**A NEW OCCURRENCE OF AMMONIOJAROSITE IN BUFFALO, WYOMING**

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**ABSTRACT**

Ammoniojarosite \( \text{NH}_4\text{Fe}_3(\text{OH})_6(\text{SO}_4)_2 \) has been discovered in a new locality near Buffalo, Wyoming. Comparison of the chemical and X-ray data for the Buffalo specimens with data from literature sources has led to the design of a quick and easy method for the identification of ammoniojarosite that distinguishes it from the more common members of the family: jarosite, natrojarosite, and hydronium jarosite.

*Keywords*: ammoniojarosite, Buffalo, Wyoming, new locality, X-ray-diffraction analysis.

**SUMMARY**

On signale un nouveau gîte d'ammoniojarosite \( \text{NH}_4\text{Fe}_3(\text{OH})_6(\text{SO}_4)_2 \) près de Buffalo (Wyoming). A la suite d'une étude comparative des données chimiques et diffractométriques portant sur les échantillons récoltés avec les données de la littérature, on propose une méthode facile et rapide pour distinguer l'ammoniojarosite des minéraux de la même famille: jarosite, natrojarosite et jarosite à hydronium.

*(Traduit par la Rédaction)*

*Mots-clés*: ammoniojarosite, Buffalo (Wyoming), nouveau gîte, analyse par diffractométrie.

**INTRODUCTION**

Ammoniojarosite was first reported in samples collected near Wamsutter, Wyoming (Erickson 1922). The ammoniojarosite occurs as a pale yellow, powdery coating associated with tschermitite veinlets and as discrete isolated nodules within blackish brown lignite shale (Erickson 1922). It was identified as ammoniojarosite on the basis of its chemical composition and similarity to jarosite.

Shannon (1929) described an ammoniojarosite from southern Utah. Chemical analyses of this sample yield 4.23 weight % \( \text{NH}_4 \text{O} \), in contrast to the 1.25 % \( \text{NH}_4 \text{O} \) in the Wamsutter sample. The theoretical formula for a pure ammoniojarosite is \( \text{NH}_4\text{Fe}_3(\text{OH})_6(\text{SO}_4)_2 \); it contains 5.43 % \( \text{NH}_4\text{O} \). Shannon (1929) believed that the Wamsutter material was a partially ammoniated jarosite rather than a true end-member. The exact location for the Utah sample was never precisely defined. The samples were originally collected by Mr. Frank Haycock of Panguitch, Utah, who decided not to disclose their exact location in view of the site's possible economic value.

Erd et al. (1964) reported the possible existence of ammoniojarosite as one mineral in a group of accessory minerals associated with the newly discovered ammonium aluminosilicate mineral buddingtonite. These minerals are thought to have been derived from the alteration of pre-existing rock by hot springs rich in ammonia at the Sulphur Bank quicksilver mine, Lake County, California (Erd et al. 1964).

One recent ammoniojarosite find in the United States comes from a lignitic black to brown shale within the Wasatch Formation of Eocene age near Buffalo, Wyoming. The outcrop is exposed in a northeast-southwest-trending roadcut on Interstate 90 about 3.7 km southeast of the junction of I-90 with U.S. Highway 16, in the NE \( \frac{1}{4} \) of the SE \( \frac{1}{4} \), sec. 5, T. 50 N., R. 81 W. Ammoniojarosite was found only on the northeast side of the highway and lies about 150 m south of an area slightly altered by the burning of the Wolters coal bed of Maple (1959).

The ammoniojarosite at this locality is found as an earthy, pale ocherous yellow powder coating on selenite crystals. The selenite crystals occur as vertical fracture-filling material within the shale. The Buffalo ammoniojarosite was compared with a sample of the Utah deposit, obtained from the U.S. National Museum, and their physical appearance is essentially identical. A sample from the Wamsutter, Wyoming, site could not be obtained for this study, but Shannon (1929) indicated that hand specimens from the Wyoming and Utah sites could not be distinguished from each other.

