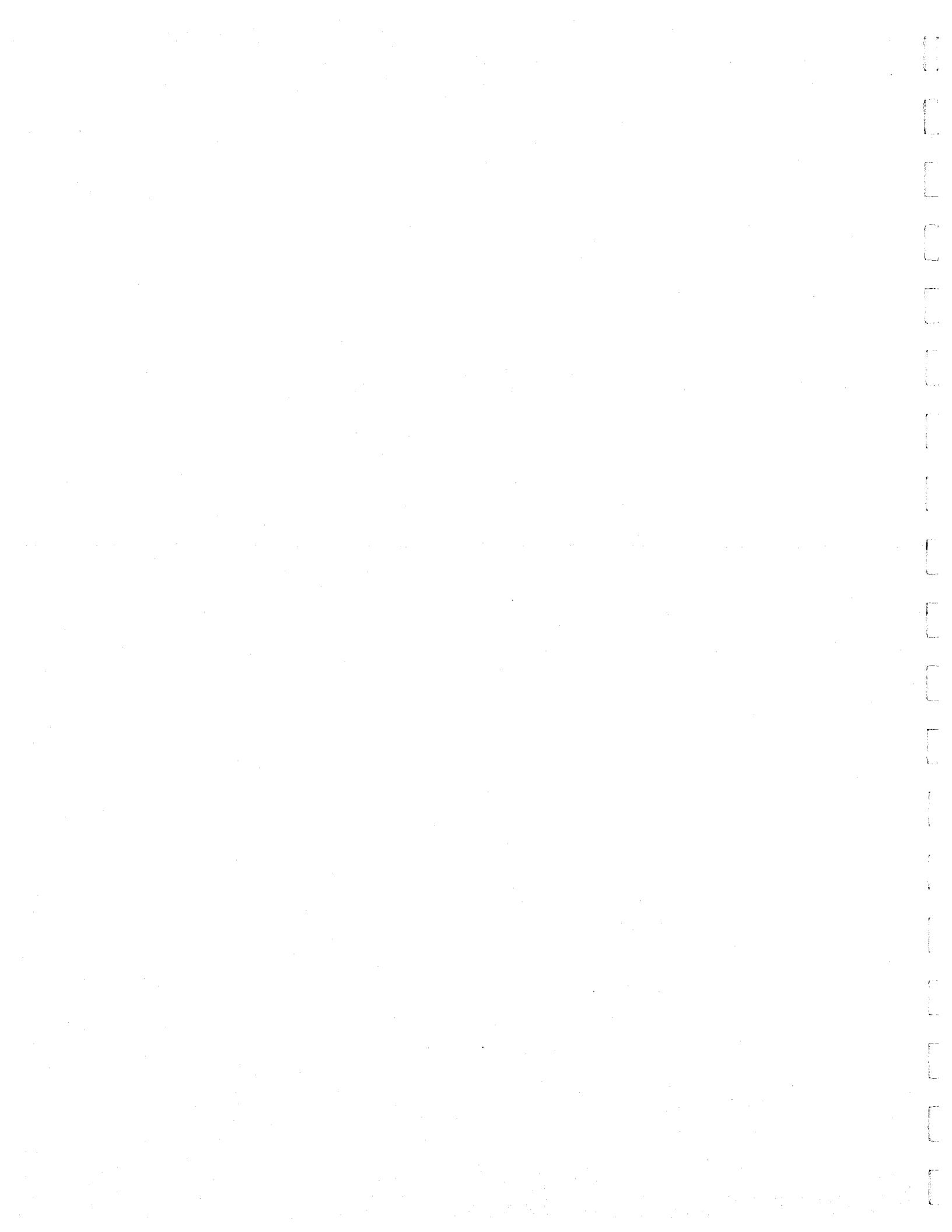C.5.   Lithogeochemical Methods for Acid Rock
Drainage Studies and Prediction

