THERMAL STUDY OF JAROSITE

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ABSTRACT. Jarosite, argentojarosite, and plumbojarosite are examined by differential thermal analysis and X-ray diffraction. The structural and chemical changes which these minerals undergo on heating are discussed and compared with alunite.

In general two endothermic peaks at about 400° C. and 700° C. are the major thermal features. The first large endothermic peak is associated with the OH loss and the jarosite structure destruction. This is followed by a small exothermic peak attributed to crystallization of Fe_2O_3 (hematite). The second endothermic peak is due to decomposition of $Fe_2(SO_4)_3$ produced during the jarosite lattice destruction. A number of thermal curves of jarosite group minerals from typical localities are discussed. Substitution is considered from a standpoint of mineral structure and geochemical conditions.

INTRODUCTION

IN recent years application of differential thermal analysis to the solution of mineralogical problems has met with considerable success.

The types of equipment, theory, and use of differential thermal analysis have been reviewed by Speil, Berkelhamer, Pask and Davies (1945), Grim and Rowland (1942), and Kerr and Kulp (1948). The method is applicable to minerals which undergo endothermic or exothermic changes within the limits of the temperature ranges ordinarily covered by available apparatus. Most work has been carried out from room temperature to about 1100°C. but at times higher temperatures have also yielded valuable information.

Although the thermal curves for alunite and jarosite have previously been published, much remains to be said concerning the thermal history, the variations in the thermal curves within the alunite-jarosite group, and the correlation of these phenomena with structure. It is the purpose of this investigation to indicate the typical thermal curve for a number of jarosite minerals, to describe the chemical reactions which produce the characteristic peaks in the thermal curve, and to examine the possible cation substitution.

The minerals of the jarosite group are:

Jarosite	$K_2Fe_6(OH)_{12}(SO_4)_4$
Argentojarosite	$Ag_2Fe_6(OH)_{12}(SO_4)_4$
Plumbojarosite	$PbFe_6(OH)_{12}(SO_4)_4$
Ammoniojarosite	$(NH_4)_2Fe_6(OH)_{12}(SO_4)_4$
Natrojarosite	$Na_2Fe_6(OH)_{12}(SO_4)_4$

Because of the frequency of occurrence, relative economic importance and availability of specimens, the potassium, silver and lead members were studied.

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TECHNIQUES AND PROCEDURE

X-ray diffraction was used to confirm the identity of the samples and to determine the structural changes of the material on heating. Debye powder photographs were taken with iron radiation. The various members of the jarosite group give sufficiently different powder patterns to permit rapid identification.

All specimens were subjected to semi-quantitative chemical analysis using the Curtman (1942) scheme. In table 1 the cations are recorded as major, minor, or trace constituents. Through analysis of samples with known metallic content it is estimated that "major" refers to greater than 5%, "minor" indicates 1-5% and "trace" considerably less than 1%.

The multiple differential thermal analysis apparatus employed is described by Kerr and Kulp (1948). A heating rate of 12.5° per minute up to 1000°C. was used. The material was ground to pass 300 mesh, packed uniformly in the thermocouple well, and heated without covering. This small particle size was found necessary to obtain comparable curves, for, although some of the specimens are reasonably coarse, others are extremely fine powders.

SPECIMEN DESCRIPTION

The specimens studied were obtained from the Egleston Mineral collection of the Department of Geology, Columbia University. In addition, a synthetic jarosite prepared by Professor Paul F. Kerr after the method of Fairchild (1933) for an earlier investigation was available.

The members of the jarosite group show few distinguishing features in hand specimen. All occur as soft masses or aggregates of fine pale-yellow to dark-brown flakes varying in luster.

Optical examination indicated the absence of impurities aside from a small quantity of an opaque red substance found associated with jarosite from several localities. X-ray examination and chemical tests showed it to be quartz coated by goethite. The optical properties of the specimens studied fell within the range recorded in the literature.

In each case the material for thermal analysis was carefully selected for homogeneity.

