The role of Na-montmorillonite in the evolution of copper, nickel, and vanadyl geoporphyrins during diagenesis[☆]

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Abstract

Sorption of a series of toluene-solvated porphyrins with differing structural characteristics and metallic centers [i.e. free-base, Cu(II), Ni(II) and VO(II)] onto Na-montmorillonite was measured to determine how this clay mineral might influence porphyrin pathways during diagenesis. In most instances, adsorption was adequately described by the Langmuir isotherm equation. The adsorption results were compared in two ways: (1) *by the metallating ion,* where predicted trends of the relative degree of adsorption are based on Buchler stability indices, and (2) *by the structural type,* where predicted trends of the relative degree of adsorption are based on the number and type of substituent groups and their corresponding steric and functional characteristics. The implications of macrocycle shape (planar, ruffle, and wave) are also discussed. In general, sorption affinity based on metallating ion followed the order: VO(II)≈Ni(II) < Cu(II) < < Free-base. In terms of functional groups, sorption affinity generally followed the order: phenyl (meso) < ethyl < methyl < ester. Ruffled shapes generally sorb less than planar shapes. These sorption trends are used to explain how clay minerals might influence the selective sorption and decomposition of porphyrins in oil shales; how clay minerals may contribute to or be responsible for the decreasing Ni(II)/VO(II) ratios observed in the fossil record; and why clay minerals probably do not play a major role in the decreasing deoxophylloerythroetioporphyrin/etioporphyrin I (DPEP/ETIO) ratio observed in the maturing sedimentary environment. Published by Elsevier Science Ltd.

1. Introduction

Biomarkers are organic compounds in petroleum, or related source rocks, which are related to known precursors through a series of progressive chemical reactions that are dependent on time, temperature, and catalytic interactions with minerals in the subsurface. The chemical form of a biomarker can give information about the maturity of a given shale or other sedimentary rock, which in turn provides information about the oil producing ability of the shale (Sundararaman and Raedeke, 1993). Biomarkers are also used in petroleum exploration for oil–oil and oil–source rock correlations to estimate the maturity of oils and determine the relationship between different oil deposits and the source rocks that produced them (Sundararaman and Hwang, 1993).

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Metalloporphyrins are important biomarkers because their structural parameters are used as a measure of thermal maturity by the petroleum industry (Sundararaman and Moldowan, 1993). By measuring thermal maturity, information is obtained that reveals whether source rocks are too immature to produce petroleum, mature enough to produce petroleum, or if they are over mature and barren. Porphyrins chelate most of the metals in the periodic table (Quirke, 1987), but the major focus of recent research has been that of the Ni(II) and VO(II) (vanadyl) porphyrins because they are the predominant porphyrins found in crude oils, sediments and shales. Geologic porphyrins escape destruction and provide a valuable fossil record because of their exceptional stability, which is enhanced through the chelation of metal ions (Baker and Louda, 1981). Ni(II)/VO(II) porphyrin ratios are important indicators of the depositional environment because they provide insights into thermal maturity (Baker and Louda, 1981, 1986; Filby and Van Berkel, 1987), kinetics (Sundararaman and Boreham, 1993) and redox conditions (Sundararaman et al., 1993; Huseby et al., 1996).

In 1936, Alfred Treibs (1936) presented an overview of his earlier research on how the geochemical process might occur when chlorophyll-a is converted to vanadyl deoxophyllo-erythroetioporphyrin [VO(II)-DPEP]. Treibs was the first to predict the structure of DPEP in petroleum. Because DPEP contains the same isocyclic ring as in chlorophyll-a, he postulated that DPEP was the product of chlorophyll diagenesis. Even though porphyrins were the first compounds of biological origin identified in petroleum, their geochemical evolution is still not completely understood (Filby and Van Berkel, 1987; Callot et al., 1990; Keely et al., 1990; Lash, 1993). Callot and Ocampo (2000) in their excellent overview of porphyrin geochemistry in *The Porphyrin Handbook*, remarked that many of the unanswered research questions noted in the 1987 review by Filby and Van Berkel are still open for investigation. One of these questions—the role of the mineral matrix in porphyrin geochemistry—is the focus of this research.

Clays are the major reactive minerals in the sedimentary environment. They have high surface areas and catalytic as well as adsorptive properties, which need to be investigated more fully in order to understand how they affect porphyrins during clay diagenesis. The adsorptive properties of clay minerals for organic compounds are well known and have been discussed in several review articles (Greenland, 1965; Weiss, 1969; Mortland, 1970; Brindley, 1970; Bailey and White, 1970; Cloos, 1972; Calvet and Chassin, 1973; Theng, 1974, 1979, 1982; Van Olphen, 1977; MacEwan and Wilson, 1980; Raussell-Colom and Serratosa, 1987; Johnson, 1996). All porphyrins are subject to sorption through the ring nitrogens, and others like mesoporphyrin IX dimethyl ester (DMEP) through their substituent groups. The relationship of functional groups to sorp-

tion is evident in the amount and polarity of bitumen adsorbed by clays during pyrolysis experiments (Tannenbaum et al., 1986). Bitumens of polar high molecular weight compounds were adsorbed strongly and they reported that as the polarity of the bitumen decreases, correspondingly smaller amounts are adsorbed.

Studies of the degree of adsorption of organic compounds on clays show a relationship between the degree of adsorption and basicity and polarity. The more basic and polar a compound is the stronger the complex is that is formed with the clay. Acidic clay minerals were found to interact with nitrogen-containing organics by acid-base and charge-transfer reactions (Siskin et al., 1987). Such acid-base interactions were found to be primarily responsible for binding organic compounds to the surface of clays in sediments (Siskin et al., 1987). Because of their ring nitrogens, porphyrins would be expected to exhibit trends in adsorption dependent upon polarity and basicity.

The objectives of our study were to demonstrate how the surface adsorptivity of a clay mineral (montmorillonite) for free-base, Cu(II), Ni(II) and VO(II) porphyrins with differing structural characteristics might influence porphyrin pathways during clay diagenesis.

