Replacements involving early carnallite in the potassium-bearing evaporites of Yorkshire.

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[Read 26 January 1956.]

Summary.—Evidence from four recent boreholes in the Yorkshire potash field suggests that carnallite was an important original constituent of the Middle Evaporite Bed, and that much of the sylvine of the potash zone is of secondary origin.

The carnallitic rocks have been affected by complex replacements, an earlier series involving sylvine, halite, and anhydrite, and a later series involving rinneite, halite, sylvine, and carnallite.

THE experimental work of van't Hoff and other workers has shown that in the evaporation of sea-water the principal potassium-bearing chloride deposited should be carnallite. Sylvine does not appear in the experimental salt succession at reasonable temperatures. In most natural deposits, however, sylvine is one of the most abundant potassium salts, and carnallite is generally subordinate in quantity. These facts have led to suggestions that sylvine is, at least partly, formed by secondary replacement of earlier carnallite, due to contemporaneous or post-consolidation reaction or solution and redeposition, involving brines originating in various ways (e.g. contemporaneous influx of sea-water, later ground water, residual trapped brines, brines formed by rise in temperature during burial, &c.).

Although in many cases direct evidence of these processes is not available, in most salt deposits there is evidence of redistribution of salts, especially in the potash zones, where the minerals are highly susceptible to solution or reaction. In the Permian potash deposits of Yorkshire evidence of wide-spread replacement and recrystallization has been described (Stewart, 1949, 1951; Armstrong, Dunham, and others, 1951; Raymond, 1953), but hitherto there has been no evidence of the former presence of primary carnallite in large quantity in the potash zones, where sylvine is abundant and carnallite relatively scarce. The home of carnallite is in the Carnallitic Marl, which separates the Upper and Middle Evaporite Beds, and most of this carnallite is secondary, occurring as veinlets in the clay.

Fisons Limited have recently sunk four boreholes in the Yorkshire potash field, sited at Robin Hood's Bay (F.1 borehole), Staintondale (F.2), Little Beck (F.3), and Hawsker (F.4) (see map in Stewart, 1954, p. 212). In these boreholes the evaporite succession is similar to that found in previous boreholes in the Whitby district. All four holes show a potash zone with abundant sylvine in the Middle Evaporite Bed, and two holes (F.2 and F.4) show a sylvine-rich zone in the Upper Evaporite Bed. In all these boreholes the writer has found structures in the potash zone of the Middle Evaporite Bed which he interprets as pseudomorphs, mainly of halite, after carnallite. These are so abundant as to indicate that carnallite was an important original constituent of this zone. The potash zone of the Upper Evaporite Bed shows no evidence of this type.

Nature of the pseudomorphs.

The pseudomorphs are normally composed of halite, which in some cases has been replaced by later minerals, as described below. Typical examples are shown in figs. 3 and 4. When enclosed in clay they are often well formed, but where clay is subordinate they tend to show poorly developed outlines. They are generally fairly small in comparison with the average grain size of chlorides in these evaporites, the well-shaped pseudomorphs reaching a diameter of a few millimetres. Many have hexagonal outlines and others are diamond shaped, while some have more than six sides. Sections of cubic halite would provide a variety of shapes, and hexagonal sections would not be uncommon, but in all such sections the cleavage traces should be parallel to the edges. In the pseudomorphs the halite cleavages are variably orientated with respect to the edges. Rectangular and trigonal sections are relatively rare where the pseudomorphs are abundant.

It seems clear that these grains are pseudomorphs. That they represent early carnallite is suggested by the fact that corroded relics of carnallite are occasionally found within them, in the form of very small ragged grains in common optical orientation. Sometimes the residual carnallite has apparently recrystallized as pseudo-hexagonal crystals, and sometimes it fills negative cubic cavities in the halite.

