

Kernite from Tincalayu, Salta, Argentina

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Abstract

The Tincalayu mine (Salta, Argentina) is essentially a monomineralic deposit of borax partly transformed to kernite with minor amounts of several rare borates. The deposit is interpreted as an old playa accumulation, buried, metamorphosed and deformed by folding and faulting. It is intercalated with clastic continental sediments of Pliocene or post-Pliocene age. The principal explored lens is more than 30 m thick and approximately 100 m in diameter.

Kernite crystals are clear, transparent and well developed; many exceed 30 cm in length and 10 cm across; no terminal faces were observed. X-ray powder data are given with the orientation: $c > a$, $\beta > 90^\circ$. The space group is $P2_1/c$; $a = 7.016 \pm 0.001\text{\AA}$, $b = 9.152 \pm 0.002\text{\AA}$; $c = 15.678 \pm 0.002\text{\AA}$. $\beta = 108^\circ 52.8' \pm 0.7'$; cell volume $952.6 \pm 0.2\text{\AA}^3$; $Z = 4$. $a:b:c = 0.7666:1:1.7131$. Cleavage: $\{100\}$ and $\{001\}$ perfect, $\{\bar{1}02\}$ poor. Optically biaxial (-); $\alpha = 1.545$, $\beta = 1.473$, $\gamma = 1.488 \pm 0.001$ (Na light); $2V = 80^\circ$, $r > v$ (slight); $X \wedge c = 70^\circ 30'$, $Z = b$. Density (calc) $1.905 \pm 0.001 \text{ g/cm}^3$, specific gravity (meas) 1.906 ± 0.003 .

A chemical analysis by wet methods gives wt percent Na_2O 23.1, B_2O_3 51.0, and H_2O 26.1 (total 100.2). DTA analysis shows endothermic peaks at 175°C (very strong), 561°C (strong) and 755°C (very strong), and exothermic peaks at 361°C (weak) and 604°C (strong).

Introduction

Kernite was discovered in 1925 during a drilling program by the United States Borax Company in the Mojave Desert, California. Although it was referred to as *rasorite* (Palmer, 1927) by the Company, it was named *kernite* after Kern County by W. T. Schaller (1927, 1930) in the first published description. The locality, originally given as the Kramer District, is today known as Boron, California, the name of the town that developed after mining began.

Boron was the only known kernite locality until Ahlfeld found the mineral in the borax mine at Tincalayu, Argentina. Only a superficial description was reported (Ahlfeld and Angelelli, 1948), and this second occurrence has gone largely unnoticed. Tincalayu is in the Province of Salta at the north-central part of the salt pan known as Salar del

Hombre Muerto. The approximate latitude and longitude are $25^\circ 20'S$ and $67^\circ 00'W$. The mine can be reached by motor vehicle from Pocitos Station on the General Manuel Belgrano Railway, 146 km to the north.

Boron and Tincalayu remain the only localities where kernite has been positively identified. However, a doubtful occurrence has been reported from the Lower Permian of the Donets Basin (Zaritskii, 1965), and a possible occurrence has been indicated in the Death Valley salt pan (Hunt *et al.*, 1966), p. B-49).

Occurrence

The Tincalayu mine is essentially a monomineralic deposit of borax partly transformed to kernite with a very minor content of several rare borates. The deposit is interpreted as an old marsh accumulation, buried, metamorphosed and deformed by folding and faulting along a predominantly north-south direction so as to be intercalated in the folded Sijes formation.

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The borax is concordantly intercalated with members of the Sijes Formation which is composed chiefly of clastic continental sediments deposited in a closed basin. The principal rocks of the formation are fine-grained sandstones and claystones variously colored white, grey, yellow and pink. These are interbedded with tuffs, evaporites, limestones, and conglomerates (Catalano, 1964; Turner, 1964; Muesig and Allen, 1957). Catalano considered the sediments post-Pliocene, whereas Pratt (1961) dated them as Pleistocene or Recent, and Turner (1964) as Pliocene.