2. Experimental

2.1. Materials

Sodium perchlorate was purchased from Aldrich, solutions of which were filtered using 0.45 μm pore size membrane filters (Millipore). Toluene (anhydrous, 99.8%) was purchased from Aldrich and used as received. Toluene was chosen as a solvent for its porphyrin solubility, ease of use in spectroscopy, minimal reactivity with clay surfaces, and to provide an organic medium to model a hydrocarbon–clay environment to elucidate how porphyrins might interact with clay surfaces during the petroleum generation process. Porphyrins were obtained from Porphyrin Products (Logan, UT) and used as received. The porphyrins used in this research were the free-base, Cu(II), VO(II), and Ni(II) forms of etioporphyrin I (ETIO), octaethylporphine (OEP), mesoporphyrin IX dimethyl ester (DMEP), and meso-tetraphenylporphine (TPP) (Fig. 1). Ni(II), VO(II) and Cu(II) were selected as the metallating ions because they are representative of metalloporphyrins observed in petroleum and in the diagenetic stages of petroleum source rocks and thus also provide insight into how variations in the metallating ion would affect adsorption. ETIO was selected for study as the Ni(II) and VO(II) complexes are abundant in petroleum and related source rocks. TPP, OEP, and DMEP were selected to determine how variations in substituent groups (alkyl, phenyl, and ester) influence the degree of adsorption relative to ETIO (phenyl is a meso sub-

stituent and the others are ring substituents). Mesoporphyrin IX was reported as bound by ester bonds to Messel oil shale kerogen (Huseby and Ocampo, 1997) so DMEP makes a good comparison. Na-montmorillonite clay (SWy-2) was purchased from the Source Clays Repository at the University of Missouri and was cleaned as described in the following section.

2.2. Na-montmorillonite preparation

The following procedure was used to obtain a <2 μm equivalent spherical diameter (e.s.d.) fraction of Na-montmorillonite. Thirty grams of the untreated clay was suspended in 125 ml of 0.5 M NaClO$_4$ and shaken for 1 h on low speed. The >53 μm diameter fraction was separated by sieving and discarded. The <2μm e.s.d. fraction was then separated by ultracentrifugation (Sorvall RC26-Plus Centrifuge and HS4 rotor) by placing the slurry into 250 ml bottles at a depth of 10 cm (shoulder line) and centrifuging for 4 min at 1000 rpm. The coarse solids were discarded. The supernatant slurries (<2 μm e.s.d. fraction) were combined and the pH adjusted to 9.5±0.1 with NaOH. The <2 μm e.s.d. fraction was washed approximately five times with 1 M NaClO$_4$/0.001 M HClO$_4$ until the pH of the supernatant was <3.0. The solids were when washed with

water approximately five times until the pH of the supernatant was >5.8. The solids were then resuspended in water, ultrasonicated (Cole-Parmer, 4710 Series Ultrasonic Homogenizer) and placed into dialysis tubing (Spectra/Por #7). Water surrounding the dialysis tubing was replaced daily until the conductivity was <1.0 μmho. The clay slurry was then freeze-dried (Labconco, model #77545–10) and ground with a mortar and pestle.

X-ray powder diffraction patterns (XRD) were recorded from 5 to 75 2θ° (Cu K_α radiation) using a Philips X'Pert MPD X-ray powder diffractometer (model # PW3040/00) operating at 40 kV and 50 mA at a scan rate of 0.02 2θ°/s. The extent of hydration of the prepared Na-montmorillonite (<2 μm e.s.d. fraction) used was determined by comparing the *d*-spacings for a sample dried at 75 °C for 16 h versus one that was equilibrated with the lab atmosphere (~20–25% relative humidity) for several months. The dried sample had a *d*-spacing of 9.9 Å at 9.0 2θ°, which indicates a dehydrated collapsed structure. The equilibrated sample had a *d*-spacing of 10.6 Å at 8.5 2θ°. A monolayer of water would yield a *d*-spacing of 12.4 Å (Suquet et al., 1975) thus indicating that the montmorillonite used had a water content of less than 1 monolayer. This result correlates well with a 30% surface coverage calculated on
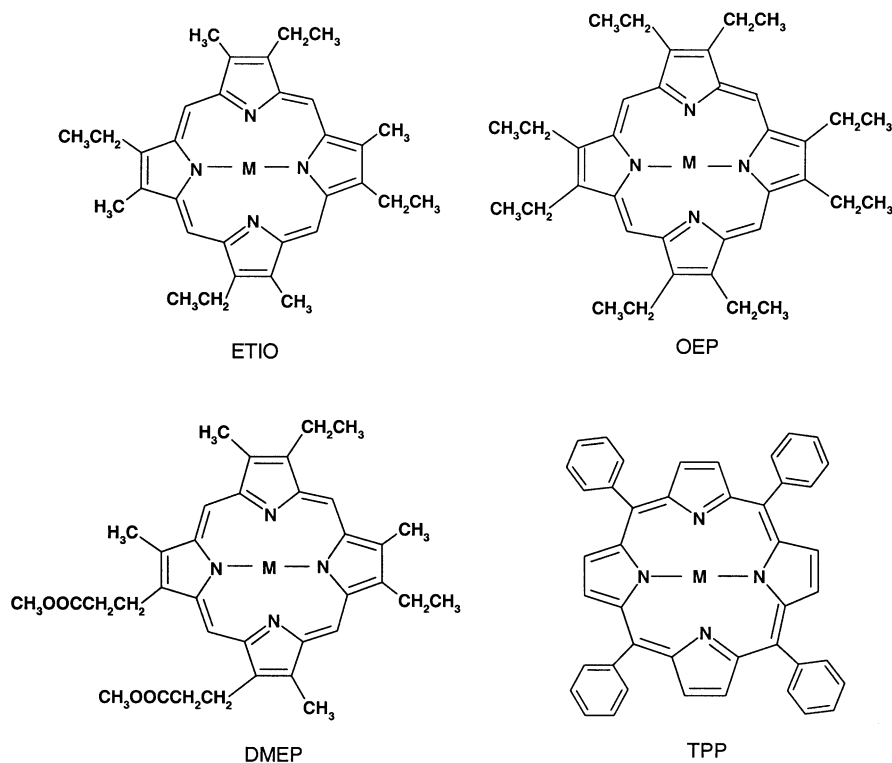

Fig. 1. Structures of the porphyrins used: etioporphyrin I (ETIO), octaethylporphine (OEP), mesoporphyrin IX dimethyl ester (DMEP), and meso-tetraphenylporphine (TPP).

the basis of a 5% water content determined by mass difference between the two samples and a reported EGME surface area of 596 m^2/g (Chorover and Amistadi, 2001).

2.3. Porphyrin analysis

Conventional UV–vis absorption spectroscopy (Shimadazu, model UV-2501PC) was used to analyze porphyrin concentrations. Absorbance spectra (wavelength maximum and molar extinction coefficient) are dependent on the specific porphyrin and the solvent. Intense Soret bands were observed near 400 nm and the weaker Q bands in the 500–600 nm region. The freebase forms of OEP, ETIO, DMEP and TPP have four weak Q bands. The metallated forms of OEP, ETIO, and DMEP only have two weak Q bands while the metallated forms of TPP have only one weak Q band (Smith, 1975; Carrado and Winans, 1990). The wavelength maximum for the Soret band and extinction coefficient for each porphyrin was determined from solutions with known concentrations (Table 1). These parameters where then used to calculate porphyrin concentrations using the Beer–Lambert Law. While here we report extinction coefficients for the Soret band, calculated coefficients for the Q(α) bands (data not shown) are in agreement for those porphyrins reported by Freeman et al. (1990). Porphyrin/toluene/montmorillonite solutions were filtered using 0.22 μm pore size syringe filters before analysis and diluted with toluene as necessary.

