A SECOND OCCURRENCE OF ANTARCTICITE, FROM BRISTOL DRY LAKE, CALIFORNIA

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Abstract

Antarcticite, $CaCl_2 \cdot 6H_2O$, occurs as divergent groups of colorless, prismatic crystals and compact aggregates in the exposed near-surface trapped brines of Bristol Dry Lake, San Bernardino County, California. The mineral has formed by the natural solar concentration of the exposed calcium chloride-rich brine of the lake playa. This general area of the Mojave Desert has a very arid climate. Associated minerals of the lake sediments include halite, gypsum, anhydrite, celestite, calcite, and chlorocalcite(?).

The Bristol Dry Lake antarcticite is hexagonal with a=7.907, c=3.95 Å, c/a=0.500; V=214.02 Å³. The strongest X-ray powder diffraction lines are: 2.16 (s) (1231), 3.96 (ms) (1120), 2.80 (m) (1121), 2.59 (m) (0221), 2.28 (m) (3030), 1.978 (m) (2240).

Antarcticite is colorless. Fracture brittle. H=2-3; the density is 1.700 g/cm^3 (calc.); the average specific gravity is 1.715 ± 0.010 (meas.). Optically uniaxial (-), ω near 1.550, $\epsilon=1.490-1.500$. Basal cleavage perfect; prismatic cleavage good to perfect.

The chemical analysis: Ca 17.25, Mg 0.015, Si 0.003, Fe 0.003, Al 0.002, Na 0.30, Cl 33.14, H₂O 49.27, sum 99.98 wt %.

INTRODUCTION

Although considered to be a rare constituent of saline lake brines, calcium chloride has been known as a prominent fraction of the subsurface brines of Bristol Dry Lake, San Bernardino County, California for over fifty years. The first claims to recover this salt were located in 1908 with production beginning in 1910. Calcium chloride is the second most abundant salt of the subsurface brines with sodium chloride being the most prominent. Gale (1951) gives an account of the mining activity to recover the calcium chloride-rich brines, which are located near the southwest shore of the playa.

Cadiz Dry Lake, 18 miles southeast of Bristol Dry Lake, also contains calcium chloride in the subsurface brines, but it is known to be in only minor amounts (Ver Planck, 1954). The occurrence of calcium chloride in California is also recorded by Hudson and Taliaferro (1925) in the Ventura County oil fields, and a general discussion of the origin of calcium chloride is given.

During the winters of 1961 and 1962, an examination of several trenches and pits was made in the vicinity of the calcium chloride plant near the southern margin of Bristol Dry Lake playa. During this examination a colorless mineral, occurring as radiating groups of compact aci-

ANTARCTICITE

cular crystals, was observed in the brine water and attached to the massive sodium chloride that bordered the brine of one pit. Samples of the brine and the colorless mineral were preserved for further study. A subsequent chemical analysis and X-ray study of this mineral proved it to be calcium chloride hexahydrate and identical with the recently described mineral antarcticite.

Antarcticite, $CaCl_2 \cdot 6H_2O$, was described by Torii and Ossaka (1965) as a new mineral crystallizing naturally from the brine water of Don Juan Pond, Victoria Land, Antarctica and associated with crystals of sodium chloride and calcium sulfate. The Bristol Dry Lake antarcticite herein described is the second reported locality for this most uncommon and highly hygroscopic mineral and represents one of the few localities where the arid-climatic conditions of low humidity and temperatures below 30°C permit its formation.

This paper describes the occurrence and properties of antarcticite from Bristol Dry Lake and includes a brief description of the area geology and associated minerals.

GEOLOGICAL SETTING

Bristol Dry Lake, together with Cadiz and Danby Dry Lakes, is situated in a trough-like valley and it is suggested by Bassett and Kupfer (1964) that it is probably of a structural origin, however it has been highly modified by abundant alluvial deposits. Blackwelder (1954) postulates that this trough was once part of a Pleistocene drainage system which connected the upper part of the Mojave Desert with the Colorado River.

