Stannoidite and cubanite from Askot polymetallic sulphide ores, Kumaun Lesser Himalaya, India

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Results of mineral, chemical and XRD investigations on stannoidite and cubanite from Askot sulphide deposit, Kumaun Himalaya are presented here. Stannoidite occurs as myrmekitic intergrowth and cubanite as exsolved lamellae in chalcopyrite. Chemical composition of this tin-bearing sulphide closely matches that of stannoidite, hitherto unreported from the Himalayan sulphides. Stannoidite and cubanite from Askot are non-stoichiometric. An average of 1.13 wt% Zn is present in stannoidite, whereas the zinc content of cubanite is very low. Cu/(Cu + Fe) ratio of about 0.326 in cubanite indicates iron enrichment. These sulphides were formed from cooling of high-temperature hydrothermal solution, possibly with higher sulphur fugacity.

Keywords: Askot sulphides, cubanite, stannoidite, sulphide mineralization.

THE polymetallic sulphide mineralization of Askot, Pithoragarh District, Uttarakhand, is the largest known metal sulphide deposit in the Western Himalaya, with an estimated reserve of about 1.14 million tonnes of copper, lead and zinc[1]. Sulphide mineralization is confined to the quartzo-feldspathic schists and gneisses of Precambrian Askot Crystallines, which occupy the asymmetrical syncline surrounded by sedimentary rocks of Berinag and Tejam formations. Askot Crystallines are considered as allochthonous, originating from the Central Crystallines and emplaced as detached klippe[2–4]. However, some investigations suggest that these and other crystallines are autochthonous or para-autochthonous[5,6]. The thrust contact between these crystallines and the underlying rocks of the sedimentary belt is characterized by intense shearing and mylonitization. Amphibolite also occurs along this contact. Schistose rocks of Askot Crystallines include chlorite–sericite–actinolite–tremolite–epidote–quartz schist, biotite–muscovite–epidote–quartz schist and garnetiferous biotite–muscovite–chlorite–sericite–quartz schists, and their gneisses are biotite-bearing. A whole-rock Rb–Sr isochron age of 1983 ± 80 m.y. has been assigned to these gneisses[7].

An encouraging prospect of polymetallic sulphides with complex mineral assemblage occurs near Berigaon, on the northern limb of the Askot Crystallines. A crude variation from chalcopyrite-rich ore, coarse-grained, galena-rich and fine-grained sulphide assemblage predominantly including chalcopyrite–sphalerite–galena–pyrite–arsenopyrite has been observed. Ghose[8] briefly described the geology, structure, mineralogy and wall-rock alteration of this mineralization. Petrographic studies[9,10] have illustrated various sulphide minerals, such as chalcopyrite, galena, sphalerite, arsenopyrite, marcasite, bornite, chalcocite, pyrrhotite and cubanite in the ore assemblage from Askot. Interesting ore textures reported include exsolution intergrowth of cubanite and pyrrhotite in chalcopyrite, exsolution intergrowth of sphalerite in chalcopyrite, inversion twins of chalcopyrite and the intergrowth of arsenopyrite with pyrrhotite. The wall-rock alteration caused by this sulphide mineralization has also been studied[11]. Seetharam[12] reported gudmundite from these sulphides and also showed stannite sternchen in chalcopyrite. He interpreted that the texture representing the breakdown of tetrahedrite to chalcopyrite–gudmundite intergrowth implies retrograde metamorphism of high-temperature ore body. Pant and Farooq[13] noticed sulphides of copper, lead and zinc in the gneisses of Askot Crystallines, wherein the sulphide zone was elongated in the direction of the major fold axes. On the basis of mineralogical and textural studies they suggested this mineralization as epigenetic replacement-type. Indications of gold were also evident[14] in the mineralized zone of Askot. Available preliminary chemical data of Askot sulphides using SEM-EDAX[15] are semiquantitative and further detailed ore chemical work would be helpful in understanding the ore minerals and genesis of these sulphides. We have carried out chemical analyses of tin-bearing sulphide and cubanite present within the chalcopyrite from Askot. Their X-ray powder diffraction (XRD) and EPM analyses are presented here. On the basis of this study, we report the presence of stannoidite in Askot sulphides. The present study also helps in understanding the thermal and compositional environment during the formation of Askot sulphides.
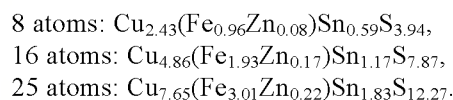
The substitution of elements in the tin-bearing sulphides at high temperature may significantly alter their composition, resulting in various derivatives. The general formula of stannite is $Cu_2(FeZn)SnS_4$, but chemical variations in the sulphides of this family greatly affect the Cu : Sn, Fe : Zn and metal : sulphur ratios. This compositional variation is a result of the thermal and chemical environment at the time of ore formation. Here we report that the tin-bearing sulphide associated intimately with chalcopyrite in chalcopyrite–cubanite–sphalerite assemblage of Askot is stannoidite. This is an unusual sulphide of copper, iron, tin and often with minor zinc. Stannoidite from Askot (Figure 1 *a*) occurs as pinkish grey brownish-coloured, curved and uneven-shaped lamellae and small globules which have myrmekitic intergrowth in chalcopyrite. It is anisotropic and shows light brown to brown pleochroism. Stannoidite lamellae are irregularly orientated in different sizes exhibiting pintch and swell, and sudden termination. In the stannoidite-bearing chalcopyrite, min-

