VITRINITE PALEOGEOTHERMICS: SOME ASPECTS

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The method of determination of paleogeothermal conditions using vitrinite reflectance data, burial history and recent geothermics is reviewed. Proposals are given to improve this method. Improvements can be made in the measurement technique for vitrinite reflectance. For the calculation of TTI-s, it is suggested that the temperature interval in which the reaction rate of the maturation of organic matter doubles, depends on the temperature. A $\triangle T(T)$ function is proposed, which is based on the Arrenhius equation. For the calculation of theoretical R_0 values from the TTI-s, a TTI vs. R_0 function is proposed. In the future, the application of monomolecular biomarker reaction (isomerization of sterane and hopane) may lead to more exact paleogeothermal determination.

Neste trabalho é revisado o método de determinação das condições paleogeotermais usando dados de refletância da vitrinita, e de geotermia histórica e recente. São indicadas propostas para melhorar esse método. Melhorias podem ser introduzidas na técnica para medições da refletância da vitrinita. Sugere-se que, para o cálculo Tempo/Temperatura (TTI) o intervalo de temperatura no qual dobra a proporção de reação de maturação da matéria orgânica seja dependente da temperatura. A função $\triangle T(T)$ é proposta com base na equação de Arrhenius. Para o cálculo do valor de R_0 a partir dos TTIs, uma função TTI vs. R_0 é proposta. A aplicação de reações monomoleculares de "biomarcadores biológicos" (isomerização de estireno e hopano) poderá fornecer, no futuro, determinações paleogeotermais mais exatas.

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INTRODUCTION

Hydrocarbon reservoirs are, generally speaking, not associated by marked geothermal anomalies. Despite this fact, geothermics has served as a useful tool in petroleum researches. Several reviews on this topic has been published in the literature, one of the recent being Stegena (1984). One of the most important application is in the determination of the thermal history of a stratum or an area, in order to evaluate hydrocarbon perspectives.

At present, the most well known methods to determine paleogeothermal conditions, are that given by Karweil (1956), Lopatin (1971) and Waples (1980). The determination is usually carried out as follows (Stegena et al. 1981, Buntebarth & Stegena 1986):

— Based on known ages of sedimentary layers in a borehole, the sedimentary history for these layers is determined (Fig. 1a). The sedimentary history is to be corrected for the effect of compaction during the geological past (Fig. 1a, solid lines).

— Based on presente borehole temperatures, the geotherms for each 10°C interval are drawn in the time-depth section (Fig. 1b). The constancy of heat flow during the past does not necessarily result in parallel and equidistant geotherms; it is possible to take into consideration the changes with time and depth of thermal conductivity of the layers. — We

construct speculative heat flow histories too, increasing or decreasing heat flows during the geological past (Fig. 1c)

— Then, we calculate Time Temperature Indices (TTI) after Lopatin (1971):

$$TTI = \Sigma \triangle t_n \, 2^n \qquad (1)$$

where $\triangle t_n$ is the time interval (in MY) the layer spent in the n-th 10°C temperature interval. The n-th temperature interval is the number of steps of the 10°C intervals above or below the 100-110°C range for which n is arbitrarily chosen as 0.

— Using Waples' (1980) correlation (Fig. 3), the calculated values of TTI for each layer of the borehole are transformed to corresponding vitrinite reflectance R_0 values.

— The calculated R_0 values are compared with the R_0 values measured in core samples taken from the borehole. Using plausible hypotheses, one makes changes in the heat flow history and repeats the comparison till a good fit between calculated and measured vitrinite reflectance is achieved (Fig. 2).

