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Abelsonite, nickel porphyrin, a new mineral from the Green River Formation, Utah

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Abstract

Abelsonite, a crystalline nickel porphyrin with the probable composition $C_{31}H_{32}N_4Ni$, has been found in eight drill cores in or near the Mahogany Zone oil shale of the Green River Formation in Uintah County, Utah. Associated authigenic minerals include orthoclase, pyrite, quartz, dolomite, analcime, and a K–Fe micaceous mineral. Abelsonite occurs as aggregates of platy crystals, as much as 3 mm long, that range in color from pink-purple to dark reddish-brown. The crystals are very soft (<3 on Mohs scale) and have a semimetallic to adamantine luster. Probable cleavage is $(1\bar{1}1)$. In transmitted light the color is red or reddish-brown, with intense absorption to reddish-brown. Its reaction with high-index liquids and its strong absorption prevented determination of optical characteristics. Abelsonite is triclinic, space-group aspect $P*$, with cell dimensions (Weissenberg), $a = 8.44$, $b = 11.12$, $c = 7.28$A, $\alpha = 90°53'$, $\beta = 113°45'$, $\gamma = 79°34'$; volume 613.8A^3, calculated density (for $Z = 1$) = 1.45 g/cm^3. The five strongest lines of the X-ray powder pattern (d value in A, relative intensity, indices) are 10.9 (100) 010, 3.77 (80) $1\bar{1}1$, 7.63 (50) 100, 5.79 (40) $1\bar{1}0$, 3.14 (40) $01\bar{2}$. Ultraviolet, visible, and infrared spectra indicate that abelsonite is a deoxophylloerythroetioporphyrin, presumably a chlorophyll derivative. The mineral is named in honor of Philip H. Abelson, President, Carnegie Institution of Washington.

Introduction

Abelsonite, a nickel porphyrin with a probable composition of $C_{31}H_{32}N_4Ni$, was first observed in 1969 by Lawrence C. Trudell (Department of Energy/Laramie Energy Research Center: DOE/LERC) in a sample from the Western Oil Shale Corporation

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Table 1. Locations of coreholes and abelsonite-bearing samples in southeastern Uinta Basin, Uintah County, Utah

Well No.		Location	Quadrangle	Depth of occurrence (in feet)
WOSCO		Sec 36 T 9 S R 20 E	Big Pack Mt. NE	2508.2 - 2508.45
ERDA/LERC	2	Sec 35 T 12 S R 21 E	Agency Draw NE	222.92 - 222.93, 223, 223.53 - 223.59, 226.47, 229.77
"	3	Sec 17 T 13 S R 22 E	Bates Knoll	65.26, 181.19, 181.35 - 181.37, 181.47, 182.17, 182.22, 190.25, 190.64, 190.70, 190.75 - 190.9
"	4	Sec 35 T 13 S R 22 E	" "	86.05 - 86.10, 86.2 - 86.3, 196.31, 195.91, 201.6
"	6	Sec 31 T 13 S R 22 E	" "	102.3 - 102.5, 234.60 - 234.62
"	7	Sec 14 T 14 S R 22 E	Pine Spring Canyon	45.07 - 45.10, 45.8 - 45.83
"	8	Sec 26 T 13 S R 23 E	Cooper Canyon	98.64 - 98.68, 102.48 - 102.52
"	9	Sec 6 T 13 S R 24 E	Burnt Timber Canyon	160.26 - 160.27, 232.2, 251.83, 253.03 - 253.2, 254.35, 254.44, 258.25

test core (Table 1, Wosco). He recorded a "tight vertical fracture from 2508.4 to 2508.8 ft. with black coatings and occasional fine pink-purple metallic patches" not over 3 mm in size (Trudell, 1970). The second observation (Table 1, No. 3) was also reported by Trudell (personal communication, November 20, 1975) as "minute purple crystalline masses." Soon thereafter, Cassandra Sever (Doe/Lerc) noted that abelsonite was found in six other cores, which are listed in Table 1.

Abelsonite (approved by the Commission on New Minerals and Mineral Names, IMA) is named in honor of Philip H. Abelson, President of the Carnegie Institution of Washington and editor of *Science,* a pioneer in organic geochemistry. Specimens of type abelsonite (NMNH 143566) have been deposited in the National Museum of Natural History, Washington, D.C.

