

Krautite, $\text{MnHAsO}_4 \cdot \text{H}_2\text{O}$ —an intracrystalline reactive mineral

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Abstract

Krautite is one of the few intracrystalline reactive minerals. Neutral molecules are intercalated between the $\text{Mn}(\text{OH}_2)\text{AsO}_3(\text{OH})$ layers and expand the lattice in the [010] direction. Best suited for lattice expansion are alkylamines. Long-chain alkylamines are aggregated to tilted bilayers between the $\text{Mn}(\text{OH}_2)\text{AsO}_3(\text{OH})$ layers. The basal spacings follow the relation $d_L = 13.4 + 1.93n(\text{Å})$ where n , the number of carbon atoms in the alkyl chain, varies from 3–18. From this result, a chain tilt of $\alpha = 50^\circ$ is derived, which is consistent with a close packing of the aliphatic chains.

Introduction

The layers of the 1:1 type clay mineral kaolinite can be separated by intercalation of neutral molecules (hydrazine, dimethylsulfoxide, urea, acid amides, pyridine-N-oxide, *etc.*; Weiss, 1961), and potassium acetate (Wada, 1961)). Intercalation reactions are of immediate interest in solid state chemistry, but the number of minerals acting as host compounds is extremely limited. Besides the kaolinite modifications dickite and nacrite, the only other intracrystalline reactive silicate mineral reported until now is silhydrite, a crystalline silicic acid (Gude and Sheppard, 1972; Lagaly *et al.*, 1975; Beneke and Lagaly, 1977). Krautite is the first reactive mineral (Fontan *et al.*, 1975) of a different chemical nature.

The layer structure of krautite is built up by (010) layers of AsO_4 and MnO_6 polyhedra that share edges and vertices (Fig. 1). Adjacent layers [composition: $\text{Mn}(\text{OH}_2)\text{AsO}_3(\text{OH})$] are related by the 2_1 operation and linked by hydrogen bonding only (Catti and Franchini-Angela, 1979).

Experimental

Synthetic krautite was used in this study. The following procedure, which differs slightly from that described by Fontan *et al.* (1975), is recommended for preparing large amounts of sample. An aqueous suspension of MnCO_3 (0.5 moles in 70 ml H_2O) was added dropwise to a solution of arsenic pentoxide hydrate (0.25 moles $\text{As}_2\text{O}_5 \cdot 5/3 \text{H}_2\text{O}$ in 1.5 l H_2O). The decomposition of the carbonate required about 3 hours. After 12 hours the solution was separated from the brown residue, and the solvent was re-

moved in a rotary evaporator at 60°C . The crystalline material was washed four times with ethanol and dried at 100°C in *vacuo*. It consisted of rectangular plates of about 2–4 μ in diameter (Fig. 2), which were very suitable for intracrystalline reactions. The X-ray powder pattern was identical with that reported by Fontan *et al.*

Amines were intercalated into krautite by direct reaction at 65°C for several hours. The formation of the intercalates was documented by X-ray powder diffractometry. In instances when guest molecules did not show any degree of reaction after several hours, the reaction times were extended up to several weeks.

The layer distance (basal spacing d_L) was taken from the (0k0) reflections (basal reflections). With increasing layer distance, the basal reflections became more intense. They were very strong after alkylamine intercalation.

Intercalation

Alkylamines R-NH_2 ($\text{R} = \text{alkyl} = \text{C}_n\text{H}_{2n+2}$, $n = 3, 4, 5 \dots 18$) expand the structure of krautite in a direction perpendicular to the (010) layers (Fig. 1). The large molecules increase the basal spacing d_L linearly with the number n of carbon atoms in the alkyl chain according to the relationship: $d_L = 13.4 + 1.93n(\text{Å})$.

