

SURFACE CHEMISTRY, COLLOIDS AND TRACE-ELEMENT SCAVENGING

Bruce D. Honeyman

Department of Marine Sciences, Texas A&M University at Galveston, Galveston, Texas 77551

(Address as of January 1992: Environmental Science and Engineering Ecology, Colorado School of Mines, Golden, Colorado, 80401)

1. Introduction

From a marine chemist's point of view, particles represent a class of ligands which are available to form complexes with many elements of interest. For example, marine particles may be represented as containing functional groups of a certain type, for example carboxylic or metal oxide groups, at a specified concentration. Furthermore, stoichiometric and mass-action expressions can be written to describe chemical interactions between particle functional groups and trace elements, and the stability of the resulting complexes can be described in thermodynamic terms. Thus, in one sense, particles, as chemical components of a system, are really no different from many dissolved ligands which are also capable of forming chemical complexes with trace elements.

However, particles pose several problems for marine chemists. First, there is the difficulty of identifying and quantifying particle functional groups. A clear example is the controversy over colloidal material. The second major problem area is the development of a consistent conceptual framework for describing interactions between dissolved components and particle-associated ligands. For example, physico-chemical models for the particle-solution interface are generally based on the notion that particles can be represented as a discrete ligand type, although most environmental particles contain chemical functional groups which exhibit polyfunctional characteristics. Another example is the complex kinetic behavior of trace element-particle interactions. Third, the origin, distribution and fate of particles in marine systems is largely unknown. The corollary is that our knowledge of the fate of many elements associated with particles is only as accurate as is our knowledge of the behavior of particles, themselves.

The first and second points mentioned above are directly interrelated. To a large extent, the kind of information needed about particle chemical characteristics, and the methods used to extract that information, are dependant on the assumed conceptual framework governing particle-solution interactions. While the third

area of concern is not a problem of particle characterization per se, the roles that particles play in regulating the chemical composition of marine systems, a central theme of marine chemistry, are inextricably connected with the fate of particles.

2. The Evolution of Surface Chemistry as Relevant to Marine Chemistry

Until the early seventies, most of the work on trace element-particle interactions was carried out by soil scientists and the emphasis was placed on the interactions of ions with fixed charged surfaces [Thomas, 1977]. The development of surface reactivity models was, in essence, a series of attempts to explain deviations of observations from ideal ion-exchange behavior. Such surface interaction models were physical models in the sense that the primary driving force for trace element-particle associations was considered to be separation of charge, for example, a positively-charged ion interacting with a negatively-charged clay surface.

In the early seventies, however, classically-trained coordination chemists began to study the interaction of metal ions with metal oxide surfaces such as γ -alumina and hydrous ferric oxide. The observation that the tendency of a metal ion to associate with a metal oxide surface correlates with the intensity of solution-phase hydrolysis product formation led to the concept of surface-complex formation [Schindler et al., 1976; Stumm et al., 1976]. Surface complexation models (SCMs) are still "physical" models in the sense that the charges of the sorbing ion and the surface of the sorbent are important factors. However, the possibility of chemical bond formation between surface-active solutes and binding "sites" on mineral surfaces is a new aspect which is a key element in SCMs but was not included in ion-exchange models. While the analogy between solution-phase and surface reactions is exact, the main difference between the various currently-available surface complexation models is the way in which the free energy of sorption is divided into electrostatic and chemical components.

Just as Sillen's model [1961] signaled the beginning of modern chemical oceanography, Schindler [1975] firmly established the link between surface chemistry and

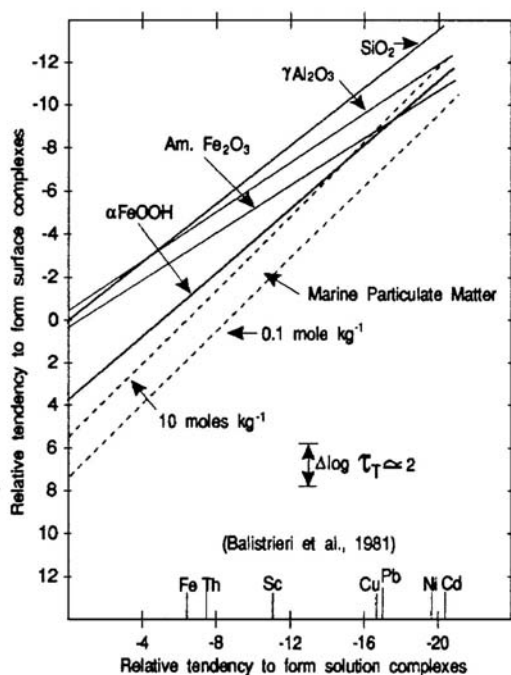


Fig. 6-50. The tendency of a metal ion to form surface complexes is related to the intensity of solution-phase complex formation. This observation led to the establishment of surface complexation models by Schindler, Stumm and co-workers [e.g., Schindler et al., 1976]. The total residence time of trace elements (Me) in the water column, τ_T , is related to the fraction of total Me associated with sinking particles, f_p , and the particle residence time, τ_p . An order of magnitude change in Me sorption intensity corresponds to a decade change in residence time, τ_T , of the trace element.

$$\tau_T = \frac{\tau_p}{f_p}$$

Sorption intensity changes with the nature of the trace element and the type and quantity of Me-sorbing particles [from Balistrieri et al., 1981, modified by Honeyman and Santschi, 1988].

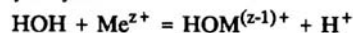
the chemical composition of the ocean with his "Zero-Order" model for the removal of trace metals from the ocean waters. In his model, the rate of removal of trace elements from seawater is related to the intensity of interaction between trace elements and particle surface sites, given a constant particle flux. The model correctly predicts the order but not the absolute value of residence times of metals in the ocean, assuming SiO_2 as the model

surface. Schindler's model was crucial for two reasons: 1) it provided a formal connection between solution-phase reactions, adsorption and trace metal scavenging; and 2) he established the notion that marine particles are chemical species which compete against dissolved ligands for complexation with trace elements. Following Schindler, Balistrieri et al. [1981] provided the next important step by investigating the extent to which variations in particle surface chemistry would affect trace element scavenging residence times.

