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RECORD

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Procedure for the isolation of kerogen from sedimentary rocks

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FIGURES

1. van Krevelen diagram showing atomic ratios for kerogens isolated from source rocks, Galilee Basin (from Jackson & others, 1981). Maturation pathways for the type I, II, and III kerogens are shown with the arrows indicating the direction of increasing maturation.

2. X-ray diffraction patterns for the 'kerogen' concentrate of a Tindelpina Shale sample during the isolation procedure.

A : after removal of pyrite by $NaBH_4$ treatment (stage 5)

B : after one treatment using heavy mineral flotation procedure

C : after second flotation treatment

D : final kerogen concentrate showing complete removal of heavy minerals

3. Schematic diagram showing stepwise isolation of low ash (inorganic free) kerogen from sedimentary rocks.

ABSTRACT

The characterisation of kerogen, the most abundant form of organic carbon in sedimentary rocks, is essential in any study of petroleum source rocks, yielding information on organic maturation and on the nature of the hydrocarbons (gas or oil) likely to be generated. This requires the isolation of low-ash (inorganic-free) kerogen. This record outlines the chemical procedures used by BMR for the removal of soluble organic matter, carbonate minerals, silicate minerals, pyrite, and other heavy minerals. The flotation method for the removal of heavy minerals has been developed in the BMR petroleum geochemistry laboratory.

INTRODUCTION

The term 'kerogen' has been applied to various forms of sedimentary organic matter. In the field of petroleum geochemistry kerogen is defined as 'the sedimentary organic matter insoluble in the usual organic solvents' (Durand, 1980a), and represents the most abundant form of organic carbon in the geologic environment. Characterisation of kerogen from potential petroleum source rock intervals is of major importance in determining the organic maturity of these rocks, and in the recognition of the dominant type of organic matter, thus enabling a prediction of gas and/or oil generative capacity to be made. The structure, characterisation, and significance of kerogen are dealt with in detail in Durand (1980b), and Tissot & Welte (1978).

Kerogen can be described by microscopic examination, X-ray diffraction, or chemical analysis. This Record describes the isolation of kerogen for subsequent chemical analysis. An application of such chemical analyses is reported by Jackson & others (1981), and is illustrated in Figure 1, a van Krevelen plot of atomic H/C and O/C ratios for kerogens isolated from possible petroleum source rocks recognised within the Galilee Basin (the majority of the data points fall below the Type III or humic kerogen curve; this implies that the source rocks in question will be gas prone).

The aim of the isolation procedure is to produce an unaltered kerogen, free of inorganic minerals. Much of the methodology described here is in common use by other laboratories (Durand & Nicaise, 1980); however, the method suggested for removing heavy minerals (the flotation method) has been developed in the BMR Petroleum Technology geochemistry laboratory.

ISOLATION PROCEDURE

The procedure for isolating kerogen from sedimentary rocks can be broken down into six stages:

1. Sample preparation
2. Removal of extactable organic matter
3. Removal of carbonate minerals
4. Removal of silicate minerals

5. Removal of pyrite
6. Removal of remaining heavy minerals such as zircon, tourmaline, and rutile.

Stage 1: Sample preparation

Great care must be taken to avoid contamination of the sample by extraneous organic matter. Where sample size permits, the external surfaces are removed by cutting it away with a diamond saw. The sample is then hammered into small chip-size pieces, the surfaces of which are cleansed by rinsing in benzene/methanol solution. The chips are then crushed to 200-mesh size in a ring crusher. The ring crusher must be cleansed with solvent and run with clean sand pre-washed in chloroform between samples to prevent cross-contamination. It cannot be emphasised too strongly that all precautions must be taken when handling the sample. The clean dry powder is best stored in sealed glass containers or wrapped in aluminium foil.

