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HUNTITE FROM A CARBONATE-EVAPORITE ENVIRONMENT

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ABSTRACT

Early diagenetic huntite is reported from a Recent, supratidal, evaporitic environment along the Trucial Coast, Persian Gulf. Initial carbonate sediments are being extensively dolomitized and a suite of early diagenetic minerals—gypsum, bassanite, anhydrite, celestite, halite, magnesite—is being developed by precipitation from interstitial, seawater-derived brines and by reactions between brines and original carbonate sediments. This occurrence of huntite is unusual because of its evaporitic environment and its association with an active belt of sedimentation, previously reported occurrences being all from weathering horizons or caves.

INTRODUCTION

Huntite was first described from Currant Creek, Nevada, and Eureka, Utah, by Faust (1953). The mineral has subsequently been identified at Dorog, Hungary (Koblencz and Nemecz, 1953), in la Grotte de la Clamouse in the Herault region, France (Baron, Caillere, Lagrange and Pobeguin, 1957), Tea Tree Gully, Australia (Skinner, 1958), Uzbek and Tadzhik, USSR (Golovanov, 1959), Crestmore, California (Carpenter, 1961), and Gabbs, Nevada (Vitaliano and Beck, 1963). J. Thrailkill (1965) has recently reported huntite from Carlsbad Caverns, New Mexico.

The geological setting and association of the Trucial Coast huntite are rather different from those of previously reported occurrences. The Trucial Coast huntite is associated with other carbonate, sulphate and chloride minerals in an environment where Recent carbonate sediments are undergoing a series of early diagenetic changes (Kinsman, 1964a, 1964b, 1966).

TRUCIAL COAST ENVIRONMENT

Along the Trucial Coast (Fig. 1), the partial infilling of marine lagoons by Recent carbonate sediments has formed a coastal plain, in places more than 10 miles wide, which lies just above the level of normal high tides. Similar supratidal surfaces have been developed around most of the offshore islands by carbonate sediment accretion. A levelled profile across the mainland supratidal surface near Abu Dhabi (Fig. 1) showed a surface relief of less than two feet, the elevation being 3 to 5 feet above mean sea level. The supratidal surfaces have an area in excess of 1000 square miles and are the product of sedimentation in response to an essentially constant sea level over the past 4000 to 5000 years.

The carbonate sediments range from very fine-grained aragonite muds, deposited in low-energy, relatively sheltered areas, to coarse skeletal sands and gravels, predominantly of aragonite, which accumulated along higher energy, unsheltered coasts. Although the mineralogy of both sediment types is similar, trace element and grain size differences have resulted in significant differences in early diagenetic developments.

Occasional flooding, by lagoon waters, of large supratidal areas sometimes occurs, particularly when strong on-shore winds coincide with spring tides. Normally, however, the surface is fairly dry. Recorded air temperatures range from 15°C to 47°C (average 28°C) and rainfall averages less than 1.5 inches per year. The area is consequently one of high net evaporation. Evaporation of water from the supratidal sediment surface results in interstitial pore fluid concentration. Along any one profile the ground water concentration normally increases away from the shore and in any one position the pore fluid concentration increases upward from the ground water table through the capillary zone (except immediately after flooding). The water table usually lies 1 to 4 feet below the surface. Temperature variation at the ground water table is 25 to 39°C, averaging 34°C. The hydrology of the area is poorly understood but it is thought that evaporation losses of water and consequent lower-

