Reverse Weathering, Clay Mineral Formation, and Oceanic Element Cycles

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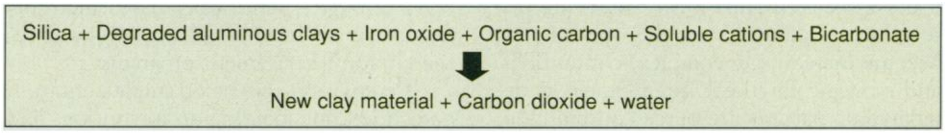
Reverse weathering as a sink of oceanic elements was proposed 30 years ago (*1*). According to this hypothesis, the formation of clay minerals in marine sediments leads to the removal of soluble cations and the release of acidity (CO_2), the opposite of the weathering reaction. Conclusive tests of this hypothesis have been difficult to make because the required quantity of authigenic (newly formed) minerals is small and thus extremely difficult to detect in deltaic sediments dominated by clays derived from continental weathering. On page 614 of this issue, Michalopoulos and Aller (*2*) demonstrate the rapid formation of aluminosilicate ("clay") minerals in marine sediments of the Amazon delta using an elegant approach. Rather than attempting to detect naturally occurring products of reverse weathering, the investigators formed their own. They affixed seed materials (including quartz grains, glass beads, and quartz grains coated with iron oxide) onto acrylic slides and inserted then into jars of Amazon sediment. Finding that clay minerals readily form, they go on to calculate that clay mineral formation processes throughout Amazon shelf sediments could consume about 10% of the present global riverine K^+ flux. The muddy deltas of tropical river systems receive about 60% of the continental river particulate flux to the oceans. If these systems have mineral formation characteristics similar to that of the Amazon, then authigenic clay mineral reactions have important implications for problems concerning the global geochemical balance of several major and minor elements.

The dissolved constituents that enter the ocean by way of rivers, ground-water flow, and hydrothermal reaction at oceanic ridge sites eventually must precipitate from the oceans or be recycled back to the continents through the atmosphere. In 1966, Mackenzie and Garrels (*1*), inspired by Sillen's paper (*3*) on the physical chemistry of seawater, calculated a mass balance for river water in which the major dissolved constituents of rivers were precipitated from the oceans as common mineral phases found in marine sediments. So that all of the constituents were balanced, part of the Na, Mg, K, and SiO_2 had to be removed by reaction with solid "degraded" aluminosilicate minerals (clays) of the suspended load of streams to make authigenic clay minerals typical of those found in muddy marine sediments. Furthermore, Mackenzie and Garrels pointed out that if the CO_2 consumed in the weathering processes producing dissolved constituents and degraded clays for riverine transport to the oceans is not returned to the atmosphere by depositional processes, there will be a decrease in the atmospheric concentration of CO_2. Seawater, because of the accumulation of bicarbonate ion from chemical weathering, would become alkaline. Any net drain on atmospheric CO_2 would arise because of failure of reversal of the reactions of silicate weathering. The depositional reactions were termed reverse weathering.



New clays for old. Generalized schematic reverse weathering reaction leading to the formation of clay minerals in Amazon delta muddy sediments. Notice that this reaction leads to the removal of soluble cations and the release of acidity (CO_2). This reaction is the opposite of the chemical weathering process.

We now know that the process envisioned by Mackenzie and Garrels is far more complex. Since their papers, discovery of large-scale hydrothermal cycling of elements at mid-ocean ridges (*4*) has displaced the site of reverse weathering to these environments and, for many scientists, made sedimentary sinks for certain dissolved constituents in the oceans unnecessary. This is despite the fact that problems concerning the river-ocean mass balance still exist and can be resolved if early diagenetic formation of clays is a viable process (*5*).