The alkylamine derivatives of krautite are more stable than those of most of the other host compounds. They can be washed several times with ethanol without removing large amounts of amines from the interlayer spaces. The stability indicates a prefer-

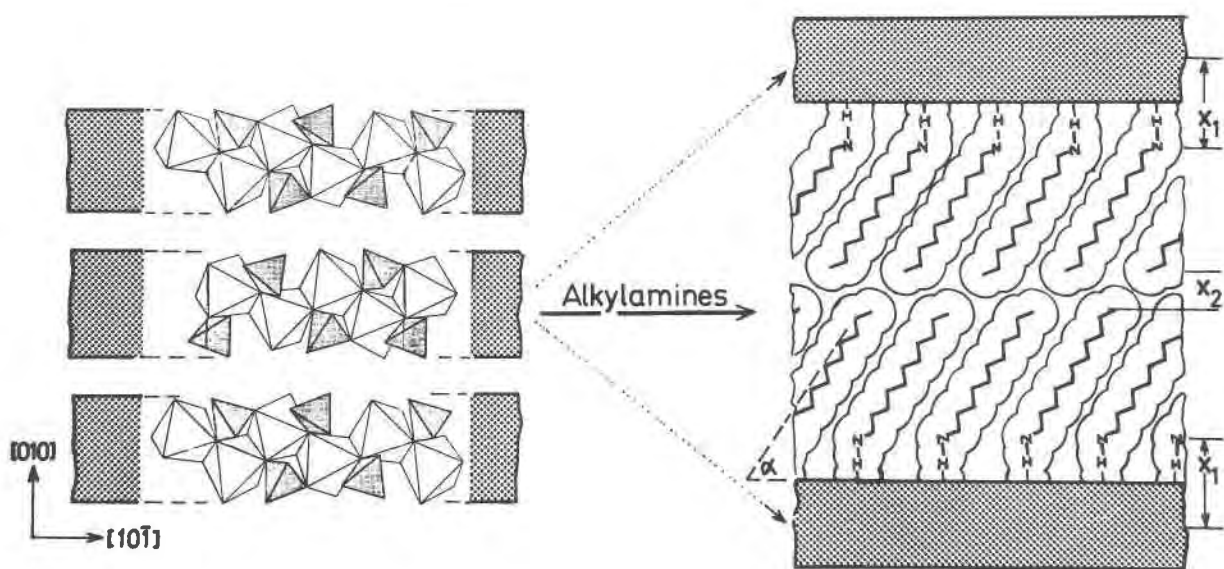


Fig. 1: Alkylamine intercalation into krautite: (a) layer structure of krautite; (b) alkylamine bilayers between the Mn(OH₂)AsO₃(OH) layers.

ential aggregation of the alkylamine molecules between the Mn(OH₂)AsO₃(OH) layers.

Single crystals of krautite disintegrate into powder after alkylamine intercalation. However, the interlayer structure can be deduced from the basal spacings measured on powdered materials. The observed mean increase of the spacings, $\Delta d_L/\Delta n$, is 1.93 Å. Alkyl chains oriented perpendicular to the layers give $\Delta d_L/\Delta n = 1.27$ Å. Therefore, $\Delta d_L/\Delta n = 1.93$ Å indicates that the chains are arranged in bimolecular layers (Fig. 1b) and are tilted at an angle of $\alpha = 50^\circ$ (from $1.93/2 \cdot 1.27 = \sin\alpha$). The interlayer structure is similar to the structure of neutral amine complexes

of vermiculite and montmorillonite. The fully extended amine molecules in the bilayers are inclined at about 65° to the silicate layers and the NH₂-groups are closely associated with pairs of surface oxygen atoms (Brindley, 1965).

