Ground Waters and Surface Waters in Exploration Geochemical Surveys

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ABSTRACT

The geochemistry of natural waters traditionally has provided an important avenue for the explorationist to evaluate mineral deposit prospectivity in a third "depth" dimension. Appreciation of basic principles in aqueous geochemistry provide a means to understanding element mobilities and interpreting dispersion patterns, with applications in both the minerals exploration and environmental disciplines. Applied hydrogeochemistry in minerals exploration peaked in the 1970s, but a new episode in hydrogeochemical minerals exploration has been opened, and investigation of robust element anomalies and dispersion patterns, at concentration levels unattainable a decade ago, can now proceed on a cost-effective basis.

This paper is divided into three parts. An abbreviated overview of some fundamentals of inorganic aqueous geochemistry controlling element mobilities, and a brief historical perspective of the use of hydrogeochemistry in minerals exploration comprise the first two parts. These are followed by two case histories illustrating how water surveys can be used in both early-stage and late-stage (pre-feasibility) exploration programs.

Inorganic aqueous geochemistry can be simplified by considering three fundamental aspects of this field: solution speciation, mineral precipitation, and element sorption onto solid substrates and solution particulates. These fundamentals are useful in interpreting hydrogeochemical survey results. Applications of hydrogeochemistry to minerals exploration and resource development are presented, with examples from a blind porphyry Cu system under pediment cover in arid terrain of the southwestern United States, and a high-sulfidation Cu ore body in a high-relief tropical environment in the Philippines. Survey results from each example may be understood in terms of hydrogeochemistry fundamentals, and demonstrate useful applications of hydrogeochemistry in minerals exploration programs.

ABBREVIATED FUNDAMENTALS OF INORGANIC AQUEOUS GEOCHEMISTRY

Geochemical mobilities in natural water are determined largely by three fundamental processes: element speciation in solution, precipitation of minerals, and surface sorption processes.

Element speciation in solution

Total element concentrations from laboratory analyses of water indicate nothing about the form of elements in the solution analyzed. For example, copper in water may be present as a free Cu²⁺ ion, a Cu-hydroxide ion complex, a Cu-carbonate neutral aqueous species, or a variety of other forms. In examining water data, it is important to consider the cationic, anionic, or neutral-charge phases, known as the element speciation, of the chemical elements of interest under the Eh-pH conditions at hand. Whether a metal will be present as a cation, anion, or neutral species in solution can be evaluated by obtaining complete water analyses for major and trace elements. Then any of a number of software programs, Minteq, EQ3/6, etc. (Allison et al., 1991; Wolery and Daveler, 1989), capable of evaluating competing complex-formation reactions can be used to determine the relative thermodynamic stabilities of metal complexes in solution, and the relative proportions of coexisting phases for a given element.

Speciation often is strongly dependent on water pH. How Cu and Zn speciation changes with pH may be seen by examining the water analysis results presented in Tables 1a and 1b.

It may be seen from Table 1b that Cu species in the analyzed solution change significantly from predominantly Cu²⁺ ion to predominantly the neutral Cu(OH)₂ aqueous species when pH is increased from 6.3 to 7.3. In contrast, Zn species in solution are almost unchanged over this same pH shift. Differences in element speciation behavior in solution affect how elements interact with each other and with charged solid materials in natural water. Speciation helps explain differences in element mobilities in nature.

Exploration Geochemistry

Mineral precipitation reactions also can remove elements from solution. Mineral-forming elements leave the solution as solid minerals precipitate. Even when elements are not expressly listed in precipitating-mineral stoichiometries, they can be removed from solution as coprecipitates, or as species sorbed onto newly formed precipitates. Solution conditions favoring mineral precipitation reactions can be determined using the same aqueous geochemistry computer software codes used for speciation evaluations, to indicate when solutions are saturated, undersaturated, or supersaturated with respect to various mineral solubility products. By determining the activities in solution of dissolved mineral components, and expressing ratios of species activities to mineral solubility products, saturation indices can be calculated to indicate the degree of saturation of a particular mineral. Saturation indices greater than one indicate supersaturation of the mineral phase.

For the solution analysis in Table 1, equilibrium saturated mineral species are displayed in Table 2 below for pH = 6.3.

