

*The mineralogy of the British Permian evaporites*

By F. H. STEWART

Department of Geology, University of Edinburgh

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*Summary.* The occurrence of the minerals is reviewed. Consideration of their genesis leads to a tentative list of primary minerals, and of early diagenetic, later diagenetic and geothermal metamorphic, and late near-surface changes.

IN 1943 Professor Tilley recorded the occurrence of polyhalite in the rocks of the D'Arcy Exploration Company's E.2 borehole at Aislaby, near Whitby; this was the first published record of a potassium-bearing salt in British evaporites. The occurrence of rocks containing sylvine (Lees and Taitt, 1946) prompted further exploration by Imperial Chemical Industries and Fisons Ltd. after the war, and this showed the presence of large deposits of potassium ores in the Whitby region. There is now a considerable literature related to these, and it seems timely to give a short review of the mineralogy of the British Permian evaporites. The writer is most grateful to Fisons Ltd. who have kindly allowed him to use unpublished information from his study of their boreholes F.1 at Robin Hood's Bay, F.2 at Staintondale, F.3 at Little Beck, and F.4 at Hawsker, in the Whitby-Scarborough district. The position of these and the other boreholes mentioned in this paper can be found in the map of Dunham (1960).

*Distribution of the minerals*

The evaporites occur in two principal areas—east and west of the Pennine Hills. In the western area (the Vale of Eden, west Cumberland, and the Furness district of Lancashire), where four evaporite beds have been recognized (Hollingworth, 1942), the mineralogy is relatively simple; carbonates, anhydrite, and gypsum are the main constituents. In the eastern area the mineralogy is much more complex. Here there are three main evaporite beds, each in general becoming thicker from the north, west, and south in County Durham, Yorkshire, and Nottinghamshire towards a central area in the Whitby-Scarborough region. In the margins of the area carbonates are the only major constituents, and these are joined successively in each evaporite bed by anhydrite (with

or without secondary gypsum), halite, and potassium-bearing salts towards the Whitby-Scarborough potash field. In this potash field, the Top Anhydrite is probably the start of a fourth evaporite cycle.

*The potash field.* Table I shows the stratigraphy of the potash field, and the distribution of the minerals so far recorded, with an indication of their relative abundance, excluding detrital and clay minerals which need further study. The table is based on publications by Armstrong, Dunham, *et al.* (1951), Beevers and Stewart (1960), Dunham (1960), Fleck (1950), Guppy (1944), Raymond (1953, 1962), Sabine (1953), Stewart (1949, 1951*a* and *b*, 1953, 1954, 1956, 1963), and Stewart, Chalmers, and Phillips (1954), together with the writer's study of the four Fisons boreholes.

*North-eastern England outside the potash field* (Dunham, 1948, 1960; Edwards, 1951; Forbes, 1958; Fowler, 1943, 1944; Hollingworth, 1942, 1948; Napier, 1948; Raymond, 1959, 1962; Sherlock, 1921; Sherlock and Hollingworth, 1938; F. H. Stewart, 1954; G. E. Stewart, 1947; other references are given in Dunham, 1960). Dolomite, anhydrite, gypsum, and halite are major constituents of certain zones. Calcite is a fairly common minor constituent, and locally a major constituent of the Magnesian Limestones. Pseudomorphs of anhydrite after early gypsum are abundant in the Upper Evaporites at Hayton. In the sulphate and chloride zones of the Upper and Middle Evaporites hematite is associated with clays and silts but is less abundant in the salts than it is in the potash field, while quartz and talc appear to be much less common than in the potash field and there is only one record of magnesite (Forbes, 1958): traces of pyrite are not uncommon and celestine has been found rarely in sulphate rocks. In the Magnesian Limestone, dolomite is predominant, calcite, gypsum, and anhydrite are common minor and occasional major constituents, accessory pyrite is widespread, and sulphur is a local minor constituent; Raymond (1962) also records traces of halite, hematite, and talc and gives the only record of magnesite.