"Argentojarosite" from Eureka, Utah, "plumbojarosite" from Almada, Mexico, and "plumbojarosite" from Pioche, Nevada, are each composed of both yellow and brown material. X-ray examination indicates the brown material from Almada to be predominantly plumbojarosite, whereas the yellow portion is apparently an intergrowth of plumbo- and argentojarosite. To verify this a 1:1 mixture of argentojarosite from Eureka, Utah, and plumbojarosite from the Eryscian mine, Chihuahua, Mexico, was artificially prepared and an X-ray diffraction powder pattern taken. The pattern obtained was identical to that of the yellow material from Almada, Mexico.

THERMAL HISTORY AND STRUCTURE

The thermal curves of the specimens studied are shown in figure 1. All are characterized by two major endothermic peaks. These are supplemented or modified by the particular chemical constitution of the mineral lattice, intergrown members of the group, and active or inactive impurities.

In order to gain a better understanding of the structural and chemical behavior of these minerals on heating and thereby to interpret the thermal curves adequately, the most typical specimens of jarosite, plumbojarosite and argentojarosite, were heated just past each significant peak, then examined by X-ray methods. For these experiments the following specimens were used: jarosite, Santa Maria mine, Jelardena, Durango, Mexico; plumbojarosite, Eryscian mine, Chihuahua, Mexico; and argentojarosite, Tintic Standard mine, Eureka, Utah.

The thermal decomposition of alunite has already been studied by Fink, Van Horn and Pazour (1931). Since the structures of alunite, $K_2Al_6(OH)_{12}(SO_4)_4$ and jarosite, $K_2Fe_6(OH)_{12}(SO_4)_4$, are similar (Hendricks, 1937), an understanding of the thermal decomposition of alunite facilitates experimentation within the jarosite group. The aluminum or iron

