The Structure of Abelsonite

Abstract. *Abelsonite, a C_{31} nickel-porphyrin of the deoxophylloerythroetioporphyrin type, is shown to have methyl groups in the 2, 3, 7, 12, and 18 positions and ethyl groups in the 8 and 17 positions by high-resolution, high-field ^1H nuclear magnetic resonance and nuclear Overhauser effect studies. Removal of the nickel by treatment with methanesulfonic acid permitted confirmation of the structure on the free base porphyrin and demonstrated structural integrity under the conditions required for demetallation. The structure is best accounted for geochemically by the hypothesis that abelsonite is derived from a chlorophyll.*

Abelsonite is a C_{31} nickel-porphyrin of the deoxophylloerythroetioporphyrin (DPEP) type found in fractures and bedding plane partings of shales from the Parachute Creek member of the Green River Formation of the Uinta Basin in Utah. It occurs in discrete purple patches, some of which exceed 2 mm in diameter, and is accompanied by small amounts of a C_{30} norisomer. Nickel-porphyrins extracted from shales surrounding the purple patches of abelsonite are a more extended series of homologues. Thus, abelsonite and its accompanying norisomer are of secondary origin.

Since the original report of the material (*1*), there have been several accounts of the spectroscopic and physical properties of abelsonite and other nickel-porphyrins found in shale deposits in the western United States which include speculations as to their structures (*2*–*4*). We have now ascertained the structure of abelsonite by means of high-field nuclear magnetic resonance (NMR) and nuclear Overhauser effect (NOE) methods.

The abelsonite studied was isolated from deposits found in fractures or bedding plane partings of drill cores taken from the Uinta Basin. The location of the cores and the details of the isolation and purification have been reported (*4*). The ^1H NMR spectra were obtained at 400 MHz with the use of a Bruker WM-400 spectrometer. Chemical shifts (δ) were measured relative to the residual $CHCl_3$ ($\delta = 7.26$ parts per million) in $CDCl_3$ and were reported relative to tetramethylsilane on the δ scale. Sufficient abelsonite was used to obtain a signal-to-noise ratio of about 40:1 after accumulation of 16 free induction decays. As is normal in the NMR of porphyrins, the line positions and line widths were dependent on concentration. The sample was heated in boiling $CDCl_3$ to ensure complete solution, and the spectra were acquired at 27°C. The NOE spectra were obtained with a low-power presaturation of 6 seconds followed by a 90-degree pulse with the decoupler off. Difference NOE's normally require 400 repetitions, but as many as 1700 were taken in some cases to obtain adequate signal to noise. Homonuclear decoupled spectra were acquired with the decoupler on at all times with a 40-degree pulse and a 3-second delay after the acquisition of the free induction decay. Spectra were collected in a 32K data block (3.3-second acquisition time) and subjected to Fourier transformation; 1-Hz line broadening was used to enhance the signal-to-noise ratio. Nickel was removed from the abelsonite by treatment with methanesulfonic acid at 110°C for 30 minutes (*5*).

Earlier high-field NMR studies narrowed the possible structures of abelsonite to the two shown in Fig. 1 (*4*). A portion of the argument for the structures in Fig. 1 was based on chemical shift assignments from the related nickel DPEP and nickel deoxophylloerythrin methyl ester and on the likely origin of abelsonite from chlorophyll. It is preferable, however, to determine the structure with minimum recourse to chemical shift analogies from models or assumptions of origin. Spin-lattice relaxation times, NOE's, and small long-range couplings have been used to make unambiguous assignments of resonances and to establish structures in porphyrins and petroporphyrins (*6*, *7*).

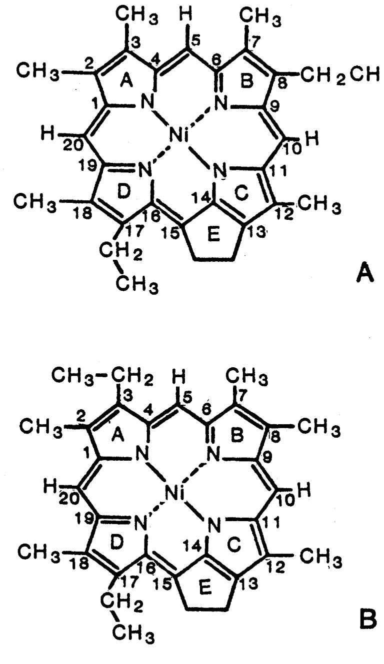

Fig. 1. Proposed structures for abelsonite (Fig. 1A was determined to be the correct structure).

