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# STUDIES ON SYNTHETIC ALKALI-HYDRONIUM JAROSITES. I. SYNTHESIS OF JAROSITE[1] AND NATROJAROSITE

A b s t r a c t. An attempt of obtaining (potassium) jarosite and natrojarosite of theoretical composition using $Fe_2(SO_4)_3 \cdot aq$ and alkali sulphates or hydroxides at temperatures ranging from about 95 to 210°C failed, in spite of using a fourfold excess of alkalies. Instead a series of hydronium-alkali jarosites with iron deficiency and excess of water resulted. The presence of excess („additional") water is responsible for the contraction of the unit cell in $K,H_3O$-jarosites (or expansion in $Na,H_3O$-jarosites, respectively). The highest alkali ($Na^+$ or $K^+$) content obtained was only 67 to 75 per cent of lattice positions available and that of trivalent cation ($Fe^{3+}$) 98 to 83 per cent, indicating some kind of intercrystalline chemical equilibrium. These values approach those found in some natural minerals formed in weathering conditions. It was put forward that the lacking $Fe^{3+}$ charge is balanced by $H_2O$ for $OH^-$ substitutions in $FeO_2(OH,H_2O)_4$ octahedra, and the iron vacancies being perhaps occupied by groupings of $H_2O$ molecules, both accounting for the excess water. Thus the general chemical formula of minerals investigated should have the form:

$$A_{1-x} (H_3O)_x Fe_{3-y} [(OH)_{6-3y} (H_2O)_{3y} (SO_4)_z]$$
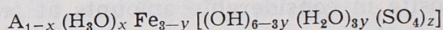
## INTRODUCTION

Investigations of about 40 jarosite samples formed in low temperature and low pressure conditions (e.g. Kubisz 1958, 1960, 1962, 1964) showed an almost constant deficiency in alkali and sometimes iron content, and excess of water. Their average composition being:

$$A_{0.75} (H_3O)_{0.25} Fe_{3.0-2.6} [(OH)_6 (SO_4)_2], \quad A = K^+, Na^+.$$

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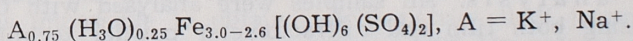
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[1] The author proposes to use the name „jarosite" as a general term like „feldspar" or „pyroxene". If used in conformity with its present meaning, for K-ferric sulphate, names like e.g. natrojarosite should consequently denote a Na, K-ferric sulphate.

This interesting phenomenon induced the author to make an attempt of establishing the chemical conditions required for the formation of jarosites with theoretical composition (Kubisz 1961, preliminary report). The procedure as given by Fairchild (1933) was followed at first. As no stoichiometric alkali jarosites resulted, the temperature, concentration of solutions, and molar ratios of starting substances were varied. A series of jarosites was obtained with various iron deficiency and alkali to hydronium ratio. On the basis of about 50 tests parameters of synthesis were settled leading to the best yield and high alkali content in the products.

The chemical constitution, X-ray data and conditions of alkali-hydronium jarosites formation in comparison with Brophy and Sheridan's (1965), results is discussed in the present paper. Thermal transformations and infrared absorption analysis are the subjects of papers to follow. Mössbauer investigations have been published earlier (Hrynkiewicz et al. 1964).

## EXPERIMENTAL WORK

S y n t h e s i s. The syntheses were performed in open glass flasks placed in an autoclave partly filled with water, in order to prevent evaporation of solutions. Temperature was varied between 100 and 210°C, 140—150°C was found to be the optimum one. Steam-bath syntheses ($\sim$ 95°C) yielded always high hydronium products. The equilibrium state of the reaction is reached after some 4 hours. Prolongation of the synthesis to 30 hours failed to increase its yield. $Fe_2(SO_4)_3 \cdot 9H_2O$, $Al_2(SO_4)_3 \cdot 18H_2O$, $K_2SO_4$, $Na_2SO_4 \cdot 10H_2O$, KOH and NaOH p.a. were used as reagents. Composition of starting solutions is given in Table 1. Only syntheses below 150—160°C yielded X-ray pure material. It must be mentioned, however, that a slight admixture of $Fe_2O_3$ and $Fe(OH)SO_4$ in the samples obtained is possible. These water insoluble substances are formed besides jarosite in considerable amounts at temperatures above 160—170°C.

The synthesized jarosite samples were thoroughly washed with destiled water and dried at 150°C before being investigated.

C h e m i c a l   a n a l y s i s. Alkalies were determined photometrically with a Zeiss photometer, iron by precipitation with ammonia, sulphur as $BaSO_4$. Total water was computed by difference. All analyses were recalculated assuming $SO_3$ molecular equivalent to be 4.00 (Tabs. 2, 3, and 4).

