Geochemical Predictions of Metal Leaching and Acid Generation: Geologic Controls and Baseline Assessment

R.J. Bowell and **S.B. Rees**

Steffen, Robertson & Kirsten (UK) Limited, Summit House, 9 Windsor Place, Cardiff CF10 3SR, UK

J.V. Parshley

Steffen, Robertson & Kirsten, Suite 300, 5250 Neil Road, Reno, Nevada 89502

ABSTRACT

An essential component in the evaluation of a mineral deposit or a mine development project is the consideration of environmental impact, particularly the leaching of deleterious elements such as As and many of the transition metals or of Acid Rock Drainage (ARD) generation. A major part of this assessment is the potential for the materials within the mineral deposit to degrade land or water.

In order to make this assessment testwork or modeling programs are conducted to predict the magnitude of impact and to assess future changes. Very often this work is carried out late in a development timetable and can lead to frustrating and costly delays for the developer. However, the prediction of geochemical impacts from a mineral deposit can be qualitatively determined at an early stage in development and used to execute a more efficient impact assessment.

The processes that can lead to geochemical impact from a mineral deposit are generally related to the geologic characteristics of the ore and host rocks. For example ARD is related to the presence of acid generating phases, especially Fe-bearing sulfides or sulfate minerals coupled with the lack of buffering agents. Consequently, the potential for metal leaching can be qualitatively based on the altered wallrock mineral assemblage that constitutes the highest proportion of waste rock and exposed wallrock. Geochemical reactions, like metal leaching, are natural processes and as such they can be interpreted in the context of geologic understanding.

This paper presents field and mineralogical observations from several contrasting ore deposit types, common to the Great Basin, along with associated laboratory assessment of geochemical leaching. A practical guideline is discussed for the field assessment of geochemical impacts that can be made during the exploration and pre-mine development phases of a project. The inclusion of geologic knowledge to that of engineering design and analytical testing and modelling is recommended in order to reduce the costs and delay associated with environmental assessment during pre-mine development.

INTRODUCTION

Metal leaching and generation of acidic drainage from a mineral deposit is a naturally occurring process. This can cause a negative impact on the receiving environment. The cost of treating problematic elements such as metals or of treating ARD can be high. But, if the major source(s) can be identified, then selective treatment may be more effective than the treatment of a much larger quantity of non-problematic material with which it is arbitrarily classified. Typically

the approach taken historically was to wait until an impact occurred and then design remediation (engineering task). Often this was costly and inappropriate technology was applied so environmental impact were not completely mitigated. A more recent approach has been to acquire estimates of reactivity from laboratory testwork and use this as input components to predictive modeling. While this approach is effective in gaining predictions, very often the predictions do not match reality and unnecessary costs are incurred by the project both in the prediction and then based on this through any work undertaken or regulatory bond applied. Rarely is the third segment of the process applied, which is to provide a detailed environmental geologic assessment at an early stage in the mineral property development.

The processes that govern generation of acidic leachate and mobilization of metals (grouped collectively as Acid Rock Drainage or ARD in this paper) can be characterized and classed (SRK, 1989; Nordstrom and Alpers, 1999a). Equally, despite individual peculiarities, mineral deposits can also be classified according to mineralogic and geologic characteristics. Logically it follows that as ARD characteristics can also be classed according to geologic rock type (Ficklin et al., 1992; Plumlee, 1994; du Bray, 1995; Plumlee and Logsdon, 1999). The geology of a mineral deposit exerts a fundamental control on interaction with the environment. Other important controls such as geochemical and biologically mediated processes, hydrogeology, hydrology, climate, topography, mining and mineral processing methods generally modify the environmental effects inferred by the geology.

This paper describes the major processes involved, the influence of geology and mineralogy for several deposit types on environmental behavior and discusses how geologists can be involved in predictions at an early stage of project development. All of which can reduce liability, operational and closure costs for a mining development.

METHODS

In this paper, ARD characteristics are assessed using conventional prediction methods (Sobek et al., 1978; SRK, 1989; Miller et al., 1997; Price, 1997). These methods have

TABLE 1. Summary of analytical methodologies.

Parameter	Rationale	Method	Task Type	Reference
Mineralogy	Assess mineral speciation	Optical/SEM/XRD	Field/lab	SRK 1989
Geochemistry expressed as a concentration, generally mg/kg	Assess total chemistry	ICPAES/XRF	Lab	SRK 1989
Paste pH/TDS with pH as su and TDS as mg/l	Assess reactive H^+ and solute release	Mix with water in field, 1:1 ratio	Field/lab	SRK 1989
Meteoric Water Mobility Procedure (MWMP) expressed in mg/l	Assess mobile constituents	Flushing of sample with one pore volume for 24 hours	Lab	NDEP 1990, 1996
Acid Base Accounting (ABA) in eq kg $CaCO_3$/t	Assess total acid that can be generated	Measure sulfide, total-, and sulfate-S, inorganic carbon; and titration with HCl/NaOH	Lab	Sobek et al., 1978; Price 1997
Net Acid Generation (NAG) in eq kg H_2SO_4/t and final pH as su	Assess total acid that can be generated	Oxidise with H_2O_2; titration with HCl/NaOH	Lab	Miller et al., 1997

been used widely in the prediction of ARD and will not be repeated in detail here but are summarized in Table 1.

Most of the laboratory work was undertaken at Sierra Environmental Monitoring, Sparks, Nevada, or at Chemex laboratories, Reno, Nevada. Additional sample characterization was conducted at the Division of Materials and Minerals, Cardiff University, Wales.

FACTORS INVOLVED IN METAL LEACHING AND ACID GENERATION

In the assessment of the acid generating potential of rock or ore types, two key factors need to be determined:
- The presence of acid generating phases
- The presence of acid consuming phases

Additionally in an arid environment, such as Nevada, the acid generating phases can constitute primary sources, such as sulfide oxidation, and secondary sources, such as sulfate dissolution.

PRIMARY SOURCES OF ACIDITY

Primary acid generating minerals are sulfides of the type, MS_2, the most common being FeS_2. The mechanisms of sulfide oxidation involve the transfer of electrons. As most sulfide minerals are electrical conductors in the semiconductor to metallic range, they can be considered as electrochemical "corrosion cells" similar to galvanic corrosion of metal alloys (Bailey & Peters, 1976; Thornber, 1975a,b, 1983, 1992, 1993; Sivenas and Beal, 1982). Sulfides are "geo-batteries" with the emphasis on "self-corrosion" by sulfide ores. These electrochemical reactions are a combination of a *red*uction reaction at a cathode, on the more noble phase and an *ox*idation reaction at the anode on the more reactive phase. Galvanic "corrosion" has been confirmed in numerous experimental studies (Thornber, 1975a; 1983; Bailey & Peters, 1976; McKibben & Barnes, 1986).

Additionally hydrogen ions are released in the process of metal hydrolysis and this is most pronounced when the cation is iron due to the further oxidation of Fe^{2+} to Fe^{3+} and hydrolysis to form $Fe(OH)_3$ (Table 2). It should be noted that not all

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TABLE 2. Oxidation reactions of iron sulfide and sulfate minerals generating acidity (after Kleinnman and Pacelli, 1991; Thornber, 1992).

Reaction 1
a) $FeS_2 + 7/2 O_2 + H_2O = Fe^{2+} + 2SO_4^{2-} + 2H^+$
b) $2FeS_2 + 7O_2 + 2H_2O = 2FeSO_4 + 2H_2SO_4$

Reaction 2
a) $Fe^{2+} + H_2O + O_2 = Fe(OH)_3 + 2H^+$
b) $2FeSO_4 + H_2SO_4 + 1/2 O_2 = Fe_2(SO_4)_3 + H_2O$

Reaction 3
$Fe^{2+} + 1/4 O_2 + H^+ = Fe^{3+} + 1/4 H_2O$

Reaction 4
$FeS_2 + 14Fe^{3+} + 8H_2O = 15Fe^{2+} + 2SO_4^{2-} + 16H^+$

Stage 1
Reaction 1: proceeds abiotically and by bacterial oxidation (reaction b more common with bacterial oxidation)
Reaction 2: proceeds abiotically, slows as pH falls (reaction b more common with bacterial oxidation)
pH approximately 4.5 or higher, high sulphate, low Fe, low pH

Stage 2
Reaction 1: proceeds abiotically and by bacterial oxidation (reaction b more common with bacterial oxidation)
Reaction 2: proceeds at rate determined primarily by activity of bacteria such as *T.ferrooxidans*
pH approximately 2.5-4.5, high sulphate, Fe and low pH. Low Fe^{3+}/Fe^{2+} ratio

Stage 3
Reaction 3: proceeds at rate determined by activity of *T.ferrooxidans*
Reaction 4: proceeds at rate determined by rate of reaction 3
pH generally below 2.5, high sulphate, total Fe and low pH. High Fe^{3+}/Fe^{2+} ratio

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sulfides on oxidation generate acidity (Thornber, 1992). Indeed sulfides of the type M_2S such as chalcocite actually consume H^+ on oxidation.

The rate of sulfide oxidation can be controlled by the rate at which oxygen is supplied and reduced at the cathode-solution interface. The separation of the cathodic oxygen-consuming, alkali-producing reaction from the anodic, oxidizing, acid-producing reaction will have a major control on the mineralogy of the resulting assemblage. The greater the distance between cathode and anode, the more extensive the conducting area and consequently the greater the potential for sulfide oxidation. Anodic reactions can occur deep within cracks, fissures and along grain boundaries where solutions can penetrate without the necessity for dissolved oxygen (Lowson, 1982; Thornber, 1975a,b; 1992).

Consequently, massive sulfide ores and sulfide-rich zones, such as those in high sulfidation epithermal systems are generally good conductors, the exception is with massive sphalerite, which is an insulator (Thornber, 1992). Where sulfides are more dispersed, such as in some Carlin-type ores, distance between oxidizing sulfides is greater and conduction is reduced so the extent of oxidation is not so great. Each sulfide grain weathers as an isolated cell and the only influence that one sulfide grain can have on another is via aqueous solution. Access by dissolved oxygen will determine leaching and sulfide composition will influence pH, water chemistry, reaction rate, and secondary mineralogy. Generally, leaching is greatest near the surface.

