

Genesis of Sylvite- and Carnallite-Bearing Rocks From Wallace, Nova Scotia

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ABSTRACT

During exploration by drilling at Wallace, Nova Scotia, potassium and magnesium mineralization was encountered within evaporites of the Mississippian Windsor Group. A potassium content of more than 4 percent was recorded in three zones in the core, sylvite being the dominant potassium-bearing mineral.

The sylvite occurs with halite and minor carnallite in a matrix of dense clay/mudstone, or with halite in a halite/mudstone breccia.

Petrographic examination of material from the most heavily-mineralized parts of the Wallace core shows that sylvite is a secondary product of leaching of carnallite. Halite pseudomorphs after carnallite are abundant, and the replacement series halite after sylvite after carnallite is well-developed. Talc developed as a reaction product between $MgCl_2$ -rich brines and the silicates of the clay matrix.

Diapiric movement of the evaporites probably produced the brecciation, and elevated the potassium-bearing zones to their present position. The original potassium-bearing sediment was probably a carnallite—and halite-rich clay.

INTRODUCTION

The rocks whose origin is the subject of this report were obtained from the core from Wallace no. 1, drilled in 1966 as part of the continuing search for potash deposits of commercial value in the Mississippian evaporites of the Province of Nova Scotia. The borehole is located at lat $45^{\circ}46.9' N.$; long $63^{\circ}23.8' W.$, in the northern part of the province (Fig. 1).

General Geology.

The distribution, stratigraphy and mineralogy of the evaporites in the Maritime Provinces of Canada have been treated in a number of publications (Norman, 1932; Goodman, 1952; Sund, 1959; Hamilton, 1961; Evans, 1967) and further such consideration here would be unnecessary and prodigal of space.

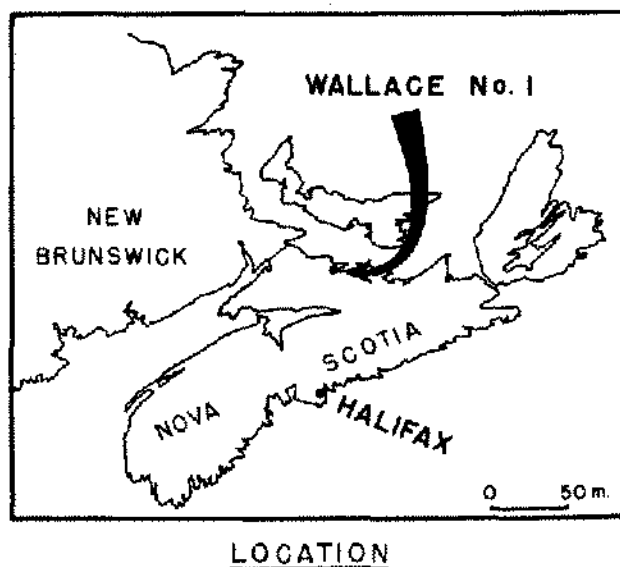


Figure 1.

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The Wallace no. 1 drill site is only six miles west of Malagash (Fig. 2) where a diapiric evaporite sequence was mined for salt for 40 years, and in which both sylvite (KCl) and carnallite ($\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) occurred (Hays, 1920; Ellsworth, 1926).

The Wallace no. 1 borehole was drilled on the south flank of a pronounced anticline in Pennsylvanian sediments. Diapiric movement has resulted in the exposure of Windsor rocks at the surface in the centre of the structure (Figs. 2, 3) and the accumulation of the low-density evaporites has produced a negative gravity anomaly over the inlet at Wallace (Fig. 2).

More than 1000 feet of evaporites were encountered in the drilling, and the rocks consist of banded halite and brecciated halite-rich mudstone. Several portions contained between 4 and 8 percent potassium and the conclusions presented here accrue from a petrographic examination of these potassium-rich rocks.

The mineralogy is simple, consisting almost entirely of carnallite and sylvite impregnation of halitic mudstone. There follows, therefore, a consideration of the relationships among carnallite, sylvite and halite, the principal mineral products of the system $\text{NaCl-KCl-MgCl}_2\text{-H}_2\text{O}$.

The System $\text{NaCl-KCl-MgCl}_2\text{-H}_2\text{O}$.