The 400-MHz ^1H NMR spectra of abelsonite and the free base porphyrin derived from it are shown in Fig. 2, D and A, respectively. The frequencies from low to high field of the 12 substituents directly attached to the porphyrin ring and the effects of irradiation of each frequency are shown in Fig. 3A.

The multiplets at 4 and 4 (Fig. 3A) are immediately recognizable as the resonances from the methylenes at C-15 and C-13, respectively, in the E ring (Fig. 1A). Irradiation of line 5 causes the collapse of line 4 and a sharpening of the singlet, line 10 (Fig. 2C). Presaturation of line 5 shows an NOE on line 4; presaturation of 4 shows an NOE on 5 and the high-field quartet at 7; presaturation of 7 shows an NOE on 9; and careful low-power presaturation of 9 shows a strong NOE on 2 and a weak NOE on 3 (see Fig. 2B for an example of a difference NOE). This establishes a connectivity of 2(H)–9(CH_3)–7($EtCH_2$)–4(15-CH_2)–5(13-CH_2)–10(CH_3). Presaturation of the low-field quartet at line 6 shows a clean NOE on lines 1 and 8; presaturation of 8 shows a strong NOE on 3 and a weak NOE on 2; presaturation of 3 shows a strong NOE on 8 and 12; 11, by the process of elimination, lies next to 12; and presaturation of 11 shows a strong NOE on 2 and a weak NOE on 3. This establishes a connectivity of 1(H)–6($EtCH_2$)–8(CH_3)–3(H)–12(CH_3)–11(CH_3)–2(H), connecting by overlap to the previous set. These connectivities fit together to give the substitution pattern at the periphery of the porphyrin molecule and require that the structure of abelsonite be as represented by Fig. 1A. The NOE's listed in Fig. 3A involving all of the frequencies determine conclusively the system and fulfill the requirements of this structure.

The metal ion is usually removed from metalloporphyrins from geological sources by treatment with methanesulfonic acid (*5*). A similar analysis of the decoupling and NOE effects in the free base porphyrin derived from abelsonite gives a connectivity of –1(H)–8(CH_3)–6($EtCH_2$)–4(15-CH_2)–7(13-CH_2)–10(CH_3)–3(H)–5($EtCH_2$)–9(CH_3)–2(H)–11(CH_3)–12(CH_3), which is the same substitution pattern as in abelsonite.

The substitution pattern observed for abelsonite is genetically related to the typical chlorophylls in that there are no bridge substituents other than the E ring, and the expected biologically mandated sequence in rings B(7 Me, 8 Et), C(12 Me, 13 Ethano), and D(17 Et, 18 Me) is present. A C_{32} acid (see Fig. 1A, 17-

desethyl, 17-propionic acid) could be the immediate precursor of this structure because of its transport potential in alkaline waters (for example, Trona Water) (*8*).

As to a more distant precursor, the product of a microbially mediated vinyl scission of chlorophyll a could be considered. Straightforward operation of normal Treibs diagenetic schemes on chlorophyll d would lead to structure A (Fig. 1); however, there are two problems with the theory of chlorophyll d origin. First, there is no evidence that nonmarine red algae, manufacturers of chlorophyll d, existed in the Eocene lakes which gave rise to the organic matter of the Green River Formation. Second, the widespread existence of chlorophyll d, even in association with overwhelming amounts of chlorophyll a, is not established. Thus, the inclusion of chlorophyll d as a precursor of abelsonite requires that the diagenetic mechanisms (*9*) operate with extraordinary efficiency on the minor component (chlorophyll d) and discard with equal efficiency the major pigment (chlorophyll a). Therefore, it is unlikely that chlorophyll d is a serious contender as a precursor of abelsonite.

