## **ESET** FEATURES

reas throughout the world have been mined for metals, sometimes for thousands of years. Metal-rich wastes resulting from this activity may be deemed to pose a hazard to human health and environmental quality. Remediation programs and monitoring of such sites may be enhanced if knowledge is available concerning the natural concentrations of metals that existed in the mineralized areas prior to disturbance by humans. In the United States approximately 50 mining sites are the subject of Superfund (CERCLA) investigation and litigation.

A difficult question that almost always arises is: What were the natural background concentrations of the metals of concern in the mined areas prior to mining? Because of the anthropogenic overprint, it is exceedingly difficult to recognize the original geochemical characteristics of the region. For example, Hosking (1) describes how the natural background geochemistry in Cornwall, England, has been obscured by more than 2000 years of mining and related activities.

If natural background concentrations in mineralized districts could be characterized, the data should be helpful in devising realistic plans for remediation and monitoring. For example, in mineralized areas it may not be scientifically reasonable or technically possible to remediate the water to standards that are lower than the natural background concentrations.

Three methods are proposed for estimating natural background chemistry of water in mineralized areas that have been mined: examination of historical documents, comparison to natural concentrations in mineralized areas that have

### DONALD D. RUNNELLS

University of Colorado Boulder, CO 80309-0250

### THOMAS A. SHEPHERD

Shepherd Miller, Inc. Fort Collins, CO 80525

### ERNEST E. ANGINO

University of Kansas Lawrence, KS 66045

## Metals 3

DETERMINING NATURAL BACKGROUND CONCENTRATIONS IN MINERALIZED AREAS

# Mater

not been mined, and theoretical geochemical modeling. These approaches range from qualitative (historical descriptions) to quantitative (geochemical modeling).

### Historical records

The geological and geochemical literature is rich in accounts of natural, metal-rich waters. Perhaps the earliest is by Agricola, who in 1546 stated (2, 3): "Now I will discuss that kind of minerals for which it is not necessary to dig, because the force of water carries them out of the veins. Of these there are two kinds, minerals—and their fragments—and juices... If the springs discharge water containing some juice, this also should be collected...."

Historical records tend to be qualitative and subjective, but investigators should examine such accounts for descriptions of "natural contamination." For example, Red Creek, Sulfur Creek, Alum Creek, Bitter Creek, Copper Creek, Red Mountain Creek, Red Dog Creek, Iron Spring, and Buttermilk Spring are actual geographic names that describe naturally contaminated waters.

In the San Juan Mountains of southwestern Colorado near Ouray,

metal-rich Red Mountain Creek drains the abandoned Red Mountain Mining District. In December 1972 a sample of the water had a pH of 3.3, with dissolved concentrations (filtered, 0.45-μm membrane filter) of 32 mg/L Fe, 0.030 mg/L Cd, and 3.5 mg/L Zn (4). Today it is visually obvious that Red Mountain Creek is affected by metal-rich drainage from abandoned mines, waste dumps, and tailings piles. However, based on early geologic publications, it is equally obvious that Red Mountain Creek was naturally contaminated by acid rock drainage before miners arrived on the scene. In fact, in the early literature the stream was called "Red Creek" rather than "Red Mountain Creek" (5). We also find such chemical descriptions as: "... all streams and springs are impregnated with mineral..." (5, p.  $\hat{7}$ 9) and "... the abundant strongly mineralized springs which issue from the surface in this district at the present day" (6, p. 108). The early geologic accounts (7, p. 98) also tell of '...abundant iron springs. ...'' A partial analysis of a spring in 1888 included (6): "SO $_3$  [sic]—very much; Fe—much; Zn—a little; Cu— 0.65 ppm."



Another example comes from the classic lead-zinc deposits of the Mississippi Valley Type (MVT) in the midcontinental United States (8). Surface waters were certainly in contact with the metallic ores of the area before mining began because the earliest mining by French explorers in the Southeast Missouri District (in the early 1700s) consisted simply of gathering chunks of galena (PbS) from the soils and weathered bedrock (9). The first discovery of ore in southeastern Kansas was in 1868 in a water well (10), again showing the shallow exposure of the sulfide mineralization. In 1879 Mudge stated: ". . . the lead and zinc ores are among the broken limestone and chert . . . the waters coming over these various minerals is more or less charged with them and with silic [sic] and sulfuric acid . . ." (11). Siebenthal (12) attributed the numerous yellowish "buttermilk" springs in the area to the presence of colloidal zinc carbonate; some springs in southeastern Kansas were reported to contain zinc in the range of 100-130 mg/L. Smith (13) attributes the high zinc content in spring waters to the oxidation of nearby deposits of sphalerite (ZnS) ore. Additional reports

of mineralized groundwater in Kansas and Missouri are found in other old scientific documents (10, 14).

In summary, historical records show clearly that natural waters in mineralized areas commonly had low pH values and elevated concentrations of metals before mining began.

# possible to remediate the water to standards that are lower than the natural background concentrations.

Mined vs. nonmined

Perhaps the most useful approach to characterizing the natural background geochemistry of water is a simple comparison of the concentrations of metals and other components in areas that have and have not been mined.

