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GEOCHEMICAL EVIDENCE FOR THE ORIGIN OF MIRABILITE DEPOSITS NEAR HOBBS GLACIER, VICTORIA LAND, ANTARCTICA

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Abstract

Numerous masses of bedded and concentrated interstitial mirabilite ($Na_2SO_4 \cdot 10H_2O$) occur in stagnant glacial ice and within and on top of ice-cored moraine near the terminus of Hobbs Glacier on the west coast of McMurdo Sound. Some are tabular bodies up to 50 m long and 4 m thick. They are thought to be deposits formed by freeze concentration and evaporation in supraglacial and periglacial meltwater ponds. Some deposits have been included within ice and deformed during glacial movement. Structural features within the ice and lithology of the morainal debris indicate the moraine is a remanent mass left during retreat of the formerly extended Koettlitz Glacier presently south of the Hobbs Glacier region.

Compositionally the salt masses are predominantly sodium sulfate, although K, Ca, Mg, Cl, and HCO_3 are also present, usually in amounts totalling less than five percent of the total salts. The mirabilite content of analyzed samples constitutes from 10 to nearly 100 percent of the total mass: the remainder is mostly ice.

Isotopically the δD and $\delta 0^{18}$ composition of water of crystallization of entrapped glacial ice falls on Craig's (1961) line for meteoric water (δO^{18} range $-6.8^{\circ}/_{oo}$ to $-37.9^{\circ}/_{oo}$, $\delta D -58.5^{\circ}/_{oo}$ to $-307^{\circ}/_{oo}$, relative to S.M.O.W.). The sulfur composition of mirabilite falls close to that of present-day seawater sulfate (δ S^{34} range $18.5^{\circ}/_{oo}$ to $22.2^{\circ}/_{oo}$; relative to meteorite standard). Sulfate oxygen of the mirabilite is compositionally similar to seawater sulfate ($\delta O^{18} +9.4^{\circ}/_{oo}$ to $+10.8^{\circ}/_{oo}$). Three samples contained anomalously light sulfate oxygen (δO^{18} $+1.3^{\circ}/_{oo}$ to $+4.0^{\circ}/_{oo}$).

Both bulk composition and isotopic data are consistent with a seawater source for sulfate and a glacial ice source for the water of crystallization of mirabilite. The data are further consistent with field evidence that indicates the mirabilite deposits formed by freeze concentration and evaporation in ponds fed largely by glacial meltwater. Anomalously light sulfate oxygen of some samples can be explained by a mechanism of bacterial sulfate reduction and subsequent reoxidation within the meltwater ponds.

Direct addition of sea water sulfate to the glacial ice by a mechanism of subglacial freezing on a floating ice shelf, as has been proposed by other investigators, is inconsistent with field evidence. Sulfate likely was added to the meltwater ponds by runoff waters from the surrounding land area. Introduction of seawater sulfate to present day land areas could occur by mechanisms involving isostatic and eustatic sea level changes, tectonic uplift, or by atmospheric precipitation of ocean-derived moisture.

Introduction

The unusual association of mirabilite ($Na_2SO_4 \cdot 10H_2O$) and glacial ice in the McMurdo Sound area has been known since the 1901–1904 British National Antarctic Expedition. The expedition geologist, H. T. Ferrar, described occurrences at Stranded Moraine, between the Ferrar and Blue Glaciers, and along the coast near the Hobbs Glacier (Fig. 1). Descriptions of these and other localities on the Koettlitz Glacier and nearby Ross Ice Shelf were made also during Scott's 1911–13 expedition (Debenham, 1920).

By far the greatest number of mirabilite deposits lie in a five-kilometer square area of stagnant ice-cored moraine between the terminus of Hobbs Glacier and the coastline (Fig. 2). Previous to 1966, however, only cursory examinations of isolated salt masses in the Hobbs area had been made. Moreover, virtually no data were available on the chemistry of the deposits.

Preliminary field observations in the Hobbs area were made by Black and Thomas E. Berg in 1963 and 1965, and by Black and Bowser in 1965. Systematic location, description, and sampling of the deposits were done during a two-week period in December 1966 by Black and Bowser and again by Black in January 1969. Nearly 160 of the deposits were located in the field and described, and an additional 19 were located on aerial photographs. Because of time limitations, they were not field-checked. Other salt bodies are known, but are not located or described.

The purposes of this paper are to summarize the results of stable isotope and wet chemical analyses from selected salt masses in the Hobbs Glacier area, to identify the source of the salts, and to discuss possible mechanisms of formation of the salt bodies.

Origin of Mirabilite in Antarctica

Early attempts at explaining the mirabilite in the McMurdo area relied heavily on evidence drawn from occurrences of mirabilite and associated marine muds on the floating terminus of the Koettlitz Glacier and adjacent Ross Ice Shelf. Debenham (1920, 1965) proposed a mechanism of subglacial freezing beneath a floating ice tongue combined with melting losses on top of the glacier to raise freeze-concentrated, seawater salts in the ice to the surface. A somewhat modified, but substantially similar, theory was proposed by Gow, *et al.* (1965) and Gow (1967, 1969). Using oxygen isotopic evidence Gow substantiated the seawater origin of the ice on the floating part of the lower Koettlitz Glacier.

Glacial deposits near the Hobbs Glacier were mapped during a general geologic study of part of the Royal Society Range by Blank, *et al.* (1963). They established the ice-