by
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LITHOGEOCHEMICAL METHODS

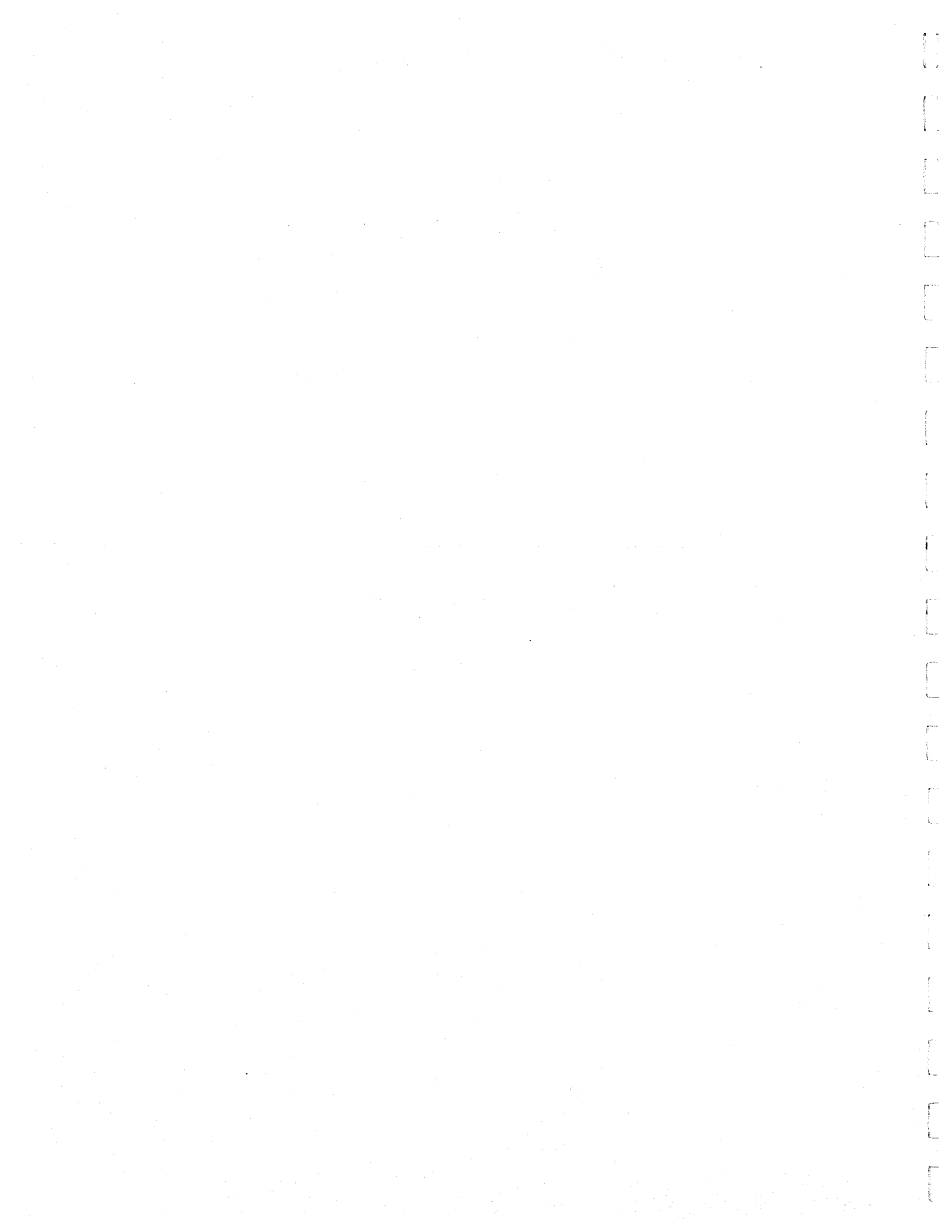# FOR

ACID ROCK DRAINAGE STUDIES AND PREDICTION

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- **WHAT CONTROLS ARD?**
  BULK CHEMISTRY OF MATERIAL

- **WHAT CONTROLS BULK CHEMISTRY?**
  MINERAL ASSEMBLAGE

- **HOW DO WE RECOGNIZE ROCK TYPES**
  VISUAL MINERALOGY (hand sample scale)
  PETROGRAPHIC STUDIES (thin section scale)
  LITHOGEOCHEMISTRY (chemistry scale)

- **CAN WE MODEL DESTRUCTION OF ROCK FORMING MINERALS?**
  Fine grained rocks
  Altered and metamorphosed

