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RUCKLIDGEITE SOLID-SOLUTION IN THE YANAHARA DEPOSIT, JAPAN

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ABSTRACT

A bismuth lead telluride mineral with variable Pb contents (up to 12.7 wt.%) is present with or without altaite in the volcanogenic massive pyritic deposit of the Yanahara mine, southwestern Japan. The mineral constitutes a solid solution between $(Bi,Sb)_2Te_3$ and PbTe, with small amounts of Ag_2Te. The member of the solid solution coexisting with altaite is rhombohedral, *a* 4.397(2), *c* 41.43(2) Å, and has a 21-layer structure. The chemical composition corresponds closely to $(Pb,Ag,Bi,Sb)_3Te_4$. The member coexisting with altaite thus is rucklidgeite, ideally $(Pb,Bi)_3Te_4$, whose Pb-rich end-member composition is suggested to be $PbBi_2Te_4$. Incorporation of the Ag_2Te component shifts the composition to $(Ag_xPb_{1-2x}Bi_{2+x})_3Te_4$; thus the variable Pb contents of rucklidgeite samples known so far can be explained.

Keywords: rucklidgeite, solid solution, Yanahara deposit, Japan.

SOMMAIRE

Nous avons trouvé un tellurure de bismuth et de plomb à teneur variable de Pb (jusqu'à 12.7% en poids), associé à l'altaïte ou non, dans un gisement volcanogénique de pyrite massive exploité à la mine de Yanahara, dans le sud-ouest du Japon. Le minéral est en fait une solution solide entre $(Bi,Sb)_2Te_3$ et PbTe, et contient une faible proportion de la composante Ag_2Te. L'exemple qui coexiste avec l'altaïte est rhomboédrique, *a* 4.397(2), *c* 41.43(2) Å, et possède une structure à 21 couches. Sa composition chimique est proche de $(Pb,Ag,Bi,Sb)_3Te_4$; c'est donc un exemple de rucklidgeïte, dont la composition idéale est $(Pb,Bi)_3Te_4$, et dont le pôle plombifère serait $PbBi_2Te_4$. L'incorporation de la composante Ag_2Te déplacerait la composition selon la formule $(Ag_xPb_{1-2x}Bi_{2+x})_3Te_4$, qui rend compte des teneurs variables en Pb des exemples connus à date de cette espèce.

(Traduit par la Rédaction)

Mots-clés: rucklidgeïte, solution solide, gisement de Yanahara, Japon.

INTRODUCTION

Zav'yalov & Begizov (1977) discovered a bismuth lead telluride mineral having an ideal formula $(Pb,Bi)_3Te_4$ in the Zod (Armenia) and Kochkar (Urals) gold deposits, and named it rucklidgeite. Rucklidge (1969) had earlier noticed a mineral of analogous composition in the Robb–Montbray deposit, Quebec. Since then, this mineral has been reported from several gold deposits worldwide (*e.g.*, Harris *et al.* 1983, Sakharova *et al.* 1984). Although few in number, available electron-microprobe data indicate that the Pb contents of rucklidgeite are variable, ranging from 21.65 to 9.4 wt.% (Table 1). Knowledge of the nature and extent of Pb incorporation is needed in order to understand the widely variable Pb contents of this mineral.

A bismuth lead telluride mineral with variable Pb contents is present, associated or not with altaite, in the Yanahara deposit, Okayama Prefecture, Japan. The mineral seems to constitute a solid solution from $(Bi,Sb)_2Te_3$ toward PbTe, with small amounts of Ag_2Te. The member of the solid solution coexisting with altaite was revealed to be rucklidgeite. The solid solution is thus called rucklidgeite solid-solution in this paper (hereafter, $rucklidgeite_{ss}$). We describe the mode of occurrence and chemistry of this solid solution and its departure toward the end-member PbTe, and discuss the substitution relationships of constituent elements.