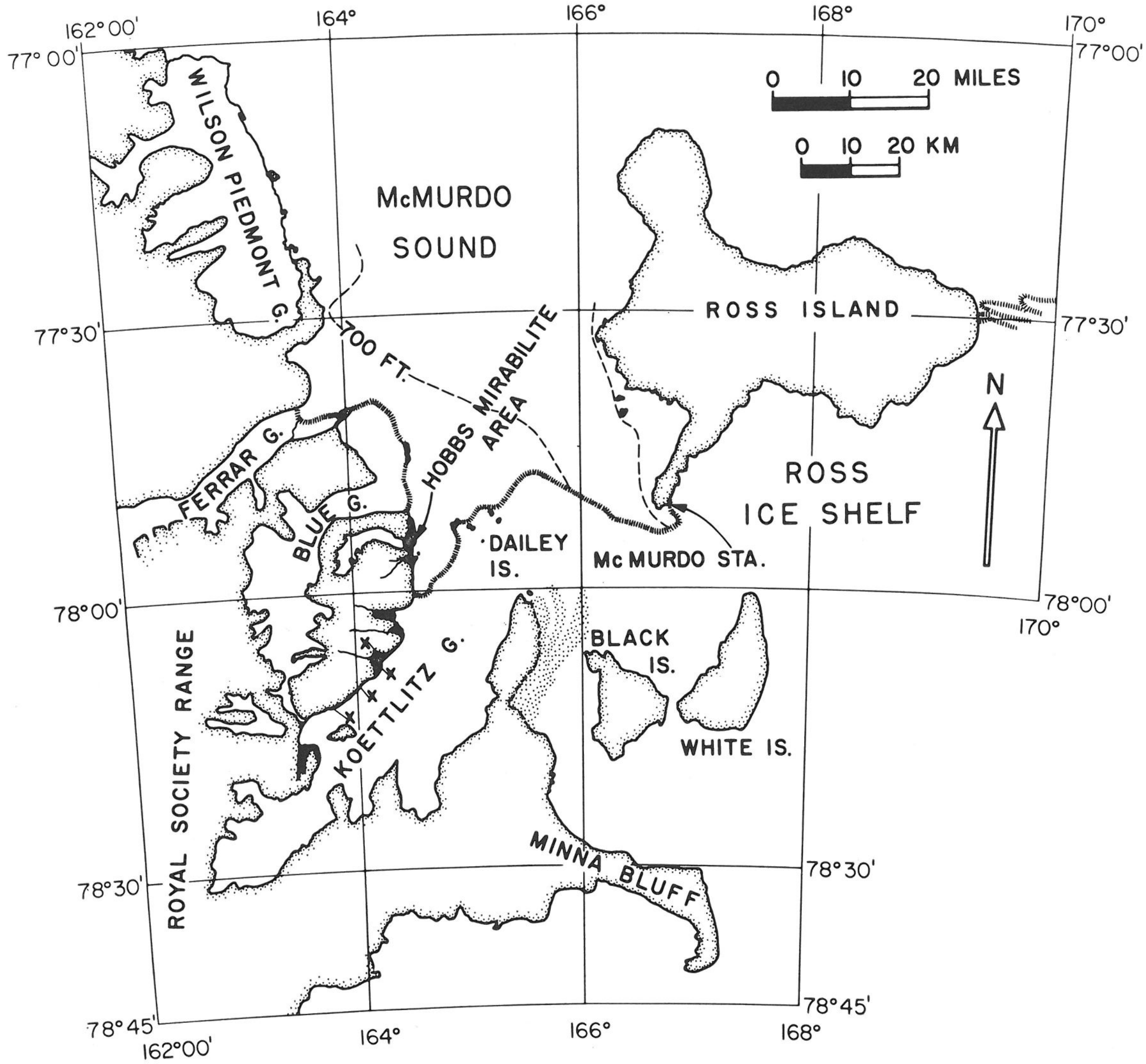

FIG. 1. Index map showing location of mirabilite deposits in the McMurdo Sound area. Areas in black indicate remnants of youngest Koettlitz Glacier morainal debris on the west side of the Glacier. Isolated mirabilite bodies like those at Hobbs glacier marked with an X. Dashed lines mark 700 foot depth in the sound.

cored moraine in front of the Hobbs Glacier as youngest, "Black Coastal," moraine from the formerly extended Koettlitz Glacier. Consequently the mechanism proposed by Gow and Debenham from the origin of the Koettlitz Glacier salts would appear to be applicable as well to the mirabilite deposits in front of the Hobbs Glacier.

Rivard and Péwé (1961) suggested that the mirabilite in front of the Hobbs Glacier is of nonmarine origin, possibly derived from volcanism in the nearby Dry Valley and Ross Island areas. Black and Bowser (1967, 1968) and Bowser and Black (1967) concluded that the mirabilite deposits were glacial pond deposits formed by freeze-concentration and evaporation of relatively small saline ponds. Because the field evidence indicates the Koettlitz ice sheet was not free floating near the Hobbs Glacier when it was last expanded, we suggested that the mechanisms proposed by Gow and Debenham were unsatisfactory for the Koettlitz morainal deposits in front of the Hobbs Glacier.

Preliminary trace element and radiocarbon data on the Hobbs mirabilite deposits were reported by Siegel and Dort (1968). Dort and Dort (1969) suggested that the Hobbs deposits as well as other lesser deposits at Skarvsnes Foreland along the Prince Olav Coast and Vestfold Hills are derived from marine waters at a time of higher sea level stand.

DESCRIPTION OF MIRABILITE DEPOSITS

Inasmuch as the major geologic features of the mirabilite deposits in front of the Hobbs Glacier have been summarized earlier (Black and Bowser, 1967, 1968 and Bowser

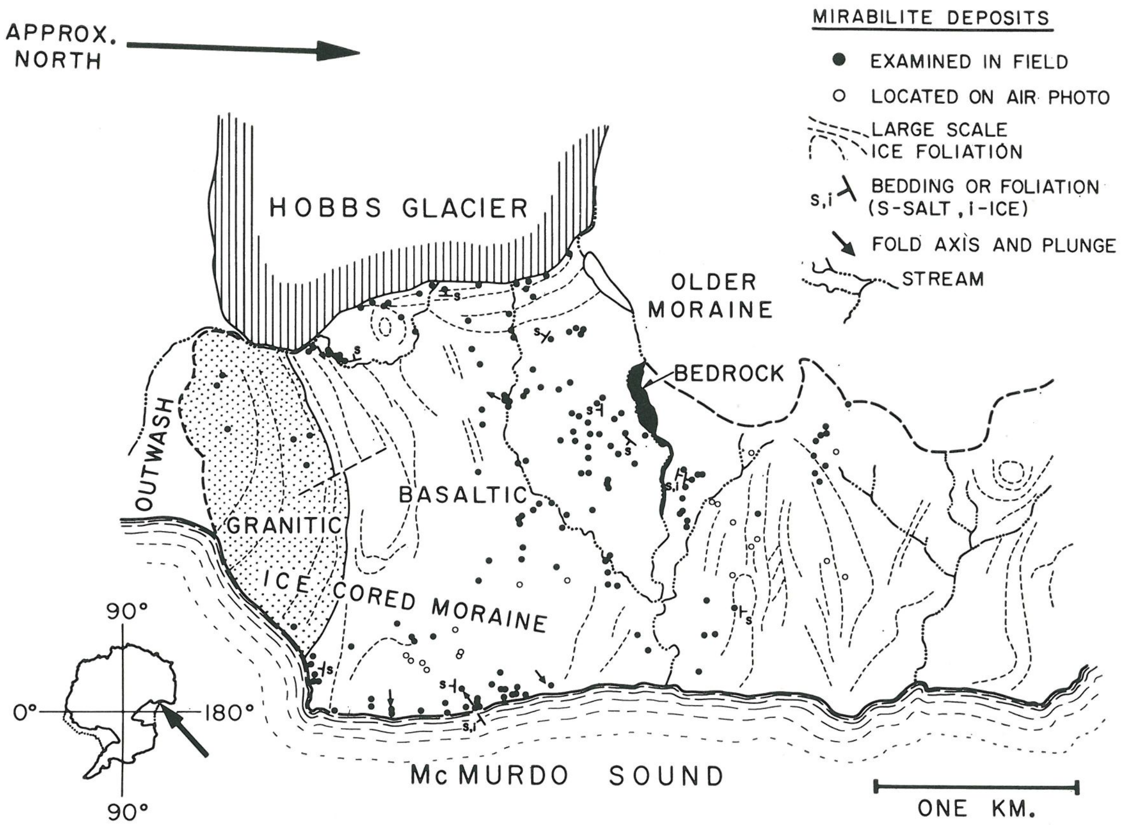

FIG. 2. Map of youngest, Koettlitz, ice-cored moraine at Hobbs Glacier locality showing location of mirabilite deposits and structural features within the ice. The area of predominantly "granitic" moraine is shown stippled, the remaining area being most basaltic and diabasic moraine.

and Black, 1967) only a brief recounting of the nature of the deposits is necessary here to provide a background for discussion of the geochemical evidence.

The location of most, but not all, isolated mirabilite bodies in front of the Hobbs Glacier is shown in Figure 2. Principal occurrences of visible salt bodies are in those morainal areas deeply dissected by modern streams and along the eroded sea coast. Undissected moraine discloses fewer salt bodies. However, numerous efflorescent crusts of thenardite (Na_2SO_4) suggest the presence of buried salt bodies.

