

Review of the stratigraphic distribution and diagenetic history of abelsonite

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Abstract—Abelsonite is a crystalline nickel (II) porphyrin, derived from one of the chlorophylls, found only in the Parachute Creek Member of the Green River Formation, an Eocene lacustrine deposit in the Uinta Basin, Utah. Since its original observation in 1969, numerous samples of abelsonite have been collected and their stratigraphic position within the formation plotted. It was observed that abelsonite occurs in six distinct narrow stratigraphic zones, which can be described with respect to the distribution of organic matter. The zones of abelsonite occurrence were designated M9, M7, M2, L6, L0, and K1 based on Green River Formation stratigraphic nomenclature. Abelsonite displays a secondary mode of occurrence, occurring in vugs, fractures, and along bedding lamina, strongly implying migration or movement. The origin of abelsonite can probably be attributed to the unique geochemical conditions of Lake Uinta, chlorophyll diagenesis, and the transport of an aqueous solution of a relatively insoluble precursor into sediments of favorable lithologic characteristics.

Key words—abelsonite, crystalline nickel porphyrin, Green River Formation, stratigraphic distribution

INTRODUCTION

Abelsonite is a crystalline nickel (II) porphyrin that to date has been found only in the lacustrine oil shale deposits of the Parachute Creek Member of the Eocene Green River Formation in Utah and Colorado. The material was first observed in 1969 by L. G. Trudell who described "occasional fine pink-purple metallic patches" occurring in a tight vertical fracture in olive-gray mudstone near the base of the L-1 oil shale zone in a core from the central part of the Uinta Basin, Utah. The discovery sample and several additional samples of similar material from other cores were sent to Charles Milton of George Washington University for identification. Milton determined the purple material to be a previously unknown nickel porphyrin mineral, which he named abelsonite in honor of Philip H. Abelson, eminent geochemist and long-time editor of *Science* (Milton *et al.*, 1978).

Since its discovery, abelsonite has been found in a number of core holes, always as very minute patches and aggregates and always in very sparse amounts. Mason and Trudell (1983) reported 16 core holes in which abelsonite was identified. Until 1985, the mineral had been found only in the Uinta Basin of northeastern Utah. In that year, abelsonite was observed in two adjacent samples from a single core hole from the western part of the Piceance Creek Basin of northwestern Colorado (Trudell *et al.*, 1986).

Milton *et al.* (1978) measured various physical and optical properties of abelsonite and determined that it is a nickel (II) chelate of a desoxophylloerythroetio-

porphyrin (DPEP) having a carbon number of 31. The structure of abelsonite (Fig. 1) was determined by Storm *et al.* (1984), who employed high-resolution proton nuclear magnetic resonance techniques. A small amount of a nickel porphyrin of carbon number 30 is usually found in association with abelsonite (Branthaver *et al.*, 1983). Additionally, some samples contain a small amount of a C-32 nickel porphyrin (Baker and Louda, 1986).

So far as it is known to the authors, abelsonite is the only known crystalline geoporphyrin. Almost all other geoporphyrins exist as a series of methylene homologues, often spanning a large range of carbon numbers (Baker and Palmer, 1978). Thus, either the origin or diagenetic history of abelsonite must differ from that of other geoporphyrins. If one assumes biochemical uniformitarianism, geoporphyrins originated from a limited number of chlorophylls. Most geoporphyrins are presumed to have been derived from chlorophyll *a*. However, some geoporphyrins have been linked to chlorophyll *b* (Chicarelli and Maxwell, 1984), chlorophyll *c* (Ocampo *et al.*, 1984; Verne-Mismer *et al.*, 1988), and bacteriochlorophylls (Ocampo *et al.*, 1985). The possibility that abelsonite was derived from chlorophyll *d* has been discussed and is largely discounted (Storm *et al.*, 1984). Therefore, it appears most likely that it is the diagenetic history of abelsonite that makes it unique. It is one purpose of this paper to examine the known occurrences of abelsonite and attempt to determine what geological factors are common to them. In this way, we may be able to account for the existence of this rare and unique material.