For example, Kepler (15) reports that Iron Spring, south of Telluride, CO, has a pH of 3.9 and contains total concentrations up to 1.5 mg/L of Fe, 0.27 mg/L Cu, and 0.40 mg/L Zn in an area that has not been mined. Farther to the south in the San Juan Mountains, Alum Creek and Bitter Creek have natural pH values between 2.7 and 3.3, with dissolved concentrations of up to 17 mg/L Fe, 0.27 mg/L Cu, and 0.94 mg/L Zn (15). If this were a mining area, the low pH values and high concentrations of metals might be incorrectly attributed to mining, not to natural processes of weathering and leaching.

Table 1 presents a summary of partial analyses of waters from mineralized areas throughout the world that have not been mined. The data show that values of pH as low as 2.6 and total (nonfiltered) concentrations of Cu and Zn as high as 68 mg/L and 16 mg/L, respectively, have been reported in stream waters draining exposed sulfide deposits in Canada. The data in Table 1 show that total concentrations of 2 to 3 mg/L Cu and Zn are fairly common in waters associated with nondisturbed ore deposits. Data for Cd and Pb are sparse, but concentrations of a few tenths of a milligram per liter represent the upper limit of natural concentrations for these metals in waters from many mineralized areas.

Three published summaries of worldwide averages of metals in stream waters from nonmineralized areas were examined (3, 21, 39); the ranges of these global averages (in mg/L) are: Cu, 0.002 to 0.007; Zn, 0.010 to 0.020; Pb, 0.0002 to 0.003; and Cd, 0.00003 to 0.00007. Compared to these global values, concentrations of metals associated with metallic mineral deposits (Table 1) are up to 3–4 orders of magnitude higher.

Shvartsev et al. (23) analyzed nonacidic (pH from 6.8 to 7.8) waters adjacent to ore deposits. They point out that the natural concentrations of metals in nonacidic waters in proximity to ore deposits can ex-

ceed nonmineralized background concentrations by hundreds to thousands of times. The maximum total concentrations (in mg/L) given by Shvartsev et al. (23) for metals in neutral waters near ore deposits include 0.26 Cd, 15 Mn, 1.0 Cu, 0.25 Pb, and 2.5 Zn, representing natural enrichment factors over nonmineralized background concentrations in waters of those regions of 5200 (Cd), 1500 (Mn), 1000 (Cu), 500 (Pb), and 1250 (Zn).

The large Red Dog ore deposit in northwestern Alaska was discovered because it was exposed at the surface of the Earth. The ore consists chiefly of sulfides of Zn, Pb, Fe, and Ag, in a host rock of black siliceous shale and chert (40). Chemical analyses from a 16-month baseline study conducted before mining began at Red Dog (41, 42) reveal natural contamination of

stream and groundwaters by leaching of metals from the nondisturbed ore body. Analyses of 16 samples of stream water (three sites) upgradient from the deposit and three samples of stream water (two sites) within the zone of exposed mineralization showed the following ranges (in mg/L) of dissolved metals (fieldfiltered, 0.45-µm membrane filters): Zn, 0.036 to 0.7 upstream, 11.0 to 272 downstream; Pb, 0.001 to 0.45 upstream, 0.004 to 2.25 downstream; Cd, 0.002 to 0.10 upstream. 0.14 to 0.80 downstream. The concentrations were highly dependent on season. Shallow groundwaters collected from pits downgradient from the nondisturbed Red Dog deposit reportedly contain total (nonfiltered) concentrations up to 3.67 mg/L Cd, 3.58 mg/L Pb, and 328 mg/L Zn (41).

In summary, stream waters and

deposits <sup>a</sup>				Cond	centration (mg/L	)	
Location (type of water sampled)	Rocks	рН	Cu	Zn	Pb	Cd	Reference
North Wales, Great Britain (stream and groundwater)	Turbidite, slate, diorite	nr	>0.10 <sup>b</sup>	nr	nr	nr	16

North Wales, Great Britain (stream and groundwater)	Turbidite, slate, diorite	nr	>0.10 <sup>b</sup>	nr	nr	nr	16
France (six deposits) (stream water)	Carbonates and siliceous	nr	0.01-0.03	0.02-0.17	<0.001-0.02	nr	17
New Zealand (stream water)	nr	nr	<0.001-0.080 (total Cu + Z		nr	nr	18
Yukon, Canada (stream water)	Intrusive igneous	2.6	0.03-2.92	nr	nr	nr	19
New Brunswick, Canada (three streams)	nr	2.7-7.0	<0.001-0.03	0.005-0.3	<0.001- 0.006	nr	20
Russia (six regions) (groundwater)	nr	nr	0.01-0.13	0.04-0.5	nr	nr	21
Northwest Territories, Canada (1 lake)	Metavolcanics, carbonate-poor	3.5-4.1	0.24-0.090	0.073-0.19	0.006-0.018	nr	22
Northwest Territories, Canada (2 springs)	Metavolcanics, carbonate-poor	3.4	0.87-2.1	1.1-2.0	0.34-0.51	nr	22
Russia (many sites; max. values in shallow groundwaters)	Shallow portions of weathered ore deposits	6.2-7.8	1.0 (max.)	2.5 (max.)	0.25 (max.)	0.26 (max.)	23
Yukon, Canada (stream)	Metamorphic and igneous, no carbonate	nr	0.005-0.1	0.11-0.14	nr	nr	24
Arkansas, Ouachita Mtns. (regional groundwater)	Shale, chert, sandstone, limestone	nr	0.001-0.85	0.002-0.14	<0.01-0.059	nr	25
Northwest Territories, Canada (three streams)	Volcanics and thin limestones	3.0-3.8	1.0-68.0	1.1-16.0	0.34 (one value reported)	nr	26
Northwest Territories, Canada (many lakes, in four areas near exposed ores)	Igneous and metamorphic, with minor carbonates	3.5-7.4	<0.001- 0.064	<0.001-0.50	<0.001- 0.010 (20 lakes)	nr	26
Puerto Rico (streams)	Intrusive igneous	3.9-8.4	<0.03-4.1 <sup>b</sup>	<0.015- 0.12 <sup>b</sup>	nr	nr	27
N.W. Arizona (one spring)	Intrusive igneous	4.0	12.0 <sup>b</sup>	3.3 <sup>b</sup>	nr	nr	na