Occurrence and localities

In the eight localities (Table 1), all in Uintah County, northeastern Utah (Fig. 1), abelsonite is present as macroscopically crystallized aggregates of platy crystals. All the samples were found in or near the Mahogany Zone, probably in the lower part (W. B. Cashion, U.S. Geological Survey, personal communication, May 11, 1976). The Mahogany Zone is the subsurface equivalent of the kerogen-rich Mahogany Ledge in the Parachute Creek member of the Green River Formation. Pink platy abelsonite was found in one sample (Wosco; the type locality) at a depth of 2508 ft.; this locality is about 16 miles northwest of the other occurrences (core samples herein designated as Doe/Lerc), where samples were found at much shallower depths, less than 258 ft. Until now, naturally occurring crystalline porphyrins have not been recognized, although Moore and Dunning (1955) solvent-extracted nickel and iron porphyrins from the eastward-extending Mahogany Ledge oil shale in Colorado; and Sugihara and McGee (1957) isolated, by solvent extraction, a nickel porphyrin from Utah gilsonite. The NW–SE trending gilsonite veins, as mapped by Cashion (1967), are a

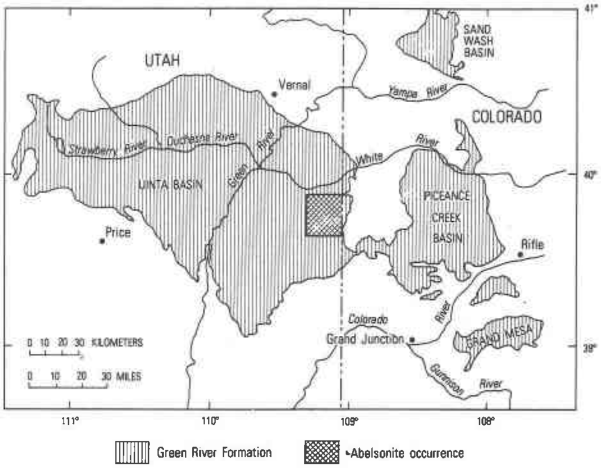

Fig. 1. Map showing extent of Green River Formation and area of abelsonite occurrences in northeastern Utah.

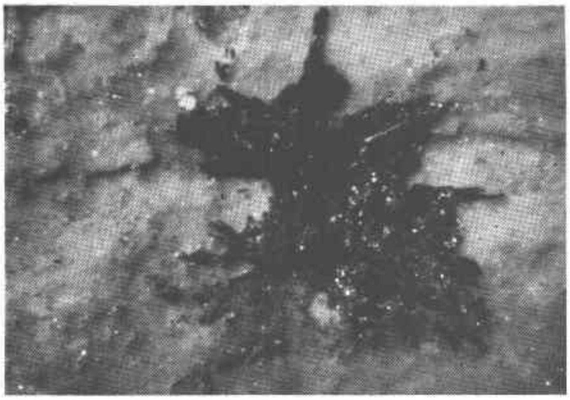

Fig. 2. Aggregate of abelsonite crystals from DOE/LERC No. 6, Uintah County, Utah. Photomicrograph, 60 ×.

few kilometers northeast and east of the abelsonite localities.

Because of the rarity and small size of the abelsonite crystal aggregates, ranging from 30 micrometers to 3 mm (Fig. 2), and superficial resemblance to "iron stains" or similar nondescript material, abelsonite may easily be overlooked in casual observation. Its identification in at least seven of ten DOE/LERC cores, from test holes scattered over an area of about 250 square miles, and in the WOSCO core (from a test hole about 16 miles northwest of the others), indicates that the mineral probably is present in a fairly extensive area in the Green River Formation.

The "black coatings," noted above by Trudell (shown in Figs. 3, 4, and 5), are a finely crystallized dark-brown micaceous aggregate, not noted in previous Green River mineralogical investigations; its precise nature is not known. Preliminary study suggests a K–Fe mica-like mineral. Other identifiable authigenic minerals associated with abelsonite are albite and orthoclase (Figs. 3, 4, and 5), pyrite, quartz, dolomite, and analcime.