Stage 2: Removal of extractable organic matter

The soluble organic matter is removed by extraction from powdered rock sample with 60:40 benzene/methanol solution using a soxhlet extraction system. Forty-eight hours is usually a sufficient time to remove the soluble organic matter; however, if colour persists in the extracting solution after this time, the extraction step should be continued. This step also removes any elemental sulphur in the sample which would otherwise persist through the subsequent acid digestion steps leading to anomalous sulphur values in the final kerogen concentrate.

Stage 3: Removal of carbonate minerals

The removal of carbonate is readily achieved by treating the extracted powder with hydrochloric acid (HCl). The extracted powder is placed in a Pyrex beaker; 0.5N HCl is slowly stirred into the mixture until effervescence (liberation of CO_2) ceases. The beaker is then covered with a watch glass and allowed to stand on a steam bath for 4 to 5 hours at a low temperature setting, about $50^{\circ}C$. Occasional stirring and/or sonication is necessary to ensure complete removal of carbonate. The mixture is then allowed to stand overnight, the supernatant solution decanted, and fresh acid added. The steam bath/stirring/sonication procedure is repeated. After decanting the supernatant solution from this second acid treatment, it is essential to wash the solid residue thoroughly with distilled water to remove cations such as Ca^{++}, which result from the acid digestion of carbonate minerals (if the cations are not removed, they may later react with the fluoride ion introduced in the next stage of the procedure, and form insoluble salts such as CaF_2). The final residue is allowed to air dry before the next stage.

Stage 4: Removal of silicate minerals

The solid residue is transferred to a hydrofluoric acid (HF)-resistant beaker and a 1:4 HCl/HF mixture is added. The suspension is allowed to stand for 8 to 10 hours with occasional stirring. The solid residue is allowed to settle and the supernatant acid solution decanted. Fresh acid mixture is added and the process repeated until the residual rock material is no longer coarse. The residue should not be left in the same HF/HCl solution for extended periods as gelatinous fluorosilicates may start forming. If this does occur, the gel-like suspension is decanted and heated in 15% (W/V) HCl at 70-80°C for 2 to 3 hours; after cooling, the mixture is centrifuged briefly at 1200 rpm, and the supernatant suspension containing the fluorosilicates decanted. The kerogen material would have flocculated or have been centrifuged down and is contained in the solid residue.

The solid residue is then mixed with distilled water; the mixture is centrifuged and the supernatant solution decanted. This washing process is repeated until the supernatant solution is neutral to pH paper. The residue is then ready for the next stage.

Stage 5: Removal of pyrite

The residue from the acid digestion stage is transferred to a 250 ml Pyrex beaker; 150 ml of distilled water is added, and 2g of $NaBH_4$ (sodium borohydride) is slowly stirred into the mixture. The beaker is then covered with a watch glass and placed on a steam bath for 3 to 4 hours (or until the effervescence due to the liberation of hydrogen ceases) with periodic stirring or possibly sonication. After cooling, about 10 mls of 5N HCl are added to destroy any excess $NaBH_4$, the mixture centrifuged, and the supernatant solution decanted. The 75-ml centrifuge tube containing the solid residue is then half to two thirds filled with 5N HCl, the mixture stirred or sonicated and allowed to stand overnight in a fume hood. The mixture is again stirred by sonication and the supernatant solution decanted after centrifuging; at this stage, the odour of H_2S (hydrogen sulphide) and a green colour due to FeS (iron sulphide) in the solution should be evident. The solid residue is washed repeatedly with warm distilled water until the washings are neutral to pH paper. A white cloudy suspension will sometimes be evident after this first $NaBH_4$ treatment. This can be removed by decanting the suspension and diluting it with a large volume of distilled water. The kerogen material is allowed to settle (do not centrifuge) and the overlying suspension is carefully decanted. This step may need to be repeated several times before the white precipitate is totally removed. The $NaBH_4$ treatment is repeated until the odour of H_2S is no longer evident. The final washed residue is allowed to dry.