X - r a y   a n a l y s i s. All samples were analysed with Cr filtered radiation using both film and diffractometer powder techniques. The diffractometer was calibrated with a silicon standard. All X-ray patterns were indexed on hexagonal axes using preliminary $c_0 (= 9d_{00.9})$ and $a_0 (= 4d_{22.0})$ values, and the accurate unit cell constant evaluated by successive approximation with a mean error of $\pm$ 0.004 Å (Tab. 2). The strongest lines of $Fe(OH)SO_4$ are: 3.257 (10), 3.203 (10), 1.587 (8), 1.553 (9), 1.282 Å (10).

Data on the synthesis of alkali-hydronium jarosites and hydronium alunite

| No. | Concentration mol/100 ml $H_2O$ | | Molecular equivalents (simplified) |
|---|---|---|---|
| | $K_2SO_4$ | $Fe_2(SO_4)_3 \cdot 9H_2O$ | $K_2O : SO_3 : Fe_2O_3$ |
| S-25 | 0.00046 | 0.043 | 1 : 280 : 93 |
| S-24 | 0.0034 | 0.043 | 1 :  38 : 12.4 |
| S-4 | 0.0092 | 0.021 | 1 :   8 : 2.3 |
| S-27 | 0.037 | 0.029 | 1 : 3.3 : 0.8 |
| | KOH | | |
| S-29 | 0.12 | 0.04 | 1 :   2 : 0.7 |
| | $Na_2SO_4 \cdot 10H_2O$ | $Fe_2(SO_4)_3 \cdot 9H_2O$ | $Na_2O : SO_3 : Fe_2O_3$ |
| S-10 | 0.0019 | 0.021 | 1 : 34 : 11 |
| S-23 | 0.022 | 0.043 | 1 :  7 : 2 |
| S-26 | 0.030 | 0.21 | 1 :  3 : 0.7 |
| | NaOH | | |
| S-28 | 0.12 | 0.04 | 1 :  2 : 0.7 |
| S-30 | 0.2 | 0.04 | 1 : 1.2 : 0.4 |
| S-17-22 S-2C | $Fe_2(SO_4)_3 \cdot 9H_2O$ | 0.025—0.05 mol/100 ml $H_2O$ pH = 0.55 | |
| S-11 | $Al_2(SO_4)_3 \cdot 18H_2O$ | 0.03 mol/100 ml  $H_2O$ | |

## DISCUSSION OF RESULTS

Using $K_2SO_4$, $Na_2SO_4$ and $Fe_2(SO_4)_3$ as starting substances it is impossible to settle freely the proper proportions of $K_2O(Na_2O) : SO_3 : Fe_2O_3$. It is seen from Table 1 that although the molar ratio of $K_2O : Fe_2O_3$ (or $Na_2O : Fe_2O_3$) added as sulphates was varied form 1 : 0.8 to 1 : 93 (or 1 : 0.7 to 1 : 11 respectively) the ratio of $SO_3 : Fe_2O_3$ was always about 3 : 1, instead of stoichiometric 4 : 3. None of the authors preparing synthetic jarosites paid any attention to this important fact. Further increase of alkali content, introduced into the starting solutions as sulphates, would diminish the relative amount of $SO_4^{2-}$ ions and the $Fe_2O_3 : SO_3$ ratio (compare the molar ratios in S-25, S-27, Tab. 1). This explains why it was impossible to obtain stoichiometric alkali jarosites in the described conditions. The same is perhaps true for natural weathering environment where $Fe^{3+}$ and $SO_4^{2-}$ ions are supplied by oxidation of iron sulphides:

$$FeS_2 \xrightarrow{+ O_2, H_2O} FeSO_4 + H_2SO_4$$
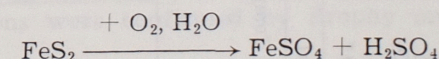
(molar ratio $SO_3 : Fe_2O_3 = 4 : 1$, similar as in discussed syntheses).

Table 2

**Chemical analyses of synthetic K, $H_3O$-jarosites and K, Na, $H_3O$-jarosite**

| | S-25 | | S-24 | | S-4 | | S-27 | | S-29 | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Weight % | Molecular equivalents | Weight % | Molecular equivalents | Weight % | Molecular equivalents | Weight % | Molecular equivalents | Weight % | Molecular equivalents |
| $K_2O$ | 1.84 | 0.19 | 5.56 | 0.56 | 6.60 | 0.68 | 7.03 | 0.71 | 7.52 | 0.75 |
| $Fe_2O_3$ | 49.31 | 2.98 | 44.54 | 2.63 | 45.14 | 2.73 | 42.30 | 2.51 | 42.13 | 2.49 |
| $SO_3$ | 33.21 | 4.00 | 34.02 | 4.00 | 33.14 | 4.00 | 33.85 | 4.00 | 33.92 | 4.00 |
| $H_2O$* | 15.64 | 8.37 | 15.88 | 8.30 | 15.12 | 8.11 | 16.82 | 8.83 | 16.43 | 8.61 |
| Total | 100.00 | | 100.00 | | 100.00 | | 100.00 | | 100.00 | |

| | S-8 | |
|---|---|---|
| | Weight % | Molecular equivalents |
| $Na_2O$ | 0.76 | 0.12 |
| $K_2O$ | 4.75 | 0.48 |
| $SO_3$ | 33.43 | 4.00 |

