

GEOCHEMICAL CONSTRAINTS ON PALEO HEAT FLOW DETERMINATIONS, A BRIEF REVIEW

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Some methods are in use to estimate paleogeothermal conditions. They approximated roughly the natural diversity in properties and environmental conditions during the geological history. Whereas the geological conditions are discussed elsewhere, geochemical constraints are accentuated here.

The degree of coalification of organic matter is most frequently used in paleogeothermal studies. Several interpretation methods have been developed in which unknown local effects are implicitly involved due to the diversity of the plant remains and the site specific chemical and depositional history of a sediment sample. The homogenization temperature of fluid inclusions is very sensitive to the chemical composition of the inclusions. This property limits its application onto a more regional scale. Stable isotope exchange reactions can be effected by recrystallisation or chemical alteration, so that the result is difficult to interpret in some cases. The diagenesis of some authigenic minerals within the uppermost few kilometers depth has been used successfully. However, the dependence of the transformation temperature on time does not yet allow a general application. The application of the different radioactive systems to reconstruct the cooling history of a rock sample yields, along with the uplift history, paleotemperature gradients, if each system is firmly closed.

Alguns métodos, atualmente em uso para estimativas de condições paleogeotermiais, aproximam grosseiramente a variação natural das propriedades e as condições ambientais durante a história geológica. Enquanto as condições geológicas são discutidas em outros trabalhos, os aspectos geoquímicos são salientados neste trabalho.

Nos estudos paleogeotermiais é utilizado, com mais frequência, o grau de carbonização da matéria orgânica. Vários métodos de interpretação têm sido desenvolvidos, nos quais os efeitos locais desconhecidos estão envolvidos implicitamente, isto devido à diversidade de restos de plantas e à história química e deposicional específica do local da amostra de sedimento. A temperatura de homogenização das inclusões fluidas é muito sensível à composição destas inclusões. Esta propriedade limita a sua aplicação numa escala mais regional. As reações de intercâmbio de isótopos estáveis podem ser afetados pela recristalização ou pela alteração química, de modo que, os resultados são interpretados com dificuldade, em alguns casos. A diagênese de alguns minerais autógenos nos primeiros poucos quilômetros de profundidade, tem sido usada com sucesso. Porém a dependência da temperatura de transformação em relação ao tempo não permite ainda uma aplicação geral. A aplicação de diferentes sistemas radioativos para a reconstrução da história de esfriamento da amostra de rocha fornece, juntamente com a história de soerguimento gradientes de paleotemperaturas, se cada sistema for firmemente fechado.

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INTRODUCTION

The efforts to map the heat flow around the globe enables one to draw a rough picture of the heat flow density of the ocean floor as well as of the continents.

The regularities in the thermal structure of the oceanic crust lead to a simple relation between heat flow and age of the oceanic crust, so that the paleo heat flow of oceanic areas is not very difficult to determine.

The surface heat flow of the continental crust, however, does not reflect a simple time dependence. The

much more complicated tectonic processes in connection with plate motions and collisions as well as orogenesis lead to a high variety in the thermal structure and in the resulting surface heat flow.

In some areas a paleo heat flow could be evaluated (Buntebarth, 1982) by applying an interpretive method to estimate the degree of coalification, and a thermal conductivity derived from the current properties of the rocks. However to evaluate the evolution of, or merely the changes in, the thermal regime within the crust, some methods are in use which are suitable for

estimating temperature gradients in the past (Buntebarth & Stegena, 1986). These methods utilize the degree of coalification of organic matter, fluid inclusions, geochemical reactions, transformation of minerals and finally, radiometric dating, and they can be applied to sedimentary basins but only the last method can be applied to crystalline rocks.

Beside geological assumptions, e.g. the subsidence history, uplift rate, and the maximum burial, each method assumes various simplified conditions which allows it to serve as a thermometer at a specific location. The basic geochemical constraints of the paleogeothermal methods which approximate more or less poorly the natural diversity in environmental condition are accentuated in the following.

