

## REPRESENTATION OF COMPOSITIONS IN THE BISMUTHINITE-AIKINITE SERIES

EMIL MAKOVICKY AND MILOTA MAKOVICKY

Institute of Mineralogy, University of Copenhagen, Østervoldgade 5-7,  
1350 Copenhagen K, Denmark

### ABSTRACT

The general formula of the bismuthinite(B) – aikinite(A) series is  $Cu_xPb_yBi_{8-1/2(x+y)}S_{12}$ ,  $x \simeq$  (ideally  $\Rightarrow$ )  $y$ ,  $0 \leq 1/2(x+y) \leq 4$ . The series is halved by krupkaite(K) at  $1/2(x+y) = 2$ . Three types of structural ribbons are recognized, corresponding to the end members B, K, A. The percentage of the krupkaite ribbons,  $n_k$ , can be calculated as  $(100 - [25(x+y) - 100])$ . The other ribbon type, present in  $(100 - n_k)\%$ , is determined by the position of the phase on the aikinite–bismuthinite join; this can be described by the hypothetical percentage,  $n_a$ , of the aikinite end-member in the phase, calculated as  $12.5(x+y)\%$ . For example, ideal gladiate,  $Cu_{1.33}Pb_{1.33}Bi_{6.67}S_{12}$ , has  $n_a$  33.33% and  $n_k$  66.67%, so that it contains 33.33% of bismuthinite ribbons.

### SOMMAIRE

La formule générale de la série bismuthinite(B)–aikinite(A) s'écrit  $Cu_xPb_yBi_{8-1/2(x+y)}S_{12}$ ,  $x \simeq$  (idéalement  $\Rightarrow$ )  $y$ ,  $0 \leq 1/2(x+y) \leq 4$ . Cette série se subdivise à  $1/2(x+y) = 2$ , à la krupkaite(K), en deux autres: B – K et K – A. On connaît trois types de rubans structuraux qui correspondent aux pôles B, K, A des solutions solides. La proportion de rubans krupkaite,  $n_k$ , peut s'exprimer (en %):  $100 - [25(x+y) - 100]$ . L'autre type de ruban,  $(100 - n_k)\%$ , dépend de la position de la phase dans la série aikinite – bismuthinite, qui s'exprime par  $n_a$  ( $12.5(x+y)$ , en %) et qui va de 0 (B) à 100 (A). Pour la gladiate idéale,  $Cu_{1.33}Pb_{1.33}Bi_{6.67}S_{12}$ ,  $n_a$  = 33.33%,  $n_k$  = 66.67%; cette phase contient 33.33% de rubans bismuthinite.

(Traduit par la Rédaction)

### INTRODUCTION

The phases of the bismuthinite–aikinite series have recently been a subject of intensive research by Welin (1966), Moore (1967), Ohmasa & Nowacki (1970 a,b), Kupčik & Veselá–Nováková (1970), Kohatsu & Wuensch (1971, 1973, 1976), Mumme (1975), Žák *et al.* (1974), Syneček & Hybler (1975), Harris & Chen (1976), Horiuchi & Wuensch (1976, 1977), Chen *et al.* (1978), Mumme & Watts (1976), Kaplunnik *et al.*

(1975). The early extreme points of view on this series suggesting a continuous solid solution (“reibanyite”) between bismuthinite and aikinite in nature (Paděra 1956) on one hand, and a densely populated series of discrete intermediate minerals with superstructures (Welin 1966, Moore 1967) on the other hand, both had to be abandoned on the basis of later data. The present understanding of the series has been formulated by Mumme *et al.* (1976), Harris & Chen (1976) and Mumme & Watts (1976). Several ordered phases have been recognized, each of which represents a structure composed of one or two of the three recognized types of quadruple ribbons: the bismuthinite-like  $[Bi_4S_8]$  and krupkaite-like  $[CuPbBi_4S_8]$  quadruple ribbons in the Bi-rich half of the series and the krupkaite-like and aikinite-like  $[Cu_2Pb_2Bi_4S_8]$  ribbons in the Bi-poor half of the series.