Lens-like bodies of borax are apparently localized by structural control along the North-South axes of the anticlines. The principal known lens is more than 30 meters thick and approximately 100 meters in diameter. The borax rests directly on a thick layer of halite and is overlain by about 50 meters of brown to reddish-brown fine-grained claystones, siltstones, tuffs and sandstones. Near the upper contact of borax and sediments are several thin claystones horizons. One of these horizons carries nodules of ulexite, another contains euhedral inyoite crystals, and a third has crystals of kurnakovite (= "inderite" of Muesig and Allen, 1957).

During the intensive folding and faulting, the sedimentary series was elevated above the playa and partially eroded; later it was covered in part by a thin flow of Holocene basalt. The folded Sijes Formation not only forms high ground at the margin of the present playa but rises as islands within it. The elevation initiated the present cycle of erosion and of deposition of clastic and chemical sediments (halite and ulexite) in the present playa.

During the tectonic deformation of the deposit, a tabular portion of the borax ore body was raised

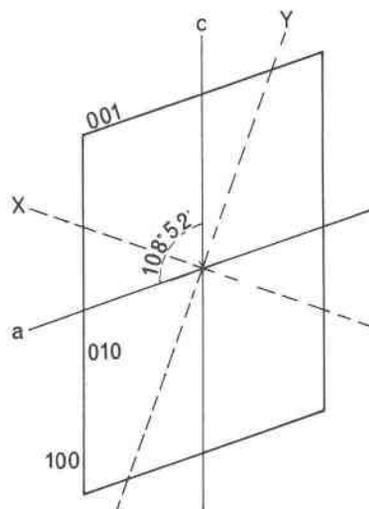


FIG. 1. Optical orientation of kernite, with $c > a$ and $\beta > 90^\circ$.

by two parallel faults. This elevated portion was the first part of the deposit to be discovered, and it led Muessig and Allen (1957) to describe it as a plug-like body.

At Boron, California, kernite is found in the lower part of the deposit as a metamorphic alteration of borax (Christ and Garrels, 1959; Barnard and Kistler, 1966; Bowser and Dickson, 1966; Smith, 1968). At Tincalayu the general relationship of the two minerals is similar. Kernite in an irregular body in places more than 10 meters thick, underlies the main deposit of borax. In addition a vein-like mass of kernite about 30 centimeters wide which cuts the upper borax probably was formed by fault action.

The portion of the Tincalayu deposit that is mined is composed of a fine-grained crystalline aggregate of borax. Occasionally, well-formed, transparent crystals of borax are found in cavities which range in size from a few centimeters to over 30 centimeters. Locally thin layers of clay and silt within the lenses reduce the B_2O_3 content, which in pure borax is 36.5 wt percent, to as low as 20 percent. Material with 28 percent or greater is sent to the dressing plant.

Associated with the borax and kernite are very small amounts of the rare borates rivadavite, ezcurrite (Hurlbut and Aristarain, 1967a, b), ameghinite, and macallisterite (Aristarain and Hurlbut, 1967a, b). There are also minor amounts of compact ulexite balls and euhedral kurnakovite crystals. Thin veins of halite and secondary tincalconite are also present.

TABLE 1. Unit-cell Data for Kernite

	Tincalayu, Salta Argentina	Ross and Edwards 1959, synthetic	Giess (1966) unknown source
System and space group	Monoclinic $F2_1/c$	Monoclinic $F2_1/c$	Monoclinic $F2_1/c$
Unit Cell			
a (Å)	7.016±0.001*	7.022	7.0172±0.0006
b	9.152±0.002	9.151±0.002	9.1582±0.0006
c	15.678±0.002	15.676	15.6774±0.0015
β	108°52'8"±0.7'	108°50'±5'	108.861°±0.002°
v (Å ³)	952.6±0.2	953.4**	953.4
z	4	--	4
ρ (calc, g/cm ³)	1.905±0.001	1.904***	1.93
sp. gr. (meas)	1.906±0.003	--	1.91
	0.7666:1:1.7131	0.7673:1:1.7130	0.7652:1:1.7118

*Initial parameters from x-ray single-crystal precession data; final parameters listed here from least-squares refinement of x-ray powder data (Table 2); morphological measurement of β gives 108° 53'±4'.