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ute exsolved bodies of sphalerite are also seen. Cubanite is closely associated with chalcopyrite of this assemblage. Elongated and tabular yellow-coloured cubanite laths and lamellae, many of them mutually perpendicular, are found exsolved in chalcopyrite (Figure 1 b). Cubanite is distinctly anisotropic, lighter in colour than chalcopyrite and shows reflectivity nearly similar to chalcopyrite. Thus the three minerals, viz. stannoidite, cubanite and sphalerite occur as exsolved phases in chalcopyrite. Other major primary minerals observed with these sulphides are arsenopyrite and pyrite. Arsenopyrite occurs as euhedral to subhedral rhomb crystals, whereas pyrite is seen in the matrix, showing mutual boundary texture with arsenopyrite. Pyrite also has a mutual boundary with chalcopyrite; however, direct boundary relations of arsenopyrite and pyrite with stannoidite and cubanite are not seen. We have verified the presence of stannoidite and cubanite through XRD study of the chalcopyrite-rich mineral concentrates from Askot sulphides. Fine powder samples were analysed using Phillips X'Pert X-ray Diffractometer and the phases were identified using X'Pert HighScore Plus software package in our XRD laboratory. XRD analyses provide well-defined peaks for stannoidite and

cubanite (Figure 2), matching well with their reference standards, and thus confirming the presence of these minerals in association with chalcopyrite.

The chemical analysis of stannoidite was carried out on the JEOL JCXA-733 super probe at the University Scientific Instrumentation Centre, Roorkee, and Cameca SX-100 at the WIHG EPMA Laboratory, Dehra Dun, under comparable operating conditions (15 kV accelerating voltage, 20 nA probe current and 2 μm beam size). Both qualitative and quantitative analyses of stannoidite were carried out. Qualitative analysis corroborates the presence of Cu, S, Fe, Sn and Zn. A total number of 14 spots of this mineral were analysed, their results along with average are given in Table 1. A variation was observed in Fe contents, but values for Cu were in close range. No compositional difference was noticed in stannoidite occurring as lamellae and globules. We have calculated structural formulae considering 8, 16 and 25 atom structures to examine various possibilities, including stannite, and the stannoidite composition accepted by various workers[16–19]. Since Pb and Mo are quite unlikely to be present in the stannoidite lattice, and that the concentrations of Pb and Mo analysed are <0.003%, the structural formula calculations reported (Table 2) are based on the elements Cu, Fe, Sn, Zn and S. The structural formulae for each of these analyses are given in Table 2, and for the average of these analyses are as follows:

8 atoms: $Cu_{2.43}(Fe_{0.96}Zn_{0.08})Sn_{0.59}S_{3.94}$,
16 atoms: $Cu_{4.86}(Fe_{1.93}Zn_{0.17})Sn_{1.17}S_{7.87}$,
25 atoms: $Cu_{7.65}(Fe_{3.01}Zn_{0.22})Sn_{1.83}S_{12.27}$.

