

Using alluvial basin ground-water chemistry to explore for concealed porphyry copper deposits in Arizona

Karen S. Bolm and Timothy S. Hayes

U.S. Geological Survey, 520 North Park Ave., Suite 355, Tucson, Arizona, 85719, USA

James G. Brown

Consulting Hydrologist, 345 North Pantano, #305, Tucson, Arizona, 85710, USA

ABSTRACT

Ground-water chemistry can aid in exploring for porphyry copper deposits that subcrop below basin-fill sediments and volcanics in basin-and-range Arizona. From up-slope of supergene enriched deposits, the general evolution of ground-water chemistry is from (1) dilute Ca-HCO₃-type water with pH near 8, with high dissolved oxygen (DO) and low trace metals, to (2) near-deposit, Ca-SO₄-type water commonly with low pH, low DO, high SO₄, and high Fe, Cu, Mn, and possibly Zn, to (3) near-downgradient, Ca-SO₄-HCO₃-type water with moderate pH, moderate-to-high DO, high SO₄, high Mo, and possibly high Zn, and to (4) ordinary basin ground water, typically Ca-Mg-HCO₃-type with increasing pH, Na, K, SO₄, Cl, and probably Fe, Mn, Zn, and Mo, and with decreasing DO toward basin low points. Near deposits, oxidation of sulfides consumes O₂, lowers pH, and releases SO₄, Cu, Mn, and Fe to the ground water. Fe and Mn appreciably dissolve only in water with almost no DO, which is unusual near the surface. Molybdenum is adsorbed at low pH but dissolves where pH is higher. Mo and SO₄ remain dissolved as DO and pH increase by mixing with ordinary ground water in contact with carbonates and feldspars, so these can migrate far from deposits. Potassic and propylitic assemblages do not produce acidic ground water, yet yield small-area, moderate-concentration Mn, Fe, Cu, and Zn anomalies, and anomalous Mo may be dispersed farther.

Lacustrine evaporite beds deep within basins yield high SO₄, low DO, and high Fe and Mn, “false anomalies” for porphyry Cu exploration. Yet other “false anomalies” may be man caused.

INTRODUCTION

Purpose and scope

There have been many earlier studies of chemical dispersal from the porphyry copper (Cu) deposits of basin-and-range Arizona, New Mexico, and northern Sonora (e.g. Lovering et al., 1950; Huff, 1970; Chaffee, 1975, 1976, 1977, 1982; Chaffee et al., 1976, 1981). Almost all of those studies sampled solid media including stream sediments, soils,

panned concentrates, and various species and parts of vegetation. Although studies of chemical dispersal in groundwater around porphyry copper deposits are limited, some results suggest the possibility that concealed porphyries may be identified by associated water geochemistry (Huff, 1970, see Fig. 1). Responding to this, we began mapping ground-water composition as a means to explore for porphyry copper deposits that are concealed beneath the basin-fill of basin-and-range Arizona. The work started as a task on the U.S. Geological Survey’s (USGS) Lifecycles of Porphyry Copper Deposits

e-mail: Bolm: kbolm@usgs.gov; Hayes: thayes@usgs.gov

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project and has continued under the Assessment Techniques for Concealed Mineral Resources project. We are trying to map ground-water chemistry of Arizona alluvial basins using a Geographic Information System (GIS), and including all publicly available data, as appropriate. The purpose is to make maps that are useful in exploration of Arizona's alluvial basins for porphyry Cu deposits.

In this paper, we describe earlier work applicable to the subject, list the data sources being used, and describe the method of our mapping and presentation of the data. Most of the paper, though, is used to illustrate a number of observations and straightforward interpretations for exploration that can be made using just the mapped data and knowledge from earlier studies of ground-water chemistry in the region. Full-coverage map products from this work will later be published as digital products of the USGS.

Earlier work

Figure 1, redrawn from Huff (1970), was the springboard for our ground-water chemical mapping. It shows concentrations of molybdenum (Mo) in ground water from shallow wells, most of them producing water from basin-fill conglomerates in the northern Pima mining district and extending into the middle Santa Cruz basin. Huff interpreted a high-Mo dispersion pattern extending downgradient from the Mission-Pima deposit area. The ground-water samples were taken in 1960. The Pima mine first produced from underground workings in 1952 (Langlois, 1978) and from the open pit in 1956, just four years before the sampling (Thurmond et al., 1954; and USGS Mineral Resource Data System database). Mission mine recorded its first production in 1961 after the time of Huff's sampling (USGS Mineral Resource Data System database). These deposits, now mined

together and with additions of adjacent resources, constituted a mineable total resource of 967 million tones of 0.65% copper (Cu) (Long, 1995). There is an area of small-scale historic mines to the southwest of Mission-Pima, and those began as early as 1880 (Ransome, 1922), but this ground-water anomaly cannot, probably, be attributed to human disturbance. The Mo-anomalous ground water stretches at least 11 km to the northeast from the mineralized area.

The Mo anomaly pattern in ground water is not like acid rock drainage. The ground water in the area is mildly alkaline. The lowest pH of any sample in the anomaly was 7.1. Most samples had pH greater than 7.5 (Huff, 1970, his Table 6). At low (acidic) pH in well-oxygenated water, Mo adsorbs to solid surfaces (Goldberg et al., 1996). This was our starting point – Mo is mobile, instead, in alkaline ground water in basin-and-range Arizona, and most of the ground water in Arizona's alluvial basins is alkaline (Robertson, 1991).

Other earlier work on ground-water chemistry of Arizona alluvial basins included the National Uranium Resource Evaluation (NURE), the Regional Aquifer Systems Analysis (RASA) program of the USGS, and work on the Pinal Creek Toxics Hydrology site. NURE produced more than 3000 ground-water analyses from eight 1:250,000-scale quadrangles in basin-and-range Arizona. Under the RASA program, the ground water of Arizona basins was extensively studied (Anderson, 1995; Anderson and Freethy, 1996; Anderson et al., 1992; Robertson, 1991). Robertson's (1991) study determined the ordinary chemical evolution of ground water in these basins. The ground-water dispersion signatures from porphyry Cu deposits have to be considered within the context of ordinary evolution. The Pinal Creek Toxics Hydrology site is below the Miami-Inspiration and Copper Cities porphyry Cu deposits. At that site, an acidic contamination plume in the

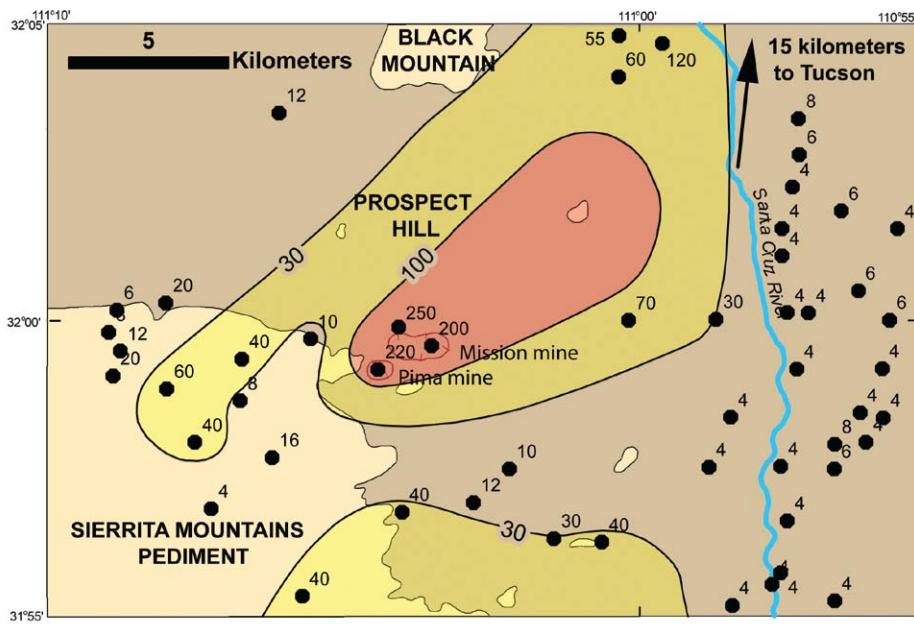


Figure 1. Concentrations, in micrograms per liter (approximately equal to parts per billion, ppb), of molybdenum in ground-water samples from the northeastern Sierrita Mountains pediment and central Santa Cruz River basin, southeastern Arizona. Redrawn from Huff (1970).

