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Preliminary data on the lithology, bromine distribution, and insoluble minerals from the A-1 Evaporite Formation, Salina Group, in the JEM Petroleum Corporation, Bruggers 3-7 core, Missaukee County, Michigan.

By

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This report is preliminary and has not been edited or reviewed for conformity with U. S. Geological Survey Standards and stratigraphic nomenclature.

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INTRODUCTION

In connection with an ongoing study of the mineralogy and geochemistry of marine evaporite deposits by the U. S. Geological Survey, the Kalium Chemical Corporation provided a drill core from their potash exploration program in the Michigan basin during the 1980s. This corehole, the JEM Petroleum Corporation, Bruggers 3-7, is located in north central Missaukee County, Michigan in section 7, T. 24 N., R. 6 W. (fig. 1). The core contains a complete interval of the A-1 Evaporite Formation, Salina Group, of Middle Silurian age in the northern part of the Michigan basin. Depth-related measurements of water-insoluble minerals and bromine content in halite are reported here and they help to define trends in brine salinity during deposition of these evaporite rocks. Temporal changes in brine salinity are important paleoenvironmental indicators that allow better predictions of the location and extent of valuable energy and mineral commodities in sedimentary basins.

Acknowledgments

Kenneth J. Esposito analysed the halite samples for bromine content by X-ray fluorescence and Carol W. Connor determined the mineral constituents of the insoluble residues by X-ray diffraction and by microscope analysis. We thank Sherilyn Williams-Stroud and Robert A. Zielinski for reviewing the manuscript.

CORE DESCRIPTION

The part of the JEM Petroleum Corporation, Bruggers 3-7 core that we received from Kalium Chemicals Corporation contains primarily the A-1 Evaporite Formation of the Salina Group of Middle Silurian age. A generalized stratigraphic column illustrates the lithologies in the core and the stratigraphic relationship of the A-1 Evaporite Formation to the overlying A-1 Carbonate Formation and the underlying carbonates of the Niagaran Formation (fig. 2). The distribution of hilgardite ($\text{Ca}_2\text{B}_5\text{O}_9\text{Cl} \cdot \text{H}_2\text{O}$) nodules is also shown on this figure as black dots.

Two hundred ninety four feet of core, between the depths of 8,081 and 8,411 ft, were furnished to the U. S. Geological Survey. The description of the core by Bruce C. Fuller was furnished by Kalium Chemicals, and is used here with permission (fig. 2). Some additional observations by the authors are included.

METHODS

Bromine analyses

The halite portion of the core was cut longitudinally, and two-foot length samples were crushed to fine-sand size and split to assure representative sampling of the core. Discrete layers of anhydrite were avoided to minimize dilution of the halite. Twenty-gram splits were pulverized in a ball mill and the resulting powder was pelletized at 25,000 psi. The pellet was analyzed for bromine in an automated ARL 8420 X-ray fluorescence (wavelength dispersive) unit at 30 kV, and 80 mA. The detector is a scintillation counter with a LiF 200 crystal. Unknown samples were compared to standards prepared with sodium bromide in a matrix of bromine-free sodium chloride. After fusion, the standard was pulverized and pelletized. Each sample was automatically analyzed three times, by

scanning the 1st order $K\alpha_1$ peak at 29.96 degrees 2θ , and the results were averaged. The analytical repetitions and the averaging greatly reduced the analytical variability in the results. The analyses for bromine content, that ranged from 24.1 to 311.5 ppm, were plotted stratigraphically (fig. 3).

Insoluble mineral analyses

The remainder of the 2-foot composite sample that was used for bromine analysis, was weighed and then dissolved in distilled water. Frequent stirring for about 2 hours insured rapid dissolution of the halite with minimum dissolution of anhydrite. The insoluble material was filtered, washed with distilled water, then rinsed with ethyl alcohol to remove excess water, and then dried over night and weighed. The percentage of the insoluble residue to the total sample was calculated and plotted stratigraphically (fig. 4).

RESULTS AND DISCUSSION

Bromine abundance and distribution in halite

The stratigraphic profile of bromine content in the halite bed of the A-1 evaporite (fig. 3) is, in general, typical of bromine profiles of marine evaporite halite beds in other evaporite basins (Holser, 1966, 1979; Raup, 1966; Raup and Hite, 1978). This profile is plotted directly from the analytical results and has not been smoothed. The bromine content at the base of the halite bed is low and then increases upward toward the top of the bed, reaching a maximum near the top. This general trend indicates a generally progressive increase in the salinity of the brines from which the halite precipitated.