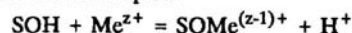
3. The Surface Complexation Approach

Figure 6-50 shows several important characteristics of surface chemistry as applied to marine chemistry. First, it illustrates the generally observed relationship between the tendency to form solution-phase hydrolysis products and the intensity of surface complexes. Similar correlations led Stumm, Schindler and co-workers to formulate the analogy between solution and surface complexes:

Aqueous hydrolysis:



Analogous surface complex:



where SOH represents a protonated particle surface site. Thus, generic stoichiometric expressions for sorption [e.g., Balistrieri and Murray, 1981] usually include the deprotonation of surface sites (or the dissociation of surface-associated water) as part of the net sorption reaction. Second, for a given particle-reactive element, there is significant variation in sorption intensity between particle types. A group of metal oxide surface site types, for example, Al_2O_3 , ferrihydrite, MnO_2 , etc., can yield a four orders of magnitude range or more in calculated binding intensities for a given metal ion. Third, a certain particle type yields marked variation in sorption intensity throughout the range of particle-reactive elements. Fourth, derived values of sorption intensity are sensitive to the specific site concentration (moles sites-mass particles), measured or assumed, for a selected particle type. A surface complexation model is a framework within which one can postulate surface reactions. In a sense, they are heuristic devices for exploring stoichiometric relationships among system chemical components. For example, Balistrieri et al. [1981], using surface complexation models in this manner, reached the important conclusion that marine particles have the trace metal binding characteristics of organic matter. It is important to recognize, also, that surface chemical

models, in their current form, are essentially solution-phase models (such as MINEQL "family" of computer codes) adapted to consider the special case of a charged particle-solution interface. The requirements for the application of surface chemical models are: 1) the representation of particles as ligands and determining their primary chemical characteristics; 2) knowledge of solution-phase chemistry; and 3) selection of a molecular hypothesis (interfacial configuration) for the sorption environment.

3.1. The representation of particles as ligands.

Conceptually, the main difference between dissolved ligands and particle ligands is that the latter are spatially constrained by the particle matrix, itself. The most common representation of particle surface sites is as moles of sites per mass of particles and the two critical parameters whose estimation is required are site density, n_s (sites nm^{-2}), and specific surface area, S_A ($\text{m}^2 \text{g}^{-1}$).

3.2. Site density.

One of the direct consequences of the analogy between solution-phase hydrolysis and surface complex formation is that trace element sorption is most frequently represented as an exchange of trace elements for surface-associated protons. Such a representation exists in both semi-generic partitioning equations [Tessier et al., 1989; Honeyman and Santschi, 1988; Balistrieri and Murray, 1983] and in the postulation of surface reactions [HYDRAQL; Papelis et al., 1988]. Thus, the most common methods used to estimate surface site density are those that include the uptake of protons by the sorbent of interest. These methods include tritium exchange [Berube and de Bruyn, 1968] and potentiometric titration [James and Parks, 1982, and references therein]. Such methods are based on the assumption that there is a one to one correspondence between sites accessible to protons and those available to the sorbate. A variety of other methods have also been employed to estimate surface site densities, including crystallographic analysis [Sposito, 1984], reacting the mineral with an OH-labile compound such as $\text{CH}_3\text{-Mg-I}$, thermographic analysis and IR spectroscopy [see James and Parks, 1982, and references, therein].

Table 6-11 [compiled by Davis and Kent, 1990] presents site densities for surface functional groups on selected hydrous oxide surfaces, as estimated by the various techniques described above. Site densities range by over an order of magnitude, from 22 sites nm^{-2} for $\alpha\text{-FeOOH}$ to less than 2 for kaolinite. While most of the

variability in estimated site densities is a direct reflection of differences in mineralogy, some differences can also be ascribed to variability in the results of various techniques for estimating site densities, as shown in Table 6-12. Differences in measured site densities are particularly stark when comparing results for the proton acid-base titrations with "saturation" isotherms for oxyanions which, compared to the proton, are relatively quite large. This indicates that "probe" molecules for surface characteristics should be physically and chemically similar to the sorbate of interest.

Davis and Kent [1990] argue, given the difficulty of accurately measuring site densities, that surface complexation constants for strongly binding sorbates should be derived using a site density of 2.31 sites nm^{-2} ($3.84 \mu\text{M m}^{-2}$). This suggestion is aimed at developing a self-consistent data set for trace element sorption in complex mixtures of sorbents and is bolstered by recent studies [Hayes et al., in press, 1991] that have shown that the ability of surface complexation models to fit adsorption data is relatively insensitive to variations in site density.

3.3. Specific surface area.

The second parameter needed to estimate the specific site concentration (M g^{-1}) of particles is specific surface area, S_A ($\text{m}^2 \text{g}^{-1}$). An enormous literature exists on the determination of surface area by various methods; Davis and Kent [1990] have recently summarized information about surface area determination of direct relevance to geochemists.

While it is possible to estimate specific surface areas by crystallographic or optical means, surface areas of importance are on a molecular scale and their accurate determination requires the utilization of probe sorbates, either a gas or solute, and then relating the amount adsorbed to the area occupied. The most common gas for surface area determination is N_2 , which is sorbed at the boiling temperature of liquid N_2 at atmospheric pressures (ca. 77° K). The most popular procedure for deriving S_A from gas adsorption measurements is the BET method [Brunauer et al., 1938]. Nitrogen adsorption onto materials with relatively low specific surface areas, i.e., less than 1 $\text{m}^2 \text{g}^{-1}$, produces erroneous results because of non-ideal N_2 gas behavior and Kr is often employed under those circumstances as an alternative sorbate. However, Kr, itself, is not an ideal sorbent, and the disadvantages of its use have been documented by Gregg and Sing [1982].

