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Solid Solution in the As_2S_3-Sb_2S_3 Series at Zarshuran Gold Deposit, Iran

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Abstract

Orpiment, getchellite and stibnite from Zarshuran deposit, NW Iran, exhibit extensive As-Sb substitution. There are four known minerals along As_2S_3-Sb_2S_3 join, i.e. orpiment (As_2S_3), Wakabayashilite [$(As,Sb)_{20}S_{30}$], getchellite ($AsSbS_3$) and stibnite (Sb_2S_3). Extensive mineralogical studies by scanning electron microscope (SEM) and electron probe micro-analyzer (EPMA) indicate that getchellite from Zarshuran exhibits large As/Sb substitution, compared to the synthetic mineral and occurrences in other deposits, which justifies further experimental studies. Natural orpiment with the highest Sb content was recorded in Zarshuran samples. Considering the possible explanation for the incomplete record of solid solution, it appears that rapid variation in fluid chemistry and variability of As and Sb concentration in the hydrothermal solution may have caused extensive solid solution in the As_2S_3-Sb_2S_3 system. The recorded solid solution may indicate that temperatures of gold mineralization were less than 250°C which is supported by fluid inclusion data.

Keywords: Getchellite; Orpiment; Stibnite; Solid solution; As_2S_3-Sb_2S_3 system; Zarshuran gold deposit

Introduction and Previous Work

Orpiment and stibnite have been recognized in several disseminated replacement type gold deposits in the western United States [1,2], China [3,4] and Iran [5-8]. There are four known minerals along the As_2S_3-Sb_2S_3 join, i.e. orpiment (As_2S_3), Wakabayashilite [$(As,Sb)_{20}S_{30}$] [9] and [$(As,Sb)_6S_9$] [$(As_4S_5$] [10], getchellite ($AsSbS_3$) and stibnite (Sb_2S_3). In contrast to the common occurrences of the end members, the occurrences of getchellite and wakabayashilite are rare.

Although arsenic and antimony have different crystallochemical behaviour and structures in their sulphides, they are chemically analogous elements. The chemical analysis of most minerals in As-Sb-S systems indicates the presence of an incomplete solid solution between orpiment and stibnite. Synthetic [11] and natural stibnite, from Nevada and Utah, exhibit 7wt% As in stibnite coexisting with orpiment [12]. The crystal chemistry of the As-Sb-S system was studied under hydrothermal condition by Nakai *et al.* [11].

Mineralogical studies and chemical analyses of ores containing orpiment, getchellite and stibnite from the Zarshuran deposit, NW Iran indicate the presence of extreme solid solution between orpiment and stibnite, which is in contrast with experimental studies by Nakai

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et al. [11]. Natural orpiment with the highest antimony content is recorded in the recent study.

Asadi *et al.* [13] reported high concentrations of antimony in orpiment (based on 16 EPMA point analysis) with an average of 4.71 wt%, and arsenic concentrations in coexisting stibnite (based on 4 EPMA point analysis) with an average of 3.79 wt%. They considered this as evidence for solid solution or the presence of fine grained inclusions. They reported getchellite as a uniform phase with an As:Sb ratio of 1:1 (based on 4 EPMA point analysis).

Phase relations in the As-Sb-S and As_2S_3-Sb_2S_3 systems were studied by Craig *et al.* [14], Dickson *et al.* [12], Sobott [15], Nakai *et al.* [11], Bernardini *et al.* [16] and Tomkins *et al.* [17]. The phase diagram of the As_2S_3-Sb_2S_3 (Fig. 1) systems shows the main phases and areas of solid solutions in these systems. Orpiment, realgar and stibnite melt at 310, 321 and 556 respectively.

Hydrothermal synthesis of the As_2S_3-Sb_2S_3 system by Nakai *et al.* [11] at 250, 300, 350 and 400°C, 1000 kg/cm^2 pressure in the presence of Na_2S, show that crystals of stibnite were formed at all temperatures, whereas those of getchellite and orpiment were formed only at 250 and 300°C. Stibnite crystals formed at higher temperatures of 350 and 400°C, have a rather narrow As substitution range. Synthetic orpiment formed at 250°C shows more Sb substitution than that formed at 300°C with the same raw material.

In view of the discrepancy between the Zarshuran occurrence and other example of solid solution, the condition of mineralization at Zarshuran will first be introduced.