The bromine content of the halite in the bottom 40 ft of the halite bed, between 8,410 and 8,366 ft, ranges from 24 to 35 ppm. From 8,366 to 8,354 ft, there is a rapid rise in the bromine content, from 35 to 103 ppm. From 8,354 to 8,279 ft there is a less rapid but steady increase in bromine content from 103 to 212 ppm. From 8,279 to 8,222 ft the bromine content is more or less constant. From 8,222 ft upward to 8,098 ft the bromine content increases irregularly upward to a maximum of 311 ppm. The highest bromine values are observed on both sides of the interval between 8,110 to 8,130 ft which is an implied zone of potash mineralization. In the upper 8 ft the bromine content decreases rapidly to 248 ppm.

The stratigraphic distribution of bromine indicates that the A-1 Evaporite Formation is the result of one depositional cycle. In most marine evaporites, the base of the halite beds have a minimum bromine content of 65 to 70 ppm. The bromine content then increases upward as the brines in the basin become more concentrated. In a situation where the brines become highly concentrated the very soluble constituents in the sea water, such as salts of potassium and magnesium are precipitated. The bromine content of halite just prior to deposition of potash minerals is usually between 250 and 300 ppm. The A-1 Evaporite Formation in this core follows this pattern for the most part. The bromine distribution in this halite bed indicates a steady increase in brine salinity up to 8,280 ft. The vertical part of the profile up to 8,220 ft indicates a period of deposition in which the salinity of the brines remained fairly constant. This was probably the result of an influx of fresh sea water into the basin that was balanced by reflux of high salinity brines out of the basin. This period of influx resulted in the addition of calcium sulfate to the basin and the deposition of increased quantities of anhydrite within the halite bed (fig. 4). Above 8,220

ft the bromine content of the halite increased rapidly to about 300 ppm. This produced the salinities necessary for the precipitation of potassium and magnesium minerals.

The bromine content of the halite in the bottom 40 ft of the halite bed, between 8,410 and 8,366 ft, is of particular interest. In that interval the bromine content ranges from 24 to 35 ppm which is significantly lower than the theoretical minimum of 65 to 70 ppm for first-deposited halite from sea water (Braitsch, 1971, Kühn, 1968, Holser, 1966, and Raup and Hite, 1978). Because these low values at the base of the halite bed grade smoothly upward into values that are considered normal for a marine halite, it is possible that these low values reflect original depositional geochemistry. This would require, however, that the partition coefficient between bromine in brines, and the bromine that is incorporated in the halite that was precipitated from those brines was different in the Silurian age Michigan basin than in other younger depositional basins or in present day sea water.

Other factors may have been responsible for the lower bromine content. Recrystallization of the originally deposited salt by meteoric waters or by other solutions with a lower bromine content would result in a secondary salt with a lower bromine content. Coarse crystal size in some of the halite at the base of the core may indicate some influence of recrystallization.

The base of the core contains abundant layers of anhydrite interbedded with the halite. Significant quantities of disseminated, fine-grained anhydrite within the halite could have diluted the bromine content in the samples that were analyzed and thus produce lower bromine values. Bedded halite normally contains a small amount (1 to 2 percent) of disseminated anhydrite. This small amount has only a minor effect on the analyses of bromine distribution in halite. Amounts above the 1 to 2 percent level would cause some dilution of bromine in the samples.

Further investigations are needed to try to determine the reasons for the unusually low-bromine content in the halite at the base of the core.

Insoluble minerals in halite

Anhydrite is the major constituent (95 to 98 volume percent) of the insoluble mineral fraction in the halite. The remainder is quartz and dolomite, with a trace of pyrite as determined by X-ray diffraction analysis. The stratigraphic distribution by weight percent of the insoluble minerals is illustrated in Figure 4. The insoluble material is not distributed evenly throughout the halite bed. An interval near the base of the halite bed, between the depths of 8,388 and 8,410 ft, contains abundant anhydrite and some limestone. This interval was transitional between the deposition of limestone below, and the chloride deposition above. In the interval between 8,200 and 8,275 ft anhydrite content increased to as much as 4 percent, indicating an influx of fresh sea water into the basin. The bromine profile (fig. 3) was also affected through this interval as indicated by an interruption from a steady bromine increase to a nearly vertical section of the profile. This indicates an interruption of the steady increase in salinity of the brine.

