Solutions in the "big laboratory": Toward a model for metals at the Earth's surface*

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Abstract: Numerous factors control the chemistry of metal ions in natural aqueous systems. These include the presence of a host of complexing agents, speciation among a variety of competing ligands, buffering due to precipitated solid phases, and the relative influences of kinetic versus thermodynamic phenomena. Natural aqueous systems are inevitably complicated, but simple, inorganic models can be constructed to characterize a variety of different environments. While available data sets for these models are large, it is clear that much further research is required in order to develop more sophisticated models. Some of the fields of research that need to be addressed are outlined, and some of the constraints on such research are briefly discussed.

Keywords: aqueous solutions; geochemistry; minerals; modeling; equilibria.

INTRODUCTION

We live in a watery world. The "big laboratory", the surface of the Earth, is a heterogeneous environment in which aqueous systems play a major role in determining the chemistry of transport of inorganic and organic species. Among other things, the transport of metal ions and their interactions with living organisms is mediated by aqueous chemistries of varying complexity. Understanding such systems is of central importance in many fields ranging from biochemistry, toxicology, and nutrition to hydrometallurgy, mineral exploration, and pollution studies [1,2].

Any approach to a model for the aqueous chemistry of the surface environment of the Earth is bedevilled by the extreme natural variation of ligands that can form complexes in solutions of widely different ionic strengths. This is certainly the case with the set of available organic ligands in that it represents a continuously evolving chemical melange subject to both biological and abiological transformations. The inorganic ligand set is much more tractable, but the number of inorganic phases that can crystallize under widely disparate conditions is enormous. These phases act as metal (and ligand) buffers and serve to limit concentrations of metals in solution. Some 4000 separate species are recognized as minerals [3], and this number is increasing by about 60 per annum. Unknown numbers of inorganic phases remain to be described in natural systems, and many of these will no doubt exert, although possibly only transiently, a buffering influence as well.

Given this background, it might well be thought that any attempt to model natural aqueous systems at the Earth's surface is doomed to failure. However, experience has shown that, even by neglecting the large set of organic ligands that are known to exist in surface and groundwaters, comparatively simple inorganic models can provide satisfactory explanations for the chemistry and mobility of metal

ions in supergene environments. This report examines some of these models applied to certain classical problems and current research aimed at deducing the extent of the dispersion of metals in natural aqueous solutions. In addition, further requirements with respect to the accumulation of thermochemical data are briefly addressed and mention is made of a need to understand kinetic influences and the relationships of inorganic systems with biological processes in order to develop a more comprehensive model.

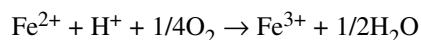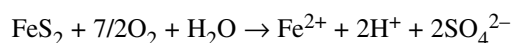## THE "SEAWATER PROBLEM" AND OTHER SOLUTE–SOLVENT EXAMPLES

The "seawater problem" is a good example of the elusiveness of the complex chemistry that operates, even in comparatively simple systems. Classically, the problem involves a knowledge of the average composition of seawater in relation to the solubility of several simple inorganic salts. Average seawater has the following composition: $[Na^+] = 0.48$, $[Mg^{2+}] = 0.054$, $[Ca^{2+}] = 0.010$, $[K^+] = 0.010$, $[Cl^-] = 0.56$, $[SO_4^{2-}] = 0.028$, $[HCO_3^-] = 0.0024$, $[CO_3^{2-}] = 0.00027$ mol dm^{-3}, with $I = 0.7$, pH = 8.15, $T = 25$ °C [4]. In simple terms, the "problem" is that multiplication of the concentrations of appropriate ions would seem to indicate that the oceans should be a milky suspension of particles of calcite, magnesite, and anhydrite or hydrated phases such as gypsum, $CaSO_4 \cdot 2H_2O$ (at 25 °C, $K_s(CaCO_3$, calcite$) = 8.7 \times 10^{-9}$, $K_s(MgCO_3$, magnesite$) = 5.6 \times 10^{-9}$, $K_s(CaSO_4$, anhydrite$) = 2.4 \times 10^{-5}$ [5,6]).

