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Uranium and organic matter: Use of pyrolysis-gas chromatography, carbon, hydrogen and uranium contents to characterize the organic matter from sandstone-type deposits

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Abstract

Organic matter seems to play an important role in the genesis of uranium deposits in sandstones in the western United States. Organic materials associated with ore from the Texas coastal plain, Tertiary basins of Wyoming, Grants mineral belt of New Mexico, and the Uravan mineral belt of Utah and Colorado vary widely in physical appearance and chemical composition.

Partial characterization of organic materials is achieved by chemical analyses to determine atomic hydrogen-to-carbon (H/C) ratios and by gas chromatographic analyses to determine the molecular fragments evolved during stepwise pyrolysis.

From the pyrolysis experiments the organic materials can be classified and grouped: (a) lignites from Texas and Wyoming and (b) hydrogen poor materials, from Grants and Uravan mineral belts and Wyoming; (c) naphthalene-containing materials from Grants mineral belt and Wyoming; and (d) complex and aromatic materials from Uravan, Grants and Wyoming.

The organic materials analyzed have atomic H/C ratios that range from approximately 0.3 to at least 1.5. The samples with higher H/C ratios yield pyrolysis products that contain as many as 30 carbon atoms per molecule. Samples with low H/C ratios are commonly more uraniferous and yield mostly methane and low-molecular-weight gases during pyrolysis.

Introduction

Sandstone-type uranium deposits, which make up more than 90 percent of the U.S. production and reserves, usually have organic material intimately intermixed in the ore. The major uranium districts are in the Wyoming basins (for example, Harshman, 1972), the Texas coastal plain (for example, Eargle and others, 1975), the Grants mineral belt in New Mexico (for example, Granger and others, 1961), and various localities in the Uravan mineral belt of eastern Utah and southwestern Colorado (for example, Shawe and others, 1959).

The Wyoming and Texas deposits are of the "roll" type, where the ore is between oxidizing updip and reducing downdip zones in sandstone beds that are sandwiched between lower permeability clays. The genesis of these ores has been discussed (Harshman, 1974) and related to a biogenic model (Rackley, 1972) and a nonbiogenic model (Granger and Warren, 1969), both involving reduction of uranium at the roll interface. Organic material is observed in these deposits as coalified or mineralized logs, millimeter-size coaly material, and amorphous organic material. The deposits are commonly in close proximity to seams of lignite. The lignite is not mineralized but could be a source of humic materials.

The New Mexico and Colorado-Utah deposits are mainly of the "tabular" type, where the ore is "floating" in sandstone bodies. The ore is generally associated with coalified wood (Breger, 1974) or with insoluble, unstructured organic material, which may have originially been of a humic acid type (Granger and others, 1961; Jacobs and others, 1970). The genesis of these ores is related to fixation of uranium by organic matter, perhaps through precipitation at an interface of two dissimilar water bodies (Granger and others, 1961; Shawe and others, 1959).

Experimental Procedure

Stepwise pyrolysis-gas chromatography has been described by Leventhal (1975, 1976), and the experimental procedure is only briefly reviewed here. First, 1 to 10 mg of finely powdered sample is placed in a 2.5-cm by 2-mm (ID) quartz tube, which is then put in the spiral heating coil of the Pyroprobe (Chemical Data Systems, Oxford, Penn.)*. The Pyroprobe is inserted in the injection port of a gas chromatograph in helium carrier gas (12 cm^3/min) and pyrolyzed for 10 seconds at 250°C. The pyrolysis products then pass into a 15-m by 0.05-mm (ID) porous-layer-open-tabular (PLOT) capillary column coated with Apiezon L on Chromsorb R-6740 and are trapped within the first 6 cm of column, which has been immersed in liquid nitrogen. The pyrolysis products are temperature programed at 6°/min from 50° to 280°C after the trap has warmed to room temperature (from liquid N_2 temperature). The procedure is repeated at 450°, 600°, 750°, and 900°C (and sometimes 1050° and 1200°C), and sometimes pyrolysis products from several steps are combined.