Michalopoulos and Aller's paper has reopened the Pandora's box of reverse weathering in sediments (*2*). These authors observed the formation of significant quantities of K-Fe-Mg clay minerals precipitated on naturally occurring substrates incubated in unaltered, anoxic, Amazon delta sediments for 12 to 18 months at 28°C. Phases formed both between substrate mineral grains as direct precipitates from solution (cements) and by alteration of FeOOH-rich coatings on substrate grains (a process of reconstitution). Painstaking scanning and transmission electron, energy-dispersive system, x-ray powder diffraction, and wave-dispersive electron microprobe analyses support the authors' conclusion that the dominant phase formed was a K-Fe-rich clay of 9.9 Å, a mica-type clay mineral. The incubation experiments demonstrate the potential for the rapid formation of clay minerals in Amazon delta muddy sediments and their likely structure and average composition. A variety of field evidence (*6*) suggests that clay minerals consistent with the composition of the experimental precipitates do indeed form in Amazon delta sediments. The formation or reconstitution of clay minerals in these sediments is responsible for the uptake of about 7% of the global riverine supply of fluorine to the ocean and about 10% of the potassium input.

The formation of clay mineral precipitates and reconstitution of FeOOH coatings in Amazon delta sediments require a source of Al and Si. The Al source may be the dissolution of relatively unstable aluminous phases typical of tropical weathering regimes or may come from the dissolution of biogenic, diatom-derived silica that has scavenged Al and been transported to the sediment. Whatever the case, Al does not act as an immobile component in Amazon delta muddy sediments and takes part in rapid dissolution-precipitation reactions involving formation of authigenic clay minerals. This finding runs counter to current scientific dogma claiming that Al is an immobile component in low-temperature environments. It appears that the major limitation on the amounts of clay minerals formed in Amazon delta sediments is the supply of reactive silica derived from diatom dissolution (perhaps also from degraded aluminosilicates). If silica does control the amount of newly formed clay mineral, then authigenic clay formation becomes a sink for biogenic silica in the ocean, as originally suggested by Mackenzie and Garrels (*1*).

The net reaction scheme proposed by Michalopoulos and Aller for the formation of new clay mineral phases in Amazon delta sediment (see figure) is remarkably similar

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to that proposed for the formation of authigenic clay minerals (nontronite and illite-smectite) in marine muddy sediments of Kaneohe Bay, Hawaii (*7*) derived from tropical weathering of basalts. This implies that reverse weathering reactions similar to those proposed by Michalopoulos and Aller may be more characteristic of nearshore muddy sediments than indicated by studies in the early 1970s of sediments in temperate environments (*8*). If so, the large quantities of degraded tropical weathering products entering nearshore environments portend substantial formation of authigenic clay minerals. Mackenzie and Garrels (*1*) pointed out that only 7% of the mass of sediments accumulating on the sea floor needs to undergo diagensis (formation of new clay phases or reconstitution of detrital phases) to resolve the mass balance between rivers and oceans. However, before reverse weathering reactions can be viewed as a significant component of elemental cycling in the ocean, it must be demonstrated that these reactions have a global significance. To do so requires more studies of the kind carried out by Michalopoulos and Aller, particularly in muddy nearshore environments of the tropical environment.

What happens to the large quantities of degraded aluminosilicates transported to these environments by tropical rivers? They are not found in shallowly buried sediments, indicating their potential for taking part in early and rapid diagenetic reactions. It is very likely that the ultimate resolution of the geochemical balance for the ocean will involve hydrothermal and low-temperature alteration of the basaltic oceanic crust and sedimentary sinks for the major and minor elements, including the incorporation of elements in newly formed or reconstituted clay mineral phases.

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Metal-Carbon Bonds in Nature

