

NUFFIELDITE FROM THE MALEEVSKOE MASSIVE SULFIDE DEPOSIT, RUSSIA

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ABSTRACT

A new occurrence of nuffieldite, a rare lead – bismuth – copper sulfosalt, is reported from a pyrite-rich massive sulfide deposit at Maleevskoe, Rudny Altai, Russia. The mineral occurs as platy crystals (0.3×0.08 mm) and as aggregates of anhedral grains up to 0.6 mm within a (Cu,Zn)-rich zone. Associated minerals are hessite, tetradyomite, electrum, aikinite, lindströmite, hammarite, cosalite, kobellite, galenobismutite, gudmundite, berthierite and nisbite. Optical properties, X-ray powder-diffraction data and results of electron-microprobe analyses are compared with those of nuffieldite from both the type locality and other localities. The mineral contains as much as 5.08 wt.% Sb, which supports the findings of Maurel & Moëlo (1990) and Moëlo (1989) that Sb is essential for the stabilization of the mineral. Calculated formulae (based on an ideal formula with 13 atoms) show an excess in Cu and a deficiency in S, which are correlated with Pb in mixed (Pb,Bi,Sb) sites. These correlations may be accounted for by assuming compensation of the substitution Pb^{2+} for Bi^{3+} by vacancies in the S site and neutral Cu atoms in excess in structural interstices. Excess Cu may be mobile, as has been established in synthetic tetrahedrite (Makovicky & Skinner 1979). The compositional field of nuffieldite may be expressed by the formula $\text{Cu}_{1-x}\text{Pb}_2(\text{Pb}_y\text{Bi}_{1-y-z}\text{Sb}_z)\text{Bi}_2\text{S}_{7-y}$, where x and y may have similar values.

Keywords: nuffieldite, electron-microprobe data, reflectance data, X-ray-diffraction data, Maleevskoe, Russia.

SOMMAIRE

Nous décrivons un nouvel exemple de nuffieldite, sulfosel rare de plomb, bismuth et cuivre, découvert dans un gisement de sulfures massifs à Maleevskoe, Rudny Altai, en Russie. Elle se présente en plaquettes (0.3×0.08 mm) et en agrégats de grains xénomorphes atteignant une taille de 0.6 mm dans une zone riche en Cu et Zn. Lui sont associés hessite, tétradyomite, électrum, aikinite, lindströmite, hammarite, cosalite, kobellite, galénobismutite, gudmundite, berthierite et nisbite. Nous comparons ses propriétés optiques, les données diffractométriques et sa composition chimique (analyses à la microsonde électronique) avec celles de la nuffieldite de la localité type et d'autres endroits. Ce matériau peut contenir jusqu'à 5.08% en poids de Sb, ce qui étaye l'hypothèse de Maurel et Moëlo (1990) et Moëlo (1989), à l'effet que l'antimoine serait essentiel à la stabilisation de ce minéral. Les formules calculées sur une base de 13 atomes démontrent un excès de Cu et une déficience de S, qui sont liées à la présence de Pb dans des sites à occupation mixte (Pb,Bi,Sb). Ces corrélations seraient expliquées en supposant une compensation de la substitution de Pb^{2+} pour Bi^{3+} par la présence de lacunes dans le site du soufre et d'un excès d'atomes de Cu, neutres, dans les interstices de la structure. Ces atomes de Cu en excès pourraient bien être mobiles, comme l'ont démontré Makovicky et Skinner (1979) dans le cas de la tétraédrite synthétique. Le champ de compositions de la nuffieldite serait bien exprimé par la formule $\text{Cu}_{1-x}\text{Pb}_2(\text{Pb}_y\text{Bi}_{1-y-z}\text{Sb}_z)\text{Bi}_2\text{S}_{7-y}$, dans laquelle x et y auraient des valeurs semblables.

(Traduit par la Rédaction)

Mots-clés: nuffieldite, données de la microsonde électronique, données de réflectance, données de diffraction X, Maleevskoe, Russie.

INTRODUCTION

Nuffieldite, a rare lead – bismuth – copper sulfosalt with a proposed formula $\text{Pb}_{10}\text{Bi}_{10}\text{Cu}_4\text{S}_{27}$, was first described by Kingston (1968) from the Lime Creek molybdenum deposit, Alice Arm, British Columbia.

