Organics in water-rock interactions

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SUMMARY AND CONCLUSSIONS

We have shown in this paper numerous examples of the role of OM in water-rock interactions. These interactions not only determine the fate of dissolved metals and OM, but also may alter the course and/or progress of different non organic reactions (e.g., mineral dissolution and precipitation), and are of interest in a variety of scientific and engineering disciplines. The literature on the interactions between a large variety of OM and many minerals includes thousands of publications. Naturally, the literature neither gives an equal representation to all minerals, nor a representation that reflects their natural abundances. Moreover, some minerals are overrepresented in the literature covering one type of interactions and underrepresented in other. For example, we found more papers that deal with adsorption on surfaces of clay minerals than on those of any other group of minerals, while we did not find papers on the effect of OM on clay precipitation. The scarcity of the latter studies is worth noting, as clay precipitation often occurs in organic-rich environment. This scarcity reflects the general deficiency in studies of the role of precipitation in natural weathering (Chu, 2009). As mentioned before, the majority of the papers that discuss adsorption deal with clays and oxides. A significant literature on adsorption of OM on carbonates exists as well. Studies of OM adsorption on sulfate and feldspars are relatively rare. Much was published on the effect of OM on dissolution of feldspars and quartz, while fewer publications were devoted to studies of the effect of OM on dissolution of clay and carbonates, and even less of sulfates. Publications studying the effect of OM on precipitation were almost entirely devoted to sulfate and carbonates.

Sorption of OM on mineral surfaces was widely studied, as it influences the fate of both OM and of metals in the environment. Adsorption affects the transport and reactivity of NOM as well as pollutants. Adsorbed OM can mask the properties of the underlying solid and present a surface with very different physicochemical properties. In addition, adsorption affects the reactivity of the mineral surfaces and therefore the dissolution and precipitation rates of the minerals. OM may be sorbed to the mineral via *chemisorption* (e.g., ligand exchange, anion exchange, cation exchange, and cation bridge) or via *physical adsorption* (e.g., Van der Waals interaction and hydrophobic effects). Often, the OM is initially sorbed onto the surface via one mechanism (e.g., Van der Waals interaction), and thereafter due to its proximity to the surface, the OM is chemisorbed via another mechanism (e.g., ligand exchange). It was shown that this initial adsorption is of time scales of seconds and minutes and depends on the environment conditions (e.g., pH). On the other hand, the chemisorption of the compound may be of longer time scale (hours) and therefore the rate of the adsorption may become significant in processes that are affected by it (e.g., dissolution and precipitation of minerals).

It is important to characterize the type of adsorption bond and coordinative structure between adsorbate and adsorbent. The organic ligand may be connected to one or more atoms on the mineral surface (i.e., mono/multinuclear). With each of these atoms, they may form one or more bonds (i.e., mono/multidentate). More than one type of complex may coexist and as we noted above, the coordination structure(s) of the adsorbed OM may change with time. Unfortunately, information on the characteristic of the bonds between a specific OM and a specific mineral is rare.

The relative charges of the functional groups of the OM and the mineral surface play an important role in adsorption. Regardless the sorption mechanism, the OM must be close to the mineral surface in order that sorption will take place. Therefore, electrostatic attraction/repulsion between the OM and the mineral surface affect sorption. Hence, sorption is influenced by the charges of the mineral surface and OM functional groups as well as the solution chemistry that affects these charges. It is important to note that although charges play an important role in sorption, often sorption may be more significant when the surfaces are less charged. For example, it was shown that as pH decreases, and both NOM acidic functional groups and surface charge of minerals become more protonated and therefore less negative, hydrophobic effects become more significant in driving organic molecules toward the mineral surface, which in turn, can increase the possibility for adsorption via other mechanisms.

Preferential adsorption of large organic molecules over small molecules was observed in many studies. This preferential adsorption was explained by the reduction of solubility with increasing size (i.e., Traube's Rule). Adsorption is also strongly influenced by the three dimensional structure of the OM. As a result, the adsorption of different isomers having the same chemical formula may be completely different. It was shown that ortho-positioned carboxyls and/or hydroxyls adsorbed more than the para- and meta- isomers. Such steric effects are important, but were poorly studied.

