DETERMINATION OF ADHESION IN BITUMEN– MINERAL SYSTEMS BY HEAT-OF-IMMERSION CALORIMETRY
II. Correlation of chemical properties with adhesion

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The strength of chemical bonds formed between eight rock-forming minerals and six bitumen samples were examined by heat-of-immersion calorimetry. The materials were characterised by their physical and chemical properties. The amount of energy released by the bitumen–mineral interaction was much larger than expected for an immersion reaction, exceeding usual values by a factor of up to 10^{2}. An oxidation mechanism, catalysed at the mineral surface, is proposed to account for this observation, and trends in the heat-of-immersion data are correlated with chemical properties of the bitumen and mineral samples.

Keywords: adhesion, bitumen-mineral system, heat-of-immersion calorimetry

Introduction

Loss of adhesion between roadstone and bituminous binder has been recognised as a significant cause of premature road failure in many parts of the world [1–3]. Previous calorimetric studies of bitumen–mineral systems [4, 5] have shown that mixing the two materials liberates an unusually large quantity of heat. A number of mechanisms have been proposed to account for this observation, including multi-layer adsorption [6], oxidation [7] and acid–base interaction [5]. In addition, some bitumens have been shown to interact more strongly with some minerals than others [5]. The present work examined the energy of interaction between eight mineral samples (quartz, orthoclase, albite, anorthite, hornblende, augite, olivine and calcite) and six bitumen samples; three of the bitumen samples were produced from Venezuelan crude oil and three from Middle East crude. The bitumen samples were chosen to represent a variety of viscosities, ranging from almost solid (50 penetration grade) to quite soft (200 penetration grade) at room

temperature. Each bitumen sample is identified below by a number, which corresponds to its penetration grade, and a letter which identifies the crude source (*V* for Venezuela and *M* for the Middle East).

Experimental

Elemental analysis of the bitumen samples has been described previously [5]. Inverse gas-liquid chromatography (IGLC) [8] was used to study the rate of bitumen oxidation [9]. The apparent molecular size distribution of the bitumen samples was determined qualitatively by high-performance gel permeation chromatography (HP-GPC) using a method reported previously [5]. Bitumen infrared (IR) spectra were recorded in carbon tetrachloride [9], analysed for trace metal content by inductively coupled plasma spectrometry, and their UV spectra recorded between 220 and 500 nm in HPLC-grade dichloromethane [5]. Thermogravimetric (TG) analyses were performed on a Stanton Redcroft TG-750 thermobalance from ambient temperature to 500°C at a heating rate of 2 deg· min^{-1}. The sample mass was 5 mg and analyses were carried out in air and nitrogen at flow rates of 10 $cm^3 \cdot min^{-1}$. The concentration of acidic and basic species in the bitumen samples was determined by potentiometric titration [9].

Preparation of the mineral samples for the heat-of-immersion work has been described previously [5]. Multipoint BET surface area measurements were made on a Quantasorb sorption analyser using the flow technique of Lowell [10] with krypton as the adsorbate. The mineral samples were analysed by X-ray fluorescence spectrometry (XRF) and the concentration of iron (II) oxide determined by titration [9]. The minerals were also analysed by X-ray diffractometry (XRD) and scanning electron microscopy (SEM) [9].

The energy released by the bitumen–mineral interaction was measured at 100°C using a Setaram C80D heatflow calorimeter [5]. Bitumen was present in excess to guarantee complete wetting of the mineral substrate.

Results

Elemental composition data for the bitumen samples [5] indicated that the Venezuelan bitumens were richer in nitrogen and lower in sulphur than the Middle East samples. Bitumen IGLC oxidation data [9] showed that the Venezuelan bitumen samples oxidised more readily than the Middle East bitumens. It was inferred from the molecular size profiles of the bitumen samples [5] that Venezuelan bitumens consisted of molecules with a smaller average molecular size compared to the Middle East samples. IR data supported this hypothesis [9].

