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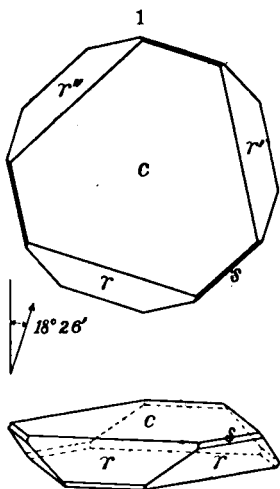
1902.

ART. XXV.—*Some Additions to the Alunite-Jarosite Group of Minerals*; by W. F. HILLEBRAND and S. L. PENFIELD.

CONCERNING two new varieties of jarosite which will be described in the present communication, one is from Nevada, and was collected by Mr. H. W. Turner of the United States Geological Survey and sent to the survey laboratory at Washington for identification; the other is from New Mexico, and was sent by Mr. J. H. Porter of Denver, Colorado, to the Mineralogical Laboratory of the Sheffield Scientific School. Except for slight differences in color the two minerals look exactly alike, each consisting of minute, isolated, tabular crystals, which, as may be seen with the microscope, consist of combinations of a rhombohedron with largely developed basal planes. By chance it happened that the present writers discovered that they were both engaged in the investigation of compounds belonging evidently to the same group, and it was decided to bring the results together into one paper.

Natrojarosite.

The material collected by Mr. Turner was obtained on the east side of Soda Springs Valley, Nevada, on the road from Sodaville to the Vulcan Copper Mine. It consists of a glistening powder, made up of perfect crystals having the habit shown in figure 1, although generally only one rhombohedron, r , is present instead of two, as shown in the figure. The largest crystals observed were 0.15^{mm} wide and 0.025^{mm} thick, and the general average would not be over half that size. In spite of being so minute, however, it was possible to measure the angles of the crystals with the reflection goniometer, the chief difficulty arising not so much from their small size as from the vicinal character of the basal planes. After repeated trials a crystal was found having a fairly good basal plane, and from this crystal the following angles were obtained:



Measured.		Measured.		Calcu-
				lated.
$c \wedge r$, 0001 \wedge 10 $\bar{1}$ 1 = 51° 53'*	$c \wedge s$, 0001 \wedge 02 $\bar{2}$ 1 = 68° 42'	68° 35'		
$c \wedge r'$, 0001 \wedge $\bar{1}$ 101 = 51 53	$c \wedge s'$, 0001 \wedge $\bar{2}$ 021 = 68 48	" "		
$c \wedge r''$, 0001 \wedge 0 $\bar{1}$ 11 = 52 26	$r \wedge r'$, 10 $\bar{1}$ 1 \wedge $\bar{1}$ 101 = 86 5 85 54			

The crystals belong to the rhombohedral division of the hexagonal system, and the angle $c \wedge r$, $51^{\circ} 53'$, which is probably very nearly correct, has been assumed as fundamental, and from it the following axial ratio has been calculated :

$$c = 1.104.$$

That the axial ratio as given is very near the truth is shown by the fact that the measurements of $c \wedge s$ and $r \wedge r$ do not vary many minutes from the calculated values; while on a number of other crystals, measurement of the angle $c \wedge r$, though varying considerably, was found to be not far from 52° . The angles of $c \wedge r$ and $r \wedge r'$ of the ordinary potassium jarosite are $55^{\circ} 16'$ and $90^{\circ} 45'$, respectively.

Under the microscope the crystals exhibit normal optical properties. Using a high power lens and convergent light, the thicker crystals show the dark cross and the beginnings of the first ring of the interference figure. The birefringence is negative. The color of single crystals, when seen under the microscope in transmitted light, is golden-yellow. Many of the crystals show numerous brown inclusions. The color shown by a mass of the crystals is yellowish-brown, and the material glistens, owing to reflections from the basal planes of the minute crystals.

