

Project 740081

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Resource Geophysics and Geochemistry Division**Introduction**

Radioactive hydrocarbons such as those which will be discussed here were first described in detail by Steacy et al. (1973). They identified discrete radioactive grains associated with amorphous hydrocarbon materials, grains of chalcopyrite and some pyrite. The host rock for the samples described from the South March area was dolomitic sandstone of the Lower Ordovician March Formation. Charbonneau et al. (1975) described this and other "thucolite" occurrences from elsewhere in the South March and nearby Marchhurst areas. In places, hand specimens of mineralized sediments contained up to 4% chalcopyrite and 0.05% U_3O_8 in hydrocarbon. Other metals including Pb, Mo, Mn and Ag are commonly associated with U in the hydrocarbons, while trace Mo probably occurs in the chalcopyrite. Not all hydrocarbon occurrences are radioactive. Typical data are presented in Table 22.1 for some oxidized specimens in which the hydrocarbons survive essentially intact.

Ford (1975) and Ford et al. (1976 and unpublished work) have made some detailed studies of the mineralogy of these U-Cu showings. Chalcopyrite was observed to be the dominant sulphide phase near the surface, however downdip pyrite seemed to be the dominant sulphide. Occasionally sulphide grains were associated with hydrocarbon material and also encased by rinds of goethite containing up to 6% Cu, possibly a product of chalcopyrite oxidation. Pyrite and marcasite were also described. Pyrite was observed to occur either as a single phase or in close association with hydrocarbon, sometimes surrounding it, other times banded or interlayered.

Ford (1975) described the hydrocarbon material as containing up to 4.7% U_3O_8 ; ThO_2 was not present. Cu, Ca, Fe, Si and Ti were also found to be common impurities. Hydrocarbon occurs as irregular grains or seams on parting planes within the carbonate sediments and within interstices between quartz grains. Some bulk

analyses (this work) of hydrocarbon grains separated from weathered bedrock from the Marchhurst occurrences were found to contain similar amounts of U.

Specimens of radioactive hydrocarbon have also been found in vertical fractures in the Oxford Formation in close proximity to U-Cu mineralization in underlying March Formation near South March. The samples were black and apparently amorphous. No discrete U or Th minerals were recognizable. Electron microprobe analyses, performed by A.G. Plant of the Geological Survey, revealed that the main mass of the sample was homogeneous hydrocarbon containing U, about 5% Ca and minor Cu, Fe, Ti, Si, Mg and S. Grains of pyrite, chalcopyrite and an Fe oxide, possibly goethite, were shown to be present within the hydrocarbon mass (Fig. 22.1).

The radioactive hydrocarbons found in both the March and Oxford formations are considered to be of epigenetic origin. The time of emplacement is in doubt, but possibilities include early deposition of fluids along bedding and in compaction or dewatering fractures during or shortly after diagenesis. In the case of the Oxford Formation occurrences, which lie in larger fractures, it is likely that the time of emplacement could be much later if the hydrocarbons have been remobilized from underlying March Formation. The regional distribution of these blanket-like Cu-U hydrocarbon occurrences as revealed by drilling results kindly provided by the Kerr Addison Company suggests that certain thin, rubbly intraformational strata are host to these minerals over a wide area. These horizons may represent ancient water tables or aquifers through which groundwaters once percolated.

Discussion

There is considerable indirect evidence that the amorphous hydrocarbons now present are relics of organic matter which was responsible for the

Table 22.1

Metal content of some hydrocarbon-rich carbonate rocks from the South March area, Ontario.
Values are in ppm except where noted.

Sample	Fe%	U%	Zn	Cu	Pb	Ag	Mo	Mn
1.	3.61	0.02	66	3200	91	4	27	1850
2.	1.54	0.01	11	320	17	1	3	600
3.	1.25	0.01	13	420	50	5	40	650
4.	1.63	0.02	25	2300	330	5	120	1070
5.	2.77	0.01	47	1500	120	5	87	1230
6.	2.23	0.02	20	790	340	36	77	1460
7.	4.41	0.04	40	4900	720	44	110	2720



Figure 22.1. Radioactive hydrocarbon: Oxford Formation. Main mass is homogeneous hydrocarbon. Bright grains are mainly pyrite with some chalcopyrite. Light grey grains are iron oxide, probably goethite. Magnification: X350. Mineral identification by A.G. Plant.

transportation of U, Cu and other trace metals into the sediments. It is further postulated that this organic matter was likely some form of the polymeric, polyelectrolyte material known collectively as humic and fulvic acids.