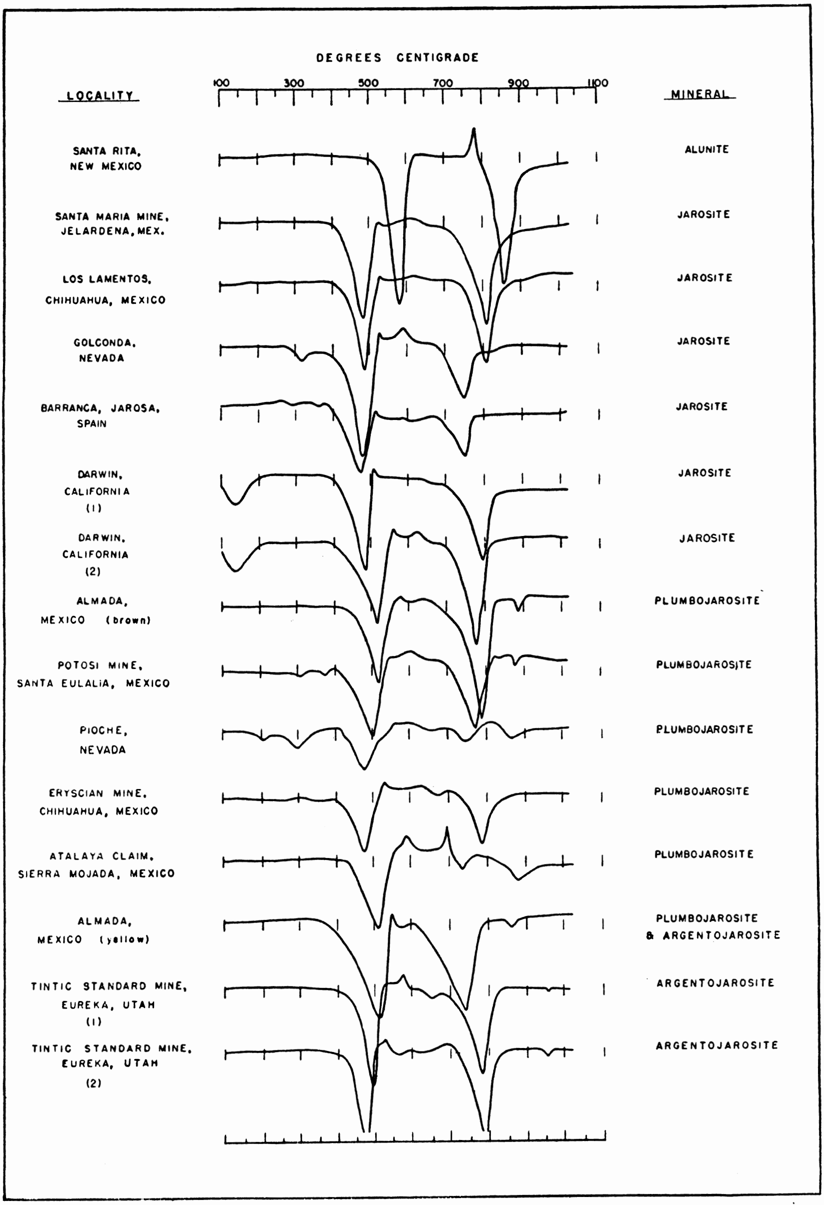

Figure 1. Differential thermal curves of alunite and jarosite specimens.

is surrounded octahedrally by four hydroxyl groups and two oxygen atoms of sulfate groups. Potassium has a coordination number of twelve, and is surrounded by oxygen and hydroxyl groups. The linkage is such that a loss of OH would cause complete decomposition of the structure, and then considerable rearrangement must take place in order to form hematite, ferric sulfate, or other possible residual products.

Fink, Van Horn and Pazour (1931) heated alunite for long periods at various constant temperatures and studied the products by means of X-ray diffraction. Alunite heated 18 to 48 hours from 250° C. to 500° C. gave only sharp lines characteristic of the mineral. Heating for 20 hours at 600° C. produced a diffuse pattern indicating a small amount of $K_2SO_4 \cdot Al_2(SO_4)_3$, while heating for 13 hours at 700° C. gave sharp lines of the potassium aluminum sulfate. At 800° C. alpha-Al_2O_3 lines became evident as did some K_2SO_4 lines, but the potassium aluminum sulfate lines were absent. Heating further to 1000° C. and 1200° C. only sharpened the alpha-Al_2O_3 and K_2SO_4 lines.

The thermal curve of the alunite from Santa Rita, New Mexico (fig. 1) can be readily interpreted in terms of the chemical changes. It should be noted, however, that the dynamic differential heating method produces peaks at somewhat higher temperature than the static equilibrium method used by Fink *et al.* (1931).

The first large endothermic peak occurs at the point of destruction of the alunite lattice according to the equation $K_2[Al_3(SO_4)_2(OH)_6]_2 \xrightarrow{550^\circ \text{ C.}} K_2SO_4 \cdot Al_2(SO_4)_3 + 2Al_2O_3 + 6H_2O$. The X-ray pattern at 600° C. is diffuse but the faint lines of the alum salt, $K_2SO_4 \cdot Al_2(SO_4)_3$, are discernible. That amorphous alumina is present at this stage is confirmed by the fact that the solution velocity in strong alkali of the mass heated to 600° C. is greater than that of alunite heated to any higher or lower temperature and results in practically complete recovery of alumina. As the temperature is increased to 700° C. the alum crystallization continues and gives sharper X-ray lines while the alumina remains in the amorphous state. The differential thermal curve reveals that the exothermic alpha-Al_2O_3 recrystallization is abrupt and immediately precedes the decomposition, $K_2SO_4 \cdot Al_2(SO_4)_3 \rightarrow K_2SO_4 + Al_2O_3 + 3SO_3$.

Above the second large endothermic peak there is little change in the structure, but crystal growth continues with increasing temperature. Presumably the heat effect of the crystallization of the Al_2O_3 produced as a result of the decomposition of the alum salt at 800° C. is incorporated into the general endothermic peak.