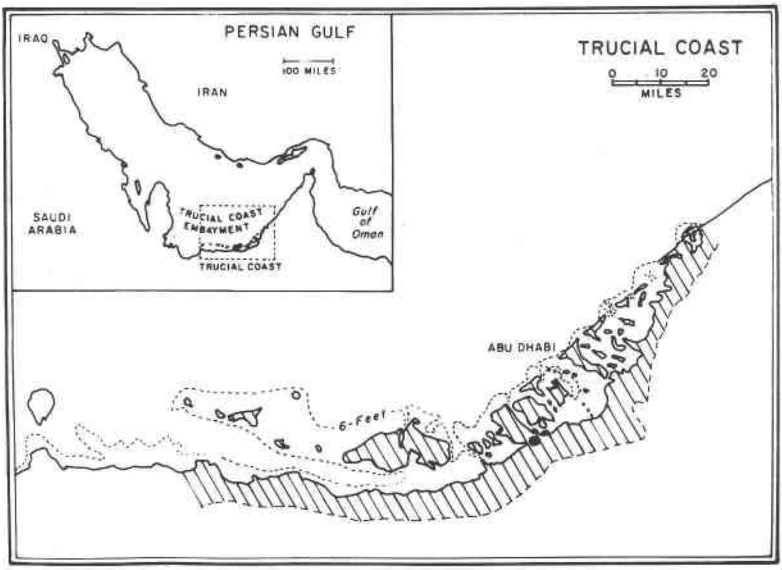

FIG. 1. Inset map shows the Trucial Coast area in relation to the Persian Gulf. Detailed Trucial Coast map shows location of Huntite (●) and approximate distribution of supratidal areas (hashed).

ing of the water table are balanced by additions of surface, lagoonal, flood waters and perhaps also by lateral flow from seaward, within the sediments. Analyses indicate that the ground waters, except at the inner margins of the mainland supratidal areas, have a definite seawater origin. Some mixing with continental ground waters does occur in areas close to the Tertiary rocks at the inner edge of the mainland supratidal surface.

HUNTITE OCCURRENCE

Huntite has been found in the unlithified sediments of the coastal plain, about 20 miles southwest of the small town of Abu Dhabi (Fig. 1: 24°15′ N, 54°15′ E). The mineral occurs in the upper 16 inches of the sediments, as irregular wisps and blebs, up to 0.3 inches in size. It is associated with a sandy mud of very fine aeolian grains of detrital quartz and carbonates, together with abundant corroded crystals of anhydrite, celestite and gypsum.

Detailed section at huntite locality:

1. Halite crust with wind ablation lag of coarse gypsum crystals and shells.	0–1 inches
2. Fine, windblown sand of quartz and carbonate grains.	1–6 inches
3. Muddy sand matrix with large gypsum crystals, some anhydrite laths; some celestite; traces of dolomite; wisps and blebs of *huntite*, forming 5–10% of sediment.	6–16 inches
4. Platy nodules of coarse-grained, dirty anhydrite in places with abnormally high amounts of celestite (up to 30%); gypsum crystals growing within anhydrite nodules and replacing earlier anhydrite.	16–18 inches
5. White, nodular anhydrite; medium-grained carbonate sand as inter-nodular matrix; celestite common in inter-nodular areas.	18–21 inches
6. Large gypsum crystals in brownish carbonate sand; occasional small anhydrite nodules (<0.04 inch).	21– inches

(Water table deeper than 27 inches)

Inside the wisps and blebs of huntite the only associated mineral is halite (this is possibly an artifact, developed because of evaporation of pore fluid after sample collection). The wisps and blebs are soft and white, and microscopic examination shows the grains to be less than 1–2μ in diameter.

MINERAL IDENTIFICATION

The mineral is relatively insoluble in water and effervesces in dilute mineral acids. Staining with an alcoholic-alkaline solution of diphenylcarbazide gave anomalous results in early stages of identification. Feigl (1958) states that magnesite, when warmed in such a solution, stains a red-violet color almost immediately and that this stain is retained even after boiling with water. Double carbonates such as dolomite remain unstained by diphenylcarbazide. A sample of huntite was washed to remove any magnesium present in interstitial pore fluids and warmed with an alcoholic-alkaline solution of diphenylcarbazide. A red-violet color appeared fairly rapidly but disappeared again on washing with boiling water. This behavior indicated a magnesium bearing mineral, other than dolomite or magnesite and the reaction with acids indicated it was probably a carbonate.

Initial X-ray diffraction work was complicated by the presence of other mineral phases. For example, the major reflection of halite (2.821 Å) lies close to the major reflection of huntite (2.833 Å) and in addition, the majority of the other reflections present could have been accounted for by dolomite, anhydrite and magnesite, which it was known were quite possibly present. A sample was picked clean from associated materials, washed and centrifuged in water. The X-ray diffraction pattern compared closely with those of earlier recorded huntites (Table 1). Only the relative intensities of the reflections of the Trucial Coast huntite are given in Table 1, but these compare fairly well with previously reported intensities.

