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Konyaite, $Na_2Mg(SO_4)_2 \cdot 5H_2O$, a new mineral from the Great Konya Basin, Turkey

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Abstract

Konyaite, $Na_2Mg(SO_4)_2 \cdot 5H_2O$, a new mineral found in the Great Konya Basin, Turkey, is associated with one or more of the following minerals: bloedite, hexahydrite, gypsum, starkeyite, halite and loeweite. Synthetic single crystals of konyaite are transparent, euhedral prismatic with a platy habit flattened on {010} and elongated parallel to {10$\bar{1}$}. The mineral is monoclinic, $P2_1/c$, with a = 5.784(3), b = 24.026(9), c = 8.066(3)Å, β = 95.37(3)°, Z = 4. Strongest lines in the X-ray powder pattern are: 12.01(40)(020), 4.541(100)(12$\bar{1}$), 4.202(40)(121), 4.017(45)(002), 3.960(45)(012), 2.597(45)(240). D (meas.) of synthetic konyaite is 2.088(6) g/cm^3; D(calc.) is 2.097 g/cm^3. Konyaite is biaxial (−); refractive indices α = 1.464(1), β = 1.468(1) and γ = 1.474(1); 2V = 74(2)°, 2V(calc.) = 79°; $\alpha \parallel b$; $\gamma \Lambda c$ = 70(2)°. Konyaite is metastable with respect to bloedite. DTA–TG curves show four endotherms at about 80, 92, 124 and 237° C due to dehydration. In addition a small exotherm is present at about 325° C. The name is for the locality.

Introduction

The new mineral konyaite was first observed on X-ray powder patterns during a study of salt minerals from the Great Konya Basin in Turkey. After subtraction of the diffraction lines of the associated minerals, 37 distinct lines remained that could not be matched with any of the minerals in the Powder Diffraction File of the JCPDS. Further study on synthetic material proved these lines to belong to a single crystalline phase. In this context it should be stressed that due to the minute size of the konyaite crystals and the intimate intergrowth with associated minerals all the data and most of the crystallographic data are derived from analyses of synthetic material. The new mineral is named konyaite ('kòn-yä-īt) after the type locality which is in the Great Konya Basin in Turkey along the road from Ereğli to Niğde near the village of Çakmak. Type material is deposited at the National Museum of Geology and Mineralogy, Hooglandse Kerkgracht 17, Leiden, The Netherlands. As this mineral is metastable with respect to bloedite, it is to be expected that it will change to bloedite with time. The description and the name were approved by the Commission on New Minerals Names IMA, prior to publication.

Occurrence

Konyaite has been found in salt efflorescences on saline soils in the Great Konya Basin in Turkey. This basin is situated on the Central Anatolian Plateau at an altitude of about 1000 m and is filled mainly with saline clayey marl soils (de Meester, 1970).

The basin is bordered on the north by the Anatolides, consisting of Paleozoic schists and igneous rocks covered by Mesozoic limestones. Devonian and Permocarboniferous limestones and schists and Cretaceous limestones and ultrabasic rocks form its southern border. Volcanics of Miocene, Pliocene and Quaternary age, varying in composition from basic to acidic, occur in and around the basin. Most rivers flowing into the basin, which has no natural outlet, come from the Taurus mountains.

Salts originate at the soil surface by evaporation of ground and surface waters. These salts consist mainly of sulphates and chlorides of sodium and magnesium (Vergouwen, 1981). Konyaite occurs in the efflorescences in the following assemblages: konyaite, gypsum, hexahydrite, bloedite; konyaite, bloedite, halite, starkeyite; konyaite, bloedite, gypsum, halite; konyaite, gypsum, hexahydrite; konyaite, loeweite, hexahydrite.

