HYDROTHERMAL ARGENTOPENTLANDITE AT EL CHARCÓN, SOUTHEASTERN SPAIN: MINERAL CHEMISTRY AND CONDITIONS OF FORMATION

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ABSTRACT

This study of argentopentlandite from El Charcón, in southeastern Spain, is the first documented report for Spain and also the first occurrence of argentopentlandite associated with hydrothermal systems related to acid-type volcanism. Ag values above 1.00 and M/S values lower than 1.125 can be explained by the presence of defects (mainly vacancies of Fe and Ni or S or both) in the argentopentlandite structure. These defects can also explain: (1) the differences observed between measured M/S and Fe/Ni values and M/S and Fe/Ni values calculated by the "cation addition – omission solid solution" model for natural argentopentlandite, and (2) the fact that most compositions of natural argentopentlandite fall outside the stability fields established for synthetic argentopentlandite at 300 and 400°C. The following modification of the argentopentlandite formula is proposed: $(Fe_{5\pm0.77}Ni_{3\pm0.75})_{\Sigma8\pm x}Ag_{1\pm y}S_{8\pm z}$, with $0 < |x| < 0.30$, $0 < |y| < 0.23$, and $0 < |z| < 0.30$. The estimated conditions of formation for argentopentlandite from El Charcón are: temperature between 400 and 450°C, salinity between 17 and 22 wt.% NaCl equivalent, log $f(S_2)$ between –9.6 to –15.7 atm., and P between 200 to 900 bars.

Keywords: hydrothermal, argentopentlandite, reflectivity, electron-microprobe data, thermochemical conditions, Betic Cordillera, Spain.

SOMMAIRE

Notre étude de l'argentopentlandite de El Charcón, dans le sud-est de l'Espagne, en établit le premier exemple connu dans un milieu hydrothermal associé à un magmatisme felsique, et aussi le premier exemple de cette espèce en Espagne. Des teneurs en Ag dépassant 1.00 atomes par unité formulaire et un rapport de métal à soufre (M/S) inférieur à 1.125 seraient dus à la présence de défauts structuraux, surtout des lacunes impliquant les sites Fe, Ni, et S. La présence de ces défauts expliquerait aussi (1) les différences observées entre les rapports M/S et Fe/Ni mesurés et calculés selon le schéma de solution solide par addition ou omission de cations, et (2) le fait que la plupart des compositions d'argentopentlandite naturelle dépassent le champ de stabilité établi d'après les études synthétiques à 300° et 400°C. Nous proposons la modification suivante de la formule structurale de l'argentopentlandite: $(Fe_{5\pm0.77}Ni_{3\pm0.75})_{\Sigma8\pm x}Ag_{1\pm y}S_{8\pm z}$, avec $0 < |x| < 0.30$, $0 < |y| < 0.23$, et $0 < |z| < 0.30$. L'argentopentlandite de El Charcón se serait formée aux conditions suivantes: temperature comprise entre 400 et 450°C, salinité entre 17 et 22% (en poids) équivalent NaCl, log $f(S_2)$ entre –9.6 et –15.7 atm., et P entre 200 et 900 bars.

Mots-clés: hydrothermal, argentopentlandite, réflectivité, données de microsonde électronique, conditions thermochimiques, Cordillère Bétique, Espagne.

INTRODUCTION

The base-metal hydrothermal-type ore deposits of the Aguilas zone are related to the potassic calc-alkaline and shoshonitic volcanism of southeastern Spain (López Ruíz & Rodríguez Badiola 1980). During the Upper Miocene, this volcanism was in turn affected by N–S compression that produced different regional sets of fractures: N70–90E, N40–60E,

N10–30E and N–120–140E (Alvarez 1987, Alvarez & Aldaya 1985). The Fe–Cu–Pb–Zn mineralization at El Charcón (Morales 1994), where the argentopentlandite was found, consists of a system of veins related to these volcanic rocks and hosted within a Triassic metamorphic complex (quartzite and quartz schists from the El Cantal unit) of the internal domain of the Betic Cordillera. The mineralization fills only the N10–30S subvertical fractures that affect the rocks of the metamorphic basement.

The mineralization consists of massive ore with minor breccia containing chalcopyrite, sphalerite, pyrite, galena, arsenopyrite, cubanite and argento-

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pentlandite, together with quartz and minor carbonates as gangue minerals. The paragenetic sequence (Morales *et al.* 1993) is divided into three stage of deposition: I) Cu–Zn–(Ag–As), with chalcopyrite, sphalerite I, argentopentlandite, cubanite and quartz, II) Fe–Zn–Cu–As, with pyrite, sphalerite II, chalcopyrite, arsenopyrite and quartz, and III) Pb, with galena and minor carbonate. The most abundant is stage II, and the least abundant, stage III.

Argentopentlandite is a scarce mineral. It has been described in no more than ten deposits worldwide, in one of four associations: a) Co–Ni skarn-type mineralization (Shishkin *et al.* 1971), b) Ni–Cu deposits associated with ultrabasic rocks, within or along the contacts of the mineralized rocks with the host rock (Vuorelainen *et al.* 1972) or near, but not in, ultrabasic sills (Scott & Gasparrini 1973), c) metamorphosed ultramafic sequences, in which case the hydrothermal origin is related to dyke emplacement (Groves & Hall 1978) or to metamorphic remobilization of tourmalinite (Benvenuti 1991), and d) as hydrothermal mineralization within paragneissic (Kontny *et al.* 1994) and metabasic rocks (Kozlovskiy *et al.* 1988), during their retrogression.