A suite of metalliferous minerals occurring mainly as veins and cavity fillings in dolomite of the Lower Magnesian Limestone (Dunham, 1948; Dunham, Claringbull, and Bannister, 1948; Fowler, 1943, 1944; Raymond, 1962) includes galena, sphalerite, chalcopyrite, pyrite, and malachite, associated with anhydrite, gypsum, barite, celestine, fluorite, ankerite, goethite, colophane, dickite, calcite, and quartz. One vein carried epsomite and sylvine (Raymond, 1962), and the only other record of sylvine is from the Billingham Anhydrite Mine in County



Durham (Raymond, 1959) where it occurs in efflorescences resulting from upward seepage of water from the Magnesian Limestone, and is associated with halite, thenardite, gypsum, epsomite, pyrite, sulphur, lepidocrocite, ?ilsemannite, ?tamarugite, talc, and other minerals. Efflorescences of trona are also found.

*North-western England* (Dunham and Rose, 1949; Hollingworth, 1942, 1948; Sherlock and Hollingworth, 1938; Stewart, 1954). Dolomite, anhydrite, and gypsum are major constituents; calcite is not abundant. Halite is practically absent, but pseudomorphs of gypsum after halite have been found in the St. Bees Shales (Hollingworth, 1942). Traces of hematite and pyrite occur, and the gypsum of the 'Daisy Bed' of the Stamp Hill Mine contains siderite. Mirabilite was found in gypsum at Kirkby Thore (Trechmann, 1901).

#### *Genesis of the minerals*

*Carbonates.* Experimental work suggests that dolomite would not be expected as a primary precipitate, and work on some modern evaporites such as those of the Persian Gulf (Curtis *et al.*, 1963; Shearman, 1963) shows that dolomite can replace aragonite and calcite at a very early stage in diagenesis. However, in the water of some Australian lakes and lagoons calcite, dolomite, and magnesite have been collected as suspended sediments (Alderman, 1959; Alderman and Skinner, 1957; Alderman and von der Borch, 1961).

In the British Magnesian Limestones there is direct evidence of some replacement of calcite by dolomite, including dolomitization of fossils and ooliths, and the distribution of the carbonates provides indirect evidence of large-scale replacement (e.g. Raymond, 1962), but it is impossible to prove how much, if any, dolomite here is of primary origin. It seems probable that most of it has replaced primary calcite and aragonite and that much of this replacement was effected early in diagenesis by the action of brines percolating from above. Later, some calcite has replaced dolomite, and this is a large-scale replacement in the concretionary limestones of County Durham.

In the calcium sulphate zones and parts of the halite zones dolomite may have been a primary constituent, but here again there is a lack of reliable criteria. Small-scale late replacement of anhydrite by dolomite has been recorded (Stewart, 1963).

Magnesite is a widespread minor constituent of the potash field, but is very scarce elsewhere. It is the normal carbonate of the potash zones of the Upper and Middle Evaporites, and the only carbonate of the zones

carrying ? primary polyhalite and kieserite in the Lower Evaporites (Stewart, 1963). It is therefore possible that it was a primary constituent in the later stages of evaporation. Its distribution in some of the calcium sulphate and carbonate zones of the potash field suggests replacement of earlier carbonates by descending solutions during the formation of higher zones. This would explain its virtual absence outside the potash field.

Small quantities of secondary magnesite accompany other salts in veins in the Carnallitic Marl (Armstrong, Dunham, *et al.*, 1951) and are also found in a few veins towards the top of the Middle Evaporites in the F boreholes. Magnesite in the Middle Potash Zone has recrystallized adjacent to clay (Stewart, 1956).

The siderite in the 'Daisy Bed' of Westmorland forms rhombohedra in secondary gypsum. The traces of ankerite found outside the potash field are of secondary origin and are associated with metalliferous minerals.

*Sulphates.* It is almost certain that all the existing gypsum in the British Permian is secondary, and most of it has formed by near-surface hydration of anhydrite. It forms porphyroblasts, veins, and patches in anhydrite, dolomite, and clastic rocks, and massive beds which pass into anhydrite with increasing depth of cover (e.g. Dunham, 1948; Forbes, 1958; Hollingworth, 1942; Sherlock and Hollingworth, 1938).