Bitumen UV spectra are shown in Fig. 1. The spectra were broadly similar, with λ_{max} at approximately 235 nm and a peak tail decreasing asymptotically with increasing wavelength. The Venezuelan samples had a small hump on the peak tail at approximately 410 nm; this feature is missing from the UV spectra of the Middle East samples. The trace–metal concentrations of the bitumen samples have been presented previously [5]. The Venezuelan samples contained significantly higher concentrations of nickel and vanadium than the Middle East bitumens. TG results showed that volatile loss commenced above 100°C [9]. In nitrogen, approximately 25% of the sample mass remained at 500°C. In air, all samples exhibited similar behaviour; weight was lost gradually up to approximately 350°C, beyond which a series of rapid weight losses occurred. From 400°C, the rate of weight loss gradually increased until, by 500°C, the sample had been completely oxidised. Again, the Venezuelan bitumens started to lose weight at a lower temperature than the Middle East samples. The TG curves of the bitumen samples are presented in Fig. 2. Results of the potentiometric acid–base titrations have been given previously [9]; the Venezuelan bitumens contained approximately ten times the amount of acidic species, and 50 to 100 times the quantity of basic species present in the Middle East samples.
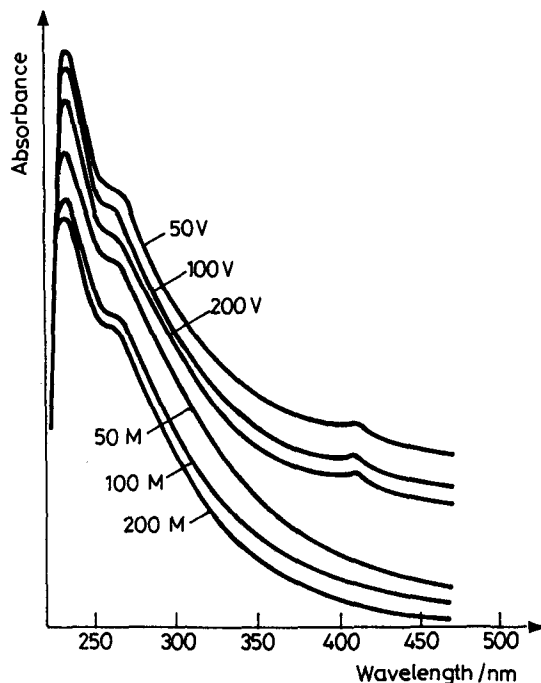