SECONDARY SOURCE OF ACIDITY

On weathering, sulfides can release all acid potential producing a range of hydroxides and oxides such as goethite. Alternatively they can release only a portion of the total acidity and store some acidity in secondary salts which are stable only in oxidizing acidic pH environments, for example the formation of jarosite (Fig. 1):

$$3FeS_2 + 9/2O_2 + 15/2H_2O + K^+ =$$
$$KFe^{3+}_3(SO_4)_2.(OH)_6 + 4SO_4^{2-} + 9H^+$$
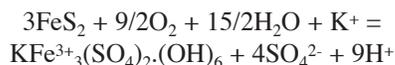
For each mole of pyrite oxidized, only a third of the available sulfate and hydrogen is released. The rest is stored as unhydrolyzed, partly oxidized iron-sulfate minerals. These sulfate minerals are termed *Acid Volatile Sulfate Salts*. As an example the most common of these salts are given in Table 3. Not all necessarily release hydrogen and sulfate on dissolution but all release sulfate anions. These minerals are highly soluble so can represent an instantaneous source of acidic sulfate-rich water upon dissolution and hydrolysis, for example the dissolution of jarosite:

$$KFe^{3+}_3(SO_4)_2.(OH)_6 + 3/2O_2 = 3FeO.OH +$$
$$K^+ + 2SO_4^{2-} + 3H^+ + 3/2H_2O \qquad (9)$$
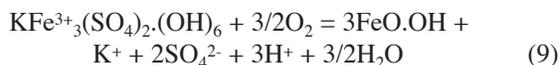
Subsequent oxidation of ferrous iron and hydrolysis of ferric iron at pH > 2 provides an additional source of acidity

(see Table 2). Hence these minerals are important as both sinks and sources of acidity, sulfate and possibly metal ions on precipitation and rapid release on exposure to moisture (Nordstrom, 1982; Fillipek et al., 1988; Cravotta, 1991, 1994).

BUFFERING OF ACID CAPACITY

Acid-neutralization reactions result from mineral buffering of H^+ in drainage. This buffering is frequently accompanied by the precipitation of secondary minerals (Kwong and Ferguson, 1997; Lawrence and Wang, 1997; Nordstrom and Alpers, 1999a). These reactions can reduce acid generation by forming an inhibitory surface coating on the reactive sulfides. Under acidic conditions, carbonate minerals (e.g. calcite, dolomite and magnesite) readily dissolve and provide bicarbonate alkalinity which results in neutralization of acid and precipitation of metal hydroxides. The major buffering mineral groups and characteristics with respect to ARD are shown in Table 4.

The order of carbonate neutralizing capacity is calcite>dolomite>ankerite>siderite. In the case of siderite and to a lesser extent ankerite the reason for the limited neutralizing capacity is that ferrous iron in these minerals are an additional source of acidity due to the strong hydrolysis of ferrous iron in solution. This order of reactivity is partly controlled by equilibrium mass-action constraints and partly by kinetic limitations (Morse, 1983). Carbonate minerals (especially calcite) have often erroneously been thought of as the only geologic source of Neutralization Potential (NP). However, carbonates dominate only limestone, dolomite and marble rock types whilst the majority of geologic materials are composed of silicates and hydroxide-oxide minerals.

Silicate weathering as a proton sink has been demonstrated in previous studies (Sverdrup, 1990; Bhatti et al, 1992; Moss and Edmunds, 1992; Kwong and Ferguson, 1997). To assess the buffering capacity of mine wastes, silicate and hydroxide minerals therefore must also be considered. From soil acidification studies, Sverdrup (1990) divided the most common minerals into six groups according to pH dependency of their dissolution rate (Table 4).

From the relative weathering rates the mineral groups show, minerals in groups 4-6 will be poor to negligible neutralizing materials due to their sluggish reaction rates. Even the intermediate and fast weathering groups, are not practical neutralizing materials unless their occur in excess of ~10% (Sverdrup, 1990).

METAL LEACHING AND
ATTENUATION PROCESSES

The primary leaching processes include sulfide oxidation and associated mineral buffering, both of which increase the total dissolved solid load in the resulting water. The accumulation of solutes in solution will lead to saturation with respect to some species. Consequently in response to either saturation or destabilization as aqueous species, these com-
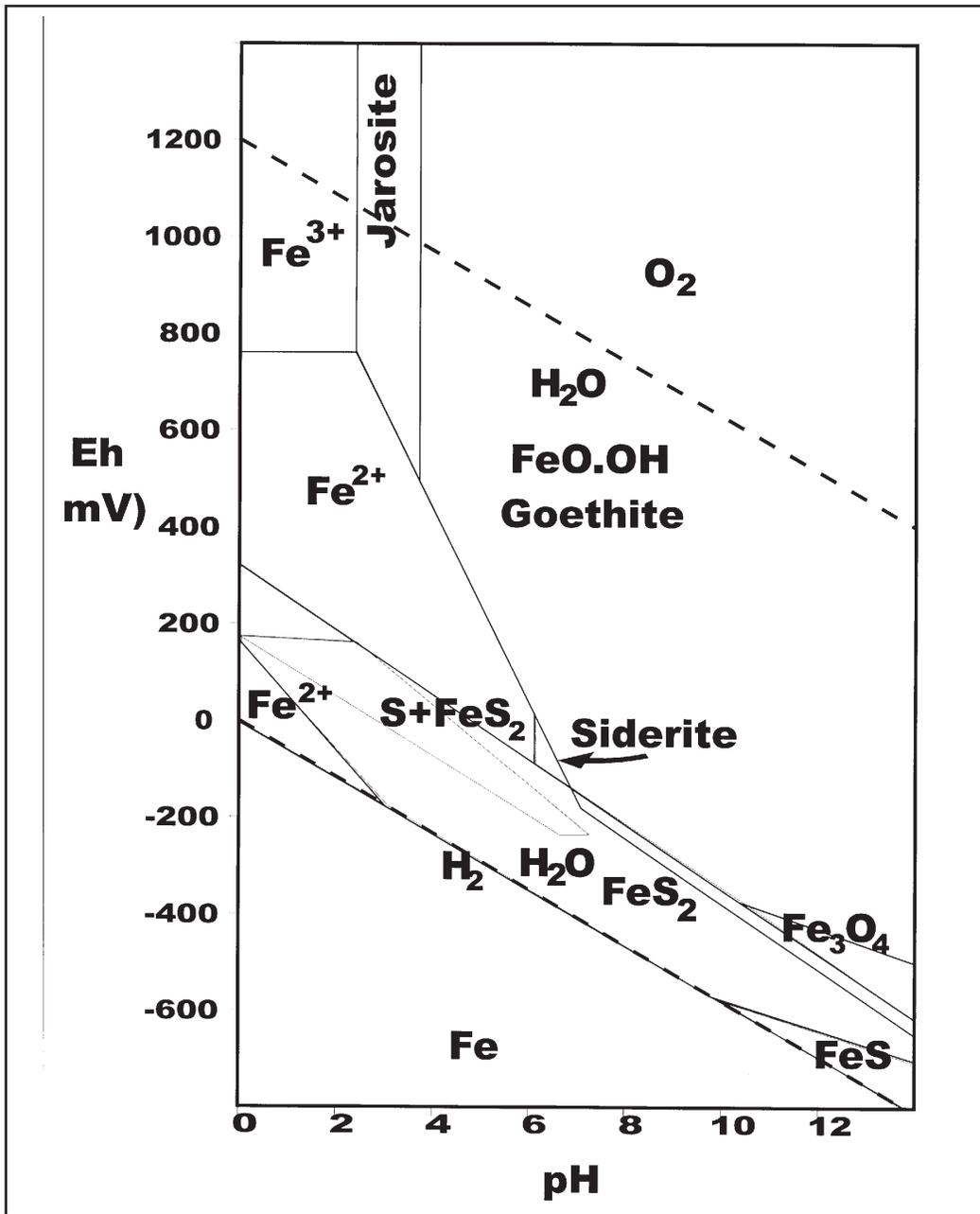
FIGURE 1. Eh-pH diagram for the Fe-S-C-O-H system at 298 K. Fe,S=10^{-6}M; P_{CO2}=10^{-2}M.

pounds precipitate as secondary minerals such as arsenates, phosphates, carbonates, sulfates or hydroxides. Additionally some of these solutes can be attenuated through surface adsorption onto mineral surfaces, noticeably iron hydroxides and clays.

This is the process of element binding at the mineral solution interface and like solubility is pH dependent, for example the adsorption of arsenic species by goethite (Bowell, 1994). Many oxide surfaces change from being positive at low pH (thus attracting anions) to negative at high pH (attracting cations). Mine drainage chemistry and particularly the level of As and heavy metals has been shown to be influenced by adsorption onto precipitated hydrous ferric oxide, or HFO (this may also include minerals like schwertmannite, goethite and jarosite amongst others; Fuge et al., 1994; Bigham, 1994; Bowell et al., 1996). It should however be noted that in many acidic environments, flushing or dissolution of these HFO can lead to high As concentrations in solution as well as competition from complexing ions mobilizing As-oxyanions.

TABLE 3. Secondary sulfate salts commonly observed in mine drainage.

Selected soluble sulfates   **Selected less soluble sulfates**

Iron minerals

Copiapite	$Fe^{2+}Fe_4^{3+}(SO_4)_6(OH)_2.20H_2O$	amerantite	$Fe^{3+}(SO_4)OH.3H_2O$
Coquimbite	$Fe_2^{3+}(SO_4)_3.9H_2O$	fibroferrite	$Fe^{3+}(SO_4)OH.5H_2O$
Ferricopiapite	$Fe_{2/3}^{2+}Fe_4^{3+}(SO_4)_6(OH)_2.20H_2O$		
Melanterite	$Fe^{2+}SO_4.7H_2O$	schwertmannite	$Fe_8O_8(SO_4)(OH)_6$
Ferrohexahydrite	$Fe^{2+}SO_4.5H_2O$	halotrichite	$Fe^{2+}Al_2(SO_4)_4.22H_2O$
Paracoquimbite	$Fe_2^{3+}(SO_4)_3.9H_2O$		
Rhomboclase	$HFe(SO_4)_2.4H_2O$		
Rozenite	$Fe^{2+}SO_4.4H_2O$		
Siderotil	$Fe^{2+}SO_4.6H_2O$		
Szomolnokite	$Fe^{2+}SO_4.H_2O$		

Ca-Mg-Na-Sr-Ba minerals

Anhydrite	$CaSO_4$	barite	$BaSO_4$
Epsomite	$MgSO_4.7H_2O$	celestite	$SrSO_4$
Gypsum	$CaSO_4.2H_2O$		
Hexahydrite	$MgSO_4.6H_2O$		
Mirabilite	$Na_2SO_4.10H_2O$		
Thendrite	Na_2SO_4		