The above scheme serves only to demonstrate the principles of paleogeothermal calculations. Some theoretical aspects of these principles are not solved
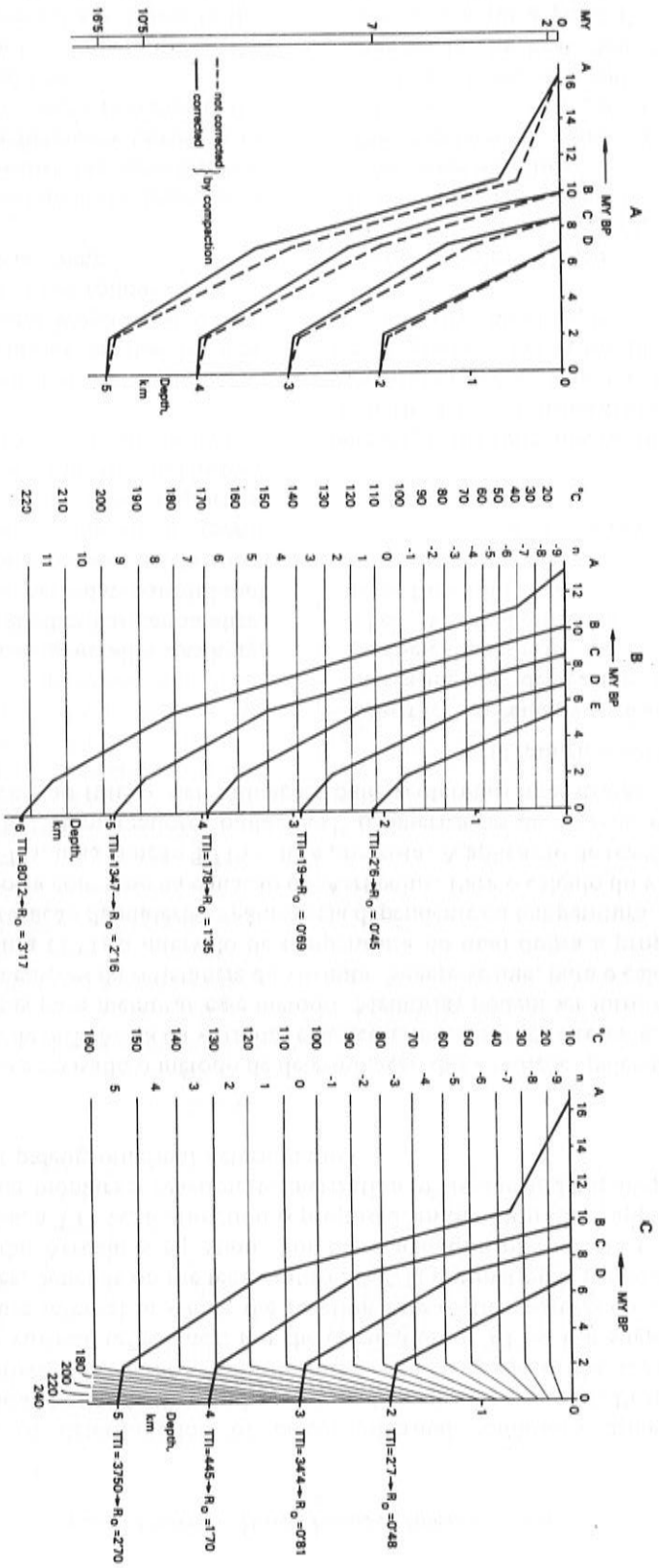
Figure 1 — A: Sedimentary history of a borehole in the Pannonian basin, with and without correction of compaction. B: Calculated TTI values for the same borehole assuming that the heat flow density was constant through the sedimentary history, and C: that the heat flow increased during the last 5 MY to the present value.
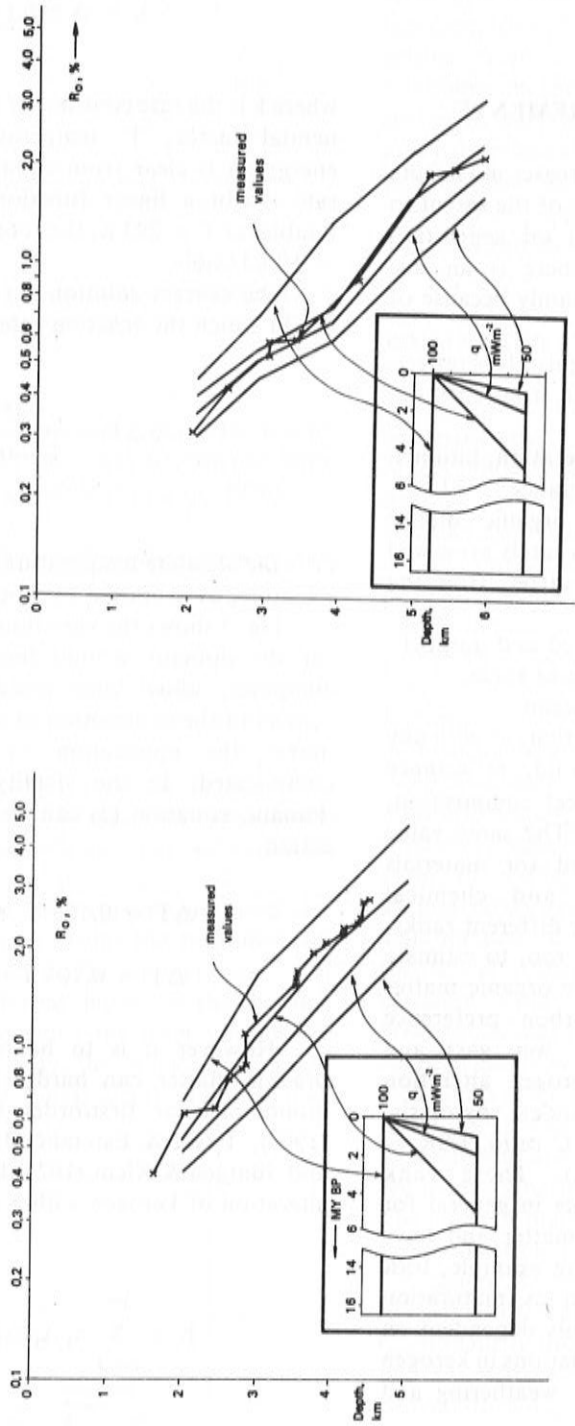
Figure 2 — Measured vitrinite reflectances in two Pannonian boreholes and the vitrinite reflectances calculated from the following heat flow histories: the heating-up of the boreholes began at ∞, 5, 2, 1 MY ago. Both vitrinite profiles suggest the same result: the basin was heated up during the last 5 MY.