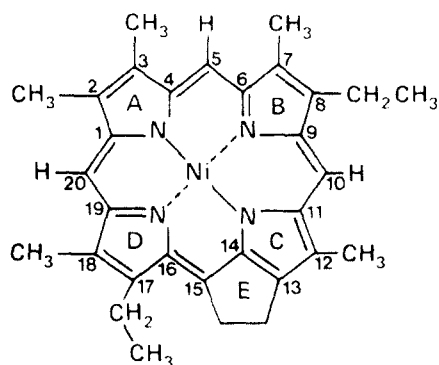


Fig. 1. The structure of abelsonite (after Storm *et al.*, 1984).

OCCURRENCE OF ABELSONITE

Geographic distribution

The names, locations, and depths of occurrence of abelsonite in 17 core holes in the Uinta and Piceance Creek basins are shown on Fig. 2 and listed Table 1. Although not all abelsonite observations have been confirmed by spectrometric analyses, the lithologic characteristics of abelsonite are so striking and unique that erroneous identification is unlikely, although compositional variations cannot be ruled out.

The unnumbered location, marked by an open circle on Fig. 2, designates Gulf Research and Development Corporation's SR-2 core. A Gulf geologist provided the authors with two samples of abelsonite from the SR-2 core, but lithologic and oil shale richness data were not made available. One additional occurrence (Table 1, No. 17) was observed in the western part of the Piceance Creek Basin, about 30 miles (48 km) east of the Utah–Colorado state line (Trudell *et al.*, 1986).

The concentration of abelsonite around the basin margin inferred by distribution may be the result of core hole placements and is not necessarily indicative of restricted occurrence. The detection of abelsonite at map locations 1 and 14 indicates that abelsonite deposition is not controlled by proximity to oil shale outcrops around the edge of the basin.

Lithologic and mineralogic associations

Typically, abelsonite occurs as minute (0.5–2 mm) flat patches or stellate masses sparsely distributed on natural fractures or bedding-plane parting surfaces. Larger patches, up to 8–10 mm, have been found very rarely. The color of abelsonite ranges from dark grayish purple to light purplish red (Munsell colors: 10P3/4 to 10RP6/8) and the luster is typically sub-metallic to adamantine. The darker colors and duller lusters may be due to organic coatings or iron oxide stains, which frequently accompany abelsonite on fracture surfaces. Abelsonite has been identified in core holes at depths ranging from 20 to 2509 ft (6–765 m).

Nearly all observed abelsonite occurrences have

been obvious secondary accumulations on natural fractures or partings. Figure 3 is a scanning electron microscope photomicrograph of abelsonite co-occurring with authigenic calcite in a vug (or small cavity) from the ERDA/LERC SUB 12 core hole from a depth of 565.5 ft. The distinct rhombohedral crystal morphology of the calcite (cube-shaped crystals) and the triclinic habit (flattened plate-like crystals) are evident from this photomicrograph. Sharp crystal edges, abundant twinning, vug habitat, and lack of a mineral matrix that is normally associated with Green River Formation oil shales, clearly indicate a secondary origin for this specimen of abelsonite. The few possible matrix occurrences have not been confirmed petrographically and were found near post-lithification fractures.

A similar nickel-petroporphyrin (C-29, DPEP) of different habit has been encountered in the Green River Formation of the Piceance Creek Basin. This porphyrin is found as apparently amorphous reddish coatings and stains on fractures and partings. It is structurally distinct from abelsonite (Branthaver *et al.*, 1982).

Organic matter content in Green River Formation rocks varies from less than 1.0 to approximately 55 wt%. Descriptive terms for oil shale richness have not been standardized. In this manuscript, "barren" implies less than 1.5 wt% organic matter; "lean" implies 1.5–9 wt% organic matter, yielding approximately 3–15 gallons per ton (gpt) of shale oil by Fischer assay; "medium" implies 9–22.5 wt% organic (15–35 gpt); "rich" implies about 22.5–37.5 wt% organic (35–55 gpt); and "very rich" implies greater than 37.5 wt% (55 to 90 gpt). One gallon per ton equals 4.17 l/tonne or about 3.45 kg/tonne. Abelsonite has been found in lean oil shales and barren mudstones yielding from 0.9 to 14.2 gpt (3.75–59.21 l/t). Thirty-six of 54 individual abelsonite observations have been in samples of rock yielding between 5 and 9 gpt (20.85–37.53 l/t); the remainder of the abelsonite observations were in oil shale of higher oil yields (9–14 gpt; 37.53–58.38 l/t).

