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THE SYNTHESIS OF BEAVERITE

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ABSTRACT

The plumbojarosite - beaverite series was synthesized at 130°C from solutions containing 2.0 M Li_2SO_4, added to increase Pb^{2+} incorporation in the jarosite structure at the expense of H_3O^+. Although in all cases the synthetic jarosite contains some hydronium ion, a formula ratio Pb:Cu of 0.937:0.973 was attained for synthetic beaverite as compared with 1:1 for the theoretical end-member. Least-squares refinements of X-ray powder-diffraction patterns indicate that the *c* dimension increases rapidly with Pb^{2+} incorporation, but that the same trend also is present for Cu^{2+}. The increases in *c* are compensated by decreases in *a*, so that little change in the cell volume occurs throughout the series.

Keywords: plumbojarosite, beaverite, synthesis, solid solution, unit-cell variations.

SOMMAIRE

On a effectué la synthèse de la série plumbojarosite - beaverite à 130°C à partir de solutions contenant 2.0 M Li_2SO_4, dont le rôle est d'augmenter le contenu en Pb^{2+} de la structure de la jarosite aux dépens de H_3O^+. Quoique toutes les compositions de jarosite synthétique contiennent de l'ion hydronium, le rapport Pb:Cu = 0.937:0.973 a été atteint pour la beaverite synthétique (Pb:Cu = 1:1 pour le pôle théorique). Les affinements des données de diffraction X (méthode des poudres) par la méthode des moindres carrés indiquent que la valeur de *c* augmente rapidement avec l'incorporation de Pb^{2+}, et qu'il en est de même pour Cu^{2+}. L'augmentation de *c*, compensée par une diminution de *a*, ne produit qu'un léger changement dans le volume de la maille d'un pôle à l'autre de la série.

Mots-clés: plumbojarosite, beaverite, synthèse, solution solide, variations de la maille.

INTRODUCTION

Plumbojarosite and cuprian-zincian plumbojarosite are of concern to mineralogists and extractive metallurgists alike because these phases are produced during the oxygen-sulfuric acid pressure-leaching of sulfide concentrates (Dutrizac 1982). In a previous study of the solid solution between plumbojarosite $Pb[Fe_3(SO_4)_2(OH)_6]_2$ and beaverite $PbCuFe_2(SO_4)_2(OH)_6$, the maximum copper content attained in the synthetic jarosite corresponds to a formula ratio $Pb_{0.714}Cu_{0.655}$ (Jambor & Dutrizac 1983). Most of the synthetic jarosite produced in that study also contains small concentrations of zinc and substantial amounts of hydronium ion. New syntheses of copper-bearing plumbojarosite have been undertaken to obtain zinc-free samples of beaverite, but principally to establish whether solid solution could be extended completely from plumbojarosite to the beaverite end-member. In addition, because compositions of synthetic jarosite are sensitive to variations in the conditions of preparation, especially with respect to the incorporation of hydronium ion, the syntheses were done under conditions that yielded low-hydronium species (*i.e.*, $Pb^{2+} > H_3O^+$).

EXPERIMENTAL

Synthesis procedures

The plumbojarosite–beaverite solid-solution series was synthesized using the optimum procedures developed previously for plumbojarosite (Dutrizac *et al.* 1980, Jambor & Dutrizac 1983). Basically, jarosite was formed by reacting excess $PbSO_4$ (30 g/L) with 1 L of 0.3 M Fe^{3+} as $Fe_2(SO_4)_3$ and 0.03 M H_2SO_4 solution at 130°C. The use of more alkaline media resulted in the precipitation of other iron compounds [*e.g.*, $Fe(OH)_3$], and more acidic media decreased the yield of product. The experiments were done in a titanium autoclave for 24 hours using a 600-rpm stirring speed. Various concentrations of Cu^{2+} (0 to 252 g/L Cu^{2+}) were maintained by the addition of reagent-grade copper sulfate. To reduce the extent of hydronium ion incorporation in jarosite, all synthesis solutions contained 2.0 M Li_2SO_4. High concentrations of Li_2SO_4 or $MgSO_4$ are known to increase Pb^{2+} incorporation into the jarosite at the expense of H_3O^+ (Dutrizac *et al.* 1980), and this effect is thought to be related to increased $PbSO_4$ solubilities in the highly concentrated sulfate media. Separate experiments established that the effect of Li_2SO_4 on solution pH was minimal. Because of the extremely high ionic strength employed in some experiments, the sulfate salts may not have been completely dissolved at the reaction temperature.