The essential mineral relationships in this system were reported by D'Ans (1933), some minor adjustments were made by Braitsch (1962) and a convenient summary in English occurs in Krauskopf (1967) and Wardlaw (1968).

The ratio of magnesium chloride to potassium chloride in sea water is shown by line 1 in Figure 4, representation of the $\text{NaCl-KCl-MgCl}_2\text{-H}_2\text{O}$ system at 20°C and saturated with NaCl . Progressive evaporation produces a change in brine concentration along line 1, leading ultimately to KCl saturation, and on further evaporation, precipitation of sylvite. With the removal of KCl from the solution, the composition of the remaining brine changes along the KCl saturation curve until the carnallite-sylvite field boundary is reached. This boundary is one of reaction, and the precipitated sylvite will, in the presence of the MgCl_2 -rich solution, alter to carnallite.

If the sylvite is removed from contact with the MgCl_2 -rich brine, it will not be altered. Continued evaporation produces crystallization of carnallite, the composition of the brine changing along the carnallite saturation curve until bischofite ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) precipitates.

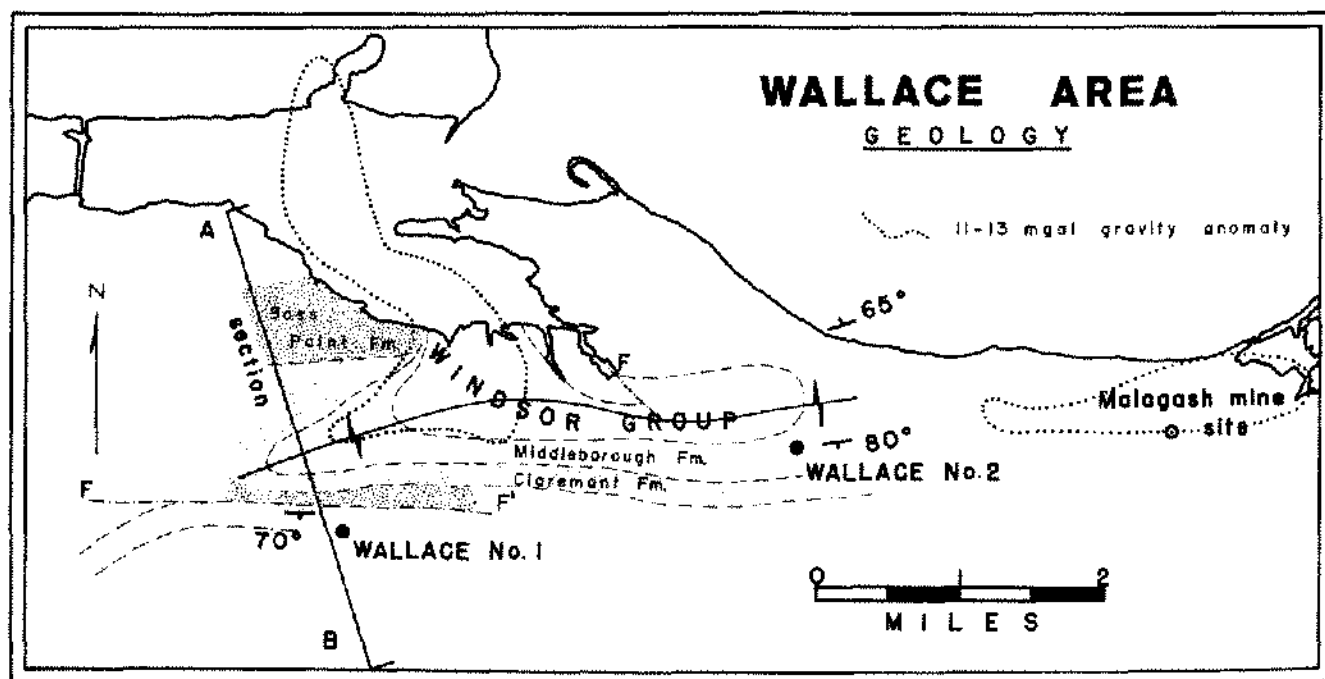


Figure 2.