Chemical composition and synthesis

Because most minerals which occur in association with konyaite contain Na_2SO_4 and/or $MgSO_4$ and semi-quantitative tests proved Na, Mg and SO_4 to be essential it was considered likely that konyaite

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also contains these components. It was found that konyaite could be synthesized by evaporation of a solution containing Na_2SO_4 and $MgSO_4$ in a molar ratio of 1:1 in a watch-glass at a temperature between 30 and 50° C. In this manner a white powder consisting of pure konyaite was formed. Below 30° C, thenardite, epsomite and sometimes mirabilite formed in addition to konyaite. Above 50° C loeweite and bloedite formed in addition to konyaite. Well-shaped crystals of konyaite (maximum size about 3 × 0.5 × 0.02 mm) formed from evaporation of a saturated solution at 35° C using a second larger watch-glass as a cover glass. White powdery salt consisting of pure konyaite formed on the rim of the watch-glass, and transparent single crystals formed in the center. The chemical analysis of synthetic konyaite is given in Table 1. Na and Mg were analyzed by means of atomic absorption spectrometry; SO_4 by means of gravimetric analysis and the water content was determined with TG. The average of two analyses leads, after normalization to 100% and on the basis of O = 8, to the empirical formula $Na_{2.03}Mg_{1.01}(SO_4)_{2.00}\cdot 5.02H_2O$ or ideally $Na_2Mg(SO_4)_2\cdot 5H_2O$.

Chemical stability

Konyaite is a very unstable mineral. It was identified in the samples taken from the Konya Basin within three months after sampling. Two years later in some samples konyaite was still present but in others it could no longer be identified. Powdered synthetic konyaite decomposed not only by further heating at the temperature of synthesis, but also at room temperature. In both cases it transformed, at least partly, to bloedite in a few days. Unground samples transformed more slowly. The large single crystals did not transform after six months. In addition, powdered samples of synthetic konyaite were altered when placed in desiccators at room temperature with 0, 20, 50 and 80% relative humidity respectively. After six weeks all desiccators contained samples which were completely or partly transformed to bloedite. It can be concluded that konyaite is metastable with respect to bloedite at room temperature. Grain-size is an important factor in this transformation.

Table 1. Chemical analyses of synthetic konyaite

	1	2	3	4
Na	13.06	13.14	13.10	13.05
Mg	6.99	6.89	6.94	6.90
SO_4	53.93	54.14	54.04	54.51
H_2O	25.25	25.63	25.44	25.54
Total	99.23	99.80	99.52	100.00

1,2: synthetic konyaite (wt.%).
3 : average of 1 and 2.
4 : theoretical $Na_2Mg(SO_4)_2\cdot 5H_2O$.

X-ray crystallography

The X-ray powder diffraction data for both natural and synthetic konyaite were obtained with a Guinier camera, equipped with a Johansson monochromator, $CoK\alpha_1$ X-radiation and corundum as internal standard. The complete data, including the calculated *d* values and indices, are listed in Table 2. The *d* values of natural konyaite and synthetic konyaite agree well. Refinement of the X-ray powder diffraction data of synthetic konyaite using the computer program of Visser (1969) shows that konyaite is monoclinic with unit-cell parameters $a = 5.784(3)$, $b = 24.026(9)$, $c = 8.066(3)$Å and $\beta = 95.37(3)°$. Refinement of the X-ray powder diffraction data of natural konyaite leads to $a = 5.786(3)$, $b = 24.029(9)$, $c = 8.060(3)$Å and $\beta = 95.38(3)°$. In addition, the unit-cell parameters were determined for synthetic konyaite using rotation, precession and Weissenberg X-ray photographs. These also show that konyaite is monoclinic. The unit-cell parameters, after transformation, are $a = 5.79(1)$, $b = 24.04(2)$, $c = 8.07(1)$Å and $\beta = 95.4(2)°$. Extinctions of $l \neq 2n$ for $h0l$ reflections and $k \neq 2n$ for $0k0$ reflections uniquely determine the space group as $P2_1/c$. The complete crystallographic data are listed in Table 3.