TABLE 6-11.

Density of Surface Functional Groups on Oxide and Hydrated Oxide Minerals From Davis and Kent [1990]

Mineral Phase	Range of Site Densities (sites nm ⁻²)	Reference	Proton acceptor groups (sites nm ⁻²)	Proton donor groups (sites nm ⁻²)	Reference
α -FeOOH	2.6-16.8	1,2	4.4	6.7	2
α -Fe ₂ O ₃	5-22	1	-	-	-
Ferrihydrite	0.1-0.9 M per M Fe	3	-	-	-
TiO ₂ (rutile)	12.2	1	2.6	4.2	1
TiO ₂ (rutile and anatase)	2-12	1	-	-	-
α -Al(OH) ₃	2-12	4	2.8	5.6	2
α -Al ₂ O ₃	6-9	4	-	-	-
SiO ₂	4.5-12	1	0	all	1
kaolinite	1.3-3	5	0.35	1.0	2

References: 1) James and Parks [1982]; 2) Sposito [1984]; 3) Dzombak and Morel [1990]; 4) Davis and Hem [1989]; 5) Fripiat [1964]

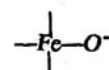
Clay minerals pose a special problem because of the porosity of interlayer regions. While N₂ and Kr gas adsorption has been used for clay mineral surface area determination [see Murray and Quirk, 1990], a common alternative is the use of polar organic compounds [glycerol: van Olphen, 1970; ethylene glycol: Dyal and Hendricks, 1950; and ethylene glycol monoethyl ether (EGME): Eltantawy and Arnold, 1973] due to their ability to penetrate clay interregions. Surface area determinations by retention of polar organics are relatively inaccurate for materials with surface areas on the order of 40 to 50 m² g⁻¹ and less. Consequently, selection of the appropriate surface area probe requires some knowledge of the mineralogy of the sorptive substrate and the adsorbate of interest.

Organic material, while not "particulate" in the way that mineral species are typically visualized, is, none the less, a major component of many sediments and provides a significant, if not dominant, contribution to the colloidal population of many systems. Organic matter is usually considered a poly-functional material whose complexation capacity (mMg⁻¹ carbon) is most often determined by potentiometric titration [see Buffle, 1987; Buffle and Altmann, 1987].

Given the relatively narrow range of measured site densities (generally, 1-7 sites nm⁻²), the largest contribution to variations in specific site concentrations

(M g⁻¹) is specific surface area, S_A. For example, α -silica (α -SiO₂) has a specific site concentration of ca. 1.5 x 10⁻⁴ M sites g⁻¹ [Benjamin, 1978] as a consequence of its relatively low specific surface area of 3-4 m² g⁻¹. Amorphous silicas have specific surface areas ranging from about 100 to several hundred m² g⁻¹, depending on the formation process [Kent and Kastner, 1985], leading to specific site concentrations on the order of a mM g⁻¹.

There is some evidence that site densities are relatively invariant among mineralogical forms of an element [Fetl and Smolkova, 1972, in their study of silicas] and that a metal oxide surface site,



has essentially the same surface chemical characteristics ("acidity") from one mineralogical form to the next e.g. hydrous ferric oxide compared to goethite. This evidence suggests that, in contrast to the enormous variability in mineralogical forms, the surface chemical behavior of chemically-similar mineral species may be relatively easier to classify. For example, iron oxides such as hematite, goethite, ferrihydrite, etc., in spite of their differences in mineralogy, may, on a per site basis, exhibit similar trace element sorptive characteristics.

3.4. Particle Ligands: Discrete or Polyfunctional Character?

Two distinctly-different approaches to representing and determining complexation properties of particle surfaces have emerged over the last fifteen years. Although both approaches explicitly include the notion that particles are ligands with a constrained spatial distribution, they depart in the conceptualization of the chemical heterogeneity of surface sites.

One approach is exemplified by the work of Buffle and co-workers [Buffle and Altmann, 1987] in their application of statistical concepts to trace metal-humic substance interactions. In this and similar approaches, macromolecules and particle surface sites display polyfunctional behavior in which complexation intensity is related, via distribution functions, to the fraction of complexant sites associated with trace elements. Thus, macromolecules or particle sorption sites are characterized by a distribution of site types rather than as a discrete chemical entity. Consequently, the interaction intensity of a trace element with a particle ligand varies with the fraction of particle functional groups which are complexed with the trace element. A distribution of site types may result from such factors as particle surface morphological variations such as edge or pit sites on mineral species or functional group type or location on macromolecules or the aggregate sorption behavior of a suite of competing particle ligands in a particle assemblage.

The second approach, and the one which occupies the largest niche in the geochemical literature, is the direct descendent of the earlier work by Schindler, Stumm and co-workers in which a particle surface is represented as a number concentration of sites of a specific type which form mono-energetic complexes with trace elements.

It makes intuitive sense that particles, especially those found in natural systems, do not have a unique chemical character but are the "sum", in some manner, of the characteristics of the particle components. To a certain extent, the inherent polycharacter of particles is at odds with what has been the major thrust of aquatic surface chemistry, i.e., the direct extension of the solution-phase, metal-discrete-ligand analogy to particle surfaces. Thus, a major question concerning approaches to trace element-particle interactions remains unresolved: What is the best approach to describing particle-trace element interactions?

TABLE 6-12.

Estimates of Site Densities for α -FeOOH by Various Adsorption Techniques From Davis and Kent [1990]

Ion	Adsorption maximum (sites nm ⁻²)	Method	Reference
OH ⁻ /H ⁺	4.0	a	f
OH ⁻	2.6	a	g
F ⁻	5.2	b	h
F ⁻	7.3	c	f
SeO ₃ ²⁻	1.5	d	i
PO ₄ ²⁻	0.8	d	i
Oxylate	2.3	b	j
Pb ²⁺	2.6	b	k
Pb ²⁺	7.0	c	k

Methods: a) Acid-base titration; b) Adsorption isotherms; c) Excess F⁻ at pH 5.5; d) Adsorption isotherm at pH_{pzc} and e) Fit with model.