Gale (1951) gives a brief description of the area, but more recently Bassett and Kupfer (1964) have made an examination of the geological features of the area with emphasis on the playas and their relation to the surrounding topography. The mountain ranges surrounding this basin principally consist of Cenozoic plutonic and metamorphic rocks. The pre-Tertiary rocks consist of gneiss, schist, and limestone of Precambrian and Paleozoic ages. A series of olivine basalt flows occur on the northwest edge of the lake and were produced by a series of volcanic vents in the vicinity of Amboy Crater. This area has been described by Parker (1963).

The playa of Bristol Dry Lake consists of a series of beds of lacustrine origin. A logged drill core of the sediments (Bassett *et al.*, 1959) penetrates lithologically similar layers of sand, silt, clays, and evaporite minerals to a depth of over 1000 feet. Bassett and Kupfer (1964) suggest that the sediments were deposited in ephemeral lakes and that the conditions of deposition have remained uniform throughout the age of the basin.

OCCURRENCE OF ANTARCTICITE

Antarcticite was observed and collected in an elongated pit 5.5 miles south of Amboy in SE 1/4 sec. 32, T. 5N., R. 12E., S.B., B.M. near the county road from Amboy to Twentynine Palms. This pit, which is one of a series of excavations in the area made to explore the subsurface salt and brine deposits, has no entrance or exit channels connecting it with the nearby trenches used to collect and transport brine to solar evaporating ponds. The base of this pit, which is about 3 meters below the playa surface, is composed of massive sodium chloride with a pool of calcium chloride-rich brine extending the length (20 m) of the pit. Acicular groups of antarcticite form in the brine and extend outward from the massive sodium chloride. The brine depth varies from 10 to 25 c over the length of the pit and has remained essentially the same depth between 1961 and 1968, when the locality was revisited. No apparent mining activity has occurred during this period. Several active trenches in the same section were examined but no antarcticite was noted. Both the California Salt Company and the National Chloride Company of America mine and process the calcium chloride-rich brines in this area.

The existence of antarcticite at Bristol Dry Lake is clearly the result of solar concentration of the calcium chloride-rich brine, which has been exposed to the arid conditions of the area by the removal of the surface sediments. Gale (1951) suggests that the calcium chloride brines were derived by the action of chlorine of volcanic origin on calcium carbonate, which is a principal constituent of the late alluvial deposits of the area. Troxell and Hofmann (1954) describe this area of the Mojave Desert as one of the driest parts of the United States with an average annual rainfall less than three inches. Daytime summer temperatures often are in excess of 120°F and fall to a low of 10 to 15°F during the winter season.

Associated Minerals

In addition to antarcticite, the evaporite minerals of Bristol Dry Lake include gypsum, anhydrite, celestite, calcite, halite, and chlorocalcite (?). The origin of the saline minerals is not definitely known but the Bristol basin has no doubt contributed many of the salts. Bassett *et al.* (1959) were unable to locate exposed saline-bearing sediments in the basin.

Gypsum. Gypsum is principally confined to the near-surface peripheral sediments and was described as early as 1920 by Hess *in* Stone *et al.* (1920). Gale (1951) and Ver Planck (1952) give brief accounts of the gypsum occurrence and describe its habit and formation in the near-surface sediments. The most abundant deposit occurs on the west and north shore areas, although it is found in small quantities around the playa. The

ANTARCTICITE

gypsum typically forms as small selenite crystals mixed with salty mud and silts. The subsurface layers are quite pure and occur as spongy white masses. Core logs of the playa given *in* Gale (1951) record gypsum crystals and layers at various depths to 142 feet. Bassett *et al.* (1959) logged gypsum in the lower sediments.

Anhydrite. Small flakes of anhydrite occur in the lower sediments and are recorded by Bassett *et al.* (1959). Allen and Kramer (1953) report bassanite from Danby Dry Lake drill cores as thin layers, and evidence is given that it has formed from the dehydration of gypsum. Bassanite probably occurs in the lower sediments of Bristol Dry Lake but its existence has remained undiscovered.