satisfactorily at present. The aim of this article is to discuss the sources of error arising in:

— measurement of vitrinite reflectance
— calculation of TTI values
— calculation of the theoretical R_0 value from TTI
— application of specific biomarker reaction instead of R_0 measurements.

VITRINE REFLECTANCE MEASUREMENTS

It became usual to assume that increases in vitrinite reflectance values were valid indicators of the extent to which organic matter maturated and oil generation occured (Waples, 1983). However, there is an uncertainty in some R_0 measurements, mainly because of the followings:

— Sometimes, it is hard to distinguish low reflecting resinite and high reflecting fusunite from vitrinites (Ho, 1978).

— During the beginning of oil generation, bitumen impregnations lower the vitrinite reflectance.

— In all red-coloured rocks organic matter is oxidized; in limestones vitrinite is very rarely preserved and if it occurs, the reflectance value differs from the value of vitrinite in the same rank.

— The distinction between recycled and authochtonous organic matter is often difficult in rocks.

— The R_0 values are quite widespread.

Ronsard & Oberlin (1984) suggest that, as with any other electronic property of any solid, reflectance depends on three parameters: chemical composition, atomic structure and microstructure. The same value for reflectance can thus be obtained for materials different in their microstructure and chemical composition, which can be of same or different ranks.

There are a lot of other methods too, to estimate the maturity by examining the soluble organic matter (percentage carbon in bitumen, carbon preference index, paraffin profile, percentage wet gas) and examining the kerogen (KAI — kerogen alteration index, TAI — thermal alteration index, pyrolysis, elementary CHO analysis, atomic H/C ratio, ESR — electron spin resonance analysis). These rank parameters however are not applicable in general for rocks with finely dispersed organic matter and have their own theoretical difficulties. As an example, ESR detects the tree radicals in kerogen as maturation parameter but ESR signals are not only dependent on temperature but are also subject to variations in kerogen type, diagenetic changes in kerogen, weathering and geologic time.

