

Characterization of insoluble organic matter from the Lower Proterozoic Huronian Supergroup, Elliot Lake, Ontario

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ABSTRACT

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Elliot Lake organic matter falls into two main groups: (1) stratiform kerogens with reflectance from 2.63 to 7.31% $R_o(\max)$, exhibit a high level of aromaticity and low atomic H/C ratios (0.41–0.60); (2) less aromatic disseminated globules, most resembling solid bitumen are of lower maturity, with $R_o(\max)$ from 0.72 to 1.32, and atomic H/C ratios 0.71–0.81.

Stratiform kerogens, originated from cyanobacteria, have $\delta^{13}C$ values from –15 to –25‰. One exception with $\delta^{13}C = -31.8‰$ may have originated from methanogenic source biota; thus two genetically distinct populations of kerogen are tentatively recognized in Elliot Lake metasediments. Globular bitumens, remobilized by hydrous pyrolysis from kerogen, exhibit $\delta^{13}C$ values ranging from –25 to –33‰. The overall isotopic bimodality among Elliot Lake organic material is explained by analogy to petroleum generation from particulate kerogen that matured under conditions of catagenesis to metagenesis and was subjected to radiation over a long time.

Barium, U, Th, Au, Pt, Pd and REE contents of Elliot Lake stratiform kerogen greatly exceed those of average black shales. Except for As, Pt, Pd and Au, all metals (Ti, V, Cr, Mn, Fe, Co, Ni, Zn, Se, Rb, Sr, Ag, Sb, Cs, Ba, Hf, Ta, W, Hg, Th and U) are more concentrated in stratiform kerogens than in the derivative bitumen. This signals a significant role for a low-temperature transfer of noble metals to migrating bitumen.

Introduction

Kerogen, the most abundant organic matter on Earth is geochemically defined as a macromolecular polymer-like fraction of sedimentary organic material, insoluble in the usual organic solvents (cf. Durand, 1980). It does not migrate following sedimentation although it can be altered to other organic substances

(e.g. bitumen), and to petroleum (Willingham et al., 1985). Although most Precambrian kerogens are believed to have been ultimately derived from prokaryotic microorganisms (Mossman and Dyer, 1985), their evolutionary pathways have only recently come under close scrutiny.

The economically most important metallic ore deposits whose genesis is linked with that of kerogen, are the Au–U ores of the Witwatersrand (Pretorius, 1981). As a first approximation, Witwatersrand kerogen has been termed a metalliferous, shale-rich organic mat-

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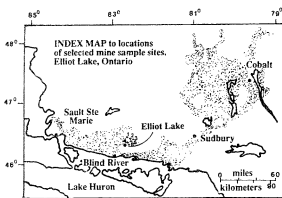


Fig. 1. Index map of distribution of Huronian Supergroup (stippled) showing Elliot Lake and the various sample locations: 1 = Quirke mine; 2 = Denison mine; 3 = Panel mine; 4 = Stanleigh mine; 5 = Stanrock mine; 6 = Nordic mine; Spine Road (not shown) is located just north and west of Elliot Lake, within the town suburbs.

ter (Nagy, 1989). Certainly it is an extreme case in terms of the enrichment in certain metals. The same is also true of organic matter in the 2.45 Ga old (Krogh et al., 1984) Lower Huronian Supergroup, Elliot Lake (Fig. 1), as documented below. Note that in view of current attempts to establish a working classification of Precambrian organic matter (e.g. Mossman and Thompson-Rizer, 1992) it is appropriate among the Elliot Lake samples to distinguish primary syngenetic kerogen, by definition of biological origin, from a secondary phase. This secondary phase, although virtually insoluble, otherwise resembles bitumen, a solid migrated form of petroleum-like material. Here, we briefly review the maturation characteristics of these organic materials and present new elemental and carbon isotopic data.

Sample description

Samples consist of eight stratiform kerogens (samples 1 to 8, Table 1) and nine globular bitumens (samples 9 to 17, Table 1), all except one (sample 6) obtained underground from mines in the Elliot Lake–Blind River region. The sample localities and nature of specific organic materials are indicated in Table 1. For

detailed description and photomicrographs of the two types of organic matter the reader is referred to Willingham et al. (1985), Mossman (1987), and to Nagy and Mossman (1992). In sample 8, obtained from paleosol at the Huronian–Archean boundary, sub-microscopic “carbon” (possibly adsorbed on clay minerals?) is present to 0.25% (Gay and Grandstaff, 1980). Sample 6, obtained from an arkosic quartz pebble conglomerate on Spine Road in Elliot Lake Township, is particulate (flake) kerogen believed to represent resedimentation of an eroded microbial mat (Mossman, 1987; V. Ruzicka, pers. commun., 1986); sample 5 is a mixture in about equal proportions of the two types of organic matter. Bitumen, the second type of organic matter, occurs either on its own as dispersed globules, or as fracture fillings, in each case distant from kerogen, or less commonly in close association with the kerogen.

Analytical procedure

Kerogen and bitumen samples were examined under a reflected-light microscope, with an oil immersion objective (N.A. 0.90×40; $N_{oil} = 1.518$ at 546 nm), and 25 maximum and minimum reflectance measurements were made on polished thin sections of each sample. A Zeiss MPM II microscope, fitted with a Zonax microcomputer and printer were used, and measurements were made under plane-polarized light (Table 1). Textures and structures of the organic matter were observed under both plane-polarized light, and partially crossed polars. Detailed visual descriptions of the organic matter types is given in Mossman (1987), and in Goodarzi et al. (1993).