* Computed by difference

Table 3

**Chemical analyses of synthetic Na, $H_3O$-jarosites and $H_3O$-alunite**

| | S-17 | | S-10 | | S-23 | | S-26 | | S-28 | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Weight % | Molecular equivalents | Weight % | Molecular equivalents | Weight % | Molecular equivalents | Weight % | Molecular equivalents | Weight % | Molecular equivalents |
| $Na_2O$ | | | 1.71 | 0.26 | 3.78 | 0.58 | 4.35 | 0.67 | 4.33 | 0.67 |
| $Fe_2O_3$ | 49.13 | 3.08 | 48.87 | 2.90 | 46.49 | 2.75 | 47.25 | 2.81 | 47.36 | 2.83 |
| $SO_3$ | 33.00 | 4.00 | 33.76 | 4.00 | 33.91 | 4.00 | 33.72 | 4.00 | 33.54 | 4.00 |
| $H_2O$* | 17.87 | 9.93 | 15.66 | 8.25 | 15.82 | 8.29 | 14.68 | 7.74 | 14.77 | 7.83 |
| Total | 100.00 | | 100.00 | | 100.00 | | 100.00 | | 100.00 | |

| | S-11 | |
|---|---|---|
| | Weight % | Molecular equivalents |
| $Al_2O_3$ | 31.15 | 2.32 |
| $SO_3$ | 42.25 | 4.00 |
| $H_2O$* | 26.60 | 11.19 |
| Total | 100.00 | |

* Computed by difference

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It is true that introduction of alkalies in the form of hydroxides improves the sulphate to iron ratio, but it increases pH of the environment leading to the formation of goethite (S-30, Tab. 1).

Addition of sulphuric acid as practiced by many authors (e.g. Brophy et al. 1962 and others) retards the synthesis, because a considerable amount of free acid is liberated in the reaction e.g.:

$$K_2SO_4 + 3Fe_2(SO_4)_3 + 12H_2O \rightleftarrows 2KFe_3\,[(SO_4)_2\,(OH)_6] + 6H_2SO_4$$

Low relative concentration of $Fe^{3+}$ ions in the starting solutions (Tab. 1) resulted in deficiency of iron in synthesized jarosites (Tabs. 2 and 3). Increasing amount of $Fe^{3+}$ vacancies is accompanied by increased incorporation of water in the jarosite crystal lattice (Tab. 4), called „additional water" throughout this work. The charge balance in the lattice is most probably maintained by joining of additional protons, leading to partial conversion of $OH^-$ to $H_2O$. Groupings of $H_2O$ molecules may perhaps occupy the vacant $Fe^{3+}$ sites too. It is interesting to note that iron deficiency and additional water content is greater in K-, than Na-jarosites with similar alkali to hydronium ratio (Tab. 4, e.g. S-4 and S-26). Perhaps it is because the higher hydrated $K^+$ ions introduce more water in the jarosite frame-work.

Table 4

Structural formulae and unit-cell constants of alkali-hydronium jarosites

| No. | Structural formulae | $c_0$ (Å) | $a_0$ (Å) | c/a |
|---|---|---|---|---|
| S-28 | $Na_{0.67}(H_3O)_{0.33}Fe_{2.83}\ [(OH)_{5.49}(H_2O)_{0.51}(SO_4)_2]$ | $16.64_3$ | $7.34_0$ | $2.26_7$ |
| S-26 | $Na_{0.67}(H_3O)_{0.33}Fe_{2.81}\ [(OH)_{5.43}(H_2O)_{0.57}(SO_4)_2]$ | $16.65_6$ | $7.33_5$ | $2.27_1$ |
| S-23 | $Na_{0.58}(H_3O)_{0.42}Fe_{2.75}\ [(OH)_{5.25}(H_2O)_{0.75}(SO_4)_2]$ | $16.71_4$ | $7.33_5$ | $2.27_8$ |
| S-10 | $Na_{0.26}(H_3O)_{0.74}Fe_{2.90}\ [(OH)_{5.70}(H_2O)_{0.30}(SO_4)_2]$ | $16.91_4$ | $7.35_0$ | $2.30_1$ |
| S-17 | $H_3O\ Fe_3[(OH)_6(SO_4)_2]$ | $17.00_5$ | $7.35_5$ | $2.31_2$ |
| S-25 | $K_{0.19}(H_3O)_{0.81}Fe_{2.98}\ [(OH)_{5.96}(H_2O)_{0.04}(SO_4)_2]$ | $17.04_9$ | $7.34_3$ | $2.32_2$ |
| S-24 | $K_{0.56}(H_3O)_{0.44}Fe_{2.63}\ [(OH)_{4.89}(H_2O)_{1.11}(SO_4)_2]$ | $17.12_4$ | $7.32_0$ | $2.33_9$ |
| S-4 | $K_{0.68}(H_3O)_{0.32}Fe_{2.73}\ [(OH)_{5.19}(H_2O)_{0.81}(SO_4)_2]$ | $17.15_3$ | $7.31_3$ | $2.34_5$ |
| S-27 | $K_{0.71}(H_3O)_{0.29}Fe_{2.51}\ [(OH)_{4.53}(H_2O)_{1.47}(SO_4)_2]$ | $17.15_5$ | $7.32_5$ | $2.34_2$ |
| S-29 | $K_{0.75}(H_3O)_{0.25}Fe_{2.49}\ [(OH)_{4.47}(H_2O)_{1.53}(SO_4)_2]$ | $17.15_9$ | $7.31_0$ | $2.34_7$ |