Degree of coalification

The application of the degree of coalification of organic matter has received particular attention as a means of estimating the geothermal history of sedimentary basins, because the degree of coalification is mainly influenced by the temperature of the environment and the duration of exposure at this temperature.

Several methods were developed for the paleogeothermal interpretation from data of distinct basins in which local effects are also involved. These local effects, e.g. different plant remains and different geochemical environment cannot be considered with simple mathematical methods.

The composition of the plant communities has changed during the evolution of the flora (Stach et al., 1982). During the Lower and Middle Devonian Psilophytes formed the early coal deposits. Because of prolific plant growth on the continent since Upper Devonian, rich coal deposits were formed by *Lepidodendron* and *Sigillaria* in swamps up to the Upper Carboniferous. Between Permian and Lower Cretaceous the Gymnosperms became more important and since then the rich Angiosperm floras. The younger the organic material the greater is the variety in the flora which leads to more heterogeneity in the plant remains in the younger geological history and more variety in the environmental conditions at which different plant communities are preserved.

The rich deposit of organic material in swamps results in seams, and the plant detritus which is covered by clastic sediments and buried, forms dispersed coaly particles in sedimentary rocks. The latter plant remains are exposed to some mechanical treatment, to the oxidizing atmosphere and to bacterial activity at the surface. The conditions only favour particles which are especially resistant, e.g. barks. Therefore, the original organic substance is not exactly the same as in the seams.

The geochemical milieu during deposition of the particles has also some effect on the properties of the coal. Organic deposits under terrestrial and subaquatic conditions are comparable but marine-influenced and

calcium-rich swamps produce coals richer in ash, sulphur and nitrogen (Stach et al., 1982).

From this follows that even with the same original material, coals with different properties can result. Vitrinite is mainly formed under slight acid conditions, but if the conditions are neutral or weakly alkaline, bituminite and vitrinite of a less matured stage are formed.

These examples demonstrate the influence of the near-surface geochemical conditions on the properties of the coal. It is not surprising that a general method for the paleothermal interpretation of the degree of coalification has not been found and that several methods were developed from data of distinct basins in which local effects are involved.

If two methods are applied to the same data sets, different results may be evaluated (Buntebarth & Middleton, 1986). The results demonstrate that the temperature gradients are in good agreement with data from recently subsiding basins. The method by Middleton appears to give higher values than the method by Buntebarth with exception of the Upper Carboniferous German basins. Other interpretation methods also agree sufficiently within the lower coalification range (Vetö & Dövényi, 1986), i.e. in young sedimentary basins.

An advantage has been gained with a method by MacKenzie & McKenzie (1983) where the reaction of a few common compounds which occur during the maturation of the organic material, were studied. Two of the reactions are isomerization, at C-20 in a sterane and at C-22 in a hopane hydrocarbon. The third reaction converts C-ring monaromatic to triaromatic steroid hydrocarbons. All three reactions satisfy the Arrhenius equation from which, however, the pre-exponential factor, the so-called frequency factor and the activation energy are not known exactly. The activation energy varies within two orders of magnitude during coalification. The frequency factor, however, varies over a range of several tens of magnitude (Lefler & Sajgo, 1986). The resulting dependence of the coalification reactions on both temperature and time makes experimental studies in the laboratory most difficult.

Fluid inclusion

In nearly all minerals, whether ores, rock forming minerals or others, small amounts of fluids are entrapped in defects of the host crystal during growth. The inclusions preserve the physical and chemical conditions of the surrounding medium during the time of the crystal growth. It is generally assumed that no subsequent change in the entrapped material takes place (Lemmelein 1956, Roedder 1967).

The fluid inclusion is a homogeneous phase at the time of entrapment. It consists mainly of water, salt (usually as sodium chloride), some carbon dioxide, and also methane and higher hydrocarbons. Since the thermal expansion of the fluid is greater than that of the

mineral, a vapour bubble is formed within the cavity when the temperature decreases.