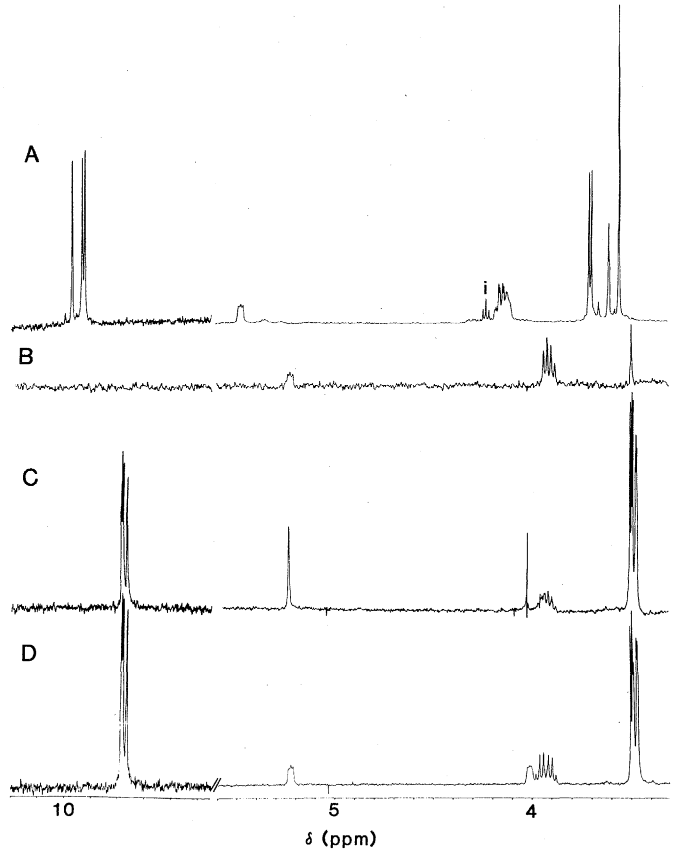

Fig. 2. (A) The 400-MHz ^1H NMR spectrum of the free base porphyrin obtained by removal of the nickel from abelsonite (*i* marks a peak from an impurity). (B) The difference NOE resulting from presaturation of the high-field triplet at δ1.68. (C) The sharpening of the singlet resonance at line 10 and the multiplet on line 4 when line 5 (see Fig. 3A) is irradiated. (D) The 400-MHz ^1H NMR spectrum of abelsonite. In all cases the low-field methine region from δ9.5 to δ10.2 and the high-field region from δ3.4 to δ5.6 are shown. The high-field triplets at δ1.68 and δ1.7 are not shown.

Lines affected

A Lines irradiated	H 1 δ9.79	H 2 δ9.78	H 3 δ9.77	CH_2 4 δ5.22	CH_2 5 δ4.01	CH_2 6 δ3.95	CH_2 7 δ3.90	CH_3 8 δ3.50	CH_3 9 δ3.49	CH_3 10 δ3.48	CH_3 11 δ3.47	CH_3 12 δ3.46
1	0					++			+	++	+	
2		0							++		++	
3			0					++	+		+	++
4				0	+		+					
5				++ S	0					S		
6	++					0		++				
7							0		++			
8		+	++			+		0				
9		++	+						0			
10	++	+			+					0		
11		++	+								0	
12		+	++									0
EtCH_3 δ1.68				++			++		++			
EtCH_3 δ1.79	++					++		++				

++,strong NOE; +, weak NOE.
S indicates sharpening due to decoupling.

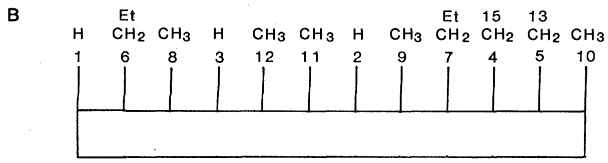

Fig. 3. The data matrix for decoupling and NOE experiments for abelsonite. (A) The vertical axis designates which line in the abelsonite spectrum (Fig. 2D) is irradiated; the horizontal axis designates which lines are affected by that irradiation. (B) The derived connectivity at the periphery of the porphyrin molecule.

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