### Table 1a: Speciation example—laboratory analysis

<table>
<thead>
<tr>
<th>Element</th>
<th>Concentration</th>
<th>Element</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na⁺</td>
<td>7.2 mg/L</td>
<td>Cu²⁺</td>
<td>27 µg/L</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>8.5 mg/L</td>
<td>Zn²⁺</td>
<td>950 µg/L</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>34.6 mg/L</td>
<td>Fe²⁺</td>
<td>18 mg/L</td>
</tr>
<tr>
<td>Al³⁺</td>
<td>60 µg/L</td>
<td>SO₄²⁻</td>
<td>170 mg/L</td>
</tr>
<tr>
<td>K⁺</td>
<td>1.2 mg/L</td>
<td>Cl⁻</td>
<td>18 mg/L</td>
</tr>
<tr>
<td>Mn²⁺</td>
<td>1.9 mg/L</td>
<td>HCO₃⁻</td>
<td>5 mg/L</td>
</tr>
</tbody>
</table>

### Table 1b: Speciation example—pH = 6.3 and pH = 7.3

<table>
<thead>
<tr>
<th>Species Distribution</th>
<th>pH=6.3</th>
<th>pH=7.3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>63.7% as Cu⁺</td>
<td>29.7% as Cu²⁺</td>
</tr>
<tr>
<td></td>
<td>29.0% as Cu(CO₃) (aq)</td>
<td>6.7% as Cu(CO₃) (aq)</td>
</tr>
<tr>
<td></td>
<td>15.4% Sorbed</td>
<td>2.3% as Cu(OH)⁺</td>
</tr>
<tr>
<td>Zn</td>
<td>81.3% as Zn⁺</td>
<td>80.6% as Zn²⁺</td>
</tr>
<tr>
<td></td>
<td>14.8% as ZnSO₄ (aq)</td>
<td>14.7% as ZnSO₄ (aq)</td>
</tr>
<tr>
<td></td>
<td>2.5% Sorbed</td>
<td>2.5% Sorbed</td>
</tr>
</tbody>
</table>

### Table 2: Saturation state of equilibrium mineral species based on solution analyses from Table 1; pH = 6.3

<table>
<thead>
<tr>
<th>Species</th>
<th>Saturation Index</th>
<th>Saturation State</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al(OH)₃SO₄</td>
<td>.09</td>
<td>Undersaturated</td>
</tr>
<tr>
<td>Boehmite</td>
<td>1.01</td>
<td>Supersaturated</td>
</tr>
<tr>
<td>Diaspore</td>
<td>2.79</td>
<td>Supersaturated</td>
</tr>
<tr>
<td>Ferrihydrite</td>
<td>4.59</td>
<td>Supersaturated</td>
</tr>
<tr>
<td>Fe(OH)₂Cl₃</td>
<td>9.35</td>
<td>Supersaturated</td>
</tr>
<tr>
<td>Gibbsite</td>
<td>.93</td>
<td>Undersaturated</td>
</tr>
<tr>
<td>K-Jarosite</td>
<td>9.45</td>
<td>Supersaturated</td>
</tr>
<tr>
<td>Na-Jarosite</td>
<td>6.76</td>
<td>Supersaturated</td>
</tr>
</tbody>
</table>

The pH-dependence of sorption is shown conceptually in the equations below, where the symbol S represents a solid surface. It may be seen that acidic, low-pH solution conditions cause positively charged solid surfaces, and that alkaline, high-pH conditions generate negatively charged solid surfaces.

\[
\text{SOH}^- + \text{H}^+ = \text{SO}^2^- + 2\text{H}^+ \\
\text{(Low pH)} \quad \text{(High pH)}
\]

Anions sorb @ low pH; Cations sorb @ high pH

\[
\text{Cl}^-, \text{SO}_4^{2-}, \text{AsO}_4^{3-}, \text{Cu}^{2+}, \text{Zn}^{2+}, \text{Cd}^{2+}, \text{SeO}_3^{2-}, \text{SeO}_4^{4-}, \text{etc.} \quad \text{Ni}^{2+}, \text{Ca}^{2+}, \text{etc.} \quad [1]
\]

For solid surfaces in nature, there is a characteristic pH value where the surface charge is zero, called the point of zero charge, or pH_pzc. At pH values below the pH_pzc for a given surface, the surface is positively charged. Conversely, at pH values above the pH_pzc for a given surface, the surface is negatively charged. Point of zero charge values for some common mineral surfaces are displayed in Table 3.