If the sample is heated up under a microscope by using a heating stage (e.g. Ohmoto & Rye, 1970; Werre et al., 1979), at a certain temperature the bubble disappears in the inclusion. The heating is then reversed to cooling until the entrapped fluid becomes an inhomogeneous phase again. The temperature at this condition is called the homogenization temperature. This particular temperature is related to the temperature of formation, but the pressure of formation has also to be involved. Generally, an increase in pressure requires a greater temperature to complete homogenization. The pressure correction is dependent on the chemical composition of the inclusions. Since the fluid inclusions contain a substantial concentration of sodium chloride, the pressure correction can be applied, if this concentration is known.

In many cases, fluid inclusion studies give minimal temperatures and only occasionally actual temperatures of inclusion formation. From these considerations of the method, it follows that the fluid inclusion is most sensitive to changes in the geochemical conditions during the growth. An unchanged chemical composition of the inclusions since their formation is not a proper assumption for higher hydrocarbons in general. The hydrocarbons can react under sufficiently high temperature within the inclusion, and the methane and/or CO₂ formed have a bearing on the homogenization temperature.

Such unknown effects may also influence the homogenization temperature in fissure quartz of the external parts of the central Alps. The composition of these inclusions changes continuously from higher hydrocarbons through methane to water-bearing fluids due to the temperature increase during the progressive Alpine metamorphism (Frey et al., 1980). The continuous change of the composition can also overlay the homogenization temperature because of uncertainties due to, for example, systematic errors in the pressure correction.

Using the density of methane-rich fluid inclusions and the homogenization temperature, the minimum pressure of formation can be estimated from the PVT data of the system (Frey et al., 1980). The pressure converted to depth and the homogenization temperature yield a paleotemperature gradient within the Axen nappe and the underlying North-Helvetian Flysch zone, situated north of the crystalline rocks of the Aar massif/Switzerland. Along a 7 km long transection, the paleotemperature gradient is estimated from 8 values, with 37°C/km during the progressive Alpine metamorphism as a mean value with a standard deviation of $s = \pm 9^\circ\text{C}/\text{km}$. Aqueous fluid inclusions which are strongly undersaturated with hydrocarbon or CO₂ generally homogenize to the liquid phase at temperatures much lower than the formation temperature and therefore, they are meaningless for paleotemperature estimations.

Geochemical reactions

Many reactions in crustal rocks, minerals and fluids are used to determine the reaction temperature, but most of them cannot support the main aim in paleo-geothermics, which is the estimation of the paleo heat flow.

The silica and the Na-Ca-K thermometers are often applied. They reflect only the thermal state of the most recent past.

The reactions mentioned here are the isotope exchange reactions which are preserved in a system of two compounds since the reactions took place. The principle of this thermometer is the temperature dependence of the partitioning of two stable isotopes of an element between two minerals. Isotopes of the elements carbon, oxygen, and sulfur are used. The isotope ratio of the two compounds is related to a standardized sample and the relative difference is the so-called δ -value (e.g. Hoefs, 1986). The fractionation factor is on the one hand approximately the difference of the δ -value of the two minerals, and on the other hand it is dependent on temperature (O'Neil, 1979).

The temperature determined in this way can be falsified by recrystallisation of minerals or chemical alteration. Thermal conditions may sometimes be indicated which are difficult to interpret, e.g. when the isotope exchange reactions took place during retrograde metamorphism (Hoefs, 1986). The application of additional paleothermal methods may confirm or assist in understanding results as Hoefs (1986) has demonstrated with homogenization temperatures of fluid inclusions and sulfur isotopic fractionation in ores.

Whereas these methods can be applied to vein mineralization of several hundreds degree or to high metamorphic regions of up to about 800°C, the following method is restricted to temperatures during the diagenesis of sedimentary rocks.

When two cogenetic minerals are in isotopic equilibrium with the ambient water, the $\delta^{18}\text{O}$ value of each mineral is temperature dependent. Calibrated $\delta^{18}\text{O}$ values of illite and quartz in dependence on the $\delta^{18}\text{O}$ value of the ambient water can be used to estimate both the temperature of formation and the $^{18}\text{O}/^{16}\text{O}$ ratio of the ambient water (Savin & Lee, 1984).