The preference of K over Na and $H_3O$ in the incorporation into the jarosite crystal lattice (Kubisz 1961) explains the rarity of natrojarosites and hydronium jarosites in nature (Kubisz 1964). Compare e.g. the molar ratios $Fe_2O_3 : A_2O$ in the starting solutions and the products for S-24 ($A = K^+$) and S-23 ($A = Na^+$) or S-10 and S-25 (Tabs. 1, 2, and 3). These observations were confirmed by Brophy and Sheridan's (1965) investigations.

It was found experimentally that dilution of starting solutions used in this work leads to a higher hydronium content in resulting jarosites.

The true dependence of unit cell dimensions of the investigated jarosites on cation substitutions is difficult to find because of several indetermined factors. Such factors in this case are: influence of iron vacancies and of „additional water". After removal of this „additional water", on heating the samples in DTA apparatus to the end of the first endothermic reaction, the unit cell of K, $H_3O$-jarosites expands (that of Na, $H_3O$-jarosites contracts) in $c_0$ and contracts in $a_0$ direction e.g. for S-29 $\Delta c_0 = +0.06$, $\Delta a_0 = -0.03$ Å, for S-28 $\Delta c_0 = -0.001$, $\Delta a_0 = -0.004$ Å (compare Brophy et al. 1962, and Parker 1962). A plot of $c_0$ and $c_0/a_0$ variations with $H_3O^+$ for $K^+$ or $Na^+$ substitutions, presented on Figs. 1 and 2 respectively, shows apparent relations only. In fact $c_0$ variation in jarosites investigated is a complex function of molar precentages of alkalies, $H_3O$ ions, and of „additional water" molecules, and perhaps indirectly of iron vacancies too. The same is valid for jarosites described by Brophy and Sheridan (1965). The non-linearity of $c_0$ variations with Na + K for $H_3O$ substitutions noticed by these authors should probably by ascribed partly to the presence of „additional water" in these jarosites. There is, however, another phenomenon observed by the present writer in „three-monovalent-cations" K, Na, $H_3O$-jarosites. If the formula for $c_0$ variations

$$c_0 = 17.01 + 0.21\, n_K - 0.51\, n_{Na} \quad (Å) \tag{1}$$

($n_K$, $n_{Na}$ — molar equivalents of $K_2O$ and $Na_2O$ respectively in relation to $n_{SO_3}$ taken as = 4.00), derived from the plot (Fig. 1) for „two-cations"
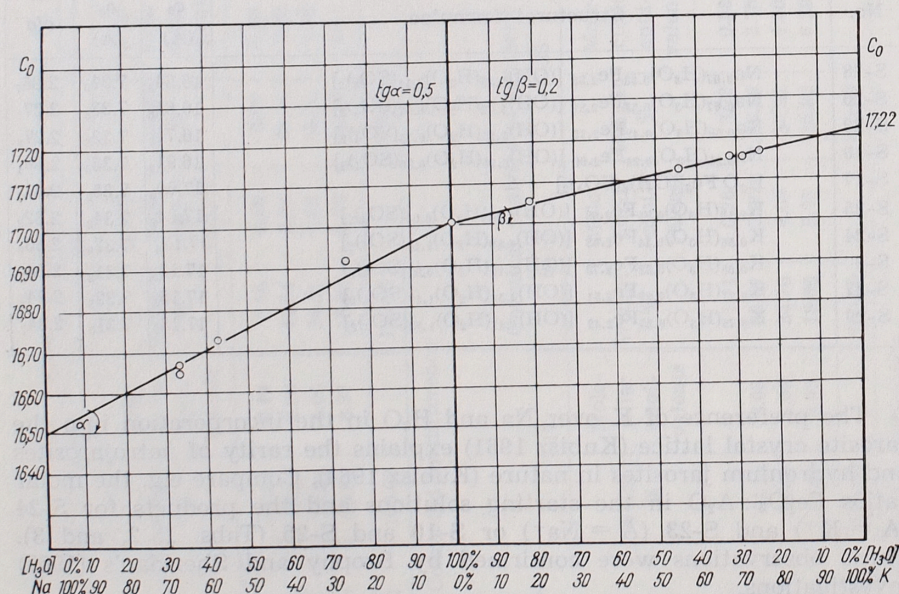