With the benefit of hindsight, of course, the "seawater problem" is seen to be illusory. By treating the ligand set as OH^-, Cl^-, SO_4^{2-}, HCO_3^-, and CO_3^{2-}, calculation of the species distribution for the major dissolved components of seawater gives the free ionic concentrations $[Ca^{2+}] = 8.13 \times 10^{-3}$, $[Mg^{2+}] = 4.70 \times 10^{-2}$, $[SO_4^{2-}] = 1.06 \times 10^{-2}$, and $[CO_3^{2-}] = 2.43 \times 10^{-5}$ mol dm^{-3}. An extended Debye–Hückel model for activity coefficients leads to $\gamma(Ca^{2+}) \approx \gamma(Mg^{2+}) = 0.28$, $\gamma(CO_3^{2-}) = 0.20$, and $\gamma(SO_4^{2-}) = 0.12$ [4]. Under these circumstances, for this *simplified* model, it is concluded that solubility product of anhydrite is not exceeded, and seawater is nearly saturated with respect to calcite, $CaCO_3$, and magnesite, $MgCO_3$. This is in accord with the manifestly extensive calcification of the exoskeletons of hosts of marine organisms.

The solution to the "seawater problem" provides an excellent example of the importance of taking speciation into account in any aqueous inorganic system and similar equilibrium-based approaches have been applied to many related phenomena. Useful overviews of a number of "simple" inorganic geochemical systems are provided by Appelo and Postma [1] and Williams [2].

METAL ION DISPERSION NEAR OXIDIZING BASE-METAL ORE BODIES

Other more recent examples of the application of speciation models concern the dispersion of metal ions in the vicinity of oxidizing base-metal deposits. In this connection, an understanding of complex solution chemistry is required to predict the extent of any groundwater contamination, the potential for application of hydrometallurgical techniques for metal extraction, and to generate models that might be applied in geochemical exploration. Sulfide deposits containing both noble and base metals are usually formed deep in the Earth under reducing conditions at elevated temperatures and pressures. Thus, it is not surprising that when these are exposed to oxidizing conditions near the surface, many react to form other, more stable, secondary species [7]. Examples include the oxidation of pyrite, FeS_2, and galena, PbS, as shown below.

$FeS_2 + 7/2O_2 + H_2O \rightarrow Fe^{2+} + 2H^+ + 2SO_4^{2-}$

$Fe^{2+} + H^+ + 1/4O_2 \rightarrow Fe^{3+} + 1/2H_2O$

$Fe^{3+} + 2H_2O \rightarrow FeOOH(s,goethite) + 3H^+$

$PbS + 2O_2 \rightarrow PbSO_4(s,anglesite)$

Primary sulfides and related sulfosalts are quite insoluble in water under ambient conditions, but their oxidized equivalents are much more soluble, and metal ions (and anionic, hydrolyzed congeners such as arsenate, molybdate, and the like) are dispersed in groundwater. This occurs under the metal-buffering control of secondary minerals (sulfates, carbonates, phosphates, arsenates, chlorides, etc.). Mineralogical diversity in oxidized zones (the supergene environment above the water table) is highly variable, but examples of comparatively simple assemblages are known.

Oxidized ores from the main pit of the Girilambone, New South Wales, Australia, deposits represent such a case. Pyrite and chalcopyrite, $CuFeS_2$, dominated the primary mineralogy, with negligible amounts of other base metals being present [8]. The secondary copper assemblage comprised only a few important species, malachite, $Cu_2CO_3(OH)_2$, azurite, $Cu_3(CO_3)_2(OH)_2$, libethenite, Cu_2PO_4OH, pseudomalachite, $Cu_5(PO_4)_2(OH)_4$, cuprite, Cu_2O, and native copper, Cu. Reliable equilibrium constants and thermochemical data for these minerals are available [2,5,9,10], and the conditions under which they preferentially form have been explored [11]. Sampling and analysis of groundwaters collected prior to mining from drill holes intersecting similar mineralization to the north of the main pit, followed by speciation calculations and comparison of ionic activity products with analogous expressions for the minerals concerned, showed that the solubilities of malachite and pseudomalachite served to limit the total amounts of copper dissolved in solution in the oxidized zone [12]. Analyses of similar samples nearby gave no such copper "signature", thus indicating that copper dispersion was highly localized and that the deposits were not a source of contamination with respect to local groundwaters.