References: f) Sigg and Stumm [1981]; g) Balistrieri and Murray [1981]; h) Hingston et al. [1968]; i) Hansmann and Anderson [1985]; j) Parfitt et al. [1977]; and k) Hayes [1987].

3.5. Surface Complexation Models of the Particle-Solution Interface

There are four basic tenets of all surface complexation models [Davis and Kent, 1990]:

- 1) The surface is composed of functional groups which react with solution species to form surface complexes. These surface complexes may be coordinative or ion pairs.
- 2) The reactions between surface functional groups and dissolved species can be described using mass-action expressions. Corrections are included to account for the work required to bring a charged species from bulk solution to a sorption plane of some net charge.
- 3) Surface charge and potential are the consequence of chemical reactions of the surface functional groups. They are secondary effects that result from surface coordination reactions.
- 4) The apparent binding constants determined for the mass-action expressions are empirical parameters related to thermodynamic constants via the rational activity coefficients of surface species [Sposito, 1983].

Hayes [1987] has suggested, since activity coefficients depend on the potentials between the plane of sorption, as well as on the charge of the reacting species, that the ratio of activity coefficients corresponding to particular mass-action expression should be equal to the electrostatic correction term.

A number of different configurations of the particle-solution interface have been developed, including the Constant Capacitance Model [Schindler and Kamber, 1968; Hohl and Stumm, 1976], Diffuse Double-Layer Model [Stumm et al., 1970] and Triple-Layer Model [Davis and Leckie, 1978]. All of these models share: 1) mass law equations for all surface reactions; 2) a mole balance equation for surface sites; 3) equations for computing surface charge; and 4) a set of equations representing the constraints imposed by the particular model (configuration) of the interfacial model. Figure 6-51 presents a schematic drawing of idealized decay of electrical potential with distance from a surface for four different interfacial configurations. The differences are found in the ways in which the free energy of adsorption is resolved into electrostatic and chemical components. More specifically, the contrasts lie in the charge-potential relationships of each interfacial configuration and the planes of assignment for the postulated surface species. For example, the Constant Capacitance Model allows only the association of specifically adsorbing solutes with the particle surfaces (i.e., the formation of inner-sphere complexes) while other ions, Na^+ , Cl^- , are considered to be inert with respect to the surface. The Triple-Layer Model, in contrast, has two planes of adsorption, the α -plane for inner-sphere complexes and the β -plane for outer-sphere, ion-pair complexes. "Inert" electrolyte ions are assigned to the β -plane where they form weak complexes with surface hydroxyls on oxides; other ions, such as Pb^{2+} or SeO_3^{2-} can be assigned to either the α - or β -plane depending on the type of surface complex which is postulated (i.e., inner-sphere or ion-pair, respectively). Because of the charge-potential relationships characteristic of each interfacial configuration, one data set will yield a different surface complexation constant for each model type used.

For example, consider the interaction of a metal ion, Me^{2+} , with a protonated particle surface site. Assuming that MeOH^+ is the only species of Me(II) sorbing, there are two possible monodentate surface complexes for consideration:

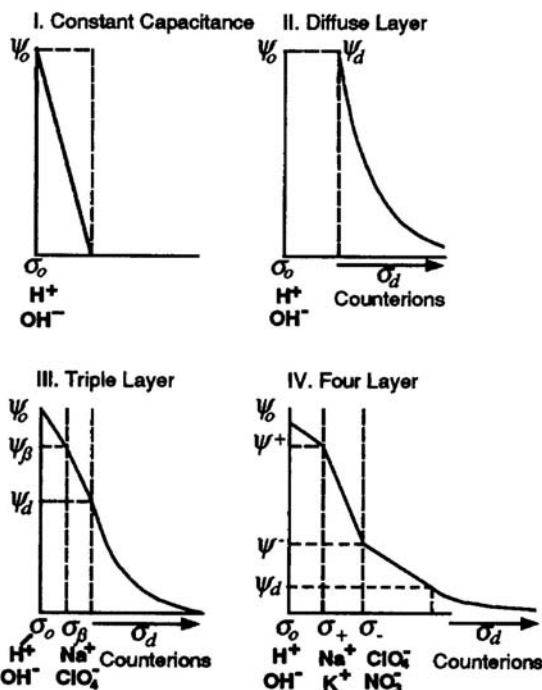
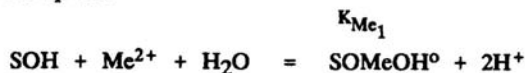
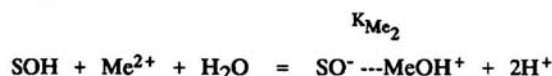


Fig. 6-51. Schematic illustration of interfacial configurations of four surface interaction models [from Davis and Kent, 1990]. The decay of potential with distance from the surface is drawn for surfaces immersed in solutions composed of simple electrolytes and at a pH other than the pH_{pzc} . In each case, the interface is conceptualized as consisting of a series of capacitors whose capacitances must be specified as a model parameter. The constant capacitance model contains one capacitor, the triple-layer model has two and the four-layer model, three. Expressions describing the relationship between charge and potential are based on the assumption that potential decays linearly with the distance between charged planes. The charge of the interface taken as a whole must obey conservation of charge. For example, in the case of the triple-layer model: $\sigma_\alpha + \sigma_\beta + \sigma_d = 0$.

