

Eugsterite, a new salt mineral

LIDEKE VERGOUWEN

*Department of Soil Science and Geology
Agricultural University, Duivendaal 10
Wageningen, The Netherlands*

Abstract

Eugsterite, $\text{Na}_4\text{Ca}(\text{SO}_4)_3 \cdot 2\text{H}_2\text{O}$ is a new salt mineral. It occurs in different parts of Kenya and in the Konya Basin in Turkey. It is associated with one or more of the following minerals: halite, thenardite, bloedite, gypsum, glauberite and nesquehonite. Eugsterite is monoclinic, $\beta = 116^\circ$. The strongest X-ray diffraction lines are (d in Å (intensity)): 9.20 (39), 5.50 (64), 4.50 (33), 3.454 (32), 3.428 (100), 2.763 (25), 2.746 (46), 1.7126 (61). It forms clusters of thin fibers. Refractive indices $1.492 \leq \alpha, \beta, \gamma \leq 1.496$; birefringence = 0.004, $\gamma \parallel b, \beta^{\wedge}c = 27^\circ$.

Introduction

A salt mineral which showed an unknown X-ray diffraction pattern was discovered during a study of the mineralogy of saline soils in Kenya and Turkey. The same mineral was also found in salt efflorescences on bricks. The mineral is called "eugsterite" after Hans P. Eugster, The Johns Hopkins University, Baltimore, Maryland, who has extensively studied the origin and mineralogy of saline lakes. Type material is deposited at the National Museum of Geology and Mineralogy, Hooglandse Kerkgracht 17, Leiden, the Netherlands. The mineral and the name were approved by the Commission on New Minerals and Mineral Names, IMA, prior to publication.

Occurrence

Kenya

Salts of saline soils with efflorescences at the surface and groundwaters from which these salts have originated through evaporation have been sampled during the autumn of 1977 in some regions in Kenya (Vergouwen, Ph.D. thesis in preparation). Most salts belong to the group of sodium carbonates and the waters are mainly of the $\text{Na}-\text{CO}_3-\text{SO}_4-\text{Cl}$ - or $\text{Na}-\text{CO}_3-\text{Cl}$ -type (Eugster and Hardie, 1978). In some sample sites, however, the groundwaters are carbonate-poor and they are of the $\text{Na}-\text{SO}_4-\text{Cl}$ -type. The groundwaters of the places where eugsterite was found belong to this latter type (Fig. 1).

Eugsterite has been found in two different regions.

It is seen at two places along the shore of Lake Victoria, at Sindo and Luanda, where it is found as a surface mineral in association with thenardite and halite (Table 1). It is also found at Kalacha, Turkana district, east of the Chalbi Desert in the north of Kenya. There vast salt efflorescences occur and eugsterite is found in association with halite and thenardite.

Turkey

Salt samples were taken in the Konya Basin in Turkey during the summer of 1978. Groundwater samples were taken at the same sites. The Konya Basin is situated on the Central Anatolian Plateau about 300 km south of Ankara. This basin, a former lake formed during the Tertiary, consists of salt-affected clayey marl soils (de Meester, 1970). The basin is bordered in the north by paleozoic schists and igneous rocks covered by mesozoic limestones. The Taurus mountains form its southern border. They consist of ultrabasics, Devonian and Permian carboniferous limestones and schists and Cretaceous limestones. In and around the basin many Mio-Pliocene volcanoes of andesitic composition exist.

Several rivers flow into the basin, especially from the Taurus mountains. In the basin itself some thermal springs occur. The climate is semi-arid with cold moist winters and hot dry summers. The lowest parts are flooded in winter and when the surface water evaporates in summer vast salt crusts occur. In other parts of the basin which are not flooded, salts form at the surface through evaporation of the groundwater.

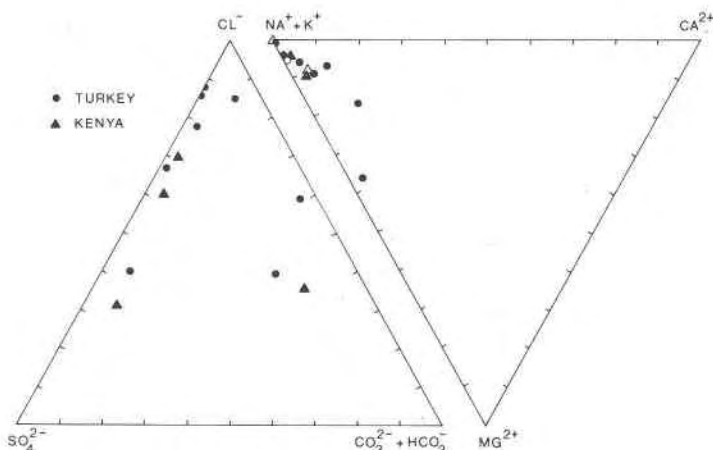


Fig. 1. Composition (mole %) of groundwaters at the localities where eugsterite has been found in the system Ca-Na+K-Mg-Cl-SO₄-HCO₃+CO₃ from the Konya Basin (Turkey) and from different regions in Kenya.