Most salt masses are in morainal debris of predominantly basaltic rocks; a few isolated deposits shown in the south part of the area of Figure 2 are in a relatively undissected zone of predominantly granitic material. In both types the morainal debris forms a 30- to 100-cm thick blanket atop glacial ice. Foliation of ice within the stagnant moraine strikes generally west southwest to west and dips gently southward. Both ice structures and morainal composition demonstrate a source to the south, *i.e.* the formerly expanded Koettlitz Glacier. Ice foliation immediately adjacent to the Hobbs terminus dips westward, indicating a possible ice source from that direction as well. This is supported by the presence of numerous metamorphic rocks on the basaltic moraine which the basal ice of the Hobbs Glacier is overriding. Moreover, ice fabrics indicate the formerly expanded Koettlitz Glacier was grounded (*i.e.* not free-floating) in this region.

Individual mirabilite deposits range in size from 1 to 50 m in length and from several centimeters up to 4 m in stratigraphic thickness. Over 30 percent of the deposits exceed 7 m in maximum dimension. The salt masses range from mirabilite-cemented till (Fig. 3a) to nearly pure masses of bedded mirabilite (Fig. 3b). The larger salt bodies are predominantly of this latter type. Both types of deposits are associated with uncemented till and algae.

Salt masses which lie on top of the ice-cored moraine at attitudes conformable to the ice foliation are tabular conformable bodies enclosed within the stagnant ice of the Koettlitz moraine (Fig. 3c), or form thin layers in the basal shear moraine of the Hobbs Glacier. Over 30 percent of the salt bodies enclosed within the Koettlitz glacial ice display tight, commonly isoclinal folding (Fig. 3d).

The bedded character of the mirabilite and its association with interstratified algae and sediments indicate the salts were formed in ponds by freeze concentration and evaporation of saline waters (Black and Bowser, 1968).

The range of structural types of deposits from highly

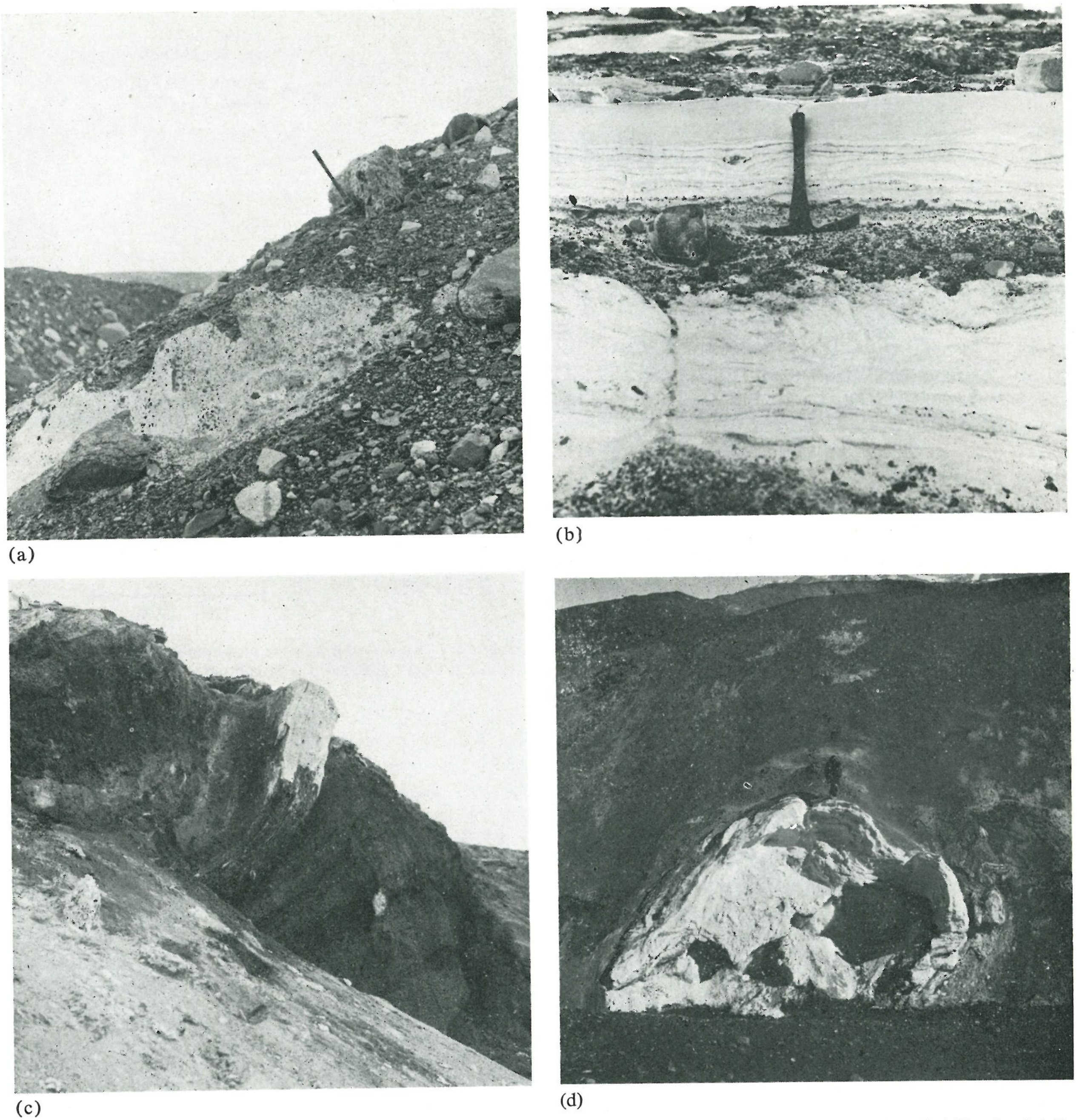

FIG. 3. Major characteristics of mirabilite deposits in the Hobbs Glacier area. (a) Glacial till cemented by mirabilite (surficially altered to thenardite) in ice-cored moraine. Trenching tool rests near a mass of algae. (b) Horizontal mass of nearly pure mirabilite showing stratification. Note ice-rafted pebble to left of pick handle. (c) Tabular body of nearly pure, bedded mirabilite (with surficial white thenardite coating) enclosed within the ice-cored moraine. Note conformity of body to ice foliation shown in lower right. Thickness of mirabilite body is approximately 45 cm. (d) Spectacularly folded, bedded mirabilite exposed in stream cut ravine in ice-cored moraine. Left dipping limbs on the left and right side of the body are nearly parallel and conformable with local ice foliation.