Eighteen samples of organic matter were analyzed for carbon isotopes in the Stable Isotope Laboratory, McMaster University, according to conventional techniques (Eckleman et al., 1962) for reduced carbon. Results (see Table 1) are reported as $\delta^{13}C_{\text{‰}}$ values

TABLE 1

Carbon isotopic compositions and sample localities of organic matter samples from the Elliot Lake-Blind River area

Field sample number	Sample number on Figs.	Organic matter type and morphology	Location	H/C	%R _o (max.)	%R _o (min.)	BRO ^a	δ ¹³ C‰	Other
84-513	1	stratiform seam of kerogen, brecciated, in matrix of pyrite	Stanleigh mine, Ryan Member	4.02	0.99	3.03	—	-15.62 -15.71	
83-01	2	stratiform seam of kerogen, 3 mm thick	Stanleigh mine, Ryan Member	0.41	6.96 ^b	1.00 ^b	5.96	-31.80 -31.81	
74-11	3	kerogen from 2.5 mm thick stratiform seam at base of quartz pebble conglomerate	Denison mine; Lower Denison reef Panel 95380	0.60	4.18	1.13	3.05	-19.15 -19.23	TOC = 6.9% ^c
84-500	4	kerogen from 5 mm thick stratiform seam; occurs in part as matrix to arkose	Stanleigh mine, Ryan Member	5.55	1.11	4.44	—	-24.32 -24.51	
85-X4NP	5	kerogen occurs as matrix to conglomerate	Quirke mine, Matinenda Fm.	4.38 0.70	1.68 (bitumen)	2.70	—	-26.9 -30.90	
81-15	6	flakes of kerogen, disseminated in conglomerate	Spine Rd. Elliot Lake Twp.	2.63	1.16	1.47	—	-24.72 -24.91	
74-12	7	kerogen forms subangular pseudoglobules	Denison mine Lower Denison reef	3.28 ^b	1.08 ^b	2.96	—	-21.20 -21.16	
38010	8	carbon (kerogen?) from (yellow) paleosol	Denison mine	—	—	—	—	-16.6	
84-501	9	bitumen globule 1 cm long in arkosic conglomerate	Panel mine Matinenda Fm.	0.88	0.77	0.11	—	-31.59 -31.80	
84-503	10	bitumen globules 2 mm dia. in calcite matrix with pyrrhotite	Panel mine Matinenda Fm.	0.81	0.72 ^c	—	—	-28.26 -28.47	S = 4.2%
84-504	11	bitumen globules < 1 mm dia.	Panel mine, Matinenda Fm.	0.94	0.90	0.04	—	-32.74 -33.00	
84-505	12	bitumen globules to 0.5 cm dia.	Panel mine, Matinenda Fm.	0.97 ^c	—	—	—	-30.21 -30.29	
84-507	13	bitumen globule (1 cm × 0.75 cm)	Panel mine Matinenda Fm.	0.79	0.73 ^c	—	—	-27.52 -27.67	S = 3.5%
84-508	14	bitumen globules 0.5 cm dia.	Panel mine, Matinenda Fm.	0.75	0.67	0.08	—	-29.26 -29.53	
84-509	15	bitumen globules enclosed in pyrite	Panel mine, Matinenda Fm.	0.76	0.73	0.03	—	-27.87 -27.88	
38983	16	bitumen globules enclosed in sepiolite in vertical fracture	Denison mine, Lower Denison Reef	0.78	1.04	1.0	0.04	-25.91 -26.04	TOC = 15.58%
95355	17	bitumen globules in calcite matrix	Denison mine, Lower Denison Reef	0.71	0.92	0.75	0.17	-32.72 -32.86	S = 6.3%

Total includes eight stratiform bitumens and nine globular bitumens. Note that stratiform kerogens occur in the morphological forms of seams, as matrix, flakes and pseudo globules (Mossman, 1987). The paleosol sample may represent an additional stratiform (syngenetic) form. Except for samples 8, 16, and 17, which follow Denison mine's cataloguing system, field numbers are those of the Geological Survey of Canada. Portions of all samples are housed in the Department of Geology, Mount Allison University.

^a Bireflectance in oil. ^b Average reflectance for two orientations (parallel to bedding, and perpendicular to bedding). ^c Percent random reflectance.

TABLE 2

Inorganic elemental analyses for selected hand-picked stratiform kerogens and globular bitumen samples from Elliot Lake uraniferous conglomerates