The descriptive data of this report, particularly the unit cell determination by Adolf Pabst, and the infrared, visible, ultraviolet, and mass spectrometric studies by P.A. Estep-Barnes and Susan Palmer, were made on the type material (WOSCO). Identification of abelsonite from the seven DOE/LERC cores is based on comparison of their X-ray powder patterns and physical properties, ultraviolet and mass spectra, and on the presence of nickel as the only metal ion.

Physical properties

Abelsonite occurs as small (<3 mm) aggregates of thin translucent laths or plates (Fig. 2). Its color varies from light "pink-purple" (Trudell, 1970) at the type locality to dark reddish-brown at the other occurrences. The luster is semimetallic to adamantine. Abelsonite does not fluoresce in long- or short-wave ultraviolet radiation.

Determination of indices of refraction by the immersion method was impossible because of the strong reddish-brown to reddish-black absorption and because the mineral is rapidly attacked by diiodomethane and other high-index liquids. Abelsonite is insoluble in water and in dilute hydrochloric and nitric acids; it is soluble in benzene and acetone.

The mineral is very soft (<3 on Mohs scale) and easily deformed by pressure. Probable cleavage is $(1\bar{1}1)$. The density of abelsonite, 1.45 g/cm^3, was computed using the X-ray cell volume (613.8 A^3) and the mass-spectrometric molecular weight (518), assuming one molecule per unit cell. During an experiment, a particle was observed to sink in dichloromethane (G = 1.33) and float in chloroform (G = 1.48); the calculated density is within the range of the experimental observations.

Chemical analysis

Microprobe analysis of six separate grains of type abelsonite showed a range in nickel content from 11

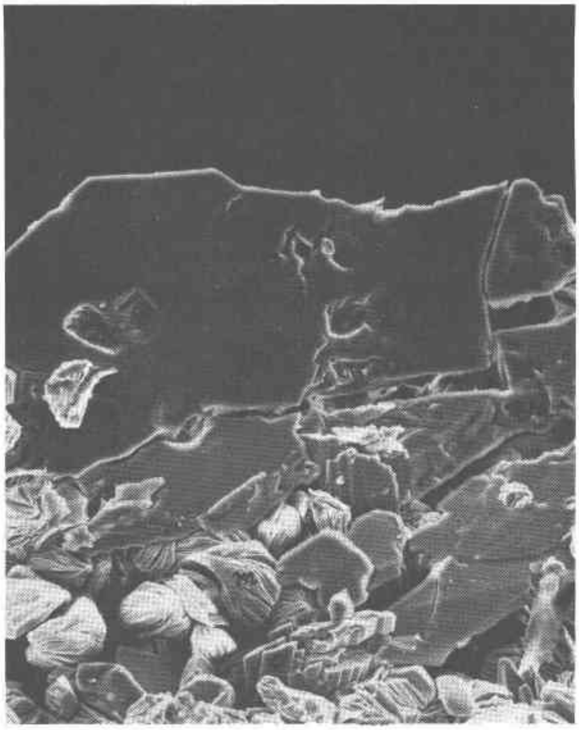

Fig. 3. Large (broken) crystal of abelsonite (a), with sheaves of an authigenic micaceous mineral (m), and orthoclase crystals (o) (WOSCO). Scanning electron micrograph, 160 ×.

to 14 percent. Approximately 10 fragments from the other occurrences were observed by using a scanning electron microscope equipped with an energy-dispersive system; the nickel content was estimated to be about 10 weight percent. In addition to the nickel determination, carbon values of 40–50 weight percent were obtained by microprobe analysis on the type material. Nitrogen could not be determined and probably was below the level of detection for the microprobe system (~10 weight percent). No other elements were detected. The intimate intergrowth of much of the abelsonite with other minerals (Figs. 3, 4, and 5) and the limited quantity available (a few milligrams) made attempts at more detailed chemical analysis impractical.

X-ray crystallography

Four fragments of type abelsonite were examined by single-crystal X-ray diffraction methods. Only two of them yielded useful results. Altogether, no more than a few score of distinct identifiable diffraction spots extend to $\sin\theta/\lambda = 0.3$. This limited range of "reflection," similar to that reported for a related compound, Ni-etioporphyrin (Crute, 1959; Fleischer, 1963), for which disorder has been postulated, is probably also attributable to disorder or other crystal imperfections.