shallow groundwaters associated with ore deposits that have not been mined can be naturally acidic (pH as low as 2.6), with documented filtered concentrations of Cu up to 12 mg/L, 272 mg/L Zn, 2.25 mg/L Pb, and 0.80 mg/L Cd. These natural concentrations of metals can far exceed the EPA primary and secondary standards for drinking water (pH between 6.5 and 8.5, 1 mg/L for Cu, 5 mg/L for Zn, and 0.010 mg/L for both Pb and Cd) as well as the EPA water quality criteria for the protection of aquatic life (43).

### Predictive geochemical modeling

A third approach, predictive geochemical modeling, can put realistic upper limits on the concentrations of chemical components to be expected in natural waters at equilibrium with rock and ore minerals (44-47). Predictive geochemical modeling allows one to vary important environmental parameters over a range of hypothetical conditions of exposure and weathering of an ore deposit. The output includes the predicted aqueous speciation and concentrations of dissolved metals at equilibrium with selected minerals, plus the state of saturation of the water with respect to a variety of minerals and solid compounds. We present below an example involving waters in the old Tri-State Mining District, Kansas (8), using the computer code PHREEQE

Important limitations are involved in predictive geochemical modeling. First, the choice of solid phases must be realistic and representative of the rocks involved. Second, such important input parameters as the E<sub>H</sub> and partial pressure of carbon dioxide gas must be reasonable and representative of the environmental conditions being explored. And third, it is assumed that chemical equilibrium is attained. Each of these assumptions is discussed below.

In this study the first two conditions mentioned above-the choice of solid phases and geochemical input parameters-were based on published summaries of mineralogy (8) and geochemical parameters (48)49) and were realistic for the site. The assumption of complete chemical equilibrium is of fundamental importance and has been the subiect of much discussion (44-47). In natural situations the kinetics of important reactions may be too slow to allow equilibrium to be fully achieved; for example, dissolved species of redox-sensitive elements are rarely in oxidation-reduction equilibrium in shallow ground-

Location (type of water sampled)	Rocks	pH	Cu	Zn	Pb	Cd	Reference
Czechoslovakia (many springs, wells, streams)	nr	nr	nr	0.05-0.25 (Zn or Pb, no	ot specified)	nr	28
Wisconsin Zn-Pb district (3766 springs)	Dolomite, chert, limestone	6.9-7.4 (21 samples)	nr	0.05-0.27 (75th percent	tile, mainly Zn)	nr	29
Wisconsin (approx. 90 springs and streams)	Dolomite, chert, limestone	7.1-8.7	<b>nr</b>	<0.002-1.5 (total heavy mainly Zn)	metals,	nr	30
Northwest Territories, Canada (lakes)	Precambrian basalts and sediments	nr	0.002-0.020	nr	nr	nr	31
Ontario, Canada (four shallow groundwaters)	Precambrian metamorphics	nr	0.003-0.070	nr	nr	nr	32
Park County, Montana (two springs)	Igneous, sedimentary, contact	2.73-3.93	0.30-7.9	0.07-1.1	<0.01	<0.0002- 0.003	33
Mt. Haldane, Yukon (nine streams)	Metamorphic, with minor limestone	5-8	<0.010-2.0 (total heavy	metals, mainly	Zn)	nr	34
Basin and Parent Creeks, Yukon (three springs)	Metamorphic, with minor limestone	4-6	0.080, 1.7, 50 (total heavy	metals, mainly	Zn)		35
Basin and Parent Creeks, Yukon (two streams)	Metamorphic, with minor limestone	4-6	0.010-7.0 (total heavy	metals, mainly	Zn)		35
Flambeau, Wisconsin (groundwater)	Precambrian volcanics	5.8-7.4	0.003- 0.085 <sup>b</sup>	0.005-1.8 <sup>b</sup>	<0.0025 <sup>b</sup>	0.0002- 0.024 <sup>b</sup>	36
Flambeau, Wisconsin (river water)	Precambrian volcanics	6.2-8.0	<0.005- 0.30 <sup>b</sup>	<0.05- 0.068 <sup>b</sup>	<0.0005 <sup>b</sup>	<0.001 <sup>b</sup>	36
Crandon, Wisconsin (groundwater)	Glacial drift, above subcrop of sulfide ore in volcanics	7.7 (mean)	<0.001- 0.09 <sup>b</sup>	<0.001-2.6 <sup>b</sup>	<0.01-0.10 <sup>b</sup>	<0.001- 0.015 <sup>b</sup>	37
Crandon, Wisconsin (groundwater)	Volcanic bedrock (six deep drillholes)	5.9-8.1	<0.001- 0.27 <sup>b</sup>	0.041-1.5 <sup>b</sup>	<0.01-0.39 <sup>b</sup>	<0.001- 0.027 <sup>b</sup>	38

<sup>&</sup>lt;sup>a</sup> Type of enclosing rock is listed if reported. Values are for total metal except where indicated; nr = not reported; max. = maximum value reported; na = not applicable, Runnels, D. D. University of Colorado, Boulder, unpublished data, 1981.