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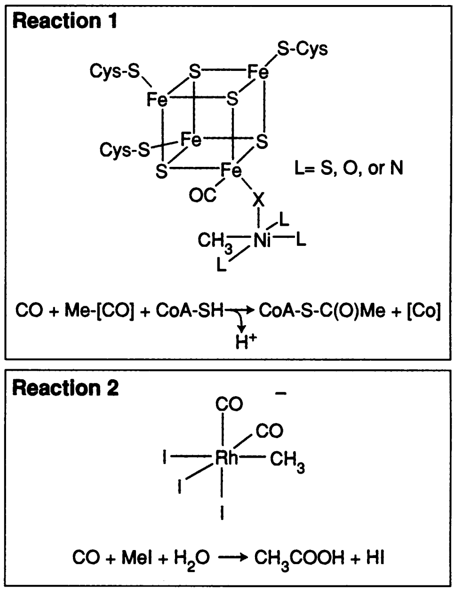
Synthetic organotransition-metal catalysts (species possessing a direct metal-carbon or metal-hydrogen bond) are frequently used in industrial processes to convert hydrocarbon fragments into industrially useful chemicals (*1*). Transition-metal alkyl ($M–CR_3$) species may, in many instances, play an important role as intermediates in these reactions. In contrast, biology tends to utilize CO_2 or CO to form metabolically useful compounds. There is, however, one biological system, which is fondly referred to as "nature's organometallic catalyst," namely vitamin B_{12} (*2*), that makes use of a $M–CR_3$ species. Vitamin B_{12} contains cobalt in a substituted corrin macrocycle (a flexible porphyrin relative) and contains an axial Co(III)–alkyl (CR_3). The macrocyclic environment imparts special properties to the cobalt center that allow it to function as nature's Grignard reagent (CR_3^- source), radical ($CR_3\bullet$ source), or Meerwein's reagent (CR_3^+ source). The reaction-type promoted by this site depends on the mechanism of Co–C bond cleavage. The accessibility of several different oxidation states (+1, +2, +3) allows the versatile behavior of this site. On page 628 of this issue, a report by Kumar *et al.* (*3*) presents strong evidence for the occurrence of a second organometallic intermediate in biology that consists of a reactive $Ni–CH_3$ fragment, which serves as a precursor to acetic acid through its reaction with CO and CoASH (acetyl-CoA synthase reaction **1**). Unlike vitamin B_{12}, the nickel ion in this enzyme, carbon monoxide dehydrogenase (CODH), is coupled to an iron-sulfur Fe_4S_4 cluster (Fig. 1).

Iron sulfur clusters are ubiquitous in nature, and analogs are accessible by means of synthetic methods (*4*, *5*). Up until the early 1980s, these clusters were thought to function solely as electron transfer and storage sites, delivering electrons to enzymes that promote substrate reduction (the most difficult being N_2 reduction to ammonia). Later, it was shown that clusters of this type can serve as enzyme active sites (such as Aconitase) and bind and activate substrate (*6*). Examples of Fe_4S_4 clusters linked to a more reactive substrate binding site M (*7*), by what is referred to as a bridging ligand X ($M–X–Fe_4S_4$), are found in an increasing number of biological systems [for instance, M= Fe(siroheme) in sulfite reductase] (*8*, *9*). If the two sites are chemically linked, they can communicate so that substrate binding at the M site triggers facile multielectron transfer, thereby avoiding toxic or unstable intermediates. In some cases the M site is incorporated into the cubane core (MFe_3S_4) in place of one of the irons (*10*).

With CODH (*4*, *11*) the properties (such as Mössbauer spectra) of the Fe_4S_4 core are not dramatically affected by the presence of the M = Ni site, suggesting that the nickel is bound externally to the cluster core. This led Lindahl, Ragsdale, and Münck to propose the cluster core structure shown in the figure (*12*). Synthetic modeling studies appear to support this structure (*13*). The identity of the bridging ligand X is unknown. Evidence for coupling between the Ni site and the Fe_4S_4 cluster derives from studies in which isotopic labels (^{61}Ni, ^{57}Fe, ^{13}CO) incorporated into the CO derivative perturbed the electron paramagnetic resonance (EPR) signal associated with this cluster site (*14*). Resonance Raman and infrared studies established that CO binds to one of the iron sites (*15*, *16*). Reaction of the CO-bound derivative with a methylated corrinoid (Me-[Co]) species results in methyl transfer to the nickel site with the formation of a CH_3-bound intermediate (see figure). Evidence



Proposed intermediates for the biological acetyl-CoA synthase reaction (reaction 1) and the Monsanto acetic acid process (reaction 2).

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