Celestite. Celestite occurs as large concretions in the near-surface sediments near the south edge of the playa. Durrell (1953) gives an account of the celestite concretions and suggests that they are being formed from the strontium-bearing waters of the playa, and that they form within the near-surface sediments. No source of the strontium has been discovered in the Bristol basin, but several sources are postulated by Durrell (1953).

Calcite. Calcium carbonate is known only as a minor constituent of the near-surface sediments. Durrell (1953) reports small rhombohedrons of a carbonate, probably calcite, in association with gypsum as a marginal part of celestite concretions. Thin layers of limestone, less than two inches thick, are recored by Bassett *et al.* (1959) in the lower sediments.

Halite. Halite is the most abundant of the saline minerals of the playa and occurs in the subsurface brines in association with calcium chloride and as a series of flat, tabular bodies interbedded with the sediments that underlie the playa. It is also found as scattered crystals within certain layers of the playa sediments. These deposits are described by Gale (1951), Ver Planck (1954, 1957) and mentioned by Wright *et al.* (1953). Bassett *et al.* (1959) show that about 40 percent of a logged core is composed of sodium chloride.

Chlorocalcite ?. Core logs reported in Gale (1951) list the occurrence of CaCl₂ crystals between 40 and 47 feet below the playa surface. The existence of this compound in the sediments of Bristol Dry Lake *must* be considered doubtful until definite proof is given. Palache *et al.* (1951, p. 41, 91) consider natural material that has been described under the name of hydrophyllite (CaCl₂) to be most likely chlorocalcite (KCaCl₃). Durrell (1953) reports K in the range of 0.15 to 0.33 percent from the brine

water in this area. Gale (1951) cites an analysis of concentrated calcium chloride which shows a small percentage of K. No evidence of $CaCl_2$ crystals was reported by Bassett *et al.* (1959) from a logged core in this area.

X-RAY DIFFRACTION DATA

Antarcticite, which is highly hygroscopic and unstable above 30°C, must be exposed to X rays under special conditions to minimize premature melting by X-ray heat absorption and atmospheric moisture attraction. To insure that a representative X-ray diffraction pattern would be obtained, the crushed mineral was exposed in a low temperature inert atmosphere by the use of a pre-cooled camera with continuous purging of liquid nitrogen-cooled helium. A GE XRD-5 unit with Ni-filtered Cu radiation and a camera diameter of 143.2 mm was used to obtain the powder diffraction pattern.

The powder data, compared with an internal standard of quartz, are given in Table 1 and compare favorably with the X-ray Powder Diffraction File for artificial $CaCl_2 \cdot 6H_2O$ and with the data of Torii and Ossaka (1965). The hexagonal lattice constants were calculated using a computer program based on Cohen's least-squares method (Klug and Alexander, 1954) on a GE 200 computer. The unit-cell data are: a = 7.907, c = 3.95 Å,

hkil	d(calc.) Å	$d(\text{obs.})^{\text{b}}$ Å	I(est.) ^a	hkil	d(calc.) Å	$d(\text{obs.})^{\mathrm{b}}$ Å	I(est.)
1010	6.848	6.9	vw	1122	1.768	1.765*	vw
$11\bar{2}0$	3.954	3,96	ms	$22\overline{4}1$	1.768		
0001	3.953			$13\overline{4}1$	1.712	1.711*	W
0111	3.423	3,42	mw	0222	1.712		
$20\bar{2}0$	3.424			4040	1.712		
$11\overline{2}1$	2,795	2.80*	m	$12\overline{3}2$	1.571	1.570*	vw
$02\overline{2}1$	2.588	2.59*	m	$40\overline{4}1$	1.571		
3030	2.283	2.28*	m	$23\overline{5}0$	1.571		
$12\overline{3}1$	2.165	2.16*	s	0332	1.494	1.495*	w
$22\overline{4}0$	1.977	1.978*	m	1450	1.494		
$03\overline{3}1$	1.977			2351	1.460	1.459*	W
0002	1.976			$22\overline{4}2$	1.398	1.395*	VW
3140	1.899	1.897*	VW	$14\overline{5}1$	1.398		
0112	1.899			1342	1.369	1.370*	VVW
				5030	1.370		