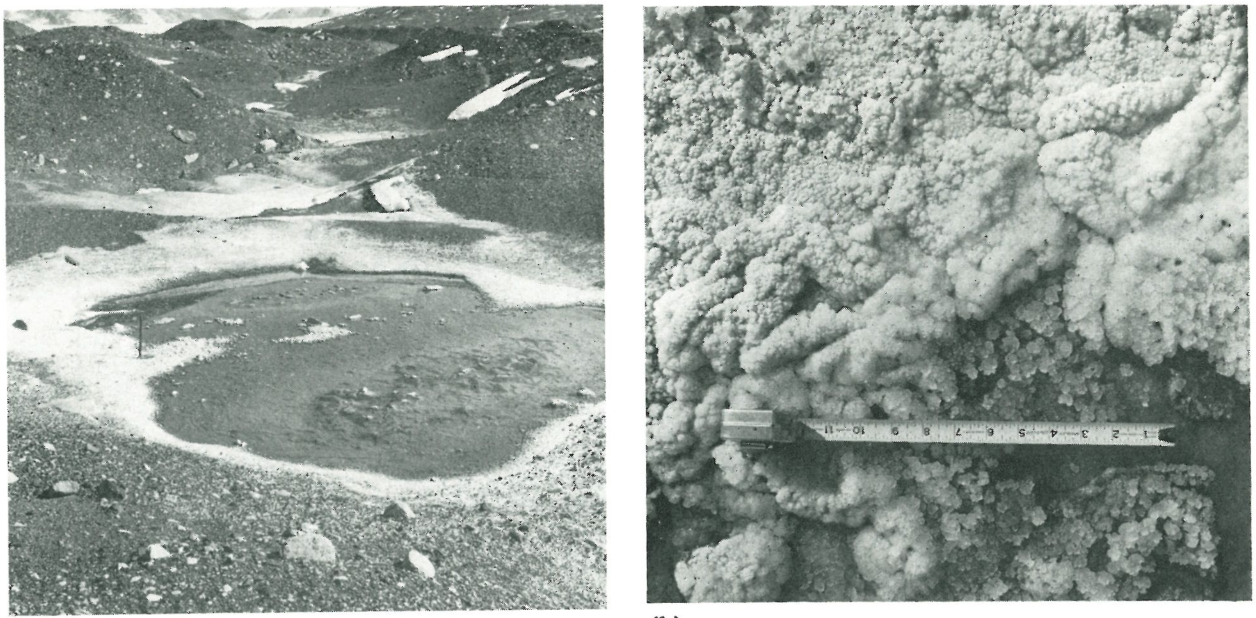
(a) (b)

FIG. 4. Modern meltwater pond demonstrating the features of mirabilite precipitation in the Hobbs Glacier area. (a) Small meltwater pond on Koettlitz derived ice-cored moraine with relatively high salt content. White efflorescent crust is thenardite formed by evaporation of capillary water surrounding pond. Algae covers bottom of pond. (b) Mirabilite precipitated on top of wrinkled surface of algae from the same pond. Photograph taken two years later.

folded masses with ice included to relatively younger undeformed formed masses on top of the moraine is presumably illustrative of the varying degrees of incorporation of pond-derived salts into the former Koettlitz ice sheet. Those in the basal shear moraine of the Hobbs Glacier clearly reflect over running of pond deposits by that glacier. The process of salt formation can be seen going on today in small meltwater ponds whose drainage area includes older salt masses. Figure 4a shows a pond containing a relatively high salt content ($1-1\frac{1}{2}\%$ by weight) with algae presently growing in the pond. The white efflorescent crust surrounding the pond is thenardite produced by evaporation of water drawn by capillary action from the pond. The nearness of the salt crust to the pond edge is a measure of the salt content of the pond. A photograph taken two years later of the same pond is shown in Figure 4b. Further evaporation of the pond water has precipitated mirabilite over an irregular mat of algae.

The field geologic data are useful in elucidating the formation of the individual salt masses, but the ultimate origin of the salts in these bodies still remains unproven.

GEOCHEMISTRY OF THE DEPOSITS

During the 1966 and 1969 field seasons samples were obtained from representative mirabilite deposits, glacial ice adjacent to the deposits, and pond waters within the ice-cored morainal area. Samples were stored frozen in sealed polyethylene bottles in the biological laboratory at McMurdo base for shipment back to the University of Wisconsin. Except during shipment most samples were stored under refrigeration until analyzed.

Stable isotopes. Seven samples of mirabilite, thenardite, and melted glacial ice from the salt deposits in the ice-cored moraine near the Hobbs Glacier were analyzed for D/H, O^{18}/O^{16}, and S^{32}/S^{34} compositions. Both sulfate oxygen and oxygen in the water of crystallization of mirabilite were determined. Two additional samples, one from the Ross Ice Shelf near its contact with the east border of the Koettlitz Glacier (Fig. 1) and another from a saline ice band at the site of the Taylor Glacier saline discharge, described by Black, *et al.* (1965) and Black (1969), were analyzed similarly. The data are summarized in Table 1 and Figures 5 and 6. Isotopic ratios for sulfate oxygen were determined by the graphite-reduction method of Rafter (1967) and Rafter and Mizutani (1967). Water of crystallization from the mirabilite samples was separated for deuterium and oxygen analysis by heating the samples in a furnace at temperatures between 200° and 300°C.

The isotopic data are reported as parts per thousand ($^{\circ}/_{oo}$) deviation from an appropriate standard of known isotopic composition according to the relationship,

$$\delta^{\circ}/_{oo} = \left(\frac{R_{\text{sample}}}{R_{\text{std}}} - 1\right) \times 1000$$

where R is the isotope ratio of HDO/H_2O, $^{18}O/^{16}O$, or $^{34}S/^{32}S$ in the sample and the standard. Deuterium and oxygen compositions are compared to Standard Mean

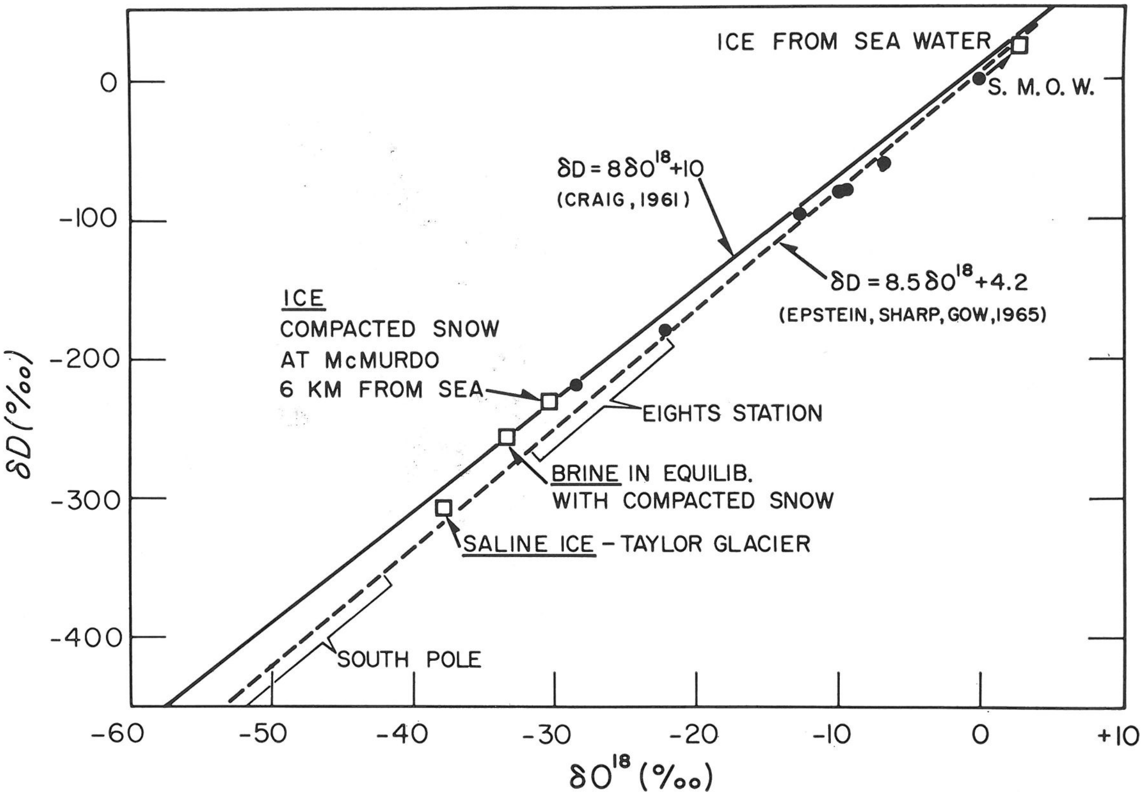

FIG. 5. δD-$\delta^{18}O$ compositions of water of crystallization of mirabilite from Hobbs Glacier area (black circles).