The proportions and arrangement of the ribbons vary from member to member, leading to unit cells with the  $a$  parameter representing a multiple ( $\times 1$ ,  $\times 3$ ,  $\times 5$ ) of the bismuthinite (or aikinite)  $a$  parameter. Each phase has a narrow to broad compositional range about the ideal composition. Chen *et al.* (1978) show with the example of friedrichite that still more intermediate phases may be found in the series.

### EXISTING SYSTEMS OF CHEMICAL REPRESENTATION

Moore's (1967)  $Z^n$  classification and Syneček's & Hybler's (1975)  $Z_a$  classification were abandoned after their predictions contradicted later experimental data. These schemes were replaced by the classification (terminology) of Mumme *et al.* (1976) based on mineral names of the recognized phases with distinct lattice geometry, space group and crystal structure.

Individual formulae of ideal phases (Table 1, after Mumme *et al.* 1976) are simple but not always directly comparable. Mumme & Watts (1976) proposed a general formula for ideal compositions,  $Cu_xPb_yBi_{12-2x}S_{18}$  ( $x = 0, 1, 2, 3, 4, 5$  and 6) actually based on a cell with a three-

TABLE 1. COMPOSITIONAL RANGES OF THE MEMBERS OF THE BISMUTHINITE-AIKINITE SERIES

Mineral Ideal formula <sup>1</sup>	Multiple of parameter a <sub>1</sub>	Type of compositional data	Empirical and/or ideal formulae			Position in the series (mol%)		Estimated chain-type ratio (mol%)			Source <sup>1</sup>
			Cu <sub>x</sub> Pb <sub>y</sub> Bi <sub>z</sub> - (based on $\frac{1}{2}(\text{Cu}+\text{Pb}) + \text{Bi} = 8$ )	$\frac{x+y}{z}$ S <sub>12</sub>	bism. (100-n <sub>a</sub> )	aikin. n <sub>a</sub>	bism. (100-n <sub>k</sub> )	krup. n <sub>k</sub>	aikin. (100-n <sub>k</sub> )		
Bismuthinite	1a	ideal		Bi <sub>8</sub> S <sub>12</sub>	100	0	100	0	0		
Bi <sub>2</sub> S <sub>3</sub>		H-CuPb, X-r.	Cu <sub>0.01</sub> Pb <sub>0.04</sub> Bi <sub>(7.95)</sub> S <sub>n.d.</sub>		98.8	1.2 <sup>2</sup>	97.6	2.4 <sup>2</sup>	0	ZSH 74	
Pekoitite	3a	L-CuPb, X-r. <sup>3</sup>	Cu <sub>0.20</sub> Pb <sub>0.12</sub> Bi <sub>7.84</sub> S <sub>12</sub>		96.1	3.9	92.2	7.8	0	HC 76	
		H-CuPb, X-r.	Cu <sub>0.43</sub> Pb <sub>0.51</sub> Bi <sub>7.53</sub> S <sub>11.79</sub>		88.3	11.7	76.6	23.4	0	MW 76	
CuPbBi <sub>11</sub> S <sub>18</sub>		ideal	Cu <sub>2/3</sub> Pb <sub>2/3</sub> Bi <sub>22/3</sub> S <sub>12</sub>		83.33	16.67	66.67	33.33	0	MW 76	
			Cu <sub>0.667</sub> Pb <sub>0.667</sub> Bi <sub>7.333</sub> S <sub>12</sub>								
		H-CuPb, n.-X	Cu <sub>0.73</sub> Pb <sub>0.76</sub> Bi <sub>7.26</sub> S <sub>10.85</sub>		81.4	18.6	62.8	37.2	0	LM 75	
Gladite	3a	L-CuPb, X-r. <sup>3</sup>	Cu <sub>1.38</sub> Pb <sub>1.18</sub> Bi <sub>5.72</sub> S <sub>11.63</sub>		68.1	31.9	36.2	63.9	0	LM 75	