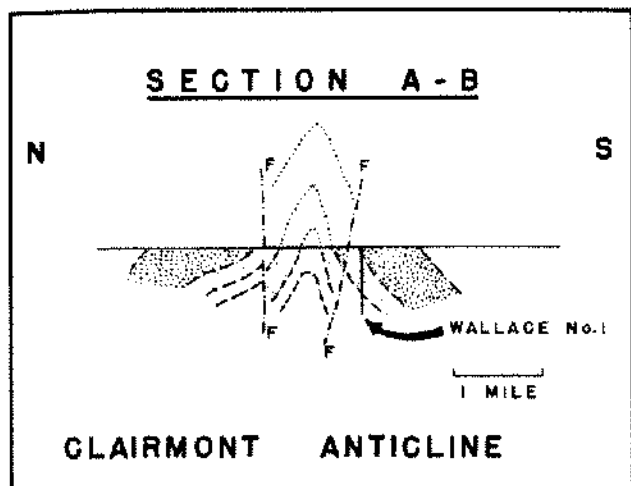


Figure 3.

Figure 4 (left column) includes the sequence of salts that will result from progressive evaporation of brine if the process proceeds without destruction of any of the precipitates by reaction with remaining brine. The right column depicts the sequence that results should the reaction at the carnallite-sylvite boundary go to completion: no sylvite is preserved, the sequence being a simple one of halite overlain by carnallitite (carnallite-halite rock) overlain by bischofite.

C.A. Baar (oral comment) assures me, however, that this reaction is a slow one and does not necessarily go to completion. Indeed were this not a slow reaction, there would be no primary sylvite found, and, Borchert and Muir (1964, pp. 193-203) notwithstanding, Baar and Kühn (1962) have produced good evidence for primary deposition and preservation of a major sylvinitic (sylvite-halite) deposit in the Rhine Graben.

In the presence of NaCl-saturated brine, carnallite is unstable, and it is important to consider the results of the dissolution of a carnallite unit. Line 2 in Figure 4 represents the ratio of KCl to $MgCl_2$ in carnallite. Attacked by a brine not saturated with $KCl \cdot MgCl_2 \cdot 6H_2O$, the mineral dissolves and the composition of the brine changes along line 2 until the point of KCl saturation is reached. Thereafter, either further dissolution of carnallite or evaporation will precipitate sylvite.

From this consideration of the phase relations among the minerals of the $NaCl$ - KCl - $MgCl_2$ - H_2O system, it may be appreciated that the relationship between carnallite and sylvite may be one of several: both minerals may be primary and coexistent,

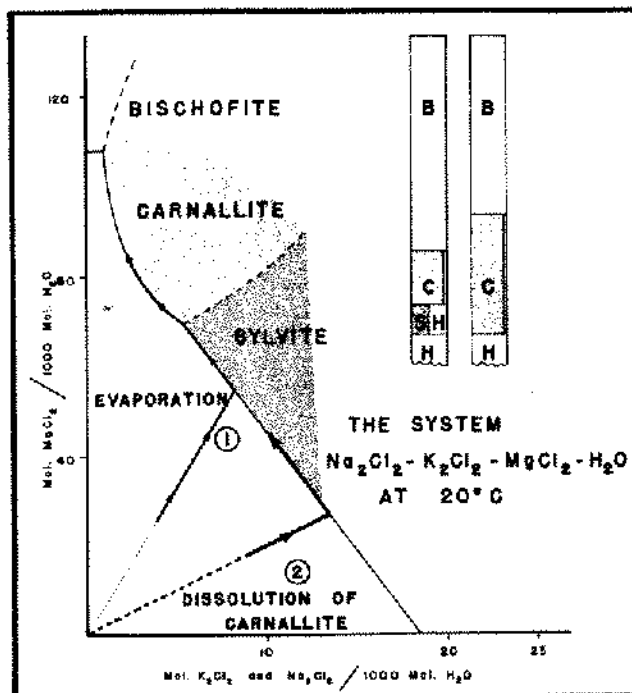


Figure 4.

each may exist alone, or sylvite may form from the secondary leaching of earlier carnallite.

Mineral Relationships and Reactions in the Rocks from Wallace.