- **CAN WE MODEL LITHOGEOCHEMISTRY AND ARD?**

- **OBJECTIVE TO DEVISE AND TEST A METHOD OF PREDICTING ARD BUFFERING CAPACITY BASED ON BULK CHEMISTRY AND MODAL MINERALOGY. DEVELOP A QUANTITATIVE THEORETICAL METHOD FOR CALCULATING NEUTRALIZING POTENTIAL, RELYING ON EASILY OBTAINABLE AND RELATIVELY INEXPENSIVE WHOLE-ROCK AND SULPHUR XRF ANALYSES, WHICH COULD SUBSTITUTE FOR CONVENTIONAL ABA PROCEDURES IN SITUATIONS WHERE THESE PROCEDURES ARE EITHER TOO COSTLY OR TOO TIME CONSUMING.**

METHODOLOGY

ABA data for mine waste samples from four different deposit types:
- anorthosite hosted magmatic sulphide nickel,
- dunite hosted magmatic sulphide nickel,
- porphyry copper-gold, and
- volcanic hosted high sulphidation epithermal silver,

- ABA BC Research method, initial pH,
- total sulphur (Leco),
- sulphate sulphur (turbidimetric method).

- Whole Rock Analyses (inductively coupled plasma emission spectroscopy (ICP-ES) using a lithium metaborate fusion),
    - provides major oxides data provide bulk chemistry
- CO_2 analyses (total inorganic carbon)
    - provides carbonate content

SAMPLING

- Assay pulps of core collected from exploration drilling, and grab samples collected from outcrop.

- Samples represent altered and unaltered host rocks, both barren and sub-ore, which were specifically collected to determine the limits of ABA for acid generating and non-acid generating material.

- Sample pulps from one of the deposits were composited to represent lithologic types, and over mining bench heights to represent mining blocks.

- Samples at the silver deposit were collected from outcrop, and had their weathering rinds cut away.

PETROGRAPHIC STUDIES:

- to determine modal mineralogy for rock classification
  (as a check on field classification),

- to examine sulphide mineralogy,

- to determine primary and secondary mineralogy and alteration variation that would impact the determination of neutralization potential.

- to determine the degree of partitioning of feldspars into calcic, sodic, and potassic end-members which may have a bearing on the silicate-based buffering capacity of these rocks.

LITHOGEOCHEMICAL STUDY:

- to determine the bulk chemistry of the waste rock;

- to classify rock types and alteration facies,

- to test CIPW normative mineralogy;

- to correlate chemistry with petrographic studies;

- to determine whether and to what extent alternative methods could be developed for the conventional ABA analytical procedures; and

- to determine complementary prediction methods and models in conjunction with the conventional or legally mandated net neutralization potential (NNP) and neutralization potential - acid production (NPR) methods.

ROCK AND ALTERATION LITHOGEOCHEMISTRY

- **LITHOLOGIC VARIATION**

- **WEATHERING POTENTIAL INDEX**

- **CIPW**
  - **NewPet software used to perform CIPW normative calculations which estimate the modal mineralogy of these rocks.**

NOTE: Data reported in weight percent have been converted to molecular proportions in order to construct the linear covariation models which relate the data to mineral formulae and chemical reactions, and specifically relate changes in the analytical data to changes in the modal mineralogy of the rocks.

LITHOLOGIC VARIATION

- Rock types can be distinguished geochemically by their conserved element ratios. A diagnostic property of rocks belonging to the same rock type, or the same cogenetic group, is that they share a common conserved element ratio, no matter how altered, metamorphosed, or weathered these rocks might be. Conserved elements are those which do not participate in mass transfer, either in rock-forming or alteration processes. In igneous rocks such elements are incompatible in the melt, and are effectively immobile in hydrothermal fluids. The loss of alkali cations from the rocks, i.e., the degree of alkali depletion, can be measured by residuals to linear molar covariation models. The degree of H^+ substitution, i.e., degree of hydrolysis of these rocks, can be estimated by the initial pH of a rock-water slurry measured as part of conventional ABA.