		ideal	Cu <sub>4/3</sub> Pb <sub>4/3</sub> Bi <sub>20/3</sub> S <sub>12</sub>		66.67	33.33	33.33	66.67	0		
CuPbBi <sub>5</sub> S <sub>9</sub>			Cu <sub>1.333</sub> Pb <sub>1.333</sub> Bi <sub>6.667</sub> S <sub>12</sub>								
		H-CuPb, X-r.	Cu <sub>1.39</sub> Pb <sub>1.36</sub> Bi <sub>6.63</sub> S <sub>12.16</sub>		65.6	34.4	31.3	68.7	0	LM 75	
		H-CuPb, n.-X	Cu <sub>1.41</sub> Pb <sub>1.45</sub> Bi <sub>6.57</sub> S <sub>11.10</sub>		64.3	35.7	28.5	71.5	0	LM 75	
Krupkaite	1a	L-CuPb, n.-X	Cu <sub>1.81</sub> Pb <sub>1.39</sub> Bi <sub>6.40</sub> S <sub>n.d.</sub>		60.0	40.00	20.0	80.0	0	W 66	
		L-CuPb, X-r.	Cu <sub>1.55</sub> Pb <sub>1.88</sub> Bi <sub>6.28</sub> S <sub>12.08</sub>		57.0	43.0	14.0	86.0	0	ZSH 74	
CuPbBi <sub>3</sub> S <sub>6</sub>		ideal	Cu <sub>2</sub> Pb <sub>2</sub> Bi <sub>6</sub> S <sub>12</sub>		50.00	50.00	0	100	0		
		H-CuPb, X-r.	Cu <sub>2.11</sub> Pb <sub>2.20</sub> Bi <sub>5.85</sub> S <sub>12.33</sub>		46.2	53.9	0	92.3	7.7	HC 76	
Lindströmita	5a	L-CuPb, X-r.	Cu <sub>2.29</sub> Pb <sub>2.38</sub> Bi <sub>5.67</sub> S <sub>n.d.</sub>		41.7	58.4	0	83.3	16.7	W 66	
		H-CuPb, X-r.	Cu <sub>2.36</sub> Pb <sub>2.36</sub> Bi <sub>5.64</sub> S <sub>12.32</sub>		41.0	59.0	0	82.0	18.0	HC 76	
Cu <sub>3</sub> Pb <sub>3</sub> Bi <sub>7</sub> S <sub>15</sub>		ideal	Cu <sub>12/5</sub> Pb <sub>12/5</sub> Bi <sub>28/5</sub> S <sub>12</sub>		40.00	80.00	0	80.00	20.00		
			Cu <sub>2.4</sub> Pb <sub>2.4</sub> Bi <sub>5.6</sub> S <sub>12</sub>								
Hammrite	3a	ideal	Cu <sub>8/3</sub> Pb <sub>8/3</sub> Bi <sub>16/3</sub> S <sub>12</sub>		33.33	66.67	0	66.67	33.33		
			Cu <sub>2.667</sub> Pb <sub>2.667</sub> Bi <sub>5.333</sub> S <sub>12</sub>								
Cu <sub>2</sub> Pb <sub>2</sub> Bi <sub>4</sub> S <sub>9</sub>		L-CuPb, X-r.	Cu <sub>2.86</sub> Pb <sub>2.86</sub> Bi <sub>5.14</sub> S <sub>12.06</sub>		28.6	71.4 <sup>4</sup>	0	57.1	42.9	HC 76	
		H-CuPb, n.-X	Cu <sub>3.00</sub> Pb <sub>3.08</sub> Bi <sub>4.86</sub> S <sub>12.50</sub>		24.0	76.0 <sup>5</sup>	0	47.9	52.1	K-M 74	
Friedrichite	3a	L-CuPb, X-r.	Cu <sub>3.13</sub> Pb <sub>3.23</sub> Bi <sub>4.82</sub> S <sub>12.28</sub>		20.5	79.5	0	40.9	59.1	CKP 78	
		H-CuPb, X-r.	Cu <sub>3.33</sub> Pb <sub>3.20</sub> Bi <sub>4.74</sub> S <sub>11.93</sub>		18.4	81.6	0	36.8	63.2	CKP 78	
Cu <sub>5</sub> Pb <sub>5</sub> Bi <sub>7</sub> S <sub>18</sub>		ideal	Cu <sub>10/3</sub> Pb <sub>10/3</sub> Bi <sub>14/3</sub> S <sub>12</sub>		16.67	83.33	0	33.33	66.67	CKP 78	
			Cu <sub>3.333</sub> Pb <sub>3.333</sub> Bi <sub>4.667</sub> S <sub>12</sub>								
Aikinite	1a	L-CuPb, X-r. <sup>6</sup>	Cu <sub>3.32</sub> Pb <sub>3.32</sub> Bi <sub>4.68</sub> S <sub>12.16</sub>		17.0	83.0	0	34.0	66.0	HC 76	
CuPbBiS <sub>3</sub>		ideal	Cu <sub>4</sub> Pb <sub>4</sub> Bi <sub>4</sub> S <sub>12</sub>		0	100	0	0	100		

