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LEWIS H. KING

FUELS AND MINING PRACTICE DIVISION

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Mines Branch Research Report R 116

ON THE ORIGIN OF ANTHRAXOLITE AND IMPSONITE

by

Lewis H. King*

ABSTRACT

Anthraxolites and impsonites are of secondary origin, but it is difficult to ascertain their point of entry in the secondary development track. They are normally described as being homogeneous and structureless; however, six of the twelve samples examined during this study possess a fine crystalline structure. The presence of crystalline material provides a basis for further speculation on their origin, as the conditions for crystallization in organic materials limit the various possibilities. It is thought that the material must have been quite aromatic in composition during deposition and that it probably migrated in an aqueous environment. It is also suggested that the migrating fraction originated as an alteration product of primary sedimented organic matter.

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Direction des mines

Rapport de recherches R 116

DE L'ORIGINE DE L'ANTHRAXOLITE ET DE L'IMPSONITE

par

Lewis H. King*

résumé

Les anthraxolites et les impsonites sont d'origine secondaire, mais il demeure difficile de déterminer de façon précise à quel moment ils sont entrés dans le processus secondaire d'évolution. On les décrit ordinairement comme homogènes et sans structure. Toutefois, six des douze échantillons examinés durant l'étude ont une belle structure cristalline. La présence de matières cristallines donne lieu à de nouvelles hypothèses sur leur origine, car les conditions de cristallisation au sein des matières organiques restreignent les origines possibles. On croit que la matière en question devait être de composition très aromatique au moment de la mise en place et qu'il y a probablement eu migration en milieu aqueux. On suppose également que la partie qui a émigré avait pour origine un produit d'altération de sédiments organiques primaires.

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INTRODUCTION

In a previous report by the author and his colleagues (1), the development and classification of organic matter in geological formations is discussed, and development tracks for a wide spectrum of organic matter of both syngenetic and epigenetic origin are defined in terms of the physical, chemical and optical properties of the samples. The tracks for primary organic matter develop progressively in response to meta morphic influence in the direction of increasing carbon and aromaticity. In addition to the metamorphic control, the course of the development tracks for the secondary organic matter is influenced by fractionation, and it is suggested that compositional changes arise from processes of selection and concentration of organic fractions from the primary organic matter. It is further contended that the organic fractions migrate in aqueous solution and can be deposited at indiscriminate stages of development along the secondary tracks.

In a later report, on the origin of albertite (2), evidence was presented to suggest that the fractionation process can take place at the lower aromatic end of the development tracks. It is the purpose of the present report to present evidence which suggests that fractionation processes must also contribute to the formation of some anthraxolites and impsonites, and, furthermore, that some anthraxolites and impsonites must enter the secondary development track as highly aromatic fractions which in some cases are not far removed in composition from that of the materials as they presently exist in the geological column.

OCCURRENCE

The samples discussed in this report are part of the larger suite of samples discussed in the earlier report (1). The majority of the samples pertinent to the discussion are from the province of Quebec, and occur along a belt of metamorphosed Ordovician rocks east of the Champlain fault. Logan (3) noted occurrences of a hardened bituminous substance at Quebec, Ile d'Orléans, Pointe Lévis, Sillery, St. Nicholas, Lotbinière, Drummondville, Acton, and many other places.

In describing the occurrences Logan states that the bituminous substance fills veins and fissures in the limestones, shales and sandstones. At other times it lines fissures encrusted with small crystals of calcite and even fills the cavities in trap rocks. In some cases it fills fissures several inches in diameter so that it has been mistaken for coal. Other deposits have been described since Logan's time; notable among these is an occurrence associated with copper mineralization and black slates of the Pohenegamook formation in Saint-Denis township, Quebec (4). Sample 107 was obtained from this locality.

Periodically, samples are sent to Ottawa from this area of Quebec for analysis at the Fuels and Mining Practice Division. A number of samples used in this investigation were obtained in this manner, and consequently their field relations are not well known.