Our study of argentopentlandite from El Charcón is the first occurrence of argentopentlandite associated with hydrothermal systems related to felsic volcanism, and constitutes the first documented report in Spain.

OPTICAL PROPERTIES

Argentopentlandite from El Charcón is reddish brown to brown in reflected light and is easily polished, but tarnishes quickly in air to a darker color. It is isotropic and has no internal reflections. The anhedral (oval, rounded or dendritic) crystals (Fig. 1) measure up to 100 μm across and *only occur as inclusions* in chalcopyrite (which shows lamellae twins), as individual grains, in some cases in common orientation, and occasionally as poorly developed dendrites. The boundaries between argentopentlandite and chalcopyrite invariably are sharp. Both the argentopentlandite and chalcopyrite commonly include sphalerite stars and skeletal crystals of sphalerite. Regular intergrowths or symplectite-like intergrowths of argentopentlandite with the chalcopyrite have not been observed at El Charcón. Argentopentlandite has never been found around the margin of chalcopyrite grains, and it never presents exfoliation features, fractures or alteration.

We determined the reflectivity of argentopentlandite using a SF Zeiss microphotometer attached to a Carl Zeiss photomicroscope, at wavelengths varying from 400 to 700 nm. Measurements were carried out in air using a Zeiss SiC standard and 16× and 40× objectives. The results obtained, together with other published values, are given in Table 1. The spectral reflectance
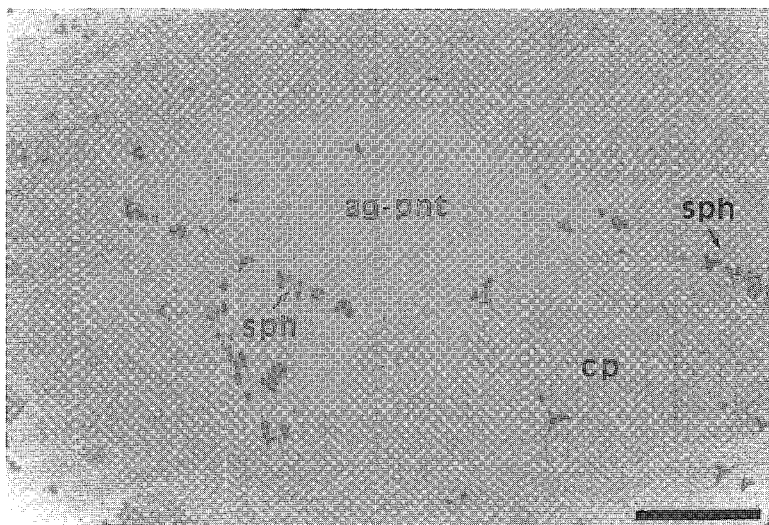

FIG. 1. Chalcopyrite (cp) including elongate and rounded inclusions of argentopentlandite (ag–pnt) and exsolved sphalerite (sph) stars aligned in parallel rows. Bar: 30 μm.

TABLE 1. REFLECTANCE VALUES (%) FOR ARGENTOPENTLANDITE

λ(nm)	1	2	3	4	5	6	7	8	9
400	23.2	20.4							
420	24.4	21.0							
440	25.7	21.9	24.1	26.4	25.4	25.3			
460	27.5	22.9							
470	27.9	23.7					25.5	26.3	
480	28.8	24.2	26.1	30.7	28.9	28.3			29.3
500	29.6	25.6							
520	31.3	27.2	31.6	33.8	32.6	31.8			
540	32.7	28.8							
546	32.8	29.1					32.8	37.4	
560	33.7	30.4	33.9	36.3	34.9	34.0			35.0
580	34.9	31.9							
589	35.6	32.7					33.7	33.0?	
600	35.7	33.3	35.5	37.2	36.9	35.5			36.5
620	36.4	34.6							
640	36.9	35.8	37.4	39.1	38.4	38.3			38.6
650	37.0	36.3					39.6	39.8	
660	37.3	36.8							
670			38.1	40.8	39.4	38.2			
680	37.7	37.8							
700	37.8	38.6							

(1) El Charcón, Morales (1994); (2) Anthony et al. (1990); (3) Karpenkov et al. (1973), Sudbury; (4) Karpenkov et al. (1973), Talnakhskoe I; (5) Karpenkov et al. (1973), Talnakhskoe II; (6) Karpenkov et al. (1973), Khovuaksinkoe; (7) Scott & Gasparrini (1973); (8) Vuorelainen et al. (1972) and (9) Shishkin et al. (1971).
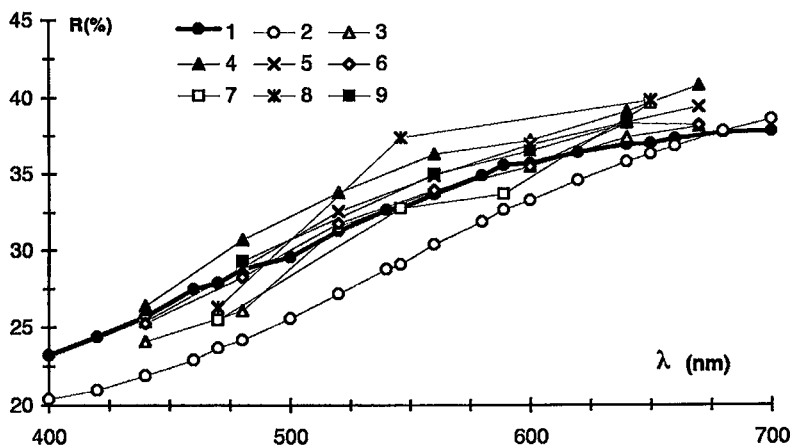