	Kerogen				Bitumen				BBC
	matrix 85-X4NP (5)	pseudo- globules 74-12 (7)	seam 84-513 (1)	seam 84-500 (4)	globules in veins 38983 (16)	globule 84-505 (12)	globule 84-509 (15)	globule 84-501 (9)	
Au (ppb)	4,170	<351	<90	27,800	850	13,000	51	134,000	3.0
Pt (ppb)	<400	200	1,100	900	<300	210	6,190	<1,200	n.a.
Pd (ppb)	700	1,200	300	1,100	800	<900	5,000	7,600	1
Ag	<42	<32	<50	<28	<3	<5	<7	91	(ppb) 80
As	45	<5	98	78	82	89	310	95	(ppb) 1.0
Ba	1	1	32,000	24,000	1	1	1	<500	250
Br	<6	<6	<6	<3	11	15	15	<2	n.a.
%Ca	<43.3	<36.3	<57.6	<31.6	<1.3	<2.3	<4.3	<3.2	5.29%
%Fe	8.75	3.05	13.5	6.33	1.76	8.03	24.2	1.68	7.07%
%Sr	<0.47	<0.37	<0.59	<0.32	<0.04	<0.06	<0.02	<0.12	260
									(ppm)
Co	220	140	410	240	19	43	130	40	29
Cr	100	<69	<110	180	6	<10	67	47	185
Cs	<11	<8.1	<12	<6.9	<0.8	<1.2	<2	<2	1.0
Hf	<9	88	140	52	3	<1	<1	<2	3.0
Hg	<81	<67	<100	<54	<9	<6	<5	<22	n.a.
Na	850	2,550	2,760	1,150	360	1,000	1,120	859	2,300%
Ni	<1,300	<1,100	<1,700	8,900	<100	<200	<200	<300	105
Rb	<270	<200	<320	<170	<15	<25	<35	<42	32
Sb	68	50	94	21	3.9	2.3	2.3	7.0	0.2
Sc	39	37	66	44	1.8	3.0	3.6	5.0	30
Se	<86	<79	<130	<69	<8	<11	<12	<26	0.05
Ta	93	69	120	60	<1	<1	<2	<2	1.0
Th	14,000	12,000	21,000	8,800	780	150	35	890	3.5
U	82,400	100,000	155,000	76,000	4,400	520	280	4,700	0.91
W	55	100	<7	<2,000	28	<1	<1	<5	1.0
Zn	2,000	1,800	<500	2,400	300	340	860	1,800	80
La	3,500	390	2,300	900	200	25	28	160	16
Ce	6,400	2,000	5,200	2,400	410	78	60	420	33
Nd	2,100	1	4,800	1	400	1	53	380	16
Sm	400	474	967	530	78	12	3.5	77	3.5
Eu	60	115	92.3	54.5	3.3	<0.4	<0.4	<0.8	1.1
Tb	200	300	280	160	14	<2	<10	13	0.60
Dy	1,500	1,500	1,700	1,100	82	<1	4.2	86	3.7
Ho	235	240	532	1,190	<5	<5	<5	<20	0.78
Yb	340	562	450	317	20.6	2.2	<0.4	21	2.2
Lu	40	1	1	38	<0.6	1	<0.5	1	0.30
Al	16,200	4,150	7,460	7,970	827	988	608	2,720	8.41%
Mn	320	456	468	251	38.3	<0.5	5.2	22.3	1,400
Ti	<1,400	<1,300	<2,000	<1,000	<120	<100	<50	<100	5,400
V	<5	<5	334	<5	<5	<5	<5	8	230
Mg	37,000	<1,900	<2,800	<3,000	<190	<140	<49	<150	3,200%

Detection limits automatically calculated from background for each element. Analysis by neutron activation except for platinum elements which were done by fire assay combined with inductively coupled plasma emissions (ICP). Values in ppm unless otherwise indicated. I=interference; n.a.=not available. See Table 1 for details of sample numbers. BBC is estimate of bulk crustal composition from Taylor and McLennan (1985, p. 67).

relative to the Peedee belemnite (PDB) standard. Precision is $\pm 0.1\%$.

The H and C contents of the organic matter were determined with a Perkin-Elmer model 240 elemental analyzer. Samples were burned in O_2 at $950^\circ C$ after carbonates, where present, were removed by digestion with hydrochloric acid or phosphoric acids.

Bitumen samples are virtually mineral matter-free. Although every effort was made to purify the kerogens (see Nagy and Mossman, 1992) complete separation was hindered due to the intimate intergrowths of some mineral substances with the kerogens.

Neutron activation analyses (see Table 2) were performed by Activation Laboratories Ltd. using aliquots (8 to 73 mg) of samples encapsulated in polyethylene vials. Samples were irradiated together with similar size aliquots of Canmet standards for one minute serially at a flux of $5 \times 10^{12} \text{ n cm}^{-2} \text{ s}^{-1}$ at the McMaster Nuclear Reactor. After a decay of 600 s the samples were counted for 200 s on a 28% efficient high-purity germanium detector linked to a Nuclear Data loss free counting system. Following a decay of 3–7 h, the samples were re-counted for 2000 s. The samples were re-counted again for 2000 s after 24 h, 7 days, and 3 weeks using a 12% efficient Ge detector with a resolution of 1.73 KeV for the 1332 KeV Co-60 peak. Net peak areas were calculated using a modification of the APOGEE peak program (Routti and Prussin, 1969) of CANBERRA. Values were determined against an internal calibration derived from multiple international and synthetic standards. Modifications were made for counting geometry based on the 5 co-irradiated standards. Results were corrected for fission production of La, Ce, Nd, Sm, Mo and Ba. Uranium interfered with the determination of Lu and Ir because of spectral overlap or high background from samples with very high uranium. Detection limits were calculated by the program APOGEE from the background for each element.

Samples 9, 12, 15, 16 were re-irradiated for

20 min at the University of Michigan reactor at a flux of $5 \times 10^{12} \text{ n cm}^{-2} \text{ s}^{-1}$. After a decay of 7 days, the samples were counted for 2000 s to obtain better detection limits on the samples with lower uranium. To obtain Pt and Pd, the same material analyzed for other elements was fire-assayed by conventional Pt fire assay methods using Ag as a collector. Following dissolution of the Ag doré bead, the solution was run by Inductively Coupled Plasma Emission spectroscopy (ICP).

Non-mineral sulfur was determined in several (sulfide mineral-free) globular bitumens using the Prompt-Gamma neutron activation analysis (PGNA) at the McMaster Nuclear Reactor.