The unit-cell dimensions, $a=9.499$ Å, $c=7.819$ Å, are similar to those calculated by Graf and Bradley (1962) for huntite from Currant Creek, Nevada, $a=9.505$ Å, $c=7.821$ Å.

CONDITIONS OF FORMATION

The Trucial Coast huntite is associated with anhydrite, gypsum, celestite and traces of dolomite, but little is definitely known of the chemistry of the precipitating solution. The mineral post-dates the phase of marine carbonate sedimentation and is definitely of diagenetic origin. There is no textural evidence to indicate that the huntite is an *in situ* replacement of a pre-existing carbonate or sulphate mineral. Natural voids similar in form to the wisps and blebs of huntite have not been observed and so it seems unlikely that the mineral is a void filling. The wisps and blebs, even though soft and composed of extremely small crystals, would seem to be capable of physically displacing the enclosing unlithified carbonate sediments (*cf.* the emplacement of multicrystalline anhydrite nodules, discussed by Kinsman, 1966).

Studies of sediments and pore fluids in other parts of the supratidal areas enable some suggestions to be made about the possible conditions of huntite precipitation.

Analyses of the marine lagoon waters show the ratio $m_{Mg^{2+}}/m_{Ca^{2+}}$ to range 5.3–5.5. Analyses have also shown this ratio to rise rapidly in the marine-derived pore fluids as concentration ensues, partly because of

Table 1. Comparison of X-ray Diffraction Data for Huntite from Trucial Coast and from Previously Described Localities

A	B	C	D	E	F	G	
d	*d*	*d*	*d*	*d*	*d*	*d*	*I*
5.69	—	5.64	—	5.67	5.66	5.63	3
4.81	—	4.73	—	4.75	4.75	4.74	2
4.16	—	—	—	—	4.16	—	—
3.67	3.65	3.63	—	3.64	3.64	3.64	5
—	—	—	—	3.53	3.52	—	—
—	—	—	—	—	3.20	—	—
3.15	3.145	3.12	3.10	—	3.15	3.125	2
2.905	2.91	2.89	—	2.89	2.89	2.881	50
2.838	2.829	2.830	2.829	2.83	2.83	2.822	100
2.74*	—	2.74	—	2.74	2.74	2.744	4
2.580	2.58	2.598	2.592	2.604	2.605	2.602	20
2.444	2.434	2.443	2.437	2.432	2.427	2.433	18
2.388	2.379	2.372	2.374	2.375	2.372	2.373	18
2.298	2.297	2.279	—	2.284	2.285	2.281	10
2.204	2.203	2.188	2.171	2.190	2.190	2.190	14
1.986	1.989	1.988	—	1.991	1.992	1.989	30
—	—	1.966	1.966	1.972	1.973	1.971	50
1.900	1.888	1.895	1.918	1.896	1.894	1.899	2
		1.888					
1.840	1.836	1.832	1.837	1.835	1.840	1.833	5
1.803	—	1.818	—	1.821	1.821	1.818	5
—	—	1.793	—	1.796	1.793	1.794	5
1.769	1.767	1.762	1.763	1.765	1.765	1.764	30
—	—	1.752	—	1.757	1.750	1.755	31
1.708	1.705	1.696	—	1.700	1.700	1.700	6
—	—	1.651	—	1.656	1.654	—	—
—	—	1.608	—	1.611	1.608	—	—
1.590	1.589	1.581	1.585	1.584	1.584	1.584	16
—	—	—	—	1.537	—	—	—
1.529	1.529	1.523	1.522	1.526	1.522	1.524	4
—	—	1.515	—	1.518	—	—	—
1.488	1.489	1.479	—	1.481	—	1.480	8

A—Huntite, Currant Creek, Nevada (Faust, 1953)
B—Huntite, Dorog, Hungary (Koblencz and Nemecz, 1953)
C—Huntite, Tea Tree Gully, Australia (Skinner, 1958)
D—Huntite, Kurgashinkin, Uzbek SSR (Golovanov, 1958)
E—Huntite, Currant Creek, Nevada (Graf and Bradley, 1962)
F—Huntite, Gabbs, Nevada (Vitaliano and Beck, 1963)
G—Huntite, Trucial Coast, Persian Gulf
*—From Skinner (1958)

calcium loss associated with aragonite precipitation, but mainly owing to the precipitation of gypsum, once concentrations of 3 to 4 times normal seawater are exceeded. By the time pore fluid concentrations have reached about ×4–5, the ratio $m_{Mg^{2+}}/m_{Ca^{2+}}$ is often in excess of 10. Dolomitization of the aragonitic sediments is under way by about this stage and the $m_{Mg^{2+}}/m_{Ca^{2+}}$ ratio thereafter falls, ultimately reaching values of less than four. In areas where the initial marine sediments are essentially aragonite muds the dolomitization is relatively rapid but where the initial marine sediments are coarser grained carbonate sands, dolomitization is retarded.