The material used for the chemical analysis was the purest that could be obtained, although crystals containing the brownish inclusions just mentioned could not be avoided, and there were occasional brown ferruginous particles mixed with the crystals. The specific gravity of the material was found to be 3.18 at 30.5° C. The results of the analysis by Hillebrand are as follows :

		Ratio.	
Fe ₂ O ₃	50.98	0.319	3.29
Na ₂ O*.....	6.03	0.094	} 1.01
K ₂ O.....	0.35	0.004	
SO ₃	30.96	0.387	
H ₂ O below 105°.....	0.12		
H ₂ O above 105°.....	11.03	0.613	6.33
As ₂ O ₃	0.20		
SiO ₂	0.23		
CaO.....	0.04		
	99.94		

The ratio of Fe₂O₃ : Na₂O : SO₃ : H₂O is evidently 3 : 1 : 4 : 6 as in ordinary jarosite, where the alkali is potash instead of

*Of the soda .22 per cent is not extracted by hot water after full ignition of the mineral and hence may belong to a feldspar or some other foreign mineral. Only 5.81 per cent is assumed to belong to the jarosite and used in deriving the molecular value.

soda. The slight excess of Fe_2O_3 and H_2O , as indicated by the ratio, is evidently due to some ferric hydroxide; probably the dark ferruginous impurities seen under the microscope are in part responsible for this, and there are also traces of some arsenate and silicate present. Regarding the excess of Fe_2O_3 and H_2O as due to impurities, it is found that 94 per cent of the material analyzed may be regarded as pure natrojarosite, as indicated below:

	After deducting impurities.		Theory for $\text{Na}_2\text{Fe}_3[\text{OH}]_{12}[\text{SO}_4]_4$.
Fe_2O_3	46.43	or	49.49
Na_2O	5.81	"	6.39
K_2O	0.35	"	----
SO_3	30.96	"	32.99
H_2O	10.45	"	11.13
	<hr/>		<hr/>
	94.00	100.00	100.00

That six per cent of impurities should be present in a crystalline powder such as analyzed is not surprising, when it is taken into consideration that it would require something like 2,500,000 crystals to make one gram of material, the estimation being based on the assumption that the crystals are 0.10^{mm} in axial diameter and 0.02^{mm} thick, which is certainly above their average size.

Among the specimens from Cook's Peak, New Mexico, sent to the Sheffield Laboratory by Mr. Porter, were some masses of a rather firmly cemented aggregate of minute crystals of a mineral of the jarosite group. The specimens are of a brownish-yellow color, and have in places the glistening appearance of a mica schist. They also look as though they had been subjected to pressure and had been somewhat sheared. The material is rather easily crushed, and the powder when examined with the microscope exhibits the properties of the natrojarosite just described. The crystals are associated with a little limonite and quartz, and pure material for analysis could not be obtained. Only a partial analysis, therefore, was undertaken with the following results:

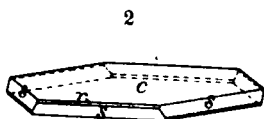
Fe_2O_3	55.60
Na_2O	4.49
K_2O	0.77
PbO	0.96

SO_3 and H_2O were present but not determined. The results are sufficient to indicate that the material is essentially natrojarosite.

Plumbojarosite.

This material is from Cook's Peak, New Mexico. It occurs as a glistening, crystalline powder and as loosely cohering

masses which may easily be crushed by pressure between the fingers. The crystals are very symmetrical, and are exactly like those of natrojarosite, figure 1, although generally only one rhombohedron r is present. On the average the crystals are a trifle smaller and noticeably thinner than those of natrojarosite. A number of crystals were measured on the reflecting goniometer, the chief difficulty arising rather from the vicinal character of the faces than from their small size. One unusually large crystal, 0.28^{mm} broad and 0.015^{mm} thick, was finally found, having the development shown in figure 2, which



is unusual, for generally r ($10\bar{1}1$) and not s ($02\bar{2}1$) is the prevailing rhombohedron. Fortunately the crystal was so taken up on a minute point of wax that the measurement of $s \wedge s$ in three rhombohedral zones

was possible. The results of five measurements of $s \wedge s$ over the upper and lower pole edges varied between $109^\circ 5'$ and $109^\circ 30'$, the average being $109^\circ 16'$; while six measurements over the middle edges varied between $70^\circ 10'$ and $71^\circ 00'$, the average being $70^\circ 36'$. The average of the two supplementary values gives $s \wedge s$, $2\bar{2}01 \wedge 02\bar{2}1 = 109^\circ 20'$, which has been assumed as fundamental, and from it the following axial ratio has been calculated:

$$c = 1.216.$$

On the crystal from which the foregoing measurements were obtained the basal plane was vicinal and hence no reliable measurements of $c \wedge s$ could be had from it. On a number of other crystals, however, the angle of $c \wedge r$ was measured with varying results, the variation resulting from the uncertainty of the reflections from the basal planes. Four measurements of $c \wedge r$, which were recorded in the note-book as derived from the best reflections, varied between $54^\circ 15'$ and $54^\circ 44'$, the average being $54^\circ 30'$, while $c \wedge r$, $0001 \wedge 10\bar{1}1$, by calculation from the fundamental measurement, is $54^\circ 32'$. Hence it may be assumed that the axial ratio as established is reasonably exact. The calculated value of $r \wedge r$, $10\bar{1}1 \wedge \bar{1}101$, is $89^\circ 42'$.