The thermal history of jarosite from the Santa Maria mine is similar but not strictly analogous to that of alunite. While the structure of the two minerals is essentially the same, the chemical reactions that ensue upon heating are different. The destruction of the lattice occurs about 100° C. lower in jarosite than in alunite. This is probably due to the OH-Fe bond being weaker than the OH-Al bond, which behavior is suggested by the large ionic radius of Fe^{+3} (0.67A°) as compared to Al^{+3}(0.57A°). The decomposition reaction is similar to that of alunite, *i.e.*, $K_2[Fe_3(SO_4)_2(OH)_6]_2 \xrightarrow{460^\circ \text{ C.}} K_2SO_4 \cdot Fe_2(SO_4)_3 + 2Fe_2O_3 + 6H_2O$ with one significant difference that, whereas the amorphous alumina does not recrystallize until about 780° C., the Fe_2O_3 produced in this decomposition is crystallized directly after the destruction of the jarosite lattice. This is reflected by the small exothermic peak at about 500° C. immediately following the endothermic decomposition. While this small sharp exothermic peak is observable on the Santa Maria mine specimen, it is more clearly developed in most of the other curves. Material heated to the end of the endothermic reaction and cooled quickly gave a diffuse X-ray diffraction pattern indicating the presence of hematite and $K_2SO_4 \cdot Fe_2(SO_4)_3$. Heating the product of the initial decomposition at 500° C. for 17 hours produced sharper lines but otherwise left the pattern unchanged. K_2SO_4 and $Fe_2(SO_4)_3$ were intimately mixed in a 1:1 molecular ratio and heated at 580° C. for several hours. The pattern produced matched the non-hematite lines in the decomposed jarosite. Since the iron oxide had crystallized by 600° C., no further reaction was observed prior to the second decomposition which appeared at about 700° C., *i.e.*,

$$K_2SO_4 \cdot Fe_2(SO_4)_3 \xrightarrow{700^\circ \text{ C.}} K_2SO_4 + Fe_2O_3 + 3SO_3.$$

The X-ray diffraction pattern of material heated past the second endothermic peak showed only K_2SO_4 and hematite lines. That the endothermic reaction corresponding to the decomposition of $K_2SO_4 \cdot Fe_2(SO_4)_3$ occurs at lower temperatures than that for the $K_2SO_4 \cdot Al_2(SO_4)_3$ in alunite, is also consistent with the structural picture.

A similar experimental procedure with plumbojarosite from the Eryscian mine yielded slightly different results. The decomposition apparently is as follows:

$$Pb[Fe_3(SO_4)_2(OH)_6]_2 \rightarrow PbSO_4 + Fe_2(SO_4)_3 + 2Fe_2O_3 + 6H_2O.$$

The material submitted to X-ray diffraction after the first endothermic peak produced $PbSO_4$ and $Fe_2(SO_4)_3$ lines with an indication of diffuse hematite lines.

The double salt $PbSO_4 \cdot Fe_2(SO_4)_3$ probably does not form due to the difference in the structure of $PbSO_4$ (barite type) as compared with the K_2SO_4 type (Evans, 1939). The "holes" in the plumbojarosite structure resulting from divalent lead ions occupying only half of the possible potassuim ion positions, probably are an additional hindrance to the double salt formation.

At higher temperatures (700° C.) the $Fe_2(SO_4)_3$ breaks down into hematite and sulfur trioxide leaving a residue of Fe_2O_3 and $PbSO_4$ at 1000° C., which was confirmed by X-ray diffraction examination.