The salts in the basin are mainly sulphates and chlorides of sodium and magnesium. Sodium carbonates were found only at a few localities; these are devoid of eugsterite, which is commonly found in the other efflorescences. It occurs in the following associations: eugsterite, halite, thenardite; eugsterite, bloedite; eugsterite, halite, gypsum; eugsterite, halite, glauberite; eugsterite, halite, glauberite, thenardite, nesquehonite. This last association was found around the historical medicinal spring of Tiana. The analyses of the waters at the sites where eugsterite has been found are plotted in Figure 1. Type locality occurs at the playa northeast of the village of Karapinar which is situated along the main road from Konya to Eregli. In summer this playa is covered with a flinty white salt crust which consists of halite, thenardite and eugsterite.

Bricks

Eugsterite has been found in salt efflorescences on bricks of Dutch river clays in association with gypsum.

Chemical analysis

In order to determine the composition of eugsterite, since the minute amounts of material available precluded conventional chemical analysis, a preliminary investigation was made by DTA. A natural sample of eugsterite with thenardite and halite shows a sharp endothermic reaction between 165° and 185°. A Mettler TA 2000 B DTA apparatus was used. The reaction product contained glauberite so it seemed likely that eugsterite could be a sodium-calcium-sulphate-hydrate. In addition, qualitative analysis with an electron microscope equipped with an

energy-dispersive system established that Na, Ca and S are the major components. The mineral was synthesized, because the naturally-occurring eugsterite always occurs with other minerals and because the grain size was very small (Fig. 2).

Solutions of sodium sulphate and gypsum were evaporated on a water bath of 60°C and eugsterite formed in considerable amounts in solutions with a molar ratio Na/Ca > 4 together with thenardite and gypsum. Eugsterite did not form from the same solutions at room temperature. Thenardite and gypsum could be separated with a heavy liquid with $d = 2.50$. Eugsterite occurred both in the heavier fraction together with thenardite and in the lighter fraction together with gypsum because of its sticky character.

The tiny eugsterite fluffs were separated from the fraction with gypsum by handpicking under a binocular. The gypsum contamination of the samples (sample size approximately 1 mg) was determined with the aid of a DTA apparatus. These samples showed in addition to the large endothermic peak of

Table 1. List of minerals used in text

bloedite	$\text{Na}_2\text{Mg}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$
eugsterite	$\text{Na}_4\text{Ca}(\text{SO}_4)_3 \cdot 2\text{H}_2\text{O}$
glauberite	$\text{Na}_2\text{Ca}(\text{SO}_4)_2$
gypsum	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
halite	NaCl
hydroglauberite	$\text{Na}_{10}\text{Ca}_3(\text{SO}_4)_8 \cdot 6\text{H}_2\text{O}$
nesquehonite	$\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$
thenardite	Na_2SO_4