There remains the vitrinite reflectance method, which is well established in geochemical laboratories of oil companies. For paleogeothermal purposes however, results of ten independent samples are necessary for obtaining reliable values, while repeating the measurement many times on each samples is an additional safeguard for minimizing errors.

CALCULATION OF TTI VALUES

Lopatin's formula is based on the assumption that the maturation process of organic matter is a first order chemical reaction and because of this obeys the Arrhenius'law,

$$k = A \exp(-E/RT) \qquad (2)$$

where k is the rate constant of the reaction, A: pre-exponential factor, T: temperature, and E: activation energy. It is clear from equation (2) that the reaction rate is not a linear function of temperature T and doubles at T = 293 K, the room temperature, only for E = 50 kJ/mole.

The correct solution for the temperature-interval ΔT in which the reaction rate doubles is given by

$$\Delta T = \frac{0.00563 \, T^2}{E - 0.00563 \, T} \qquad (3)$$

(T is the absolute temperature in degrees Kelvin, E = 42 kJ/mole, as proposed by Lopatin, 1976).

Fig. 3 shows the variation of ΔT as a function, of T for the domain around the liquid window. Use of computer, allow easy evaluation of this function, instead of the assumption of constant $\Delta T = 10°C$, and makes the application of this method not too complicated. In the vicinity of the liquid window domain, equation (3) can be approximated by linearization.

$$\Delta T = 0.105 \, T + 10.9 \text{ (in °C)}$$
$$\Delta T = 0.105 \, T - 17.8 \text{ (in K)} \qquad (4)$$

However it is to be noted that maturation of organic matter can hardly be described by a single monomolecular first-order kinetic expression. Tissot (1969), Tissot & Espitalié (1975), Tissot et al. (1975), and Jüntgen & Klein (1975) have modelled the thermal alteration of kerogen with a set of rate equations,

$$K = \sum_{i=1}^{m} n_i A_i \exp(-E_i/RT) \qquad (5)$$

where m is the number of kerogens.

This process although giving a better theoretical approximation, is hardly applicable for paleogeothermal calculations, because of the unknown mass functions n_i, pre-exponential factors A_i and activation energies E_i. Despite the fact that the activation energies
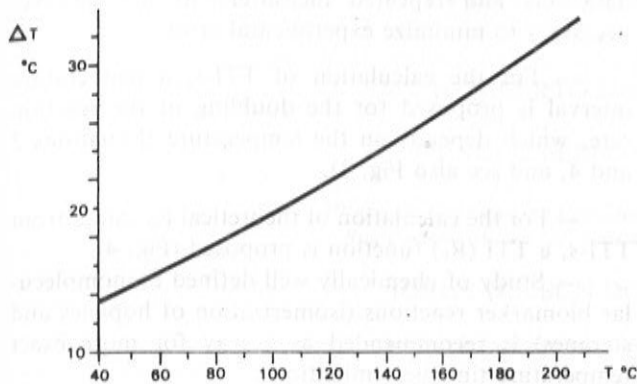
Figure 3 — ΔT, the temperature interval in which the reaction rate of the maturation of organic matter doubles, as a function of temperature T.

for geochemical reactions scatter in a range from 4 to 400 kJ/mole (Lasaga, 1981), one has to satisfied with the empirical "mean" 42 kJ/mole (Lopatin, 1976).

CALCULATION OF THE THEORETICAL R_0 VALUES

Based on 402 samples from 31 worldwide wells, Waples (1980) showed a correlation between calculated TTI values and measured vitrinite reflectance (R^0). Fig. 4 shows Waples (1980) curve, as well as later determinations by Issler 1984, Horváth et al. 1986, using independent data sets. The agreement especially between the two recent determinations, seems to be reasonable.