In some of the thin-sections examined in this study, hexagonal or pseudo-hexagonal grains of halite abound, particularly in those rocks which contain a high proportion of clay. Where the halite is surrounded by clay, hexagonal shapes are well-formed (Fig. 5), but the grains may be rounded or pseudo-hexagonal where clay is not abundant (Fig. 6). Halite cubes can appear hexagonal in cross-section, but in such a case, the cleavage traces must be parallel with the grain boundaries. This is not the case in the rocks at Wallace (Figs. 5A, B) and, therefore, these unusual grains of halite are pseudomorphs.

Several of the pseudomorphs contain small remnants of carnallite, a mineral which can develop hexagonal form and whose replacement by halite has been described from Permian rocks in Yorkshire (Stewart, 1956). The hexagonal grains are halite pseudomorphs after carnallite.

The exact nature of the replacement of carnallite by halite may be deduced from the fact that sylvite remnants are occasionally found within the



Figure 5A. Halite pseudomorphs after carnallite, nicols not crossed.

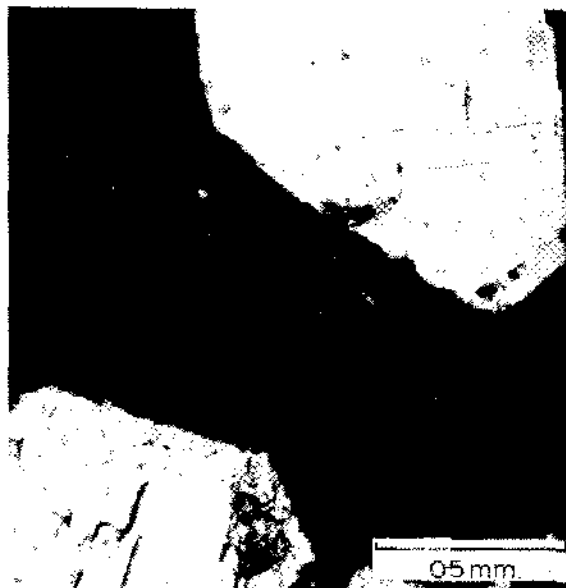


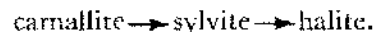
Figure 5B. Halite pseudomorphs after carnallite, nicols not crossed.



Figure 6. Rounded or pseudo-hexagonal halite pseudomorphs after carnallite, nicols not crossed.

hexagonal halite grains. Although carnallite is not found within the sylvite grains, it may be stated with confidence, bearing in mind the discussion of

the phase relations of the $\text{NaCl-KCl-MgCl}_2\text{-H}_2\text{O}$ system, that the replacement series is:



The replacement of carnallite by sylvite releases a MgCl_2 -rich brine, and it is to be expected that this brine would have some effect on the minerals of the remainder of the rock, particularly the clay minerals. Mackenzie and Garrels (1965) and Mackenzie *et al.*, (1967) have given some indication of the speed with which clay minerals react with sea water, and in view of the observations of Carroll and Starkey (1960) that Mg^{++} preferentially replaces H^+ ions in clay minerals, it is not surprising to find that in the clay-rich Wallace rocks, talc has developed at those places where carnallite has been replaced by sylvite and halite.

The talc forms rims—"reaction rims"—around the halite pseudomorphs and at sylvite/clay boundaries (Fig. 7). The talc-forming process has gone so far that rudely hexagonal accumulations developed where the earlier carnallite grains were surrounded by clay matrix. These accumulations are replacements of halite and sylvite but may properly be called talc pseudomorphs after carnallite, for the sylvite and halite are intermediate stages (Fig. 7B).

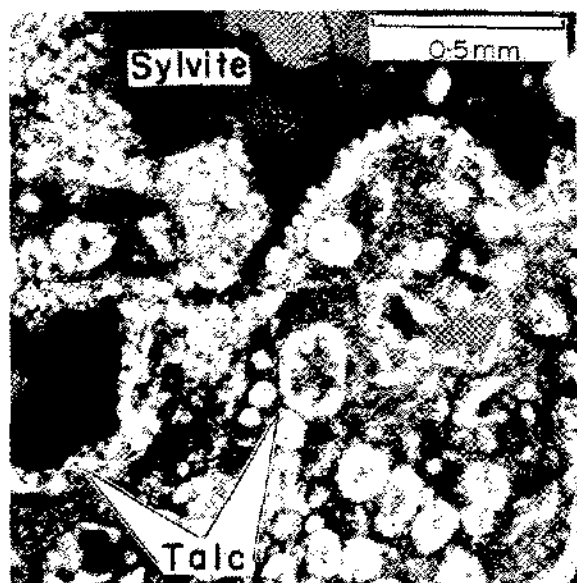


Figure 7A. Talc "reaction rims" around sylvite and talc pseudomorphs after carnallite, inclined nicols.