The shapes of the pseudomorphs are similar to those of small crystals of carnallite found, enclosed in halite, through a considerable depth range in this evaporite bed. The interfacial angles of the sharpest hexagonal sections of the pseudomorphs agree with the angles $110 \wedge 010$ and $110 \wedge 1\bar{1}0$ of carnallite, although precise measurement is impossible because of irregularities in outline. Some of the diamond-shaped sections give angles corresponding to $110 \wedge 1\bar{1}0$ of carnallite, and zoning of impurities within such crystals shows that the form 010 was present at an earlier stage of growth. Some rounded pseudomorphs may represent sections of complex carnallite crystals like those figured in mineralogical textbooks (e.g. *Dana's System of Mineralogy*, 7th edition, vol. 2, p. 93).

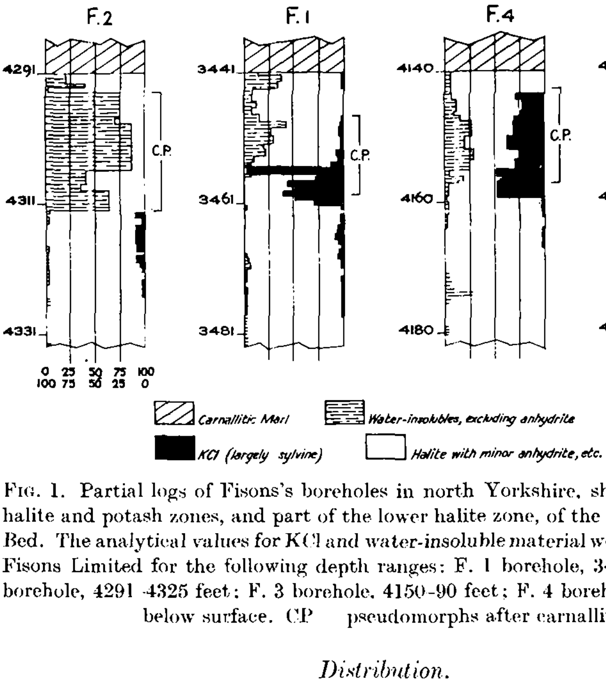


FIG. 1. Partial logs of Fisons's boreholes in north Yorkshire, showing the upper halite and potash zones, and part of the lower halite zone, of the Middle Evaporite Bed. The analytical values for KCl and water-insoluble material were determined by Fisons Limited for the following depth ranges: F. 1 borehole, 3441–78 feet; F. 2 borehole, 4291–4325 feet; F. 3 borehole, 4150–90 feet; F. 4 borehole, 4140–67 feet below surface. CP = pseudomorphs after carnallite.

Distribution.

Fig. 1 shows the range through which the pseudomorphs are found in the potash zone of the Middle Evaporite Bed of the four F. boreholes. The KCl content of the potash zone (largely contained in sylvine) and the content of water-insoluble material (largely magnesitic clay) is also shown. Within the depth ranges indicated, the pseudomorphs are extremely abundant. In the F.1 borehole, for example, it is estimated that carnallite originally formed more than 50 % of the soluble salts in the upper part of the potash zone.

It can be seen that the distribution of early carnallite does not coincide with the present distribution of sylvine, although their ranges overlap. It is believed that much of the sylvine has formed during secondary redistribution of salts. The zone rich in early carnallite is succeeded upwards by a thin zone consisting largely of halite with clay (the upper halite zone); carnallite occurs here in the form of veinlets cutting clay, and pseudomorphs after early carnallite are absent.

Pseudomorphs after carnallite occur in thin clay-rich layers within the lower halite zone of this evaporite bed, indicating periods of almost complete desiccation followed by influx of more brine.

Petrography.

The rocks have been affected by complex replacements which can be divided into two main series. The earlier series involves the replacement of original carnallite and perhaps rinneite by sylvine, halite, and anhydrite, and the later involves the introduction of new rinneite, sylvine, and carnallite. These replacements are depicted graphically in fig. 2.

First replacement series. Where least modified by the later replacements, the rocks are medium grained and consist of variable proportions of dark grey to black clay and halite, with subordinate anhydrite, magnesite, and quartz, and scarce sylvine and carnallite. Tiny hematite plates are abundant inclusions in some of the halite. Pyrite is an occasional accessory. The original bedding, approximately horizontal, is shown by variations in the quantity of clay, and the distribution of the pseudomorphs indicates an original roughly layered series of carnallite-rich and halite-rich layers.