Table 1
Millimolar extinction coefficients for metalloporphyrins in toluene

Porphyrin	Molecular weight	Soret band wavelength (nm)	Extinction coefficient (mM^{-1} cm^{-1})
H$_2$ETIO	478.68	400	164
H$_2$DMEP	594.75	400	164
H$_2$OEP	534.78	401	160
H$_2$TPP	614.74	418	444
Ni(II)-ETIO	535.38	392	203
Ni(II)-DMEP	653.45	393	205
Ni(II)-OEP	591.49	393	210
Ni(II)-TPP	673.44	414	177
VO(II)-ETIO	545.62	407	400
VO(II)-DMEP	661.70	407	390
VO(II)-OEP	599.00	407	364
VO(II)-TPP	681.68	424	528
Cu(II)-ETIO	542.23	399	176
Cu(II)-DMEP	658.30	399	216
Cu(II)-OEP	598.33	399	360
Cu(II)-TPP	678.29	416	480

2.4. Adsorption isotherms

Minimum equilibration times for porphyrin sorption on Na-montmorillonite was determined to be 3 days for the free-base porphyrins and 7 days for the metallated porphyrins. Adsorption isotherm data were obtained by placing 20 ml porphyrin/toluene solution (1–400 μM, if solubility allowed) and 0.10 g Na-montmorillonite (<2 μm e.s.d.) in a sealed scintillation vial and stirred using a stir plate for the minimum equilibration time. Each concentration was run in triplicate. Each solution was then filtered and the filtrate was analyzed using conventional UV–visible absorption spectroscopy.

The Langmuir isotherm is commonly used to describe the adsorption isotherms of natural organic matter on mineral surfaces (Schlautman and Morgan, 1994; Gu et al., 1995). The degree of adsorption of the different porphyrins on Na-montmorillonite was modeled using the Langmuir equation:

$$\Gamma = \Gamma_m(K_{ads}C)/(1 + K_{ads}C) \tag{1}$$

where Γ is the adsorption density (μmol porphyrin adsorbed/g Na-montmorillonite), Γ_m is the maximum adsorption density (μmol porphyrin adsorbed/g Na-montmorillonite), C is the concentration of free porphyrin remaining in solution at equilibrium (μM), and K_{ads} is the adsorption constant (1/μM). The Langmuir adsorption isotherm is valid up to the formation of one monolayer (Stumm and Morgan, 1995). The maximum amount that any of the porphyrins studied could theoretically sorb is 80 μmol porphyrin/g montmorillonite
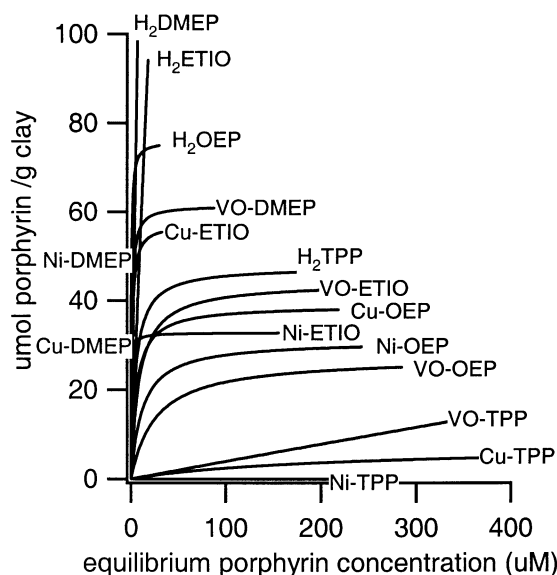

Fig. 2. Adsorption isotherms (Langmuir fits) for the free-base Cu(II), VO(II), and Ni(II) metal complexes of OEP, ETIO, DMEP and TPP on Na-montmorillonite in toluene.

(0.02 L of 400 µM porphyrin per 0.1 g clay). So, for example, if all of the H$_2$TPP (diameter = 1.76 nm; Boeckl et al., 2000) was sorbed, only 26% of the surface would be covered [based on a EGME surface area of 596 m^2/g (Chorover and Amistadi, 2001)] thus use of the Langmuir equation is valid. Modeling software (Igor, Wavemetrics Inc.) was used to calculate K_{ads} and Γ_m via the Levenberg–Marquardt algorithm (a form of non-linear least-squares fitting) to determine the best fit of the data to Eq. (1). The Langmuir fits in Figs. 2–4 are shown as solid lines. The error bars in Figs. 3 and 4 represent ±2 standard deviations of the measurements.

3. Results and discussion

The relative degree of adsorption of different porphyrins on Na-montmorillonite can be determined by examining their adsorption isotherms. Adsorption isotherms are a plot of the equilibrium concentration of a solute on the substrate verses the equilibrium concentration of the solute in a solvent measured over a range of initial solute concentrations.