By considering speciation of elements in solution, and the positive or negative surface charges on mineral surfaces at existing pH values, one can predict whether ions will be present as free species in solution, or will be sorbed to solid surfaces. The solid surfaces to which ions sorb can be present as immobile substrates, or as suspended particulates or colloids, and these can take many forms. Colloidal particles range in size from about 1 nanometer to 10 microns in diameter, and are made up of mineral grains, amorphous precipitates, bacteria, and other substances. Some examples are shown in Table 4.

Sorption

While metal sorption onto solids is a complex topic (Jenne, 1994, 1993; Smith, 1991; Anderson and Benjamin, 1990; Davis and Kent, 1990; Benjamin and Leckie, 1981; Davis and Leckie, 1978), some of the fundamental controls are readily appreciated. Sorption interactions between solution species and solid substrates are dependent on the surface charge of solid surfaces. Surface charges on solid surfaces are strongly influenced by pH (Kuo and McNeil, 1984; Harter, 1983; Kinniburgh and Jackson, 1982; Shuman, 1977). When solid surfaces are positively charged, they attract and sorb negatively charged solution species (anions). When negatively charged, surfaces attract and sorb positively-charged (cations) solution species.
An improved understanding of the three fundamental processes described above (element speciation in solution, precipitation of minerals, and surface sorption processes) can provide insight into hydrogeochemistry surveys applied to minerals exploration and environmental studies appropriate at the advanced stages of successful minerals exploration programs.

Table 3: Points of zero charge for some mineral surfaces

<table>
<thead>
<tr>
<th>Mineral</th>
<th>pH_{pzc}</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-Al_{2}O_{3}</td>
<td>9.1</td>
</tr>
<tr>
<td>α-Al(OH)_{3}</td>
<td>5.0</td>
</tr>
<tr>
<td>Fe_{3}O_{4}</td>
<td>6.5</td>
</tr>
<tr>
<td>γ-Fe_{2}O_{3}</td>
<td>6.7</td>
</tr>
<tr>
<td>Fe(OH)_{3}</td>
<td>8.5</td>
</tr>
<tr>
<td>Goethite[2]</td>
<td>7.3</td>
</tr>
<tr>
<td>MnO_{2}</td>
<td>2 – 4.5</td>
</tr>
<tr>
<td>kaolinite</td>
<td>4.6</td>
</tr>
<tr>
<td>montmorillonite</td>
<td>2.5</td>
</tr>
<tr>
<td>calcite</td>
<td>9.5</td>
</tr>
<tr>
<td>albite</td>
<td>2.0</td>
</tr>
</tbody>
</table>


The examples presented in the next section illustrate how hydrogeochemistry can be useful in minerals exploration programs.

Table 4: Types of colloids in natural water

<table>
<thead>
<tr>
<th>Colloid Type</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kaolinite particles</td>
<td></td>
</tr>
<tr>
<td>Illite and other 2:1 clays</td>
<td></td>
</tr>
<tr>
<td>Colloidal humic, fulvic acids</td>
<td>“dissolved” Fe(III)—colloidal Fe-oxides stabilized by humic or fulvic acids — important for Au transport</td>
</tr>
<tr>
<td>Biological colloids</td>
<td>Biological colloids—important for Au transport</td>
</tr>
</tbody>
</table>

Hydrogeochemistry in minerals exploration:
Two case histories—overview

Two examples presented here demonstrate how hydrogeochemistry can be successfully applied in minerals exploration. Results are described from groundwater survey work at a covered porphyry Cu system near Casa Grande, Arizona, U.S.A., completed by the U.S. Geological Survey (USGS), and streamwater orientation work carried out by Western Mining Corporation around a high-sulfidation Cu system in the Philippines.