Kohatsu & Wuensch (1973) determined its crystal structure using Kingston's chemical data and gave the structural formula as $\text{Pb}_2\text{Cu}(\text{Pb,Bi})\text{Bi}_2\text{S}_7$. Recently, Moëlo (1989) described an occurrence of nuffieldite from France that contains 2.2 wt.% Sb. Since nuffieldite had not been synthesized in the system

PbS–Bi₂S₃–Cu₂S, Moëlo (1989) proposed that antimony is an essential component for the stabilization of the mineral. Subsequent experimental studies by Maurel & Moëlo (1990) were successful in synthesizing nuffieldite at 435°C with as much as 5 wt.% Sb. Taking into account the structural role of antimony, Moëlo proposed Pb₂Cu_{1+x}(Pb_xBi_{1-x-y}Sb_y)Bi₂S₇ as the formula for nuffieldite, in which $x = 0.37$ and the Sb content is variable ($0.19 < y < 0.55$). According to this formula, an "aikinite" substitution of the type $\text{Bi}^{3+} = \text{Pb}^{2+} + \text{Cu}^+$ takes place in nuffieldite. Harris (1993) examined a cotype specimen of nuffieldite from the Lime Creek locality, confirmed the presence of 1.33 wt.% Sb, and gave compositional data on a second Canadian occurrence of nuffieldite from the Izok Lake massive Zn–Cu–Pb sulfide deposit, Northwest Territories, that contains 2.3 wt.% Sb. This paper reports on another occurrence of nuffieldite, from the Maleevskoe deposit, Rudny Altai, Russia, where it was previously described as "Cu-cosalite" (Yudovskaya *et al.* 1992).

OCCURRENCE AND ASSOCIATION

The Maleevskoe polymetallic massive sulfide deposit occurs within metamorphosed (up to greenschist facies) volcano-sedimentary rock sequences that contain several subvolcanic bodies of felsic and basic rocks. Concordant massive sulfide orebodies occur in the zone of contact metamorphism associated with the intrusion of the Zmeinogorsk granitic complex. The orebodies display a zoning sequence from footwall to

TABLE 1. REFLECTANCE DATA FOR NUFFIELDITE FROM MALEEVSKOE, RUSSIA

nm	R ₁	R ₂	nm	R ₁	R ₂
400	45.46	35.94	580	46.07	37.52
420	44.57	36.69	589	45.90	37.40
440	45.88	37.22	600	45.85	37.28
460	46.30	37.44	620	45.45	36.94
470	46.50	37.70	640	45.11	36.88
480	46.55	37.81	650	44.95	36.70
500	46.80	38.08	660	44.88	36.54
520	46.65	37.73	680	44.42	36.66
540	46.26	37.78	700	43.95	36.22
560	46.17	37.73			

Standard: WTIC. Reflectance data are expressed in %.

hanging wall of Fe – (Cu,Fe) – (Cu,Zn) – (Pb,Cu,Zn). Pyrite, chalcopyrite, sphalerite and galena are abundant, with minor tennantite and tetrahedrite.

Of particular note within this ore mineralization is the youngest association, which includes rare and minor minerals of antimony and bismuth, as well as those of silver and tellurium (hessite, electrum, tetradymite, among others). Nuffieldite occurs in this assemblage, which is usually located within the (Cu,Zn) zone. Aikinite, lindströmite, hammarite, cosalite, kobellite, galenobismutite, gudmundite, berthierite, nisbite and other Bi- and Sb-bearing minerals also have been identified (Yudovskaya *et al.* 1992).

Nuffieldite occurs as elongate platy crystals (0.3×0.08 mm) and as aggregates of anhedral grains (up to