Pinal Creek alluvial aquifer is producing a modern-day manganese concrete that is comparable in almost every way with natural manganese systems related to supergene-enriched porphyry Cu deposits. More than 100 technical reports covering various aspects of the Pinal Creek site hydrology have been published (these are listed at <http://toxics.usgs.gov/bib/bib-pinal.html>). Private mining companies had also done some prospecting using ground-water chemistry starting as early as 1961 (John C. Balla, written commun., 2007). This list of earlier work is far from inclusive, and there are tens of other studies of ground-water chemistry in Arizona alluvial basins.

Method

Large, publicly available databases of ground-water chemical data listed in Table 1 were included in our mapping of Arizona alluvial basin ground-water chemistry. A total of eight new sites were sampled for this project since 2004. The data of Huff (1970) included 51 well-water analyses. We selected and entered single-time analyses from 147 wells from 33 mines, prospects, and plant sites from Arizona Department of Environmental Quality (ADEQ) data. This is mostly data from environmental monitoring wells. Many such wells at active mines are serially sampled by personnel from the mines to ensure environmental compliance. Mine personnel or contractors also took one-time samples from other sites for the purpose of applications for state Aquifer Protection Permits, and some of these also are part of the 147 ADEQ data points. The ADEQ sites were specifically included because, in some areas, they show the upgradient sources of known anomalous ground water. They also display some of the chemical evolutionary patterns for trace metals from known deposit sources. NURE's many sites included some of the same wells

that are in the largest publicly available database, which is maintained by Water Resources Discipline of the USGS and is called QWDATA. This has over 6000 usable sites in the study area. Not all of the parameters of interest are measured at each different site, but for commonly measured parameters like sulfate (SO_4^{2-}), there are as many as 3662 different sites in QWDATA. Some of these sites have also been serially sampled. From serially sampled locations, we used only the one-time analysis that had the largest number of measured parameters of interest.

Most of the sites in the databases had little or nothing to do with exploration for porphyry Cu deposits. There were many different reasons for drilling and sampling these wells. Typical wells are used for watering stock, for drinking water, or for irrigation. With the exception of the ADEQ wells, Huff's wells, and the few of our own, the locations of sampled wells can be considered practically random.

Ground-water analyses were chosen from the NURE and QWDATA databases using the digital, 1:1,000,000-scale Arizona state geologic map (Ludington et al., 2005, as modified from Richard [2002] and Richard et al. [2000]) and a Geographic Information System (GIS). Wells in the databases were selected for study if they were located in areas underlain by Quaternary units or Tertiary volcanic and sedimentary rocks. Wells located in Laramide and Jurassic porphyry intrusions were also selected (specifically units TKg and Jg of Richard et al., 2000). Wells in areas where the outcropping units are older than the porphyries were not chosen. That probably eliminated from consideration some wells in areas where the older bedrock units are hosts to porphyry mineralization, but the method of site selection had to be automated because manual selection from among more than 9000 sites was not feasible.

TABLE 1. SOURCES FOR GROUND WATER CHEMICAL DATA, ARIZONA BASIN AND RANGE

Source	Water sample types	Geographic distribution of sites	Number of available sites/water samples
USGS Porphyry Copper Deposit Lifecycles and Assessment Techniques for Concealed Mineral Resources projects; new analyses	Spring water Well water	2 selected small areas of ongoing supergene enrichment of Cu and exotic Cu and Mn mineralization, SE Arizona	8
Huff (1970) in USGS Bulletin 1312-C	Well water	Northeastern Pima mining district and central Santa Cruz river basin, Arizona	51
Arizona Department of Environmental Quality Aquifer Protection Permit documentation	Well water Spring water	31 active, closed, or planned mine sites, 1 smelter site in closure, 1 closed mill site scattered across the Arizona basin and range	147, selected
National Uranium Resource Evaluation (NURE) databases, as selected by GIS spatial criteria	Well water Spring water	Widely distributed across 8 of the 15 quadrangles, 1:250,000-scale, needed to cover the Arizona basin and range	3003 available
USGS National Water Information System (NWIS), QWDATA database, as selected via GIS spatial criteria	Well water Spring water Miscellaneous other ground water	All of the Arizona basin and range as limited by latitude-longitude coordinates	6663 available

In preliminary work, maps were plotted on a base that showed those same two divisions from the digital state geologic map. The Quaternary, Tertiary, and source intrusive units were presented as a “basins” unit, and the pre-porphyry units were presented as a “ranges” unit. However, those divisions made the map seem unfamiliar, and locating features was confusing. So, for presentation only, Tertiary volcanic units are included within “ranges” (Fig. 2). This makes location easier, but it is still imperfect – the physiographic/hydrologic basins and geologic basins are slightly different.

All of the chemical-concentration values were then transformed to \log_{10} values and plotted on the simplified basins-and-ranges map base (pH is already a \log_{10} scale, so wasn’t transformed). For parameters where sites are sparse, we plotted “dot maps.” On these, larger chemical concentrations in ground water are shown as larger-diameter, bolder-colored dots. The ADEQ mine-site wells are colored green to distinguish them from the others, and are also plotted with dot diameters corresponding to concentrations. Analytical data have been contoured where data coverage is dense, with contours confined to drainage basins. However, many Arizona basins have multiple, stratified aquifers, so all the values within a basin should not necessarily be contoured together. Our contouring is *only* for visual effect. The contouring makes anomalies readily noticeable by allowing a high value from a single well to influence a large map area. Where data are sparse, individual values have a larger influence on contour locations.

Statistical analyses of the data was not undertaken, but

would be possible and appropriate, as long as interpretation stays within the context of the general evolution from ground-water recharge to accumulation in deep basins.

The following sections discuss a number of observations and interpretations about ground-water geochemical patterns associated with Arizona porphyry copper deposits. Figure 2 locates several detailed maps that are used to illustrate particular ground-water chemical patterns.