Small white nodules of the borate mineral hilgardite, occur in the intervals 8,170 to 8,180 ft, 8,200 to 8,210 ft, 8,237 to 8,259 ft, and 8,269 to 8,271 ft. Hilgardite ($\text{Ca}_2\text{B}_5\text{O}_9\text{Cl} \cdot \text{H}_2\text{O}$), probably the 1Tc polymorph, was confirmed by Peter Modreski (written communication, 1992). Most nodules range in size from 0.1 to 2 mm but some are as large as 6 mm. Small quantities of borate minerals are common in many evaporites of marine origin. The distribution of the borate nodules (fig. 2) coincides with the influx of

sulfate in the middle of the halite bed that resulted in the precipitation of the anhydrite. Borate minerals in other marine evaporites appear to coincide with gypsum or anhydrite such as in the Pennsylvanian age evaporites in the Paradox basin in Utah (Raup and others, 1968) and in the Permian age evaporites of the Zechstein basin in Germany (Braitsch, 1971; Kühn, 1968).

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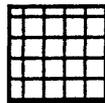
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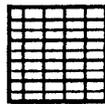
Michigan - Lower Peninsula

Figure 1. Location of JEM Petroleum Corporation Bruggers 3-7 corehole, Missaukee County, Michigan.

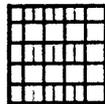
Figure 2 - Generalized stratigraphic column, and lithologic description of the JEM Petroleum Corporation, Bruggers 3-7 core, Missaukee County, Michigan.



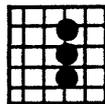
Halite with widely spaced anhydrite laminations (2-4 inches)



Halite with closely spaced anhydrite laminations (1-2 inches)



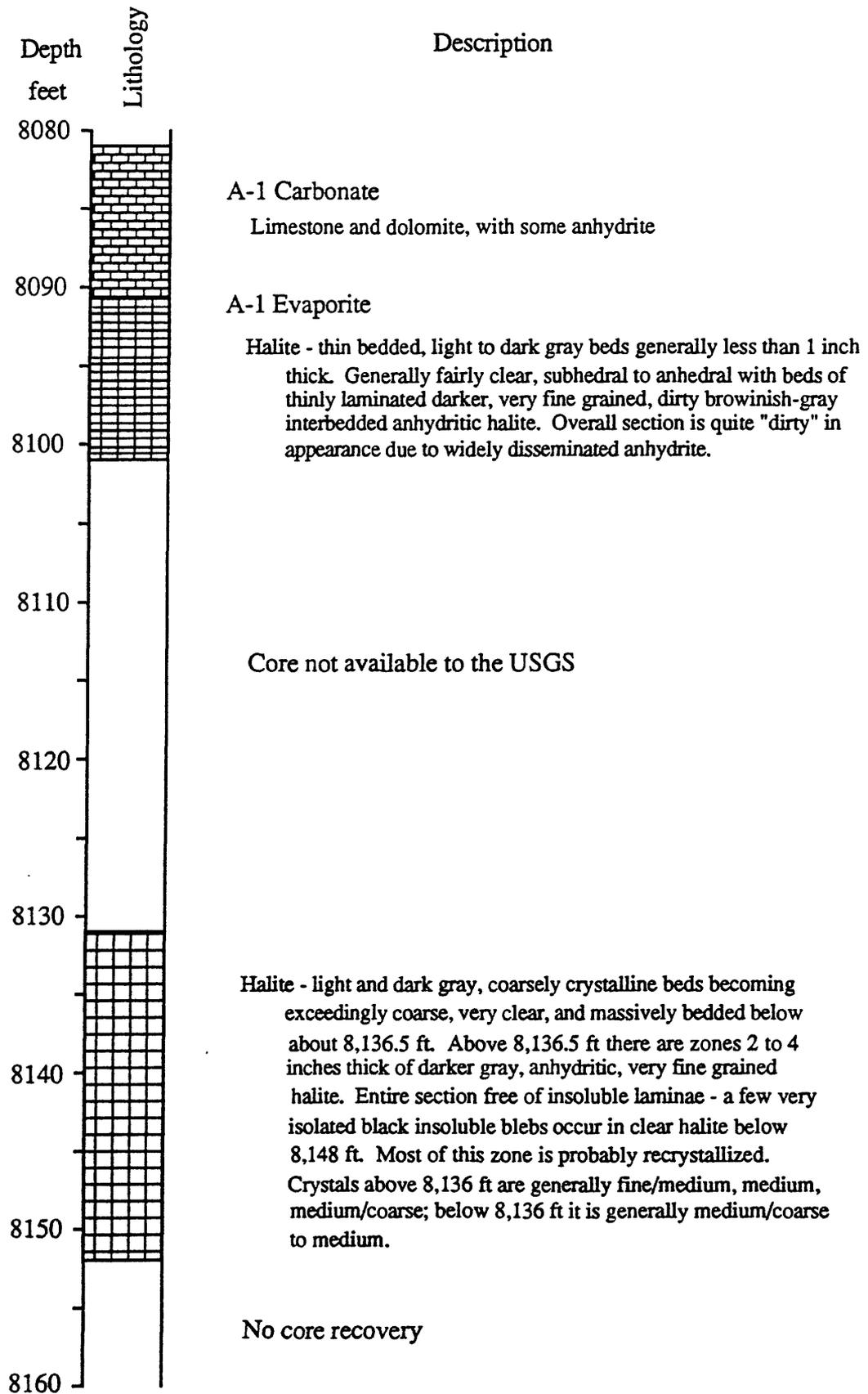
Halite crystals with cloudy centers and clear rims