Other transition metals

Alunogen	$Al_2(SO_4)_3.17H_2O$	anglesite	$PbSO_4$
Bianchite	$ZnSO_4.6H_2O$	antlerite	$Cu_3(SO_4)(OH)_4$
Chalcanthite	$CuSO_4.5H_2O$	basalumite	$Al(SO_4)(OH)_{10}.H_2O$
Goslarite	$ZnSO_4.7H_2O$	brochantite	$Cu_4(SO_4)(OH)_6$
Gunningite	$ZnSO_4.H_2O$	jurbanite	$Al(SO_4)(OH).5H_2O$
Retgesite	$NiSO_4.6H_2O$	langite	$Cu_4(SO_4)(OH)_6.2H_2O$

Alunite-Jarosite Group

Very common group of Acid Mine Drainage & Gossan minerals. Can incorporate many trace
metals and oxyanions.
$A^{2+}Fe_4^{3+}(SO_4)_6(OH)_2.20H_2O$ or $B_{2/3}^{3+}Fe_4^{3+}(SO_4)_6(OH)_2.20H_2O$
A= Ca, Cu, Fe, Mn, Mg, Zn, Co, Ni
B= Al, Fe, Cr.
Sulfate group can be partially replaced by selenite, phosphate, arsenate oxyanions.
Some examples:

Argentojarosite	$(K,Ag)Fe_3^{3+}(SO_4)_2(OH)_6$
Alunite	$K Al_3^{3+}(SO_4)_2(OH)_6$
Jarosite	$K Fe_3^{3+}(SO_4)_2(OH)_6$
Plumbojarosite	$(Pb,K)Fe_3^{3+}(SO_4)_2(OH)_6$
Osarizawaite-beaverite	$(Pb,Cu)_2(Al,Fe^{3+})_2(SO_4)_2(OH)_6$

TABLE 4. Grouping of minerals according to their neutralization potential (after SRK, 1989; Sverdrup, 1990; SRK, 1998).

Group Name	Typical minerals	Buffering pH range[1] (su)	Approx. NP[2] range	Relative reactivity[3]
1. Dissolving	Calcite, aragonite, dolomite, magnesite, aragonite, portlandite and brucite	6-11.2	7.8-14.8	1.0
2. Fast weathering	Anorthite, nepheline, olivine, garnet, jadeite, leucite, spodumene, kutnahorite diopside, siderite and wollastonite	5.5-11	2.8-0.6.2	0.6
3. Intermediate weathering	Epidote, zoiste, enstatite, hyperthene, augite, hedenbergite, hornblende, glaucophane, tremolite, actinolite, anthophyllite, serpentine, chrysotile, talc, chlorite, biotite.	4.8-7.3	1.7-5.8	0.4
4. Slow weathering	Albite, oligoclase, labradorite, vermiculite, montmorillonite, manganite, goethite, gibbsite and kaolinite.	2.4-5.1	0.5-2.9	0.02
5. Very slow weathering	K-feldspar, ferrihydrite and muscovite	2.2-4.1	0.2-0.6	0.01
6. Inert	Quartz, hematite, rutile and zircon	3.3-3.5	<0.01	0.004

[1]buffering pH range evaluated by crushing 5g of pure mineral and mixing with 5ml of distilled water and left to react for 30 minutes. The pH of the distilled water was 3.4 su.

[2]NP range assessed as equivalent buffering potential of 10 g of pure mineral to calcite and titrated with hydrochloric acid. So for example, 10g of portlandite ($Ca(OH)_2$) was found to have the equivalent capacity to neutralise HCl acid as 14.8g of calcite. Whereas 10g of hornblende was required to buffer HCl acid to a similar pH to only 3.1g of calcite.

[3]Calculated from Sverdrup's equation (1990), see below and based on 100% mono-mineral sample.

An important control on the diversity of the precipitated mineral assemblage is pH, for example in the oxidation of sulfides at low pH, Fe oxyhydroxides, scorodite and sulfates are formed while at higher pH other salts such as Ca-arsenates, smithsonite and malachite are precipitated. These mechanisms are reflected in the trace element chemistry shown for HFO precipitates from contrasting Nevada deposits (Table 5). In HFO from low pH drainage, like Goldfields, base metal content is low despite the presence of base metal sulfides in the deposit. However, As is present, most likely adsorbed onto the mineral surface. In the higher pH HFO precipitate from Goldfields (Table 5), base metal content is higher as conditions in the drainage favor precipitation. Geologic controls are clearly demonstrated in the Getchell ochre sample that shows significantly higher As content than from the other deposits with the presence of pararealgar and Ca-arsenates (austinite, pharmacolite and weilite).

Clay minerals such as smectite ($Na_3(Al,Mg)_2 Si_4O_{10}(OH)_2.nH_2O$) may also be responsible for the concentration of base metals in ochres, particularly in low pH HFO

TABLE 5. Trace element geochemistry of hydrous ferric oxide analyzed from different Nevada mineral deposits.

Deposit	Ruth Pit, Ely	Tripp/Vet pit, Ely	Goldfields	Goldfields	Ten Mile	Getchell
Drainage pH (su)	3.3	6.4	2.9	5.4	6.8	6.6
Deposit type[1]	P	P	H/S	H/S	L/S	C
HFO mineralogy[2]	Ge,Js, Sch,Cc	Fer,Ge,Sch	Ge,Js,Cc	Fer,Ge,	Fer,Ge	Caas, Ge, Fer, Sc, Pr
Elements	All analyses by LAICPMS[3]					
Co	<1	16.8	1.91	46.2	4.2	66.4
Ni	<1	25.2	2.32	89.6	7.6	58.8
Cu	316	911	88.9	732	12.4	76.1
Zn	43.4	58.9	96.5	333	84.5	149
As	169	118	890	730	1210	9670
Sc	11.2	36.3	86.5	221	415	355
Ag	67	82.3	34.8	41.5	498	87.3
Cd	2.9	4.11	4.8	12.9	1.3	11.9
Sb	1.68	3.21	2.7	21.3	16.8	492
Hg	1.76	2.49	38.6	279	109	459
Pb	441	569	1890	2130	1660	3780
U	34.6	17.6	4.2	1.6	<1	2.5

[1]P=porphyry; H/S=High Sulfidation; L/S=Low Sulfidation; C=Carlin-type

[2]Mineralogy by XRD: Caas- Calcium arsenates; Cc-Chalcanthite; Fer-Ferrihydrite; Ge-Goethite; Js-Jarosite; Pr-Pararealgar; Sc-Scorodite; Sch-Schwertmannite

[3]All analyses performed using Laser Ablation Inductively Coupled Mass Spectrometry. All samples prepared as probe blocks. Instrument used, VG Instruments PQH+ICP and VG LaserLab run in fixed Q-mode (Bowell et al., 1999).

promoting cation adsorption at a lower pH than with Fe-oxy-hydroxides (Parfitt, 1978). The formation of smectite clays in secondary mineral zones will be controlled by the geology with propylitic alteration zones more likely to produce complex clay minerals than in Carlin type illite alteration zones.

CONCEPTUAL GEOENVIRONMENTAL MODELS OF GREAT BASIN METALLIC ORE DEPOSITS

Environmental geologic models have been developed over the last few years to provide some form of initial prediction mechanism for understanding potential impacts anticipated from mining mineral deposits. These have been largely developed and applied in the USA (Plumlee, 1994; Gray et al., 1994; du Bray, 1995; Price et al., 1995; Bowell et al., 1998; Shevenell et al., 1999). A distinct correlation can be observed for a mineral deposit type and predicted metal leaching and acid generation. For example, based on a similar plot by Ficklin et al. (1992) and Plumlee (1994) a geologic grouping can be observed for mineral deposits with respect to dissolved metals and drainage pH (Fig. 2). The environmental implications of the more common mineral deposits in the Great Basin are given below.

ENVIRONMENTAL GEOLOGY OF COPPER PORPHYRIES

Porphyry deposits are typically large (typically 100-200 million tons of ore), low to medium-grade (<0.2-1wt% Cu and 0.03-0.5% Mo) deposits in which hypogene ore minerals are primarily structurally controlled showing both lateral and vertical zonation (Fig. 3). A summary of the main geologic and mineralogical characteristics of these deposits are given in Table 6 (Lowell and Guilbert, 1970; Guilbert and Lowell, 1974; Kirkham, 1972; Titley, 1993; Kirkham and Sinclair, 1996).

FIGURE 2. Metal concentration (Co+Ni+Cu+Zn+Ag+Cd+Pb) and drainage pH for different Nevada deposit types discussed in the text.

a).

PROPYLITIC
CL-EP-CB
AB-AA

PHYLLIC
QZ-MS-PY

ARGILLIC
QZ-KA-CL

POTASSIC
QZ-KF-BI
+/-MS +/-AH

CL-MS
EP-MG

b).

PERIPHERAL
CP-GA-SL
Au-Ag

PERIPHERAL
CP-GA-SL
Au-Ag

LOW
PYRITE
SHELL
PY2%

ORE
SHELL
PY 1%
CP 1-3%
Mo 0.03%
LOW GRADE
CORE
low total sulfide
CP-PY-Mo

PYRITE
SHELL
PY 10%
CP 1-3%
Mo TR

MG>PY

MG+PY

KEY
QZ quartz, MS muscovite, CL chlorite, KF potassic feldspar, BI biotite, AH anhydrite,AB albite,AA adularia,CB carbonate,EP epidote, MG
magnetite, Au gold, Ag silver, CP chalcopyrite, PY pyrite, Mo molybdenite, GA galena, SL sphalerite.