Although no gypsum is found in the potash field, pseudomorphs of anhydrite, halite, polyhalite, and other minerals after gypsum indicate that it was an abundant early mineral (probably largely primary and partly early diagenetic) in most of the sulphate zones and some halite-anhydrite zones (e.g. Stewart, 1949, 1953), and that it was a minor constituent of the Carnallitic Marl (Armstrong, Dunham, *et al.*, 1951).

Although much of the anhydrite in the sulphate zones and anhydrite-halite zones has replaced early gypsum, some of it may have been primary. Reliable criteria are rare, but textural relationships suggest that anhydrite was the primary deposit in the varved rocks of the anhydrite-polyhalite zone and higher zones of the middle cycle of the Lower Evaporites at Forden near Scarborough (Stewart, 1963). It is conceivable that the sulphate was precipitated as gypsum from surface brines and changed to anhydrite while settling through the water. In the greater part of the halite zones and in the potash zones of the Upper and Middle Evaporites there is no petrographic evidence to suggest the presence of early gypsum.

There is evidence of large-scale replacement of dolomite by anhydrite,

especially in the Lower Magnesian Limestone and towards the base of the Middle and Lower Evaporites (Dunham, 1948; Fowler, 1944; Stewart, 1949, 1951, 1954), and although there was presumably some primary sulphate in the Magnesian Limestone (Raymond, 1962), it seems likely that much of it grew during diagenesis, perhaps like the anhydrite and gypsum of recent sediments in the Persian Gulf (Curtis *et al.*, 1963; Shearman, 1963).

The writer believes that the major replacements of gypsum by anhydrite, and dolomite by anhydrite, took place in early diagenesis, by the action of interstitial waters and brines percolating through the crystal mush from above. Evidence from Forden suggests that polyhalite replaced anhydrite in this way (Stewart, 1963), and in other localities (e.g. E.2, Stewart, 1949) the anhydrite  $\rightarrow$  polyhalite change followed the gypsum  $\rightarrow$  anhydrite change. On a minor scale, secondary anhydrite formed at later stages, as a constituent of veins and patches in many parts of the succession.

Polyhalite, in exceptionally large quantity in the Lower Evaporites, is almost absent from the rest of the succession, although it is a minor constituent of the Carnallitic Marl (Armstrong, Dunham, *et al.*, 1951). It has been suggested that at Forden about half the polyhalite is primary; and that the large amount of calcium required has been derived from the pene-contemporaneous replacement of anhydrite below by a great deal of secondary polyhalite, through downward percolation of brines rich in potassium and magnesium which displaced brines rich in calcium (Stewart, 1963). The traces of polyhalite in the halite-kieserite-anhydrite subzone are of late secondary origin (post-consolidation). At other localities (E.2, Stewart, 1949; E.3 at Sleights and E.5 at Eskdalegate, Armstrong, Dunham, *et al.*, 1951, and Raymond, 1953), the polyhalite of the Lower Evaporites is largely or entirely secondary, having replaced anhydrite and halite after the gypsum  $\rightarrow$  anhydrite change.

Some kieserite has replaced secondary polyhalite in the Lower Evaporites of E.3 (Armstrong, Dunham, *et al.*, 1951). Greater quantities of kieserite at Forden may have replaced pre-existing primary magnesium-bearing sulphates such as epsomite, after consolidation. The mineral is scarce in the Middle Evaporites (F.2 and F.3).

Among the scarce sulphates, secondary apthitalite and picromerite accompany kieserite in the Middle Evaporites of the F.3 borehole. At Forden apthitalite replaces kieserite and halite, and glauberite replaces anhydrite and polyhalite, and these are late-post-consolidation effects.