FIG. 2. Spectral reflectance curve for argentopentlandite from El Charcón (curve 1) compared with others obtained from published data (same legend as Table 1).

curve for argentopentlandite from El Charcón agrees with the other curves obtained from published data (Fig. 2).

MINERAL CHEMISTRY

Analyses of the El Charcón argentopentlandite were performed on a CAMECA SX–50 electron microprobe at the Technical Service of the University of Oviedo (Spain), using an accelerating potential of 20 kV, and a beam current of 30 nA. Counting times were 10 seconds on peaks, and 5 seconds on background positions. The practical limit of detection in these routine analyses varied from 0.05 to 0.08 wt%. Results were corrected with a ZAF program. We used $CuFeS_2$ (Fe,Cu), synthetic Ag_2S (Ag), NiAs (Ni), CoS (Co) and ZnS (S) as standards.

Results of analyses (Table 2) are compared to those from other sources in Table 3, in which we have calculated all compositions from Table 3A on the basis of 17 atoms per formula, and also 8 S atoms in order to compare with the previously published data. Tables 3A, which contains a listing of compositions of argentopentlandite from various localities (in weight % and atomic %), and 3B, in which the compositions are listed as a function of Ag content (atomic %), are available from the Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario, Canada K1A 0S2.

The average value of Ag in the argentopentlandite on the base of 8 S atoms (Table 3) is 1.00 atom per formula unit (1.02 for argentopentlandite from El Charcón). This value agrees with the proposal of Scott & Gasparrini (1973), and with the demonstration of Hall & Stewart (1973) that Ag occurs in a specific site [octahedral (4b) positions] within the structure. On this basis, argentopentlandite is considered a distinct mineral species and not an end member of an isomorphous series with normal pentlandite. However, although the average Ag value is close to 1.00, values from the literature (Table 3) range from 0.77 to 1.14. Values below 1.00 were explained (Hall & Stewart 1973) by the presence of (Fe,Ni) at the octahedral position assigned to Ag. Values above 1.00 can be explained in three ways: (1) analytical errors (Hall & Stewart 1973), (2) Ag partially replacing (Fe,Ni) at tetrahedral positions, and (3) defects in the argentopentlandite structure. The first of these explanations (analytical error) is considered unlikely, as a high percentage (60%) of the compositions in Table 3 show excess Ag. Hall & Stewart (1973) demonstrated that for stereochemical and energetic reasons, it seems unlikely for Ag to occur at different octahedral positions (4b); the relative increase of Ag in comparison to (Fe,Ni) must therefore be due to vacancies in the argentopentlandite structure. To determine the structural location of these vacancies, it is better to use compositions calculated on the basis of 17 atoms per formula (Table 3). For Ag > 1 atom per formula unit (*apfu*), we can see two different groups of compositions: (a) Fe + Ni < 8 and S > 8 *apfu*, which indicates the existence of vacancies in the tetrahedral sites of argentopentlandite normally occupied by (Fe,Ni) atoms, and (b) Fe + Ni > 8 and S < 8 *apfu*, which indicates vacancies in the S position.

The Fe and Ni values for argentopentlandite from El

TABLE 2. COMPOSITION OF ARGENTOPENTLANDITE FROM EL CHARCON*

	Fe	Ni	Ag	Co	Cu	S	TOTAL
1	35,48	19,72	13,09	0,06	0,50	31,27	100,10
2	36,45	17,72	12,85	0,03	1,74	31,26	100,06
3	35,96	19,48	13,16	0,04	1,03	31,27	100,93
4	34,80	20,59	13,45	0,02	0,51	31,22	100,59
5	35,39	21,55	13,45	0,00	0,32	31,26	101,97
6	35,13	21,14	13,48	0,02	0,25	31,44	101,46
7	35,01	21,24	13,87	0,03	0,25	31,39	101,79
8	34,80	21,29	13,49	0,00	0,17	31,32	101,07
9	34,73	20,44	13,25	0,02	0,07	31,29	99,79
10	34,67	20,59	13,48	0,01	0,57	31,13	100,44
11	34,77	21,42	13,70	0,02	0,09	31,20	101,20
MIN	34,67	17,72	12,85	0,00	0,07	31,13	99,79
MAX	36,45	21,55	13,87	0,06	1,74	31,44	101,97
AVERAGE	35,20	20,47	13,39	0,02	0,50	31,28	100,85

* Compositions were determined by electron-microprobe analysis, and are quoted in weight %.