Both dissolution and precipitation of minerals are affected by the presence of OM. These effects can be due to complexation of OM with dissolved metals in solution or OM adsorption on the mineral surface. Interestingly, the different studies show that the common effects of OM are to catalyze mineral dissolution (mainly silicates) and to inhibit mineral dissolution (mainly carbonates and sulfates). The degree of saturation of the solution with respect to a mineral depends on the concentrations in solution of the lattice ions. If the concentration of any of these ions is reduced due to interactions with OM, the solution becomes more undersaturated or less supersaturated, and as a result dissolution may be faster while precipitation will be slower, respectively. One difference between dissolution and precipitation is the existence of a *dissolution plateau* (i.e., when dissolution occurs far enough from equilibrium, the degree of saturation does not affect the dissolution rate). As a result, this effect of OM on dissolution is effective only under close-to-equilibrium conditions. In contrast, there is no *"precipitation plateau"*, and precipitation rate always depends on saturation state and therefore complexation in solution of the lattice ions retards precipitation both under close-to-equilibrium and under far-from-equilibrium conditions. It is important to note that due to the inhibition effect of Al^{3+} on the dissolution of some aluminosilicates, OM complexes with Al^{3+} may enhance the dissolution rate of these minerals even at the *dissolution plateau* conditions.

Another difference between dissolution and precipitation reaction is the nucleation process. Nucleation is strongly dependent on the mineral-solution interfacial tension which is influenced by OM serving as surfactants, as well as the OM valance. These dependencies of the interfacial tension were shown to result in both promotion and retardation of nucleation kinetics.

Detailed examination of the literature data indicates that most of the experimental observations of OM effects on mineral dissolution and precipitation should be related to adsorption of OM on the surface of the minerals rather than to changes in solution chemistry. Therefore, one should examine separately each specific mineral – specific OM interaction. Whereas in some cases OM adsorption catalyzed dissolution of minerals, in othesr it may inhibit dissolution by adsorbing to reactive sites on the mineral surface and blocking them. This inhibiting effect on mineral dissolution was mainly reported for carbonate although few studies showed such inhibitory effects on silicates as well. Oppositely, catalysis by OM was mainly reported for silicates and oxides, while only few studies discussed catalysis of carbonate dissolution.

A simple ligand-promoted reaction mechanism consists of fast adsorption of the organic ion on the mineral surface followed by a slow catalyst-mediated hydrolysis step, which is the rate-determining step. It is generally agreed that organic ligands preferentially adsorb to aluminol sites of aluminosilicates and Al-oxides, Ca sites in carbonates and sulfates and probably Fe surface sites in iron rich minerals. The hydrolysis rate depends on the surface concentration of the adsorbed species, which depends both on the concentration of the ligand in solution and the surface concentration of the active site. Therefore, the increase in dissolution rate as a function of Al content of the mineral is another indication that ligand attack (as well as proton attack) occurs predominantly on Al surface sites of aluminosilicates. Correspondingly, it was found that OM that forms strong complexes with Al^{3+} in solution tends to form complexes with Al sites on silicates and oxides surfaces and therefore has a stronger catalytic effect. From the existing literature it is not possible to determine whether this stronger catalytic effect is because the stronger ligand forms more surface complexes than the weaker ligand or because the surface complexes of the former hydrolyzed faster than those of the latter. The similarity between the rate constants of oxalate attack, bioxalate attack, and proton attack on feldspar as well as the similarity between activation energies of proton-promoted and oxalate-promoted dissolution of kaolinite indicates that the magnitude of the rates of each of these reaction mechanisms is determined by the surface concentration of the various adsorbed species and not necessarily by the rate of the hydrolysis.