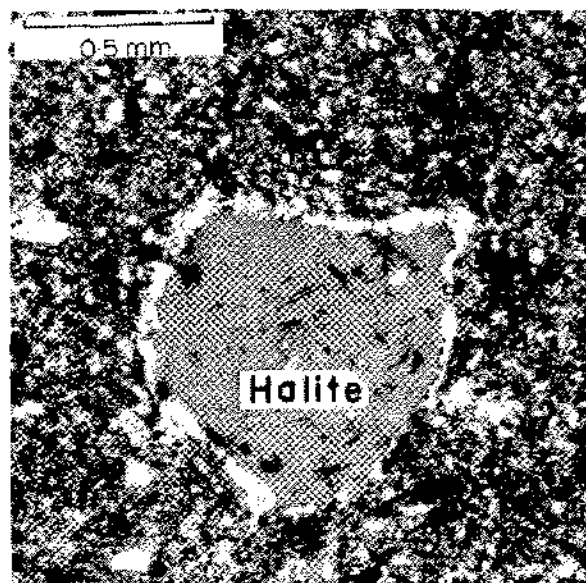
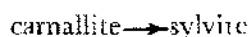


Figure 7B. Talc "reaction rim" around halite, inclined nicols.

Carroll and Starkey (1960) found that SiO_2 and Fe_2O_3 were released by clay minerals as by-products of the reaction with sea water. In their experiments, the excess SiO_2 was dissolved in sea water; in the rocks from Wallace, abundant authigenic, beautifully euhedral, often doubly-terminated quartz crystals (Fig. 8) might be the manifestations of the excess SiO_2 from the production of talc. That these quartz grains are authigenic, not transported grains is concluded from their undamaged euhedral form and from the presence within them of growth states—"phantom quartz" (Fig. 9)—outlined by hematite flakes which are similar to those characteristic of secondary sylvite grains within these rocks (see below). On the basis of the work of Carroll and Starkey (1960), one may speculate that the hematite flakes too, in addition to the talc and quartz, are products of the clay- MgCl_2 brine reaction.

The hexagonal grains of halite are commonly euhedral toward both carnallite and sylvite, a fact which indicates that development of the pseudomorphs preceded formation of these latter minerals. The relations between the later carnallite and sylvite may be deduced from the ubiquitous occurrence of carnallite remnants within the sylvite (Fig. 10). This second replacement series

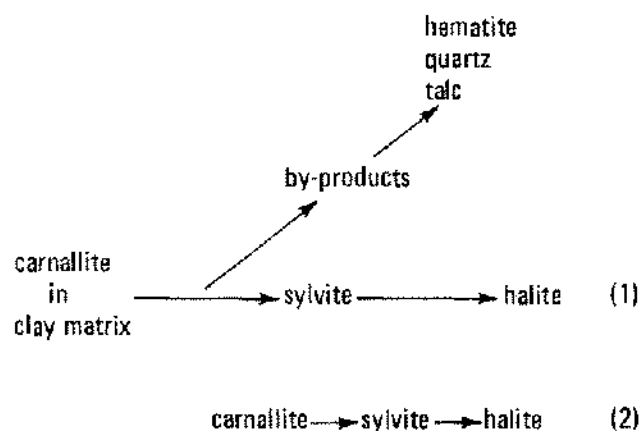


is stained red by hematite flakes (Fig. 11) and has affected many of the halite pseudomorphs of the first replacement series.

The final stage in the development of the rocks of the Wallace no. 1 borehole was the pervasive crystallization of halite at the expense of a large proportion of the earlier-formed minerals except talc, which remains as "ghost" hexagonal traces within massive halite.