Elemental analyses were done using a Perkin Elmer* C, H, and N analyzer after carbonates had been removed by acid leaching. Carbon was analyzed as follows: Total was by Leco* combustion, carbonate by acid-leach gasometry, and organic by difference (Leventhal and others, 1978).

Uranium was analyzed by the delayed neutron technique (Millard, 1976) at the U.S. Geological Survey analytical laboratories in Denver.

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*Use of brand names herein is for identification only and does not imply endorsement by the U.S. Geological Survey.

Results

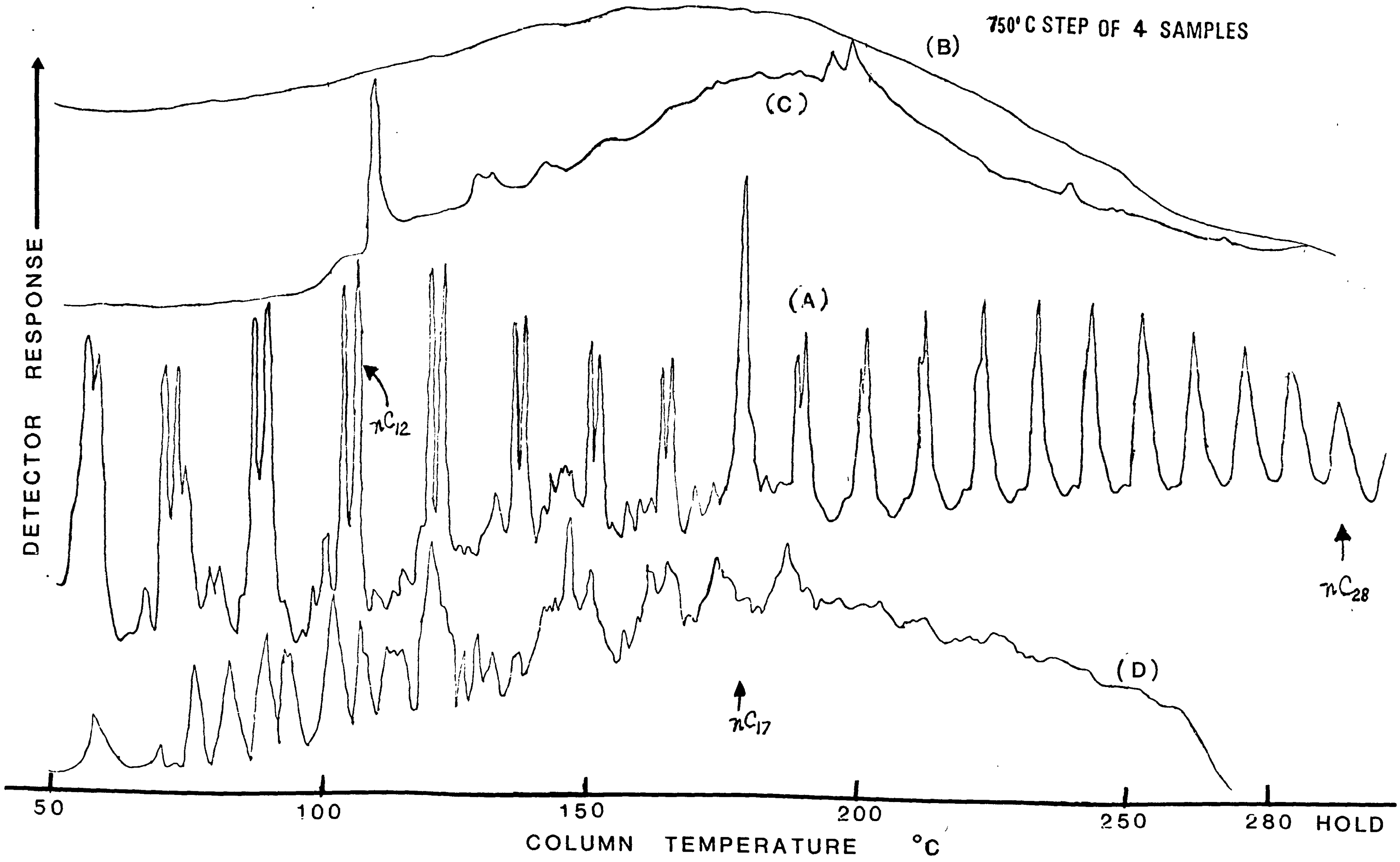
Pyrolysis-gas chromatography is used to characterize insoluble organic matter. Pyrolysis can fragment the large insoluble organic molecules into smaller pieces that can be identified. The stepwise pyrolysis procedure enables the removal of volatile or soluble molecules at low temperature without the usual chemical solvent extraction. These volatile or soluble species may be of recent origin and may not be related to the organic matter that "fixed" the uranium.