The Zarshuran Deposit

The Zarshuran deposit is located at 36° 43.390' N, 47° 08.219' E, 42 km north of Takab in the West Azarbijan province (Fig. 2). It is well known for arsenic mining, orpiment and realgar having been mined for hundreds of years, and now is a gold prospect with a reserve of 88t Au at a grade of 7.9 g/t [18].

The geology and genesis of the Zarshuran deposits and the nature of mineralization have been described by Mehrabi [5], Mehrabi *et al.* [6], Asadi *et al.* [7], Asadi *et al.* [13] and Mehrabi *et al.* [8]. The Zarshuran deposit is closely comparable with sedimentary rock-hosted disseminated gold deposits (SRHDGD) also known as Carlin-type gold deposits. Gold-bearing arsenic mineralization is semi-conformable within the presumed late Precambrian Zarshuran Black Shale Unit. The mineral assemblage includes orpiment, realgar, stibnite, getchellite, cinnabar, As-Au-bearing pyrite, base metals sulphides and sulphosalts, thallium minerals and micron to angstrom-sized gold.

The characteristic features of gold mineralization at Zarshuran are: 1) invisible disseminated gold, 2) calcareous and carbonaceous shale and limestone host, 3) presence of a low temperature hydrothermal suite of elements including As, Sb, Hg, and Tl associated with gold, 4) a complex paragenesis and lack of zoning in alteration patterns and mineralization, 5) the presence of different types of fluid inclusions and fluctuation in fluid density and chemistry, and 6) fluid PT conditions of 216±32°C at 865±375 bar, 264±38°C at 1150±150 bar and 185±40°C at 865±375 bar at early, main and late stage of mineralization, respectively [6].

An exploration program has indicated the presence of four styles of mineralization. Steeply dipping

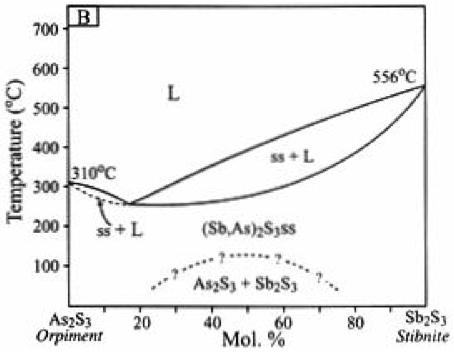

Figure 1. Phase diagram of the As_2S_3 and Sb_2S_3 system.

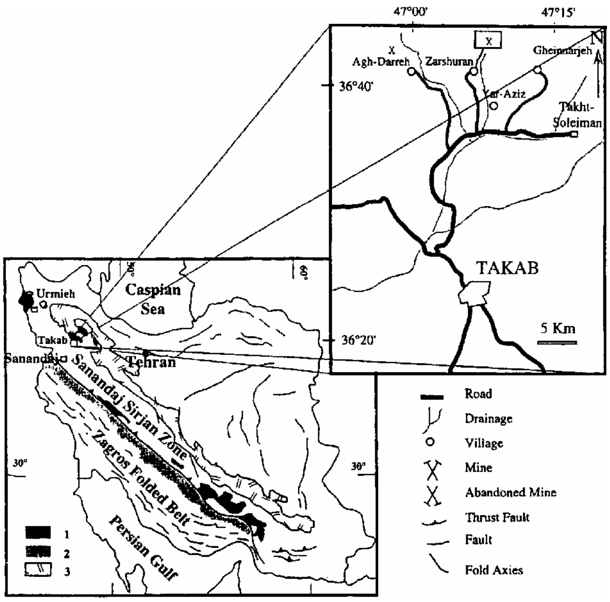

Figure 2. Location map of the Zarshuran gold deposit.