A related case was encountered during a study of the Mungana deposit, near Chillagoe in north Queensland, Australia. This polymetallic deposit, which remains unmined, is far more mineralogically complex and contains significant Pb, Zn, and As mineralization in addition to copper and a variety of accessory elements [13]. Dispersion of copper and arsenic in the oxidized zone was found to be controlled by malachite, olivenite, $Cu_2AsO_4(OH)$, and cornwallite, $Cu_5(AsO_4)_2(OH)_4$. Lead solubility was found to be limited by cerussite, $PbCO_3$, the rare phases wulfenite, $PbMoO_4$, and stolzite, $PbWO_4$ [12].

The above examples refer to situations akin to that encountered in the "seawater problem". Analytical data are available, and calculations of species distributions lead to concentrations and activities of individual ionic components of the solution. Rather more problematic is the case when an attempt is made to reconstruct the solution chemistry responsible for the emplacement of a suite of secondary minerals. The following example points to how this can be done for simple model systems that lead to practical outcomes in similar environments.

The New Cobar deposit is located in the Cobar Mineral Field, approximately 600 km west of Sydney, New South Wales, Australia. It is one of five major deposits currently being mined in the Cobar area and has been worked intermittently since 1887. In 2002–3, an open cut exposed the oxidized zone and a study of the deposit was undertaken as part of a project aimed at developing new geochemical exploration models for deposits in the region [14]. Mineralization associated with a steeply dipping fault is wholly contained within folded siltstones and sandstones [15]. Primary ores of the Cobar region are broadly similar, comprising major but variable amounts of arsenopyrite, FeAsS, pyrite, marcasite, FeS_2, chalcopyrite, galena, sphalerite, ZnS, pyrrhotite, $Fe_{1-x}S$, and magnetite Fe_3O_4. Cassiterite, SnO_2, native bismuth, bismuthinite, Bi_2S_3, and rarer tungsten, molybdenum, and selenium minerals are accessories. Quartz is the most common gangue mineral, and very little primary carbonate mineralization is present [15–17]. Only sketchy reports were available in the early literature concerning the supergene mineralogy of deposits in the area [16,18].

In a recent study of the supergene zone of the New Cobar deposit, Leverett et al. [14] identified separate suites of oxidized base-metal carbonate and arsenate minerals. The more common arsenate suite minerals include bayldonite, $Cu_3Pb(AsO_4)_2(OH)_2$, chenevixite, $Cu_2Fe_2(AsO_4)_2(OH)_4 \cdot H_2O$, duftite, $CuPbAsO_4(OH)$, gartrellite, $PbCuFe(AsO_4)_2(OH) \cdot H_2O$, mimetite, $Pb_5(AsO_4)_3Cl$, olivenite, $Cu_2AsO_4(OH)$, philipsbornite, $PbAl_3(AsO_4)_2(OH)_5 \cdot H_2O$, and segnitite, $PbFe_3(AsO_4)_2(OH)_5 \cdot H_2O$. Small quantities of agardite, $Cu_6(REE)(AsO_4)_3(OH)_6 \cdot 3H_2O$, occur as a late overgrowth on some specimens recovered from the lower oxidized zone. The arsenate minerals had a very limited spatial dis-

tribution, being confined to the highly siliceous lode channel. Superimposed on this arsenate assemblage is a copper suite dominated by azurite, $Cu_3(CO_3)_2(OH)_2$, and malachite, $Cu_2CO_3(OH)_2$. These carbonates formed later in the paragenetic sequence and are widely dispersed in the enclosing host rocks. It is possible to reconstruct the solution conditions responsible for the generation of the separate suites and thus to explain the differential geochemical dispersion of Cu and Pb ± As from the oxidizing deposit.