The organic matter associated with sandstone-type uranium deposits can be classified into four types by pyrolysis-gas chromatography (Leventhal 1975, 1976). Figure 1 shows typical pyrograms obtained from study of more than 100 samples from western U.S. sandstone deposits.

The pyrograms represent molecules with 9 to 30 carbon atoms. The large peaks of pyrogram (a) represent the normal (or linear straight-chain) alkanes and alkenes. Alkenes are molecules with an unsaturated carbon (carbon-carbon double bond). The numbers show the number of carbon atoms in the molecule (e.g. n-C_{12} is $C_{12}H_{26}$ (alkane) and $C_{12}H_{24}$ (alkene)). The samples that give pyrogram (a) are lignites (or low-grade coaly material) from beds that underlie or overlie uranium deposits in Wyoming and Texas. These pyrograms look the same as pyrograms of nonmineralized lignites from other localities.

Pyrogram (b) shows no molecules with nine or more carbons. (The "hump" represents small amounts of unresolved molecules or column bleed.) The samples that give this type of pyrogram may have carbon content as high as several percent, but the only pyrolysis products are methane and other gases (not shown on fig. 1). These gases are not part of the organic matter but are synthesized by the high pyrolysis temperature through the reaction of hydrogen from water the clays present in the samples. These samples are ores from the

Figure 1. Stepwise pyrolysis gas chromatography of organic materials associated with sandstone - type uranium ores. Detector response is shown on the abscissa and column temperature on the ordinate. See text for discussion.



Grants mineral belt and Uravan mineral belt and are amorphous-structureless organic matter intimately mixed with uranium (Granger and others, 1961). The H and C analyses (see table 1) show that they are hydrogen deficient, in some cases approaching amorphous carbon.

Pyrogram (c) shows only one large peak and several very small peaks. The large peak has been identified by mass spectrometry as having a mass/energy ratio of 128, which is characteristic of naphthalene ($C_{12}H_{10}$, two fused aromatic rings). Naphthalene is a molecule that should be stable to oxidation, temperature, and radiation. The small peaks present are below the sensitivity of the mass spectrometer and cannot be identified. The organic materials in these samples are similar to type (b): they are structureless and hydrogen poor.

Pyrogram (d) is a complex mixture, which has been partly characterized by mass spectrometry. The identified peaks are a benzene nucleus with functional groups such as hydroxyl (OH), methoxyl (OCH_3), and methyl (CH_3). These are representative of the structures of lignin (Sigleo, 1978). The samples that give pyrogram (d) are from ores that are associated with structured material that looks like coalified logs and fossil wood fragments.

Discussion

Stepwise pyrolysis gas chromatography is a useful technique which allows analysis of insoluble sedimentary organic material. Four types of organic matter have been found from western U.S.-sandstone type uranium deposits. The material represented by pyrogram (b) is the most altered, and its origin is not elucidated by pyrolysis-gas chromatography. It is possible that type (b) has evolved from type (c), and both of these could have come from either type (a) or (d). The pyrograms show the chemical building blocks of mineralized and nonmineralized lignite type (a) and mineralized coaly material type (d). Unfortunately, the amorphous material of the Grants mineral belt has not given pyrolysis products that can be related to an organic precursor.