Optical and physical properties

Konyaite is optically biaxial negative; the refractive indices are $\alpha = 1.464(1)$, $\beta = 1.468(1)$ and $\gamma = 1.474(1)$; 2V = 74(2)° and 2V(calc) = 79°; the orientation is $\alpha \parallel b$ and $\gamma \wedge c = 70(2)°$. The hardness (Mohs) is estimated to be 2.5; konyaite is readily soluble in water. The average density measured on six different rosettes of konyaite (≃ 10 mg each) by the heavy-liquid method, using a mixture of bromoform and phthalic acid dibutyl ester, is 2.088(6) g/cm^3, in excellent agreement with the calculated value of 2.097 g/cm^3 on the basis of Z = 4.

Table 2. X-ray powder diffraction data for konyaite

Natural+	Synthetic		d_{calc}**	hkl
d_{obs}	d_{obs}	I/I_o*		
12.00	12.01	40	12.013	020
7.610	7.621	8	7.616	011
	6.005	<2	6.007	040
5.756	5.759	4	5.759	100
5.662	5.674	4	5.671	031
5.192	5.195	4	5.193	120
4.809	4.806	15	4.810	041
			4.803	11$\bar{1}$
	4.677	<2	4.675	130
4.539	4.541	100	4.539	12$\bar{1}$
4.413	4.409	35	4.409	111
4.199	4.202	40	4.202	121
4.179	4.180	20	4.181	13$\bar{1}$
4.014	4.017	45	4.015	002
4.005	4.002	20	4.004	060
3.957	3.960	45	3.960	012
	3.916	<2	3.913	131
	3.797	4	3.798	14$\bar{1}$
3.592	3.592	20	3.594	141
			3.589	032
	3.448	6	3.449	10$\bar{2}$
3.431	3.434	6	3.432	15$\bar{1}$
3.413	3.413	20	3.414	11$\bar{2}$
	3.337	10	3.338	042
3.314	3.315	6	3.315	12$\bar{2}$
3.282	3.278	10	3.279	151
3.156	3.156	15	3.158	102
			3.156	071
3.129	3.130	15	3.131	112
	3.101	4	3.101	16$\bar{1}$
3.079	3.080	8	3.081	052
2.988	2.988	20	2.991	14$\bar{2}$
			2.987	161
	2.937	8	2.938	132
	2.881	<2	2.879	200
	2.855	<2	2.859	210
	2.834	8	2.835	062
2.812	2.812	8	2.813	081
			2.812	17$\bar{1}$
2.800	2.801	20	2.802	15$\bar{2}$
			2.800	220
	2.778	10	2.776	21$\bar{1}$
	2.724	15	2.726	171
			2.722	22$\bar{1}$
2.710	2.710	4	2.710	230
2.659	2.659	40	2.663	180
			2.660	013
2.637	2.639	40	2.639	152
			2.639	23$\bar{1}$
	2.611	4	2.613	023
			2.613	16$\bar{2}$
			2.609	072
	2.597	45	2.596	240
	2.572	4	2.572	221
	2.558	<2	2.561	18$\bar{1}$
	2.532	<2	2.534	24$\bar{1}$
			2.533	091
	2.504	<2	2.505	11$\bar{3}$
			2.501	231
2.479	2.479	4	2.480	162
	2.469	<2	2.470	250
			2.466	12$\bar{3}$
	2.443	<2	2.445	043
			2.438	21$\bar{2}$
2.432	2.432	8	2.433	17$\bar{2}$
	2.415	6	2.416	25$\bar{1}$
			2.412	241
2.402	2.402	20	2.405	082
			2.403	13$\bar{3}$
			2.403	0.10.0
			2.402	22$\bar{2}$
	2.337	20	2.338	260
			2.338	053
			2.334	113
2.323	2.323	8	2.324	172
			2.323	14$\bar{3}$
	2.309	<2	2.309	251
	2.300	<2	2.302	123
			2.302	0.10.1
	2.270	2	2.269	24$\bar{2}$
	2.250	<2	2.250	133

Plus 66 observed lines to 1.468A with $I/I_o \leq 10$.