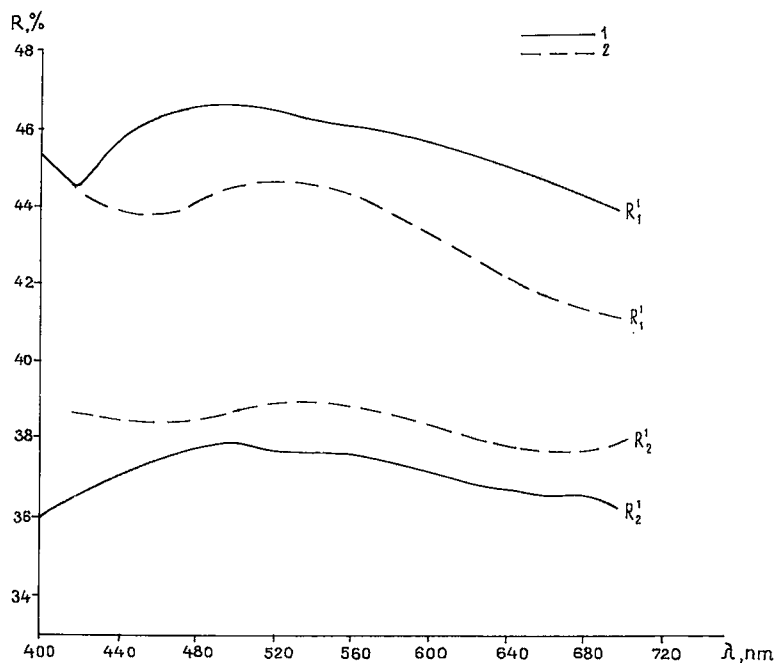


FIG. 1. Reflectance spectra for nuffieldite in air from Maleevskoe (1) and Lime Creek (2, after Kingston 1968).

0.6 mm) in association with the main ore minerals noted above. Tiny blebs of native bismuth together with chalcopyrite commonly occur on the edges of nuffieldite grains.

OPTICAL PROPERTIES

Under the reflected light microscope, nuffieldite is light grey; its color is slightly darker than galena.

TABLE 2. X-RAY POWDER-DIFFRACTION DATA FOR NUFFIELDITE

MALEEVSKOE				AKCHATAU			LIME CREEK				LES HOUCHEs	
I	d _{meas}	hkl	d _{calc}	I	d _{meas}	d _{calc}	I	d _{meas}	hkl	d _{calc}	I	d _{meas}
0.5	7.87											
1	7.20	200	7.30				1	7.30	200	7.30	0.5	7.28
0.5	6.48	130	6.39									
0.5	6.19	220	6.02									
0.5	5.39	040	5.34				0.5	5.38	040	5.34		
0.5	5.10	230	5.10	0.5	5.03	5.09	0.5	5.09	230	5.10		
0.5	4.68	310	4.75	4	4.64	4.75	0.75	4.75	310	4.75		
1	4.46	320	4.43									
0.5	4.32	050	4.27	4	4.34	4.29	1	4.29	050	4.28	0.5	4.29
		240	4.31									
1	4.09	150	4.10	1	4.15	4.10						
8+β	3.98	330	4.02	10B	3.98	4.02	9	4.00	330	4.02	5	3.97
1	3.87	011	3.96									
0.5	3.79	111	3.82									
10	3.62	400	3.650	8B	3.58	3.65	10	3.66	400	3.65	10	3.65
4	3.57	080	3.557				10	3.54	201	3.53	9	3.54
6	3.51	031	3.504									
1	3.46	420	3.454	3B	3.43	3.45	0.5	3.44	420	3.46	0.5	3.47
3	3.31	221	3.347	2	3.35	3.35	0.5	3.35	221	3.35	0.5	3.34
				2	3.33	3.25						
0.5	3.16	231	3.159	8B	3.15	3.16	8	3.16	231	3.16	9	3.16
10	3.13	141	3.139									
2	2.975	321	2.979				3	2.98	321	2.98	4	2.98
5	2.945	241	2.942	4	2.96	2.942	2	2.94	241	2.94		
6	2.909	510	2.893									
0.5	2.880	151	2.872	3	2.86	2.872	3	2.87	151	2.87	2	2.87
4	2.839	331	2.844									
1	2.812	270	2.814	2	2.79	2.814	1	2.81	270	2.82		
		520	2.817						520	2.82		
1	2.772	450	2.774				2	2.76	450	2.78		
3	2.747	251	2.718	2	2.70	2.718	2	2.72	251	2.71	3	2.73
3	2.697	530	2.702	2	2.64	2.668	0.5	2.67	080	2.67	1	2.67
5	2.649	161	2.622	1	2.61	2.622	0.5	2.62	161	2.62		
5	2.521	431	2.528	8	2.53	2.528	10	2.54	460	2.55		
		600		1	2.46	2.434						
		071		1	2.43	2.431						
2	2.372	620	2.373				2	2.40	171	2.40	1	2.40
1	2.331	361	2.338	5	2.34	2.338	2	2.34	470	2.34	1	2.35
		470				2.340						
5	2.292	630	2.303				3	2.31	521	2.31	2	2.30
0.5	2.266	560	2.257	4	2.25	2.257	1	2.22	640	2.22	1	2.23
1	2.171	371	2.175	5	2.20	2.175	1	2.16	541	2.16		
		640				2.214						
1	2.159	480	2.154	1	2.15	2.154						
0.5	2.137	0.10.0	2.134	1	2.13	2.134	1	2.13	281	2.13		
		281				2.128						
2	2.101	570	2.109	2	2.06	2.109						
		551				2.068						
7	1.998	471	2.023	2	2.01	2.023	3	2.04	621	2.04		
		631	1.999				3	2.02	471	2.02	8	2.03
		112		2	1.985	1.986						
		122		1	1.981	1.980	2	1.967	561	1.969	1	1.969
2	1.949	740	1.943	3	1.943	1.943	2	1.940	202	1.941		
		202										
2	1.931	212	1.933								0.5	1.931
1	1.906	222	1.909									
5	1.864	142	1.868	5	1.869	1.868	6	1.871	651	1.872	6B	1.878
		651				1.870						
5	1.854	312	1.853									
		242		1	1.823	1.823	1	1.821	810	1.819		
2	1.805	152	1.807	1	1.798	1.807	0.5	1.798	661	1.798	1	1.809
		661				1.797						
2	1.783	491	1.783									
		402		5	1.760	1.763	0.5	1.765	252	1.767	3	1.764
3	1.750	741	1.750				1	1.751	741	1.750		
4	1.732	1.11.1	1.736	3	1.728	1.736						
		2.12.0				1.728						
		690		4	1.693	1.698	1	1.697	690	1.699	1	1.709
1	1.684	850	1.678									
1	1.644	780	1.643									
1	1.619	831	1.619	4	1.625	1.629	1	1.631	452	1.629	2	1.639