Results

Maturation characteristics

Organic matter in the uraniferous conglomerates of the Elliot Lake region falls into two major distinct groups based on morphology, organic matter type and reflectance characteristics. Results of detailed studies (Goodarzi et al., 1993) show that stratiform kerogen (samples 1–7, Table 1) has a reflectance ranging from 2.63 to 7.31% [$R_o(\text{max})$], and shows a morphological structure similar to lamalginite and highly matured algae; thermal maturation is at the catagenesis to metagenesis stage (Tissot and Welte, 1978; Hayes et al., 1983), equivalent to sub-greenschist to lower greenschist facies of metamorphism. In contrast, globular (dispersed) materials have reflectances ranging from 0.70 to 1.32% [$R_o(\text{max})$] and are essentially isotropic bitumens; level of maturation is epi-impsonite, compatible with a virtually unmetamorphosed condition (Willingham et al., 1985; Goodarzi et al., 1993).

Stratiform kerogens are further distinguished by H/C atomic ratios from 0.41 to 0.60, in contrast to globular bitumens with H/C ratios from 0.71 to 0.81 (Nagy and Moss-

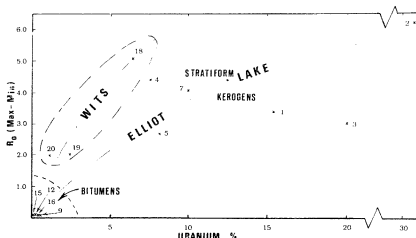


Fig. 2. Among selected samples of Elliot Lake organic matter a generally sympathetic relationship is apparent in terms of percent R_o (max-min) (bireflectance) and percentage uranium (cf. Eakin, 1989, p. 666). The trend among three selected Witwatersrand samples (18 = Blyvooruitzicht, 19 and 20 = Vaal Reef) to increased anisotropy at relatively low uranium contents may be more apparent than real, given the small sample population.

man, 1992). Materials of the latter, low-maturity group, are much less aromatic and contain more aliphatic and alicyclic groups in their structure (Khavari-Khorasani, 1975; Nagy and Mossman, 1992).

Compared to the kerogen samples (see Table 2), there is a diminishingly low content of uranium in the globular bitumens, a condition interpreted by Nagy and Mossman (1992) as reflecting the reducing conditions under which the bitumen was remobilized from the stratiform type. Also evident, is a general increase in maturity of the organic matter as gauged by the increase in the degree of anisotropy [R_o (max-min)] with increased uranium content; the same phenomenon is apparent among the several Witwatersrand kerogens (Fig. 2).

Carbon isotopes

The results of isotope analyses are included in Table 1. A graphic summary (Fig. 3) suggests that discrete fields exist for stratiform kerogen and globular bitumens as plotted against $\delta^{13}C$ and morphological types. With two exceptions, the stratiform kerogens range from -15.62 to -24.72‰ . The globular bitumens range from -25.91 to -33.0‰ , gen-

erally similar to that reported by Mancuso et al. (1989) and attributed to a process similar to that found in Phanerozoic sediments where bitumens are normally isotopically lighter than the precursor kerogen (Hayes et al., 1983). Samples 2 and 5 are exceptions to the general case for stratiform kerogens.

Interpretation of carbon isotope analyses

Sample 5 forms the matrix to a coarse-grained conglomerate. As described by Mossman (1987, fig. 4B), two different kinds of organic material are present in this specimen: one is a highly reflecting anisotropic kerogen, the other a low-reflecting ($R_o = 0.70\%$), nearly isotropic phase, penetrating fluid-like into fractures in the host rock. This physically inhomogeneous mixture of the two organic matter types doubtless accounts for the light $\delta^{13}C\text{‰}$ value of a sample initially perceived as wholly kerogen, and (probably due to sample inhomogeneity) for the spread in $\delta^{13}C\text{‰}$ values from -26.9 to -30.90‰ (Fig. 3). The phenomenon of bitumen in contact with kerogen is not unique to sample 5. A minor amount of bitumen is also visible in polished thin sections of specimen 6. Possibly it represents ma-

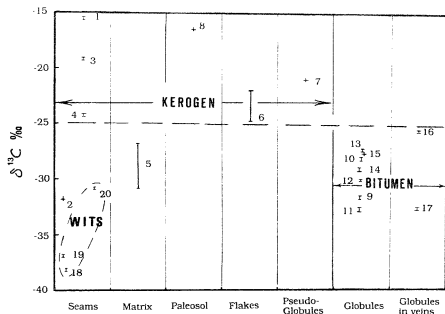


Fig. 3. Plot of $\delta^{13}\text{C}$ versus morphologies according to paragenetic succession (after Mossman, 1987) among Elliot Lake organic matter (stratiform kerogen and globular bitumen). Note that, except for specimens 83-01 (2) and 85-X4NP (5), the two groups are distinct (separated by the dashed horizontal line) in terms of $\delta^{13}\text{C}$ signature; spread in 85-X4NP (5) and in 81-15 (6) is attributed to inhomogenization in these specimens due to presence of both kerogen and bitumen. Specimen 83-01 (2) was oxidized prior to maturation and is probably of methanogenic source. Included for comparison are three stratiform Witwatersrand (WITS) kerogens: CVW-21 (20), CVD-6 (19) (Vaal Reef), 575047 (18) (Blyvooruitzicht).

terial absorbed onto the kerogen, analogous to bitumen commencing migration out of conventional source rocks (Butler and Barker, 1986), which must first saturate absorbers and fill pore spaces before expulsion occurs. Material thus absorbed, is far less likely than free bitumen in the pores to migrate out of the rocks. Specimens 5 and 6 both occur (see Table 1) in coarse-grained rocks. This lithology may have favoured the passage of (hydrothermal) fluids that affected a relatively late stage hydrous pyrolysis of the stratiform kerogens, as suggested by Willingham et al. (1985) and Nagy and Mossman (1992).