Ocean Water (S.M.O.W.) as defined by Craig (1961), and sulfur compositions are compared to the meteorite standard.

Analyses of the water of crystallization of mirabilite plot close to Craig's empirically derived line for meteoric water (Craig, 1961):

$$\delta D = 8\delta^{18}O + 10,$$

the $\delta^{18}O$ values ranging from -6.8 °/oo to -37.9 °/oo (Fig. 5). A summary plot of data from Antarctic ice (Epstein, *et al.*, 1965) is also shown for comparison. Their data plot on a line of the form:

$$\delta D = 8.5\delta^{18}O + 4.2,$$

however a more recent discussion of their results by Craig (1966b) suggests the $\delta D - \delta^{18}O$ deviations reported by Epstein, *et al.* may be analytical.

Comparison of our data for mirabilite with data on meteoric precipitation and polar cap ice involves the question of whether significant deuterium and oxygen fractionation can occur during precipitation of mirabilite from water. Data currently are lacking on mirabilite-water fractionation. However, the fact that δD and $\delta^{18}O$ data are both concordant with meteoric water suggests little if any isotope fractionation occurs. Further support for the assumption of little or no fractionation comes from samples from the Koettlitz Glacier floating ice tongue. The δD composition of water in mirabilite in our sample (A-K-7-66) is -24.7 °/oo. This corresponds to a calculated $\delta^{18}O$ composition of -4.3 °/oo, which is that expected for seawater derived ice (Fig. 5). Gow (1969) convincingly demonstrated that salts from this area are marine in origin, having formed by the subglacial freezing process. Similarly, ice from this portion of the Koettlitz Glacier is isotopically similar to sea water, $\delta^{18}O = +1.4$ to $+2.5$ °/oo (Gow, pers. commun.), indicating fractionation of no more than 4–5 per mil. between mirabilite and water.

The isotopic composition of the mirabilite structural water is therefore not likely derived from precipitation caused by freezing of seawater. Instead, the data are consistent with a mechanism involving crystallization from ponds whose water isotopic composition is derived from glacial meltwater. Two samples (A-H-19 and A-H-12) are clearly similar to polar cap ice (Fig. 5) and the remaining four are somewhat intermediate in composition between polar cap ice and sea ice. The intermediate composition of these four samples can be explained by noting that the Koettlitz Glacier in part drains the polar ice cap but also drains local accumulation basins whose precipitation is derived from lower elevations.

The isotopic composition of sulfur and sulfate oxygen provides a different picture of the mechanism of formation of the mirabilite. The analyzed $\delta^{34}S$ and $\delta^{18}O$ (SO^4) are listed in Table 1 and plotted in Figure 6. Five samples from the Hobbs area and one from the floating tongue of the Koettlitz Glacier fall very near the composition of modern seawater sulfate. (The average composition for these six samples is $\delta^{34}S = +9.9\ ^{\circ}/_{\circ\circ}$ and $\delta^{18}O(SO^4) = 19.2$). Modern seawater sulfate is remarkably uniform in isotopic composition, having a $\delta^{34}S$ composition of close to $+20\ ^{\circ}/_{\circ\circ}$ and a $\delta^{18}O$ composition near $+10\ ^{\circ}/_{\circ\circ}$ (Mizutani and Rafter, 1969a, 1969b, 1969c, Lloyd, 1967, and Longinelli and Craig, 1967). These samples clearly indicate a marine source for the sulfate in some of the Hobbs area mirabilite deposits. Moreover the sample from the Koettlitz Glacier offers further support of the subglacial freezing mechanism proposed by Gow (1967, 1969) and Debenham (1920, 1965).

Two samples from the Hobbs area and one from a point near Taylor Glacier in Taylor Dry Valley, however, are similar to sea water in $\delta^{34}S$ composition, but are 6–8 per mil lighter than sea water in $\delta^{18}O(SO^4)$ composition. The composition of these seemingly anomalous samples possible can be explained in one of three ways:

1. These mirabilite samples possibly could have formed from sulfate of a different source, such as volcanic or geothermal sulfate. However, the anomalous samples come from mirabilite deposits that are geologically indistinguishable from nearby samples having a marine sulfate source. Adjacent, geologically similar deposits with different isotopic compositions require an element of fortuity that seems unlikely.

2. A mechanism involving a change of the sulfate isotope composition within the meltwater pond would seem more reasonable. This could be brought about either by direct exchange of the sulfate oxygen with the isotopically lighter melt-water pond water or by bacterial sulfate reduction and later reoxidation within the pond. Lloyd (1968) demonstrated that either a decrease in temperature or increase in pH markedly decreases the rate of exchange between sulfate and water. "A 97 percent exchange of oceanic sulfate with ocean water having a mean temperature of 4°C and a pH of 8.2 would require of the order of 250,000 years," Lloyd (1968). These conditions are similar to those expected for the mirabilite precipitating, meltwater ponds. Four radiocarbon dates from algae associated with the Hobbs area mirabilite deposits have been published, ranging in age from 2,800 ± 100 to 12,200 ± 1,000 years b.p. (Black and Bowser, 1968, and Péwé, 1960). A recent unpublished date of a sample collected by Black within the basal shear moraine of Hobbs Glacier is 39,700 ± 1,200 yrs. B.P.[1] The life of any meltwater pond must have been only a fraction of this time. Therefore, from Lloyd's data, it seems probable that sulfate-water isotopic exchange is kinetically too slow to account for the anomalous Hobbs area samples.

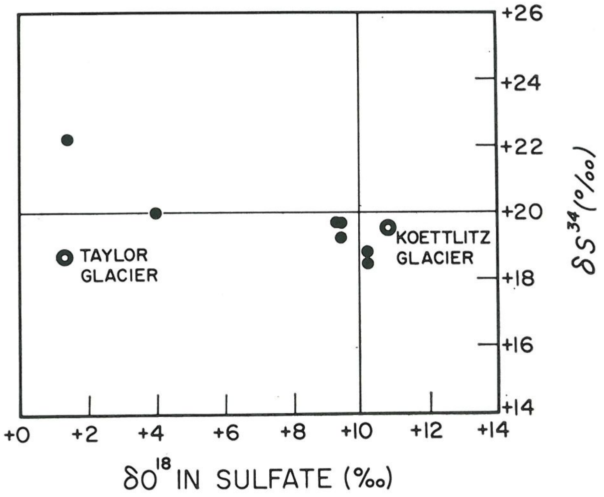

FIG. 6. $\delta^{34}S$-$\delta^{18}O$ data for sulfate in mirabilite from Hobbs Glacier area. Intersection of vertical and horizontal lines mark modern sea water composition.