** Calculated in present investigation from data of Ross and Edwards (1959) although Ross and Edwards didn't report it.

*** Calculated by Cialdi *et al.* (1967) from the data of Ross and Edwards (1959).

Morphology and Physical Properties

The kernite crystals at Tincalayu are large, but no terminal faces were observed; crystals 30 cm long and 10 centimeters across are common. Very characteristic of the occurrence are intergrowths of two large crystals giving a twin-like appearance. Freshly broken kernite is clear and transparent with vitreous luster, but on exposure to air it turns milky white on the surface and along cleavage cracks.

TABLE 2. X-ray Powder Diffraction Data for Kernite from Tincalayu

hkl	d_{hkl} (Å)	Observed*		Calculated**	
		I	I	d_{hkl} (Å)	I
011	7.79	9	7.789	35.5	
002	7.40	100	7.417	100.0	
100	6.64	85	6.638	63.3	
102	6.00	15	6.006	15.2	
012			5.762	0.0	
111			5.538	0.2	
110	5.37	2	5.374	2.2	
112	5.03	2	5.021	0.8	
111	4.68	4	4.676	5.1	
020	4.58	1	4.576	0.3	
021			4.373	3.8	
013	4.348	3	4.350	0.9	
102	4.298	5	4.303	2.7	
113	4.233	4	4.233	7.0	
022			3.895	2.2	
112	3.895	16	3.894	23.7	
121			3.823	0.1	
104	3.800	7	3.804	6.0	
120			3.768	0.3	
004	3.705	23	3.708	12.1	
122			3.640	0.9	
114	3.512	10	3.512	10.4	
121			3.502	0.6	
202			3.478	0.1	
014	3.437	6	3.437	2.7	
023	3.358	7	3.358	9.1	
200	3.312	9	3.319	2.0	
123			3.304	8.6	
211			3.260	6.5	
212	3.253	34	3.251	33.3	
113			3.240	4.2	
122	3.132	29	3.135	42.6	
210			3.120	11.3	
213			3.098	1.4	
204			3.003	0.0	
031	2.989	5	2.988	4.0	
211	2.882	29	2.882	17.2	
024			2.881	9.4	
015			2.822	0.4	
032	2.823	7	2.821	3.3	
221			2.774	3.2	
130	2.773	10	2.772	9.2	
222			2.769	3.2	
114	2.732	6	2.736	0.6	
132			2.720	0.4	
202	2.719	6	2.719	0.5	
220	2.687	7	2.687	3.8	
223	2.678	7	2.673	3.8	
106			2.609	7.8	
212	2.609	16	2.607	0.4	
215			2.577	0.4	
125	2.573	10	2.572	11.4	
133			2.571	2.2	
224			2.511	8.6	
116	2.511	8	2.509	0.0	
006	2.472	27	2.472	17.0	
124	2.430	7	2.429	3.8	
206			2.387	0.6	
016	2.387	10	2.387	4.9	
134			2.380	0.7	

*X-ray diffractometer conditions are: chart No. X3525; Cu/Ni radiation, λ CuK α = 1.5418 Å; Al used as internal standard; scanned at 1/4° 2 θ per minute.

**for $d_{hkl} > 3.000$ Å. Below this value calculated hkl listed only for observed reflections. All reflections for which $d_{hkl} \geq 2.000$ Å have been indexed. I calculated from parameters of Garrido *et al.* (1967) using computer program of Borz and Smith (1969).

TABLE 2, Continued

hkl	d_{hkl} (Å)	Observed*		Calculated**	
		I	I	d_{hkl} (Å)	I
302				2.338	0.7
222	2.340			2.338	0.0
213				2.337	0.4
216	2.308	7		2.310	3.2
231				2.296	0.3
232	2.294	7		2.294	8.9
126				2.267	1.2
112	2.266	6		2.265	1.5
041				2.261	0.4
113				2.248	1.1
304	2.246	6		2.247	0.6
230				2.246	2.1
311	2.230	6		2.230	2.6
300	2.213	10		2.213	5.8
042	2.182	7		2.186	1.5
314				2.182	4.1
204				2.152	3.5
231	2.151	6		2.151	0.2
310				2.151	0.0
234				2.140	0.4
142	2.140	6		2.138	9.4
223				2.138	0.2
214	2.095	8		2.094	5.3
322				2.082	0.9
315	2.080	9		2.080	4.9
043				2.076	3.1
321				2.055	0.1
116	2.052	5		2.051	1.6
127	2.013	5		2.012	1.8
203	2.003	7		2.002	4.3
306	1.956	4			
				1.912	13.8
				1.902	1.0
				1.881	9.5
				1.857	3.3
				1.831	4.4
				1.820	4.4
				1.799	3.3
				1.791	3.3
				1.779	4.4
				1.759	5.5
				1.745	5.5
				1.721	8.6
				1.706	3.3
				1.683	4.4
				1.659	9.4