TABLE 1. X-RAY POWDER DATA FOR ANTARCTICITE FROM BRISTOL DRY LAKE, SAN BERNARDINO COUNTY, CALIFORNIA

^a s strong, ms medium strong, m medium, mw medium weak, w weak, vw very weak, vvw very very weak.

^b Observed d marked with an asterisk were used to calculate the unit-cell dimensions.

ANTARCTICITE

c/a=0.500, and V=214.02 Å³. The calculated density is 1.700 g/cm^2 (Z=1). All d consistent with the space group P321 for artificial CaCl₂ $\cdot 6H_2O$ (Wyckoff, 1965) were calculated from the above unit-cell dimensions.

CHEMICAL ANALYSIS

A semiquantitative spectrographic analysis was performed on the crystallized antarcticite using a Jarrel-Ash 3.4 meter emission spectrograph to determine the approximate levels of the impurity elements. A standard composed of reagent $CaCl_2 \cdot 2H_2O$, together with the minor elements of the preliminary examination, was prepared and comparison of these two samples resulted in the final levels of the impurity elements. The calcium, chloride, and water were determined using standard analytical methods.

The results of the spectrographic and wet chemical analysis gave Ca 17.25, Mg 0.015, Si 0.003, Fe 0.003, Al 0.002, Na 0.30, Cl 33.14, H₂O 49.27, sum 99.98 weight percent, corresponding to $CaCl_2 \cdot 6H_2O$. K and Sr were not detected at analytical limits of 0.01 and 0.002 percent, respectively. Analysis of the brine water from two localities, one from a shallow well and the other from a drainage canal, suggest that K and Sr are present in small amounts throughout the brine of the playa (Durrell, 1953). No analysis was made of the brine where the antarcticite was collected.

PHYSICAL PROPERTIES

The mineral typically occurs as colorless, acicular groups of crystals and occasionally as jackstraw-like aggregates up to 15 centimeters in length. These groups show parallel growths of the individual crystals. Crystal terminations, often poorly developed but recognizable, were noted on material collected during the winter of 1968; however, the forms were not identified due to the friable nature of the crystals when removed from the brine. Figures 2 and 3 of Torii and Ossaka (1965) show the growth habit of antarcticite in the brine and are typical of the mineral's habit at Bristol Dry Lake.

Antarcticite is not fluorescent under short wave ultraviolet light, although the halite crystals that form in the nearby trenches fluoresce a bright red. The mineral has a perfect basal cleavage and a good to perfect prismatic cleavage; it is brittle with a Mohs hardness between 2 and 3.

The specific gravity was determined by the pynchometer method using reagent benzene as the immersion liquid. Measurements were made on five separate samples that were visually free of liquid inclusions. The mineral was crushed to about $\frac{1}{8}$ inch in size and stored at -4° C in a sealed container until the determinations were made. The average specific gravity was determined to be 1.715 ± 0.010 (14°C), which is in good agreement with the value of 1.7182 (22°C) determined by van't Hoff (1901) reported *in* Wulff and Schaller (1934, p. 48) and with that of 1.7121 (25°C) as measured by Wulff and Schaller (1934, p. 48). No specific gravity value was reported by Torii and Ossaka (1965) on type material. Specific gravity measurements made on crystalline material that contained liquid inclusions and was not crushed in size ranged from 1.63 to 1.68 at 14°C. The brine specific gravity was found to be 1.37 (17°C).