* Deceased
Fig. 1. SEM photograph of ammoniojarosite, showing its general habit (10,000x).

PHYSICAL AND OPTICAL PROPERTIES

The Buffalo ammoniojarosite occurs as aggregates of extremely fine grains; optical data were thus difficult to obtain. However, it was determined to be uniaxial negative, showed high birefringence, and had the following indices of refraction: \( \omega \ 1.800 \pm 0.005, \epsilon \ 1.750 \pm 0.005. \) Crystal habit of the individual grains is either rhombohedral or prismatic (Fig. 1). Because several different habits are present in any one photograph, the variable \( \text{NH}_4 \) content is probably not related to morphology.

UNIT-CELL PARAMETERS AND X-RAY-DIFFRACTION DATA FOR THE AMMONIOJAROSITE

The unit-cell parameters for the ammonio-jarosites listed in Table 1 were determined from their powder-diffraction reflections. A collodion mount (Gude & Hathaway 1961) of the ammoniojarosite mixed with quartz as an internal standard was run twice for reproducibility on a diffractometer from low 2\( \theta \) angles to high (12° to 70°) and then from high to low (70° to 12°). The scan was 0.5° 2\( \theta \)/min, recorded at 0.5° 2\( \theta \)/2.54 cm on the chart recorder. Other machine parameters include a high-intensity X-ray tube with a copper target and a graphite monochrometer giving CuK\( \alpha \) radiation. The resulting hand-measured 2\( \theta \) values were entered into the van Trump & Hauff (1978) version of the computer program for least-squares refinement of unit-cell parameters of Appleman & Evans (1973). X-ray powder-diffraction data from the literature cited on

| TABLE 1. THE RELATIONSHIPS BETWEEN CELL EDGES, CELL VOLUME, AND PERCENT \( \text{NH}_4 \) PRESENT FOR AMMONIOJAROSITES |
|---|---|---|---|
| Unit-cell parameters (in Ångströms) | Chemistry (percent \( \text{NH}_4 \)) | Locality | References |
| \( a \) | \( c \) | Volume | \( \text{NH}_4 \) | |
| 7.300±0.007 | 17.100±0.039 | ----- | 1.25 | Wamsutter, Wyo. | Sabine & Trelil (1960); Erickson (1922) |
| 7.310±0.001 | 17.250±0.033 | 797.46 | 2.93 | Kaineb, Utah | Shannon (1928) |
| 7.325±0.001 | 17.479±0.004 | 3.44 | Synthetic | Dutrizac & Karmann (1976) |
| \( 7.33\pm0.001 \)* | \( 17.389±0.004 \)* | \( 809.39 \)* | ---- | Synthetic | Smith & Lemper (1973) |
| \( 7.33\pm0.001 \)* | \( 17.500±0.038 \)* | 813.60 | 3.0 | Synthetic | *Value calculated is that given in the reference that would ideally satisfy the formula. |
| \( 7.33\pm0.001 \)* | \( 17.448±0.006 \)* | \( 811.48 \)* | \( 3.76 \text{ calc} \)* |
| \( 7.32\pm0.004 \) | 17.468±0.009 | 799.90 | 2.69 | Buffalo, Wyo. | Odam et al. (this study) |

*Values in parentheses were refined by computer program from the powder-diffraction data in the literature; the data reported for the Wamsutter, Wyoming, sample would not refine.

