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Zaherite, a new hydrated aluminum sulfate

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Abstract

Zaherite, $Al_{12}(SO_4)_5(OH)_{26}\cdot 20H_2O$, is a new hydrated aluminum sulfate from the Salt Range, Pakistan. It is a pearly, white, extremely fine-grained massive mineral. Aggregate hardness = 3.5, density = 2.007. Well-developed cleavage in one direction, probably basal, is seen in electron micrographs. Zaherite is anisotropic with extremely low birefringence (<0.001). Index of refraction is 1.4981 ± 0.0001. The X-ray powder pattern is dominated by an intense reflection between 15.5 and 18.1 A; all other reflections (3.22, 4.61, 4.58, 4.56 A) have $I/I_0 = 8$ or less. Zaherite hydrates and dehydrates reversibly at room temperature with a corresponding increase and decrease in the most intense reflection. It transforms to α- and γ-alumina between 900° and 1000°C.

Introduction

M. A. Zaher (1969, unpublished M.S. thesis, Michigan Technological University), in his investigation of clays from the Salt Range, Pakistan, presented X-ray powder diffraction data for a mineral that he postulated to be a new hydrated aluminum silicate or oxide, largely because of mineral associations and resemblance of powder data to some clay minerals. The physical and chemical data obtained in our study show that the material is a previously undescribed hydrated aluminum sulfate mineral. Zaherite is proposed as its name. The name recognizes its discoverer, M. A. Zaher, of the Geological Survey of Bangladesh. The new mineral and name have been approved by the Commission on New Minerals and Mineral Names, IMA.

Geologic setting

At the type locality in the Salt Range, Pakistan, zaherite is associated with kaolinite, boehmite, and aluminite. Here, zaherite is found both in relatively pure form as veinlets (up to 1 cm across) that cut massive kaolinite–boehmite rock and intimately mixed with kaolinite and boehmite in a massive white claystone. Aluminite is also found as veinlets in the vicinity. The details of geology at the type locality are not known. However, the rocks are related to the unconformity over Permian rocks in the Salt Range.

Physical properties

Zaherite in fairly pure form was found as densely packed aggregates of extremely small grains. Scanning electron micrographs (Fig. 1), show well-developed cleavage in one direction. Zaherite is white and has a pearly to earthy luster. Aggregate hardness is about 3.5. Density is 2.007, as determined with a gas pycnometer.

Zaherite is anisotropic with extremely low birefringence. A faint gray interference color is seen only on very thick grains. Birefringence is estimated to be less than 0.001. One of the indices of refraction was determined by the oblique illumination-color fringing technique to match oil and mineral. The refractive index of the oil was measured immediately with an Abbe refractometer. The index of refraction is 1.4981 ± 0.0001.

Chemical analysis

A chemical analysis of zaherite was kindly furnished by Mr. D. Rose, Analytical Chemist, Institute

Table 1. Chemical analyses of zaherite

SiO_2	0.63
Al_2O_3	37.79
MgO	0.01
CaO	0.09
Na_2O	0.03
K_2O	0.01
H_2O	36.55
CO_2	0.00
SO_3	24.87
P_2O_5	0.02
Total	100.00

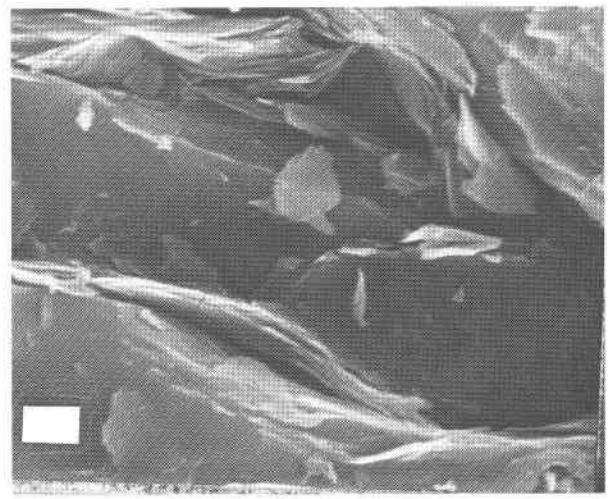

Fig. 1 Scanning electron micrograph of zaherite. Bar is 1 micron in length.

Table 2. X-ray powder data* for zaherite

1. As Received		2. Dehydrated**		3. Hydrated***	
d,Å	I/I0	15.8	100	18.1	100
17.9	100				
12.6	2				
11.9	2				
9.5	5			9.6	5
9.1	4			9.1	3
6.1	1				
5.3	3				
4.82	5	4.81	1	4.85	4
				4.80	4
4.61	7			4.60	4
4.58	7				
4.56	7	4.51	6	4.50	2
4.44	4				
4.27	3				
4.14	3				
4.08	1				
4.03	1				
3.87	1				
3.55	6			3.60	4B
3.51	3				
3.46	3				
3.44	3				
3.22	8	3.29	8	3.22	5
3.10	1				
3.06	1				
3.02	1				
2.888	1				
2.612	1				
2.579	2				
2.339	1				
1.618	1				
1.608	2				

*All data obtained with CrKα, λ = 2.2909 Å
**Dessicated at 20°C for 188 hours
***Hydrated for 50 hours over saturated $Pb(NO_3)_2$