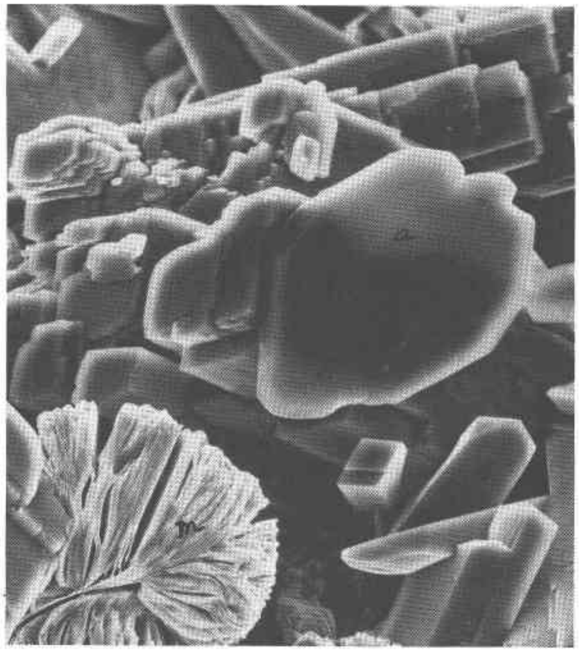

Fig. 4. Abelsonite (a) with authigenic orthoclase (o) and micaceous mineral (m) (Wosco). Scanning electron micrograph, 800 ×.

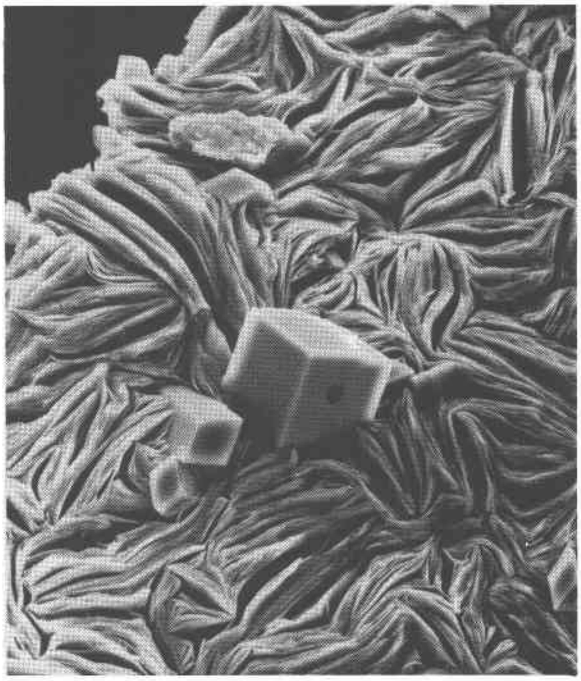

Fig. 5. Unidentified micaceous mineral with orthoclase crystals (o) (Wosco). Scanning electron micrograph, 600 ×.

The lattice derived from Weissenberg data is triclinic with diffraction aspect $P*$. From measurements on a [10$\bar{1}$] rotation pattern and the correlated 0-, 1st-, 2nd- and 3rd-layer equi-inclination Weissenberg patterns, the reciprocal lattice constants (scaled to λ = 1.54178A) were determined and the direct lattice constants calculated from these. The cell as reported in Table 2 is "reduced" in the sense that a, b and c are the shortest non-coplanar translations; it is right-handed and conforms to "rule 6" of *Crystal Data* (Donnay *et al.*, p. 2, 1963), "non-acute interedge angles α and β." This corresponds to Buerger's Type 1 crystal, orientation $abc = \bar{X}\bar{Y}Z$ (Buerger, 1963).

The lattice dimensions refined by Dr. Daniel Appleman by least-squares analysis of the powder data (indexed with the aid of single-crystal Weissenberg photographs) are listed in Table 2 for comparison with those derived from Weissenberg data.

The orientation of the translation lattice with respect to the outline of a typical lath is partly shown in Figure 6. The plane of the lath (or cleavage) (1$\bar{1}$1) has a calculated d spacing of 3.76A. There are 21 lattice planes with larger spacings. The axis of elongation, as observed on only two fragments, is [10$\bar{1}$], with identity distance *ca.* 13.18A. This is somewhat unusual, as the cleavage plane of micaceous crystals is generally that of greatest spacing, and the longest axis is ordinarily normal or nearly normal to the cleavage.