At the completion of the experiments, soluble salts and excess $PbSO_4$ were selectively leached from the jarosite by washing with four 1-litre portions of 10% ammonium acetate solution at 25°C. The jarosite residue was then filtered, water-washed and dried at 110°C prior to conventional chemical analysis and X-ray-diffraction study. The success of the washing procedure can be gauged by the fact that the jarosite typically was found to contain 0.02–0.07% Li and that $PbSO_4$ was not detected by Guinier - de Wolff X-ray powder-diffraction analysis. Lead sulfate diffracts strongly, and it has been established previously (Dutrizac *et al.* 1980) by doping experiments, chemical analyses and X-ray-diffraction work that as little as 0.3 wt.% $PbSO_4$ is detectable on the Guinier powder-diffraction patterns. Also, some of the samples of dried jarosite were rewashed with H_2O or 0.2 M H_2SO_4 at 25°C, but the rewashing did not result in a significant change in product composition.

X-ray powder-diffraction analysis

X-ray powder patterns of the jarosite were obtained using a Debye–Scherrer camera of 114.6 mm diameter, Co$K\alpha_1$ radiation (λ 1.7889 Å), and MgO as an internal standard. Refinements of the measured data were done as outlined in Jambor & Dutrizac (1983), except that the diffraction line indexed previously as 1.0.22 has been changed to 2.0.20. A hexagonal cell with $a \sim 7.3$ and $c \sim 34$ Å was adopted for all refinements for reasons discussed previously. The 11 Å diffraction line characteristic of an ordered plumbojarosite-type unit-cell was observed on a majority of the X-ray films; although this line is present for several samples with beaverite compositions, the intensity of the line is strongest for the first five compositions that are poorest in copper.

RESULTS AND DISCUSSION

Synthesis of the plumbojarosite - beaverite series

Figure 1 illustrates the variation of the Cu and Pb contents of the jarosite product as the copper concentration in solution increases from 0 to 175 g/L Cu^{2+} as $CuSO_4$; analytical data are presented in Table 1. The compositions shown in Table 1 were chosen to illustrate the compositional sequences across the solid-solution series, and data for all the experimental points are not shown. Many of the experiments yielded similar compositions and cell parameters (Figs. 2, 3); the presentation of the detailed compositional data for all the points does not add materially to an understanding of the series. In the absence of dissolved $CuSO_4$, plumbojarosite is formed with ~16% Pb (theoretical 18.32% Pb) and 0% Cu. As the concentration of dissolved copper increases, both the lead and copper contents rise rapidly; the copper and lead contents nearly level off for dissolved Cu^{2+} levels in excess of ~50 g/L. This observation is of some practical significance during the oxygen-sulfuric acid leaching of zinc concentrates that commonly contain some lead and copper. Under the preferred conditions of leaching,