In polarized light the crystals exhibit normal optical properties and negative birefringence. Being on the average thinner than crystals of natrojarosite, it is seldom that, with the highest powers and convergent light, even the beginning of the first ring of the uniaxial interference figure is visible. Individual crystals show under the microscope in transmitted light a golden-yellow color. A mass of crystals has the appearance of a glistening dark-brown powder, the color being decidedly darker than that of natrojarosite.

The analysis of the mineral was made on the very best material, having a specific gravity of 3.665 at 30° C. The results are surprising, and were wholly unlooked for, since it is found that this jarosite contains lead in the place of alkalis. The results by Hillebrand are as follows :

	I.	II.	III.	IV.	Mean.	Ratio.	
Fe ₂ O ₃	42.36	42.38			42.37	0.265	} 3.15
Al ₂ O ₃ ?*12	.08	.11		.10	0.001	
PbO	19.99	19.99	19.89	19.79	19.84	0.089	1.05
K ₂ O17				.17		
Na ₂ O21†				.21†		
SO ₃	27.05	27.07			27.06	0.338	4.00
H ₂ O below 105°02				.02		
H ₂ O above 105°	9.59	9.49			9.54	0.530	6.27
SiO ₂56	.51	.47		.51		
CuO27	.27			.27		
CaO05				.05		
MgO01				.01		
					100.15		

The ratio of Fe₂O₃ : PbO : SO₃ : H₂O is very close to 3 : 1 : 4 : 6, indicating that the mineral is a variety of jarosite, and the slight excess of Fe₂O₃, H₂O, and PbO + alkalis, may be accounted for by assuming that slight impurities are present, partly ferric hydroxide, in part some lead salt, and perhaps a soluble silicate, as shown by the complete solubility of the silica in acids. Assuming that the ratio is exactly 3 : 1 : 4 : 6, it is found that 4.36 per cent of impurities are present, and the remaining 95.64 per cent may then be regarded as plumbojarosite, as follows :

		Theory for PbFe ₃ [OH] ₃ [SO ₄] ₄ .	
Fe ₂ O ₃	40.59	or	42.44
PbO	18.86	"	19.72
SO ₃	27.06	"	28.29
H ₂ O	9.13	"	9.55
	95.64		100.00

Since it took probably 2,500,000 crystals of natrojarosite to make one gram of material, it certainly must have taken fully 4,000,000 to make a gram of plumbojarosite, for the crystals of the latter mineral, though somewhat heavier, are decidedly thinner than those of the former; hence the presence of 4.5

*The presence of alumina was not definitely proved. The figures here given are the differences between the several weights of the ammonia precipitates and those of the ferric iron in them, as determined by permanganate after reduction by hydrogen sulphide.

† Probably somewhat high.

per cent of impurities in such a crystalline product is not to be wondered at.

Jarosite and Alunite.

As seen from the analyses of these minerals which have been published, the alkali metal they contain is almost always potassium, though sodium is at times present. The formulas assigned to the two minerals are therefore $K_2O + 3Fe_2O_3 + 4SO_3 + 6H_2O$ and $K_2O + 3Al_2O_3 + 4SO_3 + 6H_2O$, which may be variously expressed, as will be indicated later.

A mineral corresponding to natrojarosite of this article, though containing a little potash, has been described by W. P. Headden* from the Buxton mine, Lawrence Co., S. D. The crystals are described as scales, consisting of a combination of base and rhombohedron. The material analyzed was evidently somewhat impure, as quartz and some As_2O_3 are reported. As the As_2O_3 evidently does not belong to jarosite, the assumption may be made that some scorodite, $FeAsO_4 \cdot 2H_2O$, is present, and the results of Headden's analysis may then be interpreted as follows:

	Original analysis.	Scorodite and quartz.	Natrojarosite.		Ratio.
Fe_2O_3	46.27	1.60	44.67	or	50.10
Na_2O	4.35		4.35	"	4.86
K_2O	1.47		1.47	"	1.65
CaO	0.39		0.39	"	0.44
SO_3	28.46		28.46	"	31.93
H_2O	10.55	0.72	9.83	"	11.02
As_2O_3	2.36	2.36	----		----
Quartz	6.10	6.10	----		----
	<hr/>	<hr/>	<hr/>		<hr/>
	99.95	10.78	89.17		100.00

Thus, assuming the presence of 4.68 per cent of scorodite and 6.10 of quartz, and deducting them, the remainder agrees very closely with natrojarosite, giving a good ratio, very near 3:1:4:6.