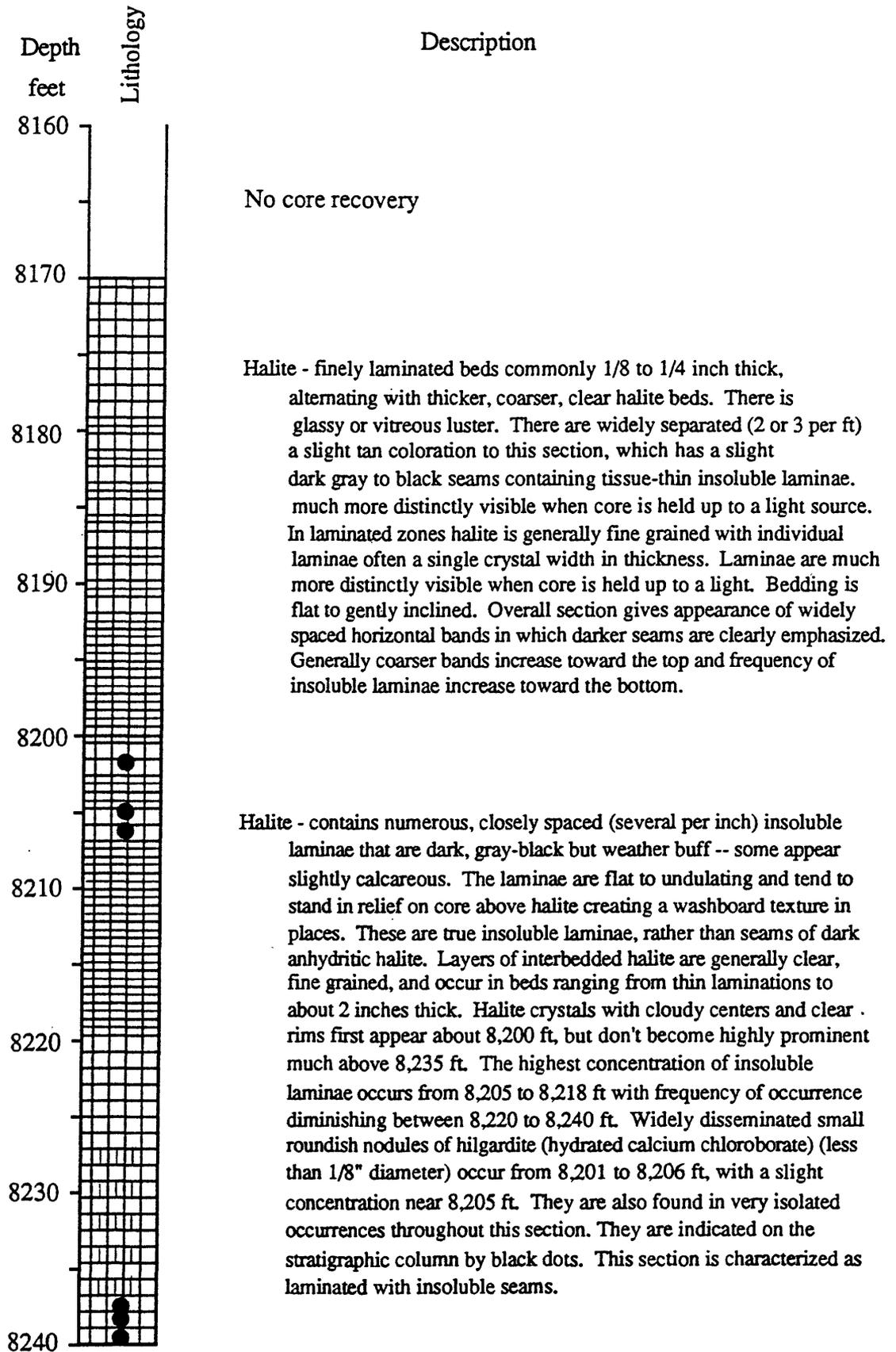


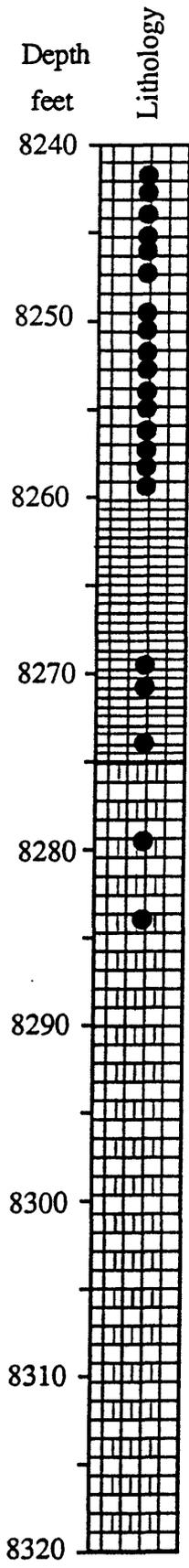
Halite with hilgardite nodules



Halite with interbedded layers of anhydrite and limestone



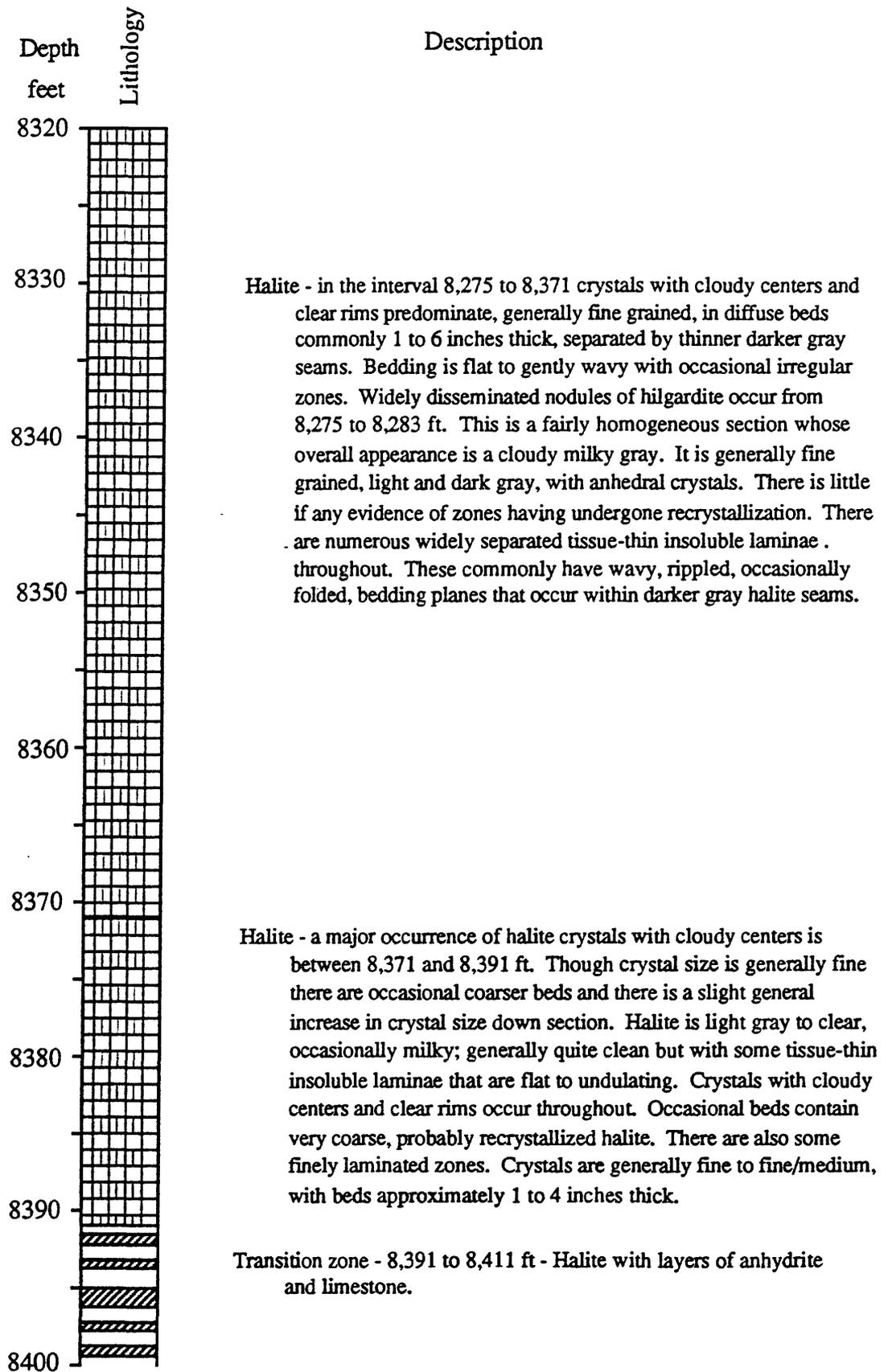


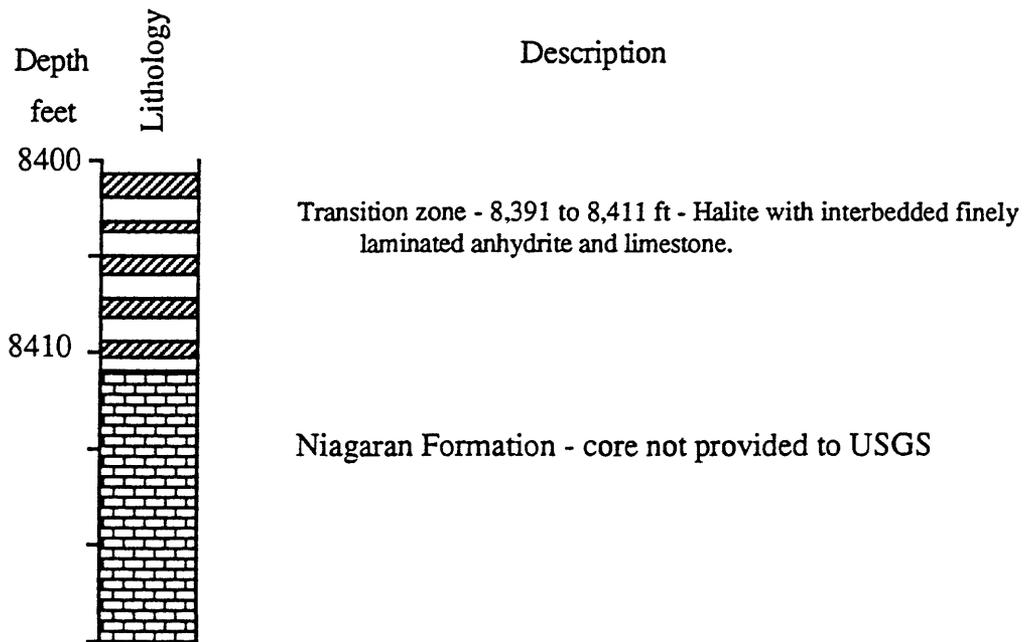


Description

Halite - with disseminated nodules of hilgardite occurring from around 8,233 to 8,260 and 8,270 to 8,274 ft. Nodules are round, white, and are generally less than 1/4 inches in diameter. They are occasionally found concentrated along bedding planes, but most are randomly distributed. Halite continues to occur in light and dark gray bands, but frequency of insoluble laminae decreases markedly and bedding tends to become thicker (1/4 to 2 inches), slightly more diffuse, and less distinctly laminated. Halite crystals become finer grained, more sugary in texture. This section is generally a definite gray, much darker than halite above 8,200 ft. Halite crystals with cloudy centers and clear rims predominate and tend to be generally fine grained. From 8,260 to 8,275 ft halite occurs in beds 1/2 to 1 inch thick often separated by tissue-thin insoluble laminae. The bed thickness in this section is intermediate between the generally thicker and diffuse bedding found below and the thinly laminated beds found above. Darker gray halite bands are probably the result of increased disseminated anhydrite. Bedding tends to be horizontal to slightly irregular and undulating.