TABLE 1. ISOTOPE ANALYSES

Sample no.	Sample condition	Mole ratio $\frac{H_2O}{Na_2SO_4}$	Sulphate		Water	
			$\delta^{18}O^a$ °/oo	$\delta^{34}S^b$ °/oo	$\delta^{18}O^a$ °/oo	δD^a °/oo
A-H[c]-5-66	liquid	—	9.8	18.8	−12.7	−93.4
A-TG[d]-12-66	liquid	—	0.9	18.7	−37.9	−305
A-H-15-66	solid, dry	—	8.9	19.7	dehydrated	
A-H-25-66	solid, dry	9.75	9.0	19.3	− 9.4	−76.6
A-H-19-66	solid, dry	9.95	3.4	20.0	−22.2	−180
A-H-26-66	solid, wet	12.00	9.8	18.5	− 9.9	−76.5
A-K[e]-7-66	solid, dry	10.00	10.4	19.5	lost	−24.7
A-H-12-66	solid, dry	10.20	1.0	22.2	−28.4	−217
A-H-31-66	solid, dry	6.15	9.0	19.7	− 6.8	−56.2

[a] With respect to S.M.O.W.
[b] With respect to meteoritic sulfur.
[c] A-H—Hobbs Glacier Region.
[d] A-TG—Taylor Glacier Region.
[e] A-K—Koettlitz Glacier Region.

3. Local reduction and reoxidation of the sulfate can, however, account for the isotopically anomalous samples. A discussion of the mechanism of oxidation of H_2S was given recently by Mizutani and Rafter (1969b and 1969c). The reaction proceeds as follows:

$$2H_2S + 3O_2 = 2H_2O + 2SO_2$$

$$SO_2 + H_2O + 1/2\ O_2 = 2H^+ + SO_4^=$$

Assuming no equilibrium or kinetic isotope effects, sulfur dioxide produced by oxidation of H_2S in contact with atmospheric oxygen should be $+23\ ^{\circ}/_{\circ\circ}$. If this SO_2 established isotopic equilibrium with water vapor of $\delta^{18}O = -22^{\circ}/_{\circ\circ}$ (a reasonable value for Hobbs area meltwater ponds), then using Urey's (1947) data the $\delta^{18}O$ of the SO_2 is calculated to be $+4\ ^{\circ}/_{\circ\circ}$ at 0°C. Conversion of sulfur dioxide to sulfate would take place according to the reaction given above. The isotopic composition of the resulting sulfate would be given by,

$$\delta^{18}O(SO_4^=) = \frac{\delta^{18}O(\text{Pondwater}) + \delta^{18}O(\text{Air}) + 2\delta^{18}O(SO_2)}{4}$$

$$= \frac{-22^{\circ}/_{\circ\circ} + 23^{\circ}/_{\circ\circ} + 2 \times 4^{\circ}/_{\circ\circ}}{4} = +2.5^{\circ}/_{\circ\circ}$$

The calculated value is in accord with the observed anomalous $\delta^{18}O$ samples. The meltwater need not be totally

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[1] Kindly obtained through the assistance of George Denton, University of Maine. Sample analyzed by Minze Stuiver (Yale Radiocarbon Lab. Sample No. Y-2640).

TABLE 2. Chemical Analyses (ppm)

	a	b	c	d	e	f	g	h	i	j	k	l	m	n	o	p
Sample no.	H-2	H-4	H-5	H-7	H-8	H-9	H-11	H-17	H-20	H-21	H-22	H-27	H-28	An-2	An-14	S.W.
Na^+	153	850	156,000	56	670	33,000	4,400	5,030	52,800	1,080	84,000	11,000	20,700	9,500	800	10,556
K^+	3.3	24	500	1.4	80	140	35	150	100	150	240	180	780	280	<40	380
Ca^{2+}	4.2	94	420	5.0	40	185	10	58.9	87	35	200	352	429	39	39	400
Mg^{2+}	0.4	3	133	0.9	19	14	8	32.3	15	4	72	39	147	88	14	1,272
Fe	—	<0.04	—	—	—	—	—	—	<0.04	<0.04	<0.16	—	4.8	<0.2	<0.2	
B	0.13	0.25	0.25	0.03	2.0	0.10	0.07	2.0	0.13	0.30	0.80	1.0	2.3	3.1	0.25	4.6
Cl^-	30	34.4	1,180	24.5	246	236	125	700	235	212	280	308	909	1,300	90	18,980
SO_4^{2-}	225	1,880	306,200	78	730	72,000	8,600	8,550	115,000	1,840	196,000	26,500	42,750	17,000	300	2,649
HCO_3^-	24.4	244	488	12.2	458	268	48.8	383	549	63.4	780	536	1,353	298	94	140
CO_3^{2-}	—	—	—	—	—	—	—	—	—	—	—	—	—	248	38	—
F	0.44	3.4	1.2	0.1	3.4	0.64	2.9	13	1.1	3.2	3.4	1.4	—	—	—	—
Total Solids	441	3,133	464,900	178	2,248	105,800	13,230	14,919	163,787	3,338	281,600	38,920	67,080	28,760	1,375	34,380
Na/K	46.4	35.4	312	40.0	8.4	236	126	33.5	528	7.2	350	61.1	26.5	33.9	>20	27.8
Ca/Mg	10.5	31.3	3.2	5.6	2.1	13.2	1.2	1.8	5.8	8.8	2.8	9.0	2.9	0.44	2.79	0.314
(Na+K)/(Ca+Mg)	34.0	9.0	283	9.7	12.7	167	246	56.8	519	31.5	310	28.6	37.3	77.0	>15.1	6.54
SO_4^{2-}/Cl^-	7.5	54.7	259	3.2	3.0	305	68.8	12.2	489	8.7	700	86.0	47.0	13.1	3.33	0.140
SO_4^{2-}/HCO_3^-	9.2	7.7	627	6.4	1.6	26.9	176	22.3	210	29.0	251	49.4	31.6	57.0	3.19	18.9
$(B/Cl) \times 10^3$	4.3	7.3	0.21	1.2	8.1	0.42	0.56	2.9	0.55	1.4	2.9	3.2	2.5	2.9	2.8	0.24
% mirabilite in ice	0.09	0.61	100	0.03	0.36	23.6	3.2	—	37.8	0.69	62.3	8.3	14.4	—	—	—

EXPLANATION OF TABLE 2

a. Glacial ice from beneath salt body no. 1:
b. Glacial ice from beneath salt body no. 4:
c. Mirabilite from salt body no. 4:
d. Glacial ice from 20″ beneath salt body no. 5:
e. Glacial ice from 10″ beneath salt body no. 5:
f. Mirabilite+interstitial ice from salt body no. 5:
g. Glacial ice from area with thenardite efflorescent crust at surface:
h. Saline pond from drainage area including an older mirabilite deposit: (See Fig. 7)
i.–j. Two samples from different stratigraphic levels in salt body 51:
k. Mirabilite plus ice from salt body no. 57:
l.–m. Two samples from mirabilite body 77 associated with carbonaceous material. (Dated at 12,000 yrs. B.P.):
n. Water from same meltwater pond as sample H-17 collected 2 years later:
o. Water from meltwater pond near sample An-2:
p. Sea water:
a.–m. Analyzed by Wisconsin State Hygiene Laboratory.
n.–o. Analyzed by Winisconsin Alumni Research Foundation.

depleted in oxygen for the sulfate reduction to take place initially (although this could occur in early spring or late fall when the pond would be ice covered). A locally reducing environment can exist beneath the mat of algae at the bottom of the pond, and, therefore, sulfate reduction could take place there while the pond water proper could still be equilibrated with atmospheric oxygen. Thus only a fraction of the total sulfur in the pond need be in the reduced state at any given time. The existence of the locally reducing environment beneath the algae mat was verified in the field in modern meltwater ponds in the ice-cored morainal area.

Major element analyses. Results of major cation and anion analyses of 15 samples are presented in Table 2. With the exception of samples H-17, An-2, and An-14, the samples were solid at the time of collection. Intercrystalline brine may have been present in some of the more concentrated salt samples, but this was not discernible in the field. Samples labelled An-2 and An-14 were analyzed at the Wisconsin Alumni Research Foundation and the remainder were done at the Wisconsin State Hygiene Laboratory.