More difficult to explain is the anomalously light carbon present in the stratiform kerogen sample 2. Under reflected (partially crossed polarized) light, this sample shows features similar to those termed by organic petrologists "botanical structures", characteristic of lamalinite and highly matured algae (Goodarzi et

al., 1993). With $\delta^{13}\text{C} = -31.81\text{‰}$, it lies within what Schidlowski (1985, p. 264) terms "... the isotopic mainstream of sedimentary organic matter through geologic time". In view of its high thermal maturity (Goodarzi et al., 1993, table 1) the sample might have been expected to show, if anything, an enrichment in ^{13}C (McKirdy and Powell, 1974). However, its H/C ratio of 0.41 (Nagy and Mossman, 1992) exceeds the 0.30 limit reported by McKirdy and Hahn (1982) as the level below which $\delta^{13}\text{C}$ of residual kerogen undergoes a marked increase (cf. Hayes et al., 1983, p. 131). Thus, the signature may be an initial depositional one, possibly that of a type I kerogen of methanogenic source.

The other stratiform samples fall within the -20 to -30‰ range, except for sample 1, which at $\delta^{13}\text{C} = -15.67\text{‰}$ (avg.) is relatively heavy. The average $\delta^{13}\text{C}$ for the eight (Table 1) stratiform kerogens is -22.63‰.

Paleosol at the Huronian/Archean boundary secured underground at the Denison mine (see figs. 2 and 3 in Farrow and Mossman, 1989) returns a $\delta^{13}\text{C}$ value of -16.6‰ for C_{ORG} , placing it well within the stratiform grouping. This is fully explicable in terms of the microbial activity in Precambrian soils during early evolution of the paleosol, as envisaged by Mossman and Wiggering (1990). Unfortunately, serial polished thin sections of the paleosol failed to reveal any recognizable carbon (kerogen) for microscopic study.

A dichotomy reminiscent of that first described from the Gunflint Iron Formation (Barghoorn et al., 1977), and later extended into the Phanerozoic by Lewan (1986) is thus evident among the isotopic data for Elliot Lake kerogens. Thus, as shown in Fig. 3, sample 2 (and the Witwatersrand kerogens) represents the light isotopic group and samples 1, 3, 4, etc. (above broken line) represent the heavy isotopic group. Note that samples 1, 2, and 4, all highly overmature, and all from the same mine, have isotopic values of -15.6 , -31.8 and -24.3‰ , respectively. Unfortunately, geologic control on these samples is poorly documented other than the fact that each was obtained at a different locality, and possibly at a different stratigraphic horizon in the Stanleigh mine. However, on the basis of hand specimen study and microscopic examination, a slight contrast of lithologies is evident. For example, sample 1 is a somewhat broken up band of kerogen set in a matrix of detrital pyrite grains. Sample 2 is of a 3-mm thick solid band of kerogen bordered by detrital pyrite grains to 1 mm in diameter. Kerogen in sample 4 is from a concentration of sub-rounded grains, which together with pyrite comprise the matrix of an arkosic conglomerate. Unfortunately, distinctive sedimentary structures are not evident. Further, although contrasts exist in precious metal and in Fe and Ba contents (see Table 1), there is nothing to suggest a systematic variation of metal content with the isotopic variation.

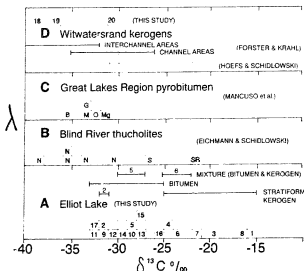


Fig. 4. Frequency distribution of Elliot Lake carbon isotopic values of various kerogens from Elliot Lake–Great Lakes region, and the Witwatersrand. (A) Elliot Lake (this study), numbers keyed to Table 1. Note the bimodal distribution between $\delta^{13}\text{C}$ values for kerogens and bitumens. Sample 2 may represent a kerogen of methanogenic source (see text for details); spread in samples 5 and 6 results from an inhomogeneous mixture of kerogen and bitumen. (B) Blind River “thucholites”, after Eichmann and Schidlowski (1974); N = Nordic mine, S = Stanleigh mine, SR = Stanrock mine. (C) Precambrian vein “pyrobitumen”, Great Lakes region, after Mancuso et al. (1989); Mg = Michigamme Fm; O = Onwatin Fm; M = Matinenda Fm; G = Gunflint Fm; B = Biwabik Fm. (D) Witwatersrand kerogens; Interchannel and Channel areas represent two populations from specific paleoenvironments (after Förster and Kralh, 1989).

Figure 4A shows a different view of the overall bimodal distribution of $\delta^{13}\text{C}$ values among Elliot Lake organic matter samples. For comparison, Eichmann and Schidlowski's (1974) isotopic data for seven “thucholites” from the Blind River District (Fig. 4B) show no hint of bimodal distribution. However, McKirdy and Hahn (1982, fig. 8, p. 133) noted a rather similar frequency distribution to this among $\delta^{13}\text{C}$ values of Witwatersrand kerogens. Note that Eichmann and Schidlowski (1974) described their “thucholites” as uraniumiferous hydrocarbons, whereas Willingham et al. (1985) and Nagy and Mossman (1992) show that the kerogen is normally uranium-rich, and the putative derivative bitumen impoverished. It therefore seems reasonable to

conclude that bitumens were somehow excluded from Eichmann and Schidlowski's suite of "thucholites".