In order for an adsorbed OM to catalyze or inhibit dissolution it should form a strong complex with a metal ion on the surface. In the case of catalysis, the complexation weakens the strength of the bond between the metal and the bulk mineral, resulting in the release of the OM and the ion to solution. In the case of inhibition, this bond should remain strong, so the OM would remain on the surface and block the ion from being removed. Commonly, the same surface sites and faces on which crystal tends to grow under oversaturation conditions are the sites in which dissolution occurs at undersaturation conditions. It is therefore reasonable to assume that OM which effectively inhibits dissolution would inhibit precipitation as well. For catalysis, this is not the case, since adsorbed OM that weakens the bond strength is not expected to catalyze precipitation.

In order for an OM inhibitor to effectively inhibit the precipitation of a mineral, a dimensional stereochemical fit between the polar group of the inhibitor and the intercationic or interanionic distances is needed. When such a structural fit exists, the OM can also act as a template or microsubstrate and promote nucleation rather than inhibit it. Indeed, it was found that some organic compounds that accelerate mineral precipitation when present at low concentrations become an effective inhibitor at higher concentrations.

A comprehensive review of the literature indicates that the common effect of OM on a wide range of minerals is to inhibit precipitation rather than to catalyze it. It is possible that this observation represent a bias of the literature and not a real effect. The Earth science literature paid little attention to low temperature precipitation of non-carbonates in general and the effect of OM on precipitation in particular. The engineering literature is motivated mainly by scale deposits and therefore tends to study inhibition of its precipitation and catalysis of its dissolution.

Bearing in mind that dissolution and precipitation are affected by OM adsorption, it is surprising that only few studies on the effect of OM on dissolution and precipitation have measured the adsorption isotherm of the OM. Taking into account the numerous published papers on OM adsorption, this seems to be a niggling point. However, the effect of sorption on dissolution and precipitation depends on the sorption mechanism (e.g., *physical adsorption* does not enhance dissolution rate). Even if the adsorption of a given compound is studied, it is not trivial to characterize the mechanisms and, more important, the relative contribution of each of them to the overall adsorption. Moreover, sorption, dissolution and precipitation depend on both the characteristics of the mineral surface and the environmental conditions, and therefore it is complicated to combine adsorption experiments from one laboratory to dissolution or precipitation experiments that were conducted at another laboratory.

Even when the adsorption isotherms are conducted at the same laboratory as the dissolution/precipitation experiments, it is not straight forward to incorporate their results. One important limitation is related to the typical duration of the experiments. As sorption is fast, adsorption experiments are usually much shorter than dissolution experiments. However, few studies showed that the coordination structures of the adsorbed OM may change with time. Therefore, it is possible that OM adsorption during dissolution experiments is different than that during the adsorption experiments. Unfortunately, monitoring sorption during dissolution experiments is not an easy task. One problem is that changes in OM concentration due to decomposition (which may be enhanced in the presence of a mineral) may be more pronounced than that due to adsorption.

The kinetics of adsorption is generally considered to be fast in comparison with dissolution reactions. Therefore, the adsorption reactions are usually regarded as being in equilibrium. For nucleation inhibition, adsorption kinetics is important, as adsorption must take place before stable nuclei are formed.

The importance of OM-water-rock interactions varied in different processes and environments. Adsorption of OM on mineral surfaces, ternary adsorption of OM and metals and complexation between OM and dissolved metals all have a very important role in controlling the fate of both OM and of metals in the environment. The effect of OM on dissolution of minerals in nature seems to be of less significant. The analysis of literature data indicates that the effect of oxalate on silicate dissolution is generally small (median enhancement factor of 2), and is much less than the between-laboratories agreement factor of 5. The possible effects of OM on precipitation of minerals in nature haven't been properly studied, and therefore, we can not estimate their importance. For industrial applications, the effect of organic antiscalants is most significant. Effective antiscalnts can decrease the nucleation rates by orders of magnitude and thereby achieving a "total inhibition". OM has important catalytic effects on dissolution of scales as well. However, much less scientific effort was devoted to such application, as it is more economical and efficient to control scale by inhibiting its nucleation rather than by dissolving it. OM may also be important in formation of surface coating that protect buildings and monuments from damaging effects of weathering. However, the stability of such coatings over time is still in question.