Table 2. Cell constants of abelsonite

	From Weissenberg data	From least squares refinement of powder data
a	8.44 Å	8.508(24) Å
b	11.12	11.185(27)
c	7.28	7.299(15)
α	90°53'	90°51(15)'
β	113°45'	114°08(12)'
γ	79°34'	79°59(13)'
V	613.8 Å^3	

Table 3. X-ray powder diffraction data for type abelsonite (Wosco)

Calculated[1]		Observed[3]	
hkℓ	d (Å)[2]	d (Å)	I
010	10.91	10.9	100
100	7.58	7.63	50
110	6.87	6.85	5
001	6.65	6.63	30
$10\bar{1}$	6.47	---	---
011	5.85	---	---
$11\bar{1}$	5.83	---	---
$1\bar{1}0$	5.73	5.79	40
$01\bar{1}$	5.53	5.51	35
020	5.46	---	---
$\bar{1}11$	5.34	---	---
120	4.91	4.90	10
021	4.36	4.39	10
101	4.22	---	---
111	4.15	---	---
$02\bar{1}$	4.09	---	---
$\bar{1}20$	4.07	---	---
$2\bar{1}1$	4.05	---	---
210	3.81	---	---
200	3.79	---	---
$1\bar{1}1$	3.76	3.77	80
220	3.44	---	---
$\bar{2}10$	3.38	---	---
020	3.33	---	---
012	3.24	---	---
$20\bar{2}$	3.24	---	---
$01\bar{2}$	3.13	3.14	40
		2.99	5
		2.60	5
		2.29	5
		2.21	5
		1.55	5

1) Indexed with the aid of single-crystal Weissenberg photographs.
2) Calculated from single-crystal Weissenberg cell constants (Table 2).
3) 114.59 mm Debye-Scherrer powder camera. V-filtered CrKα radiation (λ = 2.28962 Å). No internal standard. Intensities visually estimated.

The number of parameters required to specify all atomic positions far exceeds the number of observable reflections, even if the crystals should contain but a single type of molecule. A full crystal-structure determination of abelsonite is not possible at this time.

Nevertheless, the meager crystallographic data obtained for abelsonite do give a basis for some speculations about the structure. From lattice dimensions alone, there being but one Ni per cell, it is easy to show that distances from a Ni atom to the nearest eight Ni atoms are *a* 7.30, *c* 8.51, [101] 8.66, and *b* 11.18A, each two times, average 8.91A. In the structure of nickel etioporphyrin-I (Fleischer, 1963), with a density of 1.35 g/cm^3, distances from a Ni atom to the nearest 8 Ni atoms are 7.93A for four and 12.04A for four, average 9.98A; the molecules are nearly planar and are in a staggered arrangement by 4_1 axes with about 3.1A between the levels of the molecules. The molecules in abelsonite, if parallel to ($1\bar{1}1$), are staggered in a less symmetrical manner with a greater distance between successive levels. The mesh area of ($1\bar{1}1$) in abelsonite is 162.8A^2, whereas that of (001) in nickel etioporphyrin-I is 213.4A^2, suggesting that the molecules in abelsonite may depart more from planarity, which correlates with the slightly greater density of abelsonite. The mineral surely formed at depth under far greater pressure than the synthetic material.

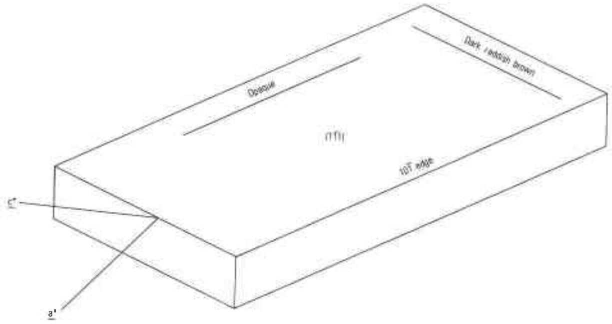

Fig. 6. Idealized sketch of orientation relations in abelsonite. The ($1\bar{1}1$) surfaces are always buckled; the [$10\bar{1}$] edge was observed as a straight line on only one fragment, and transverse surfaces are uneven though there is a suggestion of faces parallel to this edge and at a large angle to the cleavage.

Indexed X-ray powder diffraction data for type abelsonite (Wosco) are given in Table 3. Powder patterns taken of material from the other localities were virtually identical.