Carbonate-bicarbonate determinations for samples An-2 and An-14 were determined by titration with standard acid by Black in the field; the remainder of the samples were measured for HCO_3^- and CO_3^{2-} in Madison. Samples H-17 and An-2 are from the same meltwater pond (taken two years apart).

Some difficulty was encountered in analytical accuracy of the results as evidenced by the somewhat large imbalance of cation and anion equivalents (average difference 17%) from the Hygiene Laboratory analyzed samples. A plot of total solids content, obtained by summing individually analyzed constituents, versus specific conductivity (Fig. 7), however, is reasonably linear. The fact that some of the samples with the highes ttotal solids content show the largest cation-anion imbalance suggests that the sodium and sulfate determinations are the least precise. However, because of the wide variation in total solids content of the samples, intersample comparisons do seem to be meaningful, even with a 15–20 percent uncertainty in some analyses.

The pertinent cation and anion ratios for the samples are summarized in Table 2 and are plotted graphically as a function of total solids in Figure 8. It is apparent that sodium and sulfate become the predominant constituents for samples with the highest total salt content.

Differentiation of a marine versus nonmarine origin of the salts is difficult to prove on the basis of major element analysis only. Some of the analyses scatter around the ionic ratio values of sea water, suggesting it is a *possible* salt source. However, because the stable isotope data presented in the previous section indicate that the salts are marine in origin, discussion of the compositional variation of different salt bodies will be restricted to models consistent with a marine salt source.

The roughly linear dependence of the ionic ratios to the total salt content of mirabilite deposits is further evidence of their genetic relationship to one another. The ionic ratio variations among these samples are thought to be caused by fractional precipitation during freeze contraction and evaporation of brines in individual meltwater ponds and by fractionation of salts during incomplete melting of salt entrapped ice.

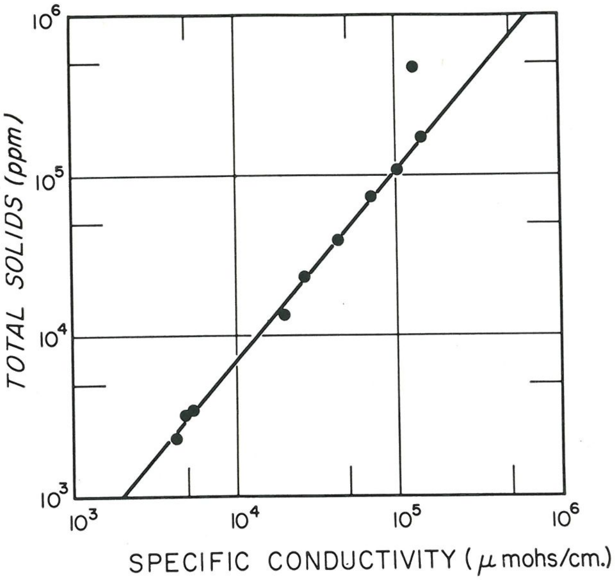

FIG. 7. Total solids content versus specific conductivity for samples listed in table 1.

Thompson and Nelson (1956) demonstrated that mirabilite is the first phase to precipitate during freezing of sea water and that other phases, such as $NaCl \cdot 2H_2O$, do not crystallize from seawater brines above −23°C; in fact, complete freezing of seawater does not take place until brine temperatures fall below −54°C. The preponderance of mirabilite in the Hobbs salt deposits is thus consistent with derivation from waters bulk compositionally similar to seawater.[1]

Surface temperatures in winter in the McMurdo area rarely fall below −38°C today, and corresponding temperatures in brines in frozen-over, meltwater pond water are likely warmer by 10 or more degrees. Even if winter temperatures in the McMurdo area had been colder when some of the salt deposits were forming, meltwater pond brines would not likely have been much colder than −35 to −40°C for short periods during the austral winter. Inasmuch as these temperatures are insufficient to completely solidify the pond brines, it seems clear that fractional pre-

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[1] Data from Thompson and Nelson (1956) show that 27 grams of mirabilite/kg of sea water can be precipitated by cooling sea water to −23°C (the temperature of initiation of crystallization of $NaCl \cdot 2H_2O$). For two meters of annual ice formation in the McMurdo area (estimated from data in Zubov, 1963) this would produce a maximum of approximately four centimeters of mirabilite in a saturated meltwater pond. The net annual mirabilite accumulation must be less than this, however, inasmuch as it is ultimately controlled by the net loss of water from a pond by combined evaporation and sublimation.

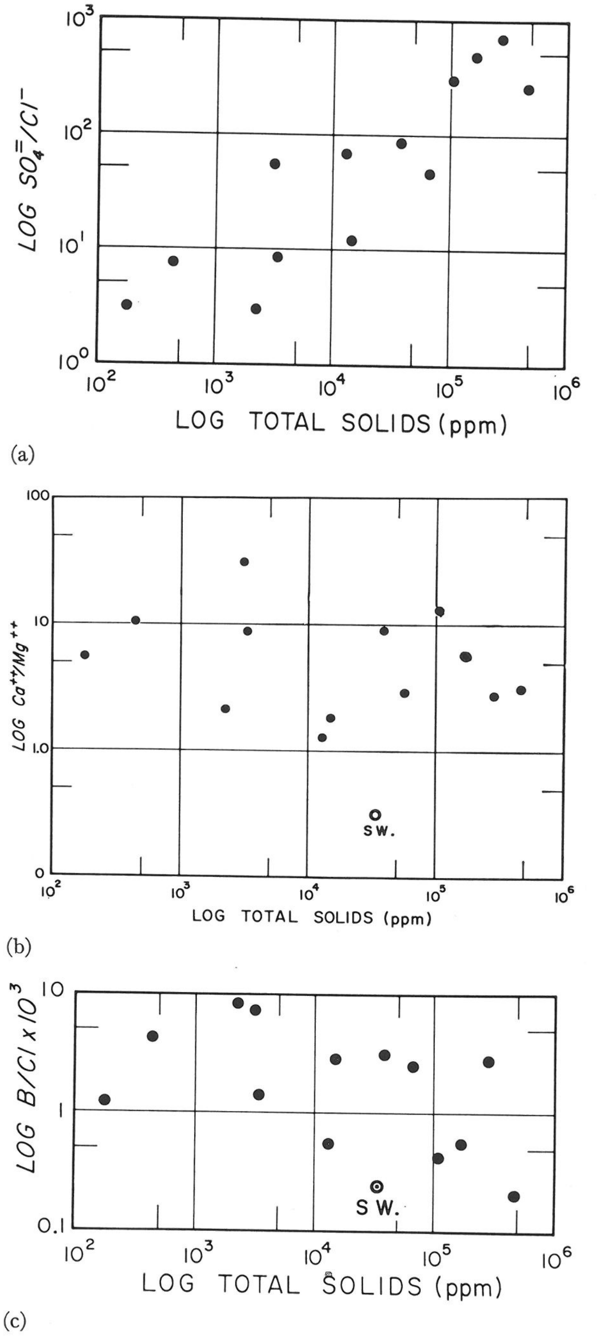

FIG. 8. Ionic ratios from mirabilite deposits, glacier ice, and pond waters from the Hobbs Glacier area. (S.W. = seawater). (a) Sulfate/Chloride, (b) Calcium/Magnesium, (c) Boron/Chlorine.

cipitation is an important control on element ratios in the resulting salt precipitate. This is further evidence by the fact that, if the salts were derived from seawater without fractionation, the chloride content should exceed sulfate by a factor of 7:1.