The argentojarosite (Tintic Standard mine) apparently decomposes in still another way. Due to the instability of Ag_2SO_4 at the temperature of argentojarosite decomposition, the following reaction is postulated:

$$2Ag_2[Fe_3(SO_4)_2(OH)_6]_2 \rightarrow 4Fe_2O_3 + 2Fe_2(SO_4)_3 + 4Ag + 12H_2O + 2SO_3 + O_2.$$

The loss of oxygen is expected as the decomposition temperature of Ag_2O is only 300° C. X-ray diffraction patterns of the material heated just past the first endothermic peak produced much more diffused lines than patterns taken after similar treatments to jarosite or plumbojarosite. Faint diffuse lines of hematite and $Fe_2(SO_4)_3$ were detected. No lines corresponding to Ag_2SO_4 were present. The absence of Ag_2SO_4 at 500° C. is indicated by two other facts. First, there is no other peak which would indicate the breakdown of Ag_2SO_4 up to its decomposition temperature at 652° C. Second, the corrosion of the nickel specimen holder is more intense than that observed after decomposing jarosite or plumbojarosite. This indicates the release of SO_3 in the presence of water vapor during the breakdown of the argentojarosite lattice.

Again at about 800° C. the $Fe_2(SO_4)_3$ decomposes into Fe_2O_3 and SO_3. The high temperature product in this case is primarily hematite and some metallic silver. The presence of this metal is shown by the endothermic peak at about 950° C. The melting point of pure silver is 960.5° C. It was found that this peak was reversible and that with each successive melting it lost some of its amplitude. This would occur if the silver gradually distilled into cooler parts of the apparatus.

From this information it is to be expected that the ammonio- and natrojarosite thermal curves will show similar characteristics. The $(NH_4)_2SO_4$ produced in the ammoniojarosite decomposition should volatilize immediately, leaving again hematite and $Fe_2(SO_4)_3$. The ammoniojarosite curve should therefore resemble the argentojarosite curve minus the 950° C. endothermic dip.

The natrojarosite may more closely resemble potassium jarosite in its thermal history, Na_2SO_4 remaining at 1000° C. Whether a double salt $Na_2SO_4 \cdot Fe_2(SO_4)_3$ would form is questionable. While the Na_2SO_4 structure is more similar to that of K_2SO_4 than to $PbSO_4$, it is nevertheless different and that difference may be enough to make the double salt formation energetically unfavorable.

Natroalunite would be expected to follow the alunite decomposition pattern closely except again for the possible absence of double salt formation. The double salt formation has relatively little effect on the thermal curve since it decomposes at only slightly higher temperatures than pure aluminum sulfate. This can be ascribed to the displacement of the equilibrium,

$$K_2SO_4 \cdot Al_2(SO_4)_3 \leftrightharpoons K_2SO_4 + Al_2(SO_4)_3 \leftrightharpoons K_2SO_4 + Al_2O_3 + 3SO_3.$$

THERMAL ANALYSIS CURVES

The thermal curves of the specimens studied in the temperature range 100-1000° C. are shown in figure 1. Table 1 gives the summary of the critical chemical and X-ray data.

The curve of the Santa Rita, New Mexico alunite has been fully discussed in the foregoing section. The jarosite from the Santa Maria mine gives a thermal curve with no evidence of foreign constituents. Chemical analysis indicates a trace of lead which does not appear to affect the thermal curve to any appreciable extent. The high-purity jarosites show at least

TABLE 1

Locality	***Mineral*** (based on X-ray data)	*Chemical Data*				
		Pb	*Ag*	*K*	*Al*	*Fe*
Santa Maria mine, Jelardena, Mex.	Jarosite	trace	X	major	X	major
Los Lamentos, Chihuahua, Mex.	Jarosite	trace	X	major	X	major
Golconda,* Nevada	Jarosite	——	—	——	—	——
Barranca,* Jarosa, Spain	Jarosite	——	—	——	—	——
Darwin, (1) & (2) California	Jarosite	X	X	minor	—	major
Almada, (brown) Mexico	Plumbojarosite	major	trace	X	X	major
Potosi mine, Santa Eulalia, Mex.	Plumbojarosite	major	trace	X	X	major
Pioche, Nevada	Plumbojarosite	major	——	X	X	major
Eryscian mine, Chihuahua, Mex.	Plumbojarosite	major	X	X	X	major
Atalaya claim, Sierra Mojada, Mex.	Plumbojarosite	major	X	X	minor	major
Almada, (yellow) Mexico	Plumbojarosite and Argentojarosite	major	major	X	X	major
Eureka, (1) & (2) Utah	Argentojarosite	X	major	X	X	major