Groundwater geochemistry at the Casa Grande porphyry Cu-Mo system

USGS open file report (Ficklin et al., 1981) describes groundwater geochemistry results from the Casa Grande porphyry Cu-Mo system. This deposit is approximately 700 m in diameter, and is found beneath interlayered Basin-and-Range valley alluvium and recent volcanics comprising a cover thickness of approximately 300 to 700 m. The mineralization occurs within the Sonora desert arid environment. In the USGS study, 78 irrigation water wells, covering an area of approximately 250 km², were sampled from April 1977 to June 1980. In the USGS report, water samples are described as having been analyzed by a combination of methods, principally flameless atomic absorption (cations), and ion chromatography (anions), for Ca, Mg, Na, K, Sr, Si, Fe, Mn, Al, Ag, As, Ba, Bi, Cd, Co, Cr, Ce, Cu, Li, Mo, Ni, Pb, Rb, U, Zn, HCO_{3}^-, SO_{4}^{2-}, NO_{3}^{-}, Cl^-, and F-. An interpretation of the USGS results is provided here.

Figures 2 through 4 show the distribution of water wells with respect to known mineralization, along with well-water pH values, and the water concentration plots for Cu, Mo, As, K and SO_{4}^{2-}.

Well-water pH values generally are elevated in this arid environment, but somewhat suppressed pH values below pH = 7.4 are observed in close proximity to and immediately northwest of the Casa Grande deposit (Figure 2). While water pH levels still are alkaline, the observed subtle lowering of pH is likely due to some minor acid generation associated with sulfide oxidation. Due to the generally elevated pH in this arid environment, copper mineralization is not indicated by Cu in solution (Figure 2). Copper mobility is strongly limited, and in accordance with the fundamentals of aqueous geochemistry, probably precipitates...
as Cu(OH)$_2$, co-precipitates with iron oxides, or sorbs onto immobile mineral surfaces. Colloid-facilitated transport probably is not an important mechanism of metal dispersion in this situation, since colloids often are trapped in pore spaces in migrating groundwater systems, and in this saline environment, charged colloidal particles are expected to readily coagulate and flocculate.

In contrast to Cu, informative anomalies with good contrast are evident for Mo, As, K, and SO$_4^{2-}$ (Figures 3 and 4). The molybdate, arsenate, and sulfate anions are not precipitated, co-precipitated, or sorbed at ambient pH, and exhibit good mobility. Elevated potassium concentrations, perhaps liberated through acid-water attack of potassic or phyllic alteration zones in the porphyry system, likewise indicate largely conservative (non-reactive) behavior of potassium in solution, and sufficient mobility to provide a clear anomaly expression associated with mineralization.

Stream water geochemistry at the Tampakan Cu deposit, Mindanao, Philippines

As part of a commitment to environmental stewardship worldwide, Western Mining Corporation maintains a science-based program to understand controls on water quality in advanced exploration and early resource development projects. With an improved understanding of controls on water quality at an early stage in a project area, the environmental impact of development can be better anticipated and alleviated. The following description of work in the Tampakan project area of the Philippines results from company commitment to understanding and maintaining water quality in the environment.

Copper mineralization at Tampakan comprises a high-sulfidation enargite-rich system, with sulfides outlined by the ground I.P. anomaly shown in Figures 5 and 6. Mineralization is hosted by "basement" andesitic volcanic rocks, and these are overlain by a younger andesite volcanic flow. Intrusive diorite crops out in a stream about one kilometer west of the defined mineralization. A significant rock alteration assemblage in the area is the mapped "silicified zone" (Figures 5 and 6), comprised almost entirely of clay, quartz, and pyrite. This alteration style exhibits substantial net acid production potential due to the contained pyrite, and the alteration assemblage contains no identified minerals with significant pH-buffering capacity. Clay-quartz-pyrite "silicified zone" alteration is found mostly west of the main copper mineralization, and is cut by flowing streams in the region.

Streamwater samples at Tampakan were collected and preserved using procedures specific for the intended analysis. Samples for cation analysis were filtered using 0.45 micron membrane filters, then acidified in the field to below pH=2. Samples for anion analysis and samples collected for field sulfate and alkalinity determinations were filtered but not acidified. Cations were run commercially by induction coupled plasma / mass spectrometry (ICP/MS), and anions by ion chromatography. Sulfate and alkalinity were determined using portable field kits, with analyses completed the same day as sample collection.