<sup>b</sup> Dissolved = filtered value.

water (50). Therefore, the concentrations of metals predicted by an equilibrium geochemical model will be in error if equilibrium is not attained.

In general, geochemical modeling involving the dissolution of minerals will yield predicted concentrations that are too high (because of kinetically slow reactions) and will represent a worst-case situation; this is almost certainly true for flowing stream water that is only briefly in contact with exposed ore minerals. In contrast, equilibrium modeling will yield predicted concentrations that are too low for dissolved species that are supersaturated in solution and kinetically inhibited from precipitating. The assumption of equilibrium is likely to be most acceptable for buried ore deposits that are in contact with slowly moving groundwater.

The data presented earlier for the Red Dog deposit illustrate that groundwaters in contact with ore contain higher concentrations of metals than stream waters just a few feet away. The differences in concentrations probably result from the longer time that the groundwaters have had to approach equilibrium with the ore minerals.

### Modeling of waters

In the Tri-State District, Kansas, the ore deposits consist chiefly of sulfides of Zn, Pb, and Fe, with minor amounts of Ni and Cd sulfide, all contained in a host rock of calcite, dolomite, and chert (8). Parkhurst (51) has investigated the discharge and metal-loadings in mine waters of the portion of the district in southeastern Kansas.

A realistic suite of primary and secondary minerals was selected from the data of Brockie et al. (8). The corresponding minerals, or reasonable proxies from the PHREEQE thermodynamic database, were defined as being at equilibrium with the water. The approach was to simulate the gradual exposure and weathering of a sulfide ore deposit that was originally deeply buried, with increasing partial pressures (fugacities) of oxygen and carbon dioxide gas. Two starting water compositions were chosen: pure water and upgradient stream water. In the modeling exercise these waters were allowed to equilibrate with representative suites of ore and gangue minerals.

The mineral assemblages and initial parameters chosen for the simulations are listed in Table 2. Values

from Figure 11.2 in Reference 50 were used to estimate the initial E<sub>H</sub>. The E<sub>H</sub> of +0.503 volts (at a pH of 7.5) was chosen as a reasonable representation of the redox status of surface water or shallow groundwater in contact with atmospheric air, whereas the negative values of EH represent the more strongly reducing environments of deeper groundwaters. Initial partial pressures of CO2 gas were estimated from Reference 49 for two of the assemblages; for the third (carbonate) assemblage an unusually high Pco, (0.32 atm) was chosen to represent a situation in which acidic waters from oxidizing sulfide minerals are in contact with carbonate rocks. In the simulations, different assemblages of solids were selected to approximate the mineral assemblages that might reasonably be expected under various intensities of oxidation of the sulfides (Table 2). To achieve a realistic model output for Mn and Cd, it was necessary to add MnCO<sub>3</sub> and CdCO<sub>3</sub> to two of the assemblages in Table 2; these minerals have not been reported by Brockie et al. (8) from the Tri-State District, but they might reasonably be expected to be present.

Initial geochemical simulations involving pure water (not presented here) showed that all of the sulfide minerals are thermodynamically stable and relatively insoluble under strongly reducing conditions, but extremely unstable and highly soluble in oxidizing environments. Oxygenated groundwaters and stream waters in contact with a sulfide ore body would therefore be subject to varying degrees of con-

tamination by metals, depending on the length of contact time.

### Predicated and observed chemistry

The Short Creek in Kansas flows generally from east to west through the abandoned mining district around the town of Galena. Chemical analyses of the stream water upgradient and downgradient from the old mining district are given in Table 3. The water in Short Creek about two miles upstream from the mining area is slightly alkaline and relatively free of dissolved metals, but after flowing through the abandoned mining area it is mildly acidic and contains higher concentrations of dissolved Cd, Cu, Fe, Mn, and Zn. [It is important to note that the downstream samples of water in Short Creek summarized in Table 3 were obtained on the same day as their upstream counterparts (52)]. The question is: Could any of the observed contamination be attributable to natural processes of weathering and leaching, in the complete absence of disturbance by humans?

### Creek water and oxidized minerals

As mentioned earlier, some of the ore bodies in this region were originally exposed at or near the surface of the Earth, but evidence for this has been removed by the subsequent mining process.