In some of these rocks irregular patches of blood-red halite, interstitial to pseudomorphs of brown halite after carnallite, suggest the former presence of an iron-bearing mineral. The red halite is crowded with minute hematite inclusions, which are often arranged in zones which do not appear to bear any definite relation to crystallographic directions in their host. The patches closely resemble patches of rinneite of the later replacement series which are partly replaced by sylvine or halite with hematite inclusions. It is therefore suggested that the red halite of the first replacement series has replaced early rinneite which may itself be a secondary mineral.

The original rocks, then, apparently consisted of carnallite, halite, magnesitic clay, and subordinate anhydrite. Rinneite may have been introduced at an early stage. The replacement of carnallite and the mineral believed to be rinneite is almost complete. Corroded relics of sylvine in pseudomorphs of halite after both the early minerals show that sylvine appeared at an intermediate stage and was then converted to halite. Secondary anhydrite sometimes accompanies the halite in

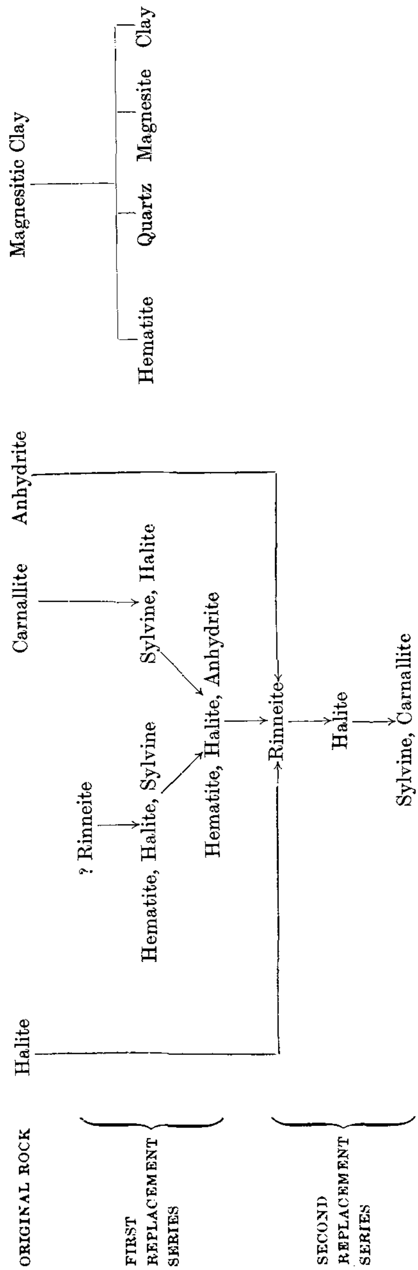
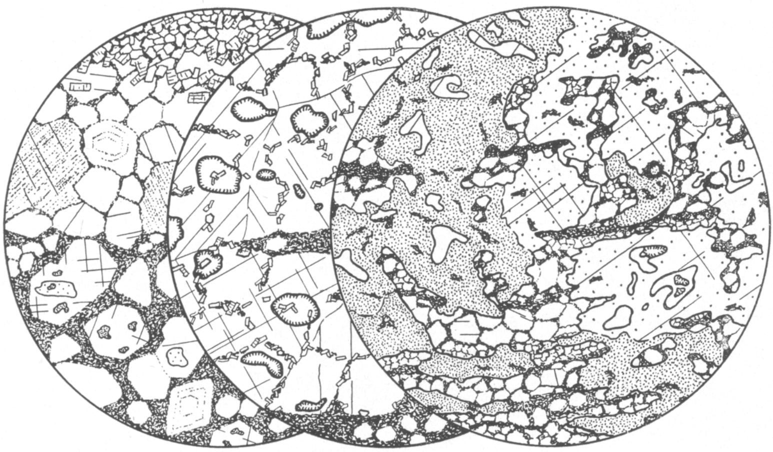


FIG. 2. Replacements in the potash zone of the Middle Evaporite Bed.

pseudomorphs after carnallite and is occasionally the dominant secondary mineral.