—— not determined
X not detected

* These specimens were subjected to X-ray examination during the course of previous investigations undertaken by Professor Paul F. Kerr and were used in this study for comparison purposes only.

two significant differences to the plumbojarosites. First, the initial decomposition begins at a slightly lower temperature, *e.g.*, most of the jarosite specimens start decomposition from 370-400° C., while practically all of the plumbojarosite and argentojarosite specimens start decomposing about 400° C. and above. A second difference is found in the temperature of the second endothermic peak. Here the jarosite is consistently higher, ranging from 810-820° C., in the high-purity specimens. The Golconda and Barranca specimens contain appreciable impurities as shown by X-ray patterns and the small amplitude of the thermal peaks. Plumbo- and argentojarosite give this high temperature endothermic peak about 780-790° C. It can also be seen that the latter minerals tend to start this final $Fe_2(SO_4)_3$ decomposition at a lower temperature. The double salt formed during the decomposition of jarosite apparently increases the stability of the ferric sulfate.

The Los Lamentos jarosite is similar to the Santa Maria specimen discussed above.

The Golconda and Barranca specimens yield typical curves. The $Fe_2(SO_4)_3$ decomposition peaks, however, occur at somewhat lower temperatures due to the presence of impurities. The Golconda specimen shows the presence of goethite in the 240° C. endothermic peak and may contain siderite along with some inert impurity.

The Darwin jarosite is not homogeneous. A sericite-like material is present which may produce the slight lowering of the high temperature endothermic peak.

The Almada plumbojarosite (brown) shows the presence of a small endothermic peak at 885° C. indicating a small amount of admixed argentojarosite. The X-ray diffraction pattern shows several faint lines of argentojarosite. It appears impossible to entirely separate this brown material from the yellow in hand specimen. The yellow material apparently contains a high percentage of argentojarosite.

The Potosi mine plumbojarosite has considerable impurities associated with it. The endothermic dips prior to the main decomposition are due to goethite and possibly some sulfide. The 875° C. endothermic peak is attributed to the melting of silver derived from the decomposition of admixed argentojarosite. The X-ray pattern of the Potosi specimen confirms the presence of argentojarosite.

The Pioche specimen appears to have considerable inert impurity, thus lowering the amplitude of the peaks. Some evidence of a clay mineral of the montmorillonite group is suggested. The high temperature peak is lowered due to dilution and the 863° C. peak may be the decomposition of a small quantity of $Al_2(SO_4)_3$, either derived from mixed alunite or substituted Al in Fe positions in the jarosite.

The plumbojarosite of the Eryscian mine appears to be of reasonable homogeneity and purity as indicated by X-ray and chemical information. This curve has already been discussed.

The plumbojarosite from the Atalaya claim is of considerable interest in that it is apparently a case of substitution of Al for Fe in the jarosite lattice. The X-ray diffraction pattern shows a shift in several strong lines toward the alunite spacings. An aluminum-substituted member of the jarosite group is to be expected on theoretical grounds but has not been previously reported. The chemical analysis indicates the presence of aluminum. The thermal curve can be interpreted most reasonably as that produced by an aluminum-substituted plumbojarosite. During the initial decomposition, amorphous Fe_2O_3, Al_2O_3, and crystalline $PbSO_4$, $Fe_2(SO_4)_3$ and $Al_2(SO_4)_3$ are formed. The Fe_2O_3 crystallizes at slightly higher temperatures to hematite and the amorphous Al_2O_3 goes over to alpha-Al_2O_3 at 692° C., followed rapidly by the ferric sulfate decomposition (733° C.). The final endothermic peak at 874° C. is presumably due to the final $Al_2(SO_4)_3$ decomposition.

The Almada, Mexico yellow material begins decomposing at a temperature near that of jarosite. The reason for this anomalous behavior lies in the extremely fine particle size of this specimen. X-ray patterns show the yellow material from Almada to be a mixture of plumbojarosite and argentojarosite in roughly equal concentrations. The small endothermic peak (950° C.) characteristic of the presence of metallic silver is also present. The two argentojarosite specimens from the Tintic Standard mine are similar and may be considered typical of the mineral.