Alunite containing considerable soda has been described by W. Cross† from Rosita Hills, Colorado, and by E. B. Hurlburt‡ from Red Mountain, Colorado, and analyses of both minerals show about equal percentages of K_2O and Na_2O , or a molecular ratio of $K_2O:Na_2O = 4:7$. The occurrence, therefore, of sodium in the jarosite-alunite group is in accordance with previous observations, but the case is quite different with lead. As far as the present writers are aware, this is the first instance on record where lead has been observed isomorphous with the alkali metals. It is interesting to note that the alunite from Red Mountain, Colorado, occurs as a crystalline powder,

* This Journal (3), xlv, p. 24, 1893.

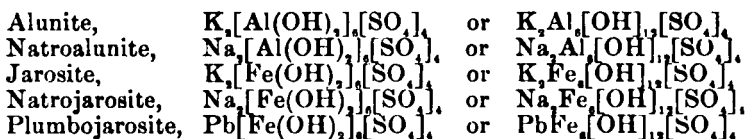
† Ibid. (3), xli, p. 472, 1891.

‡ Ibid. (3), xlviii, p. 130, 1894.

the crystals being exactly like those of natrojarosite and plumbojarosite, except that they are a trifle smaller and white, or colorless when seen under the microscope.

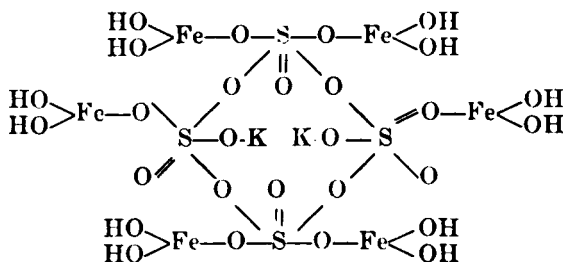
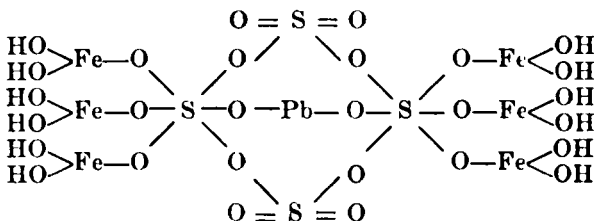
From a chemical standpoint the most interesting feature of the new minerals is the light they throw upon the isomorphism of potassium, sodium and lead. Ordinarily, even potassium and sodium are not isomorphous, as shown by the fact that their simple salts seldom crystallize in the same form. Although KCl and NaCl both crystallize in cubes, it is not certain that both salts belong to the same group of the isometric system. It has been shown, for example, by etching, that KCl crystallizes like NH_4Cl in the plagioclinal group of the isometric system, while the etchings produced on halite seem to indicate that it crystallizes in the normal group. Again at Stassfurt, Germany, sylvite and halite both occur crystallized side by side upon the same hand specimen, instead of mixing as isomorphous molecules. Even in such complex molecular compounds as the feldspars, the potassium and sodium salts crystallize as orthoclase and albite, rather than as isomorphous mixtures. Lastly potassium has a strong tendency to form alums which is not shared by sodium. In contrast to these differences in chemical nature, we have in the jarosite-alunite group of minerals not only the alkali-metals, potassium and sodium, but, what seems still more remarkable, *lead*, playing the same rôle in the compounds, and yielding crystals which are surprisingly alike in all their physical properties. The writers can at present offer no other reason for the isomorphism in the group of minerals under consideration than that the alkalis and lead play so small a rôle, and the remaining constituents so prominent a part in the complex chemical molecules, that the latter control or dominate the crystallization by virtue of what may be called their *mass effect*.