TABLE 3. RESULTS OF ELECTRON-MICROPROBE ANALYSES OF ARGENTOPENTLANDITE FOR 8 S ATOMS PER FORMULA AND 17 ATOMS PER FORMULA

Ref.	8 S atoms					17 atoms per formula						Fe/Ni	M/S
	Fe	Ni	Ag	Co	Cu	Fe	Ni	Ag	Co	Cu	S		
1	5.21	2.76	1.00	0.01	0.06	5.20	2.75	0.99	0.01	0.06	7.98	1.89	1.13
2	5.35	2.48	0.98	0.00	0.23	5.34	2.47	0.98	0.00	0.22	7.98	2.16	1.13
3	5.28	2.72	1.00	0.00	0.13	5.24	2.70	0.99	0.01	0.13	7.93	1.94	1.14
4	5.12	2.88	1.02	0.00	0.07	5.09	2.87	1.02	0.00	0.07	7.95	1.78	1.14
5	5.20	3.01	1.02	0.00	0.04	5.12	2.96	1.01	0.00	0.04	7.87	1.73	1.16
6	5.13	2.94	1.02	0.00	0.03	5.09	2.92	1.01	0.00	0.03	7.94	1.74	1.14
7	5.12	2.96	1.05	0.00	0.03	5.07	2.93	1.04	0.00	0.03	7.92	1.73	1.15
8	5.10	2.97	1.02	0.00	0.02	5.07	2.95	1.02	0.00	0.02	7.94	1.72	1.14
9	5.10	2.86	1.01	0.00	0.01	5.11	2.86	1.01	0.00	0.01	8.01	1.78	1.12
10	5.12	2.89	1.03	0.00	0.07	5.08	2.87	1.02	0.00	0.07	7.95	1.77	1.14
11	5.12	3.00	1.04	0.00	0.01	5.07	2.97	1.03	0.00	0.01	7.92	1.71	1.15
12	5.28	2.78	0.91		0.18	5.23	2.76	0.90		0.18	7.93	1.90	1.14
13	4.99	2.86	0.94	0.00	0.05	5.04	2.88	0.95	0.00	0.06	8.07	1.75	1.11
14	4.82	2.68	0.77	0.43	0.08	4.88	2.71	0.78	0.44	0.08	8.10	1.80	1.10
15	4.78	3.07	1.00	0.01	0.06	4.80	3.08	1.01	0.01	0.06	8.04	1.56	1.12
16	5.07	2.96	1.01			5.06	2.96	1.00			7.98	1.71	1.13
17	5.19	2.78	0.91		0.08	5.20	2.78	0.92		0.08	8.02	1.87	1.12
18	4.80	2.98	1.05	0.01	0.06	4.83	2.99	1.06	0.02	0.06	8.04	1.61	1.11
19	4.73	3.07	1.07	0.03	0.07	4.74	3.07	1.07	0.03	0.08	8.01	1.54	1.12
20	4.87	3.15	1.00	0.01	0.04	4.85	3.14	1.00	0.01	0.04	7.96	1.55	1.13
21	4.96	2.98	1.00	0.02	0.04	4.96	2.98	1.00	0.02	0.04	7.99	1.66	1.13
22	4.89	2.98	1.02	0.02	0.04	4.90	2.98	1.03	0.03	0.04	8.02	1.64	1.12
23	4.90	2.78	1.03	0.03	0.06	4.96	2.81	1.04	0.03	0.07	8.09	1.76	1.10
24	5.09	2.57	1.03	0.04	0.08	5.14	2.60	1.04	0.04	0.09	8.08	1.98	1.10
25	5.27	2.60	0.97	0.02	0.10	5.28	2.61	0.97	0.02	0.10	8.02	2.03	1.12
26	5.20	2.63	0.95	0.03	0.07	5.23	2.64	0.95	0.03	0.09	8.05	1.98	1.11
27	5.28	2.58	1.02	0.01	0.05	5.30	2.59	1.02	0.01	0.05	8.02	2.05	1.12
28	5.18	2.79	1.00	0.01		5.19	2.79	1.00	0.01		8.01	1.86	1.12
29	5.23	2.82	1.00	0.01		5.21	2.81	1.00	0.01		7.97	1.86	1.13
30	4.65	3.29	1.00			4.67	3.30	1.00			8.03	1.41	1.12
31	5.12	2.93	0.97			5.12	2.93	0.97			7.99	1.75	1.13
32	5.60	2.52	1.01			5.56	2.50	1.00			7.94	2.23	1.14
33	5.84	2.28	1.09			5.77	2.25	1.07			7.91	2.56	1.15
34	5.46	2.54	1.08			5.44	2.53	1.07			7.96	2.15	1.14
35	5.75	2.33	1.06			5.70	2.31	1.05			7.93	2.46	1.14
36	5.29	2.83	0.99			5.25	2.81	0.98			7.95	1.87	1.14
37	4.91	3.00	1.04			4.93	3.01	1.05			8.02	1.64	1.12
38	5.45	3.18	1.04			5.25	3.06	1.00			7.70	1.72	1.21
39	5.34	2.86	0.97			5.28	2.83	0.96			7.92	1.86	1.15
40	4.59	2.96	1.01			4.71	3.04	1.04			8.21	1.55	1.07
41	4.91	3.00	1.03			4.93	3.01	1.04			8.03	1.64	1.12
42	5.14	3.05	0.94			5.10	3.03	0.93			7.94	1.68	1.14
43	5.14	3.02	1.01			5.09	2.99	1.00			7.92	1.70	1.15