Langmuir "L" type isotherms are characteristic of molecules that adsorb flat on the substrate [e.g. Fig. 2: Cu(II)-OEP, Ni(II)-OEP, VO(II)-OEP] The shape is a
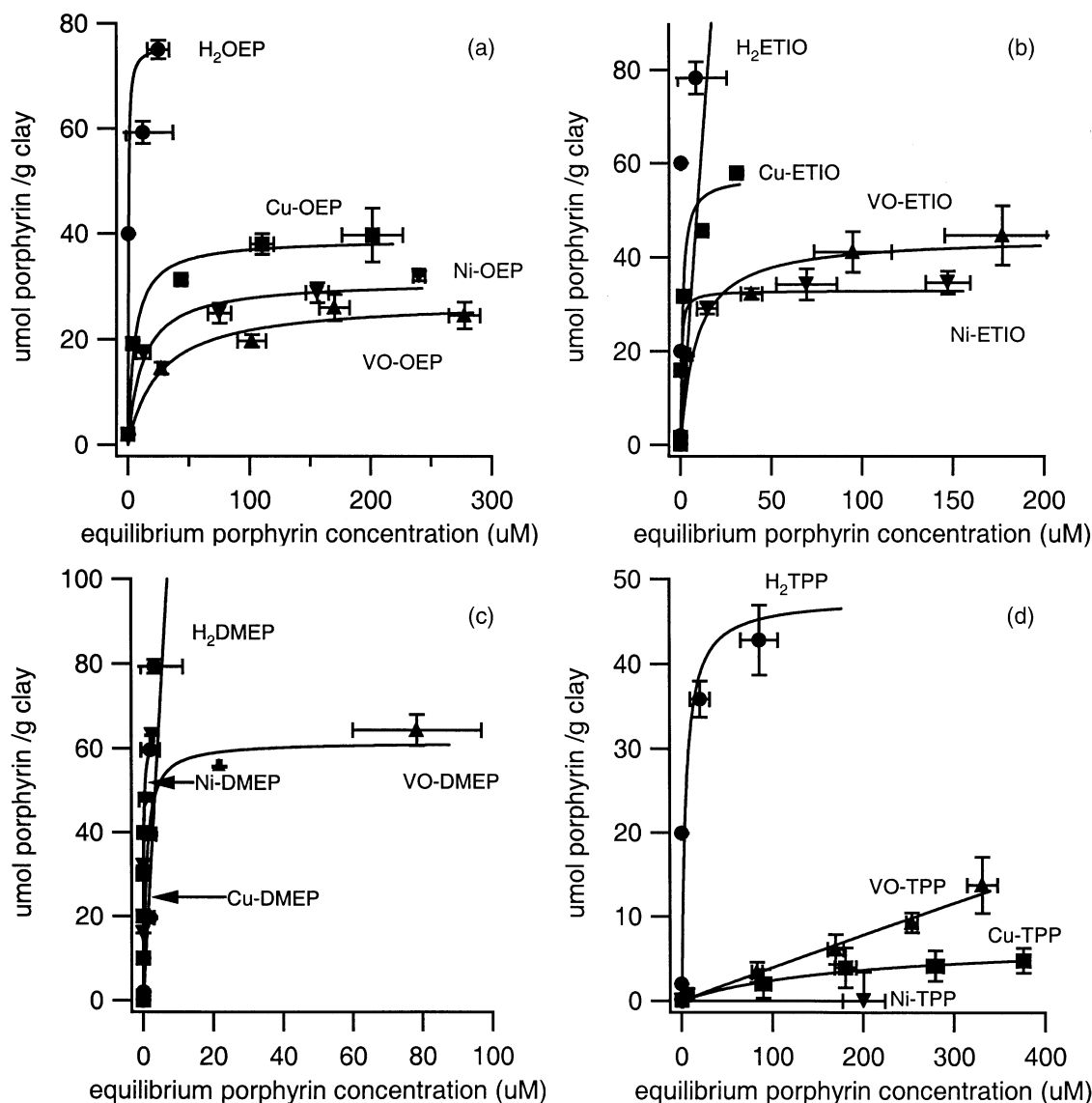

Fig. 3. Adsorption isotherms for (a) OEP, (b) ETIO, (c) DMEP and (d) TPP as a function of metallating ion: free-base (●), Cu(II) (■), VO (▲), and Ni(II) (▼) on Na-montmorillonite in toluene. The solid lines represent the Langmuir fits of the data. The error bars represent ±2 standard deviations of the measurements.

result of decreasing sites for adsorption on the substrate as system concentration rises, however, conformation of experimental data to the Langmuir equation does not necessarily imply that the hypotheses of the model are fulfilled (Stumm and Morgan, 1995). Some of the data showed extremely strong adsorption consistent with an "H" type (high affinity) isotherm. The "H" type isotherm results when the solute molecules are large or ionic and have a very high affinity for the substrate surface (e.g. Fig. 2: H$_2$OEP, H$_2$DMEP, H$_2$ETIO). Solute molecules are completely adsorbed by the substrate at lower concentrations and there are decreasing sites

available for adsorption on the substrate with increasing system concentration. Table 2 shows the Langmuir parameters (Γ_m and K_{ads}) calculated from fitting the data to Eq. (1). For type "H" (high affinity) isotherms, the porphyrins were very strongly adsorbed and porphyrin solubility was not sufficient to collect data points at higher concentrations. While the data were fit to the Langmuir equation, the resulting parameters are not useful for comparison with other tabulated Langmuir parameters. As a result, the true Γ_m values for the data "H" type isotherms are greater than determined from fitting the data.
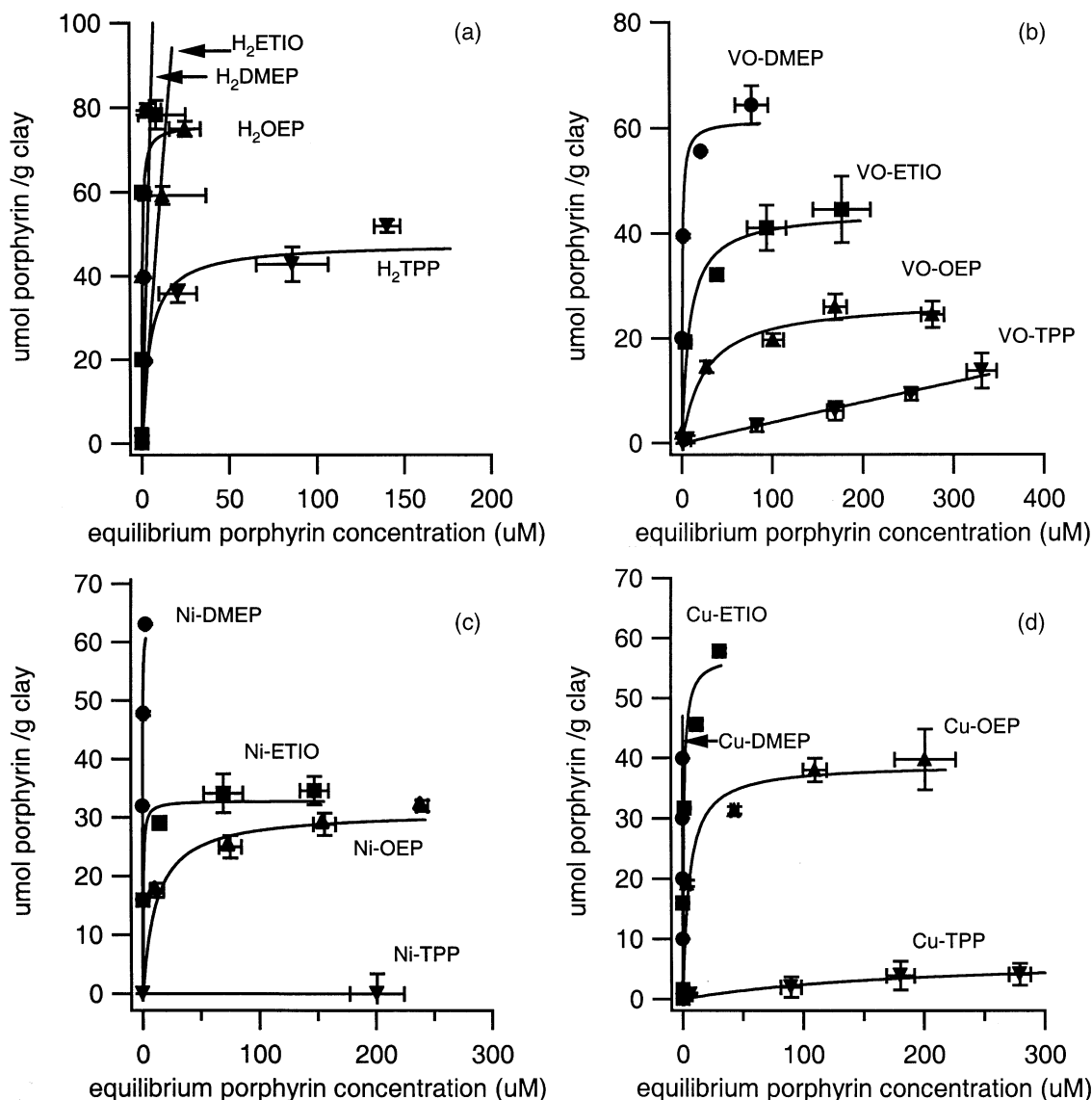