It is apparent that the structural formulae considering eight atoms do not match with stannite: $Cu_2(FeZn)SnS_4$, and the obtained variation in the ratio of Cu : Sn from 4 : 0.86 to 4 : 1.00 is also nowhere near stannite. It also does not match with mawsonite, if calculated for the 17 atom structure[16]. An average metal : sulphur ratio in the studied Cu–Fe–Sn sulphide was 12.71 : 12.21 (= 10 : 9.6) and Cu : Sn ratio nearly 4 : 1 (Table 2). The Cu : Sn ratio was much higher than 2 : 1 known for stannite. Lee et al.[16] and Moh[17] demonstrated that stannoidite shows a
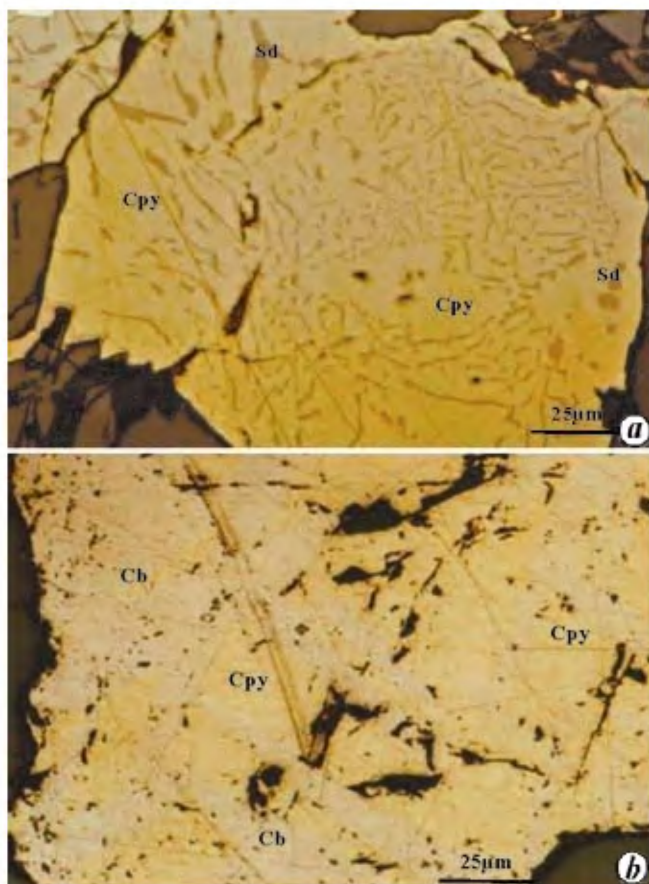

Figure 1. Photomicrograph showing (*a*) myrmekitic intergrowth of stannoidite in chalcopyrite and (*b*) cubanite lamellae exsolved in chalcopyrite. Cpy = Chalcopyrite; Sd, Stannoidite and Cb, Cubanite.
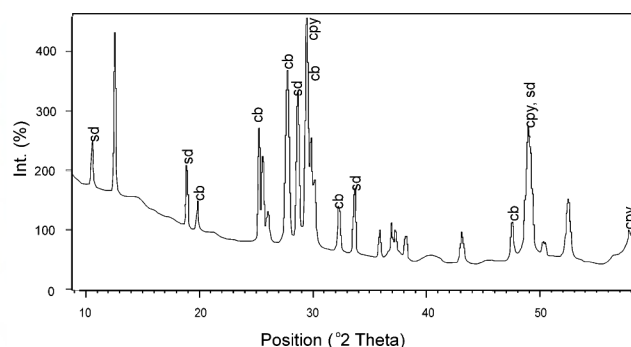

Figure 2. X-ray diffractogram showing presence of stannoidite and cubanite in Askot sulphide assemblage.

Table 1. EPM analysis of Askot stannoidite. Analyses of 14 spots and their average are given

Element	1	2	3	4	5	6	7	8	9	10	11	12	13	14	Average
Cu	36.99	36.88	36.87	37.10	37.44	37.15	37.42	37.19	37.18	37.52	37.22	36.46	37.90	36.70	37.14
Fe	13.38	12.53	13.32	11.81	11.74	12.57	12.29	13.08	13.96	11.66	11.73	16.73	12.46	12.77	12.86
S	30.08	29.62	29.89	30.80	30.26	29.63	29.83	29.80	30.28	29.86	30.03	30.71	28.85	31.41	30.07
Sn	16.16	17.01	16.12	17.05	17.49	17.21	17.27	16.74	15.85	17.28	16.96	14.65	16.96	16.21	16.64
Zn	1.13	1.07	1.06	1.24	1.12	1.09	1.21	1.20	1.00	1.23	1.21	0.89	1.17	1.20	1.13
Pb	0.22	0.78	1.17			0.54			0.82	0.37	0.73		0.29	0.40	0.38
Mo	0.28	0.33	0.31	0.21	0.30	0.18	0.24	0.25	0.30	0.28	0.25	0.30	0.21	0.34	0.27
Se		0.07		0.02	0.15			0.07			0.03	0.02	0.01	0.05	0.03
Co	0.01	0.01	0.03	0.02	0.01	0.02	0.03	0.01	0.02		0.02	0.01			0.02
Au	0.04	0.07		0.07	0.08		0.09					0.01		0.04	0.03
Total	98.29	98.37	98.77	98.32	98.59	98.39	98.38	98.34	99.41	98.20	98.18	99.78	97.85	99.12	98.57