Ultraviolet—visible spectrophotometry, mass and infrared spectrometry

Experimental procedure

Small amounts of abelsonite crystals were dissolved in benzene in acetone, and UV-visible spectra

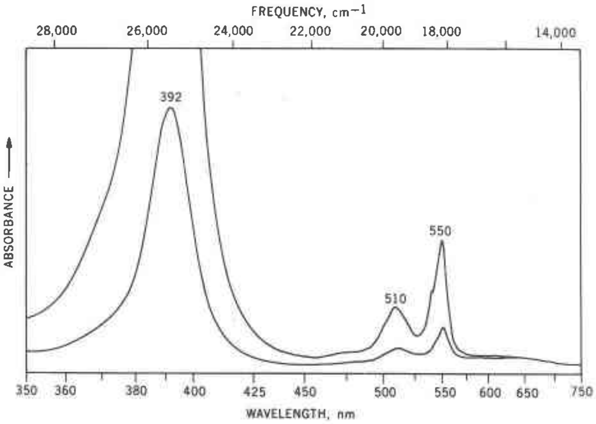

Fig. 7. UV-visible absorption spectrum of type abelsonite (in benzene solution; curves represent two different dilutions).

recorded using a Beckman[1] Acta CIII and a Perkin-Elmer Model 350 scanning spectrophotometer. The infrared spectral data were obtained on a 30 μg sample using infrared microsampling techniques described by Estep *et al.* (1973). Micropellets were scanned on a Perkin-Elmer Model 21 prism spectrophotometer (2–15 m) and a Perkin-Elmer Model 621 grating spectrophotometer (5000–200 cm^{-1}), both equipped with reflecting type 6X ultra-micro beam condensers. Mass spectrometric analyses were made using a Dupont 491-BR mass spectrophotometer equipped with a direct probe inlet system. The probe and source temperatures were 205° and 275°C, respectively.

UV-visible and mass spectrometric results

The UV-visible spectra obtained on fragments of abelsonite from two samples (WOSCO and DOE/LERC) were that of a porphyrin (Falk, 1964) having spectral bands at 392, 510, and 550 nm in benzene (Fig. 7) and 390, 512, and 552 nm in acetone. The data suggest that abelsonite is a deoxophylloerythroetioporphyrin-type (DPEP) porphyrin with an isocyclic ring. The presence of a small peak at 618 nm in the acetone visible spectrum of abelsonite from the WOSCO sample suggested the presence of about 14 percent (of total pigment) free-base porphyrin. However, only the 618-nm band was observed; other bands of the free-base porphyrin were obscured by the metalloporphyrin bands at 512 and 552 nm.

Donnay and Storm (1967) have shown that X-ray powder patterns of even the end-members of the isomorphous series tetraphenyl porphyrin (TTP) and silver tetraphenyl porphyrin (AgTTP), the free-base and silver analogs of the Green River porphyrin and nickel porphyrin, are indistinguishable. Thus, abelsonite may best be thought of as a non-stoichiometric compound.

Mass spectrometric analyses (Fig. 8) of an abelsonite sample recorded at 70eV showed that the major mass/charge (m/e) peak was 518 and a secondary