The inorganic matrix in oil shale consists of extremely fine clastic and authigenic mineral particles. Clastic particles introduced by stream and surface runoff are most abundant in near-shore depositional environments, whereas sedimentation in the center of the lakes was dominated by chemical precipitates with eolian and volcanoclastic air-fall particles. The oil shales associated with abelsonite typically contain analcime ($\text{NaAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$), an indication of volcanic ash falls. Much of the abelsonite has been found very near, or even within, discrete tuff layers. Because of the abundance of tuffaceous material throughout the section, this association is not of itself an indicator of the origin of abelsonite.

Trace-metal analyses were obtained to determine if nickel concentrations are unusually high in tuffs in or near the abelsonite zones. Analyses were run on 30 available spot samples that had been removed from

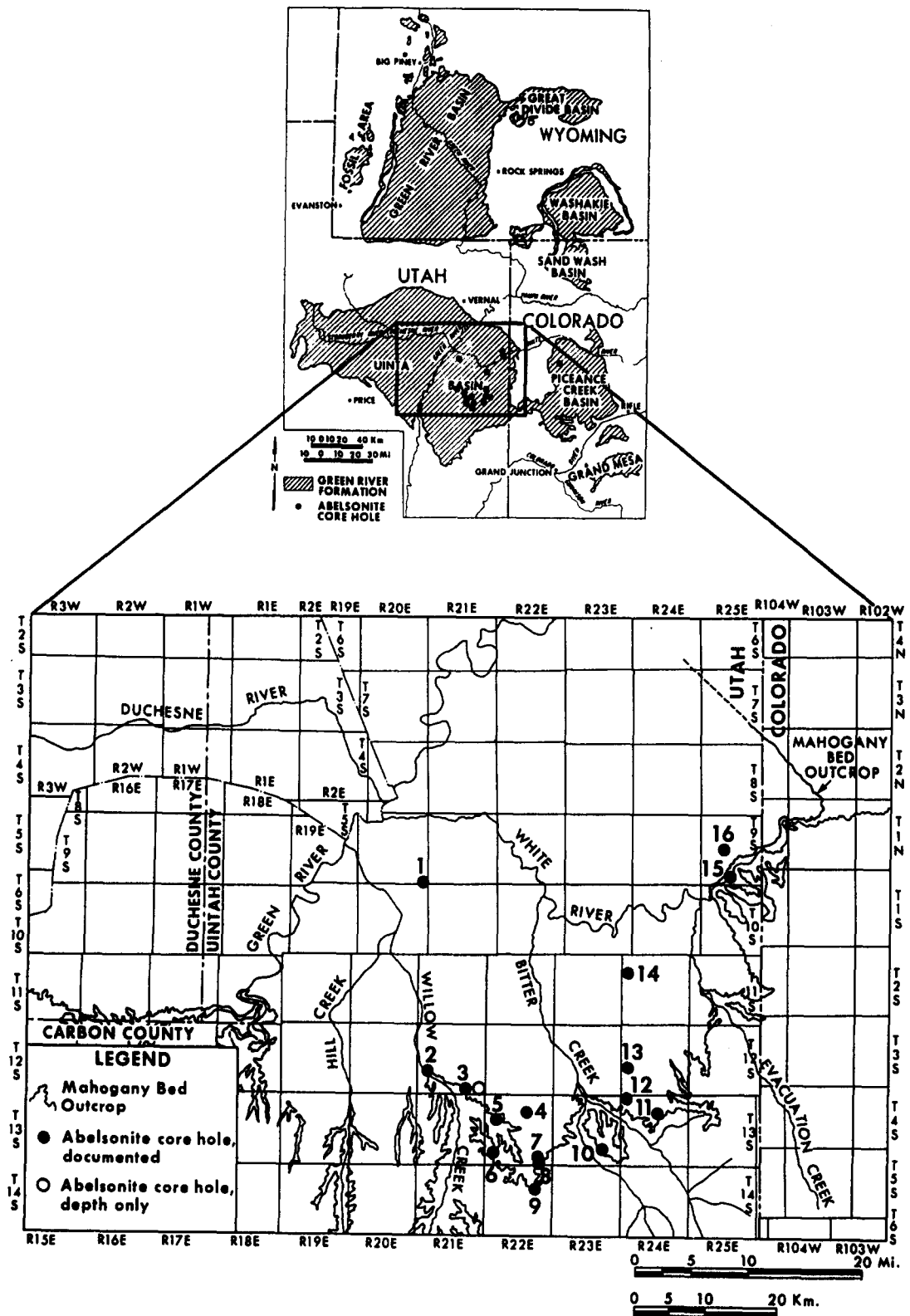


Fig. 2. Map of the Green River Formation of Colorado, Utah, and Wyoming with abelsonite sample locations.