Finally, it is worth noting that the disposition of isotopic values from Elliot Lake kerogen (this study, Fig. 4A) may find more likely analogy with the results of Förster and Krahls (1989) study of Witwatersrand kerogen. That work, which focused on specific paleoenvironments of kerogen deposition, supports rather well a case (Fig. 4D) for isotopic bimodality of kerogen. On balance, this mechanism may provide the most plausible explanation for the range of $\delta^{13}\text{C}$ among the kerogens. Note, however, that the carbon isotopic values for the

Witwatersrand populations are rather lighter than the presently reported values for Elliot Lake kerogens.

Elemental analyses

Eight new inorganic elemental analyses (Table 2) and six formerly published analyses of Elliot Lake organic matter (Nagy and Mossman, 1992) are used in calculating the averages of selected elements as given in Table 3. Minimum enrichment values for selected elements in black shales (after Vine and Tourtelot, 1970) and U.S.G.S. recommended values (Kane et al., 1990; Huyck, 1990) for the Stan-

TABLE 3

Average contents of selected inorganic elements in Elliot Lake organic matter samples, compared with minimum enrichment for average black shale (after Vine and Tourtelot, 1970) and "recommended" values for U.S.G.S. Standard Devonian Oil Shale (SDO-1) (Kane et al., 1990; Huyck, 1991) Elliot Lake samples (see Table 2) not included here.

	Shale		Elliot Lake organic matter	
	minimum enrichment values for Average Black Shale (Vine and Tourtelot, 1977)	U.S.G.S. Ref. SDO-1 (Huyck, 1990)	stratiform kerogen $n=6$	globular disseminated bitumen $n=8$
Ti	7,000	7,100 ^r	n.a.	n.a.
Mn	1,000	400 ^r	374	22
Ag	7	0.092–0.17 ^{re}	n.a.	91
Au (ppb)	n.d.	0.002–0.0035 ^{re}	8,818	21,277
B	200	128 ^{av}	n.a.	n.a.
Ba	1,000	397 ^r	39,250	50
Co	30	46.8 ^r	190	33
Cr	700	66.4 ^{av}	140	40
La	70	38.5 ^r	1,419	46
Mo	200	134 ^r	1	n.a.
Ni	300	99.5 ^r	11,450	n.a.
Sc	30	13.2 ^r	42	2
Sr	1,500	75.1 ^r	n.a.	n.a.
Rb	n.d.	126 ^{av}	n.a.	n.a.
V	1,000	160 ^r	334 ⁽¹⁾	8 ⁽¹⁾
Zn	1,500	64.1 ^r	1,680	462
U	30	48.8 ^r	155,567	1,101
Th	n.d.	10.5 ^r	22,133	245
As	n.d.	68.5	74	150

Numbers of samples analyzed are: 8 globular bitumens, including 4 reported in Nagy and Mossman, 1992 (84-503, 84-507, 95355 and 38983) (a duplicate); 6 stratiform kerogens, including 2 reported in Nagy and Mossman, 1992 (74-11 and 83-01). Values in ppm unless otherwise indicated. ⁽¹⁾ indicates ¹: analysis only. I=interference; n.a.=not available; n.d.=not determined.

^{av}=average; ^r=recommended; ^{re}=range. Note estimated compositions of Elliot Lake samples (see Table 2) not included here.

ard Devonian Shale, provide (Table 3) a general comparison. Note that Huyck (1990) defines a metalliferous black shale as one which is enriched in any given metal by $2\times$ (except for Be, Co, Mo and U, for which $1\times$ is sufficient) relative to SDO-1 shale.

Interpretation of elemental analyses

As a result of their detrital origin, uranium and thorium contents are, of course, orders of magnitude higher in the Elliot Lake stratiform kerogen than in average black shales. The same is true of barium, which in stratiform kerogen may indicate volcanic input. It may also be, in part, (cf. Mann and Fyfe, 1985) of biogenic origin. Gold is certainly far richer in the Elliot Lake kerogens than in the average black shale

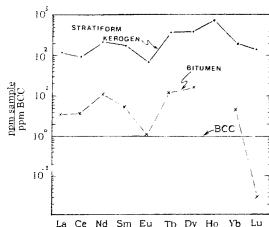


Fig. 6. Average contents of REE in four stratiform kerogens (Table 2) and eight bitumen samples (as for Fig. 5, above); analyses of REE contents are normalized to bulk crustal composition (BCC). Data on BCC from Taylor and McLennan (1985). Stratiform kerogens contain more REE than the bitumen samples.

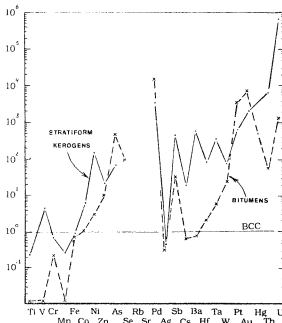


Fig. 5. Average contents of selected elements in six stratiform kerogens [four from Table 2 and two (RAD 74-11 and RAD 83-01) given in Nagy and Mossman (1992)] and in eight bitumen samples [four from Table 2 and four (RAD 84-503, RAD 84-507, 95355 and 38983) given in Nagy and Mossman (1992), all from Elliot Lake. Estimates shown in Table 2 are not used in this plot. Analyses normalized to bulk crustal composition (BCC) from Taylor and McLennan (1985). Pt is assumed to be 1 ppb for BCC. Metal content of stratiform kerogens exceeds that of bitumen in all instances, except for As, Pd, Pt and Au.