Reliable thermochemical data for most of the above minerals at 298.2 K are available [2,19,20]. Choice of this temperature for modeling the aqueous geochemistry of the deposit is appropriate given that stable oxygen isotope measurements of the carbonate minerals indicate that they crystallized at temperatures only slightly above this value [21]. Other data used in subsequent calculations were taken from [5,6,22]. A pH, lg $a(Cu^{2+})$ phase diagram for the arsenate minerals is shown in Fig. 1. In this connection, it is evident that the *present* is the key to the geochemical *past*. Field associations of the arsenate minerals indicate the general conditions under which the suite crystallized. The observation of olivenite–bayldonite–duftite intergrowths at a Pb^{2+} activity of 10^{-8} (higher values serve to obliterate the olivenite field except at unrealistically high Cu^{2+} activities) indicate a solution pH that is acidic, and the ubiquitous presence of philipsbornite–segnitite (members of the jarosite supergroup) shows that pH fell as low as 3 during the mineralizing event. This is consistent with the absence of cornwallite and clinoclase in the deposit. It is significant that anglesite, $PbSO_4$, was not detected and negligible amounts of cerussite, $PbCO_3$, are associated with the arsenates (one specimen, of hundreds recovered from the deposit, contained a minute amount of the normal Pb(II) carbonate). For the above Pb^{2+} activity, an average Cu^{2+} activity of 10^{-4} is reasonable (about the center of the bayldonite field in Fig. 1). The presence of mimetite is significant, and its stability field is contoured on the figure for varying chloride activities. Chloride activities cannot have been too high, as this would serve to obliterate the duftite and bayl-
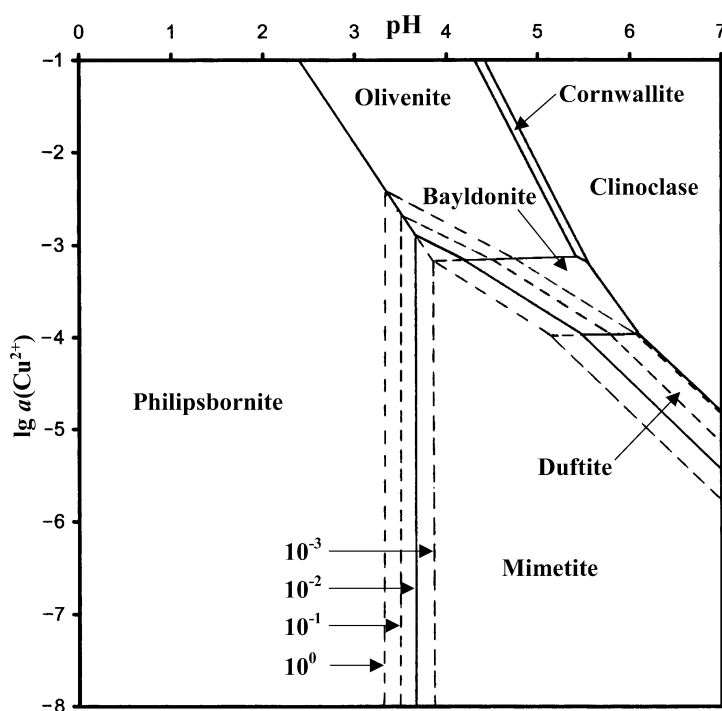

Fig. 1 Stability field diagram for Cu(II) and Pb(II) arsenates at 298.2 K in the presence of gibbsite (observed in the oxidized zone at New Cobar), with a Pb^{2+} activity of 10^{-8} and Cl^- activities of 10^0, 10^{-1}, 10^{-2} (bold), and 10^{-3} (as indicated).