Fig. 1. Dependence of $c_0$ parameter on $K/H_3O$ and $Na/H_3O$ ratio in jarosites

jarosites ($K - H_3O$ and $Na - H_3O$), is applied to K, Na, $H_3O$-jarosites (e.g. S-8), a marked discrepancy between measured and calculated $c_0$ values is observed (Kubisz 1964). Formula (1) was deduced taking 17.22 Å, 17.01 Å and 16.50 Å as $c_0$ values (extrapolated values resulting from the plot, Fig. 1) for 100 per cent K-, $H_3O$- and Na-jarosites respectively. These values are near Brophy and Sheridan's (1965) experimental ones, for coresponding jarosites (17.19, 16.98 and 16.62 Å respectively). The nonvalidity of formula (1) for „three-cations" jarosites is probably due to the different influence of „additional water" on unit cell dimensions and of different „water-introducing" abilities of $K^+$, $Na^+$ and $H_3O^+$ ions.

At it is seen from the plot (Fig. 1) $c_0$ varies linearly with $H_3O$ for K or Na substitutions in the described two-cations synthetic jarosites in contradiction to the three-cations ones described by Brophy and Sheridan (1965). The variation of $c_0$ is 2.5 times greater in the case of Na than K for $H_3O$ substitution (tg $\alpha = 0.5$). This is partly due to the ionic radii differences:

$$\Delta\, (r_{H_3O} - r_{Na}) \approx 3\, \Delta\, (r_K - r_{H_3O})$$

($r_{Na} = 0.95$, $r_K = 1.33$, $r_{H_3O} = 1.24$ Å [2]), and partly to the different „water-introducing" abilities of these ions. The amount of „additional water" (and at the same instance the deficiency of $Fe^{3+}$) which is approximately proportional to the molar percentages of alkalies increases more rapidly in $K - H_3O$ than in $Na - H_3O$-jarosites (Tabs. 2 and 3). The contracting (or expanding) influence of this water on unit cell height counteracts the expanding (or contracting) action of K (or Na, respectively) for $H_3O$ substitutions.

The influence of „additional water" is less marked on the $c_0/a_0$ ratio. Considering that $a_0$ parameter depends on the dimensions of $FeO_2(OH)_4$ coordination polyhedron (Brophy et al. 1962) it should be expected that $Fe^{3+}$ vacancies (accompanied by the increase of water content i.e. protons) will diminish this parameter. These vacancies which are greater in K-, than Na-jarosites thus influence the $a_0$ parameter of the latter in a lesser degree. It may explain why $c_0/a_0$ function is almost identical (tg $\alpha \approx$ tg $\beta$) in both jarosite solid solution series (Fig. 2).

The change of unit cell dimensions of synthetic jarosites after heating to 300°C has been noticed first by Brophy et al. (1962) and Parker (1962). These authors, however, ascribe this change mainly to the loss of $H_3O^+$, and apparently to the formation of hydronium devoided alkali minerals with stoichiometric composition whereas in the present author's opinion

[2] The effective ionic radius of $H_3O^+$ in alunite type structures was calculated on the ground of Pauling's values for $K^+$ and $Na^+$ ions and $c_0$ values of pure K-, Na-, and $H_3O$-jarosites, taken from Fig. 1 (Kubisz 1964). The $r_{H_3O}$ value 0.99 Å derived apparently from O—H distances in $H_3O^+$ ion (Parker 1962) is much too low. In all hydrogen-oxygen complexes protons are drawn inside the electronic cloud of oxygen. Thus their effective radii are greater than it appears from the O—H distances (Kubisz 1967).

it is caused by the removal of additional water. Removal of monovalent cations would rather cause general shrinking (collapse) cf the unit cell, if not connected with the simultaneous loss of corresponding amount of $SO_4^{2-}$ tetrahedra which form the basic skeleton of the crystal lattice. On the other hand from differences in $c_0$ ($\Delta c_0$, Tab. 5) between pure hydro-
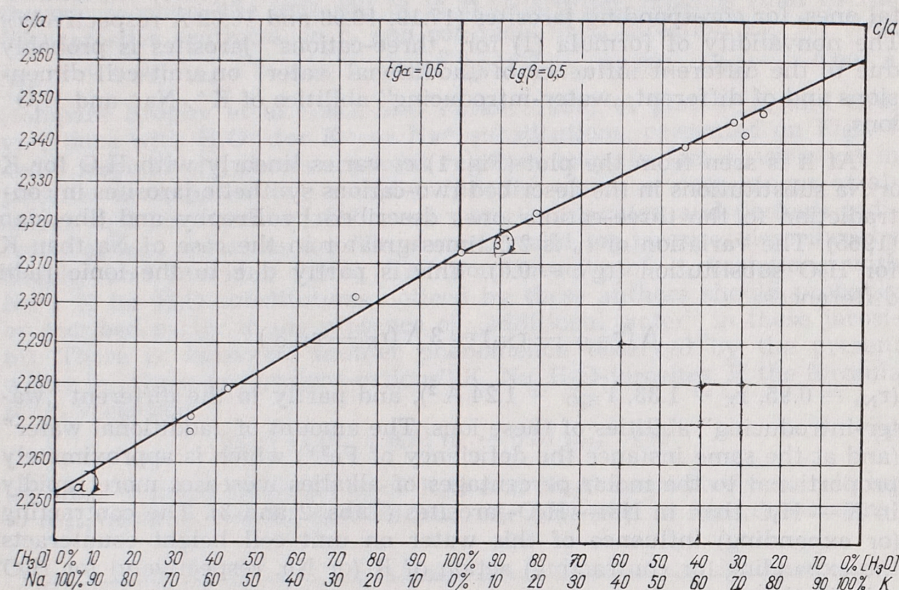