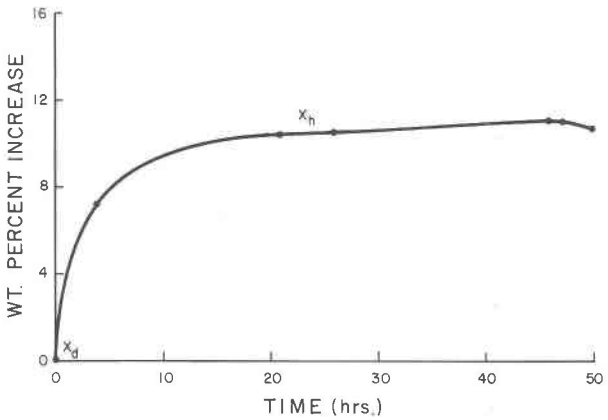

Fig. 2 Hydration curve for zaherite.

of Mineral Research, Michigan Technological University. The analysis, Table 1, represents the average of two analyses. The essential constituents are Al_2O_3, SO_3, and H_2O; all other are contaminants. The ideal formula was calculated to be $6Al_2O_3 \cdot 5SO_3 \cdot 33H_2O$, or $Al_{12}(SO_4)_5(OH)_{26} \cdot 20H_2O$.

X-ray powder diffraction data

X-ray powder diffraction data for zaherite were obtained with a General Electric XRD-6 recording diffractometer, using vanadium-filtered chromium radiation. Peak intensities were measured with a scale-counter by using pre-set time for 10^4 counts. The powder data for zaherite, as received, are given in Table 2, column 1. The data are dominated by one major reflection at 17.9 A; all other reflections have relative intensities of 8 or less. Generally, the reflections tend to be broad, indicating poor crystallinity.

Zaherite hydrates and dehydrates reversibly at room temperature in response to humidity. To test the limits of hydration–dehydration, samples of zaherite were first dessicated for 188 hours at 21°C. X-ray powder data for the dehydrated sample are given in Table 2, column 2. Following dessication, samples were allowed to hydrate for 50 hours at 21°C over a saturated solution of lead nitrate.[1] X-ray powder diffraction data for the fully hydrated sample are listed in Table 2, column 3. During hydration, a standard sample was periodically weighed. A graph showing weight gain with time is shown in Figure 2. Most weight gain was recorded during the first 10–12 hours. The total weight gain was 10.8 percent.

Reactions at elevated temperatures

A differential thermal analysis was obtained with a Stone apparatus, using a heating rate of 20°C per minute. The differential thermogram is shown in Figure 3. The endothermic reactions are interpreted as follows:

200°C	—loss of hydrated water
360°C	—loss of hydroxyl
855°C, 890°C	—loss of SO_2

The loss of hydrated water is accompanied by a large sample shrinkage. Therefore, the intensity of endotherms at 360°, 855°, and 890°C are anomalously small.

If a slow heating rate is used, the hydrated water loss is complete at 150°C, and constant weight is attained. There is a corresponding decrease in the spacing of the most intense X-ray diffraction peak to 12.2 A. No rehydration took place after this treatment.

[1] To minimize the formation of water droplets.

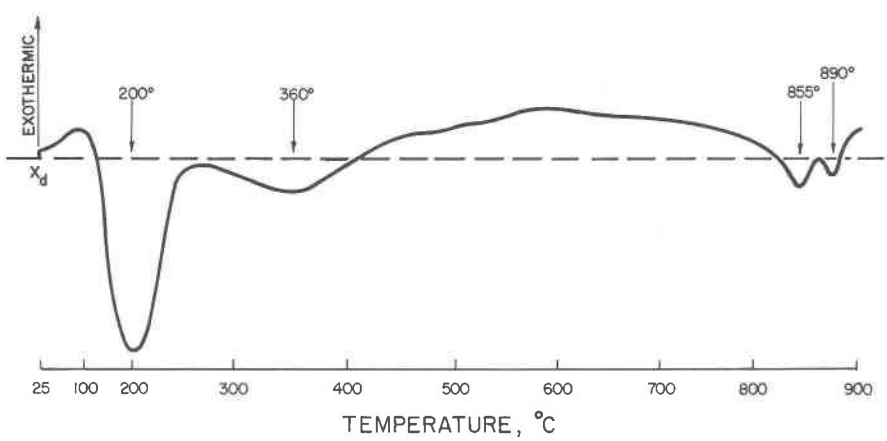

Fig. 3 Differential thermogram for zaherite.

Zaherite became amorphous to X-rays following the hydroxyl loss at 360°C. Between 900° and 1000°C, the amorphous form is transformed to a mixture of alpha and gamma alumina.

Conclusions

Cleavage, X-ray powder data, and hydration–dehydration characteristics of zaherite suggest a layered structure. Composition most nearly approximates aluminite, with which zaherite is associated. X-ray powder patterns of zaherite are not those generally found for sulfate minerals. Instead, peaks are somewhat broadened, sometimes asymetric and, except for the peak in the 15.5–18.1 A range, of low intensity. These suggest small crystallite size and poor crystallinity. It is possible that zaherite is an intermediate stage, perhaps metastable, in the formation of aluminite.

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