Cell dimensions of nuffieldite from Maleevskoe: *a* 14.602, *b* 21.375, *c* 4.026 Å (camera diameter 114.59 mm, FeK α , β radiation). Cell dimensions of nuffieldite from Akchatau (Efimov et al. 1980): *a* 14.60, *b* 21.34, *c* 4.03 Å (camera diameter 57.3 mm, FeK α , β radiation). Cell dimensions of nuffieldite from Lime Creek (Kingston 1968): *a* 14.61, *b* 21.38, *c* 4.03 Å (camera diameter 114.59 mm, CuK α radiation).

Bireflectance is weak and noticeable only on the contacts of differently oriented grains. Reflection pleochroism is absent. Anisotropism is strong, but without color effects. No internal reflections are present.

Reflectivity was measured in air on randomly oriented grains using an Opton microphotometer, with WTiC as the reflectance standard and a 20 $\times$ objective. The results are given in Table 1. The spectral curves over the wavelength range 400–700 nm for both R_1 and R_2 , along with previously published data for material from the type locality, are plotted in Figure 1. The reflectance curves are very similar, but the bireflectance of the mineral from Maleevskoe is more intense. This can probably be explained by different orientations of the grains studied.

X-RAY POWDER-DIFFRACTION DATA

X-ray powder-diffraction data for nuffieldite were obtained for an analyzed grain using a 114.6-mm

Debye–Scherrer camera and unfiltered Fe-radiation. The results are given in Table 2 and are compared to those of nuffieldite from Akchatau (Efimov *et al.* 1990), Lime Creek (Kingston 1968) and Les Houches (Močlo 1989). Our results agree fairly well with previously published X-ray data, although more lines were obtained. All the d -values except the one at 7.67 Å can be indexed on an orthorhombic cell having parameters a 14.602, b 21.375, c 4.026 Å and space group $Pbnm$.