Halite - in the interval 8,275 to 8,371 crystals with cloudy centers and clear rims predominate, generally fine grained, in diffuse beds commonly 1 to 6 inches thick, separated by thinner darker gray seams. Bedding is flat to gently wavy with occasional irregular zones. Widely disseminated nodules of hilgardite occur from 8,275 to 8,283 ft. This is a fairly homogeneous section whose overall appearance is a cloudy milky gray. It is generally fine grained, light and dark gray, with anhedral crystals. There is little if any evidence of zones having undergone recrystallization. There are numerous widely separated tissue-thin insoluble laminae throughout. These commonly have wavy, rippled, occasionally folded, bedding planes that occur within darker gray halite seams.





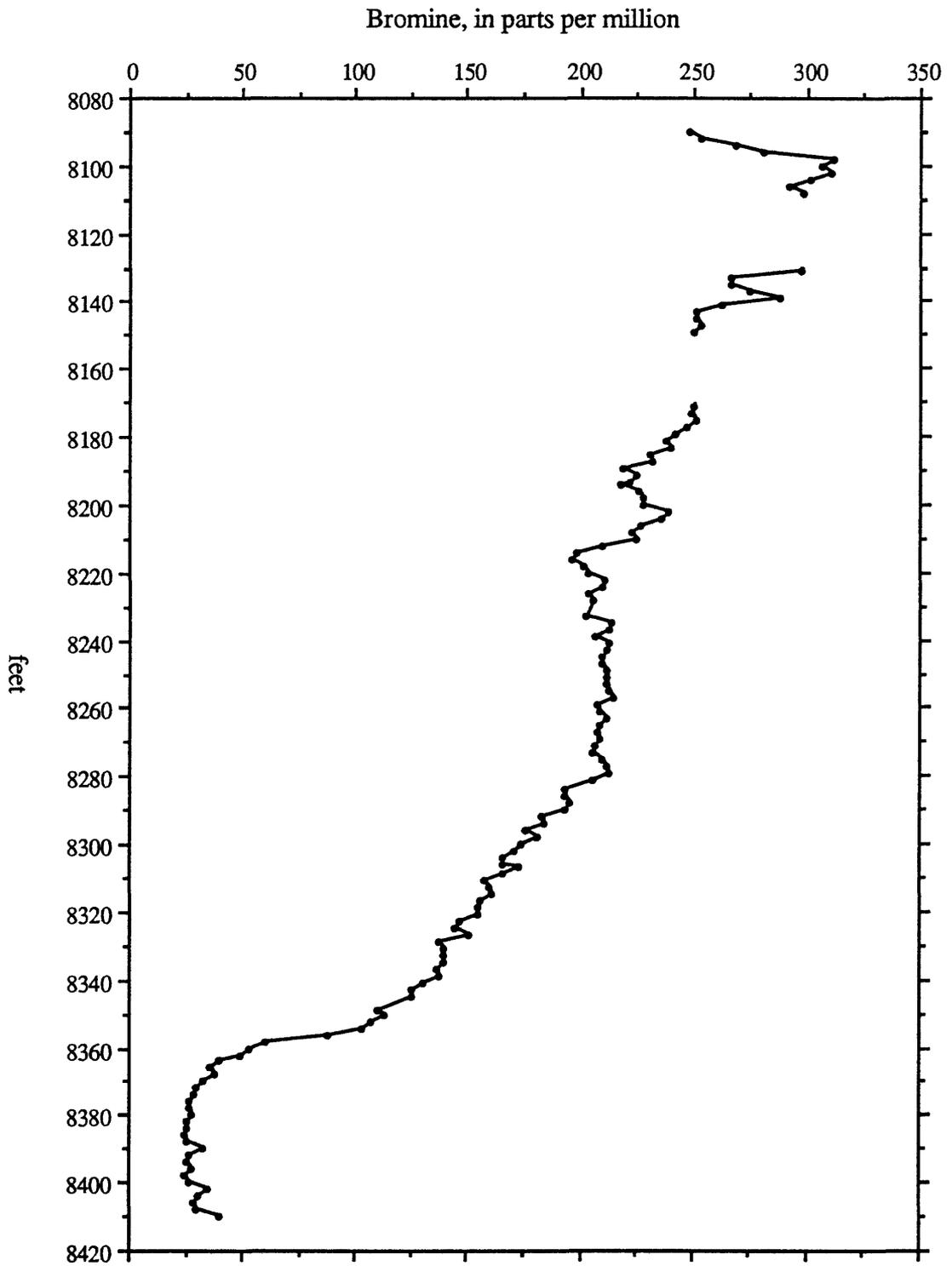


Figure 3 - Bromine distribution profile in the A-1 halite of the Salina Formation in the JEM Petroleum Corporation Bruggers 3-7 corehole.