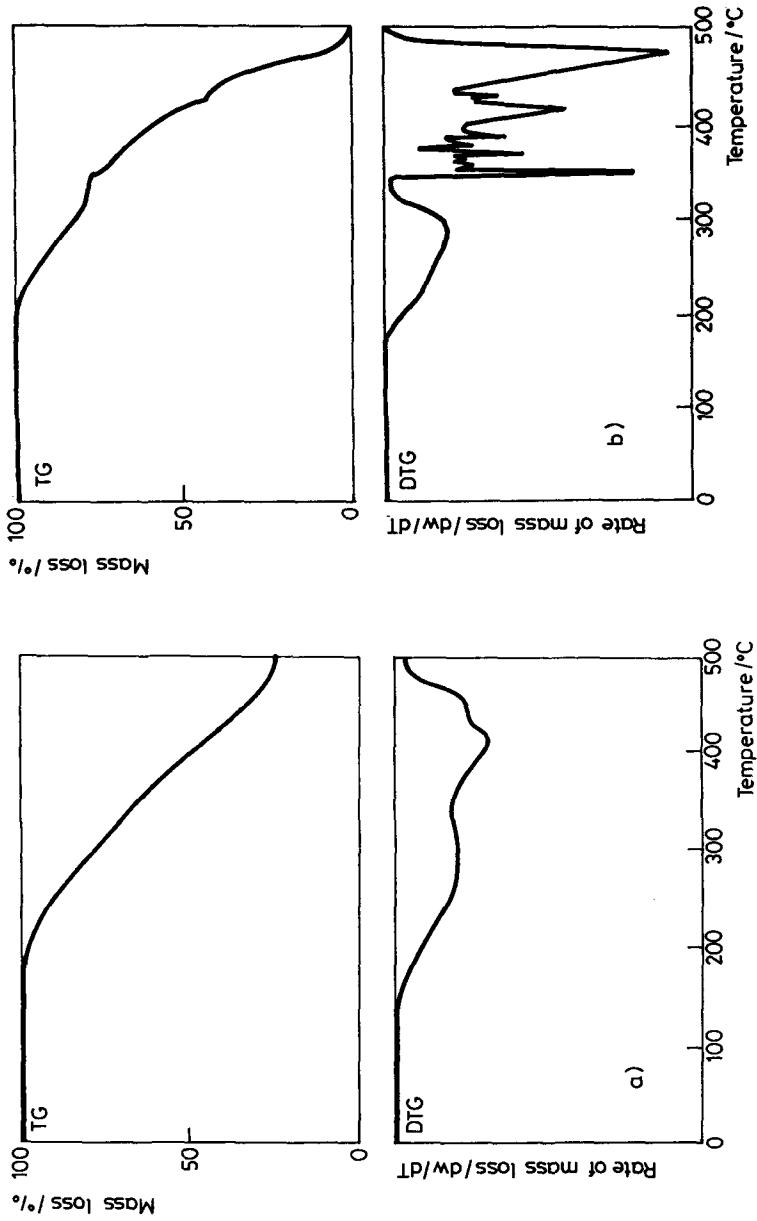Fig. 1 UV spectra of the bitumen samples

Fig. 2 Typical bitumen TG curves (a) in nitrogen and (b) in air

Table 1 BET mineral surface areas

Mineral	Surface area / $m^2 \cdot g^{-1}$
Quartz	0.105
Orthoclase	0.157
Albite	0.192
Anorthite	2.99
Hornblende	0.336
Augite	0.357
Olivinee	0.148
Calcite	0.207

Mineral surface areas are given in Table 1. Most of these are of the same order; the exception is anorthite, which has a BET surface area approximately ten times that of the other minerals. Structural formulae of the minerals, calculated from XRF data, are given elsewhere [9]. XRD data generally matched literature data for the minerals. Exceptions were orthoclase (owing to the presence of albite impurity) and hornblende (because no exact match for the chemical composition of the sample could be found). Examination of the mineral thin-sections with a petrological microscope revealed that most of the samples were monomineralic. Exceptions were orthoclase, which showed the perthitic texture typical of an intergrowth of sodium-feldspar in a potassium-feldspar matrix and anorthite, which consisted of plagioclase phenocrysts embedded in a groundmass rich in iron oxides. SEM showed that most of the mineral particles fell within the expected size range (63–125 µm) and had clean surfaces with low dust coverage. All the samples, with the exception of quartz, were cracked or pitted; the anorthite sample consisted of two types of particle: the first was angular and bounded by smooth cleavage surfaces, the second lacked cleavage surfaces and appeared to be porous, with an average pore diameter of 2.5 µm.
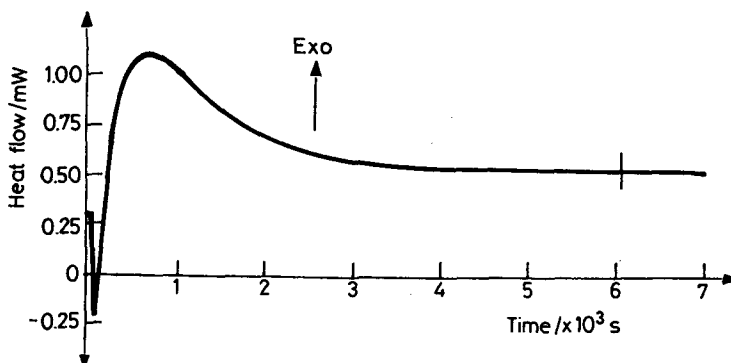

Fig. 3 Typical bitumen–mineral heat-of-immersion curve

Table 2 Bitumen–mineral heat-of-immersion results. Estimated standard deviations are shown in parentheses

Mineral	Enthalpy / $J \cdot g^{-1}$					
	50-V	100-V	200-V	50-M	100-M	200-M
Qz	1.819	2.127	2.092	1.308	1.309	1.755
	(0.069)	(0.153)	(0.118)	(0.123)	(0.113)	(0.085)
Or	1.990	2.252	1.806	1.475	1.364	1.749
	(0.076)	(0.019)	(0.036)	(0.023)	(0.234)	(0.016)
Ab	2.323	2.583	1.819	1.736	1.285	1.823
	(0.007)	(0.053)	(0.146)	(0.199)	(0.288)	(0.037)
An	2.655	2.854	2.185	2.142	1.595	1.925
	(0.070)	(0.136)	(0.076)	(0.082)	(0.136)	(0.161)
Hb	2.993	2.743	2.047	1.676	1.222	1.617
	(0.056)	(0.076)	(0.009)	(0.103)	(0.008)	(0.037)
Ag	2.820	2.419	1.960	1.770	1.112	1.535
	(0.080)	(0.150)	(0.071)	(0.061)	(0.005)	(0.008)
Ol	2.129	2.483	1.800	1.746	1.662	1.530
	(0.013)	(0.117)	(0.134)	(0.202)	(0.205)	(0.047)
Cc	2.404	2.016	1.695	1.837	1.340	1.813
	(0.252)	(0.062)	(0.071)	(0.049)	(0.112)	(0.004)