Table 2. Structural formulae calculated using analyses given in Table 1 and considering 8, 16 and 25 atom structures

Analysis no.	8 atoms	16 atoms	25 atoms	Cu : Sn
1	$Cu_{2.43}Fe_{0-.99}Zn_{0.08}Sn_{0.57}S_{3.93}$	$Cu_{4.86}Fe_{1.99}Zn_{0.14}Sn_{1.14}S_{7.86}$	$Cu_{7.60}Fe_{3.12}Zn_{0.22}Sn_{1.78}S_{12.27}$	4 : 0.94
2	$Cu_{2.46}Fe_{0.95}Zn_{0.07}Sn_{0.61}S_{3.91}$	$Cu_{4.92}Fe_{1.89}Zn_{0.14}Sn_{1.21}S_{7.83}$	$Cu_{7.68}Fe_{2.97}Zn_{0.21}Sn_{1.90}S_{12.23}$	4 : 0.99
3	$Cu_{2.44}Fe_{1.00}Zn_{0.07}Sn_{0.57}S_{3.92}$	$Cu_{4.88}Fe_{2.00}Zn_{0.13}Sn_{1.14}S_{7.84}$	$Cu_{7.63}Fe_{3.13}Zn_{0.21}Sn_{1.77}S_{12.26}$	4 : 0.93
4	$Cu_{2.44}Fe_{0.88}Zn_{0.08}Sn_{0.60}S_{4.01}$	$Cu_{4.87}Fe_{1.76}Zn_{0.15}Sn_{1.19}S_{8.02}$	$Cu_{7.61}Fe_{2.75}Zn_{0.23}Sn_{1.87}S_{12.53}$	4 : 0.98
5	$Cu_{2.47}Fe_{0.88}Zn_{0.07}Sn_{0.62}S_{3.96}$	$Cu_{4.94}Fe_{1.76}Zn_{0.14}Sn_{1.23}S_{7.91}$	$Cu_{7.73}Fe_{2.75}Zn_{0.22}Sn_{1.93}S_{12.37}$	4 : 1.00
6	$Cu_{2.47}Fe_{0.95}Zn_{0.07}Sn_{0.61}S_{3.90}$	$Cu_{4.94}Fe_{1.90}Zn_{0.14}Sn_{1.22}S_{7.81}$	$Cu_{7.71}Fe_{2.97}Zn_{0.21}Sn_{1.88}S_{12.20}$	4 : 0.99
7	$Cu_{2.47}Fe_{0.92}Zn_{0.08}Sn_{0.61}S_{3.92}$	$Cu_{4.95}Fe_{1.84}Zn_{0.15}Sn_{1.22}S_{7.83}$	$Cu_{7.74}Fe_{2.87}Zn_{0.24}Sn_{1.91}S_{12.24}$	4 : 0.99
8	$Cu_{2.45}Fe_{0.98}Zn_{0.08}Sn_{0.59}S_{3.89}$	$Cu_{4.91}Fe_{1.96}Zn_{0.15}Sn_{1.18}S_{7.78}$	$Cu_{7.66}Fe_{3.07}Zn_{0.24}Sn_{1.85}S_{12.18}$	4 : 0.96
9	$Cu_{2.43}Fe_{1.03}Zn_{0.06}Sn_{0.55}S_{3.92}$	$Cu_{4.86}Fe_{2.07}Zn_{0.13}Sn_{1.10}S_{7.84}$	$Cu_{7.59}Fe_{3.23}Zn_{0.19}Sn_{1.73}S_{12.25}$	4 : 0.91
10	$Cu_{2.49}Fe_{0.88}Zn_{0.08}Sn_{0.61}S_{3.93}$	$Cu_{4.99}Fe_{1.76}Zn_{0.15}Sn_{1.23}S_{7.87}$	$Cu_{7.80}Fe_{2.75}Zn_{0.24}Sn_{1.92}S_{12.30}$	4 : 0.98
11	$Cu_{2.47}Fe_{0.88}Zn_{0.08}Sn_{0.60}S_{3.96}$	$Cu_{4.95}Fe_{1.78}Zn_{0.15}Sn_{1.20}S_{7.92}$	$Cu_{7.73}Fe_{2.78}Zn_{0.24}Sn_{1.88}S_{12.37}$	4 : 0.97
12	$Cu_{2.33}Fe_{1.22}Zn_{0.06}Sn_{0.50}S_{3.90}$	$Cu_{4.66}Fe_{2.43}Zn_{0.11}Sn_{1.00}S_{7.80}$	$Cu_{7.29}Fe_{3.80}Zn_{0.17}Sn_{1.56}S_{12.18}$	4 : 0.86
13	$Cu_{2.54}Fe_{0.95}Zn_{0.07}Sn_{0.61}S_{3.83}$	$Cu_{5.08}Fe_{1.90}Zn_{0.14}Sn_{1.21}S_{7.66}$	$Cu_{7.94}Fe_{2.97}Zn_{0.23}Sn_{1.89}S_{11.97}$	4 : 0.96
14	$Cu_{2.38}Fe_{0.94}Zn_{0.07}Sn_{0.56}S_{4.04}$	$Cu_{4.76}Fe_{1.88}Zn_{0.15}Sn_{1.12}S_{8.08}$	$Cu_{7.44}Fe_{2.94}Zn_{0.23}Sn_{1.75}S_{12.63}$	4 : 0.94