<sup>1</sup> Nomenclature and ideal compositions after Mumme et al. (1976). Abbreviations: L-CuPb and H-CuPb are the Cu-Pb poorest and Cu-Pb richest composition limits known, respectively. X-r.: identity of the mineral was confirmed by single-crystal X-ray photographs. n.-X: identity of the mineral was not confirmed by single-crystal X-ray photographs. Source abbreviations are explained in Fig. 1. Rounding-off was carried out after calculations.

<sup>2</sup> Bi not estimated.

<sup>3</sup> Exsolution lamellae or matrix.

<sup>4</sup> The averages of the multiple chemical analyses by Welin (1966) and Povilytis et al. (1969) also fall around this value.

<sup>5</sup> Welin (1966) also gives n<sub>a</sub> equal to 76.04, with a reversed empirical Cu/Pb ratio.

<sup>6</sup> Very weak diffuse streaks parallel to a \*

fold *a* parameter. Thus, it is also applicable to cells with a simple *a* parameter but fails in the

case of the five-fold *a* parameter in lindströmita. A variety of formulae have been used to ex-

press the results of chemical analyses and the compositional ranges of individual species. In some formulae the content of Bi, or alternatively Pb or Cu, is fixed as unity (Harris & Chen 1976). Other formulae are based on a given amount of sulfur or (Pb+Bi) atoms in one unit cell (Mumme & Watts 1976, Karup-Møller 1977, Chen *et al.* 1978). Harris & Chen (1976) introduced the (Pb or Cu)/Bi coefficient to describe the degree of substitution in the bismuthinite derivatives. Its value varies non-linearly with the substitution.

#### PROPOSED SYSTEM OF CHEMICAL REPRESENTATION

A system for the representation of chemical compositions should describe both the natural ordered phases with superstructures and the synthetic disordered phases prepared at moderate temperatures (Springer 1971, Mumme & Watts 1976). It should express in a simple way the composition ranges of individual phases as well as the widths of the exsolution gaps (Borodayev & Mozgova 1971, Large & Mumme 1975, Harris & Chen 1976, Mumme & Watts 1976).

