

Two new occurrences and the Gibbs energy of burkeite

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SUMMARY. Burkeite ($\text{Na}_6\text{CO}_3(\text{SO}_4)_2$) is found as a surface mineral in the north of Kenya associated with thenardite and halite and in the Konya basin in Turkey associated with trona and halite. The cell dimensions of a natural burkeite are $a = 7.070$, $b = 9.220$, $c = 5.173$ Å. The Gibbs energy of burkeite is estimated in relation to other sodium carbonates and sulphates. $\Delta G_{f,298.15}^\circ$ (burkeite) = 3594.2 ± 3 kJ.

TWO new occurrences of the salt mineral burkeite ($\text{Na}_6\text{CO}_3(\text{SO}_4)_2$) were found in Kenya and in Turkey as a surface mineral on saline soils. Up till now burkeite has only been found in Searles Lake California (Haines, 1957, 1959). There burkeite is found in a drillhole from a depth of 28 ft to 465 ft always associated with trona ($\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$) and in association with one or more of the following minerals: halite (NaCl), hanksite ($9\text{Na}_2\text{SO}_4 \cdot 2\text{Na}_2\text{CO}_3 \cdot \text{KCl}$), borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$), thenardite (Na_2SO_4), pirssonite ($\text{Na}_2\text{CO}_3 \cdot \text{CaCO}_3 \cdot 2\text{H}_2\text{O}$), gaylussite ($\text{Na}_2\text{CO}_3 \cdot \text{CaCO}_3 \cdot 5\text{H}_2\text{O}$), and northupite ($\text{Na}_2\text{CO}_3 \cdot \text{MgCO}_3 \cdot \text{NaCl}$).

Geological setting and paragenesis

a. Kenya. Burkeite was found during a sampling trip in summer 1977 in the north of Kenya along the eastern shore of Lake Turkana (the former Lake Rudolf) near the small village of Loiengalani. Most of the area east of the lake is covered with Miocene and Pliocene basalts. Some spectacular eruption centres can be seen.

Along the shore a lacustrine laminated clay loam occurs, which was deposited when the level of the lake was a few metres higher. In some places this impermeable clay is covered by a very permeable gravelly basaltic material. Water which infiltrates the gravelly basaltic material cannot penetrate the underlying clay and moves on the interface of the gravel and the clay. This water flowing down the surface of the clay evaporates and forms a salt crust. The salt crust consists of halite and thenardite. Around some cracks in the clay the salt looks

a bit more glassy. This salt contains burkeite. Scanning Electron Microscope pictures show rosettes of thenardite needles on burkeite. Halite occurs both in cubes and in patches with no crystalline form on burkeite and between the needles of the thenardite. Sometimes the thenardite needles are overgrown with a layer of halite. Fig. 1 is a SEM of pure burkeite from Kenya.

b. Turkey. In Turkey burkeite was found during a sampling trip in summer 1978 in the Konya basin, which is a lacustrine plain in Central Anatolia. The Uplands of the basin are mostly formed of limestone formations but in some places also of andesitic volcanics. In the basin itself some strato-volcanoes occur. The plain consists of salt-affected clayey marl soils. From the edges some alluvial fans spread into the basin. Huge areas are covered with powdery and crusty salt, especially near the lower edges of the alluvial fans. These salts are mainly chlorides and sulphates of sodium and magnesium, but in the centre of the basin near Ak Göl sodium carbonates can be found. This is the only place where the pH of the ground water was found to be higher than 8. Here burkeite was found associated with halite and trona. They form a white salt crust, which formed as a result of evapotranspiration and seals the surface.

Chemical analysis

Due to the small grain-size of the burkeite (a few micrometres measured on a SEM picture) and to its intimate intergrowth with other salt minerals, it is impossible to separate burkeite from its associated salt minerals. Therefore, no quantitative analysis could be performed and only some qualitative analyses have been made by means of an electron microscope equipped with an energy-dispersive system. In this way it was established that Na, S, and C are the major components.