**Value calculated is that given in the reference that would ideally satisfy the formula.

Lodders (-----) indicate no data.
1.7 t.9 r.9 a.o

AMMONIOJAROSITE IN WYOMING


Figure 2. Computer plot of X-ray-diffraction pattern of selected specimens of ammoniojarosite. These patterns were generated using the program, XRDPLT (van Trump & Hauff 1977). 1. Specimen 800025, NH$_4$ 2.69\%, a 7.260(4), c 17.488(9) Å. 2. Specimen 800026, NH$_4$ 3.0\%, a 7.328(1), c 17.448(6) Å. 3. Specimen 800023, NH$_4$ 3.44\%, a 7.330(1), c 17.390(4) Å. 4. Specimen 800022, a 7.334(1), c 17.344(7) Å. 5. Specimen 800021, NH$_4$ 4.23\%, a 7.310(1), c 17.250(3) Å. 6. Specimen 800020, a 7.300(7), c 17.100(39) Å.

Figure 2 were also run through the program and refined where possible. The difference in $a$ values from from Table 1 is 0.063 Å; that for $c$ is 0.385 Å. These ranges indicate an insignificant variation with substitution along the $a$ dimension but a significant one in the $c$ direction.

X-ray-diffraction analysis was also used to characterize the ammoniojarosites. Powder data were obtained from the various samples used in this study and compared to those in the literature with the objective of deriving a simple and quick means of identifying the ammoniojarosites. These data with $hkl$ annotations have been computer-plotted as a function of intensity and $2\theta$ position (Fig. 2). This plot is produced on mylar and becomes the desired rapid identification tool.

As the ion in the $M$ position increases in size, the unit-cell dimension along the $c$ axis also increases. However, direct correlations of chemical versus X-ray data are potentially com-
plicated by the ease with which these ions, Na⁺, H₃O⁺, K⁺, and NH₄⁺, can substitute for one another within the monovalent position. H₂O⁺ substitution for ammonia may account for the deficiency in the ammonia content in several of the synthetic samples (Smith & Lampert 1973, Dutrizac & Kaiman 1976). Although not clearly documented, most likely this substitution also occurs in natural species. The X-ray patterns showing broad, ill-defined peaks suggesting poor crystallinity can be considered as an indicator of potential structural deterioration.

Figure 3 is a plot of the data in Table 1. Unfortunately, some of the chemistry of the samples in the study is questionable. Shannon (1929) believed that the percentage of NH₄ found in his analysis of the Wamsutter sample was too low to classify it as a true ammoniojarosite. The only other chemical and X-ray analysis of ammonia-bearing jarosite found in the literature was that of Kubis (1964). He reported an NH₄ content of 3.46% [adjusted from 5.34% (NH₄)₂O], cell parameters c 16.76 a 7.03 Å. These data are anomalous and would place this species closer to a Na⁺-H₂O⁺-bearing jarosite relative to the jarosites plotted in Figure 3. An NH₄⁺ species with that chemistry would, from Figure 3, possess a c axis somewhere between 17.30 and 17.40 Å. Obviously, more chemical and X-ray data must be added to this plot before definitive conclusions can be drawn.

**Identification of Ammoniojarosite**

Identification of the minerals of the jarosite group has become more important with their increased use in metallurgical processes (Dutrizac & Kaiman 1976). X-ray-diffraction analysis appears to be an efficient means of identifying the various phases in the solid-solution series, of which the main constituents are sodium, hydronium, potassium and ammonium. Table 2 compares the crystallographic parameters and atomic radii of the main members of the group.

The correlation of increasing radius with increasing length of the c unit-cell edge is quite apparent. This relationship manifests itself in the X-ray-diffraction pattern through 1) variable intensities of peaks common to each species, 2) shifts in the 2θ positions of these mutual peaks, and 3) the appearance or disappearance of common peaks as the chemistry varies.

This variation in an X-ray reflection with chemistry is used to advantage in the chart shown in Figure 2, which is a computer plot of diffraction data for ammoniojarosite generated from the program XRDPLT (van Trump & Hauff 1977). The differences among all the jarosites are subtle, but careful use of the major strong lines of the diffraction pattern can differentiate, not only between the species in the series, but also potentially among the phases bearing the same cation. After this approximation has been used, then chemical analysis should be performed for more specific identification.

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REFERENCES


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