In addition to the hematite derived from early rinneite (?), hematite is present in extremely small particles in most of the halite, colouring it pink or brown. The colour is most pronounced near the contact of halite

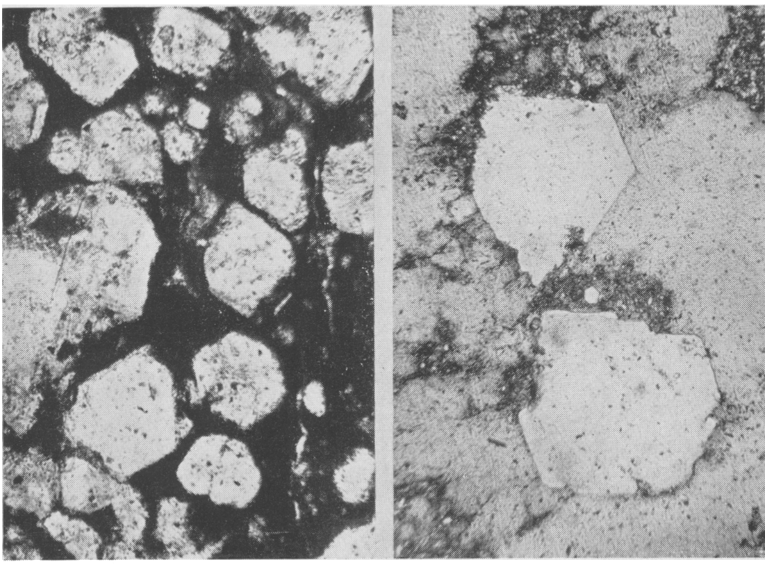


A B C

FIG. 3. A. Halite pseudomorphs after early carnallite, enclosing relics of carnallite (heavily stippled), and sylvine (lightly stippled), are partly enclosed in clay. Two large halite grains, with lines of hematite inclusions (right and left centre) may have replaced earlier rinneite. Anhydrite projects into halite at top of diagram. Magnesite and quartz, present in small quantity, are omitted. F. 1 borehole, 3452 feet below surface. ×23. B. Large colourless halite grains of the second replacement series enclose corroded, optically continuous, relics of rinneite. The rinneite has replaced earlier halite pseudomorphs after carnallite, whose boundaries are indicated by strings of anhydrite and magnesite. Some unaltered pseudomorphs are enclosed in clay layers. F. 1 borehole, 3450 feet below surface. ×23. C. Halite-clay rocks of the first replacement series (the halite is red-brown in colour) are invaded by large grains of sylvine (lightly stippled) and carnallite (heavily stippled) of the second replacement series. The latter contain corroded relics of colourless halite and rinneite, introduced at earlier stages of the second replacement series. The rinneite relics (SE. quadrant) are optically continuous, and several halite relics (NW. quadrant) have parallel cleavages. Small quantities of anhydrite, magnesite, and quartz are omitted. F. 1 borehole, 3454 feet below surface. ×8·6.

with clay, and it is believed that the iron oxide has been derived by leaching of the clay. This hematite is present in sylvine relics but not in relics of early carnallite and not in minerals of the second replacement series, which suggests that the modification of the clay took place during the early replacements.

Euhedral quartz is mainly associated with clay, and was probably formed at the same time as the hematite, the silica being derived from the clay. Some quartz crystals contain zones of hematite inclusions. Magnesite plates, often fringing clay, may have been formed by



A B

FIG. 4. A. Halite pseudomorphs after carnallite, enclosed in clay. F. 1 borehole, 3452 feet below surface. ×32. B. *Halite* pseudomorphs after carnallite, enclosed in sylvine of the second replacement series. One of the pseudomorphs has been partly replaced by sylvine, but retains some sharp boundaries. The dark material is clay, which encloses a quartz crystal near the centre of the figure. F. 3 borehole, 4060 feet below surface. ×23.

recrystallization of fine-grained magnesite. This mineral also occurs as small grains in thin anhydrite layers which are considered to be primary.

In the first replacement series the original textures of the rocks have been preserved, and there has been no appreciable mechanical displacement of material.