Crystallographic properties

X-ray powder diffraction data of the natural burkeites were obtained with a Nonius Guinier

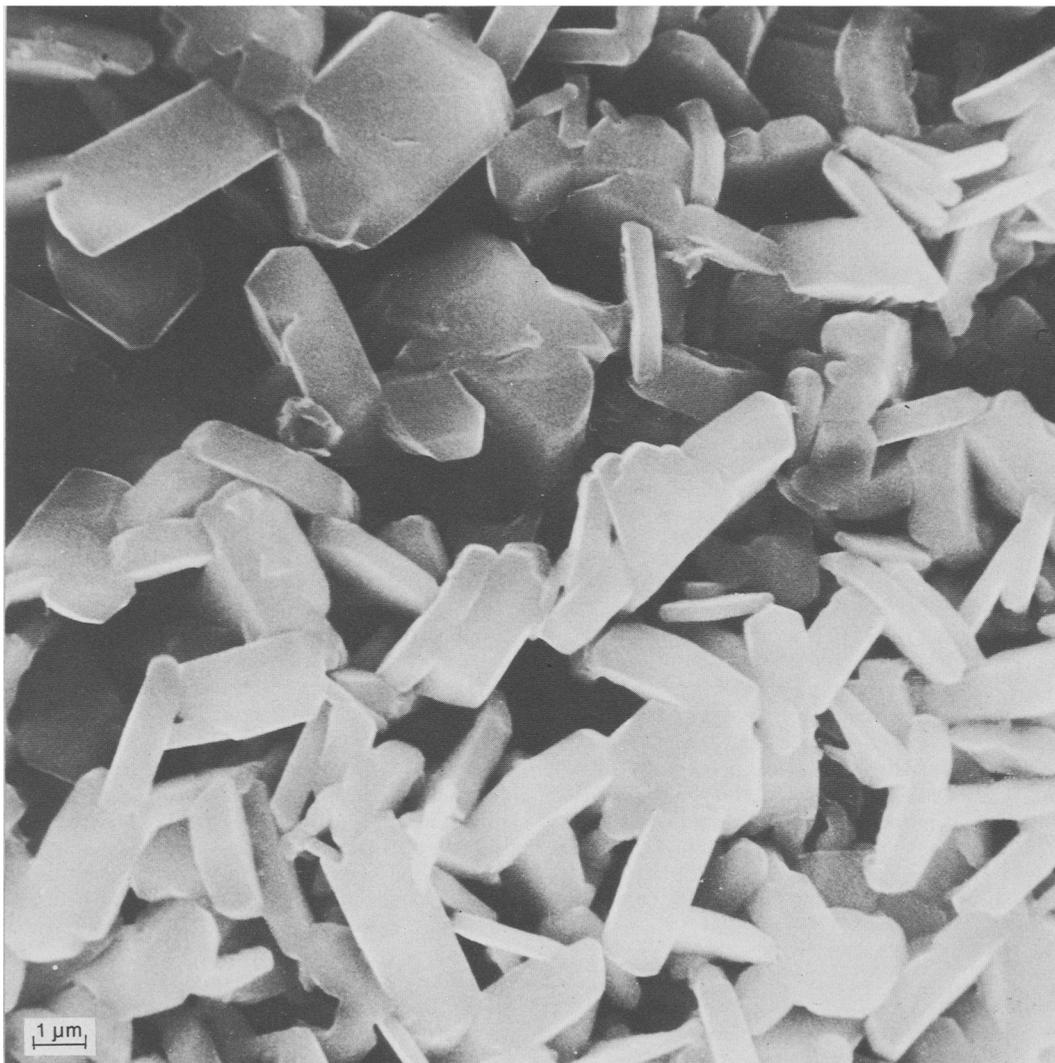


FIG. 1. Scanning Electron Micrograph of burkeite from Kenya (made by TFDL, Wageningen).