For calculating the temperature gradient of the region and subsequently, for the paleo heat flow density, the depth of the investigated reaction or the pressure must also be estimated. One way can be to estimate the pressure from fluid inclusion studies as has been undertaken, e.g., by Frey et al. (1980), if the depth is uncertain from paleogeographical studies.

Transformation of minerals

A method which is especially suitable for sedimentary basins is based on the diagenesis of some authigenic minerals within the uppermost few kilometers of depth. Clay minerals, silica polymorphs, and zeolites alter at low temperatures of up to about

200°C (Aoyagi & Asakawa, 1984). The transformation temperature of each series of authigenic minerals can be used for evaluating the geothermal history. The clay minerals give a transformational sequence of which montmorillonite alters to mixed layer minerals at a depth corresponding to a temperature range of about 80°C to 120°C. If not enough absorbable potassium is available for the transformation to illite, the reaction can be retarded even to higher temperatures (Jones, 1970). Beyond this geochemical influence, the transformation is strongly dependent on time which has been deduced not only from field observation but also from experimental and theoretical studies (Aoyagi & Asakawa, 1984).

In the middle Upper Rhine Graben/FRG, the transition zone between montmorillonite and mixed layer minerals is generally found in the same formation (Oligocene) in a depth corresponding with a recent temperature of about 70°C. The depth ranges between 700 m and 1300 m (Heling & Teichmüller, 1974). Temperature gradients between 86°C/km and 46°C/km result from this observation. If the minimum temperature of 80°C reported by Burst (1969) and Jones (1970) is considered, the paleotemperature gradients must exceed 100°C/km resp. 54°C/km because the Upper Rhine Graben is still subsiding. The higher values do not agree with the estimation of paleotemperature gradients from vitrinite reflectance data (Buntebarth, 1982).

The transformational sequences of zeolites as well as of silica minerals are also applied successfully to evaluate paleotemperature gradients of Neogene basins in Japan (Aoyagi & Asakawa, 1984).

Radiometric dating

Beside oxygen isotope exchange reactions, radiometric dating yields a thermal history of crystalline regions. Since radioactive systems such as K-Ar, Rb-Sr

and U spontaneous fission are closed at a different temperature, a thermal history of a rock sample can be evaluated when the rock passes through several closure temperatures during cooling. The cooling rate determined is combined with the rate of upheaval in order to get the paleothermal gradient during uplift.

The closure temperature in biotite has been estimated as $300 \pm 50^\circ\text{C}$ for the K-Ar and the Rb-Sr system (Purdy & Jäger, 1976). It is somewhat higher, about 350°C in muscovite (Wagner et al., 1979).

The annealing temperature of fission tracks is lower, but strongly dependent on time. Hammerschmidt et al. (1984) extrapolated from experimental results that temperatures of 50 to 150°C are sufficient to anneal fission tracks in apatite within geological ages. For the Odenwald crystalline basement/FRG, an annealing temperature of 100°C is assumed and that of the central Alps is taken as 125°C (Wagner, 1968; Wagner & Reimer, 1972). A somewhat higher annealing temperature of 170°C is assumed in detrital apatite of Cerro Prieto geothermal field, Mexico, of which the heating duration is about 10^3 to 10^4 years (Sanford & Elders, 1981).

Wagner et al. (1979) estimated the cooling history of the Bergell intrusive, Central Alps, and Werner (1986) applies the cooling rates combined with assumptions on heat sources, uplift rates and geothermal gradients to fit the data to realistic models. From this work, it follows that a paleotemperature gradient of about 20 to $25^\circ\text{C}/\text{km}$ is estimated for the Bergell intrusive.

The basic assumption in radiometric dating is that the system investigated is firmly closed. This means that diffusion of daughter nuclides is not considered. Since diffusion is most temperature dependent, it can also overlay the reconstructed cooling history by unknown systematic changes in concentrations of nuclides.

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