Key: Qz = quartz; Or = ortho-clase; Ab = albite; An = anorthite; Hb = hornblende; Ag = augite; Ol = olivine; Cc = calcite

A typical heatflow curve produced by the immersion of a mineral sample in bitumen is presented in Fig. 3. The initial endotherm was a consistent feature of the tests for which it was impossible to obtain a true correction. The resulting data were therefore proportional to, rather than equal to, the true heat-of-immersion value. The final baseline following the exothermic peak was chosen as the datum point for integration since there was a considerable offset between the initial and final baselines. The results of the bitumen-mineral heat-of-immersion experiments are presented in Table 2. Low signal-to-noise ratio, caused by the relatively small amount of energy released by the bitumen–mineral interaction, is considered to be responsible for the size of the standard deviations; the mean relative

standard deviation was 5%. Low heatflow values were expected, owing to the small surface areas of the mineral samples. Gregg [11] stated that heat-of-immersion data were best collected using samples with surface areas of several square metres per gram. This approach was impractical in the present work because of the tendency of finely-ground minerals to flocculate, causing incomplete wetting of the mineral surface by the viscous bitumen. The Venezuelan bitumens interacted more strongly with the mineral samples than the Middle East bitumens. Within each crude source group, the performance of the different grades of bitumen varied slightly: the trend for the Venezuelan bitumens was 100-V $\geq$ 50-V > 200-V, and for the Middle East bitumens 50-M $\geq$ 200-M> 100-M. The differences in enthalpy between penetration grades from the same region were less consistent than the difference between the two crude sources. The heat-of-immersion data have been presented without the customary correction for the surface areas of the mineral substrates. This approach was necessary since SEM analysis revealed cracks and pores as small as 0.2 µm in most of the mineral samples. It is extremely unlikely that the bitumen molecules would be able to wet these internal surfaces, owing to the high viscosity of the liquid, and the geometrical surface of the minerals is probably a more realistic measure of the area available to the bitumen. To enable a comparison to be made between these heat-of-immersion data and values obtained by other workers, the BET surface area of quartz $(0.105 \text{ m}^2 \cdot \text{g}^{-1})$ may be taken as an approximation of the geometrical surface area of the mineral samples, since no evidence for an internal surface was seen during SEM of this mineral. The heat-of-immersion values then fall within the range $10.59 \text{ J} \cdot \text{m}^2$ to $28.50 \text{ J} \cdot \text{m}^2$, 10^2 times higher than values reported by Gregg for the immersion of inorganic solids in organic liquids $(0.1 \text{ J} \cdot \text{m}^2$ to $0.2 \text{ J} \cdot \text{m}^2)$ [11].

Discussion

It was concluded from the presence of a Soret absorption band in the UV spectra of the Venezuelan bitumens, and the higher levels of nickel and vanadium in the Venezuelan samples, that these bitumens contained higher concentrations of porphyrin molecules than those from the Middle East. Porphyrin-metal complexes are exceptionally stable owing to π-electron delocalisation [12]. The presence of porphyrin–metal complexes and other trace–metal species in the bitumens may influence their oxidation behaviour; the Venezuelan bitumens oxidised at faster rates and at lower temperatures than the Middle East samples, and contained correspondingly higher concentrations of nickel and vanadium. The ability of transition metals to catalyse oxidation is well established [13, 14], and their relative abundance in the Venezuelan samples could account for the difference in oxidation rates between the two bitumen types.