Sample 109 was collected by the writer about two and a quarter miles south of Matane, Quebec, in the Pohenegamook Ordovician limestone. The material occurs in small tension veinlets of coarsely crystalline calcite cutting the limestone, and is probably of local origin, since the limestone is dark and contains considerable organic matter. Black slates also occur nearby. The anthraxolite occurs interstitially in particles up to a half-inch in diameter and conforms more or less to the crystal faces of the calcite, but is sometimes cut by veinlets of the calcite. It appears that the calcite and the anthraxolite were deposited simultaneously.

The Sudbury anthraxolite (sample 128) was obtained from the Geological Survey of Canada collection at Ottawa. This is the type material, and the name was proposed by Chapman (5) in 1888. Mickle (6) describes the Sudbury deposit as a fairly extensive vein cutting black slates and argillaceous sandstones. The vein is at least 70 feet in length and averages 9 feet in width. The anthraxolite occurs with quartz, some calcite, and occasionally a little pyrite. In some instances the anthraxolite occurs as rectangular fragments in a network of quartz, and in other places it is almost free of quartz.

DESCRIPTION OF SAMPLES

During the earlier examination (1), anisotropism was noted in the anthraxolites and impsonites, either as a uniform extinction across the entire field or as more or less randomly oriented anisotropic crystals 1/, generally of very fine particle size. Of the eleven samples considered, a crystalline structure was observed in the following six: 51-impsonite, St-Joachim de Tourelle, Quebec; 52-anthraxolite, Mont Joli, Quebec; 53-impsonite, Rimouski, Quebec; 109-anthraxolite, Matane, Quebec; 117-impsonite, Ile d'Orléans, Quebec; and 128-Sudbury anthraxolite, Chelmsford, Ontario.

1/ The designation 'crystal' is used throughout this report but may not be strictly correct; however, the anisotropy of the individual particles clearly indicates a certain steric regularity. The high degree of crystallinity exhibited by these samples is unique, inasmuch as anthraxolites and impsonites are normally described as being heterogeneous and structureless.

The crystalline samples represent a range from 90.2 to 94.1 atom percent carbon and 5.2 to 1.1 atom percent hydrogen, with an aromaticity ranging from 0.85 to 1.0. For a more complete description of the chemical and physical properties of these samples, the reader is referred to the earlier report (1). The classification boundary between impsonite and anthraxolite is shown to occur roughly in the area where the structure becomes fully aromatic.

Photo 1 illustrates the fine crystalline structure of sample 117. The average crystal size is 0.5 micron and can be discerned clearly only at high magnifications. The photomicrograph was taken in reflected light from a highly polished surface under oil immersion. With the exception of the Matane material (sample 109), Photo 1 is representative of all the crystalline samples, although the crystals of some exhibit a degree of preferred orientation. Sample 109 is illustrated in Photo 2, which was taken in transmitted light with crossed nicols. This material is more coarsely crystalline, with crystals in the order of 2-5 microns; these crystals resolve equally well in reflected light.

ORIGIN

The presence of randomly oriented crystals in some of the anthraxolites and impsonites provides a basis for further speculation on their origin. The nature of the occurrence of these materials indicates that they are of secondary origin, but without additional information it is not possible to infer their composition at the time of deposition, or the extent to which they have subsequently moved along the development track in response to the metamorphic factors. In other words, without additional information it is not possible to decide whether a given impsonite or anthraxolite entered the secondary track at approximately its present composition, or whether, for example, it entered as an albertite or grahamite and changed to anthraxolite under the influence of heat and pressure.