Table 1. Bulk chemical analysis of Au, As and Sb in black gouge (BG), jasperoid (JS), massive orpiment (MO) and jasperoid containing orpiment veinlets (JSOV) ore

Ore type	No. of analysis	Au (ppm)	As (%)	Sb (%)	As/Sb (Ratio)	Au-As Cc	Au-Sb Cc	As-Sb Cc
BG	81	13.52	3.89	0.19	20.47	0.23	0.01	0.04
JS	61	7.81	2.18	0.59	3.69	0.512	-0.01	-0.01
MO	17	18.04	40.50	0.27	150	0.08	-0. 04	0.32
JSOV	44	9.21	6.26	0.52	12.04	0.08	-0.02	0.24

Cc: Correlation Coefficient
Au measured by fire assay and As and Sb by AAS.

mineralization (70 degree dip or greater) include two ore types; a) black gouge with orpiment and jasperoid clasts and b) jasperoid and massive orpiment. Flat lying mineralization (45 degree or flatter) include two ore types; a) mineralized breccias and tectonites and b) sandy or powdery Chaldagh marble. The bulk of mineralization, approximately 60% of the volume, occurs in flat lying carbonaceous decalcified marble. The highest gold grade mineralization, approximately 40% of the volume, appears to occur in steeply dipping black gouge zone.

Black gouge ore formed along steep dipping faults and has the highest gold grade and As concentration. It is composed of orpiment, pyrite, stibnite, arsenian-pyrite, sphalerite and lolingite in association with organic carbon, (locally up to 11%), fluorite and barite. Jasperoid ore is composed of silicified limestone and jasperoid with erratic gold grades, microcrystalline arsenian pyrite formed along micro fractures with minor stibnite, locally cut by massive orpiment veins and veinlets. Getchellite is mainly associated with late stage orpiment and quartz veins and in silicified rocks.

Chemical analyses of Au, As and Sb in black gouge (BG), jasperoid (JS), massive orpiment (MO) and jasperoid containing orpiment veinlets (JSOV) are presented in Table 1. Au only shows a significant correlation with As. Figure 3 presents the whole rock analysis scatter diagrams of As-Sb, Au-As and Au-Sb for the jasperoid containing orpiment veinlets (JSOV) ore types. Selected orpiment, getchellite and stibnite were analysed by EPMA from this ore type.

Mineral Compositions at Zarshuran

Ores and separated pure orpiment, getchellite and stibnite were examined by XRD after conventional petrographic studies. Semiquantitative analyses were carried out by Cambridge Stereo Scan 2000 (at the University of Leeds) and LEO 1450VP (at IMPRC) SEM-EDXA, preliminary quantitative EDX analysis by Jeol JXA 8800 EPMA (at Imperial College) and quantitative analysis by Cameca SX50 fully automated EPMA (at the University of Leeds). The EPMA measurements were carried out based on following X-ray lines and standard; As Kα (pure arsenic), Sb Kα (pure antimony) and S Kα (ZnS) with 60 seconds counting time, at 15 kV and 20 nA.

Backscattered Electron mode (BSE) images show that orpiment, getchellite and stibnite crystals exhibit complex and variable chemical zonations due to variations in the As/Sb ratio (Fig. 4), though grains with uniform composition are common in arsenical ore. The chemical compositions of orpiment (selected from 189 point analyses), getchellite and stibnite from Zarshuran are listed in Table 2. The mole numbers in the formula were calculated based on As+Sb+S=5 (Table 2).

Orpiment occurs as massive coarse crystalline to microcrystalline masses in the form of veins, veinlets and lenses. One of the drill holes intersected up to 20m massive orpiment at depth of 200m and the assay results show up to 60g/t Au. Orpiment normally contains Sb, Te and Tl and shows substantial As/Sb substitution. Galkhahite and simonite were identified in orpiment as rare phases.

Stibnite occurs as needles, as needles aggregates and as subhedral crystals in jasperoid ore and massive orpiment ore. It is normally associated with quartz and occurs in clusters of acicular crystals. Stibnite shows massive substitution by As.

Getchellite is a rare mineral at Zarshuran and was recognized by Bariand *et al.* [19]. It is mainly associated with late phase quartz, orpiment and realgar in jasperoids and shows a flaky texture.

Figure 5 summarizes the solid solution range of hydrothermally synthesized [11] and natural minerals from the Zarshuran deposit. Synthetic stibnite shows As substitution up to 24 mol%. It causes elongation of the *a* axis and shortening of the *b* and *c* axes in stibnite. Natural stibnite formed at Zarshuran deposit is heterogeneous and shows up to 11 mol% As-Sb