At least some celestine is secondary, replacing anhydrite at Forden (Stewart, 1963) and occurring in veins in carbonate and sulphate rocks elsewhere (Fowler, 1944; Forbes, 1958). Epsomite is secondary (Raymond, 1962). The occurrence of langbeinite (E.3, Armstrong, Dunham, *et al.*, 1951) needs confirmation. Mirabilite (Trechmann, 1901) is presumably of late secondary origin.

*Chlorides.* Halite has suffered widespread recrystallization with some movement, so that early textures have often been obliterated. Nevertheless there is evidence of widespread early replacement of gypsum by halite in the pseudomorphous layers of the anhydrite zone of the Upper Evaporites, the halite-anhydrite zone of the Middle Evaporites and the polyhalite-bearing rocks of the Lower Evaporites. Halite has also replaced sulphates and carbonates in oolitic rocks at Forden and elsewhere. There are many records of halite replacing anhydrite in minor quantity in all the chloride zones, after movement of halite under pressure. A complex series of replacements in the potash zone of the Middle Evaporites involves three generations of halite and two of carnallite, rinneite, and anhydrite (Stewart, 1956), and here halite has replaced fairly large amounts of carnallite, perhaps during leaching of the primary potash zone soon after its formation. Veins of various ages, containing halite, are found in all chloride and many sulphate zones and in the Carnallitic Marl, and occasionally in the Magnesian Limestones.

Pseudomorphs indicate that carnallite was the main primary potassium salt of the potash zone of the Middle Evaporites, and that most of the sylvine here is secondary (Stewart, 1956). However, the writer believes that sylvine may have been primary in a layer of halite-sylvine rock, with some anhydrite and very little other impurity, which occurs below the part of the potash zone which carries pseudomorphs after carnallite in the F boreholes. Small amounts of sylvine and carnallite in the lower halite zone may have formed by crystallization partly from original interstitial brine, and partly from brines percolating from above.

The upper halite zone of the Middle Evaporites, and to a much greater extent the Carnallitic Marl, are veined and impregnated with halite, carnallite, sylvine, and rinneite (Armstrong, Dunham, *et al.*, 1951). Some similar veins cut the overlying carbonate and anhydrite zones of the Upper Evaporites, along fractures which are sometimes slickensided, and lead upwards to a subsidiary development of these potassium-bearing minerals towards the base of the lower halite zone of the Upper Evaporites: this potassium enrichment is presumably entirely secondary

and at least partly of fairly late origin, resulting from upward migration of brines from below.

Sylvine appears again in force, with scarce carnallite and rinneite, in the potash zone of the Upper Evaporites, where there is no evidence of primary carnallite.

In summary, halite, carnallite, and possibly some sylvine were primary constituents, but these minerals have also taken part in large-scale pene-contemporaneous and post-consolidation changes. Rinneite is almost certainly entirely secondary, and it is likely that the iron required for its formation has been derived from reaction of metasomatic brines with clastic material and hematite.

*Borates.* Boracite forms isolated crystals and crystal groups in well cuttings from the Middle Evaporites of the E.2 borehole (Guppy, 1944; Stewart, 1951), and radiating nodules in halite in the Upper Evaporites of E.5 (Sabine, 1953). Isolated crystals in halite, seen by the writer in slices of rocks from the Middle Evaporites (potash zone) of the F.1 borehole, show no sign of secondary origin.

*p*-Veatchite has been found only as isolated crystals in well cuttings of the Lower Evaporites of E.2 (Stewart, Chalmers, and Phillips, 1954; Beevers and Stewart, 1960). Sulphoborite replaces anhydrite in the Lower Evaporites of Forden (Stewart, 1963). No borates have been recorded outside the potash field.

*Other minerals.* Hematite is widespread in clastic rocks and salts (especially chlorides) above the Upper Magnesian Limestone. The common occurrence of flakes of this mineral in secondary sylvine and other salts, especially adjacent to clastic material, and also in some veins, suggests that much of the hematite in the salts has been formed by leaching of the clastic material by brines, during diagenesis and later geothermal metamorphism. The same applies to quartz, which is common in the Upper and Middle Evaporites of the potash field, especially in chloride zones, often fringing patches of clay or silt. There is definite evidence of late replacement of halite and anhydrite by quartz (Stewart, 1951).