For the calculation of such curves, one need the thermal history of the layers, from the beginning of sedimentation till the present. The temperature of a layer depends first on its burial depth, on the thermal conductivity of the layers above the layer considered and on the heat flow density. In many cases, it is possible to determine the burial depth and thermal
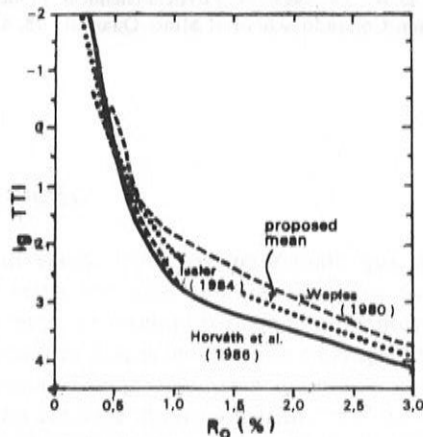

Figure 4 — Time Temperature Index vs. Vitrinite Reflectance

conductivities for every geological time, using the sedimentary history corrected by compaction and taking into calculation the changes of present thermal conductivities through geological times. The variation of heat flow density in the past are however unknown. All there curves of Fig. 4 were calculated on the assumption that the present heat flow density is representative of heat flow in the past. Systematic errors arising from such an assumption are probably a minimum in the curves of Fig. 4, since statistically sufficient data were used and it can be supposed that areas (boreholes) with increasing and decreasing heat flow histories compensate each other. The mean of the 3 curves given, is perhaps the best approximation for the TTI (R_0) function that we can reach at present.

BIOMARKER REACTIONS

Some of the problems in the use of relations suggested by Lopatin (1971), Waples (1980) and others could be avoided if chemical reactions involving only one, chemically well defined molecule are considered which occur during the maturation of the organic material. Mackenzie & McKenzie (1983) have investigated the rates of three reactions which occur before and during the early stages of oil formation. Two of the reactions are isomerization reactions, of C-20 in a sterane and of C-22 in a hopane hydrocarbon; the third reaction converts C-ring monoaromatic to triaromatic steroid hydrocarbons. All three reactions were assumed to be first order, monomolecular; the isomerization reactions are reversible, with a rate of conversion of the R to the S form of 1.174 and 1.564 respectively, while the aromatization reaction was assumed to be irreversible. This method is more reliable as it is based on clear theoretical principles and the Arrhenius equation is certainly valid for these reactions. The problem, however, is that the frequency factor and the activation energy cannot be determined in the laboratory or only very inaccurately, because of the slowness of the reactions. Because of this, McKenzie's (1978) model of stretching and crustal extension for the evolution of sedimentary basins was used to calibrate the reactions. The inverse method should however be desirable: to prove the stretching model by paleogeothermics.

Sajgó & Leffler (1986) studied in detail the isomerization reactions in a C_{29} sterane and in C_{31} and C_{32} hopane hydrocarbons and a third reaction in which two C_{29} C-ring monoaromatic steroid hydrocarbons convert to a C_{28} triaromatic one. Using core samples from boreholes of the Pannonian Basin, where the sedimentary history and geothermal temperatures which are known with a good accuracy, they determined the reaction rate of the isomerization reactions mentioned. The pre-exponential factors and activation energies are 2.4×10^{-3} s^{-1} and 91.6 kJ/mole for isomerization of steranes while the corresponding values for hopanes are 3.5×10^{-2} s^{-1} and 87.8 kJ/mole. These are in agreement

whith the value derived by Mackenzie & McKenzie (1983). The aromatization seems to be a rather complicated reaction, less applicable at present for paleogeothermal investigations. It is hoped, that by measuring the extent of the two reactions mentioned earlier as well as other reactions in a large number of layers, it will be possible to determine the temperature-time history within a better accuracy.

CONCLUSIONS

— Despite it's theoretical difficulties, the vitrine reflectance determination is at present the most suitable method for practical paleogeothermal studies. Large data sets and repeated measurements are however necessary to minimize experimental errors.

— For the calculation of TTI-s, a temperature interval is proposed for the doubling of the reaction rate, which depends on the temperature (Equations 3 and 4, and see also Fig. 3).

— For the calculation of theoretical R_0 values from TTI-s, a TTI (R_0) function is proposed (Fig. 4).

— Study of chemically well defined monomolecular biomarker reactions (isomerization of hopanes and steranes) is recommended as a way for more exact temperature-time determinations.

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