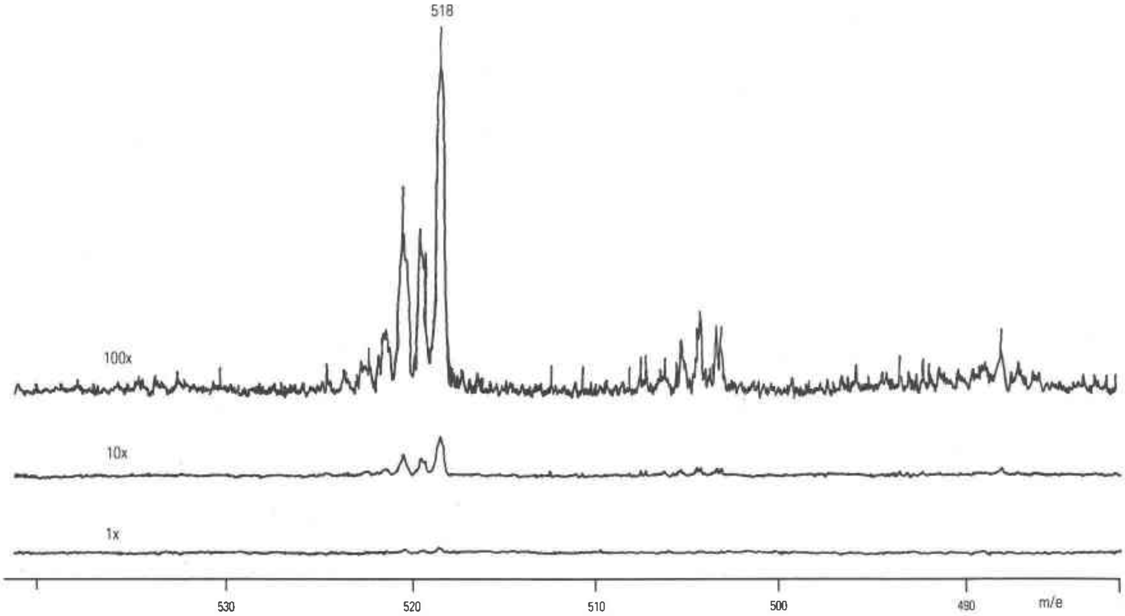

Fig. 8. Partial 12 ev mass spectrum of abelsonite from Green River Formation, Utah.

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[1] Equipment named in this report is for identification only and does not necessarily imply endorsement.

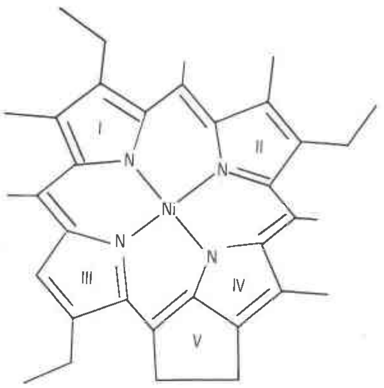

Fig. 9. Proposed molecular structure of abelsonite, $C_{31}H_{32}N_4Ni$; nickel 8-desmethyldeoxophylloerthyroetioporphyrin. Roman numerals I–IV are cyclic tetrapyrrole rings; V is a cycloalkane ring.

m/e peak was at 520. The ratio of the 518 to 520 mass spectral peak intensities roughly corresponds to the natural abundance of the two major stable isotopes of nickel (Ni^{58} = 67.8 percent and Ni^{60} = 26.2 percent).

The molecular weight of 518 indicates that this nickel porphyrin has 31 carbons and not 32 as was suggested earlier (Pabst *et al.,* 1975). The empirical formula for abelsonite should then be $C_{31}H_{32}N_4Ni$; the calculated composition for $C_{31}H_{32}N_4Ni$ (in weight percent) is: C 72.33, H 6.07, N 10.55, Ni 11.05. A proposed molecular structure for abelsonite is shown in Figure 9. It is not possible, at present, to present a more specific molecular structure.

Infrared spectrometry results

The general characteristics of the infrared spectrum appear in Figure 10, curve b (obtained on the prism instrument). Frequencies for C–H stretching vibrations, which were well resolved into three components (2970, 2915, 2860 cm^{-1}) in the grating spectrum, suggest a predominance of aliphatic groups in the structure. The absence of a strong absorption band in the C = O stretching region of 1780–1630 cm^{-1} indicates that there are no carbonyl groups in