The huntite occurs in an area where the marine sediments are essentially sandy and dolomite is developed in only trace amounts. Consequently it may be expected that in such areas, the ratio $m_{Mg^{2+}}/m_{Ca^{2+}}$ climbs to values in excess of 10 (maybe as high as 30). The development of anhydrite gives a clue to the concentration reached by the brines (Kinsman, 1966). In areas where pore fluids have been analyzed it has been found that anhydrite first precipitates where ground water concentrations are in excess of ×6. Yet in areas of fine grained sediments, by this stage in concentration, appreciable dolomitization has occurred and $m_{Mg^{2+}}/m_{Ca^{2+}}$ ratios have fallen to less than five. Thus if little dolomitization has occurred but appreciable calcium sulphate (gypsum and anhydrite) precipitation has taken place, it is probable that quite high $m_{Mg^{2+}}/m_{Ca^{2+}}$ ratios are attained ($\gg 10$). The pH of the interstitial brines, from data recorded in other parts of the coastal plain, ranges 6.5–7.5.

Stability relationships of magnesium and calcium carbonate minerals at low temperatures are not well known and experimental and natural occurrence data are often complicated by the presence of metastable phases. Many natural solutions would seem to be supersaturated with respect to dolomite, yet this phase is not readily nucleated. Similarly, there seem to be nucleation problems for calcite in solutions where $m_{Mg^{2+}}/m_{Ca^{2+}} > 1$, particularly at temperatures above 25°C. Magnesite also does not readily nucleate in solutions when it is seemingly the stable phase. In the virtual absence of the stable phases, a metastable mineral assemblage is precipitated. For example, the minerals aragonite, huntite and hydromagnesite effectively occupy the stable equilibrium fields of calcite, dolomite and magnesite (Carpenter, in Garrels and Christ, 1965, p. 375–377). Aragonite and hydromagnesite are the carbonate phases precipitated in laboratory experiments from magnesium—calcium solutions (see, for example, Alderman, 1965). Huntite has not, so far, been precipitated in similar experiments. Thus under conditions of fairly rapid precipitation the entire calcite-dolomite-magnesite field may effectively be occupied by aragonite-hydromagnesite.

The Trucial Coast data indicate the following precipitating solution conditions, (a) temperature, 20–40°C, (b) $m_{Mg^{2+}}/m_{Ca^{2+}} \backsimeq 10–30$, (c) $p_{CO_2} \backsimeq 10^{-2.0} - 10^{-3.5}$. If the ratio $c_{Mg^{2+}}/c_{Ca^{2+}}$ does not depart widely from $m_{Mg^{2+}/Ca^{2+}}$ then the solution lies in the metastable equilibrium field of huntite, as calculated by Carpenter (*op. cit.*) from published free energy data (calcite, dolomite and magnesite presumed absent). Hydromagnesite has not, so far, been recorded from this area.

OTHER HUNTITE OCCURRENCES

The huntite from Currant Creek, Nevada (Faust, 1953) occupies vugs and cavities in a bedded tuff formation. Associated minerals are magnesite, dolomite and deweylite, which are considered to have been precipitated from hydrothermal solutions rich in magnesium. Huntite was found to be a very late development associated with the meteoric water stage. Faust considered the mineral to precipitate as a very fine powder from cool ground waters which gathered their magnesium locally in traversing the magnesite deposits. The huntite had for some years been mistakenly considered to be a magnesite-dolomite solid solution (Faust, 1953, Faust and Callaghan, 1958).

The huntite from Dorog, Hungary (Koblencz and Nemecz, 1953) occurs on the walls and floors of a mine. No further data are available relating to its occurrence.