(Table 3). Also, it is one of only four elements present in greater quantity in the globular bitumens than in the stratiform organic matter.

The detailed contrasts in metal contents of stratiform kerogen, versus derivative globular bitumen, are more clearly evident in Fig. 5 when the data are normalized to the bulk crustal composition (BCC) given by Taylor and McLennan (1985). Here, the average metal content in stratiform kerogen exceeds that of the bitumens in most instances (except for As, Pd, Pt and Au). This is perhaps not unexpected, given the common enrichment in a host of metallic elements, of uraninite associated with hydrocarbons (e.g. Parnell, 1988a). Further, uraninite is a common, though not necessarily ubiquitous, phase in stratiform kerogens (Willingham et al., 1985) of the Elliot Lake and Witwatersrand conglomerates. However, what is surprising, are the notable exceptions of As, Pd, Pt and Au (and possibly Ag?) to the above generality. Acknowledging that the averages in Table 3 may be unduly influenced by high values, it nevertheless seems likely that some selective process has operated to fix these four elements preferentially in the globular bitumens.

With the exceptions noted above, the excess of metals in stratiform kerogen, as opposed to the globular type, is inclusive also of the rare earth elements (REE) (Fig. 6). It has been reported that REE-bearing minerals are more likely transported detritally than in solution (McLennan, 1984), and that secondary mobilization of REE is not normally a distinctive process. Detrital monazite is a possible residence site for REE in the stratiform kerogens. However, the widespread occurrence of authigenic monazite in the Huronian Supergroup (e.g. Sutton and Maynard, 1991) means that, at least in this instance, REE will have also been redistributed secondarily.

Discussion

The maturation data define substantial differences between the two groups of organic matter in Elliot Lake uranium ores. In the case of the kerogen, assuming that it is of cyanobacterial origin, it is of type I, and with the lowest recorded $R_o(\text{max}) = 2.63$ (Table 1), is apparently overmature. With H/C ratios of about 0.6, and TOC about 7% (Table 1), hydrocarbon generating capacity will have become virtually exhausted (Tissot and Welte, 1978, p. 455). This change will have accompanied the generation of the bitumen fraction.

Doubtless the great age of the kerogen and the high degree of ionizing radiation to which most of the samples have been subjected (Nagy and Mossman, 1992) will have further contributed to a highly overmature condition (e.g. lowered H/C atomic ratios, aromatization etc.). Thus, within the group of stratiform kerogens, increase in the degree of anisotropy accompanies increase in uranium content. The limited available data support the suggestion that H/C atomic ratios decrease with increased anisotropy (i.e. increased U content), a phenomenon reported by Eakin (1989) in the case of Mesozoic and Precambrian hydrocarbons (bitumens), and by Dahl et al. (1988), concerning the U content of sedimentary rocks.

In contrast, the bitumens form a relatively tight grouping in terms of bireflectance and H/C ratios, although they exhibit an appreciable range in $\delta^{13}\text{C}$ values. On average, between the two groups there is about a 7‰ spread (eight stratiform samples, $\delta^{13}\text{C}(\text{avg.}) = -22.63\text{‰}$; nine globular samples, $\delta^{13}\text{C}(\text{avg.}) = -29.65\text{‰}$).

To what process(es) can the spread in $\delta^{13}\text{C}$ of the two groups of organic matter most reasonably be attributed? Certainly large shifts in the isotopic composition of residual kerogen may come about at the onset of oil generation (Tissot and Welte, 1978). However, according to Hayes et al. (1983, p. 108), once the stage of an immature kerogen has been reached, all subsequent isotopic shifts are either nil or positive. The same was shown by Lewan (1983) on the basis of hydrous pyrolysis experiments. Only in the presence of carbonates is the carbon isotopic value of kerogen likely to change (become heavier) with metamorphism (Valley and O'Neil, 1981). Thus, the isotopic compositions of Elliot Lake kerogens should, in theory, represent maximum values, and precursor organic material will have been lighter, not heavier. There remains the possibility that radiation may have contributed to the enrichment of ^{13}C in kerogen relative to that in bitumen. In agreement with the results of the present study (see Fig. 4), Dahl et al. (1989) concluded that in general, irradiation tends to raise the $^{13}\text{C}/^{12}\text{C}$ ratios of residual kerogens. However, numerous exceptions are cited in the literature (e.g. Curiale et al., 1983; Leventhal et al., 1987). Alternatively, the isotopically light carbon in bitumens could be explained by derivation from methane generated by high-temperature pyrolysis of kerogen (cf. Chung and Sackett, 1979). However, this is considered unlikely because of the closely similar molecular compositions of the two organic matter types (Nagy and Mossman, 1992). More plausible, perhaps, is a process of isotopic fractionation (cf. Křibek, 1989) resulting from hydrous pyrolysis, effectively a hy-

drothermal dissolution of the kerogen. The process will have operated under catagenetic to metagenetic conditions (cf. Nagy and Mossman, 1992) possibly, in part, in the presence of CO_2 and/or H_2S with water present as a supercritical fluid.

Despite various post-depositional alterations, to which in particular the stratiform kerogens have been subjected, the wide range of isotope values (between -32 and -15‰) indicates substantial differences in the initial isotopic compositions. As noted earlier, this condition is probably linked to differences in environmental conditions and/or organic matter types, as yet unspecified. Yet the range of values is remarkably close to those (between -30 and -17‰) reported by Strauss (1986) for Proterozoic metasediments (in the Churchill Province greenstone belt).