OBSERVATIONS AND INTERPRETATIONS

Ground-water chemical signature of Cu skarn deposits in Arizona

Cu-skarn deposits like the Mission-Pima deposit (Fig. 1) and others in the northern Pima district (Ransome, 1922; Kinnison, 1966; Einaudi, 1982) include considerable amounts of unreplaceable carbonate sedimentary host rock within the calcsilicate and magnesium-silicate skarn, though the unreplaceable host rock may have been recrystallized to calcite- or dolomite-marble. Garrels and Christ (1965, p. 81-83) calculated that “...the pH of a system containing CaCO_3 in water in equilibrium with the atmosphere is 8.4.” The natural waters of the northern Pima district are incompletely equilibrated with the atmosphere and in contact with unreplaceable calcite, so they trend toward that pH as an upper limit. The pH values are probably reduced by acid produced from sulfide oxidation, but the pH values are also driven toward equilibrium with

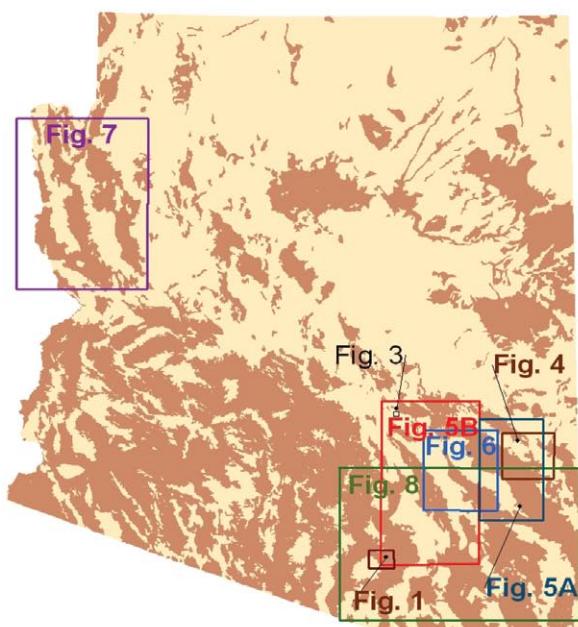
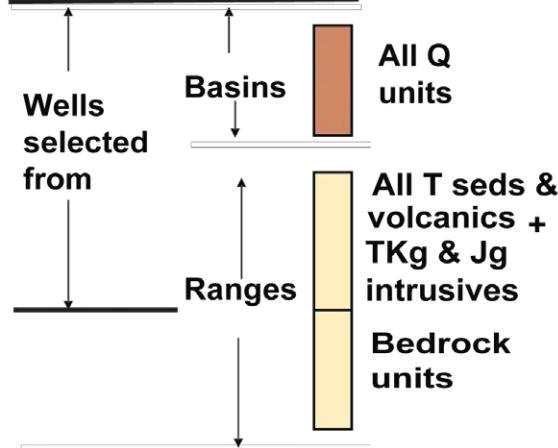


Figure 2. Map of Arizona showing (1) the division, by geologic map units, into basins and ranges for displaying ground-water chemical data, (2) the criteria, by geologic map unit, for choosing wells from digital databases for inclusion in the ground-water chemical mapping, and (3) locations of other map figures in this paper. Map units compiled from the digital Arizona state geologic map (Luddington et al., 2005; Richard, 2002).



calcite and the atmosphere. As a result of these competing influences, ground water is typically mildly alkaline, with pH values ranging from 7.1 to 8.2 (Huff, 1970, Table 6).

Huff's data and data evaluated for this study locally show anomalous metals and sulfate concentrations downgradient from Cu skarn deposits. As illustrated earlier, Mo concentrations form a classic ground-water dispersion pattern below the deposits (Fig. 1). Scattered samples near skarn deposits also have elevated zinc (Zn) and sulfate (SO_4), with zinc greater than 200 parts per billion and sulfate greater than 500 parts per million, and locally over 1000. Values like these for Zn and SO_4 are common in deep basinal ground waters from greater than ~300 m depth. SO_4 concentrations are likely even greater near buried gypsum beds. But such Zn and SO_4 values are clearly anomalous in shallower ground waters from basin flanks (as measured by Huff, 1970). Thus, in areas lacking information about deposits, elevated values from ground-water samples near basin boundaries are considered anomalous. In ground waters downgradient from Cu skarn deposits, neither Mo nor Zn are strongly correlated with SO_4 . Both metals are more frequently found at anomalous concentrations in ground water with bicarbonate (HCO_3) as its dominant anion.

Ground-water chemical signature of supergene-enriched or -enriching porphyry Cu deposits in Arizona

In Arizona, significant supergene enrichment deposits were present at Mineral Park, Bagdad, Sacaton, Santa Cruz, Copper Cities, Miami-Inspiration, Lakeshore, Ray, Silver Bell, San Xavier North, and Morenci (respectively, Eidel et al., 1968; Anderson et al., 1955; Cummings, 1982; Kries, 1995; Peterson, 1954; Peterson, 1962; Cook, 1988; Metz and Rose, 1966; Richard and Courtright, 1966; King, 1982; Parker and Stegen, 2007). Small chalcocite enrichment blankets were also found at Ajo, San Manuel, and Sierrita-Esperanza (Gilluly, 1946, p. 107; Lowell, 1968, p. 646; Lynch, 1966, p. 275), and small volumes of chalcocite enrichment are also known at the Red Mountain and Sunnyside prospects (Corn, 1975; Graybeal, 1996). In New Mexico, the Tyrone and Chino deposits were enriched (Duhamel et al., 1995; Rose and Baltosser, 1966), and in Sonora, the Cananea and La Caridad deposits were enriched (Velasco, 1966; Saegert et al., 1974). A distinctive set of ground-water chemical conditions, outlined below, results from supergene enriched or enriching porphyry Cu deposits in this region.

Iron (Fe), manganese (Mn), Cu, SO_4 , and at some places, Zn, occur in anomalously high concentrations in ground water downgradient from enriched or enriching porphyry copper deposits in Arizona. Low pH ground water may have little or no dissolved oxygen (DO), even at shallow depths. These conditions are found naturally in at least four places in Arizona. At these places the conditions cannot be attributed to exposure by mining of sulfide-rich systems, though exposing such systems by mining certainly also produces this set of anomalous

parameters in ground water. Many of the same water characteristics are found in areas of acid-rock drainage (Martin and Mills, 1976).

An undisturbed natural system in Copper Springs Wash southwest of Miami, Arizona (Fig. 3) is described below to illustrate the ground-water chemistry near and below a rock-water system where there is ongoing supergene enrichment of a porphyry Cu deposit. That system is later compared with a system that has been exposed by mining.

Copper Springs Wash drains northward off the Pinal Mountains, flowing into Bloody Tanks Wash about 3 km above the town of Miami. Over much of its course, Copper Springs Wash drains coarse, largely equigranular rocks of the Schultze Granite batholith (Creasey, 1984; Maher et al., 2005). The porphyry Cu deposits of Pinto Valley, Copper Cities, and Miami-Inspiration are each associated with Schultze porphyry dikes and apophyses on the north and northeast sides of the coarse equigranular body, and the large equigranular body is considered the parent batholith of the Schultze porphyries. Another mass of Schultze porphyry on the southeast side of the batholith in contact with Pinal Schist to its south also has associated mineralization. To the east of Copper Spring is the Lonesome Pine prospect area (Fig. 3). To the southeast is the Madera prospect drilled by Anaconda in the 1940s and described as an "immature" supergene chalcocite blanket with enriched grades of about 0.4% Cu (U.S. Geological Survey Mineral Resource Data System database). The Madera prospect is along a ridge-line that parallels the porphyry/schist contact, which is near the bottom of Copper Springs canyon. Farther west and straight uphill from Copper Spring, drilling has occurred in the area called Copper Springs Wash prospect.