Comparing the general equation for the basal spacings (Fig. 1, bond lengths N-C \approx C-C)

$$d_L = 2x_1 + x_2 + 2n\sin\alpha$$

with the relation observed

$$d_L = 13.4 + 1.93n$$

gives $2x_1 + x_2 = 13.4$ Å. Inserting $x_2 \approx 3$ Å (a mean value of the end-group distance in bimolecular films), $2x_1$ becomes 10.4 Å. As a result the distance (N—H...O) of the nitrogen atoms from the surface oxygen atoms is at least 2.4 Å: the amine group is bound to one surface oxygen atom only. On surfaces of silicates, amine groups are attached by two or even three hydrogen bonds to two or three surface oxygen atoms. This requires distinct distances (about 4.6 Å) between the surface oxygen atoms (*cf.* Fig. 3, Lagaly and Weiss, 1970a, and Fig. 16, Lagaly, 1979). The arrangement of the surface oxygen atoms of the Mn(OH₂)AsO₃(OH) layers permits the bonding of —NH₂ by one hydrogen bond only. If the N—H—O—bonds are nearly perpendicular to the layers, the chain tilting angle α is about 55° , which is in good agreement with $\alpha = 50^\circ$ observed.

The increase of the interlayer volume with n ($\Delta V/\Delta n = 1.93 \text{ a c s i n } \beta = 104 \text{ \AA}^3$) is four times the in-

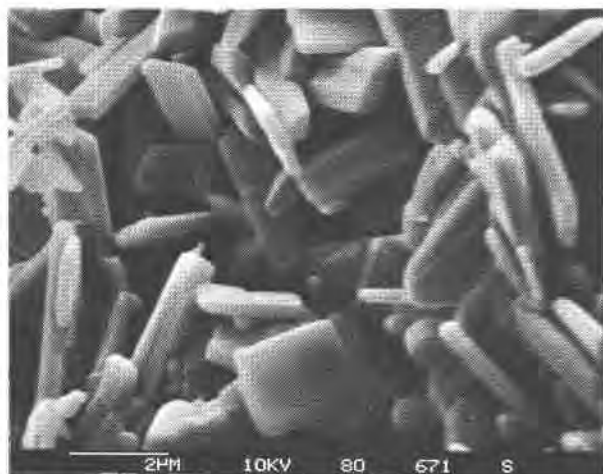


Fig. 2: Scanning electron microscope photograph of synthetic krautite (Institute of Geology of the University of Kiel).

crement for a methylene group in liquid long-chain alkylamines ($\Delta V/\Delta n \approx 26\text{\AA}^3$). Therefore, four alkylamines are intercalated per unit cell, one alkylamine per unit $\text{Mn}(\text{OH}_2)\text{AsO}_3\text{OH}$. (Analytical data: krautite: $\text{As}/\text{Mn} = 0.98$, n-decylamine krautite: $\text{Mn}/\text{As} = 1.0$, $\text{C}/\text{Mn} = 38$).

Four alkyl chains per unit cell arranged in bilayers with $\alpha = 90^\circ$ are not close-packed (area per chain: $ac/2 = 27\text{\AA}^2$). Closer van der Waals contacts are achieved by tilted chains (Lagaly and Weiss, 1970b, Lagaly, 1976). At a titling angle $\alpha \approx 50^\circ$, the chain packing density reaches the maximum value ($20\text{--}21\text{\AA}^2/\text{chain}$). Thus, the stability of the alkylamine intercalates results from (1) the direct interaction of one alkylamine molecule with one unit $\text{Mn}(\text{OH}_2)\text{AsO}_3\text{OH}$, (2) the chain orientation, which enables the bonding of each NH_2 group by one hydrogen bond to each $\text{Mn}(\text{OH}_2)\text{AsO}_3\text{OH}$ unit, and (3) the formation of close-packed tilted bilayers.

Besides n-alkylamines, a large number of other amines are intercalated. Table 1 gives selected examples which illustrate the influence of substitutions. In the case of butylamine derivatives the spacings are smaller as a result of the different packing of the end groups (denting of the chains). Substitution of $-\text{CH}_2-$ by $-\text{O}-$ also reduces the interlayer thickness by an amount ($1.4\text{--}1.6\text{\AA}$) that exceeds the chain shortening

due to the shorter C–O bonds (C–O = 1.43, C–C = 1.54 \AA). The overshortening is tentatively attributed to conformational changes in the chains (kinks or other gauche-trans sequences, Lagaly, 1976) which adapt the chain packing to the smaller volume of the ether group.