It is instructive to note that the coexistence of bitumen with kerogen at Elliot Lake has a close counterpart, at least locally, in the Witwatersrand (cf. Smits, 1984). Also, the phenomenon finds a close parallel in the recent documentation by organic petrologists in "strewn slides" from conventional Phanerozoic source rocks (Thompson-Rizer, 1987) showing solid bitumen (so-called "pyrobitumen" of some workers) derived from liquid hydrocarbons, together with kerogen. From the homogeneous "flowed" appearance of the solid bitumen, a liquid hydrocarbon origin is inferred, indicating that the hydrocarbons were generated in, or migrated through, the metasedimentary host strata (Thompson-Rizer, 1987, p. 385). It appears, therefore, that the association of kerogen and derivative bitumen is by no means a phenomenon restricted to source rocks of Cambrian age and younger.

In view of their low alumina contents, stratiform kerogens at Elliot Lake are really quite unlike black shales. Further, they are clearly atypical in terms of their Ba, U and noble metal contents by comparison with average black shales. The most plausible explanation of the anomalously high metal contents concerns

processes of biomineralization (Willingham et al., 1985; Dyer et al., 1988) combined with detrital deposition. More surprising perhaps is the fact that derivative bitumens, although depleted in Ba and U, are even more enriched in noble metals. Clearly, since impurities such as clays are lacking in the bitumens, any direct comparison with metalliferous shales is unjustified. More to the point is the question of transport and precipitation of their noble metal contents.

Evidence indicates that hydrothermal fluids may play an important role in the genesis of PGE deposits (e.g. Schiffries and Skinner, 1987). However, only recently has the phenomenon been confirmed by experiment (e.g. Wood et al., 1989). Evidently, PGE when complexed by hydroxide, bisulfide or ammonia, may undergo significant transport at low temperatures (e.g. ca. 300°C) and in restricted $\log f_{\text{O}_2}$ -pH space (Wood et al., *ibid.*).

In the case of Elliot Lake organic matter, field evidence concerning solubility/transport/precipitation of PGE centers on the existence of certain (key) elements associated with the noble metals (see Fig. 5). One possibility is that of complexing with As; another is bisulfide complexing, which is known to be quite an efficient carrier for both Au (Seward, 1973) and for Pt and Pd (Wood et al., 1989). The presence of from 1.7 to 6.3% non-mineral sulfur in Elliot Lake globular bitumens (unpublished data) makes the latter process an attractive one. Possibly several species of metallic complexes may have been involved. From a study of metal enrichments in solid bitumens, Parnell (1988b) has concluded that significant quantities of metals are unlikely to be transported with hydrocarbons; rather, incorporation of metals in bitumens occurs where metal-bearing and hydrocarbon-bearing fluids meet. However, the role of organometallic complexes may have been important here, possibly via methylation, a mechanism known (Rapsomanikis and Weber, 1986) for its efficiency in effecting wholesale transport, at low tem-

peratures, of such heavy metals as Hg and Pd. In fact, orders of magnitude more PGE can be transported by methane and other light hydrocarbons than by normal aqueous solubility.

Conclusions

Clearly, a great deal remains to be learned about the mobilization of metals in association with organic matter (hydrocarbons), and about their common occurrence together in certain ore deposits. With respect to organic matter in the Lower Proterozoic uraniferous paleoplacer ores of the Elliot Lake–Blind River region we conclude that:

(1) Two main groups of organic matter are present: stratiform kerogens, possibly of two distinct populations, originated syngenetically from microbial precursors, matured under conditions of regional metamorphism, exhibit high aromaticity, low H/C atomic ratios (0.41–0.60), large clusters of condensed aromatic lamellae and $\delta^{13}\text{C}$ values ranging from -15.0‰ to -31.8‰ (avg. -22.63‰); globular (dispersed) bitumens are of low maturity, virtually unmetamorphosed, are less aromatic, have higher H/C ratios (0.71–0.81) and exhibit $\delta^{13}\text{C}$ values from -25‰ to -33‰ (avg. -29.65‰).

(2) An overall isotopic bimodality is recognized in Elliot Lake organic matter. It is most simply explained by general analogy to petroleum generation from particulate kerogens that were subjected to radiation and low-grade metamorphism, and from which globular bitumens were remobilized by hydrous pyrolysis during one or more hydrothermal events to which the host rocks were subjected.

(3) A dichotomy (15.62‰ to -24.91‰ and ca. 31.81‰) among the isotopic data for Elliot Lake kerogens is tentatively linked to differences in paleoenvironmental conditions of the sedimentary regime, and/or to organic matter types as yet unspecified.

(4) The intimate association of bitumen with kerogen at Elliot Lake has a close parallel

with solid bitumen of liquid hydrocarbon origin present in visual kerogen strewn slides of (Phanerozoic) source rocks.

(5) Compared to metalliferous black shales, kerogens of the stratiform group are greatly enriched in Ba, U, Th, Au, Pt, and Pd. A combination of biogenic processes, detrital deposition and secondary (diagenetic) process are responsible for this enrichment.

(6) Metals are more concentrated in the stratiform kerogens than in derivative globular bitumens, except for As and the noble metals Au, Pt and Pd. This condition signals a significant role for a low-temperature ($< \text{ca. } 200^\circ\text{C}$) transfer of noble metals, possibly sourced in part from the stratiform kerogens.

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