CHEMICAL DATA

Ten electron-microprobe analyses were obtained for nuffieldite from the Maleevskoe deposit. Results of these analyses, along with published data from the four other localities, are given in Table 3. Analyses 1, 2, 4–6, and 8–10 were obtained with a JEOL JXA–5 electron microprobe using the following standards (and analytical lines): PbS (PbM α and SK α), Cu, Sb and Bi pure metals (CuK α , SbL α , BiM α). Anal-

TABLE 3. RESULTS OF ELECTRON-MICROPROBE ANALYSES OF NUFFIELDITE

#	Cu	Pb	Bi	Sb	S	Total (wt.%)	Formulae (based on 13 atoms)
Maleevskoe deposit							
1*	5.30	33.85	39.38	5.08	17.71	101.11	Cu _{1.06} Pb ₂ (Pb _{0.05} Bi _{0.39} Sb _{0.52}) ₂ 0.96Bi ₂ S _{6.98}
2*	5.74	34.16	42.00	2.11	17.29	100.94	Cu _{1.08} Pb ₂ (Pb _{0.11} Bi _{0.57} Sb _{0.22}) ₂ 0.90Bi ₂ S _{7.01}
3	5.26	34.22	42.19	2.01	17.55	101.57**	Cu _{1.06} Pb ₂ (Pb _{0.11} Bi _{0.58} Sb _{0.21}) ₂ 0.90Bi ₂ S _{7.00}
4*	5.48	33.12	42.73	1.81	17.50	100.63	Cu _{1.11} Pb ₂ (Pb _{0.03} Bi _{0.63} Sb _{0.19}) ₂ 0.85Bi ₂ S _{7.04}
5	5.37	34.59	43.16	1.84	16.83	101.79	Cu _{1.10} Pb ₂ (Pb _{0.17} Bi _{0.69} Sb _{0.20}) ₂ 1.06Bi ₂ S _{6.84}
6	5.44	33.31	42.88	1.38	16.98	99.99	Cu _{1.12} Pb ₂ (Pb _{0.10} Bi _{0.69} Sb _{0.15}) ₂ 0.94Bi ₂ S _{6.94}
7	5.50	33.80	43.29	1.98	17.01	101.78***	Cu _{1.12} Pb ₂ (Pb _{0.11} Bi _{0.66} Sb _{0.21}) ₂ 1.00Bi ₂ S _{6.86}
8	5.61	33.50	42.84	1.77	16.71	100.43	Cu _{1.16} Pb ₂ (Pb _{0.12} Bi _{0.69} Sb _{0.19}) ₂ 1.00Bi ₂ S _{6.84}
9	5.70	33.24	42.63	1.87	16.90	100.34	Cu _{1.17} Pb ₂ (Pb _{0.09} Bi _{0.66} Sb _{0.20}) ₂ 0.95Bi ₂ S _{6.85}
10	5.85	34.09	41.74	1.98	16.51	100.17	Cu _{1.21} Pb ₂ (Pb _{0.17} Bi _{0.62} Sb _{0.21}) ₂ 1.00Bi ₂ S _{6.78}
Akchatau (Efimov <i>et al.</i> 1980)							
11	5.5	33.3	40.3	3.7	16.9	99.7	Cu _{1.13} Pb ₂ (Pb _{0.09} Bi _{0.51} Sb _{0.40}) ₂ 1.00Bi ₂ S _{6.87}
12	5.7	33.6	40.0	2.9	17.1	99.3	Cu _{1.17} Pb ₂ (Pb _{0.11} Bi _{0.49} Sb _{0.31}) ₂ 0.91Bi ₂ S _{6.93}
13	6.2	35.2	40.5	2.9	17.1	101.9	Cu _{1.25} Pb ₂ (Pb _{0.17} Bi _{0.47} Sb _{0.30}) ₂ 0.94Bi ₂ S _{6.81}
14	6.4	36.2	39.1	3.0	17.1	101.8	Cu _{1.28} Pb ₂ (Pb _{0.23} Bi _{0.38} Sb _{0.31}) ₂ 0.92Bi ₂ S _{6.79}
Les Houches (Močlo 1989)							
15	6.05	36.15	37.85	2.00	16.30	98.35	Cu _{1.27} Pb ₂ (Pb _{0.33} Bi _{0.41} Sb _{0.22}) ₂ 0.96Bi ₂ S _{6.78}
16	6.20	36.35	38.10	1.90	16.60	99.15	Cu _{1.28} Pb ₂ (Pb _{0.31} Bi _{0.40} Sb _{0.21}) ₂ 0.92Bi ₂ S _{6.81}
17	6.45	36.80	37.50	2.25	16.55	99.65	Cu _{1.33} Pb ₂ (Pb _{0.33} Bi _{0.35} Sb _{0.24}) ₂ 0.92Bi ₂ S _{6.76}
18	6.55	36.60	38.05	2.20	16.65	100.05	Cu _{1.34} Pb ₂ (Pb _{0.30} Bi _{0.37} Sb _{0.24}) ₂ 0.91Bi ₂ S _{6.76}
19	6.50	36.60	38.20	2.20	16.55	100.05	Cu _{1.34} Pb ₂ (Pb _{0.31} Bi _{0.39} Sb _{0.24}) ₂ 0.94Bi ₂ S _{6.74}
20	6.55	37.15	37.95	2.25	16.50	100.40	Cu _{1.34} Pb ₂ (Pb _{0.34} Bi _{0.37} Sb _{0.24}) ₂ 0.95Bi ₂ S _{6.71}
21	6.55	36.75	38.15	2.25	16.45	100.15	Cu _{1.35} Pb ₂ (Pb _{0.32} Bi _{0.39} Sb _{0.24}) ₂ 0.93Bi ₂ S _{6.71}
Lime Creek (Harris 1993)							
22	5.81	34.12	42.00	1.33	17.52	100.78	Cu _{1.17} Pb ₂ (Pb _{0.12} Bi _{0.58} Sb _{0.14}) ₂ 0.84Bi ₂ S _{7.00}
Izok Lake (Harris 1993)							
23	5.6	34.1	39.4	2.3	16.9	98.3	Cu _{1.16} Pb ₂ (Pb _{0.17} Bi _{0.48} Sb _{0.25}) ₂ 0.90Bi ₂ S _{6.94}