Inner sphere:



Ion pair:



The equilibrium expressions corresponding to these postulated surface reactions, using the Triple-Layer Model interfacial configuration (Figure 6-51), are:

$$K_{\text{Me}_1} = \frac{[\text{SOMeOH}^0][\text{H}^+]^2}{[\text{SOH}][\text{Me}^{2+}]}$$

$$K_{\text{Me}_2} = \frac{[\text{SO}^- \cdots \text{MeOH}^+][\text{H}^+]^2}{[\text{SOH}][\text{Me}^{2+}]} \exp \left(\frac{F(\Psi_\beta - \Psi_o)}{RT} \right)$$

where Ψ_o and Ψ_β represent potentials at the surface and β planes, respectively, and F is the Faraday constant. In both cases, the empirically-determined concentration ratios are identical but the values of the intrinsic binding constants are highly dependent on the assumed molecular configuration. The exponential term in the mass-action expression for the ion-pair complex can be considered to be equal to the ratio of activity coefficients for the charged surface species. There is no correction for the inner-sphere surface complex, SOMeOH^0 , because the complex is uncharged.

It should be pointed out, also, that despite differences in self-consistent model parameters among the various models, all of the models are equally capable of reproducing a particular set of titration and sorption data [Westall and Hohl, 1980].

The complexity of natural materials, the variety of techniques used for particle characterization and the refinement of surface complexation models has led to the establishment of a multitude of inconsistent data sets. To counter this, Dzombak and Morel [1990] recently provided a self-consistent, validated data base for ferri-hydrate based on a modified form of the Diffuse Double Layer Model. This treatise is an excellent first step in providing aquatic surface chemistry with a much needed benchmark.

4. Surface Chemistry in Application

The power of the surface complexation approach is not in its predictive capability for natural systems, which is thus far minimal, but in its providing a theoretical framework for interpreting observations of trace element behavior. Surface complexation theory, and the body of experimental work supporting its basic tenets, provides a

direct linkage between solution-phase reactions and the role of particles in regulating the composition of water. It provides, for example, a rationale for understanding differences in trace element scavenging residence times in oceanic systems [Whitfield and Turner, 1987], the toxicity of trace elements to phytoplankton [Kuwabara et al., 1986] and chemical controls on particle coagulation rates [Liang, 1988]. In its present form, however, surface complexation theory, does not provide a means for understanding many interactive effects. These effects include the competition of ions for particle surface sites [Balistrieri and Chao, 1990], changes to interfacial environments from interacting particles [Prieve and Ruckenstein, 1978], and surface site heterogeneity [Zachara et al., 1989; Benjamin and Leckie, 1981]. Furthermore, it is likely that minerals which are part of mineral assemblages will not have the same surface chemical properties while in the assemblages, that they have in monomineralic systems [Anderson and Benjamin, 1990; Honeyman, 1984]. Finally, surface chemical models provide estimates of the distribution of chemical species at equilibrium. While evidence exists that metal ion sorption on monomineralic surfaces in simple electrolyte solution is rapid, on the order of milliseconds [Yasunaga and Ikeda, 1986], slow coordination reactions [Hering and Morel, 1989] or mass transport limitations [Jannasch et al., 1988; Csányi, 1986] may dramatically hinder the approach of more complicated systems to chemical equilibrium.

5. The Role of Colloidal Material in Marine Chemistry

In very broad terms, the oceanic water column contains three pools of trace-metal binding ligands: 1) macroparticles (that material a few tenths of a micron in size or larger, including marine snow and fecal matter); 2) colloids; and 3) those ligands which are truly dissolved. Not only does the nature of these ligands change spatially and with time but there is an exchange of material between these ligand pools, as well.

As described earlier, one of the basic requirements for the application of surface complexation theory is the accurate identification of chemical nature and distribution of particle-associated ligands. Until quite recently, discussions of the role of particles in regulating the composition of natural waters focussed on particles of relatively large dimension, i.e., a few microns in size and larger [Nozaki et al., 1987; Bacon et al., 1985]. There is accumulating evidence, however, that colloidal material represents a significant pool of trace element-binding ligands and that colloids may have a major impact on the distribution and fate of many particle

reactive elements [Moran and Moore, 1989]. It is important to emphasize that the "problem" of colloids is twofold. First, there are questions surrounding the identification (i.e., speciation) of colloidal material. Second, colloidal material appears to control, through its physical behavior, biogeochemical pathways of sorbed elements.

5.1. Evidence For the Importance of Colloids in the Mobility of Trace Elements

Our understanding of the role that colloids play in the geochemical life of trace elements is largely based on circumstantial evidence, although the role of submicron-sized particles in affecting the behavior of particle-reactive solutes has long been recognized. Colloid transport through porous and fractured media has been described by McDowell-Boyer et al. [1986] and Degueldre et al. [1989], respectively, in surface waters by Buffle [1987] and McCave [1984], and the literature on the formation and properties of radiocolloidal dispersions summarized by Kepak [1977]. Evidence for the importance of colloids in oceanic systems is only now emerging.

Buddemeier and Hunt [1988] studied radionuclide transport in groundwaters pumped from a nuclear bomb test cavity and found that the transition and lanthanide radionuclides, which moved considerably further than expected from ^3H and other conservative species, were essentially all associated with the less than $0.2\ \mu\text{m}$ particle fraction. Sheppard et al. [1980] concluded that much of the mobility of radionuclides in soil waters is probably due to soil constituents in the 2 to 5 nm range. Recently, Penrose and co-workers [1990] convincingly showed that colloidal material, most likely in the form of colloidal organic carbon, provided for the sub-surface transport of plutonium. Niven and Moore [1988] examined the partitioning of ^{234}Th among dissolved, colloidal and particulate fractions and found that up to 64 percent of the total ^{234}Th was associated with the colloidal (1 nm to $0.2\ \mu\text{m}$) size fraction. According to Baskaran et al. [1990], 25 to 75% of natural ^{234}Th in Gulf of Mexico water is found in the colloidal fraction. Moran and Moore [1989] estimated that colloidal material exists at about twice the mass concentration of macroparticulate material. Orlandini et al. [1990] found in their study of an oligotrophic lake that submicron colloidal material can dominate the behavior of actinides. Nash and Choppin [1980] estimated that in natural waters at $0.1\ \text{mg L}^{-1}$ DOC [humate concentration = (Hu) = $4 \times 10^{-7}\ \text{eq L}^{-1}$] the ratio of $(\text{Th-Hu})/(\text{Th}_{\text{diss}})$ would be about 4×10^{10} ,