- To test for the presence of conserved elements, concentrations of two elements are plotted on an X-Y scatterplot (see Fig. 2). Where lines can be drawn through a linear array of data points and the origin of the plot (within the limits of analytical error), the samples in such an array can be considered as belonging to one rock type, and the two elements can be considered to be conserved. It is important to keep in mind that the lines drawn through the origin of the scatterplot are constant-ratio lines, they are not regression lines. On the scatterplot of TiO_2 vs. Zr (Fig. 2) two distinct lithological populations can be distinguished: the intrusives are identified by the higher conserved element ratio; the gneisses are characterized by a linear trend approximately parallel to the x-axis. Ti and Zr are conserved elements in the intrusives, whereas in the gneisses Ti is probably not conserved. Other plots that can be used to corroborate these observations are: Al_2O_3 vs. Zr; Nb vs. Zr; and Y vs. Zr (not shown).

FIGURE 2: Rock Type Classification (MMS dataset)
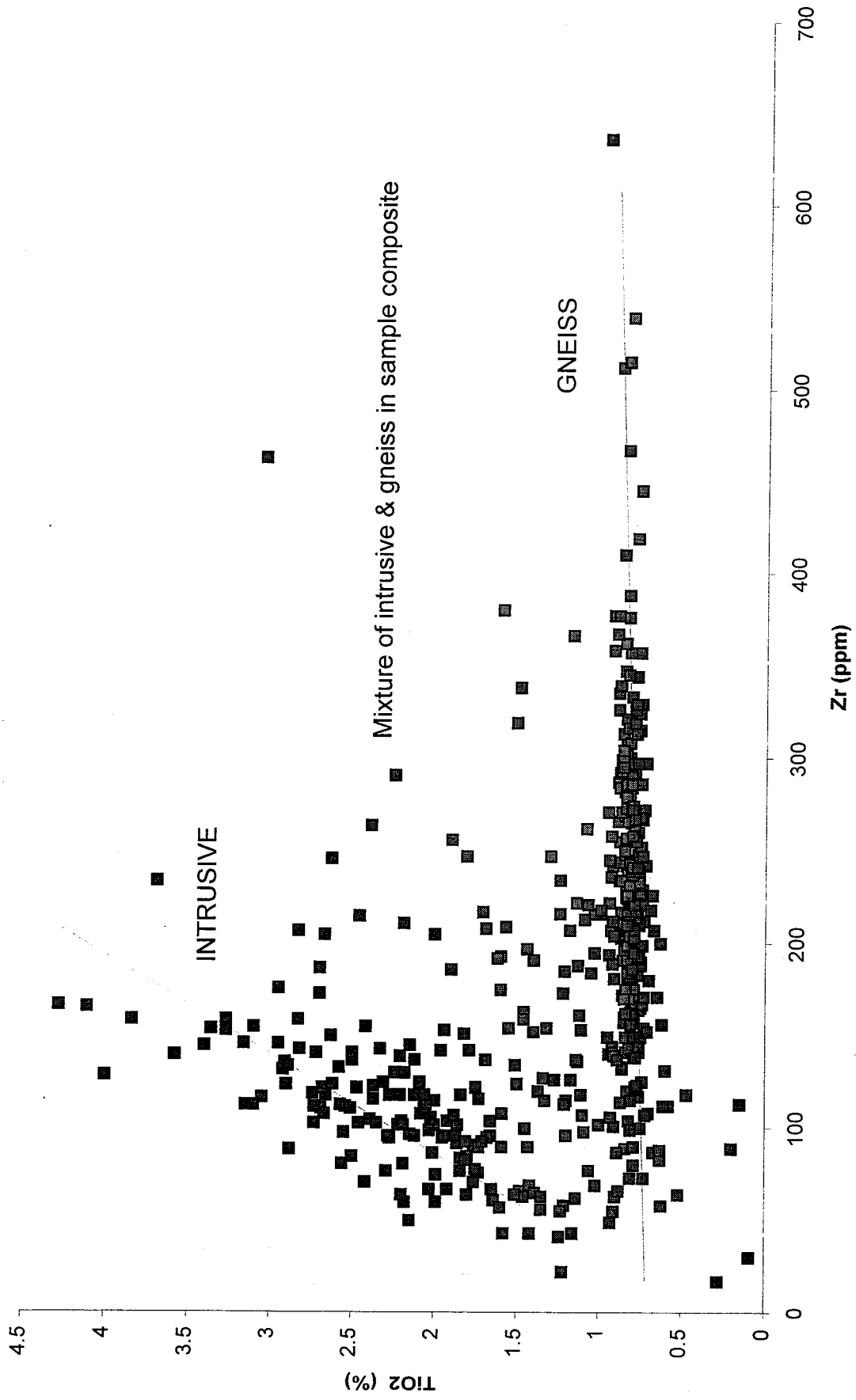
ALTERATION