TABLE 1. CHEMICAL COMPOSITIONS AND FORMULAE OF RUCKLIDGEITE AVAILABLE IN THE LITERATURE

No.	1	2	3	4	5	6
Weight percent						
Pb	15.4	9.4	16.6	21.65	13.3	11.1
Ag	1.2	1.9				1.3
Cu				0.04		
Bi	37.4	39.6	37.4	43.91	39.9	40.6
Sb		2.9				0.3
Te	43.9	44.9	44.6	18.93	45.5	44.8
Se				9.75		
S				4.33		
Sum	97.9	98.7	98.6	98.61	98.7	98.1
Atomic percent						
Pb	12.2	7.2	13.2	14.47	10.5	8.7
Ag	1.8	2.8				2.0
Cu				0.09		
Bi	29.4	30.2	29.4	29.10	31.2	31.7
Sb		3.8				0.4
Te	56.6	56.0	57.4	20.54	58.3	57.2
Se				17.10		
S				18.70		

Based on 7 total atoms per unit formula*

1. $(Pb_{0.85}Ag_{0.13}Bi_{2.06})_{3.04}Te_{3.96}$
2. $(Pb_{0.50}Ag_{0.20}Bi_{2.11}Sb_{0.27})_{3.08}Te_{3.92}$
3. $(Pb_{0.92}Bi_{2.06})_{2.98}Te_{4.02}$
4. $(Pb_{1.01}Cu_{0.01}Bi_{2.03})_{3.05}Te_{3.95}$
5. $(Pb_{0.74}Bi_{2.18})_{2.92}Te_{4.08}$
6. $(Pb_{0.61}Ag_{0.14}Bi_{2.22}Sb_{0.03})_{3.00}Te_{4.00}$

Results of electron-microprobe analyses. 1 and 2: Kochkar, Urals and Zod, Armenia, respectively (Zav'yalov & Begizov 1977), 3: Robb-Montbray, Quebec (Rucklidge 1969), 4: Oldrichov, Bohemia (Čech & Vavřin 1979), 5: Ashley, Ontario (Harris et al. 1983), and 6: Kamchatka (Sakharova et al. 1984). *Numbers of Se and S are included within those of Te.

Occurrence

The Yanahara mine is located about 35 km northeast of Okayama, southwestern Japan. The volcanogenic massive sulfide deposit, about 500 m wide, 1000 m down dip and up to 100 m thick, occurs conformably in the Permian strata of the Maizuru Group, closely associated with rhyolite lavas and pyroclastic rocks (Mitsuno 1988). The ores are dominantly composed of fine-grained pyrite, with small amounts of chalcopyrite and sphalerite. Gangue minerals, chiefly quartz and chlorite, are very minor.

Granitic rocks intruded into the Maizuru Group in the Yanahara area in late Cretaceous time imposed a thermal aureole on the surrounding rocks and ores. Pyrite was converted into pyrrhotite or magnetite in the marginal parts of the orebodies. Hydrothermal mineralization related to the intrusion of granitic magma resulted in the formation of thin sulfide veins composed mainly of pyrrhotite, jamesonite, arsenopyrite and bournonite (Higashimoto 1960). It is likely that rucklidgeite$_{ss}$ described in the present paper is related to this episode of hydrothermal mineralization.

The samples studied are thin sulfide veins, up to 5 mm thick, in rhyolitic pyroclastic rocks taken from the hanging wall of the massive pyritic orebody in the mine. Pyrrhotite, boulangerite, meneghinite, arsenopyrite, pyrite and quartz are major constituent minerals of the sulfide veins. Rucklidgeite$_{ss}$ and altaite are present in lesser amounts. Galena, chalcopyrite and sphalerite are ubiquitous in small amounts. Minute grains of electrum, up to 10 μm across, are present sporadically in and around the rucklidgeite$_{ss}$ grains, the atomic fraction of Au ranging from about 0.5 to 0.7.

The rucklidgeite$_{ss}$ is present as discrete grains with granular and tabular forms, up to 1 mm across, commonly associated with altaite, and as thin lamellae in boulangerite, usually less than 0.01 mm wide. In the discrete grains with altaite, thin lamellae of altaite or boulangerite commonly appear along the perfect basal cleavage (Fig. 1). The optical properties of rucklidgeite$_{ss}$ under reflected light are very similar to those of tellurobismuthite; the white reflectance has a faintly pinkish tint. The mineral is distinctly anisotropic between crossed nicols.

Electron-Microprobe Data on Rucklidgeitess

An electron-microprobe analysis of rucklidgeite$_{ss}$ and related minerals was carried out on a JEOL electron-microprobe analyzer operating at 25 kV and 0.02 μA specimen currents, as measured on copper metal. The standards and X-ray lines used are pure elemental Ag ($L\alpha$) and Sb ($L\alpha$), synthetic Bi_2Te_3 for Bi ($L\alpha$) and Te ($L\alpha$), synthetic Bi_2Se_3 for Se ($K\alpha$), galena for Pb ($L\alpha$), and chalcopyrite for S ($K\alpha$). The correction procedure was that of Sweatman & Long (1969). Examples of compositions of rucklidgeite$_{ss}$ with or without altaite are listed in Table 2, along with a mean composition (21 analyses) for this mineral where it coexists with altaite. Figure 2 shows the atomic ratios of (Bi,Sb), Pb and Ag for rucklidgeite$_{ss}$ with or without altaite.

