

Glossary of Terms Related to Metals and Natural Surfaces

Lewis acids and bases

Metals can be classified according to their hard and soft characteristics, based on the principle of hard and soft acids and bases (Pearson 1963, 1968).

Lewis acid – an electron pair acceptor.

All metal ions or atoms and most cations are Lewis acids and capable of accepting a pair of electrons from a Lewis base (anion). A metal that is a hard Lewis acid has a high positive oxidation state, small size, and low polarizability (e.g. potassium and calcium), while a metal that is a soft Lewis acid has a large size, low positive charge, and high electronegativity (e.g. copper and zinc). Most metals are soft or transition acids, meaning they have low positive charge and large size and form covalent bonds with ligands.

Lewis base – an electron pair donor. A hard Lewis base is an electron donor of low polarizability and high electronegativity (e.g. nitrate and sulfate), while a soft Lewis base is a donor of large size and high polarizability (e.g. iodide and cyanide) (Pearson 1963, 1968; Morris 1992; Sparks 2002).

Sorption terminology

Adsorption – the accumulation of a substance or material at the interface between a solid surface and a bathing solution.

Inner-sphere surface complex – No water molecule is present between the ion or molecule and the surface functional group to which it is bound, and the bonding is covalent or ionic. Inner-sphere complexes can be monodentate (metal is bonded to only one oxygen) or bidentate (metal is bonded to two oxygens) and mononuclear or binuclear. Inner-sphere complexation can increase, reduce, neutralize, or reverse the charge on the sorptive regardless of the original charge. Adsorption of ions via inner-sphere complexation can occur on a surface regardless of the original charge. Inner-sphere complexation is usually slower than outer-sphere complexation and is often not reversible.

Outer-sphere surface complex – A water molecule is present between the surface functional group and the bound ion or molecule (Sposito 1989). Outer-sphere complexes involve electrostatic coulombic interactions. Outer-sphere com-

plexation is usually a rapid process that is reversible, and adsorption occurs only on surfaces that are of opposite charge to the adsorbate.

Polymerization – the formation of small multinuclear inorganic species such as dimers or trimers on a surface.

Sorption – a general term that is used when the retention mechanism at a surface is unknown. Adsorption, surface precipitation, and polymerization are all examples of sorption.

Surface complex – The interaction of a surface functional group with an ion or molecule present in the soil solution can create a stable molecular entity called a surface complex. The overall reaction is referred to as surface complexation.

Surface functional group – a “chemically reactive molecular unit attached at the boundary of a solid with the reactive groups of the unit exposed to the soil solution” (Sposito 1984). Surface functional groups can be organic or inorganic molecular units. Organic functional groups are associated with humic substances (naturally occurring heterogeneous organic substances of high molecular weight and of brown to black color, i.e. humic and fulvic acids, and humin). The major organic functional groups are carboxyl [$R-C=O(-OH)$, where R is an aliphatic backbone] and phenolic ($Ar-OH$, where Ar is an aromatic ring) (Stevenson 1982; Sparks 2002). The major inorganic surface functional groups in soils are (1) the siloxane surface associated with the plane of oxygen atoms bound to the silica tetrahedral layer of a phyllosilicate (clay mineral) and (2) hydroxyl groups associated with the edges of inorganic minerals such as kaolinite, amorphous materials, and metal oxides and oxyhydroxides. Surface functional groups on metal oxide and oxyhydroxide, clay mineral, and organic matter surfaces play a significant role in metal sorption processes.

Surface precipitation – the formation of a three-dimensional phase product on a surface.

Meet the Authors



John Bargar, research scientist at the Stanford Synchrotron Radiation Laboratory since 1996,

received his BS from the Ohio State University (1990) and his PhD in geological and environmental sciences from Stanford University (1996). Bargar's research interests lie in the areas of geomicrobiology, low-temperature aqueous geochemistry, and mineral-water and membrane-water-interface geochemistry. His current research focuses on the structural chemistry and environmental reactivity of bacteriogenic minerals, with emphasis on elucidating their roles in the biogeochemical cycling of metals in the biosphere. He uses synchrotron-based scattering and spectroscopy techniques under in situ conditions.



Maxim I. Boyanov received a BSc and an MSc degree in physics from the University of Sofia and a

PhD in physics from the University of Notre Dame. In 2003, he joined the Molecular Environmental Science Group at Argonne National Laboratory as a postdoctoral researcher. His PhD work focused on using synchrotron X-ray techniques to study the molecular binding of dissolved metals to organic ligands, both on the surface and in solution. His current research aims at linking the molecular coordination of ferrous iron to its reactivity, which has implications for the biogeochemical cycling of iron and the removal of contaminants from the environment.



Michael F. Hochella Jr. is professor of geochemistry and mineralogy at Virginia Tech (USA). He received

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Shelly D. Kelly received her PhD from the University of Washington in 1999. She is currently an assistant physi-

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Kenneth M. Kemner obtained his PhD in physics at the University of Notre Dame in 1993. From

1993 to 1996 he was an NRC Post-Doctoral Fellow at the Naval Research Laboratory in Washington, DC. In 1996 he joined the Environmental Research Division at Argonne National Laboratory near Chicago, Illinois where he formed the Molecular Environmental Science Research Group, an integrated

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Ruben Kretzschmar is professor of soil chemistry in the Department of Environmental Sciences at the Swiss Federal Institute of Technology (ETH) in Zurich. He received his PhD in soil chemistry from

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Andrew Madden received his BS degree in geology at Michigan State University and his PhD at Virginia Tech where he worked with Mike Hochella in the Nano-Geoscience and Techno-

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David McNear received his BS and MS degrees from the Pennsylvania State University and currently is a graduate fellow with Dr. Donald Sparks at the University of Delaware. His research

interests include the biogeochemical processes occurring at the plant–water–soil interface and how these processes influence the mobility and bioavailability of heavy metals from geogenic and anthropogenic sources. His

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Edward O'Loughlin is a staff scientist in the Environmental Research Division at Argonne National Laboratory. He received his Bachelor's degree in biology from Cleveland State University

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Donald L. Sparks is S. Hallock du Pont Endowed Chair of Soil and Environmental Chemistry at the University of Delaware. His research focuses on the kinetics of soil chemical reactions and

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