Table 1. Abelsonite Occurrences in Utah and Colorado.

Map No.	Company	Name	Location ¹	Depth, ft	Strat. Zone
1.	Western Oil Shale Corp.	EX-1	Sec. 36, T. 9 S., R. 20 E.	2508.4-2508.8	L6
2.	ERDA/LERC ²	SUB ³ 1	Sec. 30, T. 12 S., R. 21 E.	96.1-96.8	M9
3.	ERDA/LERC	SUB 2	Sec. 15, T. 12 S., R. 21 E.	222.9-229.8	L6
4.	ERDA/LERC	SUB 11	Sec. 10, T. 13 S., R. 22 E.	431.3	M9
5.	ERDA/LERC	SUB 3	Sec. 17, T. 13 S., R. 22 E.	65.3	M9
				181.2-182.2	L6
				90.2-190.9	L6
6.	ERDA/LERC	SUB 6	Sec. 31, T. 13 S., R. 22 E.	108.3-108.5	M9
				234.6	L6
7.	ERDA/LERC	SUB 4	Sec. 35, T. 13 S., R. 22 E.	86.0-86.3	M9
				195.9-196.3	L6
				201.6	L6
8.	ERDA/LERC	SUB 5	Sec. 35, T. 13 S., R. 22 E.	20.4	M9
9.	ERDA/LERC	SUB 7	Sec. 14, T. 14 S., R. 22 E.	45.1-45.8	M7
10.	ERDA/LERC	SUB 8	Sec. 26, T. 13 S., R. 23 E.	98.6-98.7	L6
				102.5	L6
11.	ERDA/LERC	SUB 10	Sec. 10, T. 13 S., R. 24 E.	132.4-132.6	M9
12.	ERDA/LERC	SUB 9	Sec. 6, T. 13 S., R. 24 E.	160.3	M9
				232.2	M2
				251.8	L6
				253.0-254.4	L6
				258.2	L6
13.	ERDA/LERC	SUB 12	Sec. 19, T. 12 S., R. 24 E.	475.1-475.7	M9
				490.9-491.4	M7
				565.5-566.0	L6
				566.7-566.9	L6
14.	USGS ⁴	Asphalt Wash 1	Sec. 7, T. 11 S., R. 24 E.	664.8	L6
				667.7-669.4	L6
				672.1	L6
				673.2	L6
				676.2-676.9	L6
15.	DOE/LETC ⁵	Cowboy Canyon 1	Sec. 33, T. 9 S., R. 25 E.	623.3	L6
16.	Quintana Minerals Corp.	SYN-1	Sec. 16, T. 9 S., R. 25 E.	1308.3-1308.9	L6
				1312.7	L6
17.	Rio Blanco	MDP-1	Sec. 33, T. 1 S., R. 99 W.	634.9-636.1	K1
o	Gulf R & D	SR-2	Sec. 36, T. 12 S., R. 21 E.	247.9	L6
				250.7	L6

¹ All locations are Salt Lake Meridian Survey, Uintah County, Utah, except no. 17, Rio Blanco MDP-1, which is in the 6th Principal Meridian Survey, Rio Blanco County, Colorado

² ERDA/LERC = Energy Research and Development Administration/Laramie Energy Research Center

³ Southern Uinta Basin

⁴ United States Geological Survey

⁵ DOE/LETC = Department of Energy/Laramie Energy Technology Center

five cores for X-ray diffraction mineral analysis of selected tuffs. Twenty-two of the samples were from abelsonite zones and eight were from intervals between or above the abelsonite zones. Some of the tuffs in the abelsonite zones have nickel concentrations of 100-400 ppm, in contrast to whole-rock concentrations of 10-30 ppm reported for oil shales in the abelsonite-containing interval (Mason *et al.*, 1984;

Sullivan and Donovan, 1987). Other tuffs between the abelsonite zones do not have high nickel concentrations. Elevated nickel concentrations were found in selected tuffs in core Nos 9, 12, and 15, but only average or low levels were obtained for tuffs in core Nos 13 and 17. These data indicate that abelsonite distribution is not dependent on the occurrence of nearby tuffs with elevated nickel concentrations.