Nickel(II) forms a square planar complex with the porphyrin ring, whilst the vanadium species in porphyrin complexes is thought to be the vanadyl ion, $(VO)^{2+}$, which forms an octahedral complex, with the oxygen atom occupying one of the octahedral sites out of the plane of the porphyrin ring. The other site is occupied by a nucleophile, such as an electron-rich region in a polar bitumen molecule [12]. V=O groups are known to be excellent oxidation catalysts whilst nickel is known to catalyse hydrogenation [15]. It is therefore probable that the vanadyl ion plays a more important part in the catalysis of bitumen oxidation than the nickel–porphyrin complex. Oxidation may be an important mechanism in bitumen–mineral bonding, since a number of workers have identified oxygen-containing species at the bitumen–mineral interface [16–19]. GPC, IR and TG data showed that the Venezuelan bitumens contained a larger proportion of smaller molecules than the Middle East bitumens. This difference might influence the ease with which the groups responsible for bond formation migrate to, and interact with, the interface; smaller molecules would experience less resistance to movement and could therefore migrate to the interface more readily than molecules with a larger hydrodynamic volume. In addition, the polar groups assumed to be responsible for bond formation might interact more closely with the mineral surface in the absence of bulky substituents such as long alkyl chains; IR data indicated that the alkyl chains in the Venezuelan bitumens were shorter than those of the Middle East samples.
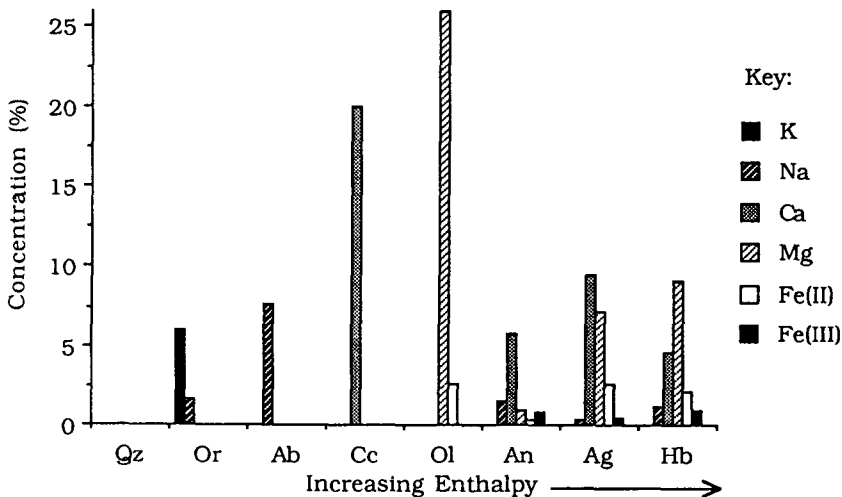

Fig. 4 Atomic proportions of the mineral cations *vs.* heat-of-immersion trend

It was previously thought that there might be a relationship between bitumen basicity and the strength of the bitumen–mineral interaction [5]. Data from the

present work casts doubt upon this hypothesis, since there is no such correlation. However, a strong relationship existed between the types of cation present in the mineral lattice and the strength of the bitumen–mineral interaction. Higher heat-of-immersion values were recorded as the electronegativities of the ionic species present increased. This trend is illustrated in Fig. 4, which shows the atomic proportions of cations present in each mineral sample. The minerals in the graph are presented in order of increasing enthalpy, and the cations in order of increasing electronegativity from left to right. The concentrations of the mineral cations influenced the strength of the bitumen–mineral interaction less than their electronegativities; quite small concentrations of iron(III) were sufficient to make
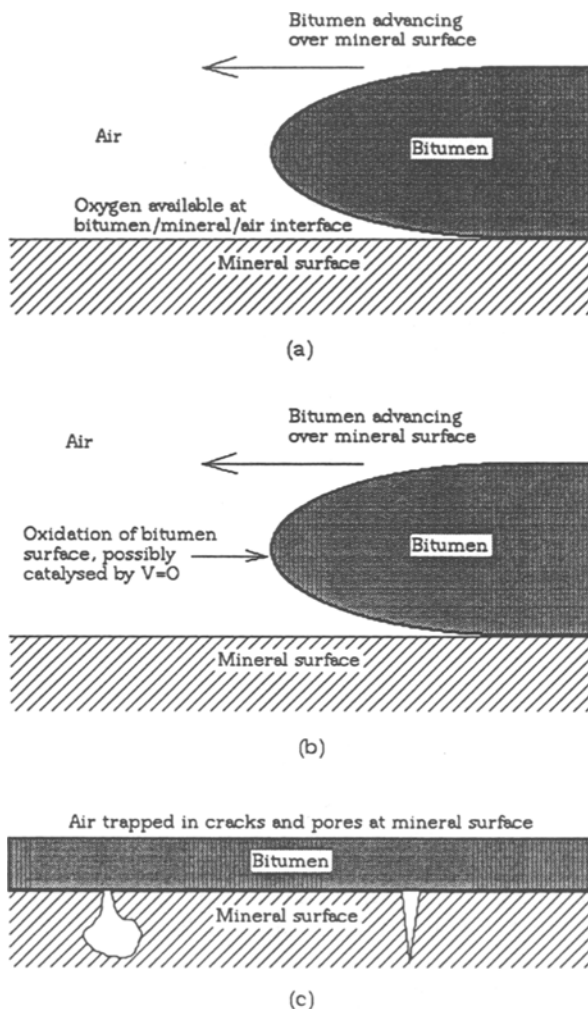