Fig. 4. Adsorption isotherms for (a) free-base, (b) VO, (c) Ni(II), and (d) Cu(II) as a function of porphyrin: DMEP (●), ETIO (■), OEP (▲), and TPP (▼) on Na-montmorillonite in toluene. The solid lines represent the Langmuir fits of the data. The error bars represent ±2 standard deviations of the measurements.

The relative positions of the plotted isotherms are directly related to Γ_m (the maximum capacity of the clay to adsorb the porphyrin) and K_{ads} (the relative strength of adsorption) (Fig. 2 and Table 3). Graphically, K_{ads} is how steeply the curve rises and Γ_m is the value at which the curve levels off. The 16 isotherm data sets collected were fitted to the Langmuir equation [Eq. (1)] and the resultant adsorption isotherms for the free-base and Cu(II), Ni(II), and VO(II) complexes of TPP, OEP, ETIO, and DMEP on Na-montmorillonite in toluene are plotted in Figs. 2–4. Table 4 shows the observed and predicted trends based on periodic and structural properties.

3.1. Global comparison

In Fig. 2 all of the adsorption isotherms are plotted on the same axes to allow for a comparison of relative adsorption for all of the porphyrins studied. The overall order of adsorption observed from least to greatest is: Ni(II)‑TPP < Cu(II)‑TPP < VO(II)‑TPP < VO(II)‑OEP < Ni(II)‑OEP < Ni(II)‑ETIO < Cu(II)‑OEP < VO(II)‑ETIO < H_2TPP < Cu(II)-ETIO ∼ VO(II)-DMEP < H_2OEP < H_2DMEP ∼ Cu(II)-DMEP ∼ Ni(II)-DMEP ∼ H_2ETIO.

The overall adsorption of the porphyrins studied are discussed by placing them in three arbitrary groups based on their Γ_m values: group 1 sorbed strongly, group 2 sorbed moderately, and group 3 sorbed weakly. Group I (strongly sorbed), consisting of Cu(II)-DMEP, Ni(II)-DMEP, H_2DMEP, H_2ETIO, and H_2OEP, produced type "H" (high affinity) isotherms. While Γ_m values are not available for these "H" type isotherms, it can be useful in the context of the discussion to think of

these porphyrins as having a Γ_m greater than 61, which is the highest value for the metal complexes for which enough data were obtained to get an accurate Langmuir fit. The porphyrins of Group 1 have several notable features that may contribute to their strong adsorption including a lack of multiple large substituent groups (all), availability of ring nitrogens (free-bases), and additional sites for adsorptive interaction [the ester group of Cu(II)- and Ni(II)-DMEP].

Group 2 (moderately sorbed), consisting of VO(II)-OEP, Ni(II)-OEP, Ni(II)-ETIO, Cu(II)-OEP, VO(II)-

Table 3
Comparison of observed relative order of plotted isotherm and Langmuir parameters calculated by fitting isotherm data to Eq. (1)

Relative order of adsorption isotherm position	Γ_m (µmol porphyrin/g clay)	K_{ads} (1/µM)	Shape
Ni(II)-TPP	–[a]	–	Ruffled[b]
Cu(II)-TPP	7.2	0.0051	Ruffled[b]
VO(II)-TPP	–	–	Planar[c,d]
VO(H)-OEP	27	0.090	Ruffled[e]
Ni(II)-OEP	31	0.08	Ruffled[b]
Ni(II)-ETIO	33	2.3	Planar[b]
Cu(II)-OEP	39	0.19	Planar[b]
VO(II)-ETIO	44	0.18	Planar[f,g]
H_2TPP	48	0.21	Planar[h], Waved[i], Ruffled[j,k]
Cu(II)-ETIO ∼	61 (VO(II) DMEP)	1.1 (VO(II)- DMEP)	–
VO(II)-DMEP			
H_2OEP	–	–	Planar[l]
H_2DMEP ∼ Cu(II)–	–	–	Planar[m] (H_2DMEP)
DMEP ∼ Ni(II)–			Planar[n] (Ni(II)-DMEP)
DMEP ∼ H_2ETIO			

[a] Langmuir parameters are of little comparative value for the type "H" type (high affinity) isotherms and are not represented in Table 3.
[b] Scheidt and Turowska-Tyrk, 1994.
[c] Scheidt, 2002. Note: VO(II)-TPP required mirror symmetry.
[d] Drew et al., 1984.
[e] Scheidt, 2002. Note: VO(II)-OEP very slightly ruffled.
[f] Scheidt, 2002. Note: VO(II)-ETIO same as Etioporphyrin II, a planar dimeric structure.
[g] Drew et al., 1984.
[h] Bymetal, 1991.
[i] Hamor et al., 1964.
[j] Silvers and Tulinsky, 1967.
[k] Silvers et al, 1964.
[l] Scheidt, 2002. Note: H_2OEP required inversion symmetry.
[m] Scheidt, 2002. Note: H_2DMEP nearly planar.
[n] Scheidt, 2002. Note: 2,4 diacetyl is planar.

Table 2
Langmuir parameters calculated by fitting isotherm data to Eq. (1)

Porphyrin	Free-base		Cu(II)		VO(II)		Ni(II)	
	$\Gamma_m{}^a$	$K_{ads}{}^b$	Γ_m	K_{ads}	Γ_m	K_{ads}	Γ_m	K_{ads}
OEP	(76)[c]	(2.5)[c]	39	0.19	27	0.090	31	0.08
ETIO	(930)	(0.01)	(58)	(0.94)	44	0.18	33	2.3
DMEP	(73)	(0.66)	(53)	(20)	61	1.1	(64)	(6.7)
TPP	48	0.21	7.2	0.0051	ND[d]	ND[d]	NS[e]	NS[e]

[a] Γ_m is in units of umol porphyrin/g clay.
[b] K_{ads} is in units of 1/µM.
[c] The numbers in parentheses are parameters from type "H" type (high affinity) isotherms where the porphyrins were very strongly adsorbed. In these cases, porphyrin solubility was not sufficient to collect data points at higher concentrations, thus while the data were fit to the Langmuir equation, the resulting parameters are not useful for comparison with other tabulated Langmuir parameters. The true Γ_m values for the data in parentheses (except for free-base-ETIO) is obviously greater than that determined from fitting the data.
[d] ND = stable parameter values could not be determined.
[e] NS = no sorption observed.