Stage 6: Removal of heavy minerals

Although the kerogen concentrate is now almost pure, there may be significant amounts of heavy minerals present, such as rutile, tourmaline, and zircon. These will be evident as a greyish-white ring at the bottom of the centrifuge tube at the end of the $NaBH_4$ treatment step.

The heavy minerals may be removed by one of two methods -

1. Sonication method

If the kerogen remained in suspension during the final aqueous washing of the $NaBH_4$ stage, repeated sonication in distilled water followed by brief, low speed centrifuging (or possibly gravity settling) and final decanting of the kerogen suspension is often sufficient to achieve its separation from the heavy minerals. The kerogen can then be recovered from the suspension by the addition of 1 to 2 drops of HCl, leading to its settling out at the bottom of the beaker.

2. Flotation method

The dry kerogen concentrate is dispersed in 100 mls of chloroform in a 250 ml Pyrex beaker; the mixture is stirred by sonication for 5 minutes and allowed to stand for 4 minutes. The suspension is carefully decanted into a second beaker and the solid residue discarded. This process is repeated a further 2 to 3 times, each time extending the settling period by 2 minutes. After the final decanting, the kerogen is recovered from the suspension by centrifuging.

The sonication method is usually not sufficient for a clean separation as the kerogen commonly wraps itself around the mineral grains. The effectiveness of the flotation method is shown by the X-ray diffraction patterns in Figure 2. After the $NaBH_4$ treatment (Stage 5), some residual pyrite, rutile, and anatase are still present in the kerogen concentrate. After three repeats of the flotation treatment, the X-ray pattern only shows the broad graphite peak due to the kerogen.

After the removal of the heavy minerals, the kerogen is dried at 60-70°C for 6 to 8 hours. The dried flakes are gently ground to a homogeneous powder using an agate mortar and pestle. The powder is then further dried in a dessicator under vacuum over silica gel for at least 12 hours.

The final yield of kerogen is low mainly due to losses; but, a low-ash (free of inorganic minerals) kerogen will be generally obtained. This is essential if further chemical characterisation of the kerogen is to be meaningful.

SUMMARY

The chemical procedures for the isolation of low-ash kerogens from sedimentary rocks are shown schematically in Figure 3. The methodology for removing soluble organic matter, carbonate minerals, silicate minerals, and pyrite are commonly used laboratory procedures. The flotation method for removing heavy minerals was developed in the BMR laboratory and is an essential step in producing low-ash kerogens. These procedures have been in use at BMR for several years, and consistently produce a low ash kerogen.

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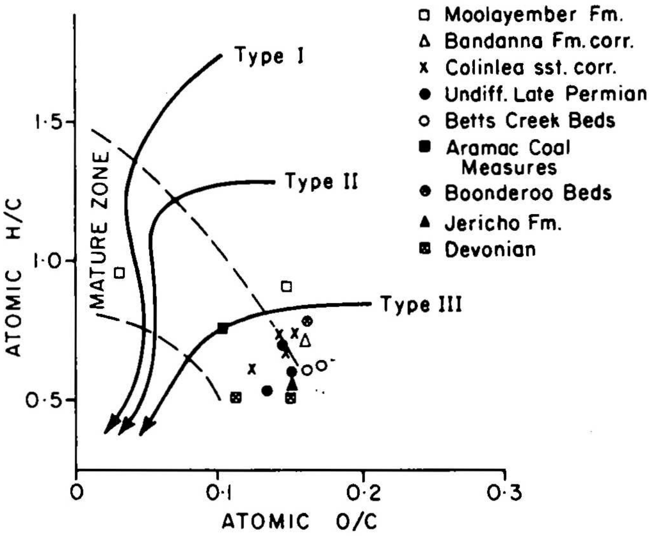