Fig. 5 Mechanisms of oxygen availability at the bitumen–mineral interface

a significant difference to the bitumen–mineral heat-of-immersion values. The presence of iron at the mineral surface may also influence bitumen–mineral bond formation by catalysing bitumen oxidation; this is particularly likely where iron oxide species are present [15]. Oxidation catalysed at the mineral surface would produce, *in situ*, some of the types of molecules thought by other workers to be responsible for bitumen–mineral bonding [15–19]. There are a number of ways in which oxygen might be available at the bitumen!-mineral interface to facilitate oxidation. These are illustrated in Fig. 5. In mechanism (a), oxidation is catalysed directly at the bitumen–mineral–air interface by the cations present in the mineral, and also possibly by catalytic metal species in the bitumen. In mechanism (b), oxidation takes place at the bitumen surface, before contact with the mineral; the catalyst is probably the vanadyl group, $(VO)^{2+}$, either complexed with a porphyrin or in some other environment. Mechanism (c) proposes that air might be available at the bitumen–mineral interface through the presence of cracks and pores small enough to exclude the bitumen, such as were observed during SEM of the mineral samples. It is interesting to note that the anorthite, augite and hornblende samples, minerals which showed the strongest interaction with bitumen, contained a significant proportion of porous particles, whilst quartz and orthoclase, which interacted relatively weakly with the bitumen samples, lacked internal surface area.

It is unlikely that a system as complex as bitumen–mineral adhesion can be fully described by a single bonding mechanism. It is possible that a number of other mechanisms also play a part in bond formation, although it is suggested that the proposed catalytic oxidation mechanism best fits the experimental data. The proposed bitumen–mineral bonding mechanism provides a chemical basis for the contention of a number of workers [2, 20–22] that 'basic' minerals (i.e. minerals containing transition metals and other electronegative cations) adhere more strongly to bitumen than 'acidic' minerals (e.g. quartz).

Conclusions

Catalytic oxidation is the mechanism believed to be most significant in bitumen–mineral bond formation. This mechanism is favoured by the presence of transition metal cations or cations of relatively high electronegativity in the mineral substrate. These cations are present in minerals found in 'basic' aggregates, such as basalt and dolerite, and are believed to be able to catalyse bitumen oxidation. The ease with which the bitumen may be oxidised has a direct bearing on the strength of the bitumen–mineral interaction; good adhesion is favoured by the use of readily oxidised bitumen. The presence of trace metals in bitumen could promote oxidation.

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Zusammenfassung — Mittels Tauchwärmekalorimetrie wurde die Stärke chemischer Bindungen zwischen acht verschiedenen gesteinsbildenden Mineralen und sechs Bitumenproben untersucht. Die Substanzen wurden anhand ihrer physikalischen und chemischen Eigenschaften beschrieben. Die durch die Wechselwirkung Bitumen/Mineral freigesetzte Energiemenge war wesentlich größer als für eine Eintauchreaktion erwartet wurde und übertraf normale Werte um einen Faktor bis 100. Es wird ein an der Mineraloberfläche katalysierter Oxidationsmechanismus vorgeschlagen, um diese Beobachtung zu erklären, weiterhin werden Tendenzen der Eintauchwärme mit den chemischen Eigenschaften von Bitumen- und Mineralproben korreliert.