Baron *et al.* (1957) have found huntite as a precipitated cave carbonate ("montmilch" or "mountain milk") in caves in dolomite in the Herault region of France. The mineral was precipitated from waters which had become relatively rich in magnesium after traversing the associated dolomite rocks.

The Tea Tree Gully huntite from Australia (Skinner, 1958) occurs at depths of up to 30 feet below the surface, as nodules associated with a dolomite horizon. Surface weathering of the dolomite has resulted in calcite being formed; the magnesium in part has formed nodules of magnesite and in part percolated down into fissures and precipitated as huntite. No evidence was found of the huntite replacing dolomite or magnesite. Skinner suggested that the evidence indicated direct precipitation of huntite from descending surface waters. There was the possibility, however, that the huntite had formed by interaction between descending surface waters and earlier formed magnesite nodules.

The huntite described by Golovanov (1958) was formed as fracture fillings in the weathered mantle of lightly serpentinized dolomites and was associated also with hydromagnesite and opal. The opal often penetrated the huntite in a network of fine fractures, while hydromagnesite occurred as very small crystals in cavities in the huntite. The huntite was considered to result from supergene conditions connected with circulation of surface waters, which in traversing the local rocks had come to have relatively high magnesium/calcium ratios.

At Crestmore, California, Carpenter (1961) found the mineral assemblage magnesium calcite-aragonite-huntite as an encrustation on brecciated calcite-monticellite rock. The minerals were very fine-grained and field relations suggested deposition from surface waters. The magnesium calcite-aragonite-huntite assemblage was considered to represent a metastable early mineral assemblage; in some places replacement by an equilibrium dolomite-calcite assemblage was found.

Vitaliano and Beck (1963) have reported huntite from Gabbs, Nevada. Early dolomite has been mineralized and in part converted to magnesite; subsequent igneous activity has resulted in brucite being developed. The huntite occurs as veinlets in the fractured and weathered mantle of the brucite and is associated with hydromagnesite. Surface waters percolating downwards are considered to have precipitated the huntite.

Thrailkill (1965) has reported huntite from Carlsbad Caverns, New Mexico, associated with aragonite, calcite, hydromagnesite and dolomite. Aragonite, calcite and hydromagnesite are being precipitated directly from solution whereas dolomite and huntite apparently are derived from the alteration of hydromagnesite. Thrailkill concluded that huntite was a metastable mineral under the cave conditions.

SUMMARY AND DISCUSSION

Huntite is now known from three different environments:

1. As a cave carbonate in areas where the country rocks are magnesium-rich, such as dolomitic limestones or dolomites. Cave carbonates comprise a range of metastable and stable calcium and magnesium minerals. The environment provides opportunities for studying the conditions under which these minerals form, but as cave deposits are not widely recognized in ancient rocks this environment is geologically not very important.
2. As a near-surface weathering product of magnesium-rich rocks such as brucite marbles, dolomites, magnesites or serpentinites. Available data indicate that the huntite is confined to the uppermost 30 feet. The development of huntite as a product of the weathering and degradation of earlier rocks does not augur well for its continued survival. Only if a continental weathering horizon be preserved would the huntite stand much chance of long continued survival. Mineral stability data of Garrels *et al.* (1960), indicate that huntite is metastable and will in time be replaced by a stable mineral assemblage such as magnesite-dolomite or dolomite-calcite.
3. As a diagenetic mineral in Recent sediment sequences such as that along the Trucial Coast. In this environment the pore solutions are magnesium-rich. The diagenetic processes could in some ways be considered an unusual form of weathering but even so a significant difference between this and the preceding type of environment can be distinguished. In this type of area active sedimentation is underway and the end product of sedimentation and diagenesis may well be preserved (as opposed to the preceding environments where the huntite is developed during a destructive, degradation cycle). Even so, the early formed

huntite will probably be replaced during later diagenesis by an equilibrium assemblage such as magnesite-dolomite or dolomite-calcite. The huntite, being extremely fine-grained will not be replaced by recognizable pseudomorphs and the individual wisps and blebs are not sufficiently distinctive to be diagnostic of the earlier presence of huntite.

Thus in ancient lagoonal/shelf carbonate sequences some of the dolomite or magnesite may originally have been huntite. In evaporite deposits the dolomite and magnesite which are often found dispersed or as stringers throughout the sequence, could have been initially huntite, at least in part.

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