The output of the predictive geochemical simulations includes the compositions of the waters after equilibration with the mineral assemblages of Table 2. The goal of the simulations was not to exactly match the observed composition of

TABLE 2 Three representative compounds used in the E <sub>H</sub> and P <sub>CO2</sub> <sup>a</sup>		
Highly oxidized (sulfate, hydroxide, carbonate minerals)	Slightly oxidized (sulfide, carbonate, sulfate minerals)	Slightly oxidized (carbonate and sulfate minerals)
Barite (BaSO <sub>4</sub> )	Barite (BaSO <sub>4</sub> )	Barite (BaSO <sub>4</sub> )
Jarosite [KFe <sub>3</sub> (SO <sub>4</sub> ) <sub>2</sub> (OH) <sub>6</sub> ]	Greenockite (CdS)	Otavite (CdCO <sub>3</sub> )
Otavite (CdCO <sub>3</sub> )	Sphalerite (ZnS)	Siderite (FeCO <sub>3</sub> )
Cerussite (PbCO <sub>3</sub> )	Galena (PbS)	Smithsonite (ZnCO <sub>3</sub> )
Manganite (MnOOH)	Cerussite (PbCO <sub>3</sub> )	Cerussite (PbCO <sub>3</sub> )
Ferric hydroxide [Fe(OH) <sub>3</sub> ]	Rhodochrosite (MnCO <sub>3</sub> )	Calcite (CaCO <sub>3</sub> )
Ni(OH) <sub>2</sub> (precipitate) Zn(OH) <sub>2</sub> (precipitate)	Calcite (CaCO <sub>3</sub> )	Dolomite [CaMg(CO <sub>3</sub> ) <sub>2</sub> ]
	Initial E <sub>H</sub> and log P <sub>CO2</sub>	
E <sub>H</sub> = (+)0.503 V	(-)0.118 V	(-)0.148 V
$P_{CO_2} = (-)3.0$	(-)2.0	(-)0.5
<sup>a</sup> Assemblages chosen to repres Last column involves carbonate	ent various degrees of oxidation minerals with high partial pressu	of a Tri-State ore body. re of CO <sub>2</sub> gas (0.32 atm).

TABLE 3
Analyses of Short Creek water from locations about two miles upstream and two miles downstream from the Galena Mining District, southeastern Kansas<sup>a</sup>

	Dissolved concentrations (mg/L)															
Location	Na	к	Ca	Mg	Alkalinity (CaCO <sub>3</sub> )	CI	SO <sub>4</sub>	SiO <sub>2</sub>	рН	Ba	Cd	Cu	Fe	Pb	Mn	Zn
Upstream	5.1	2.0	41	4.5	76	2.0	50	6.0	7.5	0.10	0	0	0.02	0	0.04	0.19
Downstream	9.3	5.0	71	6.5	8	9.0	240	17	6.0	0	0.17	0.02	0.01	0	1.7	25

water from western Short Creek, but to simply determine if it is chemically possible to release significant concentrations of dissolved metals and other species into Short Creek water under reasonable scenarios of natural weathering and dissolution. The final predicted concentrations resulting from equilibration with each mineral assemblage are listed in Table 4. Under the "highly oxidized" scenario (corresponding to the assemblage in the first column in Table 2), all of the metals and nonmetals are in their highest natural oxidation states, with the exception of Mn; an increase in E<sub>H</sub> would therefore not change any of the predicted concentrations except Mn, which would decrease.

In examining and comparing the results of the three simulations (see second through fourth columns in Table 4), it is clear that the concentrations of metals and other components in contaminated sections of Short Creek could certainly result from natural weathering of a variety of assemblages of ore minerals of the Tri-State Mining District, under realistic simulated conditions. In fact, some of the predicted concentrations are surprisingly close to those that are actually observed in the downstream creek water. Clearly, contamination from anthropogenic sources is not the only possible explanation for the present concentrations in Short Creek.

A more rigorous prediction of the concentrations of dissolved species associated with weathering ore deposits would require a more definite understanding of the mineralogy and the geochemical parameters (E<sub>H</sub>, P<sub>CO2</sub>) that control the system, as well as assurance of chemical equilibrium. As presented here, equilibrium geochemical modeling represents only a first approximation to the real situation; it does not include such complicating factors as modification of natural flow paths by mining, rubblization of the rock, fresh exposure of the minerals to air in mine workings, and the like.

TABLE 4 Predicted dissolved concentrations in water as a function of mineralogy,  $E_H$ , and  $P_{CO_2}$  (mg/L)<sup>a</sup>

Component	Highly oxidized	Slightly oxidized	Moderately oxidized	Observed at Short Creek
Final pH	7.2	7.0	6.3	6.0
Ba	0.0092	0.0059	0.20	0
Ca	41	750	210	71
Cd	0.028	0.010	1.2	0.17
Fe	0.00077	0.020	2.4	0.010
K	100	ns	ns	5.0
Mg	ns	ns	23	6.5
Ni	49.0	ns	ns	nr
Pb	0.57	0.45	0.45	0
Mn	1.6	12.3	ns	1.7
Zn	180	104	18	25
SO <sub>4</sub>	540	1900	50	240

<sup>a</sup> The second, third, and fourth "Predicted" columns correspond to columns of Table 2. The last column repeats data of Table 3, summarizing composition of Short Creek west of the mineralized area. Values are rounded to two significant figures; ns = not simulated; nr = not reported.

### Summary and conclusions

Three approaches have been presented for estimating the chemistry of waters that existed in nature in mineralized regions prior to human disturbance. These range from qualitative (historical records) to quantitative (predictive geochemical modeling).

All three approaches demonstrate that "natural contamination" of water in contact with undisturbed mineral deposits should be expected. Concentrations of metals in water may be orders of magnitude higher in mineralized regions than in nonmineralized areas, even in the absence of mining.