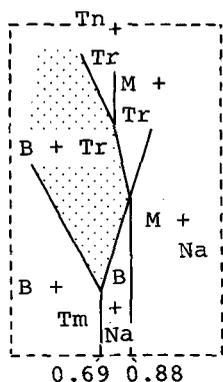
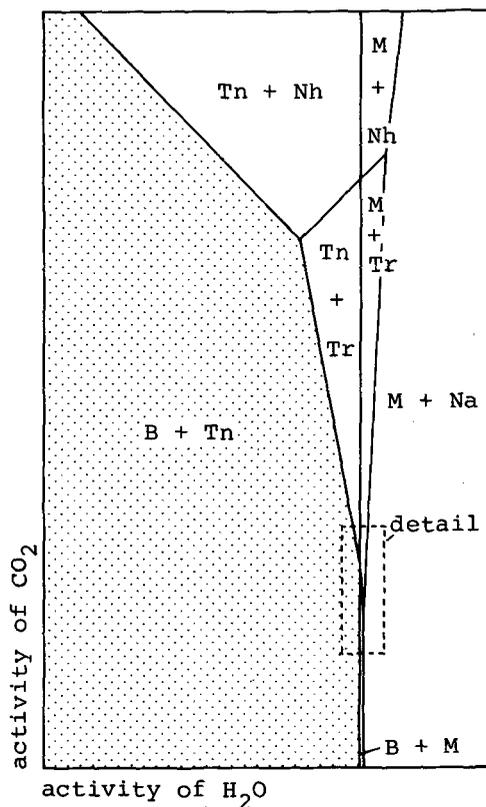
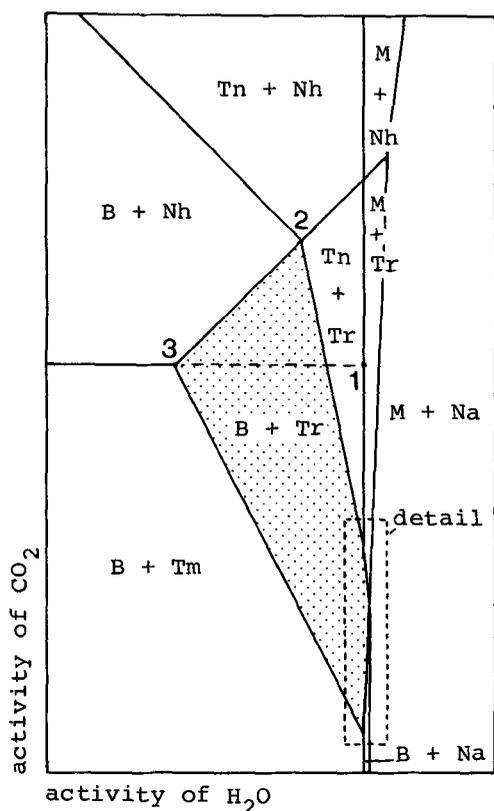
camera using $\text{Co-K}\alpha_1$ radiation, $\lambda = 1.7889 \text{ \AA}$. The data are listed in Table I. The calculated d -values show reasonable agreement with the measured ones. The cell dimensions were calculated using a program written by Visser (1969). From powder diffraction data the space group is determined to be either $Pmm2$ or $P222$.

Stability and thermodynamic properties of burkeite

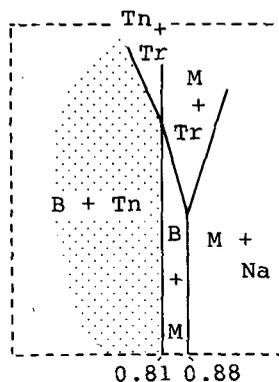
Eugster and Smith (1965) constructed an a_{CO_2} - $a_{\text{H}_2\text{O}}$ diagram for mineral reactions involving sodium carbonates and sodium sulphates. They

labelled the fields of stable associations under the assumption that burkeite (a mixed carbonate-sulphate) occurs with carbonates. This restriction is valid in the Searles Lake environment, as well as for the locality in Turkey, where burkeite has been found with trona and halite (see fig. 2a). The burkeite in Kenya is found with thenardite and halite only, so for the Kenya environment the labels of the stability fields have to be changed accordingly (see fig. 2b). Comparison of the two diagrams shows that the association burkeite + trona occurs under more restricted conditions than the association burkeite + thenardite.