Figure 3 illustrates some of the hydrology of the area around Copper Spring. That spring, at the bottom of the canyon, heads a short reach of perennial flow, shown in solid blue. Above it, in branch drainages, are Iron Spring East and Iron Spring West. Labels in Figure 3 give pH and DO measured at four ground-water sampling points in March, 2004. In the water from the iron springs, high within the gradient, DO values were essentially zero. These tiny springs vent slightly sulfidic water; there is a noticeable H_2S odor from the black sediment that clings to the bottom of cobbles or pine cones lifted out of the water. In Copper Spring the DO was only 2.8 mg/L, which was just 38% of the value of water fully equilibrated with air. Below the perennial reach, the ground-water DO was up to 7.3 mg/L, at 99% of the value fully equilibrated with air. The three springs are venting water from within the forming supergene enrichment profile of the Madera and Copper Springs deposits. The actively supergene-enriching porphyry mineralization is below the ridgeline on the southeast and south. The Iron Springs tap into the bedrock supergene system within or below the forming chalcocite blanket. Supergene mineralizing water is discharging laterally into the alluvial aquifer of Copper Springs Wash. In the alluvial aquifer, the ground water is evolving, and an exotic copper deposit (Münchmeyer, 1996) is forming. In addition to starting acidic

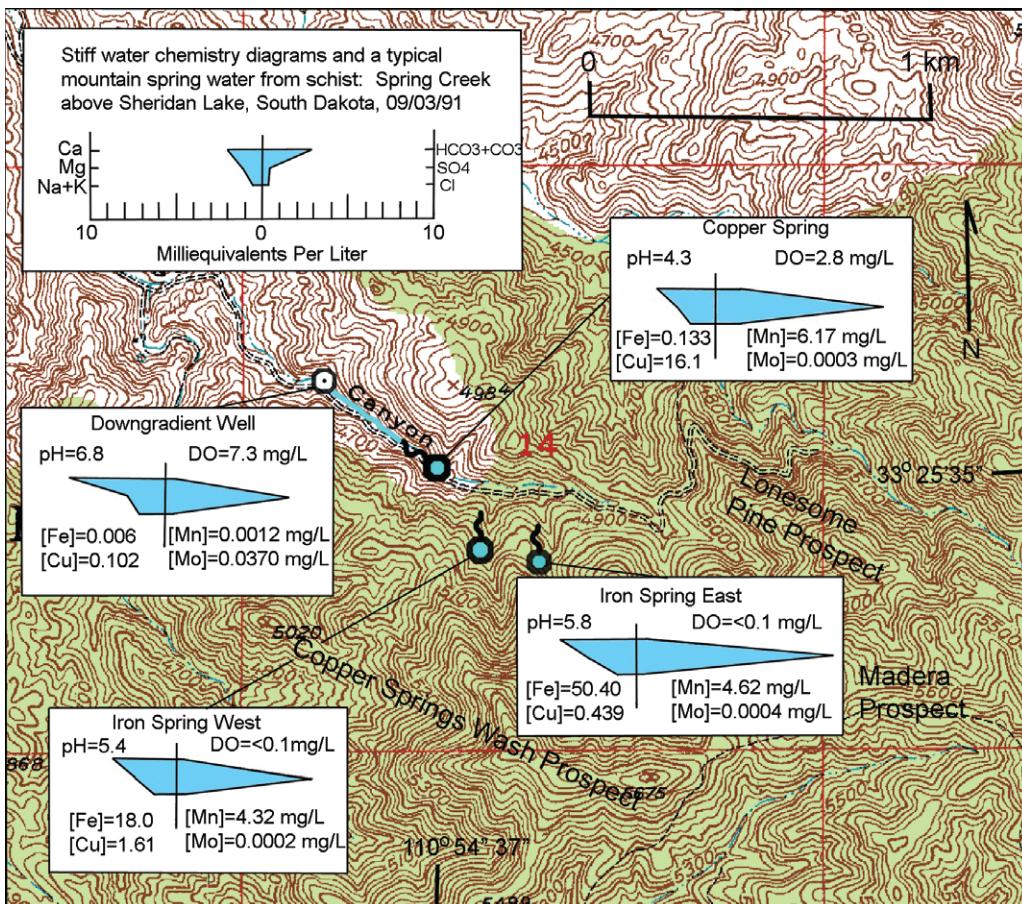


Figure 3. Ground-water and spring water sampling locations and measured water chemistry in an area of ongoing supergene enrichment of a porphyry copper deposit, Copper Springs Wash drainage southwest of Miami, Arizona. Base from U.S. Geological Survey 1:24,000-scale topographic quadrangle map, Pinal Ranch, Arizona. See text for more explanation.

and neutralizing down the gradient, the water that is discharging laterally from the enrichment profile starts oxygen-poor because it was stripped of its oxygen in reactions that are dissolving the hypogene sulfides.

Starting about 50 m below Copper Spring are bright blue and green copper-rich coatings (stream-water precipitates) on boulders in the stream bed of the perennial reach. The coatings extend downstream to the point where all the flow is subsurface. The most common copper precipitate is a powder-blue coating that forms high-water lines on the boulders. The blue coatings are amorphous to X-rays, and consist of copper aluminum silicate with small peaks for calcium and sulfur as determined from energy dispersive spectra from the scanning electron microscope. The coatings are interpreted as precursors to chrysocolla and minor gypsum. Alternatively, the coatings may be opal and an amorphous precursor to the mineral glaucocerinite (rhombodhedral $[(\text{Cu}, \text{Zn})_5\text{Al}_3(\text{OH})_{16}][(\text{SO}_4)_{1.5} \cdot 9\text{H}_2\text{O}]$), which have both been identified in a microscopic intergrowth at a second undisturbed area of ongoing supergene enrichment in Arizona.

Figure 3 also shows the concentrations of metals of interest in the water samples. The values of Fe are very high, as expected, in the iron springs, below which bright orange amorphous ferric oxide is precipitating on every solid surface including sticks, grass, moss, and pine cones. With zero DO and some sulfide, the dissolved iron measured in the samples

is ferrous iron according to speciation calculations using the program PHREEQC2 (Parkhurst and Appelo, 1999). Mn and Cu are also at quite anomalous concentrations in the water of the iron springs. Speciation calculations show that the Cu is predominantly the free (uncomplexed) cuprous ion and that Mn is predominantly the free manganese ion in the water of the iron springs. The Cu concentration is highest in Copper Spring, but PHREEQC2 speciation calculations identify that, with the greater DO there, copper is mostly cupric ion and dissolved CuSO₄⁰. Mn is also highest in Copper Spring water. Below Copper Spring, the water apparently loses Cu to the blue precipitates. Mn and Fe are also at lower concentrations in the ground water downgradient, predicting that not only the chrysocolla precursor is precipitating.

The highest molybdenum concentration (37 parts per billion) is found in the sample farthest downgradient, and is a very high value for shallow ground water. Increase in dissolved molybdenum concentration would be predicted from the higher pH (Goldberg et al., 1996), comparable with analyses of alkaline ground water from below Mission-Pima (Huff, 1970).