44	5.41	2.87	0.96			5.34	2.83	0.94			7.89	1.89	1.15
45	5.09	2.76	0.96			5.15	2.79	0.97			8.09	1.84	1.10
46	4.97	2.94	1.01			4.99	2.95	1.02			8.04	1.69	1.11
47	4.95	2.82	0.99			5.02	2.86	1.00			8.11	1.76	1.10
48	4.84	2.88	1.05			4.90	2.92	1.06			8.11	1.68	1.10
49	5.13	3.18	1.07			5.02	3.11	1.04			7.83	1.61	1.17
50	5.03	3.14	1.05			4.97	3.10	1.04			7.90	1.60	1.15
51	5.22	2.78	0.93			5.24	2.79	0.94			8.03	1.88	1.12
52	5.24	2.76	0.97			5.25	2.76	0.97			8.02	1.90	1.12
53	5.63	2.37	1.06	0.02		5.60	2.36	1.05	0.02		7.96	2.38	1.13
54	5.31	2.82	1.02		0.04	5.25	2.79	1.01		0.04	7.91	1.88	1.15
55	5.27	2.80	0.97		0.04	5.24	2.79	0.97		0.04	7.97	1.88	1.13
56	5.28	2.81	0.97		0.04	5.25	2.79	0.97		0.04	7.95	1.88	1.14
57	4.84	3.17	0.99			4.84	3.17	0.99			8.00	1.53	1.13
58	5.61	2.57	1.02	0.01	0.01	5.54	2.53	1.01	0.01	0.01	7.91	2.19	1.15
59	5.62	2.58	1.05	0.01	0.02	5.53	2.54	1.04	0.01	0.02	7.87	2.18	1.16
60	5.64	2.65	1.03	0.01	0.01	5.53	2.60	1.01	0.01	0.01	7.84	2.13	1.17
61	5.60	2.61	1.04	0.01	0.01	5.51	2.57	1.02	0.01	0.01	7.87	2.14	1.16
62	4.94	3.05	1.04			4.94	3.04	1.04			7.98	1.62	1.13
63	4.90	3.04	1.06			4.90	3.04	1.06			8.00	1.61	1.12
64	5.07	3.20	1.08	0.01		4.97	3.13	1.06	0.01		7.83	1.59	1.17
65	5.39	2.78	0.85	0.01	0.01	5.38	2.77	0.85	0.01	0.01	7.98	1.94	1.13
66	5.37	2.75	0.83	0.01	0.03	5.38	2.75	0.83	0.01	0.03	8.00	1.95	1.12
67	5.38	2.81	0.80	0.01	0.05	5.36	2.80	0.80	0.01	0.05	7.97	1.91	1.13
68	5.53	2.73	0.77	0.01	0.04	5.50	2.72	0.77	0.01	0.04	7.96	2.02	1.14
69	5.08	3.15	0.78	0.01	0.05	5.06	3.13	0.78	0.01	0.05	7.97	1.61	1.13
70	5.63	2.39	1.05	0.01	0.06	5.58	2.37	1.04	0.01	0.06	7.93	2.36	1.14
71	5.49	2.71	1.14	0.00	0.01	5.37	2.66	1.12	0.00	0.01	7.84	2.02	1.17
72	4.51	3.37	1.09	0.00	0.01	4.51	3.37	1.09	0.00	0.01	8.01	1.34	1.12
El Charcon													
MIN	5.10	2.48	0.98	0.00	0.01	5.07	2.47	0.98	0.00	0.01	7.87	1.71	1.12
MAX	5.35	3.01	1.05	0.01	0.23	5.34	2.97	1.04	0.01	0.22	8.01	2.16	1.16
AVER	5.17	2.86	1.02	0.00	0.06	5.13	2.84	1.01	0.00	0.06	7.95	1.81	1.14
Bibliography													
MIN	4.51	2.28	0.77	0.00	0.01	4.51	2.25	0.77	0.00	0.01	7.70	1.34	1.07
MAX	5.84	3.37	1.14	0.43	0.18	5.77	3.37	1.12	0.44	0.18	8.21	2.56	1.21
AVER	5.18	2.84	0.99	0.03	0.05	5.16	2.83	0.99	0.03	0.05	7.98	1.84	1.13
Bibliography+El Charcon													
MIN	4.51	2.28	0.77	0.00	0.01	4.51	2.25	0.77	0.00	0.01	7.70	1.34	1.07
MAX	5.84	3.37	1.14	0.43	0.23	5.77	3.37	1.12	0.44	0.23	8.21	2.56	1.21
AVER	5.17	2.84	1.00	0.02	0.05	5.16	2.83	0.99	0.02	0.05	7.97	1.84	1.13

1-11: El Charcón; 12-14: Kontny et al. (1994); 15: Benvenuti (1991); 16-17: Anthony et al. (1990); 18-27: Mposkos (1983); 28-29: Groves & Hall (1978); 30-35: Mandziuk & Scott (1977); 36-50: Rudashevskii et al. (1977); 51-53: Cabri & Laflamme (1976); 54-56: Imani et al. (1975); 57: Hall & Stewart (1973); 58-61: Karpenkov et al. (1973); 62-64: Scott & Gasparrini (1973); 65-69: Vuorelainen et al. (1972), and 70-72: Shishkin et al. (1971).