Figure 2 suggests that a continuous solid-solution exists from the (Bi,Sb) corner toward Pb, with small amounts of Ag. Figure 3 indicates the solid-solution relationships between Pb and related elements of rucklidgeite$_{ss}$. The atomic fraction of Bi + Sb (N_{Bi+Sb}) shows a good linear negative correlation with the fraction of Pb (N_{Pb}) (Fig. 3b). The least-squares regression is $N_{Bi+Pb} = -0.91N_{Pb} + 0.40$, with a correlation coefficient of –0.98. With increasing N_{Pb}, the atomic fraction of Te (N_{Te}) decreases according to $N_{Te} = -0.29N_{Pb} + 0.60$ (Fig. 3a), where Se and S contents are included within N_{Te} (treated likewise hereafter). The correlation coefficient is –0.86. Ag contents (N_{Ag}) also are related to N_{Pb}, according to

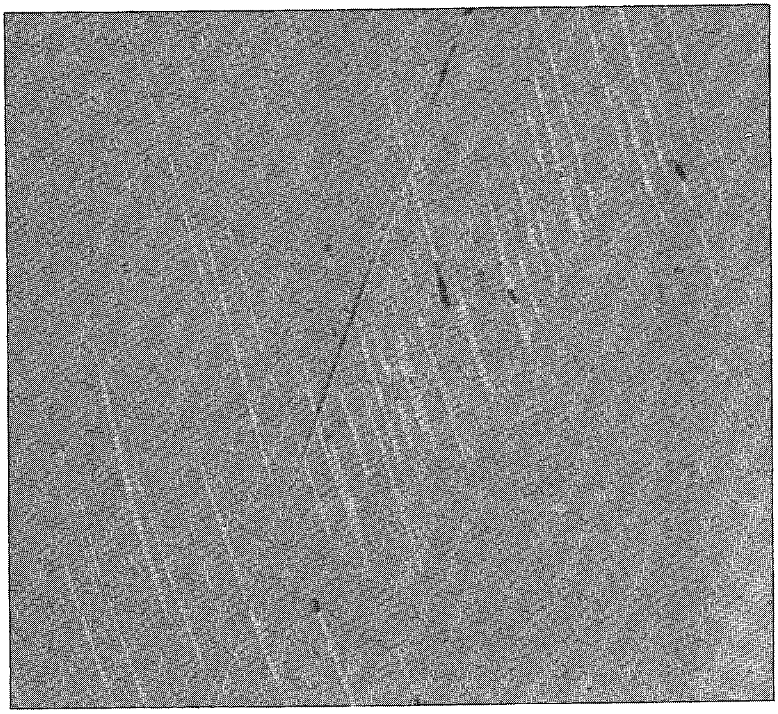

FIG. 1. Back-scattered electron image showing the thin lamellae of altaite (light) occurring along the basal cleavages of rucklidgeite$_{ss}$. Width of field of view is 0.22 mm.

TABLE 2. CHEMICAL COMPOSITIONS AND FORMULAE OF RUCKLIDGEITE$_{ss}$ WITH OR WITHOUT ALTAITE IN THE YANAHARA DEPOSIT

No.	1	2	3	4	5	6	7
Weight percent							
Pb	4.2	5.8	8.6	11.1	12.0	12.7	11.9
Ag	0.8	0.8	1.1	1.6	1.6	1.5	1.5
Bi	45.2	43.7	41.3	34.5	38.0	37.0	36.4
Sb	2.5	2.3	2.4	5.1	2.2	2.6	3.5
Te	47.1	47.7	46.6	46.3	45.4	45.5	45.8
Se	0.4	0.5	0.5	0.9	0.4	0.7	0.7
S	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Sum	100.3	100.9	100.6	99.6	99.7	100.1	99.9
Atomic percent							
Pb	3.1	4.3	6.5	8.2	9.1	9.5	8.9
Ag	1.2	1.2	1.6	2.3	2.3	2.1	2.1
Bi	33.7	32.4	30.7	25.3	28.5	27.6	27.1
Sb	3.2	3.0	3.1	6.4	2.9	3.3	4.4
Te	57.7	57.8	56.9	55.7	55.9	55.7	55.8
Se	0.8	0.9	0.9	1.7	0.9	1.4	1.3
S	0.3	0.4	0.3	0.4	0.4	0.3	0.4