Table 4
Observed and predicted adsorption trends

Porphyrin type	Observed order of adsorption	Predicted order of adsorption
TPP	Ni(II) < Cu(II) < VO(II) < < Free-base	VO(II) < Ni(II) < Cu(II) < < Free-base
OEP	VO(II) < Ni(II) < Cu(II) < < Free-base	VO(II) < Ni(II) < Cu(II) < < Free-base
ETIO	Ni(II) < VO(II) < < Cu(II) < Free-base	VO(II) < Ni(II) < Cu(II) < < Free-base
DMEP	VO(II) < Ni(II)≈Cu(II)≈Free-base	VO(II) < Ni(II) < Cu(II) < < Free-base
Free-base	TPP < OEP≈ETIO≈DMEP	TPP < OEP < ETIO < DMEP
Cu(II)	TPP < OEP < ETIO≈DMEP	TPP < OEP < ETIO < DMEP
Ni(II)	TPP < OEP < ETTO < DMEP	TPP < OEP < ETIO < DMEP
VO(H)	TPP < OEP < ETIO < DMEP	TPP < OEP < ETIO < DMEP
Overall order	NiTPP < CuTPP < VOTPP < VOOEP < NiOEP < NiETP < CuOEP < VOETP < H₂TPP < CuETP ∼ VODMEP < H₂OEP < H₂DMEP ∼ CuDMEP ∼ NiDMEP ∼ H₂ETP	

ETIO, Cu(II)-ETIO, VO(II)-DMEP, and H$_2$TPP, has Γ_m values of 31–61. These porphyrins have two notable features: a lack of multiple large substituent groups (except TPP), and the presence of complexed metal ions (except H$_2$TPP).

Group 3 (weakly sorbed), consisting of Ni(II)-TPP, VO(II)-TPP, and Cu(II)-TPP, has Γ_m values of 27 or less and are sorbed the least strongly. These porphyrins have two obvious features in common: multiple large substituent groups and the presence of complexed metal ions.

Given the diverse distribution of adsorption across the structural and metal complex combinations of the porphyrins studied, one can surmise that relative adsorption is the result of a complex interaction between the number and size of substituent groups, the presence of additional substituent groups that can serve as sites for adsorption, the presence or absence and identity of a complexed metal ion, and the overall shape of the molecules (planar, ruffle, wave, saddle, etc.). To understand how these factors may influence adsorption

Table 5
The periodic properties and stability class for Cu(II), Ni(II), and VO(II)

	Cu(II)	Ni(II)	VO(II)
Pauling electronegativity (E_n)	1.90	1.91	1.63[a]
Ionic radius (r_i)	62 pm	60 pm	59 pm
Charge (Z)	+2	+2	+4
Stability index (S_i)	6.13	6.37	11.05
Stability class	II	II	I

[a] The influence of oxidation state on electronegativity is small, such that the value for V will provide a useful comparison for V(IV) in VO(II) (Wulfsberg, 1987).

it is useful to look at adsorption isotherms as (1) a function of the presence (or absence) and identity of a metal ion, (2) as a function of the types of substituent groups present, and (3) as a function of the overall shape of the macrocycle.

3.2. Comparison by metallating ion

The influence of the specific periodic properties of a metalloporphyrin's metal ion on availability and polarity of the ring nitrogens to bind with the clay surface is predicted to influence adsorption. The metal ion would be expected to play several roles: it would influence how much attraction the metalloporphyrin ring nitrogens have for the clay surface in the initial sorption on the clay; it determines the stability of the complex once adsorbed; and it affects the overall shape of the molecule.

Buchler (1975) developed a stability index (S_i) for the metal–nitrogen bond in metalloporphyrins to predict metalloporphyrin stability. Buchler incorporates factors for the periodic properties of Pauling electronegativity (E_n), charge (Z), and ionic radius (r_i) into S_i (Table 5):

$$S_i = 100(E_n)(Z)/r_i \tag{2}$$

Quirke (1987) noted in his rationalization of the predominance of nickel and vanadium porphyrins in the geosphere that porphyrins with low S_i have more unstable metal–nitrogen bonds, which leads to easier demetallation and decomposition. Metalloporphyrin stability is rationalized to be facilitated by increasing E_n, decreasing r_i, and increasing Z. Similarly S_i should also provide a correlation to adsorption because the metal ion that would promote the greatest polarity and basi-

city of the ring nitrogens (i.e. the lowest S_i value) would also promote the rings nitrogen's sorption on the clay. VO(II), Ni(II), and Cu(II) have S_i values of 11.05, 6.37, and 6.12 respectively suggesting an order of sorption of VO(II) < Ni(II) < Cu(II). The absence of a metal ion (the free-base form) would be expected to result in the most basic ring nitrogens and therefore would be expected to have the greatest adsorption. Overall adsorption would be expected to follow VO(II) < Ni(II) < Cu(II) < free-base if the metal ion periodic properties are the dominant factors affecting adsorption of the metalloporphyrin onto the clay surface. In Fig. 3a–d, the plots of the adsorption isotherms are grouped by porphyrin structural type to compare the amounts sorbed as a function of the metal ion. For OEP (Fig. 3a) the order of adsorption observed is VO(II) < Ni(II) < Cu(II) < < free-base. For ETIO (Fig. 3b) the order of adsorption observed is Ni(II) < VO(II) < < Cu(II) < free-base. For DMEP (Fig. 3c) the order of adsorption observed is VO(II) < Ni(II) ≈ Cu(II) ≈ free-base. For TPP (Fig. 3d) the order of adsorption observed is Ni(II) < Cu(II) < VO(II) < < free-base. The adsorption trends are summarized in Table 4. There is only partial correlation between the experimental adsorption isotherms and what would be predicted on the basis of metal–nitrogen bond stability. These results suggest that more factors are involved (substituent group effects, overall shape of the molecule) in the amount a given structural type of porphyrin is adsorbed than the influence of the metal–nitrogen.

3.3. Metalloporphyrin adsorption isotherms according to structural type

Our rationalization for adsorption trends for DMEP, ETIO, OEP, and TPP considers the contribution to adsorption from the number and type of substituent groups and their corresponding steric and functional characteristics. Adsorption of porphyrins by montmorillonite occurs largely due to electropositive clay mineral sites binding to porphyrin functional groups (or through surface water polarized by the electropositive sites), most notably the ring nitrogens, or in the case of DMEP, the additional ester groups binding to the clay surface.