Charcón are very variable (Fe in the range 5.10 to 5.35 *apfu*, Ni between 2.48 and 3.01 *apfu*, and Fe/Ni between 1.71 and 2.16) and are intermediate with regard to values reported for argentopentlandite from other environments (Fe 4.51 to 5.84 *apfu*, Ni 2.28 to 3.37 *apfu*, and Fe/Ni 1.34 to 2.56). The wide range of Fe and Ni values can be explained by coupled substitution involving Fe and Ni in tetrahedral sites (32f).

The argentopentlandite from El Charcón is devoid of Co, which is characteristic (Table 3) of the other examples known (range of 0–0.04; only one is 0.43). This finding confirms the proposal that argentopentlandite does not form an isomorphous solution with pentlandite. Pentlandite and cobaltopentlandite are two isostructural species that do form a solid solution (Rajamani & Prewitt 1973). If argentopentlandite and pentlandite were end members of a

distinct solid-solution series, then Co could be expected to be significant in the argentopentlandite structure.

The metal-to-sulfur (M/S) ratio for the El Charcón argentopentlandite ranges from 1.12 to 1.16. These values are intermediate in comparison with values in the literature (1.07 to 1.21). The maximum frequency of the M/S ratio is approximately 1.125, which corresponds to the stoichiometric composition of argentopentlandite (M/S = 9/8). However, cases with values other than 1.125 were observed. Sulfur-deficient compositions (M/S > 1.125) were found in 61% of the occurrences investigated. These cases can be explained by analytical errors (Scott & Gasparrini 1973), or by the restrictive conditions of S fugacities in nature, as Harris & Nickel (1972) proposed for normal pentlandite. A relative deficiency of sulfur also is observed for other sulfide phases (pyrite, As-bearing pyrite, sphalerite and galena) in the paragenetic assemblage from El Charcón (Morales 1994). On the other hand, values lower than 1.125, indicative of a deficit in cations, can be explained by vacancies at tetrahedral sites, as proposed in pentlandite by Rajamani & Prewitt (1973).

Sixty-seven of seventy-two compositions from Table 3 are in agreement with one of the following cases (Table 3B): (1) Ag < 1 and (Fe,Ni) > 8 (22 analyses), which was explained (Hall & Stewart 1973) by the presence of (Fe,Ni) at the octahedral positions assigned to Ag; (2) Ag $\geq$ 1, (Fe,Ni) < 8 and S > 8 (17 analyses), which indicates the existence of (Fe,Ni) vacancies; (3) Ag $\geq$ 1, (Fe,Ni) > 8 and S < 8 (25 analyses), which agrees with the idea of a deficiency in S, and (4) Ag $\geq$ 1, (Fe,Ni) < 8 and S < 8 (3 analyses), which shows the simultaneous existence of (Fe,Ni) vacancies and S-deficit. As a result, deviations from the ideal formula can be explained not only by replacement of Ag by (Fe,Ni) (Hall & Stewart

1973), but also by the existence of vacancies at (Fe,Ni) positions or by a deficit of S. For argentopentlandite from El Charcón, most of the analyses indicate Ag $\geq$ 1, (Fe,Ni) > 8 and S < 8 (5 analyses).

The average formula for argentopentlandite from El Charcón (Table 3, anal. 1 to 11) is $Fe_{5.17}Ni_{2.86}Ag_{1.02}S_8$. This formula agrees with the average formula ($Fe_{5.18}Ni_{2.84}Ag_{0.99}S_8$) calculated for data in the literature (Table 3, anal. 12 to 72). Both also agree with the formula proposed by Groves & Hall (1978): $(Fe_{5\pm0.6}Ni_{3\pm0.4})_{\Sigma8+x} Ag_{1-x}S_8$, with $0 < x < 0.2$.

Nevertheless, from the values obtained for the argentopentlandite from El Charcón and those from the literature in Table 3, some modifications of the Groves & Hall (1978) formula can be proposed. These authors proposed "$\Sigma = 8 + x$" and "$1-x$" subscripts for (Fe,Ni) and Ag, respectively, to indicate that the deficit in Ag is compensated by addition of (Fe,Ni) in the octahedral sites. But, as we have seen above, there are two objections to this idea. (a) In Table 3, we found not only (Fe,Ni)-excess with Ag-deficient compositions, but also some with different combinations of (Fe,Ni) and Ag deficiencies or excesses. Therefore, modification of the subscripts "$\Sigma = 8 + x$" by "$\Sigma = 8 \pm x$" for (Fe,Ni), and "$1 - x$" by "$1 \pm y$" for Ag will be necessary. (b) If we calculate the compositions on the basis of 17 atoms per formula, we have also found variations in the subscripts of S, and consequently the ideal value of 8 for S must be changed to "$8 \pm z$". According to this idea and the values of Table 3, the formula of argentopentlandite can therefore be reformulated as:

$(Fe_{5\pm0.77}Ni_{3\pm0.75})_{\Sigma8\pm x}Ag_{1\pm y}S_{8\pm z}$,
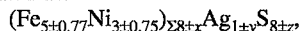
with $0 < |x| < 0.30$, $0 < |y| < 0.23$ and $0 < |z| < 0.30$. We propose this formula because it shows better the expanded compositional range of this mineral and the possibility of vacancies at different sites in the structure.
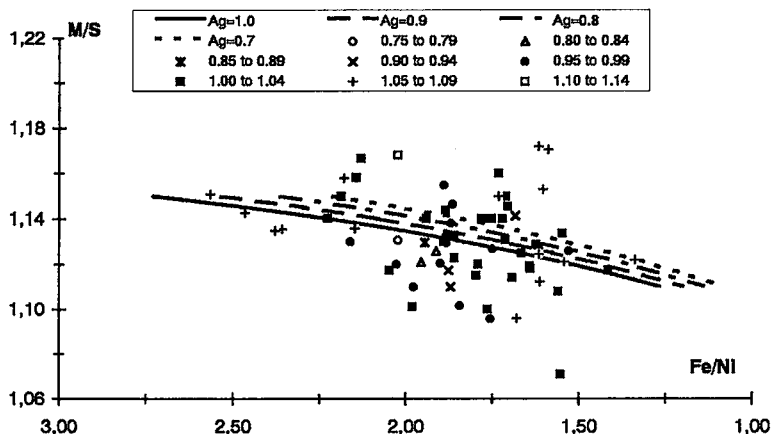
FIG. 3. Fe/Ni *versus* M/S values for argentopentlandite compositions of Table 3. Curved lines correspond to theoretical variation of metal/sulfur with Fe/Ni in argentopentlandite with different Ag values. These curves are calculated using the formula proposed by Mandziuk & Scott (1977).

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The stoichiometric composition of argentopentlandite can be predicted as a function of Ag content using the "cation addition–omission solid solution" model proposed by Mandziuk & Scott (1977). Therefore, for Ag = 1 *apfu*, Fe and Ni must be 5 and 3 *apfu*, respectively. On the other hand, Ag values from both El Charcón and the average formulae in the literature are close to 1.00 *apfu*. However, neither average formula satisfies the Mandziuk & Scott (1977) model. Measures of *M*/S and Fe/Ni values in argentopentlandite from both El Charcón and the literature (Fig. 3) show a considerable difference from values inferred by their model for different Ag contents. This model is therefore valid for synthetic argentopentlandite, but not for natural argentopentlandite. It is not clear why this is so, but owing to the absence of significant quantities of trace elements, it may be because of vacancies in the argentopentlandite structure that were not taken into account in the theoretical calculations.

PHYSICAL AND CHEMICAL CONDITIONS
AND MECHANISM OF FORMATION

P–T–X–f(S₂) conditions

Physical and chemical conditions of stage I and II of the paragenetic assemblage for El Charcón ore deposits were determined as follows.

The temperature of formation for stage I of the paragenetic assemblage is difficult to establish exactly. However, the determination of an interval of temperature is possible. Different events occurred within this interval: (a) Inversion from high- to low-temperature chalcopyrite [400 to 550°C, according to Craig & Kullerud (1969)], (b) formation of sphalerite stars [400 to 500°C, according to Sugaki *et al.* (1987)], and (c) formation of argentopentlandite [<455°C, according to Mandziuk & Scott (1977)]. The most probable interval ranges from 400 to 455°C. This interval is in accordance with the range in temperature of homogenization obtained from fluid inclusions of stage I (see below), and it is also above of determined interval of temperature for stage II of the paragenetic assemblage. This range in temperature implies an interval of log $f(S_2)$ from –9.6 to –15.7 atm. (Fig. 4).

The conditions of formation of the mineral assemblages of stage II can be estimated from the Fe content in sphalerite [4.41–11.75 at.%, according to Morales (1994)], using the equation of Craig & Scott (1974), together with the geothermometer of Kretschmar & Scott (1976) for the As content in arsenopyrite [30.29–31.98 at.%, according to Morales (1994)], both coexisting in equilibrium with pyrite. At El Charcón, temperature and log $f(S_2)$ intervals defined by the assemblage arsenopyrite + sphalerite + pyrite
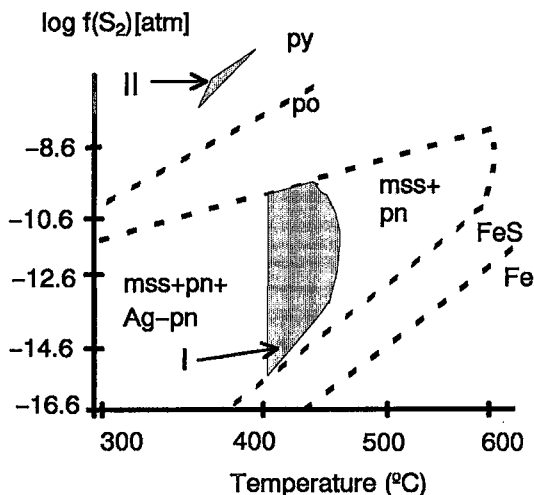

log f(S₂)[atm]

FIG. 4. Stability conditions for stages I and II of the paragenetic sequence in the temperature *versus* log $f(S_2)$ diagram. Conditions for stage I were calculated after Mandziuk & Scott (1977) using a lower limit at 400°C (see text for explanation). Conditions for stage II were calculated after Barton & Skinner (1979), Craig & Scott (1974), and Kretschmar & Scott (1976).

range from 354 to 404°C and from –6.5 to –8.4 atm., respectively (Fig. 4).