Fig. 3. Scanning electron photomicrograph of authigenic calcite (rhomboids) and abelsonite crystals (plate-like) from the ERDA/LERC SUB 12 core hole, Uinta Basin, Utah.

Stratigraphic distribution

The Parachute Creek Member of the Green River Formation was deposited during the Eocene, in a fresh to brackish water lacustrine system known as Lake Uinta. The lacustrine rocks of Lake Uinta have been divided into three primary stratigraphic units. In ascending order these are the Douglas Creek, Garden Gulch, and Parachute Creek members. The Parachute Creek Member is the primary oil shale unit of the Green River Formation in Utah and Colorado and is the only stratigraphic unit in which abelsonite has been identified. This unit is composed predominantly of organic-rich dolomitic marlstones that were deposited in a very reducing and geochemically reactive lacustrine environment. Authigenic and diagenetically altered carbonate and silicate minerals comprise the bulk of the inorganic fraction of sediments deposited in the lake during Parachute Creek time. Air-fall volcanic ash layers (tuffs) become increasingly abundant upward through the upper Parachute Creek Member. Fossil insects, ostracods, and plant fragments are known from lean, marginal parts of the Parachute Creek Member elsewhere, but they have not been found associated with abelsonite.

Oil Shales of the Green River Formation are among the most precisely stratigraphically correlative sedimentary deposits in the world. The sequence of richer and leaner oil shale layers was largely determined by climatic variations which affected sediment accumulation rates over the whole region. Oil yield bar graphs representing richness plotted against depth provide correlatable time records, somewhat analogous to tree rings for the sediments of the Green River Formation (Trudell *et al.*, 1970).

The very precise similarity of oil yield profiles at various localities permits the detailed correlations shown on Fig. 4. The correlation lines on the illustrations connect penecontemporaneous points of deposition; therefore, the stratigraphic units between lines were deposited during the same time periods. The Mahogany and L-1 oil shale zones and the A-groove and B-groove barren zones are four of about 20 widely recognized units that have been correlated over much of the Uinta and Piceance Creek basins. The Mahogany marker tuff is the most widely used lithologic reference bed in the Mahogany zone.

As illustrated in Fig. 4, all abelsonite has been found in the Mahogany zone and the L-1 zone, except for the discovery sample in core No. 1, and the Piceance Creek Basin core, No. 17, where the abelsonite is below L-1. Abelsonite occurrences fall into six relatively thin stratigraphic zones, which for convenience of reference, have been assigned the arbitrary designations M9, M7, M2, L6, L0, and K1 based on relative vertical positions within Green River Formation stratigraphic oil shale units. Stratigraphic positions and abelsonite occurrences of these zones are described below.

M9 Zone: The uppermost zone of abelsonite occurrence. The correlation is narrowly defined in the lean oil yield between two relatively rich beds near the top of the Mahogany zone. Abelsonite was found in fractures and partings in this zone in nine core holes, all in the southern part of the Uinta Basin. Two to four tuffs, ranging from 0.5 to 7 in. (1.3–17.8 cm) thick, commonly occur within 2 ft (61 cm) above and below the abelsonite.

M7 Zone: Abelsonite was found in this zone in only two cores, Nos 9 and 13. The abelsonite occurred in fractures immediately below or in the Mahogany marker tuff.

M2 Zone: Abelsonite was found at this stratigraphic location, between the bottom of the Rich section and the top of B-groove, in core No. 12. The material occurred in a lean zone between two relatively rich beds, about a foot below a 0.25 in. (6 mm) tuff. The abelsonite was about 4 ft (1.2 m) above a thick, widely correlated tuff called the Curly bed.

L6 Zone: This zone has the greatest vertical extent of any of the abelsonite zones. In core No. 14 abelsonite was observed at eight horizons through a 12-ft (3.7 m) stratigraphic sequence. Occurrences are all within a lean zone in the upper part of the L-1 zone. This zone contained abelsonite in 10 cores (including Gulf's SR-2). Three to five tuffs thicker than 1 in. (2.5 cm) are present within the lean zone in most cores. Most of the abelsonite was found in fractures. However, one occurrence in core No. 16 was described as disseminated in a tuff.

L0 Zone: The original discovery of abelsonite was in the horizon from core No. 1. Abelsonite was found in barren mudstone immediately below the L-1 zone in a tight vertical fracture. No additional occurrences have been recorded for this zone.