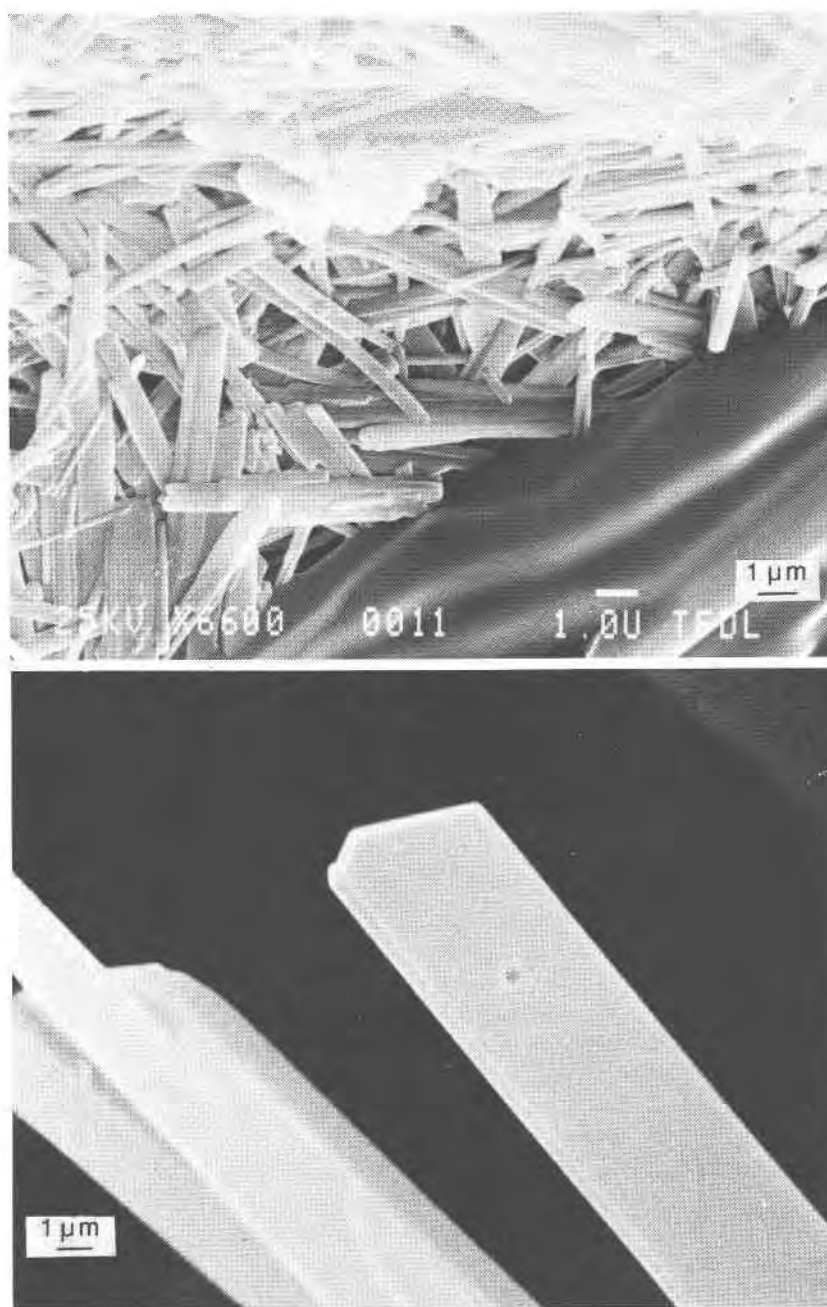


Fig. 2. (a) SEM picture of natural eugsterite together with halite; (b) Synthetic eugsterite needle indicating the monoclinic character.

eugsterite only very small negligible gypsum peaks. Na- and Ca-content of the samples were analyzed by atomic absorption. Sulphate could not be analyzed as well because of small sample size.

From the fraction of eugsterite with thenardite, weight loss after heating was determined with a TGA apparatus (Dupont TA 990). In this fraction all Ca and H₂O belongs to eugsterite so the H₂O/CaO ratio of eugsterite could be determined. These samples

were large enough to analyze sulphate as well. Sulphate was analyzed turbidimetrically. Results of an analysis are given in Table 2. Combination of these two sets of analyses leads to the ideal formula $\text{Na}_4\text{Ca}(\text{SO}_4)_3 \cdot 2\text{H}_2\text{O}$.

X-ray crystallography

The X-ray diffraction pattern (Table 3) was determined for synthetic material as these films were

Table 2. Chemical analyses of samples of synthetic eugsterite. The DTA samples contain a negligible amount of gypsum. The TGA samples contain thenardite

DTA samples	1	2	3
Na mmol	9.15×10^{-3}	9.0×10^{-3}	9.15×10^{-3}
Ca mmol	2.33×10^{-3}	2.25×10^{-3}	2.33×10^{-3}
Na/Ca	3.93	4	3.93

TGA samples	1	2
Na mmol	0.150	0.019
Ca mmol	0.0226	0.0045
SO ₄ mmol	0.10	0.0138
H ₂ O mmol	0.049	0.0087
H ₂ O/Ca	2.16	1.93

much less complicated than the films of the natural occurrences. Only the pattern of thenardite or gypsum had to be subtracted. The line positions of natural eugsterite agree exactly with those of synthetic eugsterite and comparison of many films showed no shift of lines at all.

It has not been possible to calculate the unit cell by means of the powder data. With a computer program (Visser, 1969) many solutions were obtained but none was very satisfactory. Efforts to grow larger crystals for a single-crystal analysis did not succeed.

Morphology, crystallography and physical and optical properties

The mineral forms clusters of thin fibers. The naturally-occurring fibers have a thickness of 0.5–1.5 μm and they are up to 40 μm long. The synthetic fibres are 2–6 μ thick and up to 200 μm long (measured on SEM pictures, see Fig. 2). The mineral is colorless and transparent, its hardness is very low and it is soluble in water. The density could not be measured due to its sticky nature. In the heavy liquid with $d = 2.50$ the upper fraction consists of mixtures of eugsterite and gypsum, whereas the lower fraction is composed of eugsterite and thenardite.

The SEM picture of the synthetic material shows the symmetry most probably to be monoclinic with $\beta = 116^\circ$. Optically it is biaxial, but the axial angle could not be determined on account of the fibrous habit. Refractive indices $1.492 \leq \alpha, \beta, \gamma \leq 1.496$; birefringence = 0.004, $n_\gamma \parallel b, \beta^c = 27^\circ$.