Figure 3 also shows the major-element chemistry of the same four samples. The diagrams are Stiff diagrams (Stiff, 1951), as illustrated in the upper left. On these diagrams, cation charge increases to the left, and the cations are arranged vertically in the order calcium (Ca) above magnesium (Mg)

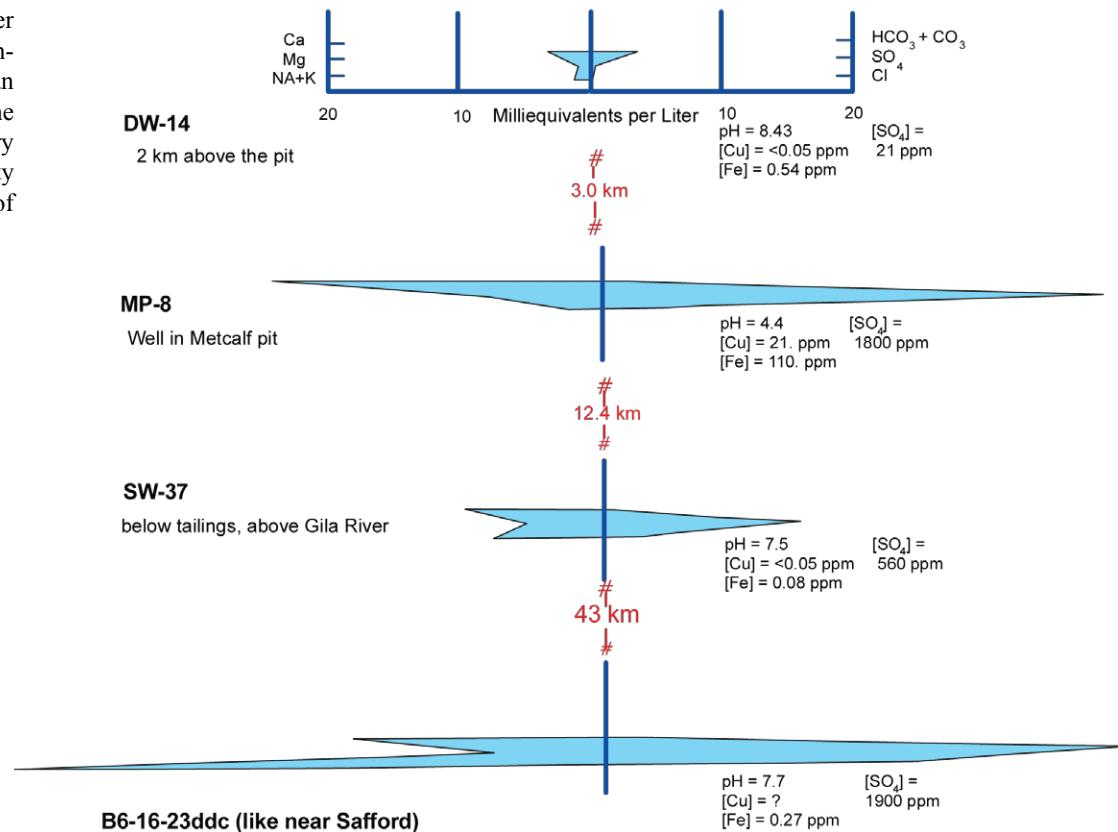
above combined sodium plus potassium ($\text{Na} + \text{K}$). Anion charge increases to the right and the arrangement is HCO_3 , above SO_4 above chloride (Cl). The total enclosed area of the diagram increases with the total dissolved solids (TDS) of the water. The water illustrated in the upper left is typical water from schist and granite terrain in the mountains of the semi-arid western U.S.A. It is very dilute, $\text{Ca}-\text{HCO}_3$ -type water. All four Copper Springs Wash waters are $\text{Ca}-\text{SO}_4$ -type with greater TDS than typical mountain-region waters. Yet, they are still relatively dilute; their average ionic strength is about 0.015. There is only minor evolution of the major ions over this short distance, and that is mostly an increase in Ca and HCO_3 . There is a slight increase in Na concentration in the neutralized downgradient water. The water at the iron springs is known from geological mapping to have percolated down through leached capping. The Pinal Schist and the granite porphyry on the ridge south of the springs are hypogene-altered to a greisen-veined assemblage (coarse-muscovite-enveloped, quartz-pyrite-chalcopyrite veins), and muscovite-bearing assemblages are typical for porphyry deposits with chalcocite blankets (Sillitoe, 2005).

The chemical changes in Copper Springs Wash are a small segment of the whole chemical evolution from mountain tops to deep basins. Figure 4 from the Morenci area shows a longer distance and similar ground-water geochemical evolution. Above the Metcalf pit, water sampled in a shallow well is typical near-recharge $\text{Ca}-\text{HCO}_3$ water-type, with very low

TDS. It has alkaline pH, very low Cu, low Fe, and very low SO_4 . The upper three ground waters in Figure 4 are from the ADEQ Aquifer Protection Permit study by Dames and Moore consultants for the Morenci mine. Water from a well at the bottom of the Metcalf pit in 1995 is much different, and it is much like the water at Copper Spring. It has low pH and very high Cu and Fe concentrations. It has high SO_4 and is $\text{Ca}-\text{SO}_4$ -type water. Enders et al. (2006) state that enrichment is ongoing at the Metcalf deposit. Twelve kilometers downgradient, in a well close to the Gila River, SO_4 concentration is lower and, as is slightly apparent in the downgradient well at Copper Springs Wash, Na increases. The water is mildly alkaline and contains low concentrations of the metals. Farther down gradient and deep into the basin, ionic strength is higher and Na and K are important. The water is still SO_4 -dominated, but both Cl and HCO_3 are elevated. The water is mildly more alkaline. Also, the Fe concentration is a little greater, probably due to decreasing DO with depth; this is also ferrous iron.

Safford Basin is the nearest deep basin downgradient from the Morenci area wells. All of the deep wells near the town of Safford and within this basin, and that are represented in QWDATA, have water concentrations of ($\text{Na} + \text{K}$) and Cl that are much greater than with Morenci area ground water. The deep basinal example well (B-6-16-23ddc) used here for comparison to Morenci area ground water is not from the Safford basin. But in chemical evolution, ground water like that from B-6-16-23ddc should lie between water like that from below

Figure 4. Ground-water chemistry from the mountains to the deep basin in an area of ongoing supergene enrichment of a porphyry copper deposit, vicinity of Morenci to vicinity of Safford, Arizona.

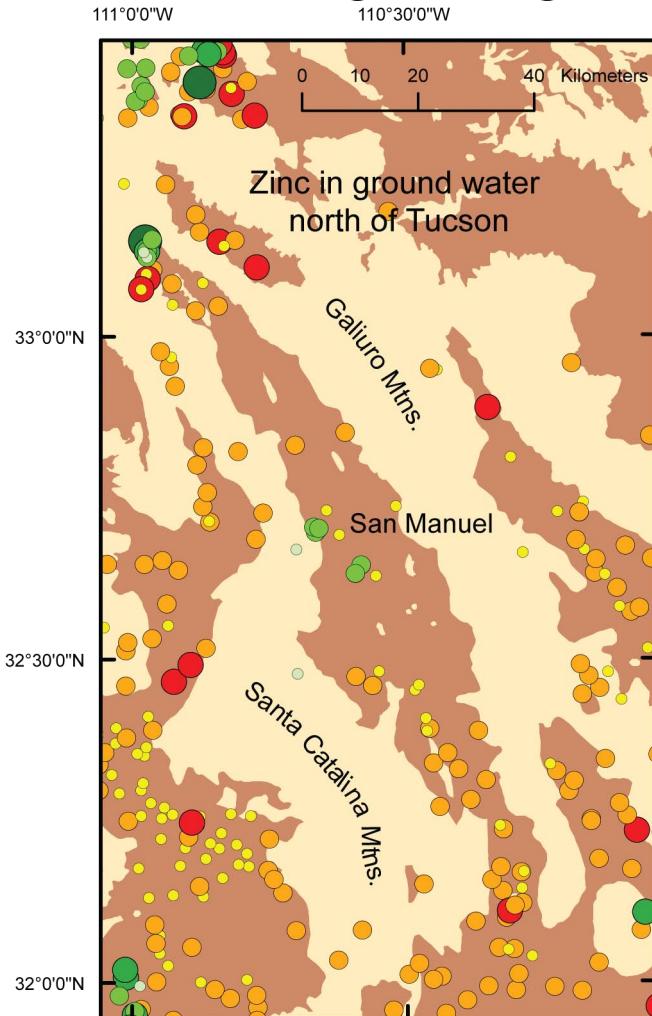


the Morenci tailings (well SW-37 in figure 4) and ground waters like those near Safford (Robertson, 1991), so B-6-16-23ddc is used to show the next step in the evolution on the way to water with much higher TDS and Na-Cl-SO₄ water-type.