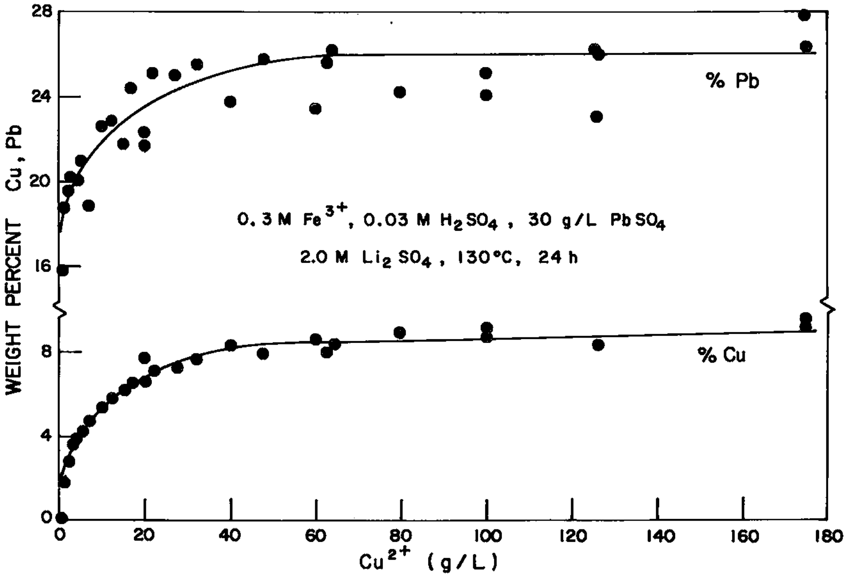

FIG. 1. Variation of the lead and copper contents of the plumbojarosite - beaverite products synthesized from solutions containing various concentrations of Cu^{2+} as $CuSO_4$.

TABLE 1. CHEMICAL COMPOSITION AND FORMULA RATIOS OF SYNTHETIC JAROSITE

	208	354	355	356	357	412	413	414	415	418	209
PbO	17.04	19.77	21.06	22.51	21.81	24.61	26.45	27.17	26.96	27.54	23.14
CuO		2.34	3.43	4.43	5.00	7.19	8.04	8.83	8.88	9.45	9.59
Fe_2O_3	40.98	37.87	37.45	36.18	36.08	30.79	29.36	28.69	28.57	29.03	28.36
SO_3	28.61	27.66	26.61	26.89	25.71	26.26	25.86	25.36	25.26	25.49	25.61
Total	86.63	87.64	88.55	90.01	88.60	88.85	89.71	90.05	89.67	91.51	86.70
Rem.*	13.37	12.36	11.45	9.99	11.40	11.15	10.29	9.95	10.37	8.49	13.30
formula contents for SO_4 = 2											
Pb	0.427	0.513	0.568	0.601	0.609	0.673	0.734	0.769	0.766	0.775	0.649
Cu		0.170	0.259	0.332	0.391	0.551	0.625	0.700	0.707	0.746	0.754
Fe	2.872	2.745	2.822	2.698	2.813	2.351	2.276	2.268	2.268	2.284	2.220
Σ_{Cu+Fe}	2.872	2.915	3.081	3.030	3.204	2.901	2.902	2.968	2.975	3.030	2.973
a(Å)	7.316(3)	7.311(3)	7.304(4)	7.293(3)	7.293(2)	7.273(2)	7.278(2)	7.265(2)	7.269(2)	7.269(3)	7.264(5)
c(Å)	33.67(2)	33.75(2)	33.87(2)	33.87(2)	33.90(1)	34.04(2)	34.08(1)	34.10(1)	34.12(2)	34.19(2)	34.19(4)

	417	210	349	416	211	212	350	213	351	352	beaverite
PbO	27.82	25.66	27.57	28.27	25.07	26.04	24.67	25.96	30.29	31.06	32.98
CuO	9.77	10.28	9.85	10.30	10.74	11.03	10.96	10.99	11.34	11.51	11.76
Fe_2O_3	28.30	27.11	28.29	27.83	26.86	25.75	26.13	24.51	24.37	24.05	23.61
SO_3	25.19	26.51	25.29	25.04	25.81	25.24	24.97	24.82	23.99	23.79	23.67
Total	91.08	89.56	91.00	91.44	88.48	88.06	86.73	86.28	89.99	90.41	92.02
Rem.*	8.92	10.44	9.00	8.56	11.52	11.94	13.27	13.72	10.01	9.59	7.98
formula contents for SO_4 = 2											
Pb	0.793	0.695	0.782	0.810	0.697	0.740	0.709	0.750	0.906	0.937	1.000
Cu	0.780	0.780	0.784	0.828	0.838	0.880	0.883	0.891	0.951	0.973	1.000
Fe	2.252	2.050	2.243	2.228	2.086	2.046	2.098	2.030	2.036	2.027	2.000
Σ_{Cu+Fe}	3.032	2.830	3.027	3.056	2.924	2.926	2.981	2.921	2.987	3.000	3.000
a(Å)	7.268(2)	7.264(3)	7.266(3)	7.256(2)	7.253(2)	7.260(4)	7.273(5)	7.257(5)	7.258(4)	7.256(4)	
c(Å)	34.21(2)	34.17(3)	34.20(2)	34.20(2)	24.20(2)	34.27(3)	34.25(4)	34.30(4)	34.32(3)	34.30(3)	

