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A CLASSIFICATION OF SULFOSALT STRUCTURES DERIVED FROM THE STRUCTURE OF AIKINITE

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Recently, Welin (1967) demonstrated the existence of several sulfosalts which have aikinite-like structures and he was able to predict compositions of other hypothetical members of this interesting group.

Stated briefly, the problem concerns quantized compositions within the series Bi_2S_3 (bismuthinite)-$CuPbBiS_3$ (aikinite). Aikinite is generated by substituting lead for part of the bismuth atoms in bismuthinite and balancing the charge by the addition of copper mole-equivalent to the lead. The small copper atoms distribute over symmetry-equivalent cavities of equipoint rank 4 in one structure cell of aikinite, containing $Cu_4Pb_4Bi_4S_{12}$. Aikinite can be considered the compositional limit of Pb:Bi substitution as there are no extra cavities remaining to accommodate copper. Welin observed that intermediate compositions were nearly stoichiometric and corresponded to superstructures described by integral multiples of the *a*-translation of aikinite in the orientation *Pbnm*.

The general structure cell formula for the aikinite derivatives can be expressed as

$$Cu_xPb_xBi_{8Z-x}S_{12Z}$$

where Z is the integral multiple of the *a*-translation in aikinite for the superstructure.

First, x must be a multiple of 4 to satisfy the equipoint requirements for the space groups observed for the aikinite structural derivatives mentioned by Welin. Since superstructures are observed, the copper (and lead?) atoms are evidently ordered over the sites available to them, including the cavities. Secondly,

$$\frac{12Z}{x} > 3 \quad \text{or} \quad 4Z > x$$

since the limiting case is aikinite, beyond which no cavities are available for copper atoms. Thirdly, the classification is based on Z^n where $n = x/4$, the number of lead (copper) atoms in the asymetric unit. Evidently, for given Z, $n < Z$ since aikinite is the limiting case; consequently there is a possible maximum of $Z-1$ compositions. If both Z and n have a factor in common, factoring out results in a formula already accounted for in some smaller Z. These are the conditions for quantizing compositions

within the bismuthinite-aikinite series. Hence, from the general formula, the specific formulae can be generated as listed in Table 1 for multiples of a less than 7.

Of the eleven unique formulae, three have been found to exist in nature (Welin, 1967) and no doubt as more detailed analyses are undertaken, other members will be found. It is interesting that these three compositions as well as aikinite were found among the sulfosalts from Gladhammar, Sweden, and the various members are quite indistinguish-

TABLE 1. FORMULAE OF AIKINITE DERIVATIVES WITH $Z<7$

	Z^n	Structure Cell Formula	Asymmetric Unit	Name
$Z=2$	2^1	$Cu_4Pb_4Bi_{12}S_{24}$	$CuPbBi_3S_6$	
$Z=3$	3^1	$Cu_4Pb_4Bi_{20}S_{36}$	$CuPbBi_5S_9$	gladite
	3^2	$Cu_8Pb_8Bi_{16}S_{36}$	$Cu_2Pb_2Bi_4S_9$	hammarite
$Z=4$	4^1	$Cu_4Pb_4Bi_{28}S_{48}$	$CuPbBi_7S_{12}$	
	$4^2=2^1$			
	4^3	$Cu_{12}Pb_{12}Bl_{20}S_{48}$	$Cu_3Pb_3Bi_5S_{12}$	
$Z=5$	5^1	$Cu_4Pb_4Bi_{36}S_{60}$	$CuPbBi_9S_{15}$	
	5^2	$Cu_8Pb_8Bi_{32}S_{60}$	$Cu_2Pb_2Bi_9S_{15}$	
	5^3	$Cu_{12}Pb_{12}Bi_{28}S_{60}$	$Cu_3Pb_3Bi_7S_{15}$	Welin's new composition
	5^4	$Cu_{16}Pb_{16}Bi_{24}S_{60}$	$Cu_4Pb_4Bi_6S_{15}$	
$Z=6$	6^1	$Cu_4Pb_4Bi_{44}S_{72}$	$CuPbBi_{11}S_{18}$	
	$6^2=3^1$			
	$6^3=2^1$			
	$6^4=3^2$			
	6^5	$Cu_{20}Pb_{20}Bi_{28}S_{72}$	$Cu_5Pb_5Bi_7S_{18}$	

able without recourse to single crystal or chemical analytical techniques. Table 2 lists the weight percentages, arranged in decreasing bismuth content. The greatest Z/n values are for the highest bismuth and the lowest lead (copper) contents.

These known and hypothetical compounds pose problems in nomenclature. To give a different name to the mineral having each composition would be a burden to the literature. It is suggested here, that since the code Z^n designates both the length of the a-translation *and* the composition of an asymmetric unit of structure, it should suffice to describe a particular member. In fact, from the code, the composition of any member can be immediately obtained. Thus, retaining aikinite as the limit of

the quantized series, the other members can be referred to as Z^n-aikinites. Hence, 'gladite' = 3^1-aikinite; 'hammarite' = 3^2-aikinite; and Welin's new member is 5^3-aikinite.

I have no idea why the copper (and lead?) atoms do not distribute statistically over the sites available to them. Since lead and copper enter molewise in the same amount there may be an important interaction between them. Nor can I predict the nature of the ordering over the sites.

Though the 3^1 and 3^2 members apparently have structures compatible with the space group of aikinite (*Pbnm*), the 5^3 member is devoid of an

TABLE 2. COMPOSITION OF AIKINITE DERIVATIVES WITH $Z<7$

Z^n	Bi	Pb	Cu
6^1	73.1%	6.6%	2.0%
5^1	71.4	7.9	2.4
4^1	69.1	9.8	3.0
3^1	65.1	12.9	4.0
5^2	62.1	15.4	4.7
2^1	57.5	19.0	5.8
5^3	53.1	22.5	6.9
3^2	50.2	24.9	7.6
4^3	46.6	27.7	8.5
5^4	44.5	29.4	9.0
6^5	43.1	30.5	9.4

axial glide plane (*Pmnm*) indicating a different manner of ordering in the aikinite subcells, though the aforementioned conditions still hold since the equipoint number of this space group is compatible with *Pbnm*. Informative in this aspect would be a crystal structure analysis of one of the members. It may be mentioned that a crystal structure study of 3^1-aikinite ('gladite') is now under way.

ACKNOWLEDGMENTS

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REFERENCES

WELIN, E. (1967) Notes on the mineralogy of Sweden. 5. Bismuth-bearing sulphosalts from Gladhammar, Sweden. *Ark. Min. Geol.* (in press).