Coordination chemistry of carboxylic acids at the water-mineral interface

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The ground-breaking work by Paul Schindler and Werner Stumm laid the foundations for coordination chemistry of organic ligands at water-mineral interfaces. They proposed stoichiometries and structures for a wide range of organic ligand-mineral surface complexes based on careful adsorption and dissolution experiments in combination with surface complexation modelling. Recent advances in IR spectroscopic data collection and analysis have provided new insights into ligand-mineral interactions, and a more complex picture has emerged. An intricate relationship exists between the structure and composition of the organic ligand and the modes of ligand adsorption. A logical approach to discern these relationships has been to begin with the simplest ligands and subsequently add complexity by systematically introducing more functional groups. Thus, obvious starting-points for carboxylic acids are acetate and benzoate, which both form two types of outer sphere surface complexes on goethite. In contrast dicarboxylates form inner and outer sphere complexes, and inner sphere coordination is favoured by low pH. The stability of inner sphere complexes is directly related to the chelatering size and decreases according to: 5-ring (oxalate) > 6- ring (malonate) > 7- ring (o-phthalate). Even more carboxyl groups favour the formation of outer sphere complexes, and mellitate, a benzehexacarboxylate, bonds to goethite surfaces solely via outer sphere interactions. This phenomenon will be discussed, and new spectroscopic data unravelling the relation between ligand coordination modes and their desorption kinetics will be presented.

Evidence for mobilization and recycling of boron in the continental crust of the Central Iberian Zone (Spain)

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Tourmaline-bearing rocks are widespread minor lithologies within the Central Iberian Zone, Spain, particularly in the Alamo complex. This complex consists of structuralmetamorphic domes surrounded by low-grade metasedimentary rocks of Upper Proterozoic to Lower Cambrian age that form part of the Schist Graywacke Complex. Tourmaline is ubiquitous throughout the domes, which occurs in stratiform tourmalinites, psammo-pelitic schists, quartzites, gneisses, migmatites, leucogranites, aplopegmatites and quartz veins.

Field relations and petrographic observations, combined with geochemical and isotopic data provide evidence of intense metasomatism affecting this region. Preliminar boron-isotope data of different types of tourmalines show a total range of δ^{11} B values from -15.6 to 6.8‰ that are typical for continental crust. Tourmaline 40 Ar/ 39 Ar data obtained from tourmaline-rich rocks (from ~370 to ~300 Ma) are consistent with different stages of tourmaline formation.

The occurrence of tourmaline in a variety of rocks denotes a significant mobilization of boron in the continental crust of this region, which may have been important for the genesis and evolution of granitic magmas in the CIZ. The original boron may have derived from: (i) pre-Variscan tourmalinerich rocks resulting from the metasomatic activity of B-rich fluids related to the Cambro-Ordovician magmatism, which recycled by deformation, metamorphism and anatexis with important feedbacks between these processes; and/or (ii) infiltration and cycling of B-rich aqueous fluids into the midcrustal zone derived from some thousands of meters of the SGC sediments during the Variscan orogeny. Boron was removed from the rocks via solution in aqueous fluids released by devolatilization reactions during prograde metamorphism. Though there is no compelling evidence for metasomatic events driven by Cambro-Ordovician boron-rich magmatic fluids, some petrographic and geochemical features make this hypothesis tenable. Further investigation, nevertheless, is necessary to assess the boron source and the precise timing of tourmalinization.