A cross-section of an idealised porphyry copper deposit showing (a) alteration zones and (b)
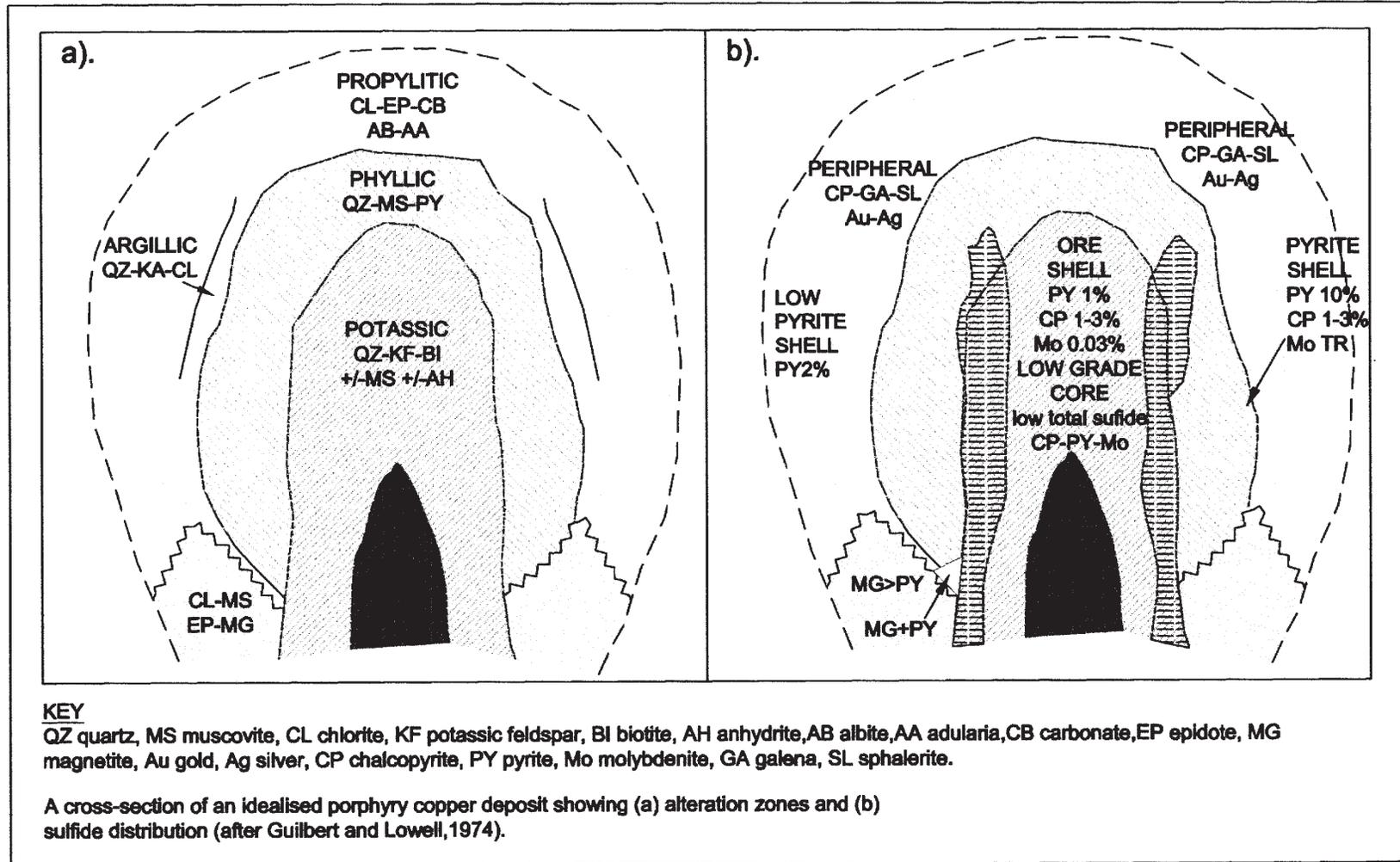sulfide distribution (after Guilbert and Lowell,1974).

FIGURE 3. Schematic cross-section of a porphyry copper system (modified from Guilbert and Lowell, 1974).

Hypogene mineralization can host from <1-20 % sulfide chiefly as pyrite with accessory chalcopyrite, molybdenite, bornite, chalcocite and covellite (Table 6). The most important environmental zone is the pyrite-rich "ore shell" halos with up to 20% volume (Guilbert and Lowell, 1974). Typically these zones carry sub-economic grades and thus the potentially most acid generating rock is waste.

Alteration minerals are also zoned with peripheral propylitic alteration, containing carbonates, being the only significant buffering. Despite this, due to the coarse idiomorphic nature of sulfides they tend to be sluggish in their oxidation reaction. Consequently ARD is not always a significant issue with Copper porphyries.

The contrast in porphyry deposits for ARD is shown in Figure 4. The majority off porphyry waste rocks are low metal, non to low-acid generating, but some zones within the porphyry can produce a high potential. Typically these are from the silicified sulfide-bearing zones that have been partially oxidized and so have associated with the sulfides, a series of Cu-Fe sulfate salts and other sources of secondary acidity such as jarosite. Another sulfide zone is also shown on this figure that has a predicted high total acid to be generated but a circumneutral paste pH. These samples are from a zone of supergene enrichment in a copper porphyry deposit, this typically comprises of goethite, cuprite, chalcocite and covellite with minor jarosite and relict pyrite. Due to the configuration of chalcocite it does not produce protons on oxidation but hydroxyl ions and consequently produces alkaline drainage. Within this drainage, metal levels are low. Consequently for chalcocite-rich ores traditional Acid Base Accounting (Sobek et al., 1978) fails to reflect this and over estimates acid potential. Supergene copper zones are common in copper porphyry deposits of the western USA (Lowell and Guilbert, 1970; Guilbert and Lowell, 1974) and also in Nevada such as in the Ruth Pit in the Robinson mining district (Smith, 1976).

ENVIRONMENTAL GEOLOGY OF CARLIN-TYPE DEPOSITS

Carlin-type deposits are probably the most significant source of gold in the Great Basin (Berger and Bagby, 1991; Kuehn and Rose, 1995; Teal and Jackson, 1997). These deposits are typically large-tonnage, low grade epigenetic deposits hosted predominantly in carbonate rock formations (e.g. Carlin mine, Getchell pits). They are formed through the focusing of hydrothermal fluids along zones of weakness (Fig. 6), such as deep fault zones and mixing of deep crustal waters with meteoric recharge (Berger and Bagby, 1991; Kuehn and Rose, 1995; Bertensen et al., 1996; Teal and Jackson, 1997). Host rocks are often carbonaceous and contain abundant calcite and dolomite (Table 6). Sulfide levels in the mineralization can range from <1% to 20-30% and are dominated by abundant marcasite and pyrite that show morphologies from idiomorphic crystals to porous, microcrystalline grains (Bowell et al., 1999; Simon et al., 1999). Possible accessory minerals include realgar and orpiment (noticeably at Getchell where ores can grade up to 30% As), stibnite, Hg-Tl-As sulfosalts, and rarely arsenopyrite, sphalerite and galena (Berger and Bagby, 1991).

Carlin deposits tend not to have anywhere near the same potential for acid generation or metal leaching as other mineral deposit types in the Great Basin (Fig. 5 and Table 7). Similarly with metal leaching, base metal sulfides are volumetrically lower in Carlin deposits so there is less potential to discharge first row transition metals (Hofstra et al., 1995; Price et al., 1995). Trace elements associated with Carlin deposits are however environmentally of concern and include As, Sb, Hg, Tl, Ag, Ba, W, and Se (Kuehn and Rose, 1995). Most of these elements generally show a low mobility in acidic systems due to the strong adsorption potential for their oxyanions by mineral surfaces (Sigg and Stumm, 1980; Deng and Stumm, 1994; Bowell et al., 1996). But in alkaline systems these oxyanions may be dispersed and be readily mobilized in the circumneutral groundwaters observed in Nevada (Table 8). Natural controls are dependent on the availability of Ca and Fe to bind with these oxyanions. High concentrations can persist and mobility can be exacerbated in the environment by evapoconcentration (Eary, 1998).

ENVIRONMENTAL GEOLOGY OF HIGH SULFIDATION DEPOSITS

These deposits are classed as High Sulfidation precious metal Epithermal deposit (Table 6). Typically they are vertically zoned with the highest sulfide content associated with the silicified and leached zones (Fig. 7). The characteristic geologic, mineralogical and geochemical features of this class of deposit influence the environmental behavior of altered rocks and ore found within them.

These deposits typically show high sulfide content, typically from 20-50% of the ore zone and altered wallrock with up to 50% sulfide, chiefly pyrite but several other sulfides can also be important (Table 6). This is reflected in the acid generation potential and reactivity of these deposits (Table 7) and drainage chemistry (Table 8).

These deposits also commonly contain secondary minerals such as chalcanthite, jarosite, scorodite and effervescent iron-sulfate salts. For example at Borealis (Eng, 1991), jarosite is common in the oxidized wallrock and additionally halotrichite, melanterite, and szomolnokite have also been observed by the authors.

The high acid generating capacity of these deposits not only reflects sulfide content but also the leaching of carbonates that accompanies formation of the hydrothermal deposit (Heald et al., 1987; White and Hedenquist, 1995). Such that, even low-sulfide clay-alunite caps to the mineralization and much of the wallrock display highly acidic paste pH indicating high reactivity (Table 8). The only potential buffering capacity is observed in peripheral zones and at depth where propylitic alteration occurs or where a carbonate overprint has been produced post deposit formation. Veins are generally subordinate to disseminated ore types, thus although conduits to deep unexposed sulfides are low the actual surface

TABLE 6. Summary of geological characteristics of the Great Basin deposit types discussed in the text.

Deposit class	Geology	Ore Mineralogy	Alteration characteristics
High Sulfidation (Quartz-Alunite)[1] (H/S)	Felsic volcanic rocks hosted in older sedimentary, volcanic or crystalline rocks. Often associated with composite volcano complex	High sulfide component, dominated by pyrite (up to 50% of ore zone) also quartz and alunite are abundant. Accessories include gold or electrum, then in the shallow zones Ag-sulfosalts, cinnabar, orpiment and realgar. Deeper in the hydrothermal system, chalcopyrite, enargite-luzonite, tennantite-tetrahedrite, galena and sphalerite	Zoned, deep argillic alteration surrounds quartz-pyrite core; intermediate areas propylitic and argillic alteration around core; near surface vuggy silica, quartz-alunite and peripheral propylitic alteration (calcite-epidote-quartz-pyrite-clays)
Low Sulfidation (Quartz-Adularia)[2] (L/S)	Andesitic to felsic volcanics and volcanoclastic rocks. Associated with sedimentary basins and may extend into underlying volcanic sequence	Native gold or electrum, with low to moderate sulfide. High variability between deposits, some have tellurides or selenides, other abundant base metal sulfides such as chalcopyrite, galena and sphalerite. Most contain quartz-adularia veins as the main ore although in some cases pervasive silicification can also occur.	Strongly zoned, central silica unit and potassic (adularia), grading out to quartz-sericite-illite and low temperature clays and zeolites and propylitic assemblages (chlorite-epidote-calcite-quartz-pyrite)
Porphyry Copper[3] (P)	Intermediate to felsic intrusives, associated with breccia pipes, volcanic, calcareous sedimentary rocks and basins	Chalcopyrite-bornite-molybdenite ores with pyritic shell. Gangue and alteration minerals grade outwards. Late stage quartz, clay, pyrite, electrum veins or supergene halos of chalcocite-covellite. Accessory minerals include enargite, tetrahedrite, galena, sphalerite and barite	Strongly zoned, inner silica and potassic zones, argillic and propylitic. A pyrite shell is often present around the ore zone. Overprinting common.
Carlin type[4] (C)	Calcareous or dolomitic sedimentary rocks, can also be associated with arenaceous sedimentary rocks and volcanics. In some cases clear association with felsic magmatic activity	Disseminated micron gold, quartz, pyrite, marcasite, dolomite, calcite, sericite, clays, orpiment, realgar, barite. Base metal sulfides rare to absent. Oxide ore has high goethite content.	Primary ore-sulfide associated with silicification, sulfidation, argillization and decalcification. Oxide ores appear as vuggy silica, pseudo-gossans