+ Lines not resolved from lines of associated minerals are omitted.

* Intensities estimated visually.

** Calculated on basis of monoclinic cell with a=5.784, b=24.026, c=8.066A and β=95.37°.

Thermal analysis

The thermal analyses were performed with a Du Pont 990 Thermal Analysis System using a DSC-cell and a 951 thermal balance. About 15 mg of powdered synthetic konyaite was weighed in an aluminum sample pan covered with a pierced lid. Al_2O_3 was used as reference material. DTA and TG were carried out in an atmosphere of static air with a heating rate of 5° C/min and temperature ranging from room temperature to 375° C. The DTA and TG curves are shown in Figure 1. The DTA curve is characterized by four endotherms and one small exotherm. From several analyses it appears that the peak temperature of the first endotherm varies. The peak temperatures of the four endotherms are 80±10° C, 92±4° C, 124±3° C and 237±2° C respectively. The peak of the exotherm is at 325±2° C.

The TG and DTA curves show that all endo-

Table 3. Crystallographic data for konyaite

	Synthetic*	Synthetic**	Natural**
a(A)	5.79(1)+	5.784(3)	5.786(3)
b	24.04(2)	24.026(9)	24.029(9)
c	8.07(1)	8.066(3)	8.060(3)
β	95.4(2)	95.37(3)	95.38(3)
V(A^3)	1118(2)	1116.0(5)	1115.7(5)

Crystal system: Monoclinic
Space group: $P2_1/c$
Cell contents: 4 $Na_2Mg(SO_4)_2 \cdot 5H_2O$
Density(calc): 2.097 g/cm^3
Density(meas): 2.088(6) g/cm^3

* From single-crystal techniques.
** From refinement of X-ray powder diffraction data.
\+ Estimated standard deviations in parentheses refer to the last decimal place.

therms are due to dehydration. The weight losses after the three dehydration steps (there are actually four, but the first two are not well resolved) are 4.90, 9.25 and 11.29% respectively. The first two percentages agree well with the theoretical weight loss of 5.11 and 9.48% for the transition of konyaite to bloedite and the transition of bloedite to loeweite respectively, which were identified as intermediate products. The last two endotherms are due to dehydration of bloedite and this part of the dehydration curve is in agreement with the result of the thermal study of bloedite by Madsen (1966). The X-ray powder patterns of the crystalline products before and after the exotherm are different. Both patterns could not be matched with any pattern in the Powder Diffraction File of JCPDS.

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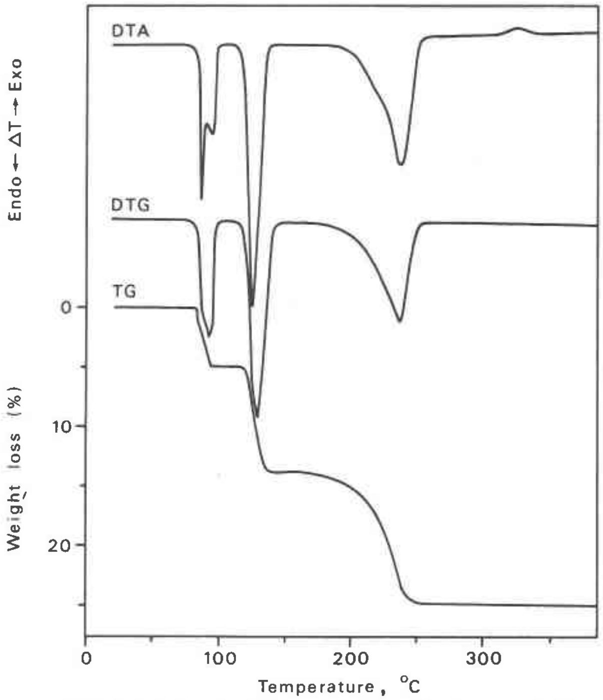

Fig. 1. TG, DTG and DTA curves of synthetic konyaite in an atmosphere of static air. Heating rate: 5° C/min

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