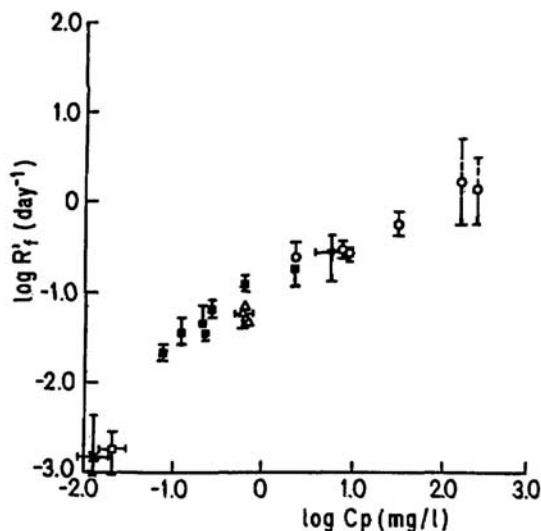


Fig. 6-52. Log of the scavenging rate constant, R'_f , versus the log filterable particle concentration, C_p . R'_f was calculated using oceanographic data from the literature [Honeyman et al., 1988, and data sources cited therein] using the following expression

$$R'_f = \log \left[(R_r + \lambda_{234} + \lambda_p) \left(\frac{A_{\text{Th part}}}{A_{\text{Th diss}}} \right) \right]$$

where R_r is a "desorption" rate constant (assuming $0.007\ \text{d}^{-1}$) for the appearance of Th in the filter-passing fraction of bulk solution and λ_{234} and λ_p are the ^{234}Th decay ($= \ln 2 / 24.1$ days) and particle removal rate constants, respectively, and A represents thorium activity.

suggesting that truly-dissolved thorium is unlikely when macromolecular DOC is present. Sequential extraction and ultrafiltration experiments by Santschi et al. [1983, 1987] have shown that radioisotopes of particle reactive elements are involved in the dynamic cycles of coagulation and disaggregation of macroparticles and colloids in the water column of coastal marine ecosystems; and Buchholtz et al. [1986] demonstrated the aggregation effect of colloidal radionuclides in laboratory batch experiments with marine sediments. Buffle and co-workers [Buffle, 1987, and references therein] have documented trace metal associations with colloidal material.

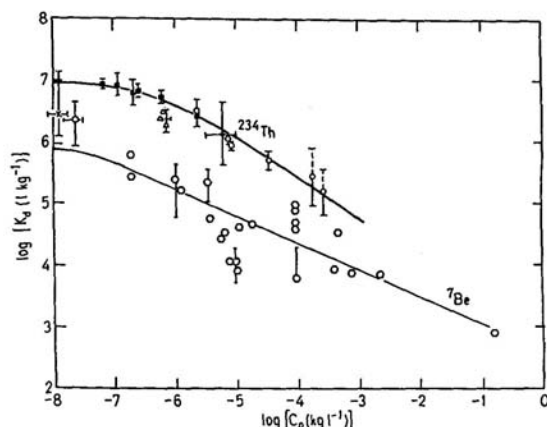


Fig. 6-53. $\log K_d$ versus $\log C_p$ [from Honeyman and Santschi, 1988]. Refer to Honeyman et al. [1988] and Honeyman and Santschi [1988] for sources of data. Physico-chemical theory indicates that the intensity of sorption (represented by K_d) should be independent of the ligand concentration (i.e., C_p). This is not observed in many cases. A postulated cause of the "particle concentration effect" is the presence of trace element sorbing colloids in the operationally defined "dissolved" fraction [Morel and Gschwend, 1987]. In other words, it is an artifact of incomplete phase separation.

5.2. Kinetic and Equilibrium Effects of Colloidal Material on Trace Element Behavior

Colloidal material affects our ability to describe trace element behavior for two reasons: 1) it is a large pool of trace element binding ligands which are very difficult to accurately characterize; 2) while often operationally considered as part of the "dissolved" fraction, trace elements associated with colloids will likely have a physico-chemical behavior different from truly dissolved species of the trace element; furthermore, it is likely that there is a significant, albeit slow, transfer of material between the colloid and macroparticle pools.

Thorium associated with colloidal material and operationally considered part of the "dissolved" (i.e., filter-passing) fraction has been implicated [Honeyman and Santschi, 1989] in producing: 1) scavenging rate constants which are relatively small in magnitude and which increase value with particle concentration and 2) the so-called "particle-concentration effect".

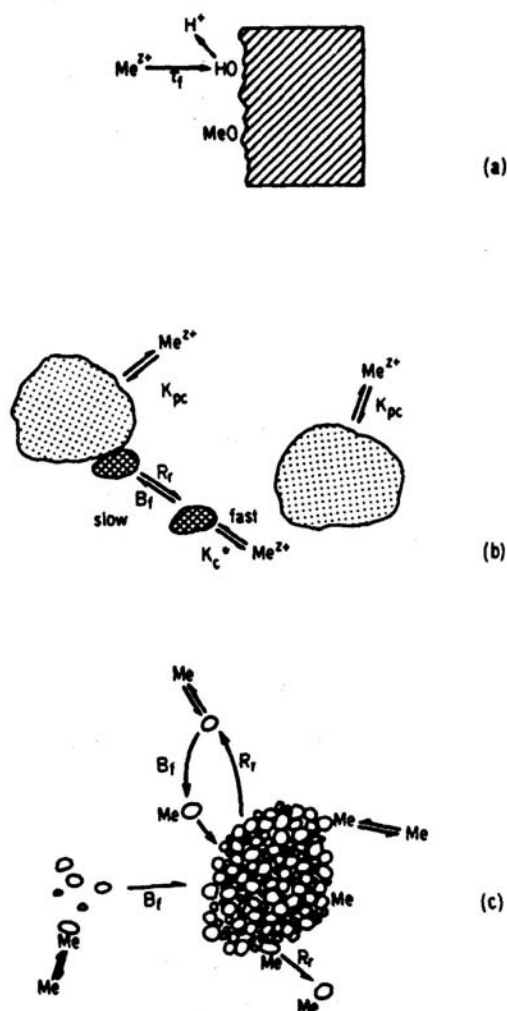


Fig. 6-54. Schematic of colloidal pumping model: coagulation coupled to adsorption [Honeyman and Santschi, 1989]. a) Rapid sorption of trace elements onto particle surfaces. Formation of surface complexes is rapid compared to rates of particle-particle interactions. K_{pc} and K_c^* represent conditional sorption constants. b) Slower aggregation, B_f , of colloids with larger particles. Colloidal material includes organic macromolecules, mineral fragments and condensation nuclei. c) Natural particle clusters most likely contain materials of varied size, history and composition.