Andesitic rocks containing mafic silicate minerals provide considerable pH-buffering capacity in the chemical weathering system at Tampakan, and serve to keep the stream waters flowing over these rocks from becoming acidic. Natural streamwater alkalinities are high in stream waters flowing over andesitic volcanic rocks. Where acid is produced from weathering of sulfides in the silicified zone, alkalinity in the incoming stream water is consumed by acid generated upon sulfide oxidation, and the pH values are low (below pH=5). Upstream and downstream from the silicified zone, stream waters flow over andesitic rocks, and the water-rock interaction rapidly raises streamwater pH to values above pH=7. The pH distribution is bimodal (there were no recorded pH values between pH = 5.5 and pH = 6.9 in the survey), and is clearly controlled by water-rock interactions.

Metal contents in water increase directly with the drop in stream pH, and decrease directly with the increase in stream pH, as displayed in Figure 5 where pH and Cu water concentrations are plotted. Within the reach of stream flowing over the mapped silicified zone, stream water copper concentrations are elevated. In fact, stream waters in this relatively short section of stream naturally exceed set copper concentration limits for some of the recreational and fishery water usage classifications specified in 1990 Filipino legislation. These elevated Cu concentrations are natural, not the result of any disturbance or activity by man. In reaches of stream beyond the silicified zone, where water flows over andesitic rocks with greater pH-buffering capacity, metal
Figure 2: pH and Cu in irrigation well waters in the Casa Grande area, Arizona, U.S.A.
Figure 3: Mo and As in irrigation well waters in the Casa Grande area, Arizona, U.S.A.
Figure 4: K and SO$_4^{2-}$ in irrigation well waters in the Casa Grande area, Arizona, U.S.A.
values are much lower in water, and legislated concentration limits are not exceeded. Mineral precipitation, co-precipitation, and increased metal sorption with increasing pH likely explain the reduced solution concentration levels of Cu observed when stream water flows over andesitic rocks.

Just as copper concentrations in water increase in the more acid reach of stream water shown in Figure 5, copper concentrations in stream sediments along this same portion of the stream decrease to a level below the regional geochemical anomaly threshold for this part of Mindanao island. Acid water generated by the natural, unbuffered weathering of sulfides leaches copper from the stream sediment and raises the Cu concentrations in streamwater solution. The stream then redeposits copper (through mineral precipitation, co-precipitation, or sorption reactions) from the stream water back onto stream sediment as the pH increases, due to water interaction with acid-buffering minerals in the mafic volcanic rocks.

Figure 5: pH and Cu in stream waters of the Tampakan area, Mindanao, Philippines.
This phenomenon has potentially important implications in minerals exploration. Low Cu values in stream sediment may be encountered relatively short distances downstream from major Cu-mineralized sources, if the reach of stream sampled occurs in a naturally acid zone. Measurement of water pH and sulfate (Figure 6) can help identify these acid zones in routine exploration programs.

There also are potentially important environmental implications resulting from this understanding of natural controls on streamwater quality. High-quality environmental baseline studies must account for the geological controls on water quality, with specific identification of important water-rock interactions in the baseline area. The rapid improvement of water quality observed in this study, as naturally acid water flows downstream over rocks with high pH-buffering capacity, suggests that local acid-absorbing geological materials might be useful in mine planning and development. Streamwater alkalinites (Figure 6) can help indicate the most promising source areas for acid-consuming
rocks for use in mine planning. In fact, complete water analyses of the most alkaline stream water in the survey (102 mg/L CaCO₃ alkalinity) indicated that calcium carbonate is supersaturated in this water based on a MINTEQ (Allison et al., 1991) computer simulation.

An understanding of the metal speciation in stream waters also has important environmental implications, since the free ion forms of metals are much more toxic to aquatic life than the same metals in the form of metal-complexed species. A knowledge of the thermodynamically favored metal forms in stream waters allows some appreciation of the toxicity of natural stream waters, and how this toxicity might change based on various strategies of resource development. Strategies can be developed to increase metal complexing in stream waters exiting a project, and thereby reduce the metal toxicity to aquatic life.

Stream waters at Tampakan represent a classic example of how rock mineralogy can control water geochemistry, and the relationship between rock and water is fundamental to understanding the trace element aqueous geochemistry and element dispersion patterns in minerals exploration. A good understanding of local water-rock interactions Likewise is important for planning and executing strategies to maintain high water quality during resource development.

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