metal to sulphur ratio of $13 : 12$, whereas it is $1 : 1$ in stannite. Wang[18] gave a metal : sulphur ratio between $10 : 9.7$ and $10 : 9.9$ for stannoidite. The accepted 25 atom structural formula for stannoidite was $Cu_8Fe_3Sn_2S_{12}$ with minor Zn, whereas Ramdhor[19] considered the 16 atom formula for stannoidite as $Cu_5(FeZn)_2SnS_8$. In all of these considerations the Cu : Sn ratio is significantly higher in stannoidite than in stannite. Our above-mentioned calculations based on 16 as well as 25 atom structures closely match the stoichiometric composition of stannoidite. Most published EPMA data of sulphosalts and complex sulphides show that their natural occurrences do not strictly match with the stoichiometric compositions; this has also been verified experimentally[20]. Stannoidite is likely to show variation in composition because of variation in Zn content. The EPMA-based composition of many stannoidite, including that from the type area – Konjo Mine, Japan[21]: $(Cu_{7.22}Ag_{0.01})(Fe_{2.76}Zn_{0.23})\,Sn_{1.71}S_{12.00}$ and others from Vila Apacheta, Bolivia: $Cu_{7.74}\,(Fe_{2.74}Zn_{0.16})\,Sn_{2.03}S_{12.00}$ are also non-stoichiometric, and compare well with the composition of the studied stannoidite. Overall, optical and XRD study, chemical composition, Cu : Sn and metal : sulphur ratios recommend that the tin-bearing sulphide myrmekitic intergrown in chalcopyrite from

Askot is stannoidite. Askot stannoidite is deficient in sulphur and tin. Its deviation from the stoichiometric stannoidite is a consequence of initial composition of the hydrothermal system, the activity of metals in it and their partitioning into sulfosalts[20]. It is possible that the stannite sternchen noticed by Seetharam[12] in chalcopyrite could be stannoidite. We have also analysed cubanite exsolved within chalcopyrite from Askot. Four EPM analyses of cubanite are furnished along with the structural formula for each of these analyses (Table 3). Askot cubanite shows slight Fe enrichment, but absence of Zn. The Cu/(Cu + Fe) atomic% for this cubanite is <0.33 with values 0.326 ± 0.001.

Experimental studies on various sulphide-mineral species along with studies on natural occurrences are significant to understand their stability conditions and genesis[16,17,21–24]. The intergrowth between common tin-bearing sulphide–stannite and chalcopyrite may result from (i) simultaneous formation from a hydrothermal fluid, (ii) complex mineral chemical reaction or (iii) exsolution[19]. Stannoidite generally forms a solid solution with chalcopyrite and often occurs with chalcopyrite, bornite and cubanite in complex vein-type hydrothermal ores, wherein it is typically noticed in xenothermal depo-

Table 3. EPM analysis of Askot cubanite. Structural formulae for these analyses are also calculated