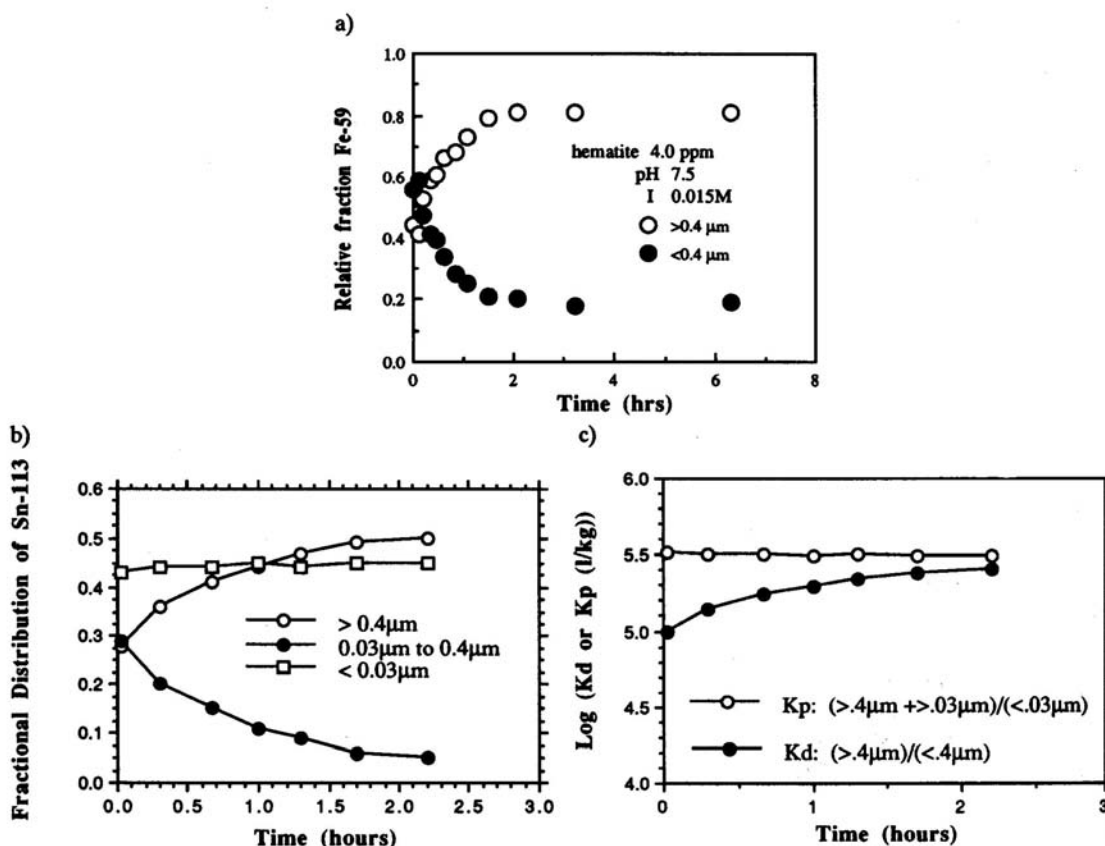


Fig. 6-55. a) Relative amount of $0.25 \mu\text{m}$ ^{59}Fe -labelled hematite in fractions of bulk solution passing and retained by $0.4 \mu\text{m}$ Nuclepore filters, as a function of time. b) The effect of particle aggregation on the distribution of ^{113}Sn between the colloidal ($0.03 \mu\text{m}$ to $0.4 \mu\text{m}$), particulate (greater than $0.4 \mu\text{m}$ size fractions) and dissolved (less than $0.03 \mu\text{m}$) pools with time. Sorptive equilibrium is rapidly attained (note that the dissolved concentration is constant); Sn is transferred between the particle pools by coagulation. c) K_d is smaller in value than K_p because the $0.4 \mu\text{m}$ filter-passing fraction, the operationally defined "dissolved" fraction in the K_d determination contains, colloidal ($0.03 \mu\text{m}$ to $0.4 \mu\text{m}$) particles. K_p , in contrast, is based on the ratio of sorbed to truly dissolved Sn, its value is time-independent.

Examples of these effects of colloidal material on the behavior of thorium isotopes, and by extension other particle-reactive elements, are shown in Figures 6-52 and 6-53.