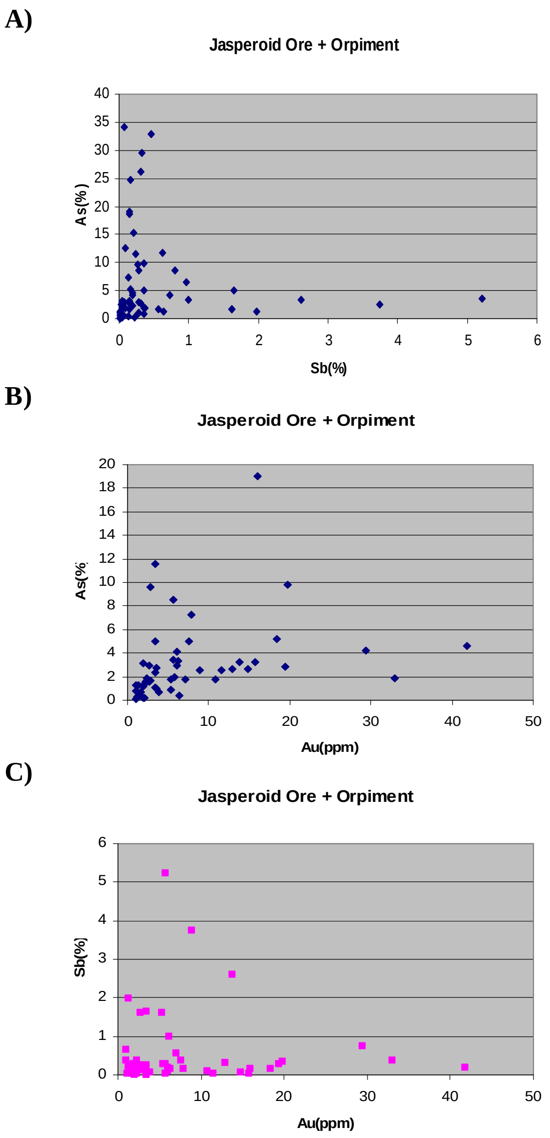

Figure 3. Whole rock analysis scattered diagram showing A) As-Sb, B) As-Au and C) Sb-Au content of Jasperoid containing orpiment mineralization at Zarshuran gold deposit. Orpiment, getchellite and stibnite phase were selected for EPMA analysis from this ore type. (Au measured by fire assay and As and Sb by AAS).

substitution. The chemical composition of getchellite was reported to be $As_{0.98}Sb_{1.01}S_3$ which is idealized as $AsSbS_3$ [20]. The chemical composition of synthetic getchellite deviates from the ideal $AsSbS_3$ component only toward As rich side [11]. Getchellite from the Zarshuran deposit shows extensive substitution of As-Sb, which is spread symmetrically around a As/Sb ratio of 1 (Fig. 3). The upper limit of the substitution of Sb for As in synthetic orpiment is 17 mol%. Natural orpiment from the Getchell mine, Nevada (associated with getchellite samples of the US National museum) contains 11 mol% Sb_2S_3, which is the highest antimony content recorded previously in natural orpiment [11]. Zoned orpiment from the Zarshuran deposit shows brighter zones with up to 12 mol% Sb_2S_3.

Discussion

The lower level of solid solution recorded in natural orpiment and stibnite, relative to those in synthetic minerals, raises the question of the existence of such a difference. The possible explanations are: 1) natural minerals may have formed originally with an extensive solid solution that subsequently readjusted by exsolution, 2) synthetic minerals grew metastably and incorporated more foreign elements in their structure [13], 3) the properties of arsenic and antimony such as, covalent radii and coordination geometry are different, thus the As-Sb substitution causes distortion and deformation of the unit cell, therefore the limit of such a deformation may be responsible for the limited solid solution [11], and 4) different condition of formation.

Natural getchellite from the Zarshuran deposit shows a wider range of solid solution than in the synthetic system. This observation challenges some of the results obtained from synthesizing getchellite, and justifies further experimental studies. Considering the condition of mineralization at the Zarshuran deposit may help to find a realistic explanation for the paradox recorded in the As_2S_3-Sb_2S_3 solid solution. Notably the temperature of formation at the Zarshuran was below 250°C, which is supported by fluid inclusion data [6].