Cu	Fe	S	Se	Mo	Sn	Total	Cu	Fe	S	Cu/(Cu + Fe)
22.63	41.34	35.05	–	0.29	0.19	99.50	0.976	2.028	2.996	0.325
22.51	40.61	35.30	0.06	0.39	0.23	99.10	0.974	1.999	3.027	0.327
22.62	40.79	34.76	0.05	0.29	0.46	98.97	0.984	2.018	2.997	0.327
22.61	41.03	34.14	0.03	0.33	0.34	98.48	0.991	2.045	2.963	0.326
						Average	$Cu_{0.981}Fe_{2.023}S_{2.996}$			

sits[24,25]. It is characteristically reported from complex polymetallic hydrothermal deposits[26], as well as from the pegmatitic and pyrometasomatic ore deposits[27,28]. The observed occurrence of stannoidite as myrmekitic intergrowth in chalcopyrite refers to a solid solution between chalcopyrite and stannoidite at high temperature. In the chalcopyrite solid solution at high temperature significant Zn content was also present, as evident from the sphalerite occurring as exsolved phase within the same grain of chalcopyrite along with stannoidite. Although genesis of stannoidite is not fully resolved, however the stability fields of stannoidite have been demonstrated in the solubility range and phase behaviour of Cu–Fe–Zn–Sn–S system[16–18]. It is known that the formation of stannite–stannoidite–mawsonite of this system not only depends on the temperature, but also on the sulphur fugacity. The ratio of metal to sulphur is 1 : 1 in stannite, 13 : 12 in stannoidite and 9 : 8 in mawsonite, i.e. decreasing sulphur. However, stannoidite formation requires higher sulphur fugacity than stannite; a further increase in sulphur fugacity at constant temperature helps in the formation of mawsonite instead of stannoidite[16]. Occurrence of stannoidite at Askot may indicate a higher sulphur fugacity during ore formation than required for the formation of stannite. Elsewhere, stannoidite is known to occur in high sulphidation mineral deposits[29]. Experimental investigations on the mutual exsolution of chalcopyrite–sphalerite–stannoidite also indicate that stannoidite can be deposited from solid solution at a wide temperature range[16,17] of 390–800°C. Stannoidite is stable above 390°C and below this temperature mawsonite exists, i.e. the phase transformation occurs. The minimum decomposition temperature for stannoidite also sets a limit of 390°C to the observed intergrowth of stannoidite in chalcopyrite. Furthermore, this decomposition temperature and hence the stability of stannoidite are also greatly affected by the variation in Zn concentration. Synthetic zinc-free stannoidite is stable up to 800°C, whereas addition of 3% Zn reduces its decomposition temperature[16] to 500°C. Hence an increase in Zn concentration reduces the temperature of stability of stannoidite, but this broad understanding does not provide any idea about their relationship – whether it is linear or not. Therefore, with the knowledge that an average 1.13 wt% Zn is present in Askot stannoidite, we can only suggest that the Askot stannoidite was formed below 800°C, probably at about 600°C. On the basis of 1.2 wt% Zn in stannoidite from Langban ore, Sweden, Burke[30] has also considered a decomposition temperature of 600°C.

The exsolution of cubanite and chalcopyrite (Figure 1 b) can also help in this thermal assessment, as this is believed to be a useful thermometer for the sulphide ore deposits[31,32]. The exsolution of cubanite in chalcopyrite indicates a temperature[19] above 250–300°C. Transformation of isometric, tetragonal and orthorhombic forms of cubanite also occurs as a function of temperature[22,33]. Isocubanite, a cubic high-temperature cubanite[22,23], shows an overall decrease in Cu contents, increase in Fe content and Cu/(Cu + Fe) of 0.33. Askot cubanite has low Fe (<41.34 wt%) and higher Cu (22.51–22.63 wt%) than isocubanite. Its Zn content (0.001–0.023 wt%) is low and shows Se up to 0.063 wt%. Analyses of Askot cubanite reveal slight deviation from the stoichiometric composition of cubanite, with minor Fe enrichment and Cu/(Cu + Fe) of <0.33. Its XRD (Figure 2) is similar to that of cubanite. The laths of cubanite in chalcopyrite as observed in Askot, are considered as a product of the subsolidus process, wherein the isocubanite first formed was transformed to cubanite[33,34]. Experimental work[22] also demonstrated that repeated homogenization and annealing in nature may have caused the removal of isocubanite and formation of cubanite in ancient ores. Since the observed Fe enrichment and Cu/(Cu + Fe) of 0.0326 ± 0.001 are inclined to higher temperature, Askot cubanite is likely to be the result of natural transformation from the isocubanite first formed. Together, the studied minerals favour the initial formation of Askot ore assemblage from high-temperature hydrothermal solution.

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