Table 1.--Pyrolysis type, uranium content, carbon content, and H/C (atomic) ratio for organic matter associated with uranium sandstone ores

Sample	ppm U	% C org	H/C*
Type (a) Alkanes and alkenes			
18.3 lignite, Wyoming	352		16.6
Lignite, Powder River Basin, Highland Mine, Wyoming	3	2.0	
Beiker Mine, lignite, Texas	1,000	--	
Stoeltje Mine, lignite, Texas	133	49	
Powder River Basin 472 ft, fossil vegetal matter, Wyoming	5,450	19.1	
Powder River Basin 447 ft, Wyoming	544	0.72	
Coal, New Mexico	0.9	51.4	0.61
Stoeltje Mine, lignite 12, Texas	--	20.1	1.12
Stoeltje Mine, upper lignite, Texas	--	48.9	1.10
Searcy Mine, middle lignite, Texas	--	13.2	1.36
Type (b) H-poor			
1972975 Uravan, amorphous, Utah	15,640	1.7	
3072375 Uravan, amorphous, Utah	5,987	0.7	
8 Jackpile, amorphous, New Mexico	4,450	1.8	
15.5 Paguate, amorphous, New Mexico	11,000	3.7	
26G61 i, Ambrosia Lake, New Mexico	15,000	0.7	
Searcy Mine, Texas	5,077	0.1	
Shirley Basin, Wyoming	363	9.1	
Sec 30 Mine, amorphous, New Mexico	10,800	1.1	
Sec 30 Mine, amorphous, New Mexico	27,700	5.0	
KL #3, Shirley Basin, Coaly Wyoming	10,860	45.1	0.62
7-11-67 Coaly, Ore, Utah	5,930	26.5	0.67
Type (c) Naphthalene			
35G62 Poison Canyon, Ambrosia Lake, New Mexico	3,145	62	0.39
2-6-8-75 Salt Wash, Coaly, Utah	39,462	33	0.88
U 16 Stoeltje, lignite, Texas	1,414	28	
16.1 Pawelek (black), lignite, Texas	1,586	26	
16.2 Pawelek (red), Texas	866	2.5	
16G58 Wood? Bone? Asphalt?, New Mexico	--	39.8	(1.67)
37G62, Coal N58, New Mexico	--	55.6	0.49
1960 Kermac Sec 30, fracture filling, New Mexico	--	39	0.46
Type (d) Complex and aromatic			
44G58 amorphous, New Mexico	20,000	30	
1572975 coaly, Uravan, Utah	8,960	73	
1672975 coaly, Uravan, Utah	9,030	61	
Cottonwood Wash Mine, coaly, Uravan, Utah	125	70	
KL2 Shirley Basin, Wyoming	5,483	2.8	(1.51)
KL4 Shirley Basin, Wyoming	806	13	0.85
WYSBA2 Shirley Basin, coaly, Wyoming	11,460	42	
Black Diamond Mine, New Mexico	210	2.6	
Highland Mine, Powder River Basin, Wyoming	692	57	
9-11-7 lignite, Rajah, Utah	65	35.2	0.83
Stoeltje, Texas	51	2.3	0.67
Coaly seam, Phosphoria Fm GD6075, Wyoming	44	34.2	0.68
5 of 9/26/74 ore, Utah	130,000	32.2	0.69
Black Diamond Mine, Dakota Fm, New Mexico	180	2.6	3.4
44G58a, Ambrosia Lake, coaly, New Mexico	80	40.8	0.67
44G58d, Ambrosia Lake, coaly, New Mexico	155	31.1	0.77
45G58a, Ambrosia Lake, coaly, New Mexico	--	4.4	0.75
Highland Mine, #4 Wyoming	171	57.5	0.69
Highland Mine, #1 Wyoming	692	57.1	0.70
Highland Mine, Mudstone, Wyoming	329	9.4	0.92
Highland Mine, #3 Wyoming	--	46.9	0.72
Utah Int, Shirley Basin, Wyoming	--	63.9	0.74
Log, Uravan, Utah	125	70.4	0.89
17-7-29-75, Utah	105	69.7	0.71
19.2 Gas Hills, Wyoming	3,700	60.9	0.67

*All H/C data may include inorganic H from water (in clays, etc); numbers greater than 1 given in parentheses are not considered reliable for this organic material.

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