Fig. 2. Dependence of $c/a$ on $K/H_3O$ and $Na/H_3O$ ratio in jarosites

Table 5

Differences in unit cell parameters between jarosites and alunites with various monovalent cations

| Difference Δ between: | Alunite | Jarosite |
|---|---|---|
| $\Delta c_0$ (K — $H_3O$) = | (17.34 — 17.18 =) 0.16 Å | = (17.22 — 17.01 =) 0.21 Å<br>= (17.19 — 16.98 =) 0.21 Å |
| $\Delta c_0$ ($H_3O$ — Na) = | (17.18 — 16.70 =) 0.48 Å | = (17.01 — 16.50 =) 0.51 Å<br>= (16.98 — 16.62 =) 0.36 Å |
| $\Delta a_0$ ($H_3O$ — K) = | (7.01 — 6.98 =) 0.03 Å | = (7.36 — 7.31 =) 0.05 Å<br>= (7.36 — 7.29 =) 0.07 Å |
| $\Delta a_0$ ($H_3O$ — Na) = | (7.01 — 6.98 =) 0.03 Å | = (7.36 — 7.34 =) 0.02 Å<br>= (7.36 — 7.31 =) 0.05 Å |

Combined data of the present author, Parker (1962) and Brophy & Sheridan (1965).

nium and alkali minerals follows that the change of this parameter after heating, if caused by removal of only several (10—20) molar per cent of $H_3O^+$ ions, should be by for smaller in K, $H_3O$ ($\Delta c_0 = + 0.02$ Å for 10% of $H_3O$) and greater in Na, $H_3O$ minerals ($\Delta c_0 = 0.05$ Å for 10% of $H_3O$). Similarly the change of $a_0$ should be much smaller ($\Delta a_0 = 0.003$ Å for 10% of $H_3O$) than follows from results of Parker's (1962) investigations of synthetic K, Na, $H_3O$-alunites.

## CONCLUSIONS

An attempt of synthesizing stoichiometric alkali jarosites from iron and alkali sulphate or hydroxide solutions with as great as fourfold molar excess of $K_2O$ over $Fe_2O_3$ failed both in low and elevated temperatures. The highest achieved occupancy of monovalent cation position with alkali ions being only 67 per cent in natrojarosite and 75 per cent in potassium jarosite, and the occupancy of $Me^{3+}$ positions with ferric ions only 83—97 per cent. These results seem to be partly confirmed by Brophy & Sheridan's (1965) investigations of mixed-cation K, Na-jarosites.

Comparison of the chemical composition of natural jarosites formed in weathering conditions with that of synthetic ones (Kubisz 1964, Brophy & Sheridan 1965) leads to the conclusion that alkali and perhaps iron deficiency, and consequent excess of „water" (= hydronium ions plus „additional water") should be regarded as their constitutional property.

It seems impossible to obtain stoichiometric pure alkali jarosites and alunites from sulphate reagents used up to now, as proposed first by Mitscherlich (1861), because of constant excess of sulphate ions. A proper molar ratio of $Fe_2O_3$ to $SO_3$ can not be settled in this case, and the progressing acidifying of solutions in the course of the synthesis increases the relative amount of $H_3O^+$ ions. Thus the resultant products are iron deficient and always contain hydronium in monovalent cation positions. Most probably natural chemical environment in the weathering zone provides similar conditions for the jarosite formation. Iron and sulphur are commonly supplied by decomposing pyrite (marcasite) in which Fe : S ratio is much lower than in jarosite. The lacking positive charge is balanced by incorporation of protons which most probably join the OH groups situated around trivalent $Me^{3+}$ ions forming $H_2O$ molecules. The influence of these (additional) water molecules on unit cell dimensions makes it impossible to establish the true dependence of its parameters on alkali for hydronium substitutions. Namely it has been found that the $c_0$ parameter decreases considerably in potassium minerals and remains unchanged (or increases) in sodium minerals with increasing conversion of OH into $H_2O$ in $FeO_2$ (OH, $H_2O$)$_4$ octahedra.