* By difference from 100%

plumbojarosite is formed, and near-maximum losses of copper (and zinc as well) into the plumbojarosite will occur at fairly modest concentrations of these elements in the processing solution (Dutrizac & Chen 1983). Above ~50 g/L dissolved Cu^{2+}, the contents of both Pb and Cu in the jarosite become nearly constant. There is more scatter in the lead data, and possibly this indicates slight variations in the Pb^{2+}/H_3O^+ ratio from test to test. Under the best conditions, beaverite near its end-member composition has been synthesized (Table 1).

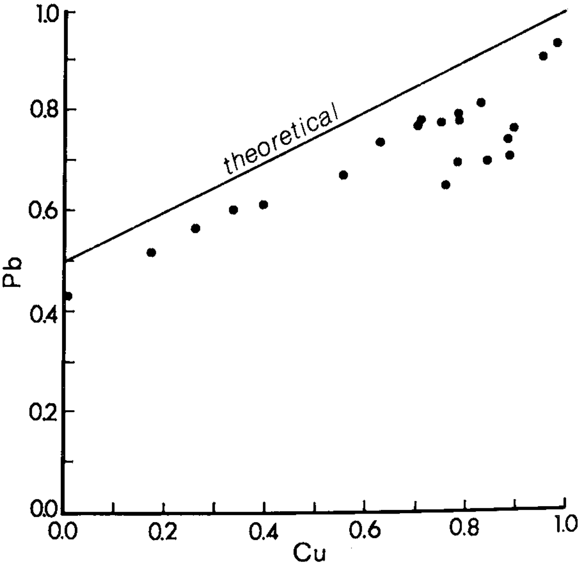

FIG. 2. Formula content of Pb *versus* Cu for the jarosite compositions synthesized, plotted relative to the theoretical join plumbojarosite–beaverite.

Compositions

The formula of the jarosite samples was calculated on the basis of $SO_4 = 2$, since this procedure yields the most consistent interpretations from both the chemical and structural points of view. The substitution of H_3O (which cannot be directly measured) for Pb or other alkali-site elements precludes using Pb as the basis. The substitution of Cu for Fe, as well as evidence of Fe vacancies (Kubisz 1970), rules out iron as a basis for comparison as well. The hydroxyl ion is determined by difference and is not accurately or directly known. Thus SO_4 is the best