The presence of a wide range of As/Sb ratio (150-3.69), different fluid inclusion types, locally even in a single sample, and variation in composition, salinity, temperature and pressure of the mineralizing fluid during the main stage of orpiment, getchellite and stibnite formation have been recorded at the Zarshuran deposit [6]. Possibly rapid variations in the fluid chemistry, availability of enough As and Sb in solution and variation in PT condition are responsible for extensive solid solution among the As_2S_3-Sb_2S_3 join minerals of the Zarshuran deposit. The wider range of As-Sb substitution in getchellite compared to the synthetic one, which formed at 250°C indicate that the Zarshuran gold mineralization formed at a temperature below 250°C, which is supported by fluid inclusion data [6]. The natural variation of As-Sb ratio in natural minerals in Zarshuran justifies further experiments at temperature of less than 250°C in the As-Sb-S system to find out the possibility of getchellite formation as a stable phase or support the existence of metastable phases in the As_2S_3-Sb_2S_3 system.

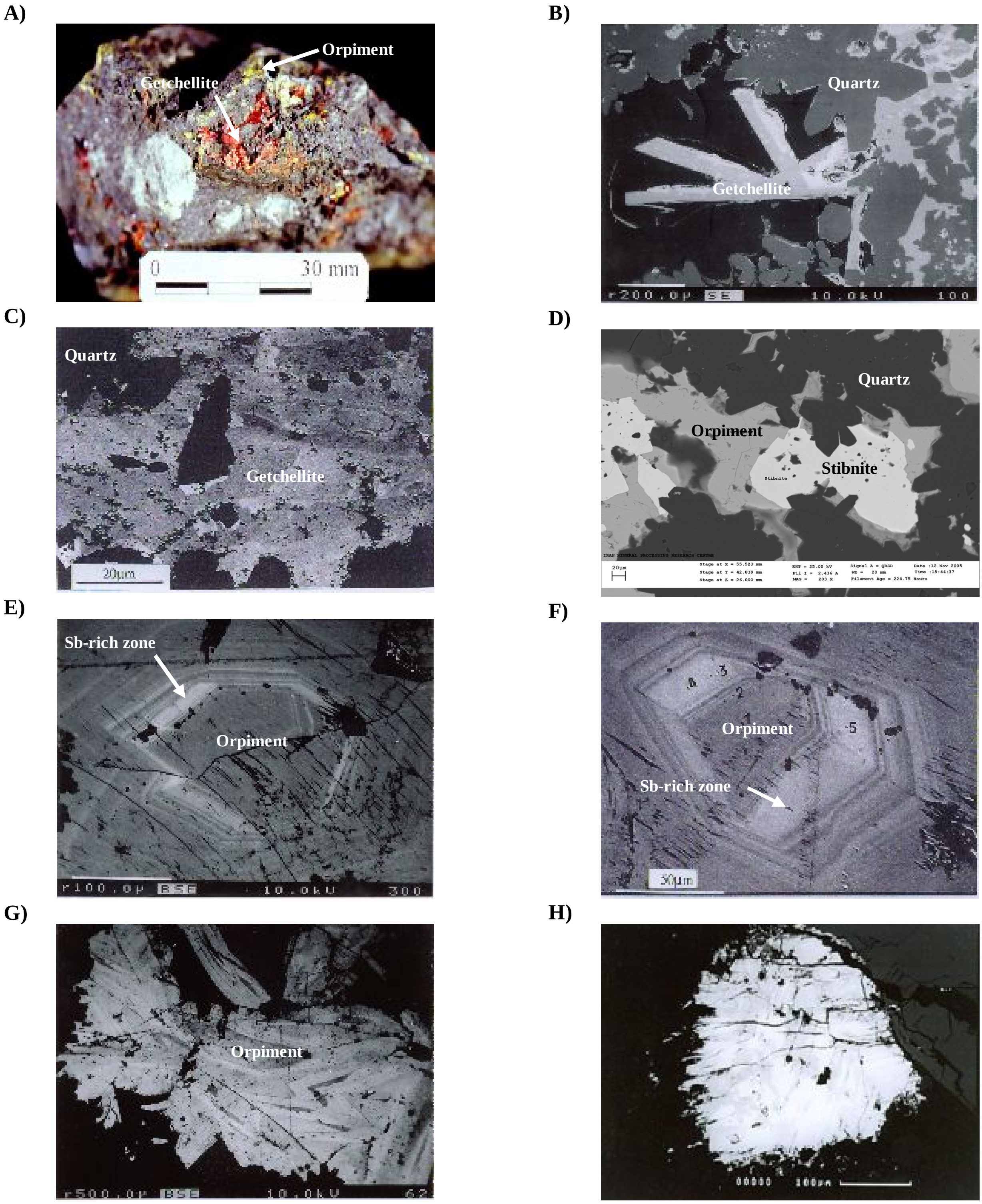

Figure 4. Photograph, BSE and SE images from sulphosalt minerals in Zarshuran showing As-Sb substitution. A) getchellite and orpiment in jasperoid; B) subhedral to euhedral getchellite formed in open spaces in association with quartz showing negligible substitution; C) heterogeneous getchellite with patchy zonation; D) stibnite and orpiment in association with quartz with negligible substitution; E&F) oscillatory zoning in orpiment (bright area contains more Sb); G) complex zoning in orpiment and H) As-Sb substitution in unknown minerals of twinnite-guettardite series.

Table 2. Chemical analysis of orpiment (O), getchellite (G) and stibnite (S) by EPMA, from Zarshuran deposit. Empirical formula calculated on the basis of As+Sb+S=5