There are no thermodynamic data available for



(a)



(b)

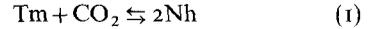
FIG. 2a and b. a_{H_2O} - a_{CO_2} diagrams for the system Na_2CO_3 - Na_2SO_4 - H_2O . For abbreviations see Table II. B = burkeite. In fig. 2a fields are labelled assuming that burkeite occurs with carbonates. In fig. 2b fields are labelled assuming that burkeite occurs with sulphates. The coordinates of points 1, 2, and 3 in fig. 2a are: 1 $P_{CO_2} = 10^{-4}$ atm., $a_{H_2O} = 0.81$; 2 $P_{CO_2} = 10^{-2.6}$ atm., $a_{H_2O} = 0.29$; 3 $P_{CO_2} = 10^{-4}$ atm., $a_{H_2O} = 0.01$. In the enlargements of the details the slopes of the field boundaries are arbitrary but their relative steepness has been maintained.

TABLE I. X-ray data for burkeite

Burkeite from Kenya			NBS synthetic burkeite		
d_{obs}	d_{calc}	hkl	d	hkl	I/I_1
9.199	9.220	010	9.215	010	8
4.609	4.610	020	4.607	020	5
4.510	4.512	011	4.507	011	17
4.175	4.175	101	4.172	101	4
3.862	3.862	120	3.854	120	40
3.804	3.803	111	3.795	111	75
3.537	3.535	200	3.526	200	80
3.440	3.442	021	3.439	021	19
3.300	3.301	210	3.307	210	3
3.075	3.073	030	3.072	030	17
2.806	2.805	220	2.801	220	100
2.778	2.783	211	2.777	211	55
2.643	2.642	031	2.640	031	75
2.588	2.587	002	2.583	002	75
2.490	2.490	012	2.488	012	5
2.347	2.349	112	2.345	112	6
2.305	2.305	040	2.305	040	11
2.283	2.283	310	2.279	310	4
2.191	2.192	140	2.191	140	3
2.150	2.149	122	2.147	122	14
2.145	2.145	301	2.142	301	11
2.106	2.105	041	2.105	041	6
1.980	1.979	032	1.978	032	12
1.925	1.931	240	1.929	240	30
1.906	1.906	132	1.904	132	25
1.899	1.902	222	1.898	222	30
			1.784	150	2
1.768	1.768	400	1.764	400	17
1.737	1.737	051	1.735	051	8
			1.722	003	3
1.680	1.675	103	1.673	103	2
1.647	1.648	113, 340	1.645	113, 340	3
1.635	1.635	250	1.635	250	4
			1.627	322	4
1.616	1.615	023	1.614	023	4
1.559	1.559	251	1.557	251	5
1.549	1.550	203	1.548	203	6
1.546	1.547	242	1.545	242	5
1.537	1.537	060	1.536	060	6
1.529	1.528	213	1.526	213	5

a 7.070 b 9.220 c 5.173 Å a 7.055 b 9.215
 $Pmm2$ or $P222$ c 5.167 Å

burkeite, but an approximate Gibbs energy of burkeite can be calculated from the Gibbs energies of the other minerals plotted in fig. 2 (see Table II). The equilibrium f_{CO_2} between thermonatrite and nahcolite can be calculated as follows:



$$\Delta G_{\text{R}} = -RT \ln K = +RT \ln f_{\text{CO}_2};$$

at 298.15 K $f_{\text{CO}_2} = 10^{-4}$ bar.