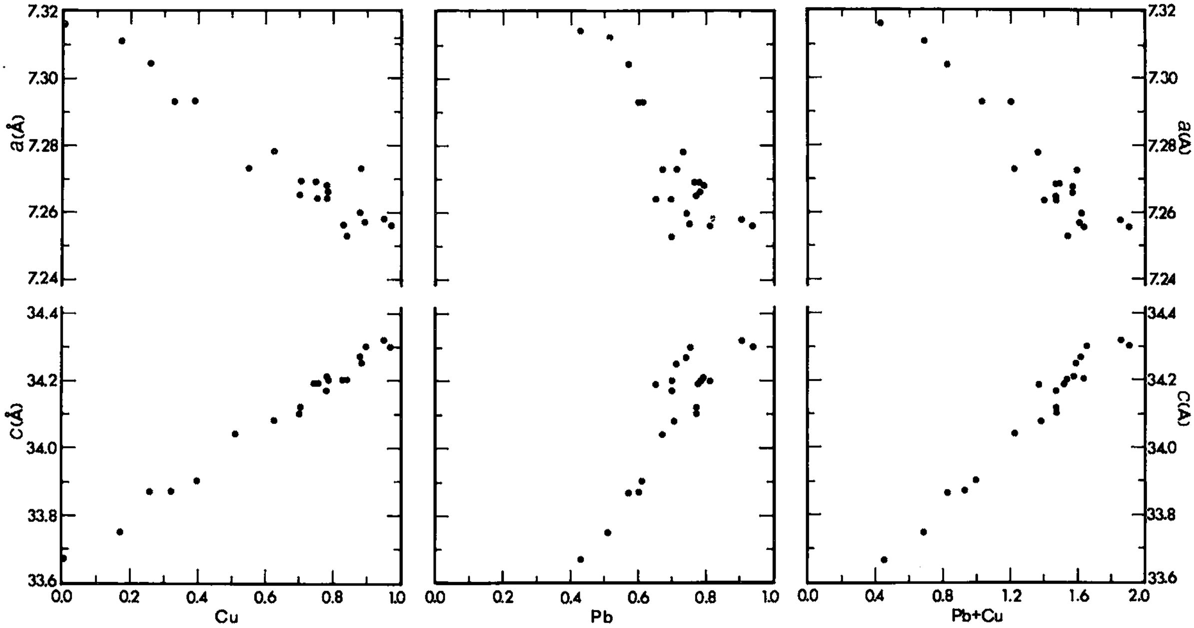

FIG. 3. Variations in *a* and *c* dimensions of synthetic jarosite plotted against formula contents of Cu, Pb, and Pb + Cu.

basis for chemical comparison and has the further structural advantage of being saturated in the jarosite structure; *i.e.*, an excess or deficit of SO_4 is unlikely to be structurally tolerated. For the theoretical series from plumbojarosite $Pb[Fe_3(SO_4)_2(OH)_6]_2$ to beaverite $PbCuFe_2(SO_4)_2(OH)_6$, lead exceeds copper except in the beaverite end-member, where Pb is equivalent to Cu (Table 1). Figure 2 shows the theoretical variation in the Pb and Cu contents as well as the formula ratios obtained for the synthesized jarosite; in all cases, the jarosite contains less lead than the theoretical amount. Nevertheless, these jarosite compositions, particularly those with low copper contents, plot closer to the theoretical join than does the series obtained previously (Jambor & Dutrizac 1983). The difference is that more lead and less hydronium ion are present in jarosite of the newer series, thus permitting a better opportunity to examine the relationship between Pb–Cu incorporation and unit-cell dimensions. Although the H_3O^+ ion cannot be determined directly, it is postulated to account for the observed deficiencies in alkali-site occupancy. All efforts to confirm H_3O (including room-temperature and low-temperature IR and low-temperature laser-Raman spectroscopy) have been inconclusive, although NMR may eventually solve this problem. The "remainder" noted in Table 1 includes the structural OH, hydronium ion and excess water that may occupy the alkali sites and result from $H_3O^+ + OH^-$ interactions. Because of the presence of this excess water, the H_3O^+ contents can only be assumed and estimated.

X-ray powder-diffraction study

Unit-cell parameters calculated for the various products are given in Table 1. Plots of the cell dimensions *versus* the formula contents of Fe^{3+}, Cu^{2+} and Pb^{2+} show that there are good correlations between *a* and each of these elements, and also good correlations between *c* and each element. It should be noted that although Fe^{3+} and Cu^{2+} occupy the same structural position, plots of each element give slightly different results because of nonstoichiometry. Similarly, each Cu^{2+} atom incorporated in the structure permits the entry of ½Pb^{2+} to maintain charge balance, but charge neutrality also is affected by the Fe^{3+} and H_3O^+ contents.