[1]Heald et al. (1987); du Bray (1995); White and Hedenquist (1995)
[2]Heald et al. (1987); du Bray (1995); White and Hedenquist (1995)
[3]Lowell and Guilbert (1970); Guilbert and Lowell (1974); Titley (1993); du Bray (1995)
[4]Berger and Bagby (1991); Hofstra et al. (1995)

FIGURE 4. NAG value versus MWMP leachable metals (Co+Ni+Cu+Zn+Ag+Cd+Pb) for different Nevada deposit types discussed in the text.
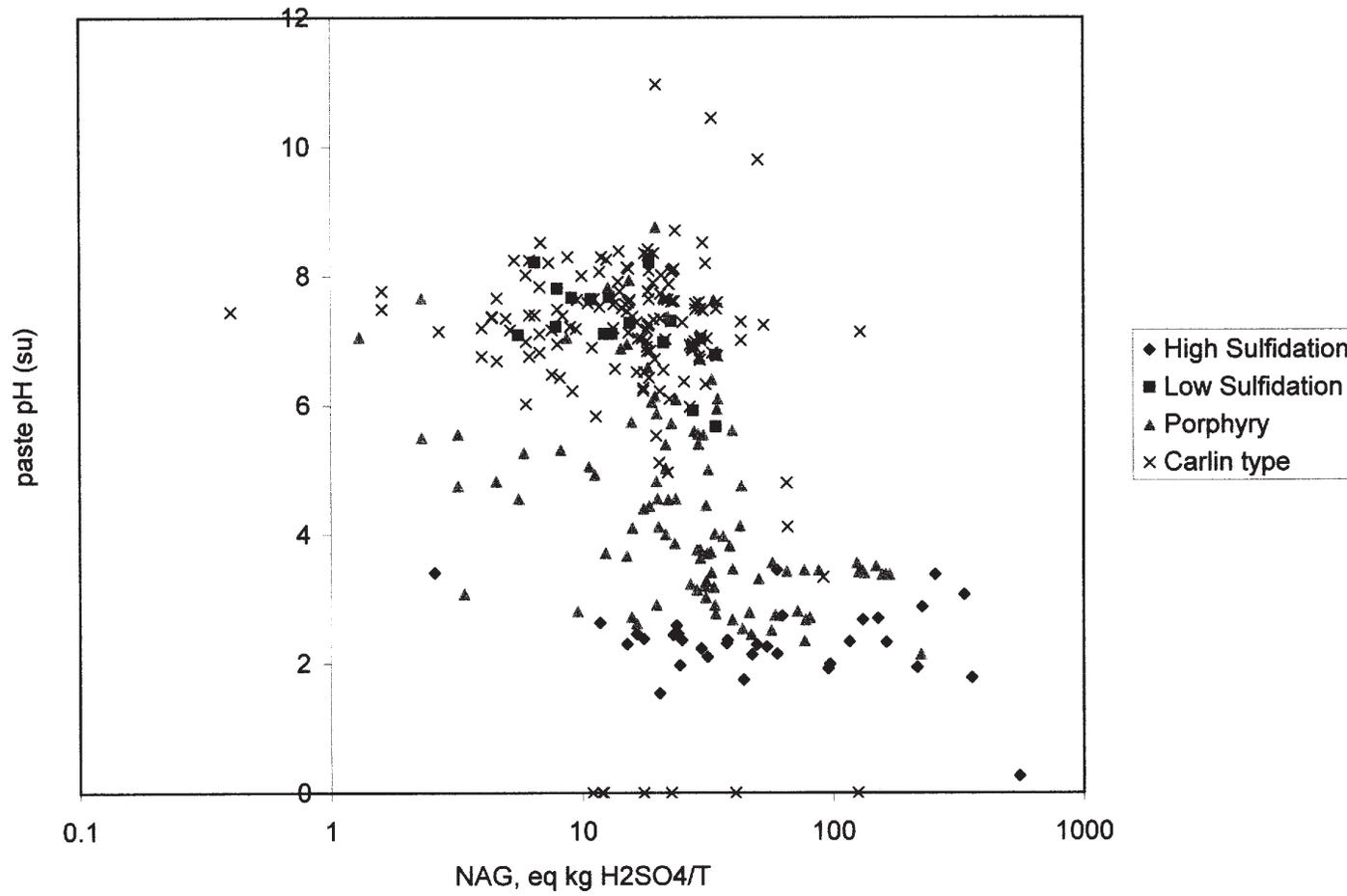
FIGURE 5. NAG value versus paste pH for different Nevada deposit types discussed in the text.

TABLE 7. Summary hydrogeochemical characteristics of surface water at deposits that appear in the geoenvironmental models discussed in the text (data from NDEP records; Price et al., 1995; Getchell data from SRK, 1999).

Deposit	Class	pH, su	TDS	Fe	Mn	As	Cu	Zn	Sulfate
Goldfields	H/S	2.2	3100	485	17.1	8.6	17.5	23.6	2850
Borealis	H/S	2.73-3.19	580-1240	0.4-28	0.51-1.1	<0.005-0.005	0.59-1.5	0.12-0.27	570-1020
Aurora	L/S	7.31-7.42	313-491	<0.05-0.07	0.022-0.091	<0.005-0.005	<0.005	<0.05-0.01	36-265
Tuscarora	L/S	7.2-8.68	192-800	0.05-1.1	<0.005-0.021	<0.005-0.023	<0.005-0.01	<0.005-0.026	51-190
Liberty pit	P	2.86-7.29	2870-7010	0.033-105	22.8-144	<0.005-0.005	0.014-50.6	7.51-66.7	1910-3940
Yerrington	P	7.98-8.25	450-645	<0.01	0.03-0.05	0.003-0.01	<0.005-0.158	<0.005-0.016	65-277
Tonapah	P								
Cortez	C	7.55-8.13	425-553	<0.05-0.257	<0.003-0.135	0.007-0.04	<0.005	<0.005-0.013	82-157
Boss	C	8-8.19	8510-15700	<0.05-3.2	<0.05	0.91-3.1	<0.05-0.19	<0.05	3270-4860
Getchell SCP lake-surface	C	6.67-8.7	245-1720	0.09-2.4	0.002-3.7	0.034-11	<0.002-0.008	<0.002-3.6	58-1000
Getchell SCP lake-metalimnion	C	7-8.6	600-1370	0.05-0.72	0.06-0.7	0.44-3.5	<0.002-0.01	<0.002-0.15	380-700
Getchell SCP lake-hypolimnion	C	3.3-7.6	500-5100	0.25-410	0.72-2.7	0.53-18	0.003-0.15	0.3-38	400-2900

STAGE 1

EARLY JASPEROID

Flow of entrapped meteoric
waters in sedimentary rock
section

Magmatic fluids

GRANODIORITIC INTRUSIONS

STAGE 2

Relatively shallow
meteoric-water flow

Deeply circulating
meteoric water flow

Mixed magmatic &
deeply circulating
meteoric water

GRANODIORITIC INTRUSIONS

SCHEMATIC MODEL FOR THE DEVELOPMENT OF A CARLIN - TYPE DEPOSIT.
STAGE 1- Initial mineralization consists of probable skarn and possible stockwork
metallization in the immediate vicinity of the intrusive complex and concurrent formation
of early jasperoid distal to the complex.
STAGE 2- Schematic model for the development of a Carlin gold deposit. Gold
mineralization may occur either close in, or distal to, the intrusive complex. Gold
deposition typically coincides with early, pre-ore jasperoid.The early jasperoid may be
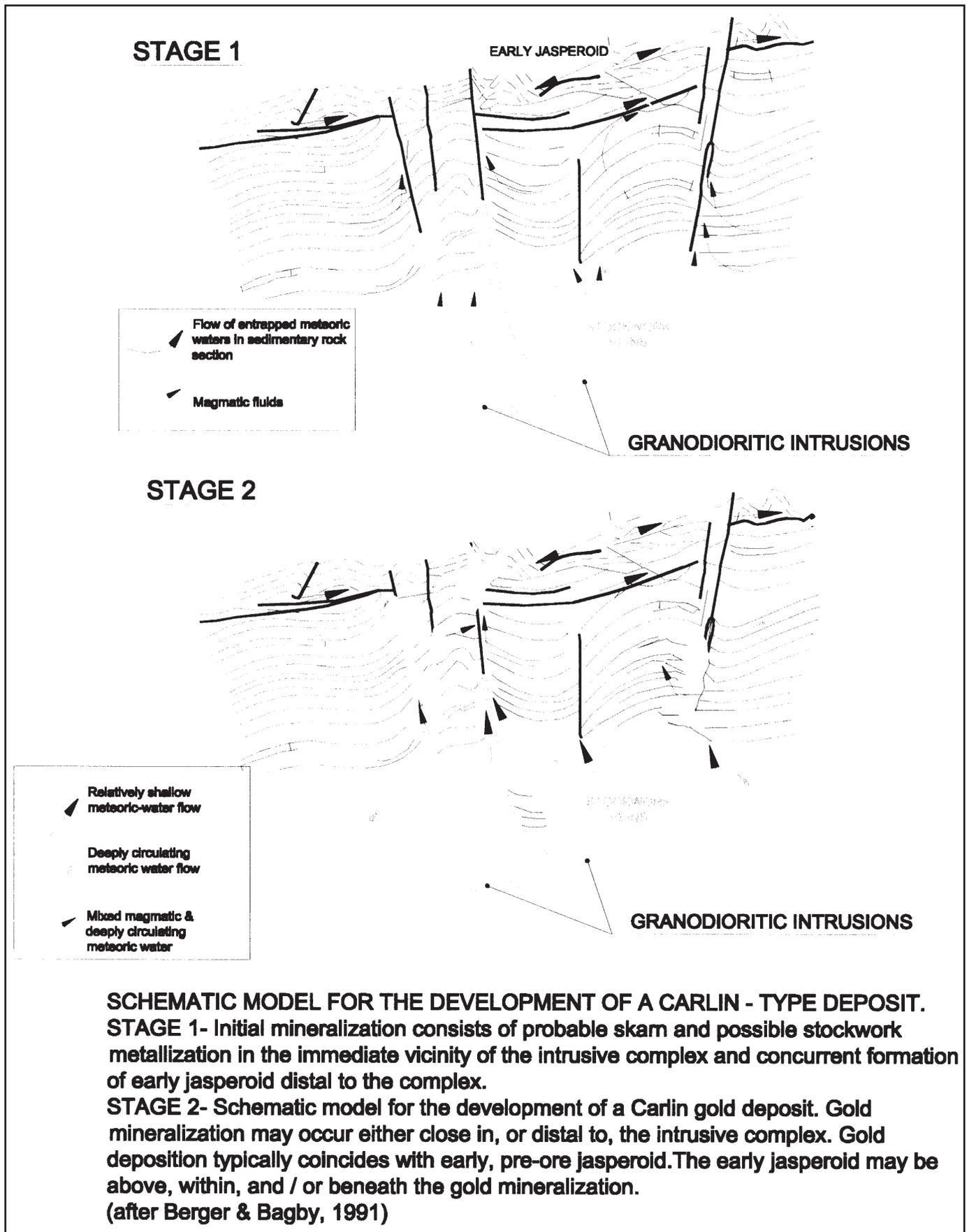above, within, and / or beneath the gold mineralization.
(after Berger & Bagby, 1991)

FIGURE 6. Schematic summary of the development of a Carlin-type deposit (after Berger and Bagby, 1991. Reproduced from Figure 7.7, page 241 of Gold Metallogeny and Exploration, editor: R.P. Foster, 1991, Chapman & Hall, London).