Previous studies by Tannenbaum et al. (1986) show a relationship between the degree of adsorption and the basicity and polarity of a compound's functional groups: the more basic and polar a compound is the stronger the complex is that is formed with the clay. In the case of the metalloporphyrins studied in our research, the primary focus is the basicity, polarity, and availability of the ring nitrogens. Any factors that influence the basicity and polarity of ring nitrogens would be predicted to influence adsorption. From a structural standpoint, differences in the degree of adsorption are rationalized to relate to the number and kind of functional groups available to bind with the clay surface, their relative amount of steric hindrance, and the inductive (electron withdrawing or donating) effects that might affect the stability of the metal–nitrogen bond of the macrocycle. Substituent groups can have a significant effect on the basicity of ring nitrogens. For example, titrations of porphyrins where two formyl groups replaced two ethyl groups showed a thousand-fold depression in basicity (Phillips, 1960).

ETIO and OEP are similar from a structural standpoint, differing only in the alkyl substituents on the pyrrole rings. ETIO has four methyl ($-CH_3$) groups and four ethyl ($-CH_2CH_3$) while on OEP, all eight substituents are ethyl groups. DMEP differs from ETIO in that one methyl and ethyl group are each replaced by ester groups ($-CH_2CH_2COOCH_3$). TPP has large phenyl substituents in the meso positions that are perpendicular to the porphyrin ring plane. DMEP may have a higher degree of adsorption than TPP, ETIO, and OEP due to the additional ester groups that could bind to the clay surface. The degree of adsorption to the clay surface for ETIO, OEP, and TPP may follow a trend related to the relative steric hindrance provided by the individual functional groups. ETIO and OEP would be predicted to have similar degrees of adsorption with ETIO showing a slightly greater degree of adsorption. ETIO would have slightly less steric hindrance from its methyl groups than OEP would have from its ethyl groups allowing it to be adsorbed easier. TPP would be predicted to have the greatest steric hindrance due to its large phenyl groups and thus a correspondingly lower degree of adsorption. The adsorption trend based on the number of functional groups that would favor adsorption would be predicted to be TPP < OEP < ETIO < DMEP. The trend predicted in this structural rationalization is generally reflected in the experimental results.

In Fig. 4a–d the plots of the adsorption isotherms are grouped as free-bases and by the metallating ion to compare the relative amounts adsorbed as a function of structural type. For free-bases (Fig. 4a) the order of adsorption observed is TPP < OEP ≈ ETIO ≈ DMEP. For vanadyl complexes (Fig. 4b) the order of adsorption observed is TPP < OEP < ETIO < DMEP. For nickel complexes (Fig. 4c) the order of adsorption observed is TPP < OEP < ETIO < DMEP. For copper complexes (Fig. 4d) the order of adsorption observed is TPP < OEP < ETIO ≈ DMEP. The experimental versus the predicted adsorption trends are summarized in Table 4.

The sorption of DMEP, OEP, and ETIO free-base porphyrins shows little diversity, all sorbing similarly strongly. Ni(II) and VO(II) porphyrins sorbed in the predicted order of TPP < OEP < ETIO < DMEP. Cu(II) and free-base porphyrins were less clear cut as to the influence on absorption by the substituent groups. The freely available nitrogens of free-bases tend to moderate

the influence of substituent groups on adsorption, except for the steric hindrance caused by the phenyl groups in the case of TPP. The presence of a Ni(II) or VO(II) metal ion moderates the dominance of the ring nitrogens on adsorption allowing the influence of the substituent groups to emerge.

The free-base forms of DMEP, ETIO, and OEP sorb strongly in similar amounts, suggesting that availability of the ring nitrogens for bonding with the mineral surface may be the single most important factor in sorption—even the additional ester sites did not contribute to increased sorption for the free-base porphyrins. The ring nitrogens on TPP are not as accessible due to the steric hindrance of the phenyl substituent groups and thus it sorbs less. The additional steric hindrance of the metal ion and the decreased availability of the ring nitrogens to bind to the surface can account for the decreased adsorption of metallated porphyrins compared to the free-base porphyrins.

Ni(II) and VO(II) metalloporphyrins sorb according to TPP < OEP < ETIO < DMEP as predicted based on the effects of their substituent groups. Among the metalloporphyrins studied, the stability gained by the presence of the metal ion appears to allow the influence of the various substituent groups on sorption to emerge in comparison to free-bases. Cu(II) metalloporphyrins sorb according to TPP < OEP < ETIO ≈ DMEP.

3.4. Macrocycle shape and adsorption isotherms

There has been significant interest recently in investigating non-planar porphyrins. *The Porphyrin Handbook* (Senge, 2000) lists 2189 tetrapyrrole crystal structure determinations in its database, and offers a comprehensive review of the systematics of the stereochemistry of porphyrins and metalloporphyrins (Scheidt, 2000). There are four non-planar porphyrin types cited in the

literature: saddle, wave, dome, and ruffle conformations. Some porphyrins, such as H_2TPP have multiple conformations (planar, ruffled, waved). Table 3 lists the known conformations of the porphyrins studied. The conformation type of the porphyrins seems likely to influence adsorption by affecting accessibility to the ring nitrogens or other substituent groups. The ruffled porphyrins generally sorb less strongly than the planar porphyrins or those porphyrins with at least one planar conformation (H_2TPP). How the shape may be influenced by sorption onto clay minerals is unknown. The influence of porphyrin shape on adsorption is intriguing and deserves additional study.

4. Summary and conclusions

The identity of the metallating ion, the number and kind of substituent groups, and the overall shape of the macrocycle has a significant influence on the relative amount of adsorption of metalloporphyrins on clay minerals. The complex interrelationships of the metallating ion and the number and kind of substituent groups makes it difficult to predict the outcome of adsorption by easily used rules of thumb. Ultimately this data implies that clay minerals may play a significant role in the biogeochemistry of porphyrins.

The relative degrees of adsorption of TPP, OEP, ETIO, and DMEP in their free-base, Cu(II), Ni(II), and VO(II) forms on Na-montmorillonite under similar conditions can be used to infer how clay minerals may influence the formation and degradation of geoporphyrins during diagenesis or post diagenesis. Montmorillonite interacts with porphyrins by three pathways (Bergaya and Van Damme, 1982): (1) adsorption and desorption, (2) metallation, demetallation, and trans-metallation, and (3) protonation and deprotonation