Remediation can be a necessary and accepted activity in historic mining districts. However, standards for remediation should take into account the fact that the natural chemical quality of water in mineralized regions will usually not be as good as in nonmineralized regions. Data of the type presented here can offer alternative targets for remediation that are more reasonable than standards that do not recognize the probable effect of natural processes

of weathering and leaching of metalliferous ores. In the absence of meaningful information on natural background concentrations, targets for cleanup may be set that require water to be purer than that which existed originally; such targets may be scientifically unrealistic and economically unachievable.

### Acknowledgments

Sincere appreciation for assistance is expressed to Dave Baker, Newmont Mining Company; Glenn L. Anderson, ASARCO Inc.; Ralph Hargrave and Charlotte L. MacCay, Cominco Alaska; Gary Uphoff, Environmental Management Services, Inc.; Lisa Kirk and Dan McLaughlin, Crown Butte Mines, Inc.; and Robert Ramharter, Wisconsin Department of Natural Resources.

### References

- Hosking, K.F.G. In Proceedings of Third International Geochemical Exploration Symposium; Boyle, R. W.; McGerrigle, J. I., Eds.; Canadian Institute of Mining and Metallurgy: Toronto, Ontario, 1971; (CIM) Special Vol. 11, pp. 176–89.
- (2) Agricola, G. De Re Metallica; Hoover, H. C.; Hoover, L. H., translators; Dover: New York, 1912.



Donald D. Runnells is a professor and chair of the Department of Geological Sciences at the University of Colorado, Boulder. He received a B.S. degree in geology from the University of Utah and an M.S. degree and Ph.D. from Harvard University. He has published and consulted extensively in the fields of ore deposits, mineralogy, geochemistry, rockwater interactions, and contamination of water by wastes. He serves on the editorial board of Applied Geochemistry.



Thomas A. Shepherd is president of Shepherd Miller, Inc., a consulting firm in Ft. Collins, Colorado, specializing in environmental and geotechnical services to the minerals and energy industries. He received a B.S. degree in chemistry from Duke University, an M.B.A. in finance from Indiana University, an M.S. degree in resource planning from Colorado State University, and a Ph.D. in resource planning and geotechnical engineering from Colorado State University. He served on technical advisory committees for the Nuclear Regulatory Agency to develop criteria for management of uranium mill tailings.



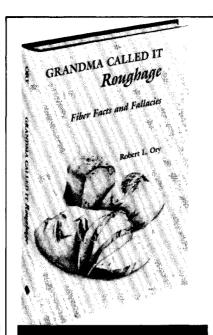
Ernest E. Angino is professor of geology at the University of Kansas, Lawrence. He received a B.S. degree in geophysics from Lehigh University and an M.S. degree and a Ph.D. in geology from the University of Kansas. He is an associate editor of Environmental Geology and director of the Water Research Center at the University of Kansas. He is the author of more than 100 papers and author or editor of six books. His research is in the area of aqueous geochemistry and water quality.

- (3) Levinson, A. A. Introduction to Exploration Geochemistry; Applied Publishing: Calgary, Alberta, Canada, 1974; pp. 33-34.
- 1974; pp. 33-34.
  (4) Moran, R. E.; Wentz, D. A. Effects of Metal-Mine Drainage on Water Quality in Selected Areas of Colorado, 1972-73: Colorado Water Conservation Board and U.S. Geological Survey: Denver, CO, 1974; Circular No. 25.
- (5) Schwartz, T. E. In Proceedings Colorado Scientific Soc., III; Colorado Scientific Society: Denver, CO, 1888; pp. 77–85.
- (6) Ransome, R. L. Economic Geology of the Silverton Quadrangle, Colorado; U.S. Geological Survey: Washington, DC, 1901; Bulletin 182.
- (7) Emmons, S. F. In Proceedings Colorado Scientific Soc., II; Colorado Scientific Society: Denver, CO, 1885; pp. 85–105.
- (8) Brockie, D. C.; Hare, E. H., Jr.; Dingess, P. R. In Ore Deposits of the United States, 1933/1967; Ridge, J. D., Ed.; American Institute of Mining, Metallurgy, and Petroleum Engineers: New York, 1968; Vol. 1, Chapter 20.
- (9) Snyder, F. G.; Gerdemann, P. E. In Ore Deposits of the United States, 1933/1967; Ridge, J. D., Ed.; American Institute of Mining, Metallurgy, and Petroleum Engineers: New York, 1968; Vol. 1, Chapter 17.
- (10) Winslow, A. Lead and Zinc Deposits of Missouri; Missouri Geological Survey: Columbia, MO, 1894; Vol. 6, pp. 544–600.
- (11) Mudge, B. F. In First Biennial Report of State Board of Agriculture, Kansas, 1877–1878; State Printer: Topeka, KS, 1879; Vol. 6, pp. 82–84.
  (12) Siebenthal, C. E. Origin of the Zinc
- (12) Siebenthal, C. E. Origin of the Zinc and Lead Deposits the Joplin Region, Missouri, Kansas, and Oklahoma; U.S. Geological Survey: Washington, DC, 1915; Bulletin 606.
- (13) Smith, W.S.T. In Contributions to the Hydrology of the Eastern United States; U.S. Geological Survey: Washington, DC, 1905; Water Supply Paper 145.
- (14) Haworth, E.; Crane, W. R.; Rogers, A.F.R. Lead and Zinc; University Geological Survey of Kansas; State Printer: Topeka, KS, 1904; Special Report, Vol. 8.
- (15) Kepler, K. Water Quality Investigations in Mineralized Areas of the San Juan Mountains: Red Mountain Creek, Howard's Fork, and Henson Creek; Colorado District 10 Planning Commission: Montrose, CO, 1980.
- (16) Mehrtens, M. B. In Reviews in Economic Geology, vol. 3; Exploration Geochemistry: Design and Interpretation of Soil Surveys; Robertson, J. M., Ed.; Economic Geology Publishing: El Paso, TX, 1987; Chapter 8.
- (17) Wilhelm, E.; Laville-Timsit, L.; Le-