In fig. 2a it can be seen that at this f_{CO_2} and at an $a_{\text{H}_2\text{O}}$ where thenardite and mirabilite are in equilibrium with each other (point 1 in fig. 2a) burkeite is unstable with respect to the assemblage thenardite + trona, which means that at these conditions the ΔG_{R} of the following reaction must be positive:



at $f_{\text{CO}_2} = 10^{-4}$ bar $\Delta G_{\text{R}} > 0$

$$3G_{\text{B}} > 6G_{\text{Tn}} + 2G_{\text{Tr}} - G_{\text{CO}_2}^{\circ} - RT \ln f_{\text{CO}_2} - 5G_{\text{H}_2\text{O}}^{\circ} - 5RT \ln a_{\text{H}_2\text{O}}. \quad (3)$$

$a_{\text{H}_2\text{O}}$ can be calculated from the equilibrium:



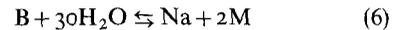
$$\Delta G_{\text{R}} = +10RT \ln a_{\text{H}_2\text{O}};$$

at 298.15 K $a_{\text{H}_2\text{O}} = 0.81$.

Substituting this value as well as $f_{\text{CO}_2} = 10^{-4}$ in the inequality (3), the following result is obtained:

$$G_{\text{B}} > -3596.02 \text{ kJ}. \quad (5)$$

In fig. 2b it can be seen that the equilibrium between burkeite and natron + mirabilite is situated at a higher $a_{\text{H}_2\text{O}}$ than the equilibrium between thenardite and mirabilite (where $a_{\text{H}_2\text{O}} = 0.81$).



at $a_{\text{H}_2\text{O}} = 0.81$ $\Delta G_{\text{R}} > 0$

$$G_{\text{B}} < G_{\text{Na}} + 2G_{\text{M}} - 30G_{\text{H}_2\text{O}}^{\circ} - 30RT \ln a_{\text{H}_2\text{O}} \\ G_{\text{B}} < -3592.40 \text{ kJ}. \quad (7)$$

From (5) and (7) it follows:

$$-3596.02 \text{ kJ} < G_{\text{B}} < -3592.40 \text{ kJ}.$$

The accuracy of these values depends on the accuracy of the Gibbs energies of the individual minerals which take part in the reaction equations (1, 2, 4, and 6). As there are no uncertainties given

TABLE II. Gibbs energies of the minerals

Name	Formula	$\Delta G_{f, 298.15}^{\circ}$ kJ/mol	Reference
Nahcolite (Nh)	NaHCO_3	-851.86	1
Natron (Na)	$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$	-3428.98	1
Thermonatrite (Tm)	$\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$	-1286.55	1
Trona (Tr)	$\text{NaHCO}_3 \cdot \text{Na}_2\text{CO}_3 \cdot 2\text{H}_2\text{O}$	-2386.55	1
Thenardite (Tn)	Na_2SO_4	-1269.985	2
Mirabilite (M)	$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$	-3646.540	2
Carbon dioxide (g)	CO_2	-394.375	2
Water (liq.)	H_2O	-237.141	2

References: 1. Garrels (R. M.) and Christ (C. L.), 1965. (1 cal. = 4.184 J).
 2. Robie (R. A.), Hemingway (B. S.), and Fisher (J. R.), 1978.

for the Gibbs energies of the sodium carbonates, we cannot give an exact uncertainty for the Gibbs energy of burkeite. Therefore, we estimated:

$$\Delta G_{f, 298.15}(\text{burkeite}) = 3594.2 \pm 3 \text{ kJ.}$$

The Gibbs energy of burkeite is calculated from equilibrium relationships with respect to other minerals. As soon as the values of the Gibbs energies of the other minerals change, the Gibbs energy for burkeite has to be changed accordingly. Once the Gibbs energy of burkeite is known, the positions of all other equilibria in the diagrams can be calculated. It can be seen that burkeite can form under the atmospheric condition $f_{\text{CO}_2} = 10^{-3.5}$ atm and that during formation the solution must be rather concentrated (activity of H_2O less than 0.88), a stage which is easily reached during evaporation.

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