$$[M^{2+} \text{ - } (H_2O)_n \text{ - } Mont] + H_2Porph$$

adsorption   desorption

$$[M^{2+} \text{ - } (H_2O)_n \text{ - } H_2Porph - Mont]$$

metallation   demetallation   protonation   deprotonation

$$[MPorph - 2H^+ \text{ - } (H_2O)_n \text{ - } Mont] \qquad [M^{2+} \text{ - } 2OH^- \text{ - } (H_2O)_{n-2} - H_4Porph^{2+} \text{ - } Mont]$$
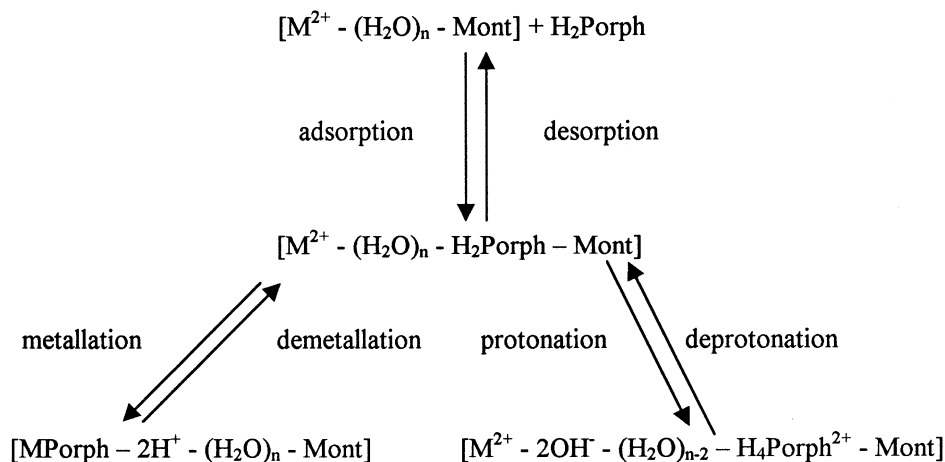
Fig. 5. Porphyrin interactions with montmorillonite (adapted from Bergaya and Van Damme, 1982).

(Fig. 5). These pathways can contribute to the selective survival and degradation of geoporphyrins. How the clay minerals influenced decomposition would correlate with decomposition in the larger geological environment is uncertain as overall decomposition trends may be primarily thermal and related to kerogen composition changes.

4.1. Geochemical implications of porphyrin adsorption trends

From the isotherm data, it can be generalized that the greater the number of functional groups that can bind to the surface and the lower the steric hindrance of the substituent groups, the greater the adsorption of the free-base or metalloporphyrin. The geochemical implications of this are that those free-base, Cu(II), Ni(II), and VO(II) metalloporphyrins sorbed onto montmorillonite to the greatest extent in the depositional environment would also be expected to decompose to the greatest extent. This research has several implications related to DPEP/ETIO ratios, Ni(II)/VO(II) porphyrin ratios, as well as the disappearance of Cu(II) porphyrins observed in the geological environment.

4.1.1. DPEP/ETIO ratio
Given that ETIO is sorbed strongly by clays and that DPEP could be considered a more substituted ETIO (that would be predicted to sorb less strongly), one would predict that the DPEP/ETIO ratio would increase over geological time if clay minerals were a major factor for the DPEP/ETIO ratio. However, just the opposite is observed in hydrous pyrolysis experiments (Huseby et al., 1996): the DPEP/ETIO ratio decreases with increasing temperature, suggesting that DPEP is degraded by thermal stress rather than converted to ETIO. Analysis of Kimmeridge clay source rocks show a decreasing DPEP/ETIO ratio with increasing thermal maturity, also suggesting that clay minerals do not play a major role in the decreasing DPEP/ETIO ratio observed in the sedimentary environment (Huseby et al., 1996).

4.1.2. Disappearance of Cu(II) porphyrins
Cu(II) porphyrins are not in evidence in the petroleum producing geological environment where geoporphyrins occur in high abundances only in their Ni(II) and VO(II) forms. Generally, the isotherm results show that Cu(II) metalloporphyrins, which have a lower S_i value, are sorbed in greater amounts than the Ni(II) and VO(II) metalloporphyrins. The lower S_i value suggests that Cu(II) metalloporphyrins would degrade on clay surfaces relative to Ni(II) and VO(II) metalloporphyrins, everything else being equal (Quirke, 1987). The disappearance of Cu(II) porphyrins is observed in the petroleum producing geological environment, but to what extent clay minerals play a role is uncertain.

4.1.3. Ni(II)/VO(II) ratios
VO(II)-OEP and VO(II)-DMEP sorb less than their Ni(II) counterparts. VO(II)-ETIO and VO(II)-TPP sorb more than their Ni(II) counterparts. For those VO(II) geoporphyrins that are sorbed less than their Ni(II) counterparts, the additional sorption and the stability of the VO(II)-nitrogen bond may result in a decreasing ratio of Ni(II)/VO(II) over geologic time, as is observed in the fossil record. This suggests that clays in the sedimentary environment may contribute to the decreasing ratio of Ni(II) to VO(II) over time as observed in the fossil record. These types of clay mineral adsorption interactions might in part explain the results of the analysis of Kimmeridge clay source rocks by Huseby et al. (1996) where low abundances of Ni(II) porphyrins were observed relative to VO(II) porphyrins.

Ni(II) porphyrins have been reported in the literature to be more thermally stable than VO(II) porphyrins (Rosscup and Bowman, 1967; Baker and Louda, 1981), which would imply increasing Ni(II)/VO(II) ratios with increasing depth of burial for thermal assisted degradation. However, other investigators (Van Berkel et al., 1989; Beato et al., 1991) found that VO(II) porphyrins persist to higher temperatures than Ni(II) porphyrins in hydrous pyrolysis studies of New Albany kerogen. Mackenzie et al. (1980) observed that the Ni(II) geoporphyrins disappear from the fossil record faster with depth and increasing temperature than VO(II) geoporphyrins indicating that thermal stability is not the primary factor in the decreasing Ni(II)/VO(II) ratios observed. Ni(II) porphyrins may be thermodynamically more stable but decompose at a faster rate than their VO(II) counterparts. The question of thermal stability for Ni(II) versus VO(II) porphyrins is not yet clear.

A fairly complicated interrelationship was observed between the number and types of substituent groups, the identity of the metallic centers, and the overall shape of the macrocycle on the sorption of porphyrins on Na-montmorillonite. The most important factor in adsorption seems to be the availability of the ring nitrogens to bind with the clay surface followed by the influence of the substituent groups and to a lesser extent the identity of the metallic center. In most instances, adsorption was adequately described by the Langmuir isotherm equation. In general, sorption affinity based on metallating ion followed the order: VO(II) ≈ Ni(II) < Cu(II) << Free-base. In terms of functional groups, sorption affinity generally followed the order: phenyl < ethyl < methyl < ester. Ruffled shapes generally sorb less than planar shapes. These sorption trends suggest how clay minerals might influence the selective sorption and decomposition of porphyrins in oil shales; how clay minerals may contribute to the decreasing Ni(II)/VO(II) ratios observed in the fossil record; and why clay minerals probably do not play a major role in the decreasing   deoxophylloerythroetioporphyrin/etiopor-

phyrin I (DPEP/ETIO) ratio observed in the maturing sedimentary environment.

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