- leau, M. In Proceedings Seventh International Geochemical Exploration Symposium; Watterson, J. R.; Theobold, P. K., Eds.; Association of Exploration Geochemists: Rexdale, Ontario, Canada, 1978; pp. 185–99.
- (18) Brooks, R. R. In Proceedings of the Second Seminar on Geochemical Prospecting Methods and Techniques, UNESCO; University of Ceylon: New York, 1970; (UNESCO) Mineral Resource Development Series 38; pp. 73–87.
- (19) Archer, A. R.; Main, L. A. In Proceedings of Third International Geochemical Exploration Symposium; Boyle, R. W.; McGerrigle, J. I., Eds.; Canadian Institute of Mining and Metallurgy: Toronto, Ontario, 1971; (CIM) Special Vol. 11, pp. 67–77.
- (20) Nigrini, A. In Proceedings of Third International Geochemical Exploration Symposium; Boyle, R. W.; McGerrigle, J. I., Eds.; Canadian Institute of Mining and Metallurgy: Toronto, Ontario, 1971; (CIM) Special Vol. 11, p. 235.
- (21) Rose, A. W.; Hawkes, H. E.; Webb, J. S. Geochemistry in Mineral Exploration, 2nd ed.; Academic Press: London, 1979; p. 359.
- don, 1979; p. 359. (22) Cameron, E. M. *J. Geochem. Explor.* **1977**, 7, 327–48.
- (23) Shvartsev, S. L.; Udodov, P. A.; Rasskazov, N. M. J. Geochem. Explor. 1975, 4, 433–39.
- (24) Horsnail, R. F. J. Geochem. Explor. 1975, 4, 83–88.
- (25) Wagner, G. H.; Steele, K. F. Water, Air, Soil Pollut. 1985, 25, 339–47.
- (26) Cameron, E. M. J. Geochem. Explor. 1978, 10, 219–43.
- (27) Miller, W. R.; Ficklin, W. H.; Lerned, R. E. J. Geochem. Explor. 1982, 16, 217-33.
- (28) Pokorny', J. In Geochemical Exploration 1974; Elliott, I. L.; Fletcher, W. K., Eds.; Elsevier Sci. Publ. Co.: Amsterdam 1975; pp. 77-83
- Amsterdam, 1975; pp. 77–83. (29) De Geoffrey, J.; Wu, S. M.; Heins, R. W. Foon, Cool. 1967, 62, 679–97.
- R. W. Econ. Geol. 1967, 62, 679-97.

  (30) Kennedy, V. C. Geochemical Studies of the Southwestern Wisconsin Zinc-Lead Area; U.S. Geological Survey: Washington, DC, 1956; Bulletin 1000-E.
- (31) Allan, R. J.; Hornbrook, E.H.W. In Proceedings of Third International Geochemical Exploration Symposium; Boyle, R. W.; McGerrigle, J. I., Eds.; Canadian Institute of Mining and Metallurgy: Toronto, Ontario, 1971; (CIM) Special Vol. 11, pp. 53-66.
- (CIM) Special Vol. 11, pp. 53–66. (32) Thomson, I. J. Geochem. Explor. 1975, 4, 168–72.
- (33) Application for a Hardrock Operating Permit and Proposed Plan of Operation, New World Project; Vols. 4, 4a, Environmental Baseline Data, Appendix B, Crown Butte Mines, Inc.: Cooke City, MT, 1990.
- (34) Boyle, R. W.; Pekar, E. L.; Patterson, P. R. Geochemical Investigation of the Heavy Metal Content of Streams and Springs Waters in the Galena Hill Mount Haldane Area, Yukon Territory; Geological Survey of Canada: Ottawa, Ontario, 1956; Bulletin 36.
- (35) Boyle, R. W.; Illsley, C. T.; Green, R. T. Geochemical Investigation of