Without the Morenci deposit, the evolution would not move to sulfate dominance until the ground water is well down into the basin, and the metals would not increase and then decrease down gradient. According to Robertson (1991), initial dilute Ca-HCO₃-type water would have become more concentrated in Ca and HCO₃ down gradient, followed by an increase in Mg and SO₄, in turn followed by increasing Na, K, and Cl towards the deep basin interiors.

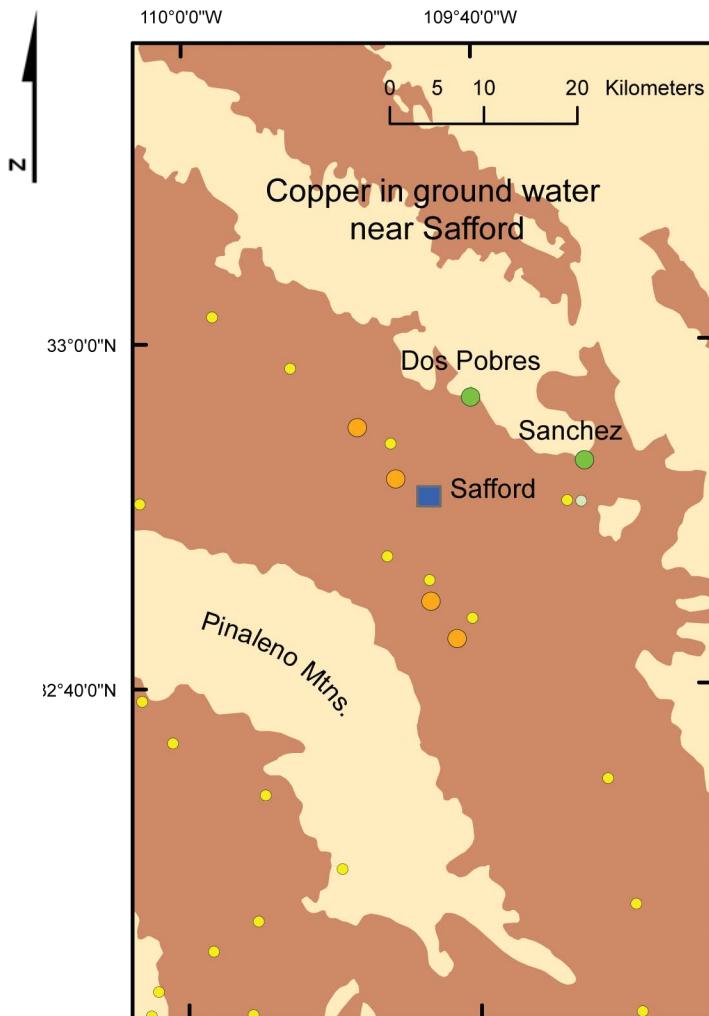
Figure 5. Example patterns of metals in ground water associated with Arizona porphyry copper deposits that are dominated by potassic alteration. Values are in micrograms per liter (ppb) of metal dissolved.

DEQ wells	Basin wells
Log Cu or Zn	Log Cu or Zn
0.0 - 1.5	0.0 - 1.5
1.51 - 3.0	1.51 - 3.0
3.01 - 4.0	3.01 - 4.0
>4	>4



Ground-water chemical signature of porphyry Cu deposits with potassic alteration in Arizona

The past two sections showed that the ground-water chemical signature for a Cu-skarn is mildly alkaline water with anomalously high Mo and possibly anomalous Zn and SO₄, and that the ground-water chemical signature for a supergene enriched or enriching porphyry Cu deposit is water with low pH, high Cu, high Fe, high Mn, and perhaps low DO. The ADEQ data show another chemical signature variant; that from porphyry Cu deposits dominated by potassic alteration. A well producing directly from rocks of a porphyry Cu deposit dominated by biotitic alteration shows mildly anomalous metal concentrations and near-neutral pH. The monitoring well that is producing water from the Dos Pobres deposit (Fig. 5B) has ground water with 640 ppb Cu at a pH of 7.13. That high Cu value is certainly higher than typical ground water of the Safford basin. Zn, Mn, and Fe also are mildly anomalous at places that are in and very near porphyry deposits dominated by potassic alteration. The Zn value in the monitoring well below San Manuel is 440 ppb, a



relatively high value for a shallow well (Fig. 5A). Mo is also found in anomalous concentrations in mildly alkaline ground water from deposits dominated by potassic alteration, but Mo has not been measured in as many places.

Water types

The various changes in ground water can be summarized in evolving from up- to downgradient and including parameters that are in anomalous concentrations due to porphyry Cu deposits. From up-slope of the Cu deposits, the general evolution of ground-water chemistry is (1) dilute Ca-bicarbonate (HCO_3^-)-type water with pH near 8, high dissolved oxygen (DO), and low trace metals, (2) near-deposit Ca- SO_4^- -type water, commonly with low pH, low DO, high SO_4^- , and high Fe, Cu, Mn, and possibly Zn, (3) near-downgradient, Ca- SO_4^- - HCO_3^- -type water with slightly alkaline pH, moderate-to-high DO, high Mo, high SO_4^- , and locally high Zn, and (4) ordinary basin ground water, typically Ca-Mg- HCO_3^- -type with increasing pH, Na, K, SO_4^- , and Cl and decreasing DO toward basin low points. Fe, Zn, Mn, and Mo may also increase with depth towards basin centers. Near deposits, oxidation of sulfides consumes O_2 , lowers pH, and releases SO_4^- , Cu, Mn, and Fe to the ground water. The Fe and Mn are appreciably soluble only in water with almost no DO, and low-DO water is unusual near the surface. Molybdenum is adsorbed at low pH but dissolves where pH is higher. Sulfate, Mo, and Zn remain dissolved as DO increases by mixing with ordinary ground water and remain dissolved as pH increases in contact with carbonates and feldspars, so these can migrate far from deposits as type 3 water. Unreplaced calcite in porphyry Cu-associated skarns produces near-deposit water of type 3 that evolves downgradient to type 4. Potassic and propylitic alteration assemblages do not produce acidic ground water, yet yield small-area, moderate concentration Mn, Fe, Cu, and Zn anomalies, and Mo anomalies may also be present and farther reaching, though less frequently measured.

Multi-parameter anomalies in single wells

In the state-wide data there are quite a number of analyzed ground-water samples that have anomalous values in more than one parameter, and multi-parameter anomalies in isolated single wells may be of significant interest. Each frame of Figure 6 shows a different mapped parameter over the same area. A single well collared about 2 km from the contact between Middle Tertiary sedimentary rocks and metamorphosed Proterozoic rocks near the southwestern flank of the Pinaleño Mountains is anomalous in Mo, Mn, SO_4^- , and, to a lesser degree, Zn. Not shown, the sample also had DO that was low for a well that is so close to the surface and to the range boundary.