	Composition (element wt%)						Composition (element wt%)				
No.	S	As	Sb	Total	Empirical Formula	No.	S	As	Sb	Total	Empirical Formula
O01	39.05	60.31	0.39	99.75	$As_{1.99}Sb_{0.01}S_{3.01}$	G08	30.57	19.81	50.13	100.51	$As_{0.81}Sb_{1.26}S_{2.93}$
O02	38.54	58.99	2.23	99.76	$As_{1.96}Sb_{0.05}S_{2.99}$	G09	31.73	26.99	41.73	100.44	$As_{1.06}Sb_{1.01}S_{2.92}$
O03	37.95	55.96	6.21	100.12	$As_{1.88}Sb_{0.13}S_{2.99}$	G10	31.64	24.49	44.38	100.51	$As_{0.97}Sb_{1.09}S_{2.94}$
O04	37.59	54.08	9.10	100.77	$As_{1.83}Sb_{0.19}S_{2.98}$	G11	31.00	23.93	45.22	100.15	$As_{0.97}Sb_{1.12}S_{2.92}$
O05	37.36	54.78	8.85	100.99	$As_{1.86}Sb_{0.18}S_{2.96}$	G12	31.57	25.54	43.72	100.83	$As_{1.18}Sb_{1.07}S_{2.92}$
O06	38.62	59.30	2.24	100.16	$As_{1.96}Sb_{0.01}S_{2.99}$	G13	31.36	24.87	44.76	100.99	$As_{0.99}Sb_{1.10}S_{2.92}$
O07	38.32	58.49	3.18	99.99	$As_{1.95}Sb_{0.07}S_{2.98}$	G14	31.64	25.52	43.42	100.31	$As_{1.00}Sb_{1.06}S_{2.94}$
O08	37.45	54.04	8.76	100.25	$As_{1.84}Sb_{0.18}S_{2.98}$	G15	31.52	25.43	43.90	100.85	$As_{0.99}Sb_{1.10}S_{2.92}$
O09	37.46	56.06	6.18	99.70	$As_{1.90}Sb_{0.13}S_{2.97}$	G16	31.70	25.51	43.39	100.60	$As_{1.01}Sb_{1.06}S_{2.93}$
O10	37.94	56.75	5.18	99.87	$As_{1.91}Sb_{0.11}S_{2.98}$	G17	31.24	24.55	44.24	100.03	$As_{0.98}Sb_{1.09}S_{2.93}$
O11	38.22	56.78	5.20	100.20	$As_{1.90}Sb_{0.11}S_{2.99}$	G18	31.63	26.59	42.00	100.22	$As_{1.05}Sb_{1.02}S_{2.92}$
O12	38.01	54.67	7.69	100.37	$As_{1.84}Sb_{0.16}S_{3.00}$	G19	31.89	26.10	42.49	100.84	$As_{1.03}Sb_{1.03}S_{2.94}$
O13	37.55	56.18	6.13	99.66	$As_{1.91}Sb_{0.13}S_{2.96}$	G20	31.76	26.08	42.98	100.82	$As_{1.03}Sb_{1.04}S_{2.93}$
O14	38.40	59.60	2.18	100.18	$As_{1.98}Sb_{0.04}S_{2.98}$	G21	31.88	26.47	42.08	100.43	$As_{1.04}Sb_{1.02}S_{2.94}$
O15	37.52	53.85	8.70	100.07	$As_{1.83}Sb_{0.18}S_{2.98}$	G22	31.60	25.00	44.08	100.68	$As_{0.99}Sb_{1.08}S_{2.93}$
O16	37.85	55.34	7.07	100.26	$As_{1.87}Sb_{0.15}S_{2.99}$	G23	31.46	24.83	44.12	100.41	$As_{0.99}Sb_{1.08}S_{2.93}$
O17	38.31	57.83	3.64	99.78	$As_{1.93}Sb_{0.07}S_{2.99}$	S01	27.77	1.43	72.63	101.72	$Sb_{2.01}As_{0.06}S_{2.93}$
O18	38.23	58.49	2.92	99.64	$As_{1.95}Sb_{0.06}S_{2.99}$	S02	28.03	2.57	71.26	101.86	$Sb_{1.96}As_{0.11}S_{2.93}$
O19	38.54	60.25	1.18	99.97	$As_{1.99}Sb_{0.02}S_{2.98}$	S03	28.22	3.52	70.39	102.67	$Sb_{1.93}As_{0.16}S_{2.92}$
O20	37.78	54.28	8.15	100.21	$As_{1.84}Sb_{0.17}S_{2.99}$	S04	27.53	1.20	72.59	101.32	$Sb_{2.03}As_{0.03}S_{2.92}$
O21	38.17	57.19	4.25	99.61	$As_{1.92}Sb_{0.09}S_{2.99}$	S05	28.50	4.01	70.02	102.53	$Sb_{1.89}As_{0.18}S_{2.93}$
O22	38.62	59.15	2.16	99.93	$As_{1.96}Sb_{0.04}S_{2.99}$	S06	27.58	0.99	72.46	101.03	$Sb_{2.03}As_{0.04}S_{2.93}$