Schaller (1927) first described the mineral as orthorhombic with c parallel to the intersection of the two prominent cleavages. Later he recognized the monoclinic symmetry and reoriented the crystal, making old $c =$ new b , $c > a$ and $\beta < 90^\circ$ (Schaller, 1930). Garrido (1932) reporting unit cell dimensions followed the rule $a > c$ and $\beta > 90^\circ$.

A third orientation in which $c > a$ and $\beta > 90^\circ$ was used by Minder (1935), and followed by Ross and Edwards (1959), Giese (1966) and Cialdi *et al.* (1967), in their respective studies of kernite structure. Schaller's a value obtained from morphological measurements is double the true value as used by all of these authors. Except when otherwise indicated, the Minder orientation is used in this present paper. The transformation formula from Garrido to Minder, *i.e.*, from orientation, $c < a$ to $c > a$ ($\beta > 90^\circ$ in both) is: 001/010/100.

Most of the following physical properties of kernite from Tincalayu are in close agreement with those of kernite from Boron as determined by Schaller (1930) and reported in Dana's System of Mineralogy

(Palache, Berman and Frondel, 1951). The cleavages are {100} and {001} perfect, {102} poor. As given in Dana's System for orientation $c < a$, the cleavages are respectively {001}, {100} and {201}, with {100} perfect and {001} less so.

The Mohs hardness is $2\frac{1}{2}$, the specific gravity (meas) 1.906 ± 0.003 ; the calculated density, from the composition $\text{Na}_2\text{O} \cdot 2\text{B}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$, $Z = 4$ and unit cell volume, $952.6 \pm 0.02\text{\AA}^3$, is $1.905 \pm 0.001 \text{ g/cm}^3$; calculated using the analysis of Table 3 the value is 1.910 g/cm^3 .

The optical properties are: $\alpha = 1.454$; $\beta = 1.473$; $\gamma = 1.488$ all ± 0.001 (Na light); $2V = 80^\circ$, biaxial negative, $r > v$ (slight); $X \wedge c = 70^\circ 30'$ and $Z = b$ (Fig. 1). With orientation $a > c$, $X \wedge c = 38^\circ 30'$ and $Z = b$.

X-Ray Data

The unit cell dimensions for the Tincalayu kernite, as obtained from precession photographs ($\text{MoK}\alpha$) and refined from powder diffraction data ($\text{CuK}\alpha$), compare closely with previously described specimens (Table 1). The interplanar spacings for the powder data were indexed (Table 2) using the automatic computer method of Evans *et al.* (1963). Intensities were calculated from the atomic parameters given by Cialdi *et al.* (1967), using the computer program of Borg and Smith (1969). Observed and calculated intensities are in reasonable accord, considering the strong preferred orientation due to the perfect {001} and {100} cleavages. To avoid hydration to tincalconite the sample was ground under methanol; no lines of this material were found. Other powder data for kernite were given by McIntosh and Matthews (1948), Muessig and Allen (1957), Cipriani (1958) and Bowser (1965).

Chemistry and Structure

Pure fragments of a large kernite cleavage piece were selected for chemical analysis. Atomic proportions resultant from the wet chemical analysis carried out by Dr. Jun Ito, Harvard University, yield (Table 3) the empirical formula: $1.02\text{Na}_2\text{O} \cdot 2\text{B}_2\text{O}_3 \cdot 3.97\text{H}_2\text{O}$, which is very close to the ideal formula of $\text{Na}_2\text{O} \cdot 2\text{B}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$. Table 4 summarizes several known analyses of the mineral.