donite fields, as indicated. A value for the chloride activity was chosen as 10^{-2}, consistent with observations of chloride contents of other groundwaters in arid environments, but well below chloride levels in seawater (see above). Likewise, a choice of a similar sulfate activity (10^{-2}) is justified by reference to related groundwater compositions in other deposits [2], and the absence of anglesite for the given lead ion activity. Thus, a good proxy for the bulk ionic composition of the mineralizing solutions corresponds to 10^{-2} M NaCl plus 10^{-2} M Na_2SO_4. This bulk composition can then be used to derive ionic activity coefficients for concentrations of species containing Pb^{2+}, Cu^{2+}, and $H_2AsO_4^-$. Use of the extended Guggenheim relationship lg $\gamma = -Az^2[I^{1/2}/(1 + I^{1/2}) - 0.3I]$ at $T = 298.2$ K (the temperature adopted for all model calculations) gives $\gamma = 0.83$ and 0.49 for univalent and divalent ions, respectively. It is then possible to calculate $H_2AsO_4^-$ (the only significant arsenate species between pH 3 and 7) activities in the solutions through any equilibrium expression involving the dissolution of any of the arsenate-bearing phases, on the basis of the other chosen activities, including a pH of 5 as an indicative measure of the acidic nature of solution conditions responsible for the crystallization of the arsenate suite (this is in line with the considerations above, by reference to Fig. 1).

Of course, further calculation steps are required to move from activities of base-metal species to total concentrations. This is achieved by using the activities of Cl^-, SO_4^{2-}, Pb^{2+}, Cu^{2+}, and $H_2AsO_4^-$ to calculate activities of dissolved complexes. These can then be converted to concentrations and summed. CO_2 was included in the calculations at a pressure (p/p_o) of $10^{-3.5}$, equivalent to atmospheric levels. Species included in the calculations were $CuCl^+$, $PbCl^+$, $PbCl_2°$, $PbCl_3^-$, $PbCl_4^{2-}$, $CuH_2AsO_4^+$, $PbH_2AsO_4^+$, $CuSO_4°$, $PbSO_4°$, $CuCO_3°$, $Cu(CO_3)_2^{2-}$, $PbCO_3°$, $Pb(CO_3)_2^{2-}$, $CuHCO_3^-$, $PbHCO_3^-$, and $Pb(SO_4)_2^{2-}$. Higher chloride species of Cu(II) and hydrolyzed species were neglected. As a result, for the secondary arsenate-mineralizing event, total concentrations of Cu, Pb, and As are 4.90×10^{-4}, 7.94×10^{-8}, and 1.45×10^{-5} M, respectively [21].

For the separate copper carbonate-mineralizing event, a different model needs to be adopted. Use here is made of the observation at New Cobar of the fact that azurite and malachite are intimately intergrown, with no sign of preferential replacement, thus indicating that they crystallized under equilibrium conditions. Thermochemical data taken from the above sources gives an equilibrium pressure (p/p_o) of CO_2 equal to $10^{-1.36}$ at 298.2 K for the following reaction:

$$3Cu_2CO_3(OH)_2(s) + CO_2(g) \leftrightarrow 2Cu_3(CO_3)_2(OH)_2(s) + H_2O(l)$$
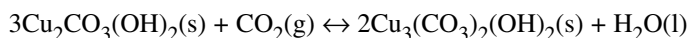
Iterative calculations lead to a pH of 4.59, again too low for the formation of cerussite, and the concentrations of other carbonate species can be derived. Using the same general method as outlined above, with $[Na^+] = 0.012$, $[Cl^-] = 0.01$, and $[SO_4^{2-}] = 0.001$ mol dm^{-3}, a total dissolved copper concentration of 1.22×10^{-2} mol dm^{-3} was found, a value almost two orders of magnitude higher than in the case of the arsenate mineralization. This in turn implies that more copper was transported in solution in the carbonate event and this is exactly in line with observations concerning the extent of azurite–malachite deposition versus the basic copper and lead arsenates. Furthermore, perturbation of the model with respect to the activity values chosen, within limits imposed by field assemblages and relationships indicated by Fig. 1, do not significantly alter the outcome. Leverett et al. [21] used this line of argument to propose a model for geochemical exploration in the Cobar Basin based on the differential mobilities of copper lead and arsenic in the supergene zone.