The above sequences of replacement may be summarized:

ORIGINAL PRECIPITATE REPLACEMENTS



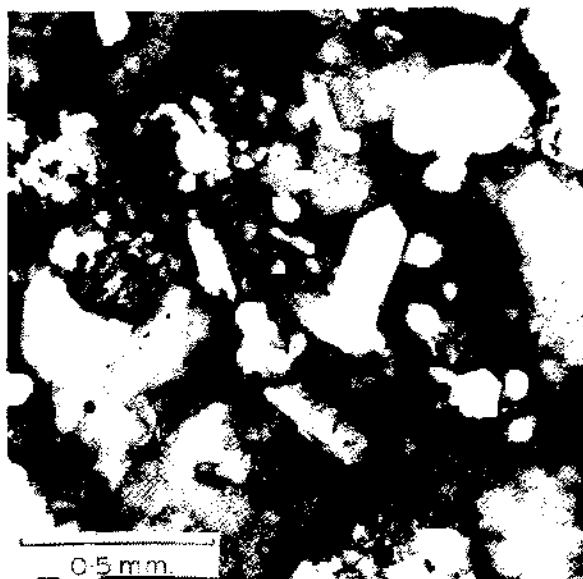


Figure 8. Euhedral quartz, nicols inclined.

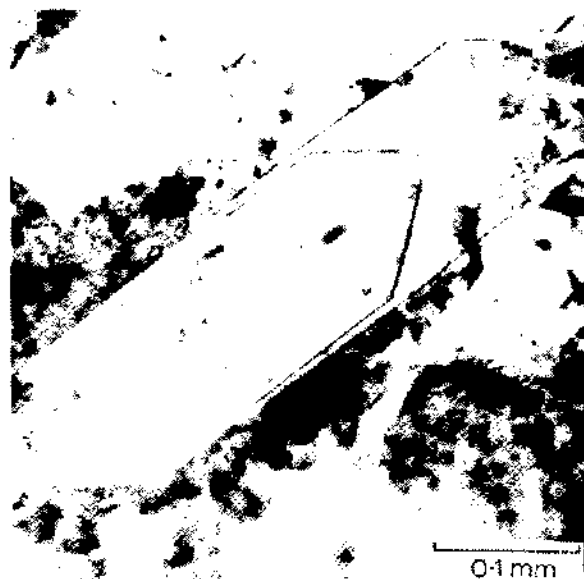


Figure 9. "Phantom quartz" growth stage, nicols not crossed.

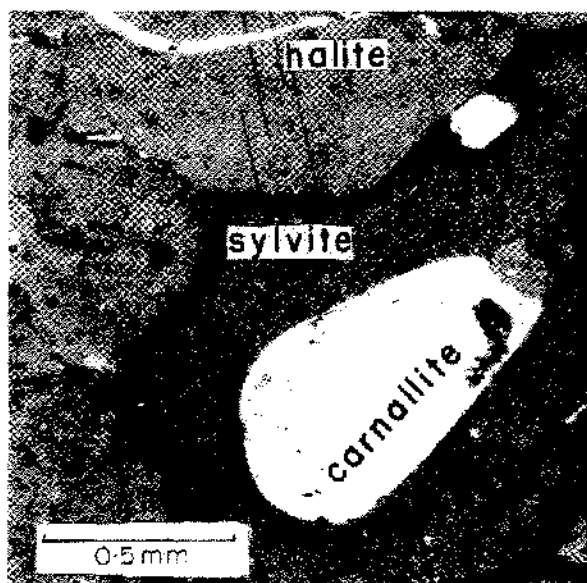


Figure 10. Halite pseudomorph after carnallite, and euhedral toward sylvite containing carnallite remnant, inclined nicols.