TABLE 8. Summary geochemical characteristics of the geoenvironmental models for ore zone material.

Class	Paste pH, su	% Sulfide, range	NAG, eq.kg H_2SO_4/T	NAG, final pH	NNP, eq.kg $CaCO_3$/T	Metals[1] enriched in rocks	Major MWMP leachable metals (>2 SD regulatory limit)
H/S	0.45-6.7	3.4-31	8-550	0.78-4.56	-325 - -5.9	Fe, Mn, Co, Ni, Cu, Zn, As, Se, Mo, Ag, Cd, Sn, Sb, Te, Au, Hg, Tl, Pb, Bi	Fe, Mn, Co, Ni, Cu, Zn, As, Se, Mo, Cd, Sn, Sb, Hg, Pb, Bi
L/S	3.2-8.3	<0.1-6.3	0-23.5	2.82-6.54	-22.1- 112	Cu, Zn, As, Se, Ag, Cd, Te, Au, Hg	As, Se, Cd, Pb
P	2.2-8.1	0.2-21.6	0-129	1.65-5.87	-108-12.1	Fe, Mn, Cu, Zn, As, Se, Mo, Ag, Cd, Sn, Au	Mn, Cu, Zn, As, Se, Mo, Cd
C	3.6-11.2	<0.1-18.8	0-98	2.44-6.11	-55.4 – 7.6	As, Ag, Cd, Sb, Ba, W, Au, Hg, Tl, Pb	As, Cd, Sb, Hg, Tl, Pb

1.Geochemical anaomaly

H/S High Sulfidation

L/S Low Sulfidation

P Porphyry

C Carlin-type

area of the mineralization can be significant (Heald et al., 1987).

Due to the high level placement, mineral grains tend to be very fine, thus have a high surface area: volume ratio and consequently tend to be more reactive. Typical grain size is of the order of < 5mm indicating fine grains. Complex mineral parageneses are common leading to mixed assemblages of pyrite and base metals. The result is that sulfides with widely different electrochemical characteristics occur together and thus range promote sulfide oxidation through the localized formation of anode-cathode "self-generating" sulfide battery cells (Thornber, 1983).

Geochemically the anomalous elements associated with such deposits include ore grades of Au, Ag and Cu and pathfinder elements such as As, Sb, Bi, Hg, Te, Sn, Pb, Mo and Se (White and Hedenquist, 1995). These latter pathfinders are all potential pollutants and in the case of As, Hg and Pb particularly, exhibit "low environmental tolerance. In summary, this style of mineralization can be predicted to be both acid generating and contain a significant potential for release of pollutants (Fig. 2).

ENVIRONMENTAL GEOLOGY OF LOW SULFIDATION EPITHERMAL DEPOSITS

Low sulfidation Epithermal deposits are formed in a similar environment to high sulfidation systems (Fig. 7), but from circumneutral hydrothermal fluids rather than acidic solutions (Barton and Skinner, 1979). These deposits typically show low sulfide content, from <5-20% of the ore zone and altered wallrock even less, usually being < 5% sulfide (Table 6).

Secondary minerals associated with these deposits tend to reflect the circumneutral to alkaline nature of the mineralization with carbonates such as siderite, malachite, azurite, smithsonite and cerussite being common.

By contrast to high sulfidation systems, abundant mineral buffering is available with calcite forming a major component of the vein mineralization and the extensive adularia-sericite and propylitic alteration halos. Consequently the field paste pH and NAG values indicate a low potential for acid generation (Fig. 5) with little metal leaching (Figs. 2, 4).

Low sulfidation deposits are formed in vuggy open space veins comprising the major form of mineralization with minor disseminated or replacement styles of mineralization. Due to the open space nature of the mineralization, sulfides tend to have a wide range in grain size (<0.1 to > 50 mm) and are often idiomorphic implying a greater degree of stability than for fine grained porous sulfides often observed in the high sulfidation deposits.

Geochemically the anomalous elements associated with such deposits include ore grades of Au and Ag and pathfinder elements such as high Ag/Au, As, Sb, Hg, Tl, Zn, Pb, Te and K (White and Hedenquist, 1995). In the case of As, Sb and Tl, mobility can be enhanced in alkaline environments so whilst acid generation and mobilization of base metals is unlikely to occur, a potential environmental impact related to geologic characteristics still exists.

FIELD ASSESSMENT OF ENVIRONMENTAL IMPACT

The environmental impact of a metallic ore deposit, can be viewed in terms of:
- Potential for contaminant generation (metals, acid and salts)
- Potential for contaminant buffering

Both these parameters can be estimated on the basis of mineralogical and geochemical attributes of the ore and waste to be mined. In reality, complications occur due to differences in petrology, rock competency, biogeochemical processes, background hydrogeology and hydrogeochemistry of the mineral property area, as well as the limitation of mineral weathering data. Yet despite this, field estimates are useful in identifying those rock units or ores that contain a high concern for impact at an very early stage in the mining project.

FIELD EVIDENCE FOR ACID GENERATION AND METAL RELEASE

Definitive identification, characterization and assessment of ARD requires a combination of field observations, laboratory tests and predictive modelling. However a valid field assessment can be made based on mineralogical and geologic evidence and from simple field tests. An outline of these procedures is provided below.

PRIMARY MINERALOGY

From the above conceptual geoenvironmental models it is evident that key criteria can be identified for metal leaching and acid generation including sulfide and carbonate mineralogy and the presence of Ca-Mg fast weathering silicates. Several ABA schemes have been proposed on a mineralogic balance but are often poorly applied. Using one of the more useful schemes, the comparison of mineralogical and laboratory derived NNP values from Nevada deposits, of the classes discussed above, is presented below.

The method used here, proposed by Kwong (1993), relates the number of protons released from sulfide oxidation (from experimental work by Thornber, 1975a,b; 1983; 1992; 1993) to buffering capacity (defined by cation release from theoretical calculations of Sverdrup, 1990). The complete derivation of the equations can be found in Kwong (1993) essentially the main derivatives are:

Estimate of proton release

$$\text{Number of } H^+ \text{ per sulfide atom} = 2(1-r) \qquad (1)$$

Where r = average metal/sulfur atomic ratio in the sulfide mineral. If the metal concerned is Fe, the Thornber (1975) formula is modified to account for ferrolysis (Table 2).

The modified Thornber formulae (Thornber, 1993) would read,

$$AGP_{field,Fe}= \text{Number of } H^+ \text{ per sulfide atom} =$$
$$2(1-r+p) \qquad (2)$$

Where p = proportion of ferrous iron in the metal sulfide assemblages and AGP=Acid Generation Potential. The modification is required whenever Fe^{3+} is not stable relative to
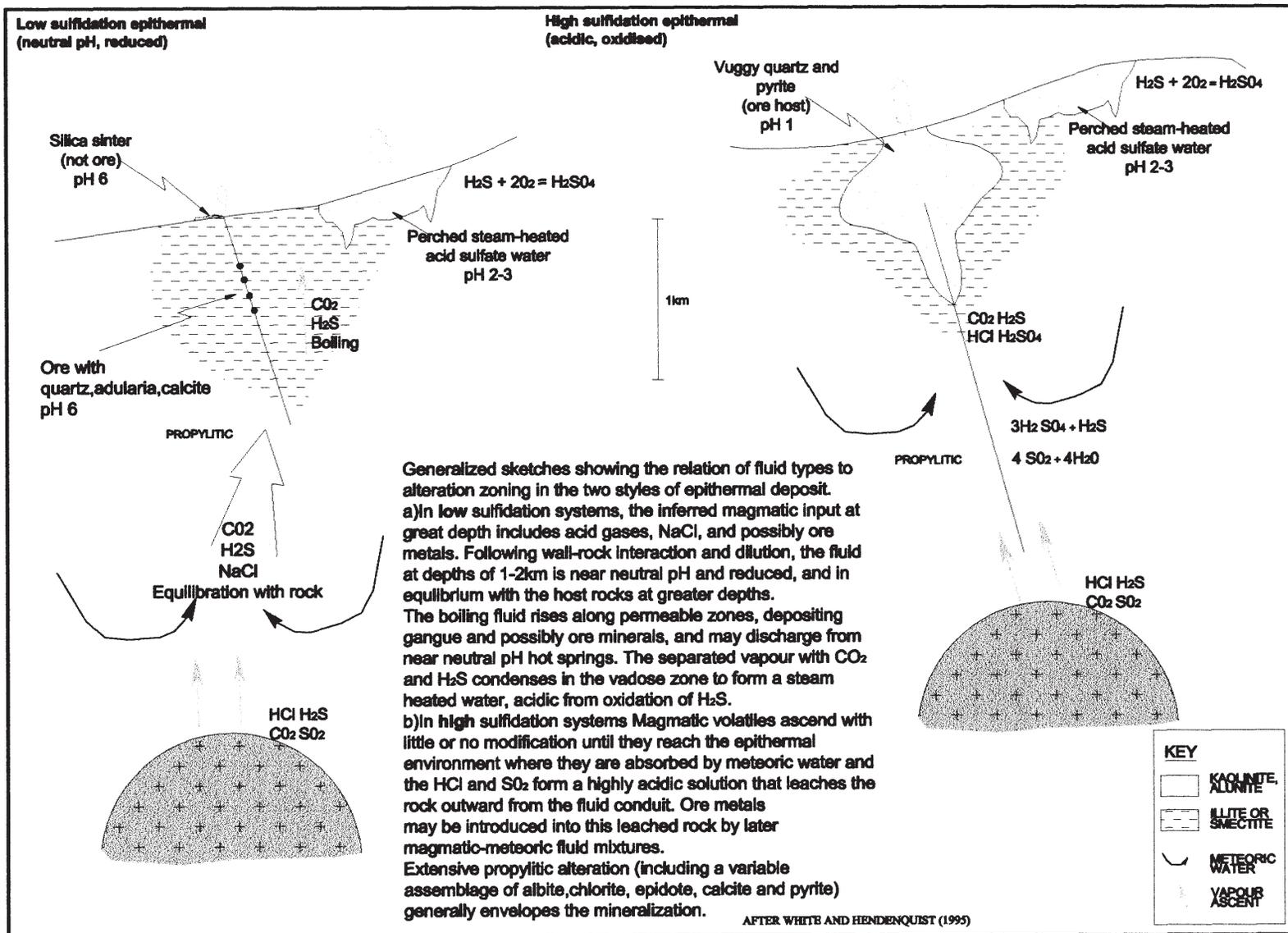
Low sulfidation epithermal
(neutral pH, reduced)