O23	37.09	53.56	8.89	99.54	$As_{1.84}Sb_{0.19}S_{2.97}$	S07	27.30	1.12	71.26	100.34	$Sb_{2.03}As_{0.05}S_{2.92}$
O24	37.28	53.52	8.95	99.75	$As_{1.83}Sb_{0.19}S_{2.98}$	S08	27.69	1.05	70.39	101.22	$Sb_{2.02}As_{0.05}S_{2.93}$
O25	38.38	59.72	1.24	99.34	$As_{1.99}Sb_{0.03}S_{2.99}$	S09	27.75	0.98	72.59	100.02	$Sb_{2.00}As_{0.04}S_{2.96}$
O26	37.10	52.40	11.07	100.57	$As_{1.80}Sb_{0.23}S_{2.97}$	S10	28.34	2.26	71.20	101.80	$Sb_{1.95}As_{0.10}S_{2.95}$
O27	38.72	57.91	3.63	100.26	$As_{1.92}Sb_{0.07}S_{3.00}$	S11	28.37	3.77	68.22	100.36	$Sb_{1.97}As_{0.17}S_{2.96}$
O28	38.66	58.70	1.21	98.57	$As_{1.96}Sb_{0.02}S_{3.02}$	S12	28.37	2.73	70.70	101.80	$Sb_{1.93}As_{0.12}S_{2.95}$
O29	38.78	59.70	0.76	99.24	$As_{1.98}Sb_{0.02}S_{3.00}$	S13	28.42	4.20	98.60	101.22	$Sb_{1.87}As_{0.19}S_{2.94}$
O30	38.57	59.76	0.65	98.98	$As_{1.99}Sb_{0.01}S_{3.00}$	S14	28.05	1.11	71.33	100.49	$Sb_{1.99}As_{0.05}S_{2.96}$
O31	38.97	60.11	0.75	99.83	$As_{1.98}Sb_{0.02}S_{3.00}$	S15	28.05	1.54	71.89	101.48	$Sb_{1.99}As_{0.07}S_{2.94}$
O32	38.88	57.76	2.12	99.76	$As_{1.95}Sb_{0.04}S_{3.01}$	S16	28.75	4.02	69.15	101.71	$Sb_{1.88}As_{0.18}S_{2.95}$
O33	37.28	51.78	10.98	100.04	$As_{1.78}Sb_{0.23}S_{2.99}$	S17	28.32	2.68	70.10	101.20	$Sb_{1.93}As_{0.12}S_{2.95}$
O34	38.01	52.95	9.00	99.96	$As_{1.80}Sb_{0.19}S_{3.01}$	S18	28.18	1.18	71.35	100.71	$Sb_{1.98}As_{0.05}S_{2.97}$
O35	37.81	51.37	11.46	101.00	$As_{1.76}Sb_{0.24}S_{3.00}$	S19	28.14	1.17	71.71	101.20	$Sb_{1.99}As_{0.05}S_{2.96}$
O36	37.41	51.63	10.31	99.37	$As_{1.78}Sb_{0.22}S_{3.01}$	S20	28.14	2.98	69.27	100.39	$Sb_{1.91}As_{0.13}S_{2.95}$
O37	37.57	51.98	10.97	100.52	$As_{1.77}Sb_{0.23}S_{3.00}$	S21	28.05	1.59	70.76	100.40	$Sb_{1.97}As_{0.07}S_{2.96}$
O38	37.28	51.32	10.96	99.56	$As_{1.77}Sb_{0.23}S_{3.00}$	S22	27.49	1.21	71.23	99.93	$Sb_{2.01}As_{0.06}S_{2.94}$
O39	37.21	51.92	10.39	99.52	$As_{1.79}Sb_{0.22}S_{2.99}$	S23	28.44	2.87	70.06	101.37	$Sb_{1.92}As_{0.13}S_{2.96}$
G01	32.02	23.99	44.73	100.74	$As_{1.79}Sb_{1.09}S_{2.96}$	S24	27.97	1.07	71.22	100.26	$Sb_{1.99}As_{0.05}S_{2.96}$
G02	32.01	25.92	42.81	100.74	$As_{1.02}Sb_{1.04}S_{2.94}$	S25	28.97	4.18	68.57	101.72	$Sb_{1.85}As_{0.18}S_{2.97}$
G03	31.45	24.15	45.72	101.32	$As_{0.96}Sb_{1.12}S_{2.92}$	S26	27.65	1.17	70.68	99.50	$Sb_{1.99}As_{0.05}S_{2.96}$
G04	31.11	24.87	44.67	100.65	$As_{0.99}Sb_{1.10}S_{2.95}$	S27	28.05	1.39	71.18	100.62	$Sb_{1.98}As_{0.06}S_{2.96}$
G05	31.44	24.09	43.79	99.32	$As_{0.97}Sb_{1.08}S_{2.95}$	S28	28.94	4.02	68.93	101.89	$Sb_{1.86}As_{0.18}S_{2.96}$
G06	32.36	30.56	37.38	100.30	$As_{1.18}Sb_{0.98}S_{2.95}$	S29	28.69	5.12	67.79	101.60	$Sb_{1.83}As_{0.22}S_{2.94}$
G07	31.90	28.39	39.90	100.19	$As_{1.11}Sb_{0.96}S_{2.92}$	S30	27.78	1.55	70.98	100.31	$Sb_{1.98}As_{0.07}S_{2.95}$