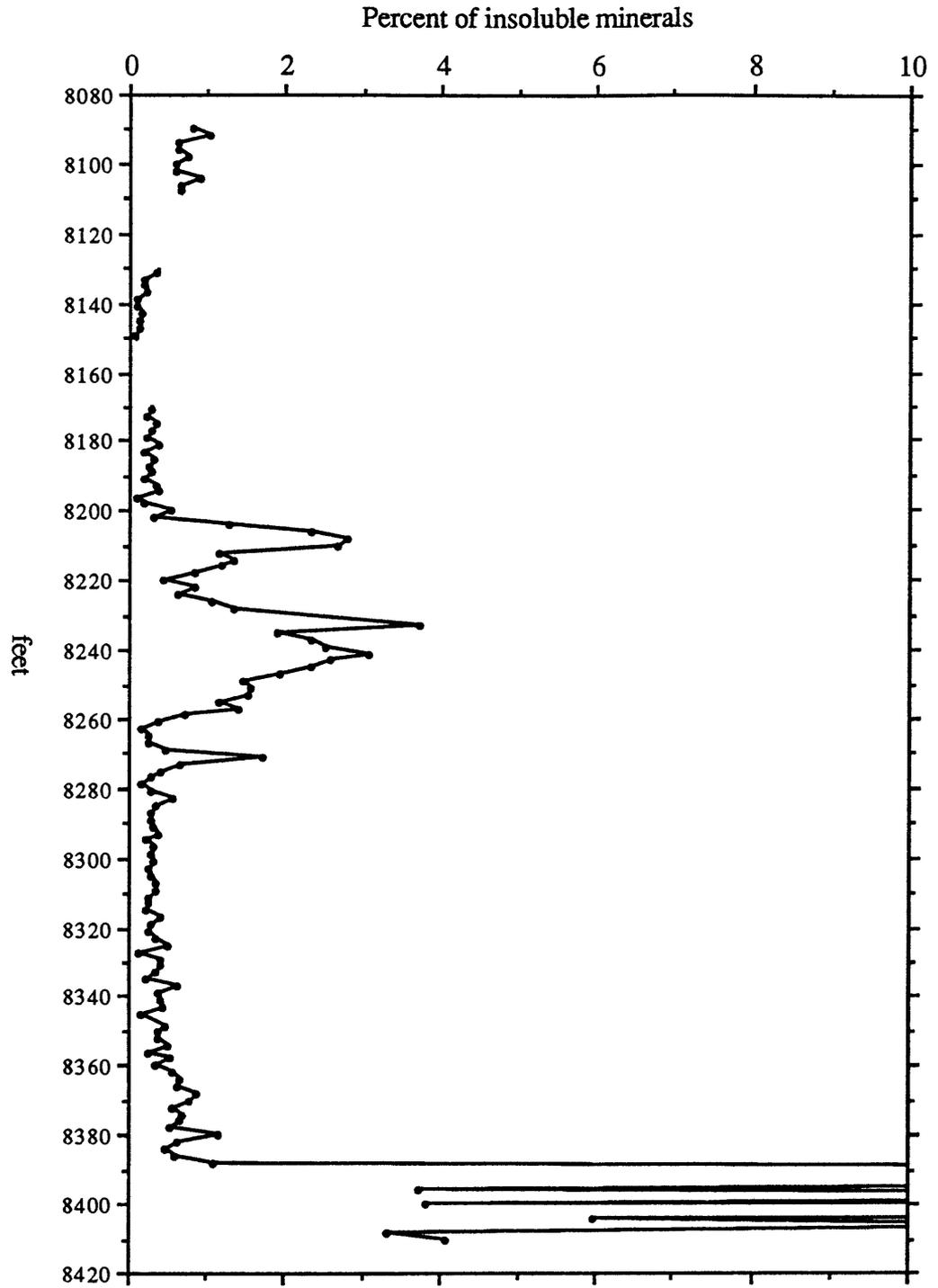


Figure 4 - Insoluble mineral profile in the A-1 halite of the Salina Formation in the JEM Petroleum Corporation Bruggers 3-7 corehole.