykite Standard (A) (JCPDS Data Card No.9-333)			Interplanar spacings of studied alpha-domeykite (B)
d Å	I/I_1	hkl	d Å
3.95	40	112	3.9469
3.41	20	022	3.4086
3.05	40	013	3.0539
2.57	30	123	2.5404
2.42	20	004	2.4154
2.15	40	024	2.1493
2.05	100	233	2.0599
1.965	50	224	1.9667
1.888	70	015, 134	1.8895
1.558	20	116, 235	1.5642
1.519	10	026	1.5117
1.486	20	145	1.4805
1.415	5	136	-
1.361	20	017, 345	1.3633
1.308	50	127, 255	1.3072
1.264	10	037	1.2638
1.218	40	156, 237	1.2120
1.185	30	147	1.1876
		(Plus 22 reflections upto 0.7800 Å)	

	(A)	(B)
Cell parameter	a_0 = 9.62 Å	9.646 Å
Cell volume	-	897.68 $Å^3$

DISCUSSION

The arsenides of copper are two types i.e., lower and higher. The lower arsenide mineral species are whiteneyite, algodonite, alpha-domeykite and beta-domeykite, whereas the higher arsenides are represented by koutekite, novakite and paxite (Skinner and Luce, 1971). Higher arsenides are rare. Among lower arsenides, alpha-domeykite is commonly found in relatively pure masses and other minerals of this

Table 3. X-ray data of meta-domeykite standard (A) compared with interplanar spacings and cell parameters of beta-domeykite (B) from Romehra area, Hamirpur district, Himachal Pradesh

Meta-domeykite standard (A) (JCPDS Data Card No14-454)			Interplanar spacings of studied beta-domeykite (B)
d Å	I/I_1	hkl	d Å
3.63	40	002,110	3.642
3.21	20	111	3.206
2.56	10	112	2.541
2.37	30	202	2.362
2.23	30	211	2.220
2.13	5	-	-
2.08	100	300	2.061
2.02	100	113	2.012
1.973	20	212	1.967
1.804	30	302	1.793
1.752	20	104,221	1.751
1.672	10	311	1.668
1.637	5	114	1.641
1.445	50	223,214	1.438
1.399	10	321	1.388
1.329	40	322	1.323
	(Plus 17 reflections upto 0.890 Å)		
	(A)		(B)
Cell parameters	a_0 = 7.16 Å		7.151 Å
	c_0 = 7.33 Å		7. 304 Å
Cell volume	-		323. 430 Å^3

Table 4. X-ray data on koutekite standard (A) compared with interplanar spacings and cell parameters of koutekite (B) from Romehra area, Hamirpur district, Himachal Pradesh

Koutekite standard(A) (JCPDS Data Card No13-581)			Interplanar spacings of studied koutekite (B)
d Å	I/I_1	hkl	d Å
3.32	60	030	3.3568
2.88	10	005	2.8732
2.747	10	015	2.7253
2.660	20	222	2.6496
2.567	10	132	2.5757
2.482	20	223	2.4720
2.443	70	041	2.4402
2.356	20	042	2.3621
2.304	10	125	2.3063
2.242	20	224	2.2629
2.161	50	140	2.1209
2.081	100	142	2..0599
2.023	100	126	2.0125
1.989	100	050	1.9870
1.934	10	234	1.9355
1.786	60	333	1.7928
1.743	50	054	1.7446
1.497	50	336	1.5117
1.451	50	163	1.4375
1.400	10	255	1.3882
1.377	70	261, 443	1.3581
1.346	10	165	1.3462
1.324	80	170, 3 54	1.3199
1.198	80	266, 272	1 .1980
1.179	80	084	1.1790
1.148	90	085	1.1480
		(A)	(B)
Cell parameters		a_0 = 11.51 Å	11.578 Å
		c_0 = 14.54 Å	14.55 Å
Cell volume		-	1689.27 Å^3

species, due to less arsenic (As) content, are more malleable and, thus, difficult to separate them individually. Lower arsenides (Cu content about 75 atomic percent) are known to occur generally as fine-grained intergrown assemblages that include (1) whitneyite and algodonite, (2) algodonite and alpha-domeykite, (3) algodonite and beta-domeykite and (4) alpha-domeykite and beta-domeykite (Skinner and Luce, 1971). In the Romehra area, the fourth assemblage is present in intimate association with koutekite. The cupriferous sandstones from Kazakhstan also contain koutekite in association with domeykite (Abulgazina et al. 1991). Because of their very fine-grained and malleable nature, we could not separate them individually for study. A fraction comprising all the three minerals has analysed 78.5% Cu and 19.3% As (chemical data), besides 2481 ppm Ti, 72 ppmV, 5114 ppm Mn, 13 ppm Ni, 18 ppm Y, 363 ppm Zr and 264 ppm Pb (spectrographic data).

Formation of alpha-domeykite is known to take place below 90°C temperature (Skinner and Luce, 1971). Accordingly, we believe that studied alpha-domeykite of Romehra area might also have been formed under similar temperature condition. This is further supported by its association with sandstone type of uranium mineralisation, in which low-temperature groundwaters are known to be the mineralising solutions (Finch and Davis, 1985). Also, it would thus mean that uranium mineralisation in Siwaliks of the Romehra area took place below 90°C temperature, because uranium and copper arsenide minerals commonly occur in intimate association in the matrix of sandstones of Romehra, and alpha-domeykite can be used directly as a geothermometer (Skinner and Luce, 1971). Even in hydrothermal system domeykite is known to crystallise from low temperature solutions in an environment of extremely low sulphur fugacity (Burke and Dunn, 1988). In all probability, beta-domeykite has formed from the breakdown of alpha-domeykite at low temperatures (*cf.* Skinner and

Luce, 1971; Gaines et al. 1997). In natural samples where both the polymorphs co-exist, beta-domeykite is known to be copper deficient, and their co-existence need not necessarily represent a case of disequilibrium (Skinner and Luce, 1971). Compounds richer in arsenic do not form at normal pressure conditions (Heyding and Despault, 1960). By analogy, therefore, koutekite might have been formed at a pressure higher than the pressure (about one atomosphere; Skinner and Luce, 1971) required for the formation of alpha-domeykite.

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