Based on 7 total atoms per unit formula*
4. $(Pb_{0.58}Ag_{0.16}Bi_{1.77}Sb_{0.45})_{2.96}Te_{4.04}$
5. $(Pb_{0.64}Ag_{0.16}Bi_{2.00}Sb_{0.20})_{3.00}Te_{4.00}$
6. $(Pb_{0.67}Ag_{0.15}Bi_{1.93}Sb_{0.23})_{2.98}Te_{4.02}$
7. $(Pb_{0.62}Ag_{0.15}Bi_{1.90}Sb_{0.31})_{2.98}Te_{4.02}$

Results of electron-microprobe analyses. Samples from 1 to 3 are not associated with altaite and their formulae are not shown (see text). Samples from 4 to 7 are with altaite, in which 4 and 6 are compositions with the minimum and maximum Pb contents, and 7 is the mean of 21 analyses with altaite. *Numbers of Se and S are included within those of Te.

the relationship $N_{Ag} = 0.20N_{Pb} + 0.0033$ (Fig. 3c), with a correlation coefficient of 0.89.

In contrast with the widely variable Pb contents in the overall compositions of rucklidgeite$_{ss}$, its variation in Pb content where associated with altaite is limited, between 11.1 and 12.7 wt.%, with a mean content of 11.9 wt.% (Table 1). The coexisting altaite contains 46.9–48.6 atomic % Pb, 0.2–1.1% Ag, 1.5–1.8% (Bi + Sb) and 49.7–50.5% Te.

X-RAY-DIFFRACTION RESULTS

X-ray powder-diffraction data were obtained for rucklidgeite$_{ss}$ samples associated with altaite with a Guinier camera, with silicon as the internal standard; the data are listed in Table 3, along with those for rucklidgeite in the Kochkar deposit, Urals (Zav'yalov & Begizov 1977). No powder data could be obtained for material not associated with altaite because of insufficient sample. Several reflections in the sample of the Kochkar deposit are not observed in the sample of the Yanahara deposit, but the characteristic reflection near

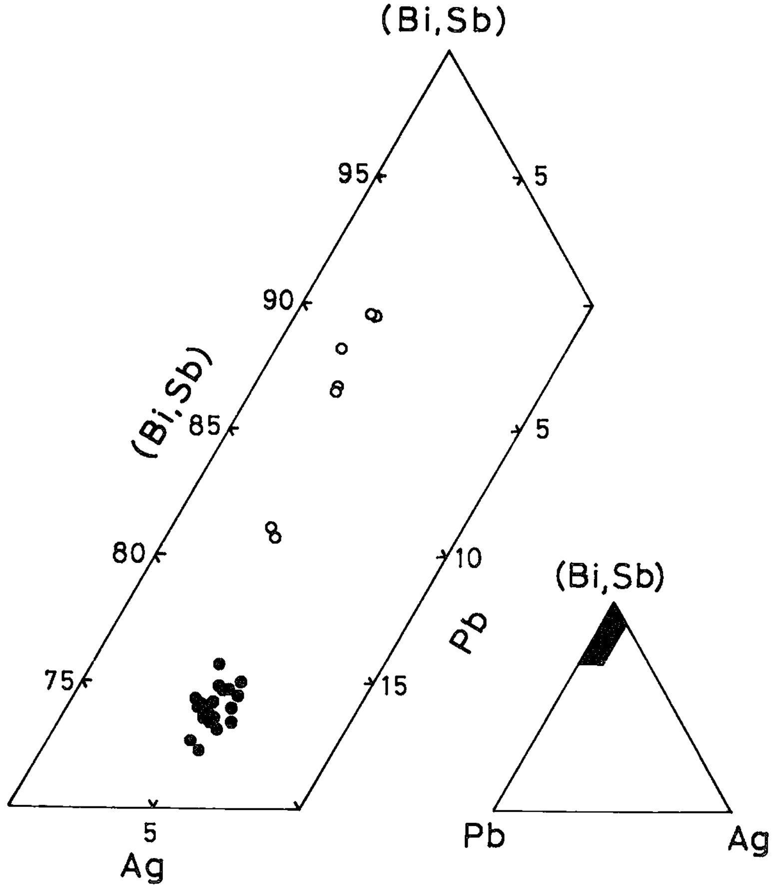

FIG. 2. Atomic ratios of (Bi,Sb), Pb and Ag of rucklidgeite$_{ss}$. Solid circles: altaite is associated. Open circles: no altaite is present.