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Fig. 1

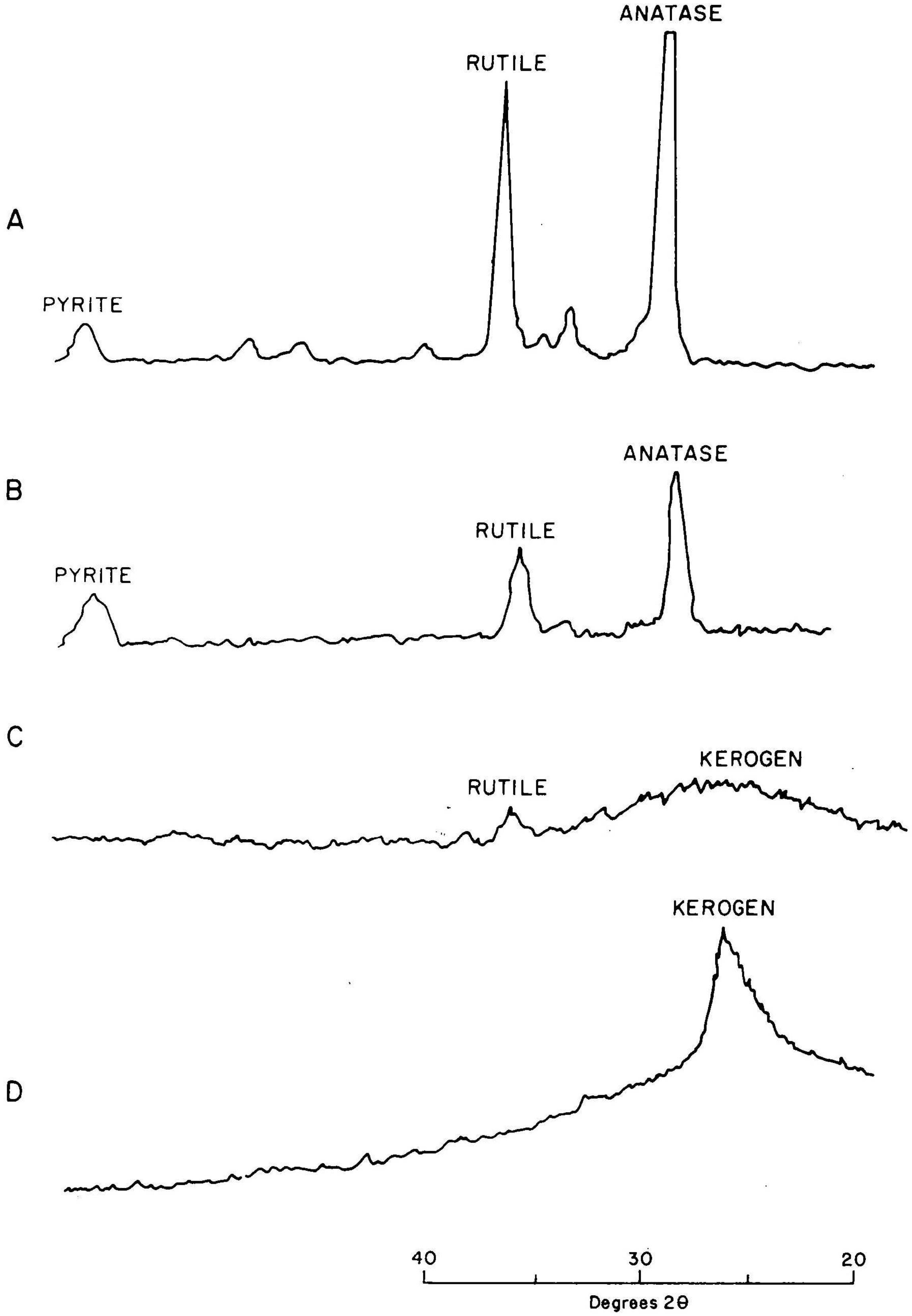
ANATASE
RUTILE
A
PYRITE
ANATASE
B
RUTILE
PYRITE
C
KEROGEN
RUTILE
KEROGEN
D
40
30
20
Degrees 2θ