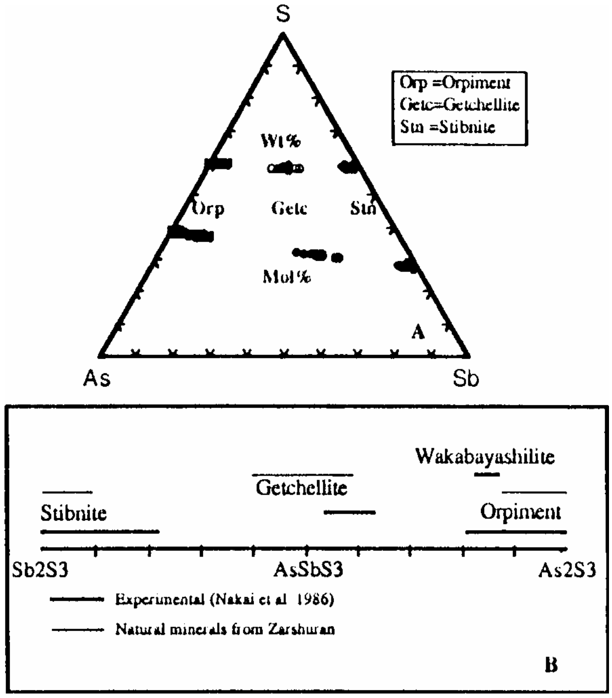

Figure 5. Ternary (A) and binary (B) diagrams showing the variation in chemical composition of orpiment, getchellite and stibnite, indicating the extensive As-Sb solid solution compared to experimental data.

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