These examples illustrate the point that comparatively simple solution models can provide answers to quite complex geochemical questions in the natural environment. However, it is fair to question how more sophisticated models might be developed and just what are the limitations and deficiencies in our knowledge of the chemistry of the natural environment.

CONTROLS ON METAL ION SPECIATION IN NATURAL WATERS

Speciation in natural aqueous systems is controlled by the usual parameters of temperature and pressure. For most model systems at the Earth's surface, values of 25 °C and 10^5 Pa are used. Apart from some exceptions, these seem adequate for most purposes. Thus, it is possible in general to set out requirements for developing more sophisticated models. This in essence reduces to a more comprehensive knowledge of the species that do form in solution with a given set of metal ions and ligands, the stability constants that apply to their formation, and stabilities of the solid phases that can be generated and which serve to buffer metal and ligand concentrations under the appropriate conditions.

As far as the first requirement is concerned, it is emphasized that interactions with naturally occurring organic ligands, except for simple ligands such as amino acids, are not well understood. This is in large part due to the fact that the most important kinds of ligands such as humic and fulvic acids are not stoichiometrically fixed species, but rather represent immensely large families of related compounds. Many studies have been directed toward studies of metal interactions with such ligands (see, e.g., [23,24], and references therein). While ranges of stability constants for metal ions are available for these important complexing agents, details of the coordination chemistry remain sketchy and these kinds of complexes are beyond the scope of this article. For "simple" inorganic ligands, a number of data sets are available (see, e.g., [6,25,26], and references therein). These represent excellent sources of data, with the usual caveats. First, not all data have the same degree of reliability. Secondly, a host of other complexes exist for which no data are available. The latter certainly applies to mixed complexes of simple ligands, for example. However, these represent areas of research that will be addressed more fully in time and which could feasibly be tackled in terms of the size of the problem. It is appropriate to consider here the scale of the ligand set concerned.

Below are listed some simple inorganic ligands that need to be included in a comprehensive data set arranged by group according to the donor atom. The metal set, of course, comprises the bulk of the Periodic Table. Many oxyanions and their conjugate acid anions and polymeric derivatives are present in natural aqueous systems and it might be the case that modeling techniques, as opposed to direct experimental determinations, may need to be brought to bear in such cases.

Group 14: CN^-
Group 15: NH_3, SCN^-, $As(OH)_3$
Group 16: H_2O/OH^-, CO_3^{2-}, SO_3^{2-}, SO_4^{2-}, $S_2O_3^{2-}$, NO_3^-, PO_4^{3-}, AsO_4^{3-}, SiO_4^{4-}, MoO_4^{2-}, WO_4^{2-}, numerous other oxyanions, SCN^-, SO_3^{2-}, $S_2O_3^{2-}$, other sulfur oxyanions, Se and Te analogs
Group 17: F^-, Cl^-, Br^-, I^-, complex halides

Much more problematic, as alluded to above, concerns the requirement for data for solid phases in equilibrium (or metastable equilibrium) with aqueous solutions. Aside from perhaps one-half of the known mineral phases, data will be required for compounds known only as synthetic phases. Inevitably, many of these will ultimately find their way into the mineralogical literature. Otherwise, knowledge of their stabilities will aid in the definition of the limits of natural chemistry of aqueous chemistry. Here, a strong case can be made for the paramount need for better predictive models for thermodynamic parameters, simply because the experimental task would be so huge. Nevertheless, an important constraint for such theoretical studies is the need for accuracy. At 298.2 K, a change of 1 order of magnitude in an equilibrium constant corresponds to an energy difference of about 5 kJ mol^{-1}. It is suggested that this is the level of accuracy, or better, that needs to be achieved.