- the Heavy Metal Content of Stream and Spring Waters in the Keno Hill Galena Hill Area, Yukon Territory; Geological Survey of Canada: Ottawa, Ontario, 1955; Bulletin 32.
- (36) Final Environmental Impact Statement, Flambeau Mining Co.—Copper Mine, Ladysmith, WI; Department of Natural Resources, State of Wisconsin: Madison, WI, 1990.
- (37) Final Environmental Impact Statement, Exxon Coal and Minerals Co., Zinc-Copper Mine, Crandon, Wisconsin; Department of Natural Resources, State of Wisconsin: Madison, WI,
- (38) Environmental Impact Report, Crandon Project; Exxon Minerals Company, prepared for Wisconsin Department of Natural Resources, Madison, WI, 1982.
- (39) Forstner, U.; Wittman, T. W. Metal Pollution in the Aquatic Environment; Springer-Verlag: Berlin, 1979.
- (40) Moore, D. W.; Young, L. E.; Modene, J. S.; Plahuta, J. T. Economic Geol. **1986**, *81*, 1696–1727.
- (41) Water Quality Report; Chapter 3 of report by Dames and Moore, Inc., prepared by L. A. Peterson and Associates, Inc., for the Red Dog Mine Project, Cominco Alaska, Inc., 1983.
- (42) Ott, A. G. Memorandum on Historical Water Quality Data from Wulik River Drainage: Alaska Department of Fish and Game: Anchorage, AK, February 14, 1990.
- (43) van der Leeden, F.; Troise, F. L.; Todd, D. K. The Water Encyclopedia, 2nd ed.; Lewis: Chelsea, MÍ, 1990.
- (44) Parkhurst, D. L.; Thorstenson, D. C.; Plummer, L. N. PHREEQE—A Computer Program for Geochemical Calculations; U.S. Geological Survey: Washington, DC, 1980; Water-Resources Investigations 80-96.
- (45) Plummer, L. N.; Parkhurst, Geochimica et Cosmochim. Acta **1983**, *47*, 665–85.
- (46) Plummer, L. N. In Proceedings of First Canadian/American Conference on Hydrogeology; Hitchon, B.; Wallick, E. I., Eds.; National Water Well Assoc.: Worthington, OH, 1984, pp. 149-77
- (47) Ground Water Models-Scientific and Regulatory Applications; National Research Council: Washington,
- (48) Garrels, R. M.; Christ, C. L. Solutions, Minerals, and Equilibria; Freeman, Cooper, and Co.: New York, 1965.
- (49) Lindsay, W. L. Chemical Equilibria in Soils; Wiley-Interscience: New York, 1979.
- (50) Lindberg, R. L.; Runnells, D. D. Science 1984, 225, 925-27.
- (51) Parkhurst, D. L. In Proceedings of the Second Technical Meeting, U.S. Geological Survey Program on Toxic Waste—Ground-Water Contamination; U.S. Geological Survey, Reston, VA, 1988; (USGS) Open-File Report 86-481, pp. D5-D9.
- (52) Summary of Water Data Indexed by the National Water Data Exchange (NAWDEX), A Catalog Prepared by the U.S.G.S. Office of Water Data Coordination and NAWDEX; U.S. Geological Survey: Reston, VA, 1981.



## Grandma Called It Roughage

### **Fiber Facts and Fallacies**

his semi-technical volume, written specifically for non-scientists, is must-reading for anyone concerned about health and nutrition. With scientific facts to support the statements made about the known health benefits of fiber, Dr. Ory offers an interesting, sometimes humorous, approach that will appeal to the general reader.

Although not intended to be the final word on dietary fiber (research goes on continually), the book is intended to quell rumors about dietary fiber and to inform those who don't understand enough about fiber's benefits and limitations.

The author also offers some of his own recipes for simple and tasty high-fiber foods, including Bread Pudding, New Orleans Style Red Beans, and Eggplant Lasagna.

### **Contents**

- Fibermania and How It Began
- What Is Fiber and Where Do We Find It?
- Fiber and Metabolism vs. Fat and Cholesterol
- Can Fiber Fight Fat?
- Fiber and the Big "C"-Constipation!
- Can Fiber Cure Cancer, Diabetes, or Other Diseases?
- Fiber and Mineral Nutrition
- Is Fiber an Essential Nutrient?
- Breakfast Cereals: The Battle of the Brans
- Fiber in Fruits and Vegetables
- Can Fiber Be Good for You and Still Taste Good? Robert L. Ory, Ph.D.

160 pages (1991) Clothbound: ISBN 0-8412-1749-1 **\$22.95** 

Paperbound: ISBN 0-8412-1764-5 \$12.95

### O · R · D · E · R F · R · O · M

American Chemical Society Distribution Office, Dept. 21 1155 Sixteenth St., N.W. Washington, DC 20036

or CALL TOLL FREE

(in Washington, D.C. 872-4363) and use your credit card!



At Anderson Laboratories, we specialize in customer satisfaction.

Anderson has an in-stock selection of more than 500 specific standardized solutions, reagents and chemicals - but there's more.

We prepare solutions every day. labeled to meet specific requests variable strength solutions, quantities and sizes - without sacrificing the rigid quality control standards Anderson has always emphasized

When you need a STANDARD prepared to customized specifications, Anderson is your best source.

To find a dealer near you, look in the Laboratory Equipment and Supplies section of your Yellow Pages or call 1-800-433-7751.

Because of our large network of U.S. distributors in every major metropolitan area, we fill and ship most orders within 48 hours.

### Choose from:

- Standardized Laboratory Solutions
- Reagent Grade Laboratory Solvents
- Water Testing Solutions
- APHA, ASTM and AOAC Test Solutions
- Buffers (Standard and Color Coded)
- Indicating Solutions
- Biological Staining Solutions
- In-Vitro Diagnostic Reagents
- Custom Preparations



Anderson Laboratories, Inc. 5901 Fitzhugh Avenue Fort Worth, Texas 76119 (817) 457-4474 1-800-433-7751 Fax (817) 451-8349

CIRCLE 1 ON READER SERVICE CARD