The presumption of the location of additional $H_2O$ molecules in $FeO_2(OH, H_2O)_4$ groupings, which control the $a_0$ values, is supported by remarkable decrease of this parameter in heated minerals. The $c_0$ contracting ability of additional water in K minerals (expanding in Na

minerals) may be connected either with the number of protons (H-bonds), or with the different relationship between unit cell height in jarosite--alunite series and $A^+$—$Me^{3+}$ ions content. Namely the $c_0$ parameter is very sensitive to $Me^{3+}$ ions substitutions when large $K^+$ ions are present: in natural alunite ($Me^{3+} = Al^{3+}$, $A = K^+$) $c_0 = 17.34$ Å, and in jarosite ($Me^{3+} = Fe^{3+}$, $A = K^+$) $c_0 = 17.19$ Å ($\Delta c_0 = 0.15$ Å). In Na minerals $c_0$ varies far less on $Me^{3+}$ exchange: in natural natroalunite $c_0 = 16.69$ and in natrojarosite $c_0 = 16.62$ Å ($\Delta c_0 = 0.07$ Å). Most probably the dimensions of monovalent cation cavities between sulphur tetrahedra and $Me^{3+}$ octahedra sheets of the framework are greater than the radius of $Na^+$ ions. Thus in natroalunite and natrojarosite the manner of fitting of $MeO_2(OH, H_2O)_4$ octahedra does not affect considerably the $c_0$ parameter.

It is worth mentioning how remarkably similar results to those discussed in the present paper were obtained for alunites by Parker (1962); the Na, K-alunites synthetized by him show almost the same, as jarosites, iron and alkali deficiency — the average composition of these products can be expressed by the following formula:

$$H_3O_{0.14}(Na, K)_{0.86}Al_{2.72}[(SO_4)_2(OH)_6]$$
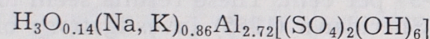
The considerable shrinkage of $a_0$ after heating to 300°C ($\Delta a_0 = 0.03$ Å) shows that some change in the size of $AlO_2(OH)_4$ octahedra has taken place, which can not be ascribed to the removal of 0.14 molar per cent of $H_3O^+$ ions only ($\Delta a_0$ between pure K,Na-alunites and $H_3O$-alunite is of the same size, Tab. 5). The differences in $a_0$ after heating seem to depend rather on Al than on alkali deficiency, and that in $c_0$ on the kind of alkali ion present and not on $H_3O$ content ($c_0$ increases by about 0.15 Å in synthetic K,$H_3O$-alunites and decreases by 0.02 Å in Na,$H_3O$--alunites obtained by this author).

Intercrystalline equilibrium in the jarosite structure controls the proton distribution between three coexisting hydrogen-oxygen complexes: $OH^-$, $H_2O$ and $H_3O^+$. Because of periodic inhomogeneity of the electric crystal field this equilibrium is not a simple function of ionic concentration. It depends on polarization state and site symmetry of different oxygens (Kubisz 1967) in the structure. There are four different kinds of oxygens in jarosites:

1) hydroxyl (or water) oxygens coordinated to $Fe^{3+}$ ions ($O_z$),
2) sulphate oxygens coordinated simultaneously to $Fe^{3+}$ ions ($O_{II}$),
3) sulphate oxygens on $C_3$ axes ($O_I$),
4) oxygens in monovalent cation positions (= hydronium oxygens) ($O_h$).

The $O_{II}$ and $O_h$ oxygens should display strongest acidic, and $O_z$ strongest basic character. Statistical distribution of protons corresponds most probably to the scheme represented by chemical formulae as proposed in Table 4. It is however possible that for a given period of time some other proton-oxygen configuration exists in the jarosite crystal lattice. Of course the threefold site symmetry of $O_h$ will favorize its triangular coordination i.e. formation of $H_3O^+$ complex.

*

After completing of the work here presented there appeared a paper (J. B. Brown, Canad. Mineral., 1970, 10, 696—703) on low temperature jarosite synthesis. This paper estabilishes the important role of $Fe^{2+}$ (Eh) in jarosite formation and their alkali (hydronium composition. The lack of correlation between cell-edge and K/$H_3O$ content points, however, to some kind of anomaly of their chemical composition — probably iron deficiency due to low Fe : $SO_4$ ratio in the strating solutions (full chemical analyses are needed to confirm this presumption). This leaves the problem of obtaining stoichiometric jarosites from sulphate reagents still unsolved.

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**BADANIA SYNTETYCZNYCH JAROSYTÓW ALKALICZNO--HYDRONIOWYCH. I. SYNTEZA JAROSYTU POTASOWEGO I SODOWEGO**

S t r e s z c z e n i e

Próby uzyskania syntetycznych jarosytów o teoretycznej zawartości sodu lub potasu z roztworów $Fe_2(SO_4)_3 \cdot aq$ i siarczanów lub wodorotlenków alkaliów w zakresie temperatur od 95 do 210°C nie powiodły się.

Nawet w przypadku użycia czterokrotnego nadmiaru jonów Na⁺ lub K⁺ otrzymano jarosyty z niedoborem alkaliów, zamiast których zostaje wprowadzony w więżbę krystaliczną jon hydroniowy $H_3O^+$. Jarosyty te charakteryzują się również deficytem jonów $Fe^{3+}$ i podwyższoną zawartością wody. Obecność dodatkowych drobin wody powoduje w przypadku jarosytów K, $H_3O$ zmniejszenie komórki elementarnej, a w przypadku jarosytów Na, $H_3O$ jej zwiększenie.