Talc (Raymond, 1962; Stewart, 1949, 1951, 1963) is a widespread minor constituent of the potash field and occurs sporadically outside it. Its common occurrence along cleavages of recrystallized halite, and in veins with halite cutting halite and silt (in the Upper Evaporites of the F boreholes), suggests formation during geothermal metamorphism.

A biogenic origin for the small quantity of sulphur found in patches



and veins has been suggested by Raymond (1962). Sulphur has replaced some anhydrite (Stewart, 1949; Raymond, 1962).

In the potash field traces of fluorite have been recorded in anhydrite rock (Lower Evaporites, E.2; Stewart, 1954), in dolomite in the Upper Magnesian Limestone filling rods of the fossil *Filograna permiana* (E.2, Trechmann in discussion on Raymond, 1953), and in dolomite veins in the Lower Magnesian Limestone, with traces of a mineral tentatively identified as northupite (E.5, Raymond, 1962). The origin of the suite of metalliferous minerals, with fluorite, barite, etc., found in the Lower Magnesian Limestone outside the potash field is discussed by Fowler (1943) and Dunham (1948, 1960). Dunham points out that their emplacement appears to be epigenetic, but that they might originate from Hercynian mineralizing fluids from depth or from fluids squeezed out of the Permian Marl Slate during diagenesis.

### *Conclusions*

Our present knowledge of these evaporites suggests the following tentative history.

*Primary minerals:* Probably calcite, dolomite, magnesite, gypsum, anhydrite, polyhalite, epsomite, halite, carnallite, sylvine, boracite; possibly aragonite, celestine, fluorite, *p*-veatchite.

*Early diagenetic (pene-contemporaneous) changes,* resulting largely from reaction with brines percolating downwards during evaporite formation: Large-scale replacement of calcite (and aragonite?) by dolomite, dolomite by anhydrite (and gypsum?), gypsum by anhydrite and halite, anhydrite and halite by polyhalite, and carnallite by halite and secondary sylvine; smaller-scale replacement of dolomite by magnesite; leaching of magnesium sulphates by fresher brines in the Lower Evaporites; development of some hematite and quartz by alteration of clastic material.

*Later diagenetic and geothermal metamorphic changes,* involving rise of temperature and pressure during burial: Some dolomitization of calcite, conversion of remaining gypsum (if any) to anhydrite, widespread but moderate scale replacement of anhydrite by halite, and development of kieserite from earlier magnesium-bearing sulphates; veining and impregnation of upper part of Middle Evaporites and Carnallitic Marl with halite, carnallite, sylvine, rinneite, magnesite, and quartz, and introduction of these minerals from below into the lower part of the Upper Evaporites; development of quartz, hematite, rinneite, talc, partly through reactions with clay and silt; widespread migration of

halite, anhydrite, and other minerals forming veins and patches in both evaporites and overlying sediments; many minor changes including replacement of anhydrite by dolomite, of polyhalite and anhydrite by glauberite, of glauberite, anhydrite, polyhalite, and magnesite by halite, of halite and kieserite by apthitalite, and development of scarce late polyhalite; large-scale recrystallization of halite, with some movement. The suite of metalliferous minerals and their associates, galena, chalcopyrite, sphalerite, barite, fluorite, etc., were probably formed by upward migration of fluids from below the evaporites.

*Near-surface changes*, involving the action of meteoric water, and fall of temperature and pressure on erosion of the overburden: Large-scale hydration of anhydrite to gypsum (with release of some celestine?); solution and removal of halite and gypsum; the replacement of dolomite by calcite in the concretionary limestones may belong here; development of mirabilite.