K1 Zone: The identification of abelsonite in this horizon from core no. 17 is the only known occurrence of the material in the Piceance Creek Basin. Abelsonite was found in fractured rock, in a relatively lean interval, in the lower part of the rich oil shale zone that Cashion and Donnell (1972) have designated the R6 zone. Reddish porphyrin stains were also observed on fracture surfaces. A thin tuff layer was observed immediately below the abelsonite occurrence; otherwise tuffs are sparse in this stratigraphic interval.

DISCUSSION

Abelsonite differs from almost all other geophorphyrins by its existence in nature as a single compound not in association with significant amounts of methylene homologues. This poses many chemical and geochemical questions to which some informed speculation may be offered. Four possibilities to

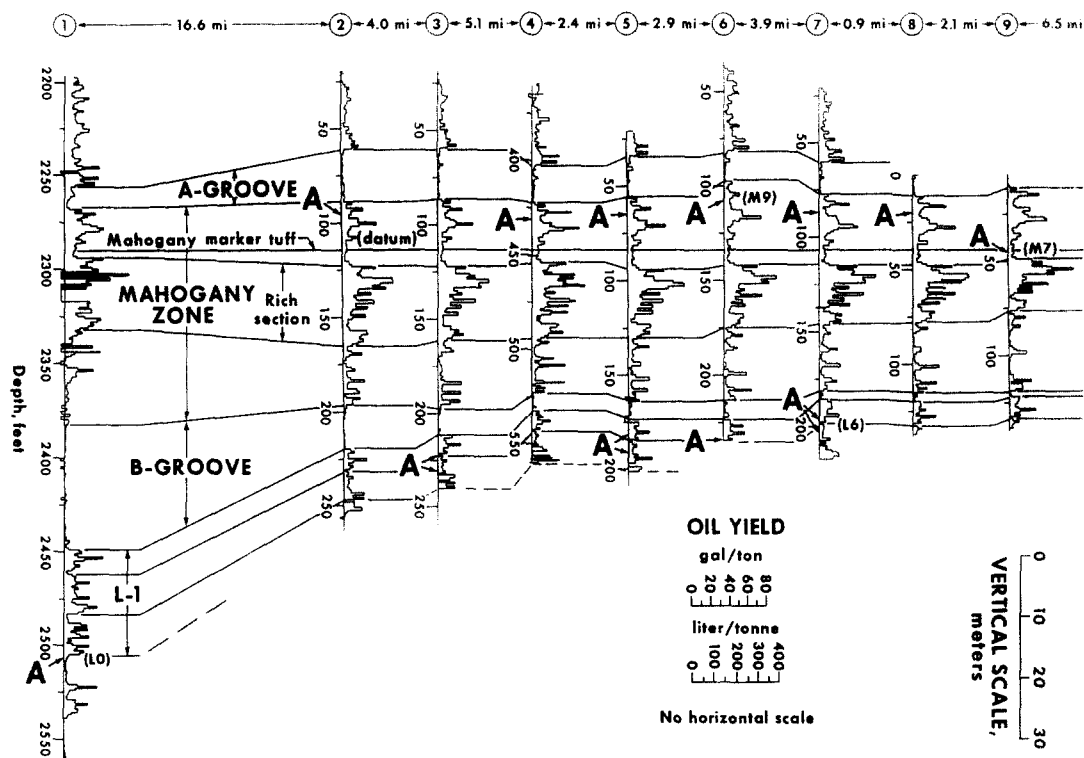


Fig. 4(a). Correlation diagram showing abelsonite locations related to oil shale richness profiles. Sample locations 1-9, Uinta Basin, Utah.