We have not used the GIS location of this well to return to the original database and recover more information about the well and the sample, but the GIS tables linked to the

locations will simplify for the users the processes of returning for additional data. Returning to the original databases for a sample location or for an area that looks interesting is strongly recommended, because with more than 9000 locations, unusual well or sampling conditions or special sampling purposes cannot be readily identified but should be ignored in searches for porphyry copper deposits.

Long-traveled element/ion anomalies

Two analytes are notable for showing large dispersion halos that are probably attributable to porphyry deposit sources. These are Mo, as shown by Huff (1970; Fig. 1) and SO_4^- . The pattern of elevated SO_4^- below the Mineral Park deposit may be in excess of 17 km long, assuming that the source of sulfur is only the known deposit (Fig. 7). In this anomaly, the northern part is acidic water, but the southern part is alkaline. For these two parameters, particularly, the anomalies may extend into the typically alkaline water-type of the basins. Though these two may help target a deposit beneath the basin fill from more than 10 km away, they also illustrate that using ground-water chemistry from the basin-fill typically does not, itself, generate a target for drilling. Such maps may be useful as one of several data sets analyzed in a search for undiscovered and concealed porphyry copper deposits.

“False anomalies”

There are many areas with high values of the geochemical parameters discussed above where the sources are not porphyry Cu deposits. Some high sulfate concentrations are due to lacustrine evaporites within the basin-fill sedimentary rocks. There are concentric-contoured high values of SO_4^- beneath the Willcox Playa (Fig. 8). High values are found, also, along the axis of the Safford Basin and centered on the Benson area. Robertson (1991, p. C8) showed that each of these areas along with at least 9 more Arizona alluvial basins contain Tertiary lacustrine evaporites. Also, the Permian section of southeastern Arizona contains marine bedded gypsum (Blakey and Knepp, 1989).

Fe and Mn are generally greater with depth in moving toward the centers of basins, probably because the water is losing dissolved oxygen with depth. Zn and Mo may also be generally greater with depth.

Also, because of the varied purposes for analyzing ground water within the large databases, the data is likely to include a few contaminated waters. Contaminated water is not always easy to detect. We cannot examine the data site by site to try to exclude such points. But the GIS data tables linked to each site allow the user to go back to the source databases for any particular point of interest.

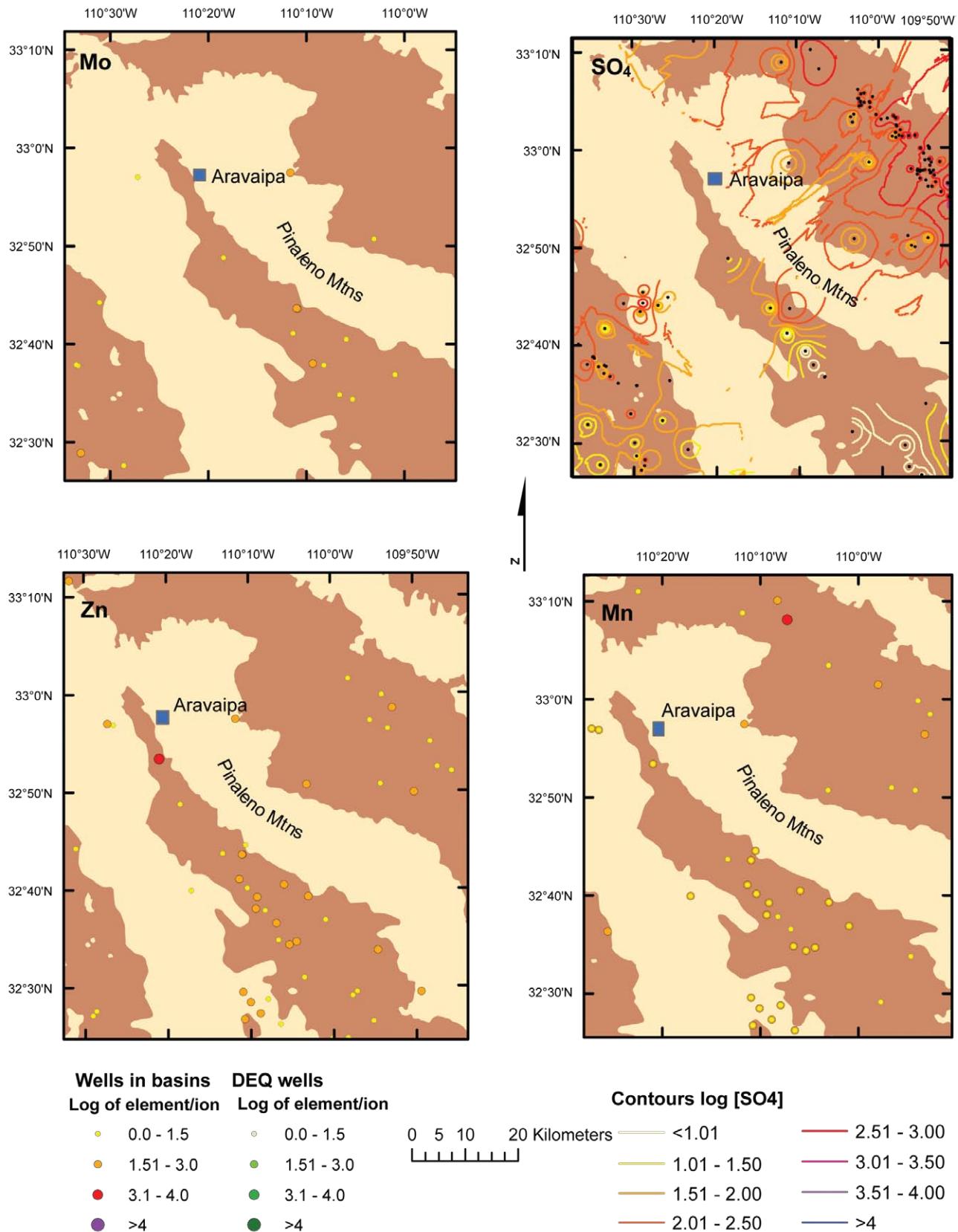


Figure 6. Example of a single-well, multi-parameter anomaly. The ground-water sample nearest to and southwest from the letter "o" in "Pinaleno Mtns." is anomalous in molybdenum and mildly anomalous in sulfate, zinc and manganese. The well is in a relatively upgradient position, near the bedrock/basin-fill contact, in the Aravaipa Creek basin. Values for Mo, Zn, and Mn are in micrograms per liter (ppb). Values for sulfate are in milligrams per liter (ppm). On the Mn map, note the doubled symbol where both NURE and QWDATA reported analyses for the single well. For Mn, NURE values were systematically lower than those in QWDATA.