Optical Properties

The optical properties of antarcticite were determined with some difficulty due to the unfortunate tendency of the mineral to absorb water when exposed to a non-arid atmosphere. Crushing the mineral for optical study necessarily caused rapid surface melting, hence the examination was conducted within the shortest time possible after the mineral had been placed in the immersion oils. Antarcticite was confirmed to be uniaxial (-) with ω near 1.550 and ϵ between 1.490 and 1.500. These values show good agreement with those given by Winchell and Winchell (1964) for artificial crystals and by Torii and Ossaka (1965) on type material.

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References

- ALLEN, R. D., AND HENRY KRAMER (1953) Occurrence of bassanite in two desert basins in southeastern California. Amer. Mineral., 38, 1266–1268.
- BASSETT, A. M., D. H. KUPFER, AND F. C. BARSTOW (1959) Core logs from Bristol, Cadiz, and Danby Dry Lakes, San Bernardino County, California. U. S. Geol. Surv. Bull. 1045-D, 97-138.
- , AND D. H. KUPFER (1964) A geological reconnaissance in the southeastern Mojave Desert. *Calif. Div. Mines Spec. Rep.* 83, 43 p.
- BLACKWELDER, ELIOT (1954) Pleistocene lakes and drainage in the Mojave region, southern California. Calif. Div. Mines Bull. 170, chap. V, 35–40.
- DURRELL, CORDELL (1953) Geological investigations of strontium deposits in southern California. Calif. Div. Mines Spec. Rep. 32, 48 p.
- GALE, H. S. (1951) Geology of the saline deposits of Bristol Dry Lake, San Bernardino County, California. Calif. Div. Mines Spec. Rep. 13, 21 p.
- HUDSON, F. S., AND N. L. TALIAFERRO (1925) Calcium chloride waters from certain oil fields in Ventura County, California. Amer. Ass. Petrol. Geol. Bull. 9, 1071–1088.
- KLUG, H. P., AND L. E. ALEXANDER (1954) X-Ray Diffraction Procedures. John Wiley and Sons, New York, 715 pp.

- PALACHE, C., H. BERMAN, AND C. FRONDEL (1951) System of Mineralogy ..., vol. 2, 7th ed., John Wiley and Sons, New York.
- PARKER, R. B. (1963) Recent volcanism at Amboy Crater, San Bernardino County, California. Calif. Div. Miens Spec. Rep. 76, 21 p.
- STONE, R. W., AND OTHERS (1920) Gypsum deposits of the United States. U. S. Geol. Surv. Bull. 697, 81-82.
- TORII, TETSUYA, AND JOYO OSSAKA (1965) Antarcticite, a new mineral, calcium chloride hexahydrate, discovered in Antarctica. *Science*, **149**, 975–977.
- TROXELL, H. C., AND WALTER HOFMANN (1954) Hydrology of the Mojave Desert. Calif. Div. Mines Bull. 170, chap. VI, 13–17.
- VER PLANCK, W. E., JR. (1952) Gypsum in California. Calif. Div. Mines Bull. 163, 47–48.
 (1954) Salines in southern California. Calif. Div. Mines Bull. 170, chap. VIII, 5–14.
 (1957) Salt in California. Calif. Div. Mines Bull. 175, 23–25.
- WINCHELL, A. N., AND HORACE WINCHELL (1964) The Microscopical Characters of Artificial Inorganic Solid Substances. Academic Press, New York, 439 p.
- WRIGHT, L. A., R. M. STEWART, T. E. GAY, JR., AND G. C. HAZENBUSH (1953) Mines and mineral deposits of San Bernardino County, California. *Calif. J. Mines Geol.* 49, 49–192.
- WULFF, P., AND D. SCHALLER (1934) Refraktometrische Messungen und Kristallen und Vergleich isomorpher Salze mit edelgasähnlichen und edelgasunähnlichen Kationen. 8. Mitteilung über Refraktion und Dispersion von Kristallen. Z. Kristallogr. 87, 43-71.
- WYCKOFF, R. W. G. (1965) Crystal Structures, vol. 3, 2nd ed. John Wiley and Sons, New York, 981 p.

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