Second replacement series. These replacements involve the introduction of rinneite, halite, carnallite, and sylvine in irregular patches and vein-like masses. The original structures are sometimes largely obliterated, the older material being partly displaced and broken up, including the clay. In other cases a network of anhydrite, quartz, magnesite, and clay indicates the original structure.

The first change is the introduction of rinneite, and this is well seen in material from the F.1 borehole, near the top of the potash zone. The mineral forms large irregular grains, which have replaced halite. It is normally colourless, and it is possible that the pre-existing hematite in the halite has contributed iron to the secondary rinneite. Plentiful relics of brown halite are found in the rinneite. The secondary mineral forms fairly large grains, up to about a centimetre in length, but these are often represented by optically continuous relics in later minerals. Anhydrite has been partly attacked at this stage.

The second change is the replacement of rinneite by colourless halite, and most of the rinneite now seen has been partly replaced and occurs as small relics enclosed in the halite.

The third change is the replacement of the early red halite, the rinneite, and the late colourless halite by sylvine and carnallite, which enclose optically continuous relics of these minerals, and occur as irregular veins penetrating them. The sylvine and carnallite form irregular grains, of variable size and occasionally very large (up to 2 inches across in the veins). They may have formed simultaneously, as there is no evidence of the one replacing the other. The carnallite is honey-yellow in hand specimen, and the sylvine white or red, or white with red edges, the red colour being due to inclusions of hematite.

Rinneite and carnallite of this replacement series are abundant only in the upper part of the potash zone of the F. 1 borehole. Sylvine is the main late replacing mineral in the F. 3 and F. 4 boreholes, and is also abundant in the lower part of the range of pseudomorphs after carnallite in the F. 1 borehole. In the F. 2 borehole the upper part of the potash zone is extremely rich in clay, and the late potassium-bearing salts are present only in very small quantity.

In all these rocks veinlets of halite and carnallite, sometimes with slickensided walls, penetrate clay and all the minerals so far described.

Conclusions

It is suggested that carnallite was an important original mineral of the potash zone of the Middle Evaporite Bed, occurring in a layered series of carnallite-rich and halite-rich rocks. This accords with the experimental evidence. Pseudomorphs after carnallite have been seen in all the F. borings and in one of the few specimens recovered from the potash zone in the E. 2 boring.

In the first replacement series this primary carnallite has been almost completely replaced; $MgCl_2$ and then KCl have been removed, and

$NaCl$ and $CaSO_4$ introduced, the end-products being halite and anhydrite. In the thin pseudomorphous layers within the lower halite zone these replacements have probably been effected by influx of less saline marine brine after periods of almost complete desiccation. A similar origin may be invoked for the main pseudomorphous range, in the potash zone, the new brines being responsible for deposition of the upper halite zone. The absence of pseudomorphs after carnallite in the upper halite zone supports this origin, rather than that of post-consolidation leaching.

The second replacement series involves local introduction of $MgCl_2$ and $FeCl_2$, and general introduction of KCl, at the expense of NaCl and some $CaSO_4$. The fact that sylvine is the main secondary mineral suggests either that the replacements were effected at a relatively high temperature (perhaps resulting from burial under a considerable thickness of later rock), or that the brines responsible had compositions lying off the liquid line of descent from sea-water. After removal of $MgCl_2$ the second stage of the first replacement series involves the removal of sylvine, and this would result in brines rich in KCl. The migration of these brines might lead to re-deposition of sylvine at different levels of the potash zone. Potash-rich brines might, however, arise in various other ways (e.g. from connate waters, geothermal metamorphism, post-consolidation leaching). Whatever may be the cause or date of the later replacements, it is apparent that the present distribution of potash salts does not coincide with their original distribution in a vertical sense, although it approximates to it. This also appears to be true in a horizontal sense; for example, pseudomorphs after carnallite are widely distributed but sylvine is scarce in the F. 2 borehole. This horizontal redistribution of salts is an important factor to be taken into account in exploration of the potash field for economic purposes.

In conclusion I wish to record my sincere thanks to Fisons Limited for permission to publish data on their material and to use the results of analyses carried out in their laboratories.

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