4.6 Å in the Kochkar sample also is present in the Yanahara sample. The powder patterns of the samples from both deposits are thus essentially analogous (Table 3). All of the reflections for rucklidgeite$_{ss}$ in the Yanahara deposit are indexed consistently in terms of a rhombohedral cell with an *a* of 4.397, and *c* of 41.43 Å (Table 3). The cell dimensions are very similar to those in the Kochkar deposit (Table 3). The powder pattern and cell dimensions also are very similar to those of pilsenite (Bi_4Te_3) from Deutsch-Pilsen, Hungary (*a* 4.446, *c* 41.94 Å: Ozawa & Shimazaki 1982).

NATURE AND EXTENT OF Pb INCORPORATIONS AND CHEMICAL FORMULA OF RUCKLIDGEITESS

The N_{Bi+Sb} and N_{Te} of rucklidgeite$_{ss}$ in the Yanahara deposit are negatively correlated with N_{Pb}. The slopes of least-squares regression equations for these relationships are –0.91 and –0.29, respectively. Supposing that rucklidgeite$_{ss}$ is on the Bi_2Te_3 – PbTe join, N_{Bi} and N_{Te} are related to N_{Pb}: $N_{Bi} = -0.8N_{Pb} + 0.4$, and $N_{Te} = -0.2N_{Pb} + 0.6$. Incorporation of Ag_2Te makes the slopes of these equations steeper. The compositions of rucklidgeite$_{ss}$ in the Yanahara deposit are, therefore, explained by the substitution of PbTe for $(Bi,Sb)_2Te_3$, not of Pb for Bi,Sb), accompanied with a limited incorporation of Ag_2Te, indicating that rucklidgeite$_{ss}$ is a compound where electrostatic neutrality is maintained, with charges of the constituent elements as follows: Bi and Sb (+3), Pb (+2), Ag (+1) and Te (–2).

Discrete grains of rucklidgeite$_{ss}$ associated with altaite commonly involve altaite lamellae, exsolved from the solid solution. Therefore, the maximum extent of PbTe substitution is expected in rucklidgeite$_{ss}$ coexisting with altaite. The Pb contents vary only slightly, but are not fixed in the Yanahara deposit.

The cell parameters of the rucklidgeite$_{ss}$ coexisting with altaite are analogous to those of pilsenite and of rucklidgeite in the Kochkar deposit; the chemical formula can be discussed in terms of an analogy with

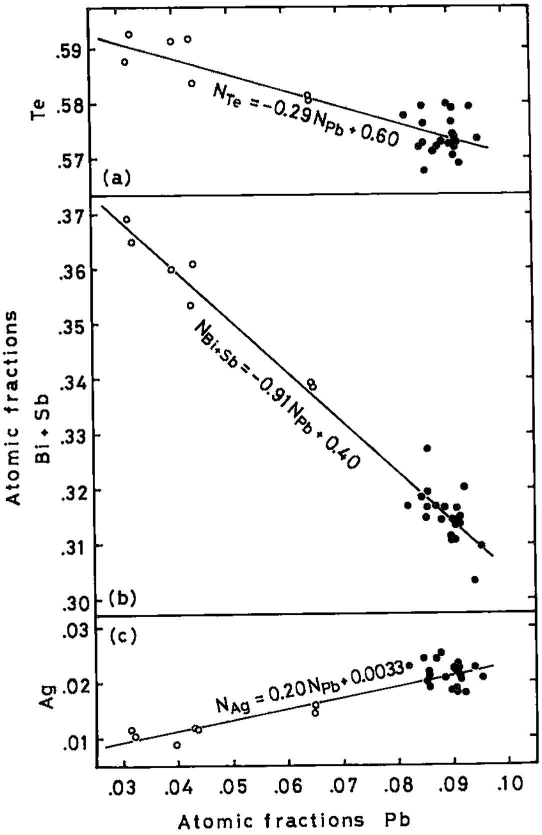

FIG. 3. Relationships between N_{Pb} and (a) N_{Te}, (b) N_{Bi+Sb} and (c) N_{Ag} in rucklidgeite$_{ss}$. Atomic fractions of Se and S are included within N_{Te}. The correlation coefficients for three regression equations are referred to in the text. Symbols as in Fig. 2.