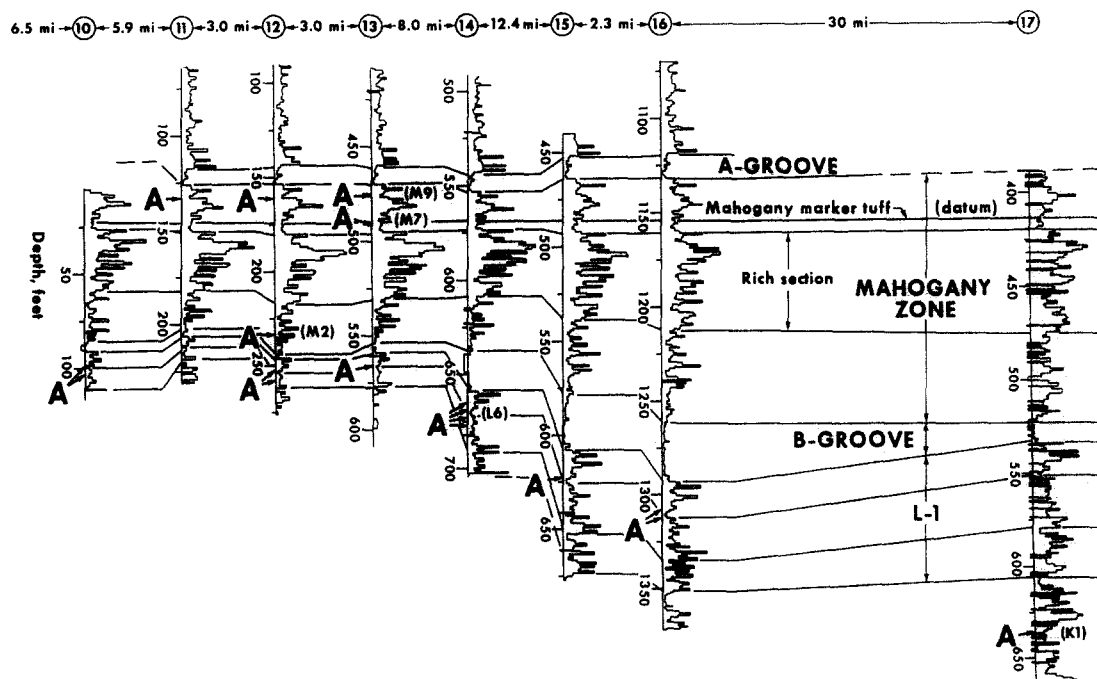


Fig. 4(b). Correlation diagram showing abelsonite locations related to oil shale richness profiles. Sample locations 10-17, Uinta and Piceance Creek basins, Utah and Colorado.

account for the existence of abelsonite are considered: (1) abelsonite is authigenic and was formed penconemporaneously with the deposition of the lake sediments; (2) abelsonite is allogenic—i.e. it formed some place else and was transported or migrated into its

current place, origin unknown; (3) abelsonite was derived from the sediments in which it is found; (4) abelsonite was formed from the episodic blooming of an unknown organism.

It is unlikely that abelsonite is authigenic. All

observed occurrences of the material appear secondary in nature. Abelsonite has been identified in bedding planes, fracture zones, and tuffs. It could not be determined that any sample of abelsonite was of primary origin. Abelsonite is biological in origin and organisms usually do not produce megacrystalline structures.

It is unlikely that abelsonite was derived from organic matter in surrounding shales. Nickel porphyrins can be extracted from these surrounding shales after manual removal of abelsonite crystals (Branthaver *et al.*, 1983). These porphyrins are a series of methylene homologues, one of which probably is chemically identical with abelsonite. If it is assumed that the porphyrins extracted from the shales surrounding abelsonite are representative products of kerogen alteration, then the surrounding kerogen probably was not the source of abelsonite. Otherwise, abelsonite would more closely resemble its geochemical "neighbors". The authors know of no process that would selectively remove a single porphyrin from a closely related group of porphyrins.

The hypothesis that abelsonite is derived from some unusual organism is difficult to test. Chlorophyll alteration to porphyrins presumably would proceed in the same manner upon the demise of any organism. It has been observed that abelsonite can be derived from chlorophyll *d* on paper in a straightforward manner, but it is not known if organisms that synthesize chlorophyll *d* ever inhabited the lacustrine system that deposited the Green River Formation sediments. Such organisms would presumably have left other traces of their existence. In addition, abelsonite would likely be authigenic in this case because it would have been incorporated into the organic matter of the shales derived from the bodies of such organisms.

If abelsonite was not formed penecontemporaneously with the lake sediments, and if it was not derived from the sediments in which it is found, and if it was not formed from the episodic blooming of an unknown organism, the most likely mode of genesis remains an allogenic origin. The secondary occurrence of abelsonite indicates that the material was formed elsewhere (near or far) and was transported to its presently observed location by migration along fractures and bedding lamina of the surrounding sediments. It must have entered the sediments after lithification had occurred, either early or late in their history. Whenever the introduction of abelsonite occurred, the process must have involved a solution of abelsonite or a precursor to effect the transfer. It seems plausible that the volcanoclastic units, often found in close association with abelsonite, served as conduits for fluids because of their porosity and permeability.