According to Schnitzer and Khan (1972) the following ions form very stable strong complexes with fulvic acid: Fe^{3+} , Al^{3+} , Cu^{2+} , Pb^{2+} , Ca^{2+} ; Zn^{2+} , Mn^{2+} and Mg^{2+} form weaker complexes. Roughly the same order of stability is followed for metal ion-humic acid complexes as well. It is generally considered that the strong complexes are true inner-sphere or chelate types whereas the weaker complexes are outer-sphere types. For example, van Dijk (1971) assigned the following order of increasing stability for divalent metal ion-humic acid complexes:

Ba, Ca, Mg, Mn, Co, Ni, Fe, Zn, Pb, Cu, (Fe III).

Little work has been done to date on UO_2^{++} complexes, however Pauli (1975) has conducted experiments which indicate that UO_2^{++} forms very strong soluble humic acid complexes, at least as strong as Cu^{2+} .

No work has been published on the complexes which might form between U^{4+} ions and soluble humic matter. It is likely that such complexes do form and are stable under the reducing conditions normally experienced in groundwaters. Kovalev and Generalova (1968) have reported that normally immobile species such as the hydrolyzate ions of Ti^{4+} , Zr^{4+} and Th^{4+} are readily stabilized in solution by the complexing action of humic and

fulvic acids. U^{4+} is chemically a very similar ion to Th^{4+} and therefore might be expected to be similarly mobile in the presence of natural organic acids.

The strength of complexes formed and the related ability of humic and fulvic acids to dissolve silicate minerals are further illustrated by the work of Huang and Keller (1972) who found that fulvic acid can extract Al, Si, Fe and Mg from clays and other silicate minerals. Moreover, Fotiyev (1971) has demonstrated that "aqueous humus" from marsh waters contains considerable dissolved silica which forms a 1:2 complex with fulvic acid. Carbonates and sulphides are also readily solubilized by aqueous humic acids (Baker, 1973).

The presence of sulphide ion in the groundwater system does not appear to be a total deterrent to the migration of metal-humate complexes. Kovalev and Generalova (1974) investigated the effects of organic acids on the formation of Fe sulphides. They observed that the presence of organic acids, especially fulvic acid, suppressed the formation of pyrite. Pauli (1975) studied the system humic acids: metal ions, Cu, Zn, Pb, Ni, Cd: saturated H_2S . Although some 60 per cent of the metal humates were transformed into sulphides, some 30 per cent remained with acid precipitable humus. Boulegue and Michard (1974) noted that polysulphide ions, species common in reducing groundwaters, serve as good acidity and redox buffers as well as strong complexers. Humic acid-polysulphide interactions result in the stabilization of the organics by incorporating polysulphide into their structure. The complexing ability of these addition complexes towards metal ions is also further strengthened. Other ions such as S_2O_3^- (Listova, 1966) are commonly present in groundwaters and have been shown to form very stable complexes with ions such as Pb^{++} under weakly acid conditions.

Conclusions

The relevance of this work to the formation of Cu-U hydrocarbon residues in Paleozoic rocks can now be demonstrated. The ability of humic acids to transport UO_2^{++} , Cu^{++} , Pb^{++} , Ca^{++} , Fe^{++} and ions is undoubted. There is good evidence that reduced species, such as U^{4+} and ions normally considered to be immobile, Th^{4+} , Zr^{4+} , Ti^{4+} , Si^{4+} , Al^{3+} , are also rendered quite mobile by humic acids. Thus interactions between them either in solution or as coalescing gels become possible. Fotiyev (1971) has suggested that kaolin could form from the interaction of organic complexes of Si and Al; Huang and Keller (1972) consider that bauxite may form as a result of leaching and accumulation of Al-fulvate complexes. Similarly it can be suggested that uranotitanates, of which brannerite is an end member, could also form in this way, or coffinite could exsolve from a hydrocarbon-rich

solution containing both U and Si. Of course, other related mechanisms involving adsorption of U ions onto pre-existing hydrocarbon residues, titania or silica skeletons likely complicate the model. But in the absence of matching quantities of counter ions, uraninite itself may exsolve from a degrading hydrocarbon complex along with some sulphides of Cu and Fe. Given sufficient time this would likely occur spontaneously, but there is one further aspect which may be important to the formation of U-rich hydrocarbon residues and that relates to the well known ability of prolonged radiation (X-ray, gamma, UV) to promote dehydrogenation and polymerization and accelerate precipitation of organic compounds.

It is therefore proposed that the very even distribution of U, and certain other trace ions such as Ca^{++} , in the South March area hydrocarbons are the result of catalytic polymerization of soluble humic materials which have also contributed to the collection of these ions en route. Ions then become trapped at their complexation sites rather than migrating to crystallization loci as might happen in gel reactions. Ca^{++} is abundant in these hydrocarbons because of its ability to form strong humate complexes and most importantly, because of its easy availability in carbonate rocks. Its content may well represent the saturation complexing capacity of the original transporting organic acids.

This mechanism is proposed as a strong possibility for this particular environment. It does not exclude other adsorption-precipitation mechanisms or the involvement of other complexing agents in the mineralizing process.

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