At first glance the fact that the Na/K, Na+K/Ca+Mg, SO_4/Cl, and SO_4/HCO_3 ratios of the Hobbs area samples increase with increasing total salt content would seem to be inconsistent with Thompson and Nelson's data. One could reason that salt bodies with higher total solid content are ones that are completely crystallized, and that, therefore, they should contain *higher* amounts of K, Cl, and carbonate relative to sodium and sulfate. A more satisfactory explanation for the element ratio data, however, is that analyzed constituents other than sulfate and sodium are entrapped within the ice phase of the samples. Inasmuch as the samples are composed essentially of ice and mirabilite the two phases must, of course, be inversely related to one another in relative proportions. Thus, if the other cations and anions occur in brine pockets in the ice, the ratio between sulfate and another anion (Fig. 8a) or sodium and another cation (see Table 2) would also be expected to show an inverse relationship.

Ion ratios that do not include sodium or sulfate should, then, reveal the fractionation trends expected for freeze precipitation of marine salts. The B/Cl and Ca/Mg plots show just that (Figs. 8b–8c). The average Ca/Mg and B/Cl ratios are greater than seawater by factors greater than 10 (respectively 24 and 12). Boron is a conservative element during freezing of normal seawater (Blinov, 1965), hence, it might be concentrated relative to chloride in brines formed by partial melting of saline ice. The data of Thompson and Nelson (1956) indicate that calcium would tend to remain in the unfrozen brine relative to magnesium when cooled below −36°C. Consequently it would be expected that increased Ca/Mg ratios could be explained by the same mechanism as that causing the higher B/Cl ratios in the salt deposits.

The relatively high degree of scatter of the B/Cl and Ca/Mg ratios in samples from the different mirabilite bodies indicate that some chemical fractionation of the meltwaters takes place *before* they reach the meltwater ponds. Thus, fractional melting of saline ice must also have played a role in determining the composition of the meltwater ponds from which the mirabilite was precipitated. Partial melting of the ice-cored moraine, of permafrost-cemented older moraine, and of ice in bedrock occurs regularly in the austral summer months. Capillary draw of the meltwater to the surface combined with evaporation leads to the formation of extensive, powdery crusts of thenardite in the Hobbs Glacier and adjacent Dry Valley regions. Both of these processes acting together produce a compositionally modified salt. Also the notably low concentration of chloride in the mirabilite deposits indicates that the source waters were considerably enriched in sulfate relative to chloride before they reached the meltwater ponds.

DISCUSSION

The stable isotope data for sulfate oxygen and sulfur clearly indicate an ultimate marine source for the mirabilite sulfate, and the isotopic composition of the water of crystallization indicates a nonmarine, *i.e.*, glacial, source of water from which the mirabilite precipitated. Satisfactory explanation of these data requires a mechanism to separate the marine salts from seawater or to dilute the seawater with a larger volume of isotopically much lighter glacial melt water.

The mechanism of subglacial freezing of marine waters beneath the floating tongue of the Koettlitz Glacier proposed by Debenham (1920, 1965), Gow *et al.* (1965) and Gow (1967, 1969) fails to explain the data from the Hobbs area on more than one basis. Structurally the ice-cored moraine enclosing the mirabilite deposits exhibit features of grounded, not floating, ice. Moreover, at the time the Koettlitz Glacier expanded into this area sufficiently to leave ice 200 meters above present sea level, ice thickness was such as to have grounded the glacier in all this part of McMurdo Sound (note the position of the minus 700-foot contour in McMurdo Sound, Fig. 1). Eustatic lowering of sea level at the time of the Koettlitz Glacier advance would have moved the grounding line of the glacier even further north of the Hobbs area. However, isostatic depression of the land would have compensated, at least in part, for the eustatic change which here is ignored.

Evidently, then, the salts were derived from a landward source which was itself derived from seawater. Older marine evaporite deposits are totally absent in the adjacent area, ruling them out as possible source (Blank, et al., 1963). Efflorescent crusts of thenardite are present, however, in nearly all the ice-free areas of the McMurdo Sound area (Black and Bowser, 1967, 1968). These salts are concentrated by evaporation of capillary-drawn water in the dry zone above permafrost. Older areas with thick dry zones have more salts in the soil profile than younger areas with thin dry zones. These salts from the permafrost and overlying dry zone in the drainage area near the Hobbs Glacier are likely direct sources for much of the salts in the meltwater ponds in which the mirabilite precipitated. Although isotopic data are not available for sulfate from the permafrost in the region, there is some evidence to suggest it is compositionally similar to seawater. If it were compositionally dissimilar, it would have diluted the sea water derived sulfate producing a shift in isotopic composition of the salt. No evidence for this is seen in the Hobbs Glacier area. Moreover, as is discussed in the section on major element chemistry, the growth of efflorescent crusts is probably one of the processes which chemically fractionate the salts before they reach the saline ponds. Further examination of the process involved in the formation of salts and their stable isotope chemistry is presently in progress.

The process of adding marine salts to high elevations in the McMurdo Sound region is not clearly understood. Mirabilite bodies like those in front of the Hobbs Glacier are found to elevations of at least 800 meters (Parker, E. Calkin, written commun., Dec. 1, 1969). These are seemingly too high to have been deposited directly from a marine source. Past eustatic and isostatic changes of sea level during the past few tens of thousands of years should have involved at most a few tens of meters of change. Only striking tectonism could have accomplished such changes. Evidence for such an event has been suggested by Black and Berg (1968) from studies in Taylor Valley.

Abundant mirabilite is deposited annually on the sea ice in McMurdo Sound (Wellman and Wilson, 1963). Only rarely do winds in winter blow from the north and northeast to transport those salts to the coastal areas on the west side of the Sound and less frequently into the Dry Valleys and highlands. However, it is well known that precipitation carries minute quantities of salts from evaporated sea water. Long-term concentration of such salts in meltwater from snow and ice in the highlands of the Dry Valley region is a possible source, and, therefore, a likely alternative to the proposed mechanism of tectonic uplift. It should be possible to decide among the alternatives by appropriate stable isotope and bulk compositional studies of permafrost and associated dry zones at a number of different elevations from the coastline inland from McMurdo Sound.

Isotopic studies have been published on the origin of salts in saline lakes of the Dry Valley area, specifically Lakes Vanda and Bonney. Jones *et al.* (1967) and Jones and Faure (1967) argue that the strontium in the lakes is derived from weathering and not seawater or volcanic sources. On the other hand Craig (1966a), using D/H data, and Rafter and Mizutani (1967) and Mizutani and Rafter (1969b) using $\delta^{18}O$-$\delta^{34}S$ data, have shown that their results are consistent with a marine source for the water and sulfate respectively. The data could be rationalized by arguing a separate source for the strontium and sulfate. It is important to note, however, that the strontium content of these lakes is very small relative to chloride and sulfate. From mass balance considerations, a very large amount of rock weathering would be required to produce the amount of sulfate and chloride in these lakes. Evidence for significant chemical weathering in the McMurdo region is lacking. Again, the isotopic composition of salts from the Hobbs area are inconsistent with sulfate derived from weathering, at least in the past 40,000 years. More complete studies are necessary to tie these contrasting arguments together. Other arguments for the origin of saline lakes in Antarctica based solely on bulk chemical data have largely failed because of the significant amount of chemical fractionation these waters have undergone.

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