In dealing with solids, mention ought to be made of metastable phases and kinetic phenomena. Here, we are on somewhat more shaky ground in that very little is known of the solution characteristics responsible for the promotion or inhibition of nucleation of solid phases. Nevertheless, such species abound in geochemical systems under ambient conditions. One or two related examples will suffice to illustrate the point. The titration of aqueous solutions of $CuSO_4$ with aqueous NaOH at 25 °C is non-

commutative [27]. Addition of base to the metal solution initially yields a precipitate of metastable posnjakite, $Cu_4SO_4(OH)_6 \cdot H_2O$, which changes with time, in contact with the reaction solution, to the thermodynamically stable phase at this temperature, brochantite, $Cu_4SO_4(OH)_6$. Titration in the reverse sense gives a precipitate of spertiniite, $Cu(OH)_2$, which is also metastable with respect to brochantite or tenorite, CuO, depending upon the relative amounts of reagents added. A more spectacular example of this manifestation of the Ostwald effect [28], a phenomenon widespread in many geochemical systems [29], involves the similar titration of aqueous $CuCl_2$ with base. Depending on solution conditions chosen, the order of precipitation is claringbullite, $Cu_4Cl(OH)_7$, followed by botallackite, $Cu_2Cl(OH)_3$, then atacamite, $Cu_2Cl(OH)_3$, then clinoatacamite, $Cu_2Cl(OH)_3$, and each phase can be separately isolated over time [30]. Addition of excess chloride ion to the reaction mixture almost completely inhibits the nucleation of the most stable product at 25 °C, clinoatacamite. It is apparent that solution speciation exerts a kinetic control on the nature of compounds that may form in metastable equilibrium with the aqueous phase, but details of just how this happens are virtually unknown. Since some related systems, such as assemblages of certain phases associated with acid mine drainage trains [31], are of considerable importance from an environmental point of view, these phenomena must surely represent a fruitful area for future research.

Finally, it should be recognized that aqueous inorganic systems in the natural environment are rarely if ever disconnected from biological processes. Aside from the importance of organic ligands in metal speciation, what are recognized as inorganic species may have a biological origin, at least in part. Carbonate is an example, and sulfate, sulfide, and intermediate valency sulfur oxyanions may all be generated catalytically by certain organisms (see, e.g., [32]). Other more bizarre cases illustrate how pervasive biological interactions may be in systems that might have been thought of as being "purely inorganic." A single-crystal structure of a member of the connellite–buttgenbachite series from the Great Australia mine, Cloncurry, Queensland, Australia, showed that it contains considerable nitrate substituting for sulfate in the lattice [33]. The derived formula is $Cu_{36}Cl_{7.82}(SO_4)_{0.52}(NO_3)_{0.48}(OH)_{62.66} \cdot 5.14H_2O$. It is associated with the other copper nitrate minerals gerhardtite, $Cu_2NO_3(OH)_3$, and likasite, $Cu_3NO_3(OH)_5 \cdot 2H_2O$, in the oxidized zone of a copper ore body. Measurements of nitrogen isotope ratios of the nitrate in the ore (unpublished results) show that much of it is derived from nitrogen fixation to ammonia and oxidation to nitrate in and around termite mounds at the surface.

CONCLUDING REMARKS

The chemistry of metal ion solution, speciation, transport, and precipitation in the "big laboratory" is undoubtedly complex. Perhaps surprisingly, however, given the number of parameters involved, simple models can be used to great effect in describing and understanding a range of important processes. Nevertheless, it is apparent that much remains to be done to understand fully the more complicated cases and to develop more sophisticated models that adequately describe them. Advances will involve the application of both experimental and theoretical approaches in intimate association. However, it is patently obvious that a multidisciplinary effort is required. Such a combination is bound to yield a wealth of valuable data that can be applied to a better understanding of the environment in which we live.

ACKNOWLEDGMENTS

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