Table 3. X-ray diffraction powder pattern of synthetic eugsterite. Line positions measured by Dr. J. W. Visser at the Technisch Fysische Dienst at Delft using a Guinier camera with CuK_α1 radiation, $\lambda = 0.15406$ nm, and a special densitometer for Guinier films

d	I	d	I
12.62	1	1.9431	4
9.20	39	1.9291	2
6.32	4	1.9199	<1
5.96	1	1.9081	<1
5.50	64	1.8935	<1
5.35	1	1.8835	3
4.64	5	1.8494	5
4.60	5	1.8406	1
4.58	8	1.8313	5
4.50	33	1.8125	6
4.20	4	1.7998	4
3.860	7	1.7922	2
3.819	5	1.7648	1
3.622	3	1.7619	2
3.590	2	1.7273	3
3.454	32	1.7126	61
3.428	100	1.6999	4
3.233	4	1.6809	5
3.211	10	1.6632	6
3.150	4	1.6530	4
3.118	<1	1.6459	<1
3.065	15	1.6198	3
3.054	6	1.6053	2
2.973	2	1.5901	1
2.936	16	1.5829	2
2.893	8	1.5523	3
2.797	19	1.5418	<1
2.763	25	1.5318	<1
2.746	46	1.5234	<1
2.727	8	1.5148	2
2.671	13	1.5046	<1
2.545	5	1.4963	3
2.458	5	1.4645	1
2.291	5	1.4599	<1
2.284	2	1.4536	1
2.231	2	1.4293	2
2.214	2	1.4178	3
2.178	2	1.4021	2
2.170	<1	1.3869	1
2.158	<1	1.3820	<1
2.148	2	1.3654	1
2.132	2	1.3555	2
2.112	2	1.3470	<1
2.043	1	1.3353	3
2.013	7	1.3299	<1
1.9837	2	1.3234	2
1.9546	3		

Discussion

Eugsterite is a very common salt mineral which forms during evaporation of nonalkaline waters. The mineral is synthesized easily at 60° while at room

temperature it did not form. This may be an indication that it is a metastable mineral under natural circumstances.

Hydroglauberite is the only other known sodium-calcium-sulphate-hydrous mineral. However, the X-ray pattern of hydroglauberite differs essentially from that of eugsterite (Slyusareva, M.N., 1969). An unknown sodium-calcium-sulphate-hydrate, called phase X, has been found by L.A. Hardie, Johns Hopkins University, Baltimore, in Saline Valley and by R. C. Erd of the U.S. Geological Survey in the Death Valley salt pan associated with glauberite, thenardite and gypsum (both from L. A. Hardie, unpublished Ph.D. thesis, Johns Hopkins University). This mineral was not chemically analyzed, but Hardie assumed it to be the same as what is known as "labile salt", a synthetic double salt ($2\text{Na}_2\text{SO}_4 \cdot \text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) (Hill and Wills, 1938). No X-ray data are available for "labile salt". The X-ray powder diffraction pattern given to "labile salt" by Conley and Bundy (1959) is for thenardite, which is already noted by Braitsch (1971, p. 76). The line positions of the X-ray powder pattern of Hardie's phase X agree fairly well with that of eugsterite. There are, however, some differences in intensities. It is very probable that eugsterite is the same as Hardie's phase X and as "labile salt".

Acknowledgments

I thank Dr. Akira Kato, Drs. E. L. Meijer and Dr. L. van der Plas for their helpful suggestions, Mr. E. Velthorst, Mrs. A. Baas and Mr. J. D. J. van Doesburg for the chemical analysis, Mr. F. Thiel for operating the SEM and Dr. J. W. Visser for measuring the X-ray powder pattern. Miss A. Bouter typed the manuscript.

References

- Braitsch, O. (1971) Salt deposits, their origin and composition. Springer Verlag, Berlin.
- Eugster, H. P. and L. A. Hardie (1978) Saline Lakes. In A. Lerman, Ed., Lakes: Chemistry, Geology and Physics. Springer Verlag, New York.
- Hill, A. E. and Wills, J. H. (1938) Ternary Systems XXIV. Calcium sulfate, sodium sulfate and water. *Journal of the American Chemical Society* 60, 1647-1655.
- Meester, T. de (1970) Soils of the Great Konya Basin, Turkey. Pudoc, Wageningen, the Netherlands.
- Slyusareva, M.N. (1969) Hydroglauberite, a new mineral of the hydrous sulfate group. *Zapiski Vsesoioznogo Mineralogicheskogo Obschestva* 98, 59-62. (In Russian).
- Visser, J. W. (1969) A fully automatic program for finding the unit cell from powder data. *Journal of Applied Crystallography* 2, 89.

*Manuscript received, July 15, 1980;
accepted for publication, January 5, 1981.*