Fluid-inclusion studies of quartz from stage I and II of the paragenetic sequence show two populations (Morales 1994). In those associated with stage I, the temperature of homogenization ranges from 405 to 508°C, and the salinity, from 17 to 22 wt.% NaCl equivalent. For stage II, the temperature of homogenization ranges from 160 to 310°C, and the salinity, from 2 to 8 wt.% NaCl equivalent. Isochores calculated following Zhang & Frantz (1987) for fluid inclusions from stage I can be bracketed between 400 and 450°C (see above). Fluid pressure in this temperature range varied from 200 to 900 bars.

All values for argentopentlandite in Table 3 were plotted in terms of Ag–Fe–Ni, established by Mandziuk & Scott (1977) for synthetic argentopentlandite. Most of the values (included compositions of argentopentlandite with a temperature of formation lower than 400°C) fall beyond the stability fields at 300 and 400°C (Fig. 5), which indicates that this diagram is not useful for determination of temperature of formation. There are two possible explanations for this: (1) the stability fields are valid for synthetic argentopentlandite, but not for natural argentopentlandite, in which case other factors must be taken into account, or (2) the displacement of values for
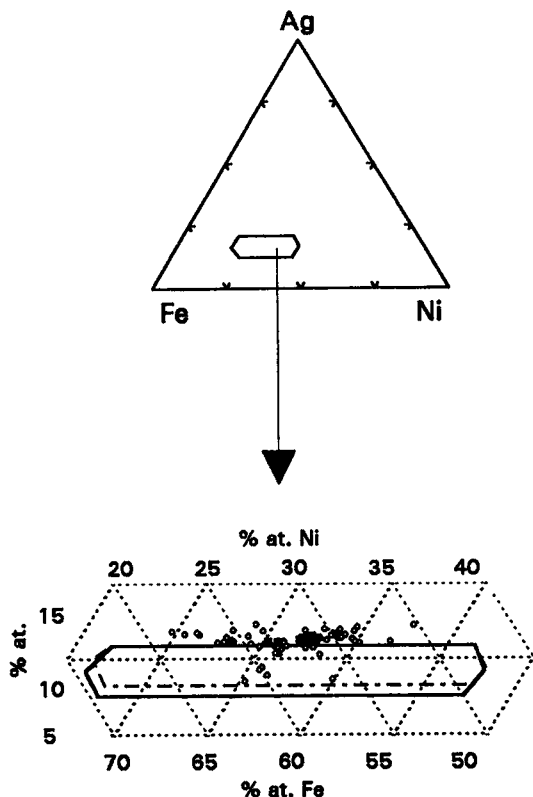
FIG. 5. Ag–Fe–Ni plots for argentopentlandite compositions from Table 3. Dark circles: argentopentlandite from El Charcón; open circles: argentopentlandite from other occurrences. Stability fields at 400°C (dashed lines) and 300°C (full lines) from Mandziuk & Scott (1977).

exsolution has been inferred for star-shaped sphalerite (Morales 1994) on the basis of textural features of sphalerite and also by calculating the bulk chemical composition of chalcopyrite containing star-shaped sphalerite, using the method by Sugaki *et al.* (1987). (3) The textures described by Groves & Hall (1978) as being characteristic of genesis by subsolidus reactions are not found in the argentopentlandite from El Charcón. There is therefore a connection between the origin of argentopentlandite, the presence of star-shaped sphalerite and the inversion of chalcopyrite from a high- to a low-temperature form. The formation of lamellae twins in the chalcopyrite seems to have occurred "simultaneously" with the exsolution of sphalerite and argentopentlandite.

In summary, we contend that both argento-pentlandite and sphalerite exsolved from Ag- and Zn-rich chalcopyrite (or *iss*) during cooling of ore-bearing solutions. We can suggest further lines of research on argentopentlandite. Work must be done on: (1) the electronic model for stabilization of the argentopentlandite structure, (2) the stability fields of natural argentopentlandite, and (3) verification of its space group.

natural argentopentlandite toward the Ag corner of the diagram is the consequence of relative enrichment in Ag because of vacancies. The latter agrees with the conclusions obtained by study of argentopentlandite chemistry (see above).

Mechanism of formation

Three factors can be mentioned to explain the genesis of argentopentlandite from El Charcón as the result of exsolution. (1) Argentopentlandite is invariably enclosed in chalcopyrite, as individual grains with sharp boundaries, in some cases with common orientation and occasionally as poorly developed dendrites. This last texture was described by Scott & Gasparrini (1973) as a characteristic product of exsolution. (2) Argentopentlandite always occurs associated with star-shaped sphalerite. Genesis by

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