The alunite from Red Mountain, described by Hurlburt, was analyzed in the Sheffield Mineralogical Laboratory under the direction of one of the present writers, and it was found that water was first expelled from the compound at a rather high temperature, thus indicating that the mineral contains hydroxyl and no water of crystallization: accordingly it was shown that the seemingly complex formula of the mineral, expressed by the ratio $\text{Al}_2\text{O}_3 : \text{K}_2\text{O} : \text{SO}_3 : \text{H}_2\text{O} = 3 : 1 : 4 : 6$, may be much simplified to $\text{K}[\text{Al}(\text{OH})_2]_2[\text{SO}_4]_2$. In the light of the present investigation it now seems best to abandon the above simple formula and adopt one containing double the number of atoms, in order to make clear the isomorphism between K_2 , Na_2 , and Pb . The formulas of the minerals of the group would then be expressed as follows :



In the case of the lead compound one atom of lead, and in the others two atoms of either potassium or sodium, are combined in complex molecules containing fifty other atoms; hence that the complex of fifty atoms, to the right of the K_2 , Na_2 , and Pb in the foregoing formulas, should control or dominate crystallization by virtue of *mass effect*, and condition an isomorphism between such unlike elements as sodium, potassium and lead, is not so surprising as would at first appear.

Having adopted the double formulas, as given above, there are numerous ways of writing developed formulas, of which the following are perhaps the simplest and most satisfactory :



It is interesting to note that although K_2 , Na_2 , and Pb play so small a rôle in the alunite-jarosite molecules, the substitution of Na_2 for K_2 is attended by quite a marked variation in the angles of the crystals, greater in fact than is generally observed in isomorphous replacements. That alunite and jarosite containing potash would be nearly alike in their angles is expected, since crystals of corundum and hematite are surprisingly alike as shown by the following comparison :

	Axial length.	$r \wedge r'$	$c \wedge r$
Corundum, Al_2O_3 ,	1.3630	$93^\circ 56'$	$57^\circ 34'$
Hematite, Fe_2O_3 ,	1.3656	$94^\circ 00'$	$57^\circ 37'$

The relations of the minerals of the alunite-jarosite group are as follows :

	Axial length.	$r \wedge r'$	$c \wedge r$	Birefringence.
Alunite -----	1.252	90° 50'	55° 19½'	positive
Jarosite -----	1.245	90 45	55 16	negative
Natrojarosite ...	1.104	85 54	51 53	negative
Plumbojarosite..	1.216	89 42	54 32	negative

From the foregoing table it is seen that the substitution of sodium for potassium in jarosite has brought about greater variation in the angles of the crystals than the substitution of the bivalent metal lead for potassium.

The three minerals, natrojarosite, plumbojarosite and the Na-K-alunite from Red Mountain, are very interesting when studied together as microscopic mounts, the crystals being practically alike in size and development, and illustrating very beautifully on the one hand the isomorphism of aluminum and iron, on the other the isomorphism of potassium, sodium and lead. The three substances must have formed under like conditions, and it is believed that they are solfataric products, formed under the combined action of heat and pressure. Being difficultly soluble, they have formed, like many precipitates, as fine crystalline powders.

The three products just mentioned, when heated in closed tubes behave alike; they suffer no change on gentle heating, but when the temperature is sufficiently high to decompose the chemical molecules, the crystals break up into fine powder or dust, which is carried along by the escaping vapors and deposited for a considerable distance along the sides of the tubes. In addition to water, SO₂ and SO₃ are copiously given off during decomposition. In the case of natrojarosite, and the same would doubtless hold true for the Na-K-alunite, it is found that after ignition, one-fourth of the sulphate radical has been retained by the alkali metal, and may be extracted by water. In the case of plumbojarosite, however, all of the sulphate radical is expelled by ignition, doubtless because the ferric-oxide present serves to decompose any lead sulphate which might have a tendency to form. Anglesite, PbSO₄, when heated alone in a closed tube suffers no decomposition, but when finely triturated with limonite and heated, acid water is given off. Finely powdered natrojarosite and plumbojarosite are slowly but completely soluble in boiling hydrochloric acid. Plumbojarosite when fused with sodium carbonate on charcoal yields globules of lead and a coating of lead oxide.

It has seemed to the writers best to designate the new compounds described in this article as natrojarosite and plumbojarosite, the names signifying their relation to a well known

species. Other members of this group will doubtless be found, and the name natroalunite might be employed to designate the two varieties of alunite from Colorado mentioned on page 216, where the proportion of the soda to the potash molecule is 7:4. It is highly probable that a series of alunite-jarosite compounds could be made artificially.

It is with pleasure that the writers acknowledge their indebtedness to Messrs. Turner and Porter for calling attention to the interesting compounds described in this article.

Laboratories of the U. S. Geological Survey, Washington, and of the
Sheffield Scientific School, Yale University, New Haven,
Feb., 1902.