High sulfidation epithermal
(acidic, oxidised)

Vuggy quartz and
pyrite
(ore host)
pH 1

$H_2S + 2O_2 = H_2SO_4$

Perched steam-heated
acid sulfate water
pH 2-3

Silica sinter
(not ore)
pH 6

$H_2S + 2O_2 = H_2SO_4$

Perched steam-heated
acid sulfate water
pH 2-3

1km

CO_2
H_2S
Boiling

$CO_2 H_2S$
$HCl H_2SO_4$

Ore with
quartz,adularia,calcite
pH 6

PROPYLITIC

$3H_2SO_4 + H_2S$

PROPYLITIC $4 SO_2 + 4H_2O$

Generalized sketches showing the relation of fluid types to
alteration zoning in the two styles of epithermal deposit.
a)In low sulfidation systems, the inferred magmatic input at
great depth includes acid gases, NaCl, and possibly ore
metals. Following wall-rock interaction and dilution, the fluid
at depths of 1-2km is near neutral pH and reduced, and in
equilibrium with the host rocks at greater depths.
The boiling fluid rises along permeable zones, depositing
gangue and possibly ore minerals, and may discharge from
near neutral pH hot springs. The separated vapour with CO_2
and H_2S condenses in the vadose zone to form a steam
heated water, acidic from oxidation of H_2S.
b)In **high** sulfidation systems Magmatic volatiles ascend with
little or no modification until they reach the epithermal
environment where they are absorbed by meteoric water and
the HCl and SO_2 form a highly acidic solution that leaches the
rock outward from the fluid conduit. Ore metals
may be introduced into this leached rock by later
magmatic-meteoric fluid mixtures.
Extensive propylitic alteration (including a variable
assemblage of albite,chlorite, epidote, calcite and pyrite)
generally envelopes the mineralization.

CO_2
H2S
NaCl
Equilibration with rock

HCl H_2S
$CO_2 SO_2$

HCl H_2S
$CO_2 SO_2$

AFTER WHITE AND HEDENQUIST (1995)

KEY

KAOLINITE,
ALUNITE

ILLITE OR
SMECTITE

METEORIC
WATER

VAPOUR
ASCENT

FIGURE 7. Schematic summary of the development of Epithermal deposits (after White and Hedenquist, 1995).
Reproduced from the October 1995 issue, No. 23, of the SEG Newsletter with permission of the Society of Economic Geologists, Inc.).

$Fe(OH)_3$, which is the case at pH> 3.3 su under atmospheric conditions (Fig. 1).

Buffering Capacity

From the work of Sverdrup (1990) from which the weathering rate of a rock, R, can be approximated by the following equation:

$$R = {}^6 xm_n.k_n \qquad (3)$$

Where n is the number of mineral weathering classes in the Sverdup classification (Table 4), xm_n and k_n are the fraction and weathering rate of each mineral class, respectively. The weathering rate is expressed in terms of kilo-equivalents (of cations released) per hectare per annum from a one meter thick segment of rock or soil with a paste pH (1:1 soil to water) of 5 su. However such a field estimate of neutralization potential, ignores the dependency of weathering rate on mineral concentration in a rock and rather defines "a relative reaction rate with respect to carbonates", on a mono-mineral basis (Kwong, 1993). From the predicted values shown in Table 4, the slow weathering, very slow weathering and inert groups do not participate in acid neutralization as they provide negligible buffering and essential only carbonates are considered. Consequently an effective neutralization potential, NP_{field} can be considered as being equal to the equivalent moles of carbonate present for buffering. The maximum buffering for one mole being 2. Consequently for classes 1-3 of Sverdup's classification, the field Neutralization Potential (NP) can be calculated as being:

$$NP_{field}/\text{no.of moles of H}^+ \text{ neutralized by rock} =$$
$$2\sum xm_n K_n' \qquad (4)$$

Where xm_n' = molar proportion of minerals in class "n" and K_n' is the relative reactivity of mineral class "n". As shown in Table 4, W_n' = relative reactivity of the mineral group n. Consequently taking both of these values a field NNP, can be estimated as:

$$NNP_{field}=NP_{field}-AGP_{field} \qquad (5)$$
$$\text{Or} \qquad NNP_{field}= 2\{[\sum xm_n-k'_n]-[x_s(1-r+p)]\} \qquad (6)$$

Where x_s is the fraction of sulfide in the mine waste. If Net Neutralization Potential (NNP_{field}) is negative then the material is classed as being potentially acid generating. As an example field NNP values were calculated for four deposits in Nevada, on the basis of mineralogy and compared to traditional ABA results (Price, 1997). As can be observed the field estimates show slight to significant variation for each of the mineral deposits, related to mineralogical controls, but generally show a similar trend for low and high NNP estimates.

High sulfidation deposits show the best correlation as mineralogy is dominated by pyrite and by inert buffering materials such as quartz (Fig. 8). Variance occurs in material in the laboratory NNP range of (-10 to 10 eq. kg $CaCO_3$/t. This is because in this range reactive silicates and carbonates provide buffering component of propylitic and argillic alteration zones. As silicates do not buffer to the same rate as carbonates, the laboratory or actual buffering capacity is less than that derived empirically. Consequently NP is over-estimated by the mineralogical method. Additionally Al released from dissolution of silicates, will hydrolyze like Fe^{3+} and release protons on formation of a hydroxide. This reduces the actual buffering capacity and again is not accounted for by empirical calculations.

Another difference between the two methods for high sulfidation deposits, often ignored, is that laboratory ABA analyses often account for non-acid generating refractory sulfate, such as alunite and barite in the sulfide fraction. This leads as shown to spurious over assessment of AGP. Another cause of this difference is that by a mineralogical ABA balance, the only sulfides considered are Fe-sulfides but by laboratory analysis all sulfide sulfur is included in the assessment. Consequently the mineralogical methods also have a use in validating or highlighting potential problems with laboratory assessment techniques.

In the case of porphyry and low sulfidation systems the problems of aluminosilicate buffering outlined above is even more noticeable (Fig. 8). Consequently caution has to be used in applying mineralogical methods of ABA to these types of deposits, even as a field method. At high NP values in low sulfidation systems, where carbonates are abundant a good correlation is observed and in porphyry samples with high sulfide content (Fig. 8). Otherwise there is little or no correlation.

In the case of the Carlin deposits with high NP a good correlation is observed as the carbonates dominate the ARD characteristics of the samples. Where sulfide is higher, this correlation is lost as well as the problems of aluminosilicate buffering in these samples that typically have low carbonate and the accessory minerals are clays and quartz. In some samples, laboratory AGP is considerably higher than would be estimated empirically. This again is due to the presence of non-acid generating sulfides, but in this case from realgar. Additionally in some high As-sulfide content samples when back titration is undertaken, it appears that some protons are consumed, through formation of $H_nAsO_4^{3-n}$ species (Bowell et al., in prep). As these minerals are not assessed as having a buffering capacity by the Sverdrup equation they are not accounted for and consequently the calculated NNP is underestimated and the laboratory AGP is overestimated.

SECONDARY MINERALIZATION

The neutralization of ARD results in the formation of mineral precipitates along drainage channels, waste rock piles and wall rock. Such phases include jarosite and iron oxyhydroxides (yellow to red color), aluminum hydroxides (white), metal salts that can be green (Ni), pink (Co), bluish-green (Cu), deep blue (Mo), red (Pb), or white. On the basis of composition of these salts the mobile metals can be described and this information used to select appropriate target elements in chemical testwork augmenting information from geologic and bulk rock geochemistry studies.