The influence of pressure on the orientation of aromatic nuclei under natural conditions is evident from our knowledge of coal (7) (8). As coals increase in rank and become more aromatic as a result of metamorphism, pressure brings about an alignment of the aromatic nuclei parallel to the bedding of the coal. This alignment and stacking of molecules is manifest in the optical properties of the coal, and since the alignment is continuous it gives rise to uniform optical properties on a macroscopic scale. Coal examined microscopically under crossed nicols will extinguish simultaneously over the entire field of view. For purposes of this discussion it is important to note that coal does not develop as a mass of interlocking crystals of variable orientation, as is the case with some of the impsonites and anthraxolites. Nevertheless, coal can be described, at least as a first approximation, as having

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a uniaxial negative birefringence.

Since our knowledge of coal development indicates that the application of pressure to aromatic systems under geological conditions is not conducive to the formation of crystalline growth of the type illustrated in the photomicrographs, the most obvious conclusion appears to be that the crystals developed at the time of deposition. Furthermore, the composition of the material during deposition must have been quite aromatic in order that highly anisotropic but randomly oriented crystals could form. The anisotropy would develop as a consequence of the strong attraction between the polynuclear aromatic molecules. Assuming this to be the mechanism by which the crystals formed, it can be further inferred that the deposits formed from materials of a restricted chemical and molecular distribution, since crystallization would otherwise have been strongly retarded. The crystals of several samples show a degree of preferred orientation which probably resulted from pressure subsequent to deposition.

From what is known of the occurrence of the samples under consideration and their association with calcite, an aqueous environment of deposition is implied. Dunn and Fisher (9) postulated an aqueous environment for the deposition of the anthraxolites of the Mohawk valley. They contend that the presence of an aqueous fluid before, during, and after the solidification of the proto-anthraxolite is demonstrated by the overlapping of the deposition of quartz and calcite with the entry and alteration of protoanthraxolite.

The association of the impsonites and anthraxolites with sedimented organic matter of shales and limestones, in all cases where the field relations are known, suggests that the secondary deposits originated from the primary organic sediment. This is also true of the Mohawk Valley deposits. If such an origin is to be entertained, and it is certainly the simplest and most logical, then a satisfactory reason must be given to explain the mobility of the secondary materials. Since the impsonites and anthraxolites appear to have been deposited under more intense metamorphic conditions than some of the less aromatic vein deposits, for example albertite (2), it might be expected that the primary organic sediment acting as the source would have previously become completely leached of any material capable of migrating in aqueous solution. However, it is possible that, during or after such leaching, the primary sediment became altered under metamorphic conditions and became regenerated as a source. The experiments of Berl (10)(11) and others (12) on the hydrothermal alteration of cellulose and related products to materials resembling asphaltites suggest that the above assumption is within the realm of possibility. Dunn and Fisher (9) have suggested that "the conditions during the Lower Paleozoic in the Mohawk Valley may well have been duplicated by Berl's experiments so as to create anthraxolite".

Berl produced coal-like material of bituminous rank by heating cellulose and other carbohydrates in a weakly alkaline solution in an autoclave at temperatures as low as 230°C. The substances altered first to a viscous black material similar to asphalt and then, with further heating, to coal. Schuhmacher, Huntjens and van Krevelen (12) confirmed the work of Berl and placed greater emphasis on the hydrogen ion concentration. Under alkaline and neutral conditions at 340°C, cellulose, wood and peat altered to black asphalt-like products, but under acid conditions altered to a brown powder. Lignin altered to a brown powder under all conditions of pH.

Replacing the accelerated reaction conditions of these investigators with geological time, it seems probable that similar reactions could occur under certain natural conditions at lower temperatures. Primary sedimented organic matter could be altered, at least in part, to more mobile organic fractions. These alteration products would have a true hydrocarbon aspect as a result of the elimination of foreign atoms, but the products would undoubtedly have a wide molecular weight and chemical type distribution and this would inhibit crystallization. The alteration products would, therefore, require modification to a clean aromatic fraction, through fractionation and concentration processes, before crystalline impsonites and anthraxolites could form. Anthraxolites formed in this manner would, of course, be restricted to the high hydrogen end of the group; that is, in the area where the structure just becomes fully aromatic near the classification boundary between impsonite and anthraxolite. Further metamorphism would be required to advance anthraxolite much beyond its lower boundary, and this would probably be a process of pyrolysis.