* Reported as Cu-cosalite (Yudovskaya *et al.* 1992).

** Includes 0.34 wt. % Ag.

*** Includes 0.20 wt. % Ag.

TABLE 4. COMPARISON OF S ATOMS VERSUS Cu EXCESS (Cu_{exc}) AND Pb IN MIXED SITES (Pb_{mix}) IN NUFFIELDITE

Anal. #	S	Cu_{exc}	Pb_{mix}	Anal. #	S	Cu_{exc}	Pb_{mix}
4	7.04	0.11	0.03	8	6.84	0.16	0.12
2	7.01	0.08	0.11	13	6.81	0.25	0.17
22	7.00	0.17	0.12	16	6.81	0.28	0.31
3	7.00	0.10	0.11	14	6.79	0.28	0.23
1	6.98	0.06	0.05	10	6.78	0.21	0.17
6	6.94	0.12	0.10	15	6.78	0.27	0.33
23	6.94	0.16	0.17	17	6.76	0.33	0.33
12	6.93	0.17	0.11	18	6.76	0.34	0.30
11	6.87	0.13	0.09	19	6.74	0.34	0.31
7	6.86	0.14	0.11	20	6.71	0.34	0.34
9	6.85	0.17	0.09	21	6.71	0.35	0.32
5	6.84	0.10	0.17				

ysis 3 and 7 were obtained with a CAMECA MS-46 electron microprobe using the following standards (and analytical lines): PbS ($\text{PbL}\alpha$, $\text{SK}\alpha$), CuFeS_2 ($\text{CuK}\alpha$), and Ag, Sb and Bi pure metals ($\text{AgL}\alpha$, $\text{SbL}\alpha$, $\text{BiL}\alpha$).

As shown in Table 3, all examples of nuffieldite contain between 1.33 and 5.08 wt.% Sb. The highest Sb content occurs in a sample from the Maleevskoe deposit; this composition supports the observations of Maurel & Moëlo (1990) that nuffieldite can be synthesized with as much as 5 wt.% Sb. The existence of Sb thus confirms Moëlo's (1989) proposal that Sb plays an important structural role in nuffieldite. As much as 0.5 wt.% Ag also was detected in some grains.