WEATHERING

Acid generation, buffering, metal mobilization and secondary mineral precipitation are part of the natural geochemical cycling of elements. As weathering progresses downwards,
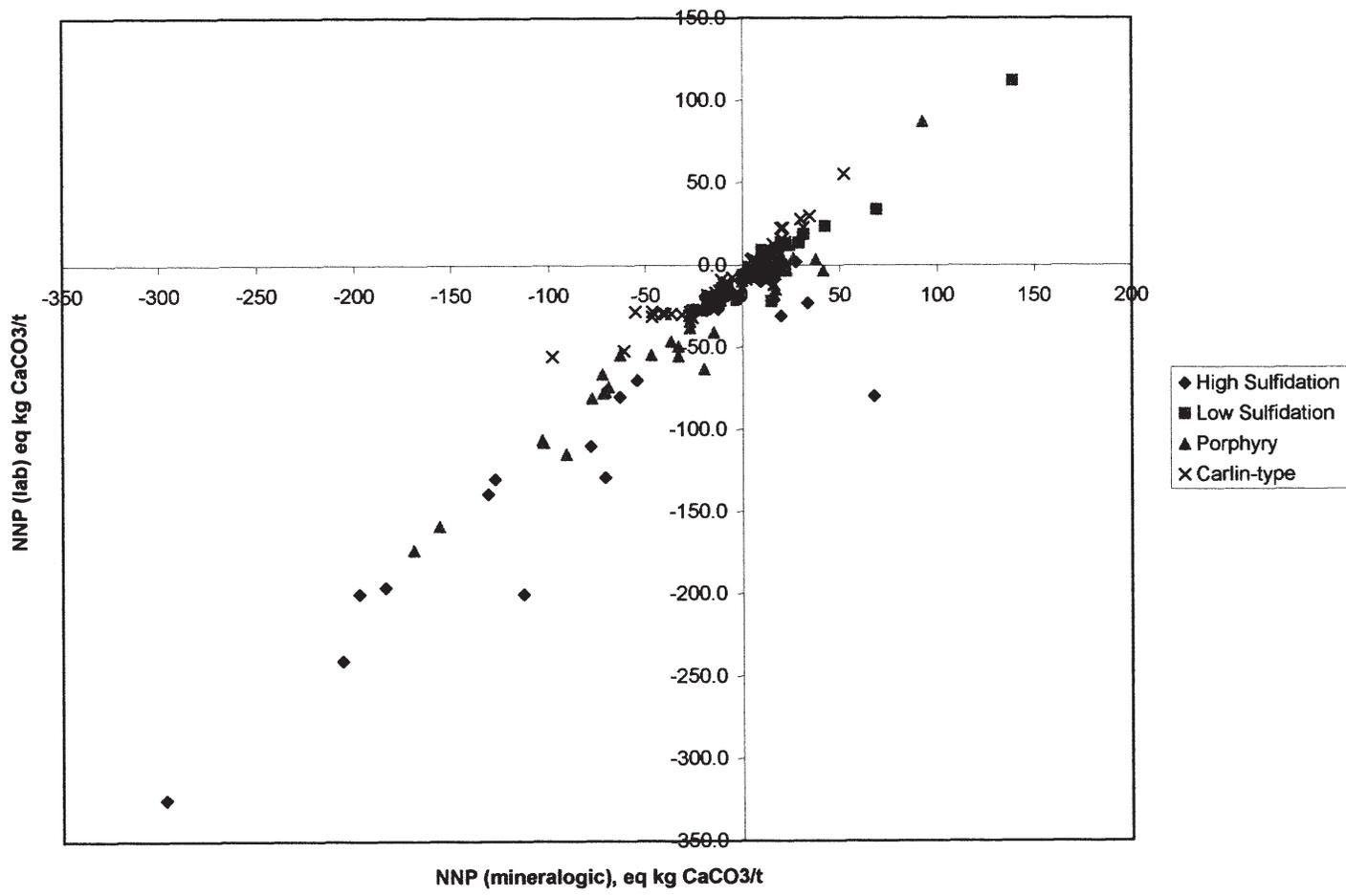
FIGURE 8. Correlation between field and laboratory NNP for different Nevada deposit types discussed in the text.

distinct horizons are formed. A typical sequence includes an acidic weathered surface layer, a moderately acidic layer dominated by iron oxyhydroxides and an underlying circumneutral layer.

FIELD INDICATORS IN DRAINAGE WATERS

Water coming into contact with a rock mass will transport the products of acid generation and metal leaching including dispersed sulfate salts. Typically such waters have a yellow to orange to red discoloration from the presence of dispersed $Fe(OH)_3$ particles (pH>3 su) or dissolved Fe^{3+} (pH < 3 su). These waters often have high electrical conductivity (>5 μS/cm). These waters are different from acidic waters resulting from humic acid dispersion as is found in peat wetlands which have a black to brown color, pH is rarely below 5 su and the water has a low electrical conductivity (typically ~ 100-200 (S/cm).

FIELD INDICATORS FROM THE ROCKS

Additional to the qualitative observational information above, the potential reactivity of a rock unit can be assessed from measuring pH and electrical conductivity of a paste. The paste is formed by crushed rock and water mixed in a ratio of 1:1 for arid climates (such as the Great Basin) or 2:1 (respectively) for material in more temperate climates.

The paste pH result infers potential acid generation if the pH reading is < 4 su. Where Fe-sulfate salts are strongly developed, such as in high sulfidation systems paste pH can commonly be as low as pH 1.5-2 su. The paste pH result is a reasonable indicator for high sulfidation, porphyry and Carlin deposits described above of potential acid generation when compared to traditional NNP analyses (Fig. 9). Although in detail the ordering of strong and moderate acid generation potential is not always the same, the test distinguishes between high and low reactivity. In the case of the low sulfidation deposits the presence of scarce idiomorphic crystals of sulfides and abundant reactive alkalinity from carbonates results in a masking of the "geologic potential"(defined by the NNP) and the "reactive potential" of the lithologies.

CONCLUSIONS

In this paper we have attempted to describe some of the important geologic controls on the environmental impacts associated with metal mineral deposits that are common to the Great Basin. The importance of understanding geologic processes that generate and control environmental impacts is proposed here to be fundamental not just in evaluation but also in future prediction and mitigation of the effects of acid generation and metal leaching.

The processes that generate acidity and leach metals are essentially the reaction between rocks and the environment as the rock mineralogy attempts to define equilibrium with prevailing environmental conditions. Consequently an assessment of ARD can gain considerable benefit from a geologist's knowledge of the geochemical behavior of mineral deposits as well as the changes that can be anticipated over the property with respect to structural changes, groundwater flow and mineralogical variations in the lithologies.

At the reconnaissance stage, the main task is the identification of the major acid-generation or acid-neutralizing rock units. This can be achieved by examining the mineralogical content of the known rock types, their competency, petrology and extent of weathering. In highly weathered outcrops, secondary minerals can be identified and natural runoff characterized.

Once a mineralized target has been delineated a more valuable assessment can be acquired with information on mineralogical variations, porosity and structural integrity of relevant lithologies. These data are essential in the rapid assessment of acid-generating/neutralizing potential. Petrology of representative core samples will allow the description of the relationship between various sulfide and gangue minerals to be assessed. Examination of exposed sub-outcrop will reveal the nature and extent of oxidation and chemistry of secondary mineral products if not identified elsewhere. A further task is to delineate likely deleterious trace elements. This information is best collected from whole rock geochemistry acquired during exploration activities.

At the feasibility stage, a comprehensive environmental impact statement for permitting purposes is generally prepared with various detailed monitoring programs and specific studies. Any ARD studies can be significantly enhanced by allowing field geologists an opportunity to be involved in the selection of representative material to reflect the broad range of potential environmental interactions anticipated from exposed underground and pit wall lithologies, waste rock and ore stockpiles.

The geo-environmental understanding of mineral deposits is essential in defining remediation objectives. In many situations, natural drainage is poor and it is inappropriate and in a few cases impossible to remediate a site to "pristine conditions" with water quality required to drinking water standards. However, in many states in the USA and in many national government agencies the natural occurrence of ARD has yet to be accepted. The development of valid geo-environmental models provides a challenge to current regulatory requirements. In the future they may support the need for more realistic closure objectives to be set, that account for local geologic variations.
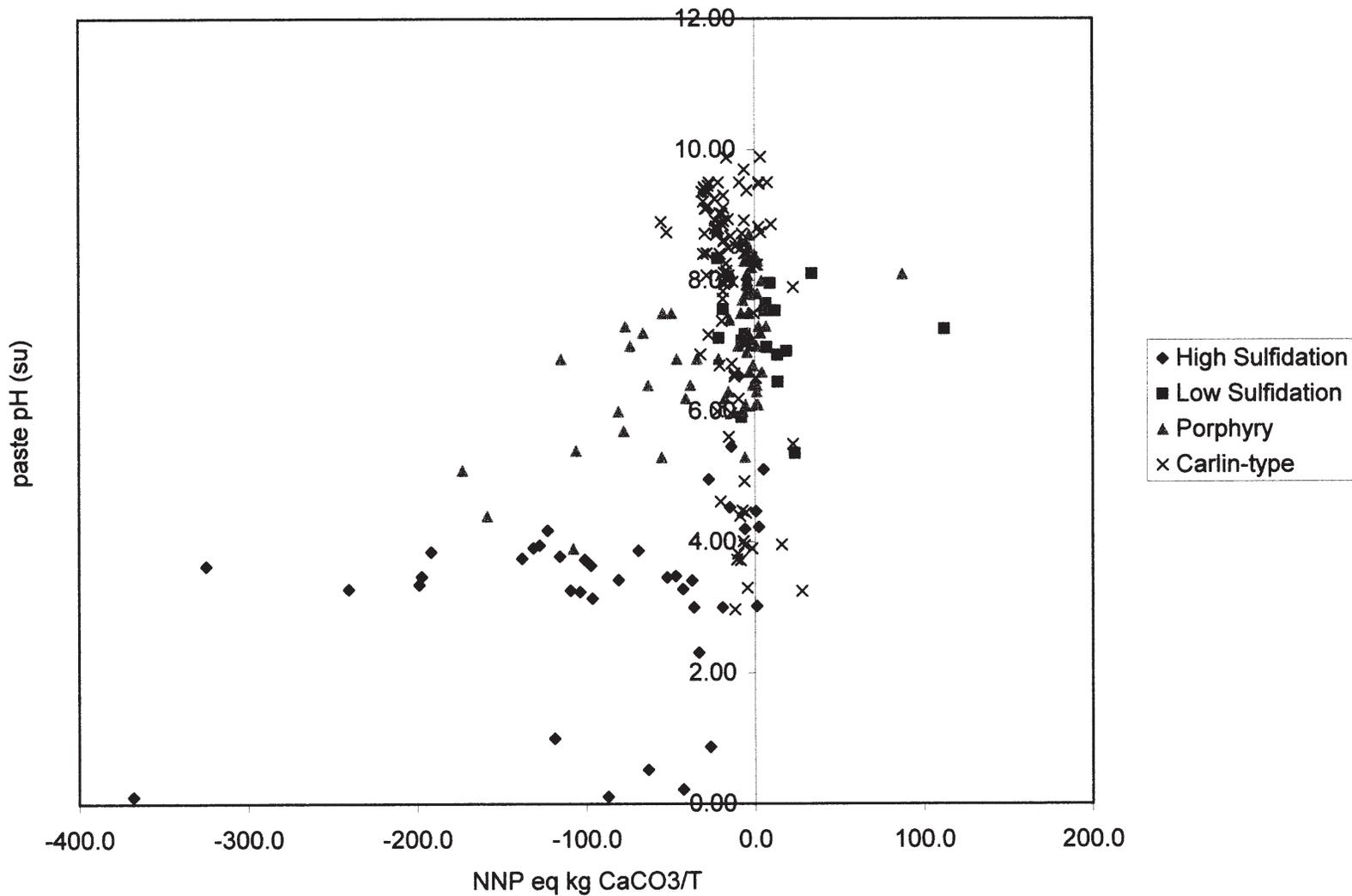
FIGURE 9. Correlation between paste pH and laboratory NNP for different Nevada deposits discussed in the text.

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