#### References

- ALDERMAN (A. R.), 1959. *J. Geol. Soc. Australia*, vol. 6, p. 1.  
 — and SKINNER (H. C. W.), 1957. *Amer. J. Sci.*, vol. 255, p. 561.  
 — and VON DER BORCH (C. C.), 1961. *Nature*, vol. 192, p. 861.  
 ARMSTRONG (G.), DUNHAM (K. C.), HARVEY (C. O.), SABINE (P. A.), and WATERS (W. F.), 1951. *Min. Mag.*, vol. 29, p. 667.  
 BEEVERS (C. A.) and STEWART (F. H.), 1960. *Ibid.*, vol. 32, p. 500.  
 CURTIS (R.), EVANS (G.), KINSMAN (D. J. J.), and SHEARMAN (D. J.), 1963. *Nature*, vol. 197, p. 679.  
 DUNHAM (K. C.), 1948. *Proc. Yorks. geol. Soc.*, vol. 27, p. 217.  
 — 1960. *Ibid.*, vol. 32, p. 229.  
 — CLARINGBULL (G. F.), and BANNISTER (F. A.), 1948. *Min. Mag.*, vol. 28, p. 338.  
 — and ROSE (W. C. C.), 1949. *Proc. Geol. Assoc.*, vol. 60, p. 11.  
 EDWARDS (W.), 1951. *The concealed coalfield of Yorkshire and Nottinghamshire. Mem. geol. Surv.*  
 FLECK (A.), 1950. *Deposits of potassium salts in north-east Yorkshire. Chemistry and Industry* (separate, 17 Oct.), 15 pp. (This work was issued and is paginated independently of the volume for 1950.)  
 FORBES (B. G.), 1958. *Proc. Yorks. geol. Soc.*, vol. 31, p. 351.  
 FOWLER (A.), 1943. *Geol. Mag.*, vol. 80, p. 41.  
 — 1944. *Ibid.*, vol. 81, p. 193 and p. 254.  
 GUPPY (E. M.), 1944. *Min. Mag.*, vol. 27, p. 51.  
 HOLLINGWORTH (S. E.), 1942. *Proc. Geol. Assoc.*, vol. 53, p. 141.  
 — 1948. *Proc. Yorks. geol. Soc.*, vol. 27, p. 192.  
 LEES (G. M.) and TAITT (A. H.), 1946. *Quart. Journ. geol. Soc.*, vol. 101, p. 255.  
 NAPIER (E.), 1948. *Proc. Yorks. geol. Soc.*, vol. 27, p. 210.  
 RAYMOND (L. R.), 1953. *Quart. Journ. Geol. Soc.*, vol. 108, p. 283.  
 — 1959. *Min. Mag.*, vol. 32, p. 172.  
 — 1962. *Quart. Journ. geol. Soc.*, vol. 118, p. 39.

- SABINE (P. A.), 1953. Petrog. Dept. Report. Summ. Prog. Geol. Surv. for 1951, p. 60.
- SHEARMAN (D. J.), 1963. Abs. Proc. Geol. Soc., no. 1607, p. 63.
- SHERLOCK (R. L.), 1921. Rock salt and brine. Spec. Rep. Min. Resources, G.B., Geol. Surv., no. 18.
- and HOLLINGWORTH (S. E.), 1938. Gypsum and anhydrite and celestine and strontianite. Spec. Rep. Min. Resources, G.B., Geol. Surv., no. 3.
- STEWART (F. H.), 1949. Min. Mag., vol. 28, p. 621.
- 1951a. *Ibid.*, vol. 29, p. 445.
- 1951b. *Ibid.*, vol. 29, p. 557.
- 1953. Proc. Geol. Assoc., vol. 64, p. 33.
- 1954. Proc. Yorks. geol. Soc., vol. 29, p. 185.
- 1956. Min. Mag., vol. 31, p. 127.
- 1963. Proc. Yorks. geol. Soc., vol. 34, p. 1.
- CHALMERS (R. A.), and PHILLIPS (R.), 1954. Min. Mag., vol. 30, p. 389.
- STEWART (G. E.), 1947. Trans. Instn. Min. Metall., vol. 56, p. 113.
- TILLEY (C. E.), 1943. Min. Mag., vol. 26, p. lvii.
- TRECHMANN (C. O.), 1901. *Ibid.*, vol. 13, p. 73.
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