Structural formulae calculated from the analytical data on the basis of 13 atoms are given in Table 3. These formulae show a significant deviation from the

ideal formula with seven atoms of S. The deviations in proportion of S are compared with the excess of Cu and the Pb mixed sites in Table 4. The results indicate that with decreasing S contents, there is a general increase in Cu and in Pb contents in the mixed site. Thus both of these values are negatively correlated with concentration of S in nuffieldite.

DISCUSSION

The chemical data reported for nuffieldite from the Maleevskoe deposit and those from other localities permit some conclusions about possible schemes of substitution. 1) Sb probably enters the mixed site by the simple substitution $\text{Bi}^{3+} = \text{Sb}^{3+}$, as proposed by Moëlo (1989) and Maurel & Moëlo (1990). 2) There is an uncertainty concerning the mechanism of substitution of Pb^{2+} for Bi in the mixed site. Positive correlation between Cu_{exc} and Pb_{mix} can be interpreted in terms of the substitution scheme $\text{Cu}^+ + \text{Pb}^{2+} = \text{Bi}^{3+}$. However, the observed negative correlation between S and Cu_{exc} , and that between S and Pb_{mix} , do not agree with this scheme. Such correlation may be explained if we assume that the substitution Pb^{2+} for Bi^{3+} in the mixed site is compensated for by vacancies in S sites, and that the excess Cu occurs in structural interstices as neutral atoms. In this latter case, the compositional field of nuffieldite may be expressed by the formula $\text{Cu}_{1+x}\text{Pb}_2(\text{Pb}_y\text{Bi}_{1-y-z}\text{Sb}_z)\text{Bi}_2\text{S}_{7-x}$, where x and y are commonly the same value.

It is not excluded that Cu_{exc} is mobile. On this reasoning, an additional Cu site (one site per unit cell), as proposed by Moëlo (1989), has not been substantiated by the structural studies of Kohatsu & Wuensch

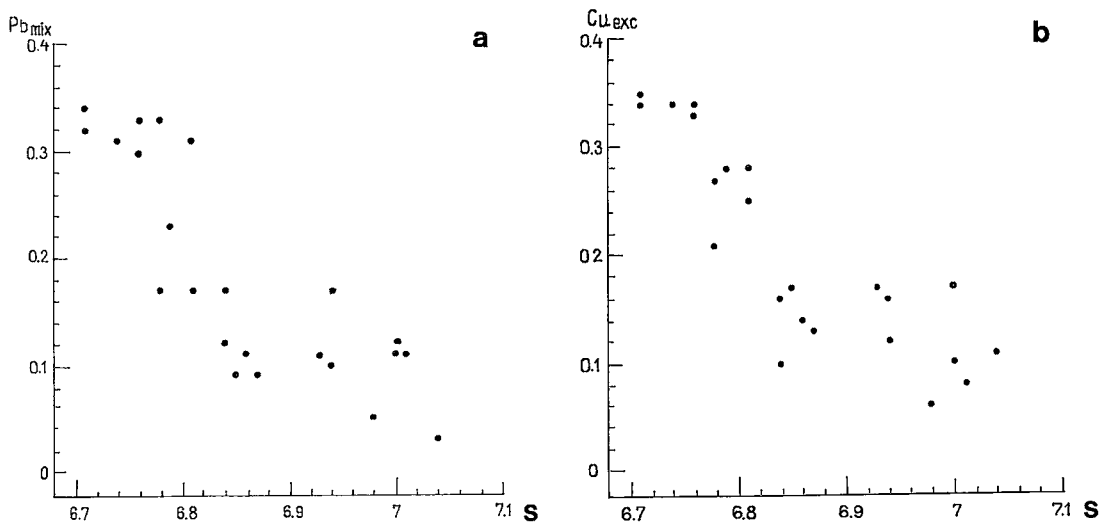


FIG. 2. Proportions of a) Pb_{mix} and b) Cu_{exc} versus S in nuffieldite (in atoms per formula unit).

(1972). These proposals need further investigation. However, similar problems have been found in the fahlore minerals. Reduction of S content and the appearance of vacancies at the S(2) site in the tetrahedrite structure, where Ag substitutes for Cu, were found by single-crystal X-ray-diffraction structural studies (Rozhdestvenskaya *et al.* 1989). Mobile Cu also has been determined by structural studies on synthetic tetrahedrite (Makovicky & Skinner 1979). Because of this feature, the tetrahedrite was referred to as a solid electrolyte.

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