Fig. 2

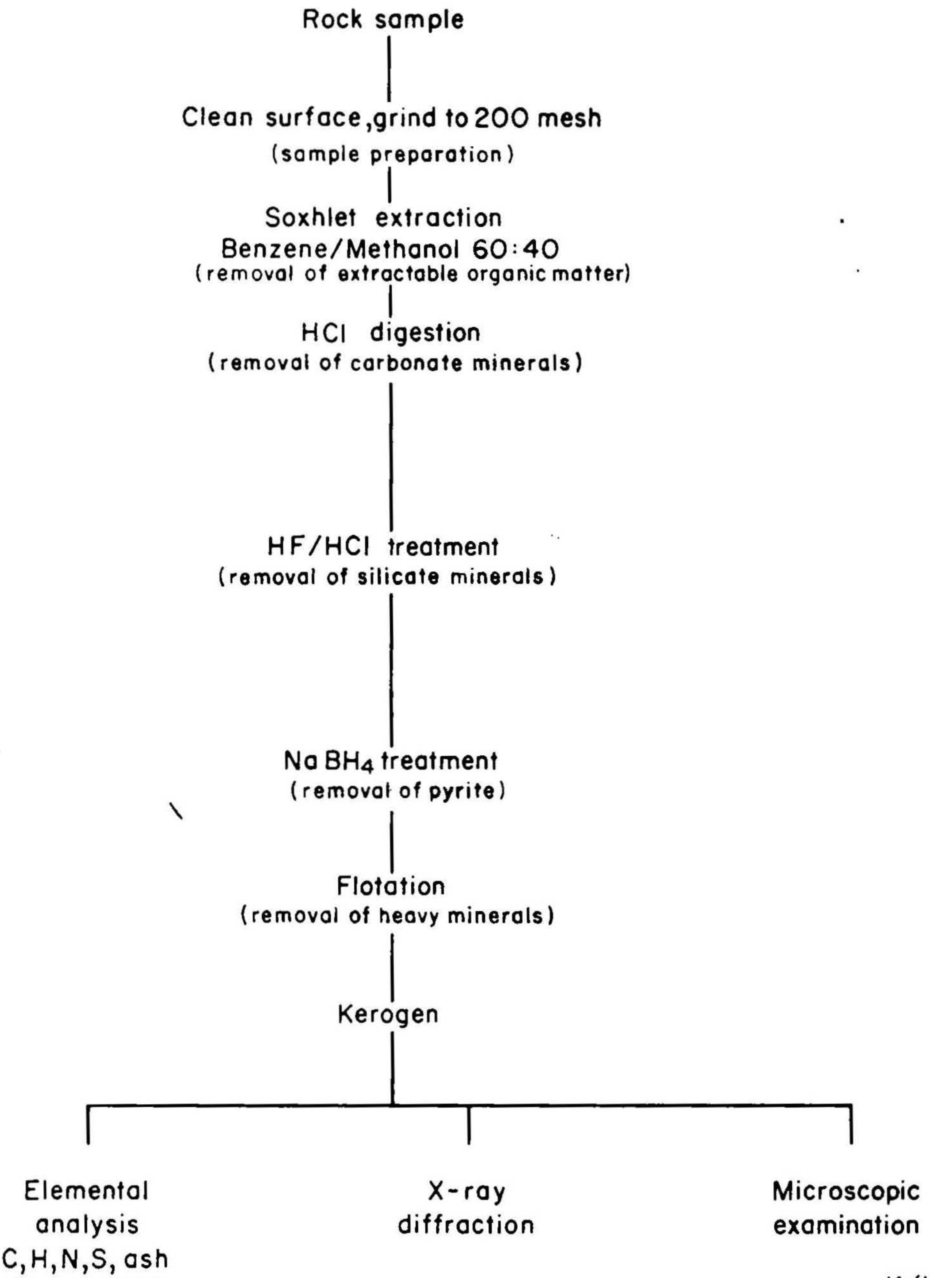

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Fig. 3