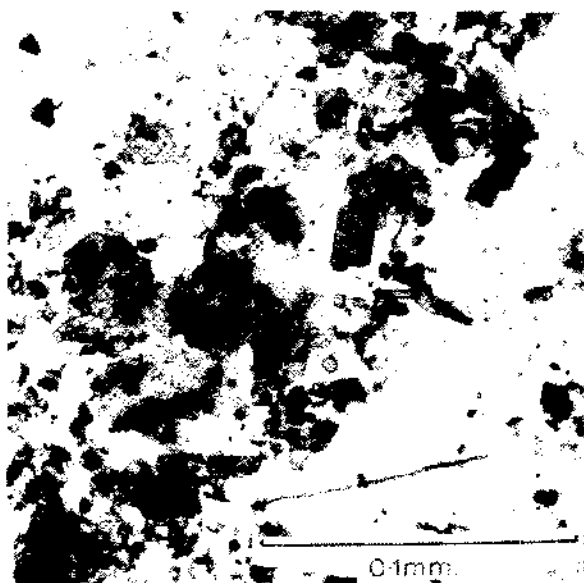


Figure 11. Hexagonal hematite flakes, nicols not crossed.

Précis.

(1) Potash mineralization in evaporites in a core obtained from drilling in a diapiric anticline near Wallace, Nova Scotia, consists of sylvite and carnallite in a clay matrix.

(2) Phase equilibria studies show that sylvite and carnallite can be primary precipitates and that sylvite can form as a result of the dissolution of carnallite.

(3) In the material from the Wallace core, two distinct sequences of replacement can be recognized. In both sequences, carnallite is replaced by sylvite and the sylvite by halite. In the first replacement series good halite pseudomorphs after carnallite are present.

(4) Talc developed as a by-product of the dissolution of carnallite, forming by reaction of the clay matrix and $MgCl_2$ -rich brine. SiO_2 and Fe_2O_3 released during the formation of talc appear as euhedral quartz and hexagonal hematite flakes respectively.

(5) The original sediment was probably a carnallite- and halite-rich clay.

REFERENCES

- D'Ans, J., 1933, Die Lösungsgleichgewichte der Systeme der Salze ozeanischer Salzablagerungen: Berlin, Kali-Forschungs-Institut G.m.b.H.
- Baar, A., and Kühn, R., 1962, Der Werdegang der Kali-salzlagerstätten am Oberrhein: Neues Jahrb. Mineralogie Abh., v. 97, p. 289-336.
- Borchert, H., and Muir, R.O., 1964, Salt deposits: London, Van Nostrand, 338 p.
- Braitsch, O., 1962, Entstehung und Stoffbestand der Salzlagerstätten: Berlin, Springer-Verlag, 232 p.
- Carroll, D., and Starkey, H.C., 1960, Effect of sea water on clay minerals, in *Clays and clay minerals* (7th Conf.): New York, Pergamon Press, p. 80-101.
- Ellsworth, H.V., 1926, Chemistry of potash-bearing horizon of the Malagash salt deposits, Nova Scotia: Canada Geol. Survey Sum. Rept., 1924, Part C, p. 181-198.
- Evans, Robert, in press, Evaporites in the Mississippian of the Canadian Maritime Provinces: Sixth Int. Cong. Carboniferous Strat. and Geol., Sheffield, U.K.
- Hamilton, J.B., 1961, Salt in New Brunswick: Mines Branch, N.B., Mineral Resource Rept. 1, 73 p.
- Hayes, A.O., 1920, The Malagash salt deposits, Cumberland County, N.S.: Canada Geol. Surv. Mem. 121, 24 p.
- Krauskopf, K., 1967, Introduction to Geochemistry: New York, McGraw-Hill, 721 p.
- Mackenzie, F.T., and Garrels, R.M., 1965, Silicates: reactivity with sea water: Science, v. 150, p. 57-58.
- Mackenzie, F.T., Garrels, R.M., Bricker, O.P., and Bickley, F., 1967, Silica in sea water: control by silica minerals: Science, v. 155, p. 1404-1405.
- Norman, G.H.W., 1932, Salt deposits of Nova Scotia and New Brunswick: Canada Geol. Survey. Sum. Rept., 1931, Part D, p. 28-35.
- Stewart, F.H., 1956, Replacements involving early carnallite in the potassium-bearing evaporites of Yorkshire: Mineralog. Mag., v. 31, p. 127-135.
- Sund, J.O., 1959, Origin of the New Brunswick gypsum deposits: Can. Min. and Metall. Bull., v. 52, p. 707-712.
- Wardlaw, N.C., 1968, Carnallite-Sylvite relationships in the Middle Devonian Prairie Evaporite Formation, Saskatchewan: Geol. Soc. America Bull., v. 79, p. 1273-1294.