TABLE 2. EQUATIONS FOR CELL PARAMETERS VERSUS COMPOSITION*

equation	standard deviation	equation	standard deviation
$a(\text{Å})=7.3672-0.1319(\text{Pb})$	0.0186	$c(\text{Å})=33.1410+1.3579(\text{Pb})$	0.1700
$a(\text{Å})=7.3171-0.06593(\text{Cu})$	0.0043	$c(\text{Å})=33.6563+0.6812(\text{Cu})$	0.0183
$a(\text{Å})=7.1324+0.06086(\text{Fe})$	0.0052	$c(\text{Å})=33.5359-0.6169(\text{Fe})$	0.04585
$a(\text{Å})=7.2104+0.02121(\text{Cu+Fe})$	0.0517	$c(\text{Å})=34.3967-0.09808(\text{Cu+Fe})$	0.5183
$a(\text{Å})=7.3370-0.04639(\text{Pb+Cu})$	0.0035	$c(\text{Å})=33.4512+0.4772(\text{Pb+Cu})$	0.0216
$V(\text{Å}^3)=1558.4+5.7780(\text{Pb})$	4.9395	$V(\text{Å}^3)=1560.6+2.8791(\text{Cu})$	2.1696

* Where Pb etc. is the formula content of the element as given in Table 1 and the standard deviation is for the last term of the equation.

The jarosite structure is sheet-like, and the large cations such as Na^+, K^+, Pb^{2+} or H_3O^+ fit in 12-co-ordinated positions between the sheets. Theoretically, therefore, the size of the 12-co-ordinated cation has a pronounced effect on the *c* dimension, whereas *a* remains unchanged (Menchetti & Sabelli 1976). Figure 3 shows that *c* increases markedly as the Pb content rises; *a* apparently has the reverse trend, but the scatter at the lead-rich end of the series is such that the correlation is not precise. Similar scatter also occurs in the plots involving Fe^{3+} (Table 2). The best correlation is for *a versus* Cu^{2+} (Fig. 3), which is in accord with the conclusion of Menchetti & Sabelli (1976) that the length of *a* is directly related to the (Cu^{2+}, Fe^{3+})-OH bond length in the jarosite sheets. Although an increase in *a* would be expected because of the larger ionic radius and lower charge of Cu^{2+} compared with Fe^{3+}, a well-defined decrease occurs instead. Furthermore, even though the *c* parameter follows the expected trend of increasing as the Pb^{2+} content increases, the most precise correlation is with Cu^{2+} rather than Pb^{2+} (Table 2, Fig. 3). The middle diagram of Figure 3 shows a cluster of samples in which Pb is ~0.7 and the *c* values are above the main trend. These samples (*e.g.*, 209–213 inclusive in Table 1) have a relatively low Pb/Cu ratio; if the low Pb content of these samples were attributable to above-average H_3O contents, the *a* dimensions also should have increased rather than decreased (Fig. 3). Thus Cu^{2+} must exert an extraordinarily strong influence both on the length of the sheet-like structure and on its thickness. Accommodation of Cu^{2+} in the structure also occurs without an appreciable change in volume (Table 2). In osarizawaite, which is the aluminum analog of beaverite, the copper atoms have the effect of elongating the (Cu,Al) octahedra, thereby stretching the thickness of the sheets (Giuseppetti & Tadini 1980). Presumably this elongation of the octahedra through their apices in the *c* direction permits a corresponding contraction in the plane of the sheets, thereby accounting for both an increase in *c* and decrease in *a* with rising copper content in the beaverite.

CONCLUSIONS

The plumbojarosite – beaverite solid-solution series, including near-end-member beaverite, has been synthesized from highly concentrated sulfate media at 130°C. Although hydronium ion seems to be present in all products, its amount has been significantly reduced as a result of the modified procedure of synthesis. Good correlations were obtained for the formula contents of Fe^{3+}, Cu^{2+} or Pb^{2+} and the *a* and *c* cell parameters. Copper exercises a major influence on the cell parameters, although it has little effect on cell volume. Substitution of Cu^{2+} for Fe^{3+} in the sheet structure of jarosite apparently distorts the (Cu,Fe) octahedra such that *c* expands whereas *a* contracts by a corresponding amount.

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