TABLE 3. X-RAY POWDER DATA

1			2		
I	d(obs)	d(calc)	I	d	h k 1
4	4.614	4.604	10	4.61	0 0 9
5	3.745	3.745			0 1 2
100	3.203	3.203	100	3.22	1 0 7
21	2.336	2.337	90	2.34	1.0.14
34	2.198	2.199	40	2.21	1 1 0
			20	2.15	1.0.16
			10	2.07	1.0.17
			50	1.976	0.0.21
14	1.813	1.813	40	1.822	2 0 7 1.0.20
			10	1.731	1.1.15
			20	1.632	1.0.23
12	1.601	1.601	40	1.607	2.0.14
7	1.470	1.468	60	1.473	1.1.21 1.0.26
12	1.398	1.399	30	1.405	2 1 7 2.0.20
			40	1.382	1.0.28 0.0.30
			10	1.363	1.1.24
			5	1.314	2.0.23
5	1.295	1.294	30	1.300	1.2.14
3	1.269	1.269	10	1.276	3 0 0

1	2
a 4.397(2)A	a 4.422A
c 41.43(2)A	c 41.49A
V 693.7(8)A^3	V 702.6A^3

Hexagonal, $R\bar{3}m$, Z=3, Alpha=Beta=90, Gamma=120.

1: Rucklidgeite$_{ss}$ associated with altaite in the Yanahara deposit. Guinier camera method. Ni-filtered Cu-radiation with silicon as the internal standard. 2: Rucklidgeite in the Kochkar deposit, Urals (Zav'yalov & Begizov 1977).

layered bismuth chalcogenide phases, as Zav'yalov & Begizov (1977) did. According to Strunz (1963) and Stasova & Karpinskii (1967), the number of layers in the unit cell of bismuth chalcogenide phases is three times the number of atoms in the formula unit. The number of layers in the rucklidgeite$_{ss}$ coexisting with altaite, with a c periodicity of about 41.4 Å, is expected to be 21 (Strunz 1963). Accordingly, the number of atoms in the unit formula must be 7. Based on 7 total atoms per unit formula, the chemical composition of the present mineral is calculated to be very close to $(Pb,Ag,Bi,Sb)_3Te_4$, or ideally $(Pb,Bi)_3Te_4$ (Table 2), which is identical with the ideal formula given by Zav'yalov & Begizov (1977). Rucklidgeite is thus considered to be the member with the maximum extent of Pb-for-(Bi, Sb) substitution and incorporation of Te in the solid solution from Bi_2Te_3 toward PbTe.

A balance of electrostatic charges is maintained in rucklidgeite, and thus the composition of Ag-free rucklidgeite is considered to be $PbBi_2Te_4$. Actually, the compositions represented closely by this formula are known in the Robb–Montbray and Oldrichov deposits (Table 1). A small extent of incorporation of Ag into the structure may shift the composition of $PbBi_2Te_4$ to $(Ag_xPb_{1-2x}Bi_{2+x})_3Te_4$. The relationship in number of Ag, Pb and Bi atoms expressed by this formula qualitatively corresponds to that in the Ag-bearing rucklidgeite reported previously and in the rucklidgeite of the Yanahara deposit. Widely variable Pb contents and a number of Pb + Ag atoms nearly always smaller than unity in the chemical formula of rucklidgeite described so far are well explained by a small extent of incorporation of Ag (see Table 1). Pašava *et al.* (1986) reported the presence of Cu-rich rucklidgeite (up to 1.77 wt.% Cu) in the Jílové deposit, Czechoslovakia. It is likely that Cu plays the same role as Ag, but the formulae calculated from their compositions deviate significantly from the ideal, and the hypothesis is not proven.

In order to obtain the chemical formulae of rucklidgeite$_{ss}$ with intermediate compositions, we need to know the number of layers in the unit cell, which is probably variable in accordance with the variable compositions of this solid solution. For the members with a fixed number of layers in the intermediate solid-solution, the constraint that a balance of electrostatic charges is maintained suggests that Ag contents should correlate negatively with Pb contents. The positively correlated relationship between them indicated in material from the Yanahara deposit seems to be inconsistent with this rule. The inconsistency probably arises from the fact that the relationship was obtained for members with various numbers of layers in the solid solution.

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