In summary—the thermal characteristics of the jarosite group are such that the presence of thermally active or inactive impurities can be readily detected. Also, if the material is monomineralic, the particular member of the jarosite group is identifiable from the thermal curve. Furthermore, argentojarosite can be detected in intimate intergrowths by the presence of the 900-950° C. melting peak for silver. The potassium jarosite differs from the lead and silver varieties by having a lower temperature for the initiation of the lattice destruction and a higher temperature for the second endothermic peak.

SUBSTITUTION

Theoretically a number of possibilities exist for substitution in the jarosite group. The structure is composed of three main cation positions which in ordinary jarosite are occupied by potassium, iron, and sulfur. The possible replacements based on ionic radii (Palache *et al.*, 1944) are shown in table 2.

TABLE 2

Potassium position		Iron position		Sulfur position	
Ion	Ionic Radii	Ion	Ionic Radii	Ion	Ionic Radii
*Na^{+}	0.98 A°	*Fe^{+3}	0.67 A°	*S^{+6}	0.29 A°
*K^{+}	1.33	*Al^{+3}	0.57	*P^{+5}	0.34
**Rb^{+}	1.48	Cr^{+3}	0.65	As^{+5}	0.47
*Ag^{+}	1.20	Co^{+3}	0.65		
*Pb^{+2}	1.32				
Sr^{+2}	1.18				
Ba^{+2}	1.36				
Ca^{+2}	1.01				
Au^{+2}	1.37				
Hg^{+2}	1.11				
**Ce^{+3}	1.10				

* These cations form known jarosite-alunite minerals.

** These cations form synthetically prepared jarosites (Fairchild, 1933).

The wide range of ionic radii possible in the potassium position is attributed to the relative openness of the structure.

The extent to which substitution is found in these minerals will be determined in large measure by the geochemical environment present during their formation regardless of the substitution theoretically possible. As Hendricks (1937, p. 783) points out, "There is no explanation in the structure for the observation that the various minerals are usually found free of extensive isomorphous replacement."

In this study none of the samples indicates substitution for the sulfate group by either phosphate or arsenate. The substitution of aluminum for iron has been indicated in the specimen from the Atalaya claim and may be present in the Pioche specimen to a lesser extent. No other substitution has been demonstrated. It is entirely conceivable, however, that a chromium jarosite could be formed, if a unique combination of potash-iron-acid-bearing solutions passed through a chromite deposit. The probability of such an unusual set of conditions is so small that it accounts for the absence of this mineral. Complete substitution in the potassium positions by other cations gives rise to the various jarosite minerals. It is interesting to note that analyses in the literature seldom reveal the presence of more than one of the potassium position cations in a single specimen. In the present study partial substitution of silver or lead in jarosite, or of silver in plumbojarosite, and lead in argentojarosite, has not been observed. The one or two plumbojarosite specimens that do give evidence for the presence of silver probably contain a small quantity of argentojarosite. The striking absence of substitution is evident from X-ray diffraction patterns in the case of the yellow material from Almada, Mexico. Since both argentojarosite and plumbojarosite are indicated the most reasonable interpretation is the existence of two generations. Because of the low temperature of formation and relative insolubility in dilute acids, it is to be expected that once jarosite has formed in one geochemical environment, any change in the composition of the solutions with regard to the potassium-substituting cation (either Ag or Pb) will not rework the member already formed but simply deposit the new member. Apparently this is the case with the Almada material and may be the situation in the Potosi specimens. In view of the relative solubilities and the sources of lead-bearing as against potash-bearing solutions, it is not too likely that potassium and lead would be present in roughly equal concentrations at the time of formation of the jarosite mineral. As long as the concentrations differed by as much as a 1:20 ratio no appreciable substitution would be detected by inspection of thermal curves or X-ray patterns.

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