As mentioned previously, the evidence suggests an aqueous environment for the deposition of anthraxolite and impsonite, but it is difficult to extend the hypothesis and postulate specific migration and deposition mechanisms for the mobile aromatic fraction. One possibility is that the source rocks were very local and the fractions migrated through fractures as an emulsion. It is also possible that the migrating fractions were of low molecular weight, and thus a solution hypothesis would be plausible. Dissociating polar groups would also lend support to a solution hypothesis, but the metamorphic conditions prevailing at the time of deposition make their existence unlikely. In either case it would be necessary to invoke subsequent polymerization to explain the present high molecular weights of the anthraxolites and impsonites.

Where high temperatures are indicated it seems possible that anthraxolites and impsonites, among other secondary products, could originate from the distillation of primary sedimented organic matter. Although such an origin seems unlikely for the samples under consideration, it is, nevertheless, quite a widely held point of view. Mueller (13) has presented an interesting discussion in this respect on the organic matter associated with the hydrothermal deposits of the Derbyshire district of the British Isles. Mueller stresses distillation and the differentiation of distillation products to explain the origin of a wide variety of "organic minerals".

CONCLUSIONS

Anthraxolites and impsonites probably originate in at least three ways: (1) as metamorphic products of less aromatic materials such as albertite and grahamite; (2) as products of aqueous fractionation and concentration processes, whereby they enter the secondary development tracks as highly aromatic materials sometimes close to the composition at which they presently occur; or (3) as distillation products of primary sedimented organic matter. It is difficult to ascertain the nature of the development of any given occurrence, but where organic crystalline material is in evidence the second postulation appears most desirable.

The crystalline structure probably forms at the time of deposition. In order for crystallization to occur, the material being deposited would have to be quite aromatic and of a restricted chemical and molecular distribution. Such material could originate as fractions of primary sedimented organic matter, formed and transported in an aqueous environment. The experimental evidence of Berl (10)(11) and others (12) suggests that temperatures of the order of 200-300°C could produce mobile fractions from primary organic sediment under alkaline conditions.

Anthraxolites and impsonites, as well as thucholite and some of the less aromatic secondary deposits, are quite often associated as minor constituents with mineral deposits but have never attracted widespread interest. This is unfortunate, since a broad knowledge of the organic geochemistry of this class of material could probably elucidate some of the problems pertaining to the genesis of certain classes of mineral deposits. Mueller (13)(14) has indicated a number of avenues for research.

ACKNOWLEDGEMENT

The author is grateful to Drs. D.S. Montgomery and M.F. Millson for constructive criticism of this report.

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DESCRIPTION OF PHOTOMICROGRAPHS

Photo 1 -

Crystalline structure of impsonite (Sample 117) from Ile d'Orleans, Quebec. Taken from a polished section in plain light, under oil immersion, at a magnification of 1700X. The average crystal size is approximately 0.5 micron. Crystals are strongly anisotropic. The white and the light grey materials are impsonite; the black areas are cavities where the impsonite crystals were eroded by polishing.

Photo 2 -

Crystalline structure of anthraxolite (Sample 109) from Matane, Quebec. Taken from a thin section, under oil immersion, with crossed nicols, at a magnification of 1000X. The average crystal size is approximately 2-5 microns. The crystals are strongly anisotropic. Both the black and the white materials represent anthraxolite; the black areas are at the extinction position. The elongated black area at the bottom is a scratch. Crystals resolve equally well in reflected light.

George Mueller (Univ. Coll." London, "The The Theory of Genesis of Oil Through Hydrothermal Alteration of Coal Type Substances Within Certain Lower Carboniferous Strata of the British Isles", Congres Geologroup Huesdenkaf, Completers, Strata of the Striftsh Isles", Congres 1952: No. 12, 270-327 (1976) (Completers) (Congress)

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Photo 1



Photo 2

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