Najwyższa ilość jednowartościowych jonów (Na⁺ lub K⁺), jaką udało się wprowadzić w więżbę jarosytów, nie przekracza 67—75% pozycji sieciowych, a w przypadku jonów $Fe^{3+}$ 98—83%. Wskazuje to na utworzenie pewnego rodzaju wewnątrzkrystalicznej równowagi. Podobne zawartości alkaliów i $Fe^{3+}$ charakteryzują większość jarosytów tworzących się w naturalnym środowisku wietrznym. Na tej podstawie przyjęto więc, iż deficyt alkaliów i $Fe^{3+}$ stanowi konstytucjonalną cechę niskotemperaturowych i niskociśnieniowych jarosytów. Wysunięto także przypuszczenie, że brakujący (wskutek deficytu $Fe^{3+}$) ładunek sieci krystalicznej jest równoważony przez podstawienie w tetraedrach $FeO_2(OH)_4$ jonów $OH^-$ przez drobiny $H_2O$, a puste pozycje sieciowe po jonach $Fe^{3+}$ obsadzone są przypuszczalnie przez ugrupowania dalszych drobin wody. Oba zjawiska tłumaczą podwyższoną zawartość $H_2O$ w analizowanych jarosytach. Opierając się na uzyskanych rezultatach badań zaproponowano dla jarosytów następujący ogólny wzór konstytucyjny:

$$A_{1-x}(H_3O)_x Fe_{3-y}[(OH)_{6-3y}(H_2O)_{3y}(SO_4)_2]$$
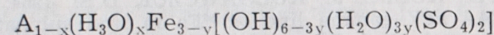
## OBJAŚNIENIA FIGUR

Fig. 1. Zależność parametru $c_0$ od stosunku K/$H_3O$ i Na/$H_3O$ w jarosytach
Fig. 2. Zależność c/a od stosunku K/$H_3O$ i Na/$H_3O$ w jarosytach

Ян КУБИШ

# ИССЛЕДОВАНИЕ СИНТЕТИЧЕСКИХ ЩЕЛОЧНО-ГИДРОКСОНИЕВЫХ ЯРОЗИТОВ. I. СИНТЕЗ КАЛИЕВОГО И НАТРИЕВОГО ЯРОЗИТОВ

Р е з ю м е

Попытки получения синтетических ярозитов с теоретическим содержанием калия или натрия из растворов $Fe_2(SO_4)_3 \cdot$ aq и сульфатов или гидроокислов щелочных металлов, в температурах от 95° до 210°C, не увенчались успехом. Даже в условиях четырехкратного избытка ионов Na⁺ или K⁺ были получены ярозиты с недостатком этих элементов, а их место в кристаллической решетке занимал гидроксониевый ион $H_3O^+$. Кроме того, такие ярозиты отличаются недостатком ионов $Fe^{3+}$ и повышенным содержанием воды. Дополнительные молекулы воды вызывают уменьшение элементарной ячейки у K, $H_3O$- ярозита и увеличение ячейки

у Na, $H_3O$- ярозита. Самое большое число олновалентных ионов (Na⁺ или K⁺), какое удалось ввести в решетку ярозитов, не превышает 67—75% позиций решетки, а в отношении ионов $Fe^{3+}$ 98—83%. Это говорит о возникновении своего рода внутрикристаллического равновесия. Такого порядка содержания щелочных металлов и $Fe^{3+}$ наблюдается у болшинства ярозитов, образованных в естественной среде зоны выветривания. Исходя из этого было принято, что дефицит щелочных элементов и $Fe^{3+}$ является конституционный признак ярозитов, образующихся при низких температуре и давлении. Выдвинуто также предположение, что недостающий (вследствие дефицита $Fe^{3+}$) заряд кристаллической решетки уравновешивается подстановкой в тетраэдрах $FeO_2(OH)_4$ вместо ионов $OH^-$ молекул $H_2O$, а пустые места решетки после $Fe^{3+}$ заняты, по-вероятности, дальнейшими группировками молекул воды. Эти явления объясняют повышенное содержание $H_2O$ в исследованных ярозитах. Исходя из полученных экспериментальных данных предлагается следующая общая формула ярозитов:

$$A_{1-x}(H_3O)_x Fe_{3-y}[(OH)_{6-3y}(H_2O)_{3y}(SO_4)_2]$$
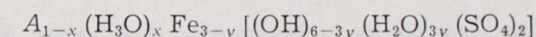
## ОБЪЯСНЕНИЯ К ФИГУРАМ

Фиг. 1. Зависимость параметра $c_0$ от отношения К/$H_3O$ и Na/$H_3O$ в ярозитах.
Фиг. 2. Зависимость c/a от отношения К/$H_3O$ и Na/$H_3O$ в ярозитах.