Figure 6-54 presents the elements of the colloidal-pumping model described by Honeyman and Santschi [1989]. The conceptual model attempts to couple two characteristics of colloidal material: 1) its participation in chemical reactions; 2) its aggregation with, or transfer to, large particles. When sorption of trace elements onto colloids is rapid (Figure 6-54a) compared to time scales for particle coagulation, the transfer of colloid-sorbed

elements to the macroparticle (filter-retained) pool is limited by particle aggregation rates (Figure 6-54b). In this figure large particles are distinguished from colloids by the comparative ease at which they can be separated from bulk solution, for example, with relatively large pore sized filters ($0.45 \mu\text{m}$). A critical element is the explicit consideration of complexes between trace elements and colloidal (i.e., filter-passing) material. The transport of scavenged trace elements to their final repository on the ocean floor is likely circuitous as the material making up particles periodically cycles through various pools as the consequence of aggregation,

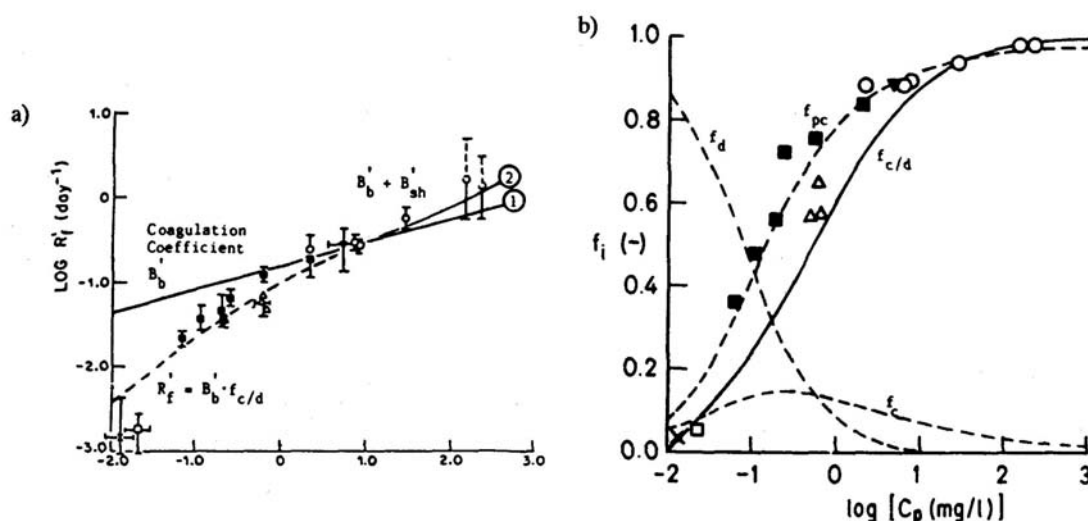


Fig. 6-56. Coupling Farley and Morel's [1986] sedimentation model with sorption and its application to oceanic Th scavenging. [from Honeyman and Santschi, 1989]. a) Data are the same as shown in Figure 6-52. Critical parameter values: Brownian collision efficiency factor, $\alpha_b = 0.5$, particle density, $\rho_p = 2.5 \text{ gcm}^{-3}$ and mean depth, $h = 6 \text{ m}$ (the average depth of a water column that a sorbed ^{234}Th atom will be in contact with before decay). Solid lines represent the scavenging rate constant when a trace element or radionuclide in the filter-passing fraction is completely associated with colloidal particles (i.e., K_c^* is "infinite"): 1) Brownian coagulation; 2) Brownian + shear coagulation. In other words, only particle-particle interactions are considered. The dashed line includes the effect of Th solution/colloid partitioning on scavenging rate with $\log K_c = 10^7$. b) Calculated distribution of Th between dissolved, f_d , colloidal, f_c , and filter-retained, f_{pc} , fractions. $f_{c/d}$ represents the portion of the bulk solution passing the filter but which is associated with colloids. Note that as $f_{c/d}$ approaches 1, that is, when little truly dissolved Th exists, that the scavenging rate constant approaches the maximum rate of coagulation + sedimentation. Actual values of f_{pc} correspond to the data in Figure 6-52.

disaggregation and remineralization processes.

Laboratory evidence demonstrating the validity of colloidal pumping is shown in Figure 6-55 [Honeyman and Santschi, in press]. Figure 6-55a shows the transfer of $0.25 \mu\text{m}$ ^{59}Fe -labeled hematite particles between filter-passing and filter-retained fractions of bulk solution. This transfer occurs because singlet particles ($0.25 \mu\text{m}$) pass the $0.4 \mu\text{m}$ filter while aggregates of doublet size and larger are retained. As the particle size distribution of the initially homodisperse system evolves, total particle mass shifts from the pool of singlets to larger and larger aggregates.

The addition of a sorbing element (Sn as ^{113}Sn) shows the effect of particle aggregation (followed simultaneously by ^{59}Fe activity) on Sn transfer to the filter-retained particle pool (Figure 6-55b). Note that truly-dissolved Sn, represented by the less than $0.03 \mu\text{m}$ portion of bulk solution, remains constant, and that

sorptive equilibrium is rapidly attained. Thus, the observed kinetic effect, the transfer of ^{113}Sn between particle pools, is the consequence of particle aggregation. When a clear distinction between sorbed and dissolved is made, the conditional binding coefficient, K_p , is constant in value while the operational coefficient, K_d , increases in value with time, approaching K_p as the fraction of colloidal Sn decreases (Figure 6-55c).

Figure 6-55 illustrates a critical point. While the chemical characterization of colloidal material, and knowledge of the extent of its interaction with trace elements, is important, it is also crucial to understand the physical behavior of colloids. These two aspects of the colloid "problem" are reiterated in Figure 6-56 [Honeyman and Santschi, 1989]. In this case, thorium sorption onto colloidal material and the removal of particle mass (and sorbed thorium) through coagulation-sedimentation are invoked as the primary rate-

controlling processes in trace element scavenging. The rate of thorium scavenging depends on 1) the rate of particle aggregation leading to sedimentation and 2) the fraction of thorium associated with colloidal material (i.e., the chemical speciation of thorium and colloidal material).

6. Summary

Surface chemical theory has provided a sound framework for aiding in the interpretation of observations of trace element behavior in many natural systems. Its main contributions have been: 1) systematizing the way in which particles are viewed as chemical species whose surface-bound ligands are available for complexing trace elements and 2) providing a linkage between solution chemistry and the role of particle surfaces. However, several research areas need particular attention. These include: 1) studies of particle assemblages rather than the current focus on monomineralic systems; 2) development of methodologies for quantifying components of the colloid pool; 3) striving for the development of a consensus in configurations for interfacial models and in representations of particles as ligands; and 4) greater effort in understanding the physical behavior of particles.

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