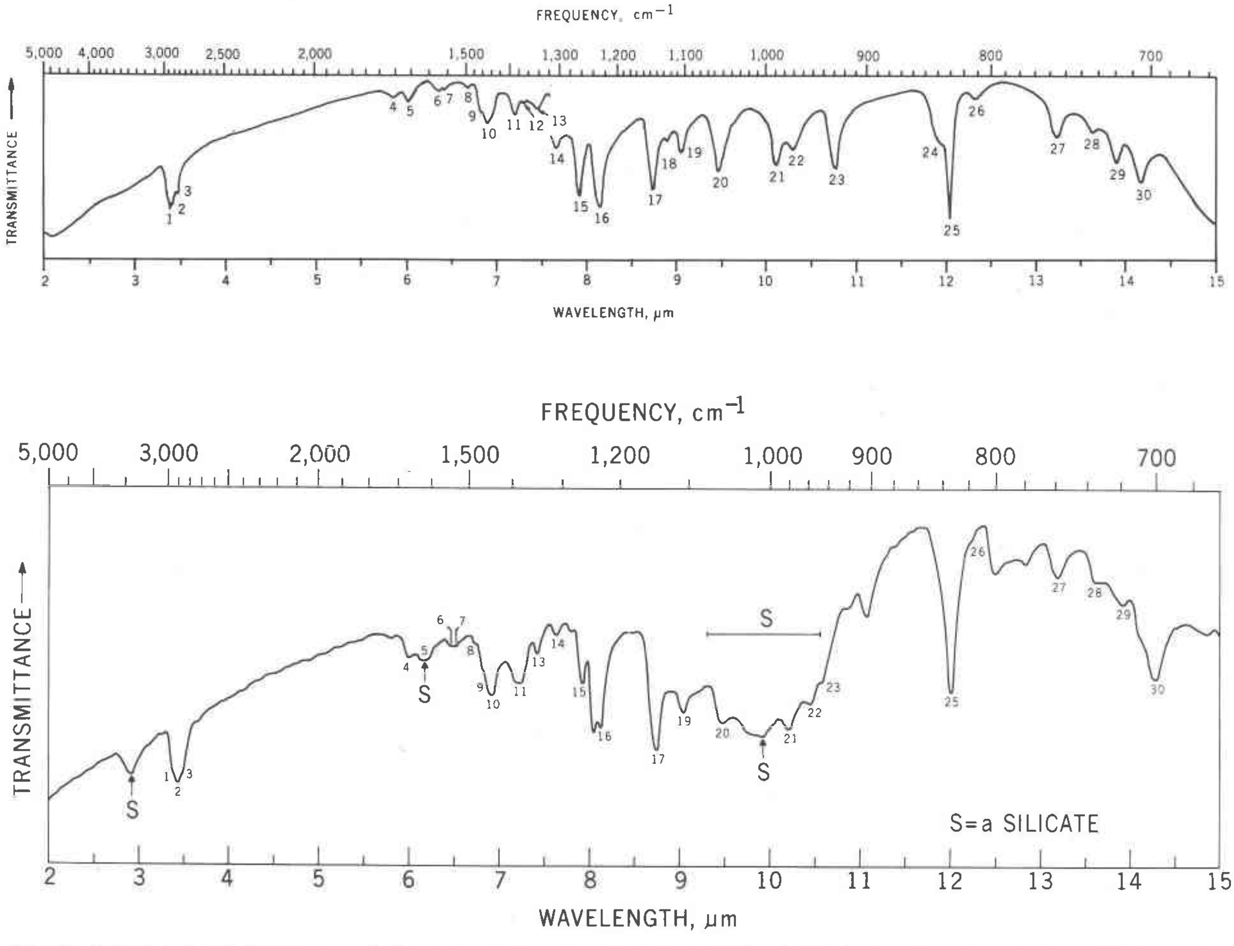

Fig. 10. Infrared absorption spectra of nickel–porphyrin complexes. (a) Nickel-etioporphyrin I (synthetic API No. 1906, nujol and fluorolub mulls); (b) Abelsonite (Wosco, CsI micropellet).

the structure. Additional absorption bands in the low-frequency mid-infrared region of the spectrum were observed at 620 (w = weak) 602 (w) 535 (w) 512 (w) 441 (s = strong) and 392 (w) cm^{-1}. Absorption bands at 3430 (m = medium) 1635 (w), 995 (w) cm^{-1} (labeled "S" in Fig. 10, curve b) and at 440 cm^{-1} (s) (observed in the grating spectrum) matched well with the major absorption bands in the spectrum obtained for the fine-grained black material that abundantly coated the surface of the host rock. A microscopic examination of the three translucent grains of abelsonite used to obtain the infrared spectrum showed several occluded black specks. The spectrum of the black material isolated from the host rock indicates that it is an hydroxyl-containing layer silicate (presumably the "micaceous mineral" referred to above). Since the infrared spectrum of a nickel desmethyl DPEP was not available from the literature for comparison with that of abelsonite, a comparison was made with that of nickel-etioporphyrin I (Fig. 10, curve a, American Petroleum Institute, 1957). There are gross overall similar spectral characteristics, but minor differences indicate a different structure, as was verified by UV-visible and mass spectral data.

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