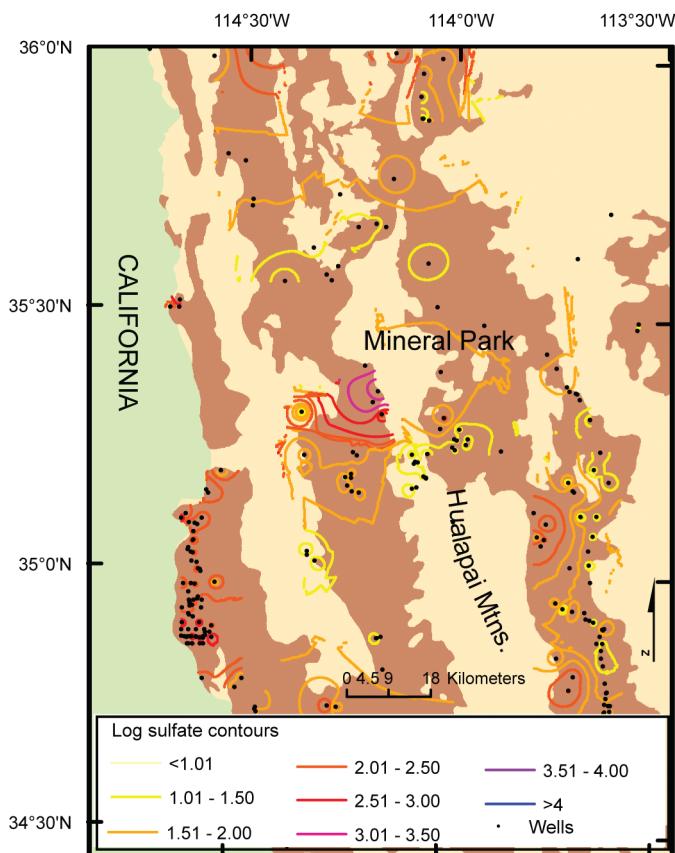


Figure 7. Example of an apparently extensive ground-water chemical anomaly probably attributable to an Arizona porphyry copper deposit: sulfate west and south from the Mineral Park deposit in the Sacramento Valley. Contours are for sulfate in milligrams per liter (ppm) in ground-water samples.

CONCLUSIONS

Ground-water chemical mapping in exploration for concealed deposits does not appear to uniquely identify drilling targets. As one method within an integration of several, however, it is probably useful.

More specifically, Cu, Zn, Mn, Fe, SO₄, low alkalinity or pH, and low dissolved O₂ in ground water appear to be anomalous downgradient from porphyry Cu deposits that have supergene enrichment blankets. These are from rocks that are affected by quartz-sericite-pyrite, argillic, and maybe advanced argillic alteration. Cu, Mn, Fe, or Zn also may form small-area, moderate-concentration anomalies in the mildly alkaline water that evolves from silicic rock-hosted deposits dominated by potassie alteration. Mo may also be anomalous below such deposits. Ground water below Cu-skarns is also mildly alkaline and can have anomalous Mo and SO₄. Mo and SO₄ can form large ground-water anomalies that, at places, are almost certainly derived from porphyry Cu deposits. Molybdenum and sulfate stay in solution in the typically alkaline water-type of the alluvial basins. They may provide evidence of distant concealed deposits. Single isolated wells

that have anomalous values in two or more parameters may be clues to the location of undiscovered sulfide mineral deposits. However, high values may be the result of geologic features other than porphyry copper deposits. The most obvious of these is high SO₄ due to lacustrine evaporites in the basin-fill sediments. There are other additional possible problems with individual data sites such as contamination, so we urge caution in using the maps.

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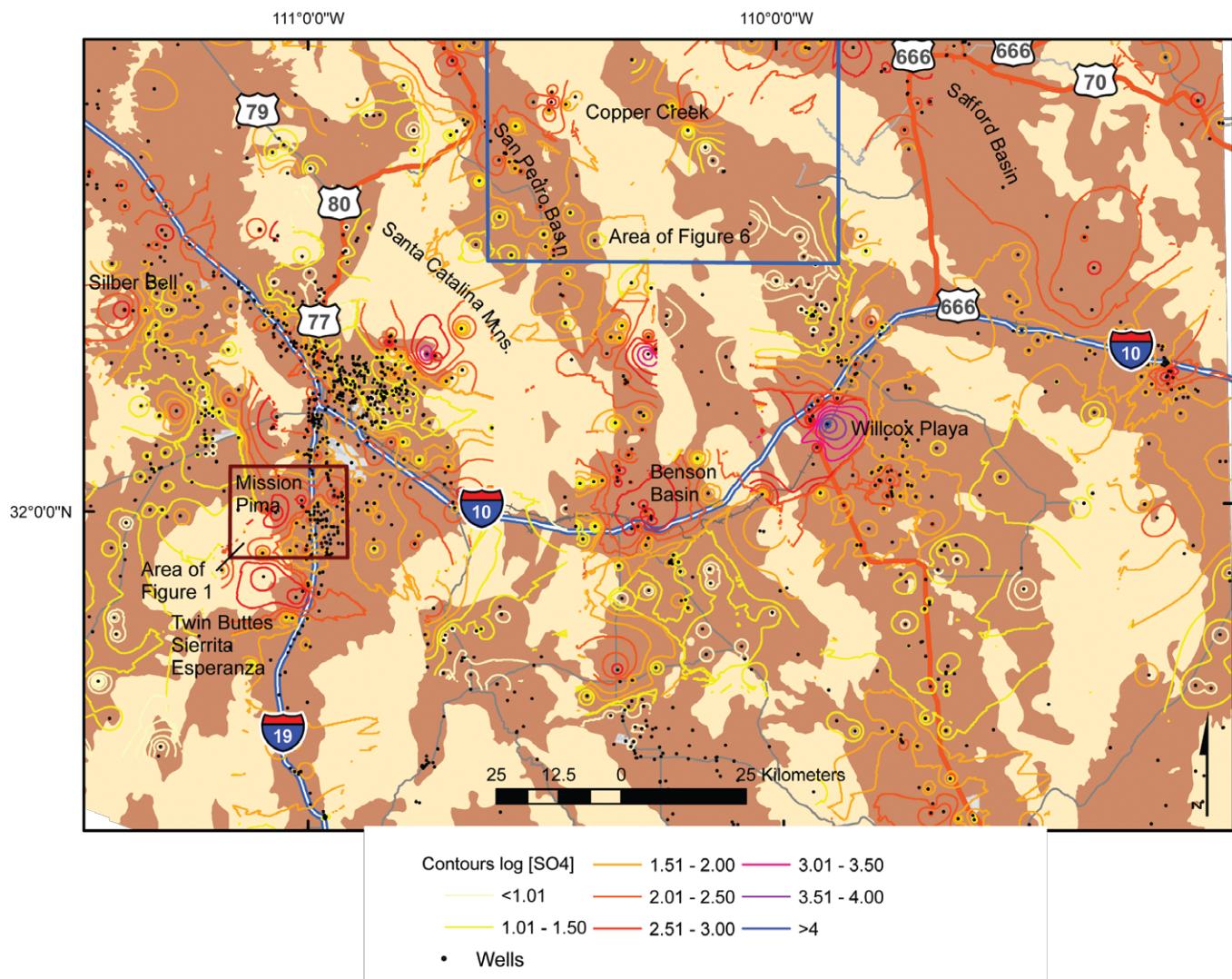


Figure 8. Anomalous sulfate concentrations in ground water are probably attributable to lacustrine evaporates in the basin-fill sediments in the Safford Basin, the Willcox Playa, the Benson Basin, and the northern San Pedro Basin, Arizona. Other sulfate anomalies, however, are associated with porphyry copper deposits and prospects, at post-mining Silver Bell, Mission-Pima, Sierrita-Esperanza-Twin Buttes, and Copper Creek. The causes of several additional anomalies are not known.

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