According to all available data, the bismuthinite-aikinite series represents bismuthinite derivatives obtained by a combination of metal substitution with the filling of vacant tetrahedral positions:  $\text{Cu} + \text{Pb} \rightleftharpoons \square + \text{Bi}$ . The Cu:Pb ratio is assumed to be 1:1 in all phases and the deviations from this ratio are ascribed to experimental errors or to impurities (Harris & Chen 1976, Mumme *et al.* 1976). No indications of Pb (Cu) or S vacancies have been reported. Thus, the best procedure to satisfy the outlined requirements is to recalculate the analyses of bismuthinite derivatives to the unit-cell content of the bismuthinite (or aikinite)-like subcell,  $\text{Cu}_x\text{Pb}_x\text{Bi}_{8-x}\text{S}_{12}$ , as did Welin (1966). The compositional ranges (and gaps) of real phases expressed in this way are given in Table 1. In the ordered cases the coefficient  $x$  can be interpreted as a fraction, the denominator of which is equal to the multiplicity of the resulting  $n \times a$  supercell parameter; the numerator describes the number of Bi atoms in the supercell that are replaced by Pb. For example, idealized gladite has the formula  $\text{Cu}_{4/3}\text{Pb}_{4/3}\text{Bi}_{20/3}\text{S}_{12}$ , whereas the gladite richest in Cu and Pb (Table 1) has the empirical formula  $\text{Cu}_{4.23/3}\text{Pb}_{4.35/3}\text{Bi}_{19.71/3}\text{S}_{11.10}$ .

Because of the accuracies in microprobe analyses for the elements involved, the formulae should be based on a constant sum of metals which substitute for each other, *i.e.*, Pb + Bi. For the same reasons, they should be evaluated

by the compromise normalization formula (atomic basis):  $1/2 (\text{Cu} + \text{Pb}) + \text{Bi} = 8$ , resulting in an empirical formula  $\text{Cu}_x\text{Pb}_y\text{Bi}_{8-1/2(x+y)}\text{S}_{12}$ , with  $x$  approximately equal (in the ideal case equal) to  $y$ .

The averaged Cu+Pb content of the analyzed phase,  $\frac{1}{2}(x+y)$ , then differs from ideal aikinite,  $\text{Cu}_4\text{Pb}_4\text{Bi}_4\text{S}_{12}$ , by  $[4 - \frac{1}{2}(x+y)]$ . The position of the phase in the bismuthinite-aikinite series can be expressed using the  $\frac{1}{2}(x+y)$  value, which varies linearly from 0 to 4 with substitution. It also can be expressed by the hypothetical percentages of the aikinite and bismuthinite end-members: aikinite ( $n_a$ )-bismuthinite ( $100 - n_a$ ). The two values are interconnected:  $n_a = \frac{25(x+y)}{2}$ . The accuracy of the analysis may be conveniently expressed as a difference between aikinite molar percentages based on Pb concentration estimates alone and on Cu percentages alone:  $\Delta n_a = 25(y-x)$ . The above analysis of Cu-Pb rich gladite has  $n_a$  equal to 35.7% with a minimal error of 3%.

As mentioned above, the crystal structures of all the intermediate phases in the bismuthinite-aikinite series are composed of only three types of quadruple ribbons. Compositional ranges of the basically ordered phases, and complete disorder of the ribbon types at higher temperatures, indicate that the structural (*i.e.*, ribbon-type) errors in the basic ordered ribbon patterns are common and connected with relatively small energy differences. Therefore, we may reasonably expect that any real phase of this series will have all three types of ribbons present in the structure; only two occur in substantial amounts and were detected in structure determinations and included in the latest classifications (Mumme *et al.* 1976; Horiuchi & Wuensch 1976, 1977; Chen *et al.* 1978). As noted by the above quoted authors, the ideal ratio of the two principal (or exclusive) ribbon types can be successfully estimated from the chemical composition. The bismuthinite derivatives thus represent ordered or disordered "mixtures/intergrowths" of three basic "members": bismuthinite, krupkaite and aikinite. The composition of an examined phase expressed in terms of two of these end-members will directly suggest the expected percentages of the corresponding principal ribbon types in its structure.