The fact that abelsonite is crystalline suggests crystallization from a transporting liquid. Crystals form from melts or from solution. In the case of abelsonite, a melt need not be considered. It may be

that a carboxylated precursor of abelsonite existed in an aqueous solution, and as decarboxylation of this precursor proceeded, abelsonite crystals developed on surfaces confining such a solution (Baker and Louda, 1986). Solutions of carboxylated nickel porphyrins, along with other dissolved organic matter, are known to exist in the bedding planes of Green River Formation oil shales (Smith *et al.*, 1980). Abelsonite is virtually insoluble in water. Therefore, an aqueous solution occupying the small volume in sediment fractures and bedding planes could not contain enough material to precipitate even the minute crystals observed. The crystals could only build up if a solution of abelsonite were continuously replenished. The same considerations would probably apply to a more soluble carboxylated precursor.

If abelsonite is of secondary origin, the question of its primary origin arises. It is presumed to be derived from a chlorophyll or porphyrin known to be synthesized by living organisms. A number of chemical transformations must occur in order to form geoporphyrins from any known possible precursor. Among these transformations are demetalation and rechelation with nickel, deesterification, dehydrogenation, reduction of carbonyl groups, and decarboxylation. These reactions must have taken place before abelsonite formed as a crystalline mass.

As mentioned earlier, abelsonite is unique in consisting of crystals of a Ni(II)-2,3,7,12,18 pentamethyl-8,17-diethyl DPEP not associated with significant amounts of other geoporphyrins. This particular nickel porphyrin is a common geoporphyrin but usually occurs in association with other DPEP homologues and isomers, as well as other porphyrin types. Therefore, it would seem that speculation about a primary source of abelsonite might consider a geochemical environment resulting in the exclusive formation of the above C-31 nickel porphyrin (or its carboxylated precursor), the extraction of this porphyrin from a mixture of porphyrins, or derivation from a unique organism. The authors do not consider the latter two hypotheses to be very likely.

Abelsonite has been identified in sediments that correspond to low levels in the lakes from which the Green River Formation oil shales were derived. The waters in these lakes had high magnesium concentrations at such times and probably were strongly alkaline as well. The first step in chlorophyll diagenesis is normally loss of magnesium to form pheophytin, a process that is usually rapid. Nissenbaum *et al.* (1972) report that in high-Mg Dead Sea sediments, chlorophyll *a* is found in substantial amounts, as well as pheophytin *a*, but not chlorophyll *b*. In the case of the precursor chlorin of abelsonite, some other reactions such as saponification may have preceded loss of magnesium. Such a metallated chlorin acid might be more soluble in water than would a pheophytin. A solution of such a compound may have percolated into lithified sediments through fractures and/or more porous beds within the formation.

Fractures are more abundant in leaner oil shales than in richer oil shales. Solutions of porphyrin precursors, along with other organic matter, might have existed long enough for the transition to a porphyrin to take place, followed by deposition as crystals.

CONCLUSIONS

Abelsonite is found in distinct narrow stratigraphic zones in lean oil shales of the Green River Formation. The evidence of stratigraphic control appears overwhelming; therefore, a relationship to the deposition of the original material implies a correlation strongly favoring lithologic characteristics. The secondary nature of abelsonite crystals strongly implies some migration or movement. Its occurrence may be related to episodes in which the lakes that gave rise to the lean oil shales were at very low levels. Abelsonite might be considered pseudoauthigenic because its chemical origins are related to formation in place, but then at some later date it migrated short distances to its present locations within the formation.

Abelsonite was probably transported to its present locations as an aqueous solution of some relatively soluble precursor. The reason abelsonite exists as a single compound rather than a series of homologues is probably related to the special chemical environments in the lakes at the time the precursor chlorin was synthesized and a subsequent lack of intimate association with the bulk organic matter of the sediments in which abelsonite eventually came to reside. These conditions would allow a somewhat different diagenetic history than that of most geoporphyrins. Derivation from an organism synthesizing a chlorophyll different from the common chlorophylls *a* and *b* does not seem likely. Therefore, it is proposed that abelsonite was not derived from other chlorophylls, but was a product of chlorophyll *a* diagenesis under the exceptional geochemical conditions that existed in Lake Uinta.

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