The crystal structure of kernite was determined almost simultaneously by Giese (1966, 1967) and Cialdi *et al.* (1967), and its structural formula determined to be $\text{Na}_2\text{B}_4\text{O}_6(\text{OH})_2 \cdot 3\text{H}_2\text{O}$. The crystal contains infinite chains of composition $[\text{B}_4\text{O}_6(\text{OH})_2]^{2-}$

TABLE 3. Chemical Analysis* and Atomic Proportions of Kernite from Tincalayu

	Wt %	Weight percent recalculated to 100	Atomic proportions if Boron = 4
Na_2O	23.1	23.05	Na 2.0356
B_2O_3	51.0	50.90	B 4.0000
H_2O	26.1	26.05	H 7.9127
TOTAL	100.2	100.00	O 10.9740

*Dr. Jun Ito, Harvard University, analyst. A spectrochemical analysis indicates: Si, Al, Ca, Li, K (0.01 - 0.001) and Mg, Mn, Ba, Sr, Fe, Cu (<0.001) percent.

as predicted by Christ and Clark (1957), and Christ and Garrels (1959). There are two chains per unit cell that run parallel to the b -axis. As shown by Giese (1966), the linkage between the boron-oxygen chains along the c -axis is through hydrogen bonding, and along the a -axis through hydrated sodium ions. The bonding within the chains themselves is much stronger than the bonding between chains, and thus the perfect {100} and {001} cleavages and the fibrous nature of kernite are readily understood on the basis of the crystal structure.

A differential thermal analysis of Tincalayu kernite gave three endothermic and two exothermic peaks, as represented in Figure 2. The peaks of endothermic reactions are at 175°C (very strong, very broad), 561°C (strong, broad), 755°C (very strong, sharp). The exothermic peaks are at 361°C (weak, broad) and 604°C (strong, sharp).

The alteration of kernite from Tincalayu appears to proceed more rapidly than that from Boron, California. Fragments of kernite from Boron that have been in the Harvard University Museum for 25 years are still essentially transparent, and have only a thin white coating. Material from Tincalayu stored under similar conditions has become partly chalky white in two years time.

TABLE 4. Chemical Analyses of Kernite (Wt Percent)

	Synthetic		Boron, California			Tincalayu, Salta, Argentina		Calculated composition
	1	2	3	4	5	6	7	
Na_2O	22.65	22.63	22.66	22.62	22.7	23.1	22.68	
B_2O_3	50.80	50.76	50.90	50.52	51.1	51.0	50.95	
H_2O	26.55	26.50	27.07	26.37	26.6	26.1	26.37	
TOTAL	100.00	99.89	100.63	99.51	100.4	100.2	100.00	

1) Schaller (1930), B_2O_3 , by difference.

2) Schaller (1927, 1930).

3) Cipriani (1958).

4) Laboratorio Químico del Instituto de Geología y Minería, Jujuy, Argentina; Ahlfeld and Angelelli (1948).

5) R. Herzenberg, analyst; Ahlfeld and Angelelli (1948).

6) This study, Jun Ito, analyst.

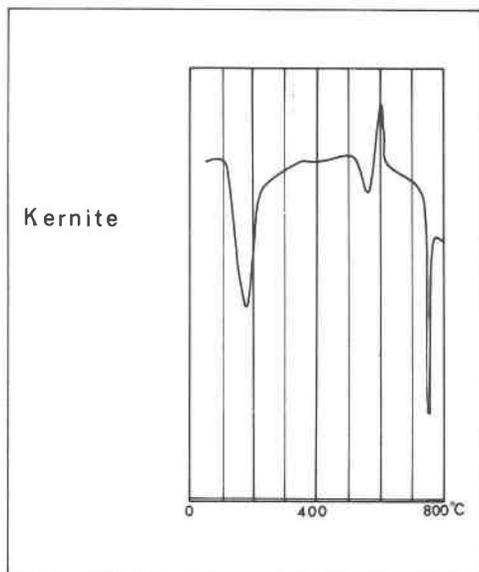


FIG. 2. Curve showing the differential thermal analysis of kernite; heating rate 20°C per minute, reference junction 0°C; thermocouple Pt/Pt + 13 percent Rh, reference material Al_2O_3 .

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