In a similar manner as that for  $n_a$ , the percentage of krupkaite,  $n_k$ , in the phase can be obtained by comparing its normalized formula with that of ideal krupkaite,  $\text{Cu}_2\text{Pb}_2\text{Bi}_6\text{S}_{12}$ . Then,  $n_k = (100 - |25(x+y) - 100|)$  or  $n_k = (100 - |2n_a - 100|)$ . The  $n_a$  (or  $\frac{1}{2}[x+y]$ ) and  $n_k$

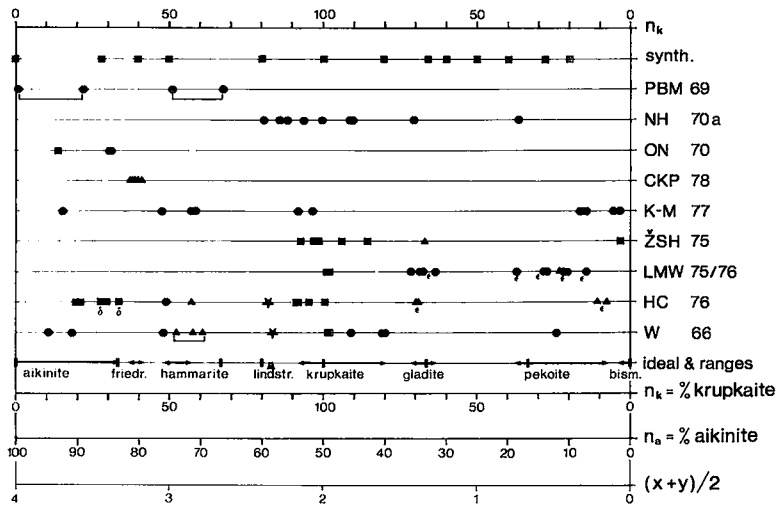


FIG. 1. Ideal compositions (Mumme *et al.* 1976, Chen *et al.* 1978), compositional ranges and selected individual analyses of bismuthinite-aikinite derivatives. Circles: chemical data without X-ray single-crystal data; squares: 1a derivatives; triangles: 3a derivatives; stars: 5a derivatives with both chemical and single-crystal data.  $\delta$ : streaks parallel to  $a^*$  in predominantly ordered 1a phases.  $\epsilon$ : exsolution products. Results of distinct analyses of the same sample are bracketed. Data sources for W66: Welin (1966); HC76: Harris & Chen (1976); LMW75/76: Large & Mumme (1975), Mumme & Watts (1976); ZSH75: Žák *et al.* (1974), Syneček & Hybler (1975); K-M77: Karup-Møller (1977); CKP78: Chen *et al.* (1978); ON70a: Ohmasa & Nowacki (1970a); NH70: Nicolaou & Häkli (1970); PMB69: Povilytis *et al.* (1969); synth.: Mumme & Watts (1976).

coefficients are not meant to replace the nomenclature by Mumme *et al.* (1976); they simply allow a refinement of its chemical basis. However, to a large extent they do not depend on the degree of structural order/disorder nor on the subsequent changes of the standing nomenclature. As  $n_a$  is purely descriptive,  $n_k$  has very interesting structural implications. For example, pekoite has the ideal composition ( $n_a$  16.67,  $n_k$  33.33) but the chemical data indicate a percentage of krupkaite chains ranging from  $n_k$  7.8 to 37.0; hammarite ( $n_a$  66.67,  $n_k$  66.67) has only been observed with analytically determined  $n_k$  values between 47.9 and 57.1 (Table 1).

The linear relationships for the above coefficients describing the substitution  $\text{Cu} + \text{Pb} \rightleftharpoons \square + \text{Bi}$  can only be retained in the  $\text{Bi}_2\text{S}_3 - \text{Pb}_2\text{S}_2 - \text{Cu}_2\text{S}$  (*i.e.*, Bi-Pb-Cu) diagram (as in Fig. 1).

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