Conclusion

The $\text{Mn}(\text{OH}_2)\text{AsO}_3\text{OH}$ layers of krautite can be separated by intercalation of organic molecules. Only molecules with donator groups for hydrogen bonds are intercalated. Most of these molecules are amines, and acid-base reactions of the type



may be of decisive influence. In this way, krautite reacts very differently from kaolinite. Kaolinite does not intercalate alkylamines in direct reaction, but intercalates small molecules with high dipole moments and with acceptor and donator groups for hydrogen bonds. Such molecules include dimethylsulfoxide (DMSO), acetamide, formamide (FA), N-methylformamide (NMFA), urea, methyl and ethyl ureas, etc. (Weiss *et al.*, 1966). Most of these molecules are not intercalated by krautite in direct reaction.

The different behavior results from the different type of bonding between the layers (pronounced dipole-dipole interactions in addition to hydrogen bonds between the kaolinite layers) on one hand, and the increased acidity of surface OH groups with the possibility of acid-base reactions on the other. Due to their intracrystalline reactivity and the driving force for intercalation, krautite and kaolinite represent the end members according to the scheme in Table 2.

Surface acidities of $\text{pK}_a < 7$ enable the direct intercalation of alkylamines. However, there is no general relation between basicity, surface acidity, and intercalation (Lagaly, 1979).

In contrast to kaolinite, the increased surface acidity of krautite ($4.9 < \text{pK}_a < 6.8$) enables the exchange of OH-protons by metal cations in aqueous solution. The exchange capacity increases with pH, reaching, for example, 0.5 moles of sodium ions per mole krautite at $\text{pH} = 6\text{--}7$. The beginning decomposition at $\text{pH} \approx 8$ affects the quantitative exchange.

Noted that the reactivity with long-chain alkylamines provides a specific, sensitive, and simple method for detecting traces of krautite in a manner similar to that used for clay minerals (Lagaly, 1981).

Table 1: Alkylamine intercalates of krautite

Alkylamine	basal spacing of krautite (\AA)
$\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{NH}_2$	21.2
$\text{CH}_3 - \underset{\text{CH}_3}{\text{CH}} - \text{CH}_2 - \text{CH}_2 - \text{NH}_2$	19.8
$\text{CH}_3 - \underset{\text{OH}}{\text{CH}} - \text{CH}_2 - \text{CH}_2 - \text{NH}_2$	19.0
$\text{CH}_3 - \underset{\text{OCH}_3}{\text{CH}} - \text{CH}_2 - \text{CH}_2 - \text{NH}_2$	20.1
$\text{CH}_3 - \text{CH}_2 - \underset{\text{NH}_2}{\text{CH}} - \text{CH}_3$	17.7
$\text{CH}_3 - \text{CH}_2 - (\text{CH}_2)_3 - \text{NH}_2$	22.4
$\text{CH}_3 - \text{O} - (\text{CH}_2)_3 - \text{NH}_2$	20.8
$\text{CH}_3 - (\text{CH}_2)_3 - \text{CH}_2 - (\text{CH}_2)_3 - \text{NH}_2$	28.8
$\text{CH}_3 - (\text{CH}_2)_3 - \text{O} - (\text{CH}_2)_3 - \text{NH}_2$	27.4

Table 2: Intracrystalline reactivity of intercalating minerals

interaction between the layers	kaolinite	silhydrite and crystalline silicic acids		krautite
	hydrogen bonds + dipole - dipole interactions	$H_2Si_{14}O_{29} \cdot 5H_2O$	$H_2Si_2O_5$	hydrogen bonds
surface acidity	$pK_s > 7$	$pK_s < -3$	$pK_s = 2-3$	$pK_s = 4.9 - 6.8$
direct intercalation of alkylamines	-	+	+	+
of DMSO	+	+	±*	-
of NMFA	+	+	±*	-
of urea	+	+	-	-

* depending on the modification of $H_2Si_2O_5$

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