- **When rocks become hydrothermally altered or weathered, their bulk chemistries and modal mineralogies change, and consequently their neutralization potentials (NP) change.**

The magmatic massive sulphide nickel deposit is hosted in mafic intrusives and mafic-derived hornblende gneisses. The appropriate lithogeochemical model for these rocks is the three-phase petrologic model for mafic rocks $(.25Al+.5Fe+.5Mg+1.5Ca+2.75Na)/Zr$ vs. Si/Zr. This model is based on the bulk stoichiometric covariation of Al, Fe, Mg, Na, and Na with Si in the rock-forming silicates olivine $((Fe,Mg)_2SiO_4)$, clinopyroxene $(Ca(Fe,Mg)Si_2O_6)$, and plagioclase $(CaAl_2Si_2O_8)$ in ultramafic and mafic rocks. On this model (Fig. 3), unaltered rocks plot along the model line of slope 1; if the rocks contain hornblende, they plot below that line depending on the composition of hornblende and on how much is present. Altered rocks plot below or to the right of the model line, depending on whether they have lost Ca and Na, or have gained Si, respectively. On Figure 3, the mafic intrusive (anorthosite gabbro) plots along the model line of slope 1, and the hornblende gneiss plots along a model line of slope 0.75. The fact that these samples plot along, and not too far away from, these two model lines suggests that these rocks are unaltered; the scatter of samples between the two model lines is probably due to the compositing of rock types into mining blocks.

The main metasomatic process associated with host rocks of hydrothermal sulphide deposits is the loss of Ca, Na, and (to a lesser extent) K cations from rock-forming minerals. In hydrothermally altered rocks the lost cations are replaced by both H and K ions resulting in a modal mineralogy dominated by micas and clays, whereas in weathered rocks these cations are substituted mainly by H ions, leading to a clay dominated modal mineralogy. A useful model for dealing with unaltered and altered igneous rocks and feldspathic sedimentary rocks is the feldspar-biotite model $(2Ca+Na+K)/Zr$ vs. Al/Zr, which is based on the stoichiometrically defined covariation of the sum of the alkalis with aluminum in anorthite $(CaAl_2Si_2O_8)$, albite $(NaAlSi_3O_8)$, orthoclase $(KAlSi_3O_8)$, and biotite $(K(Fe,Mg)_3AlSiO_{10}(OH)_2)$. Unaltered intermediate to felsic rocks plot on the model line of slope 1, regardless of their actual feldspar compositions or feldspar-biotite mixing proportions. Altered rocks can plot above or below this model line, depending on whether they have gained or lost alkalis in the alteration process. Since Al is generally immobile in hydrothermal fluids, rocks plotting below the model line are interpreted to have undergone alkali loss, while felsic rocks plotting above the model line are interpreted to have experienced carbonate alteration. Rocks plotting on the line with slope 1/3 are fully sericitized, and rocks plotting on the X-axis have completely lost their alkalis (e.g, advanced argillic alteration due to acid leaching). For any sample which plots below the model line, the extent of alkali loss can be measured by its relative residual, which is calculated by taking the slope of the line through the sample and the model line intercept (in this case a line through the origin) and subtracting this slope from the model line slope.

This model is sensitive to carbonate metasomatism, because Ca must be included in the sum of the alkalis. For example, in many epithermal environments the lateral margins and hanging wall of the alteration zone host calcite veins. Carbon dioxide analyses are required to accommodate the effect of carbonate alteration. To deal with carbonate altered rocks the Y-axis term of the above model is modified. For rocks whose CO_2/Ca molar ratios are <1, the Y-axis term $(2Ca(1-CO_2/Ca)+Na+K)/Zr$ is

6

Figure 3: Olivine, Clinopyroxene and Plagioclase Fractionation - Crystal Sorting Model
(MMS dataset)
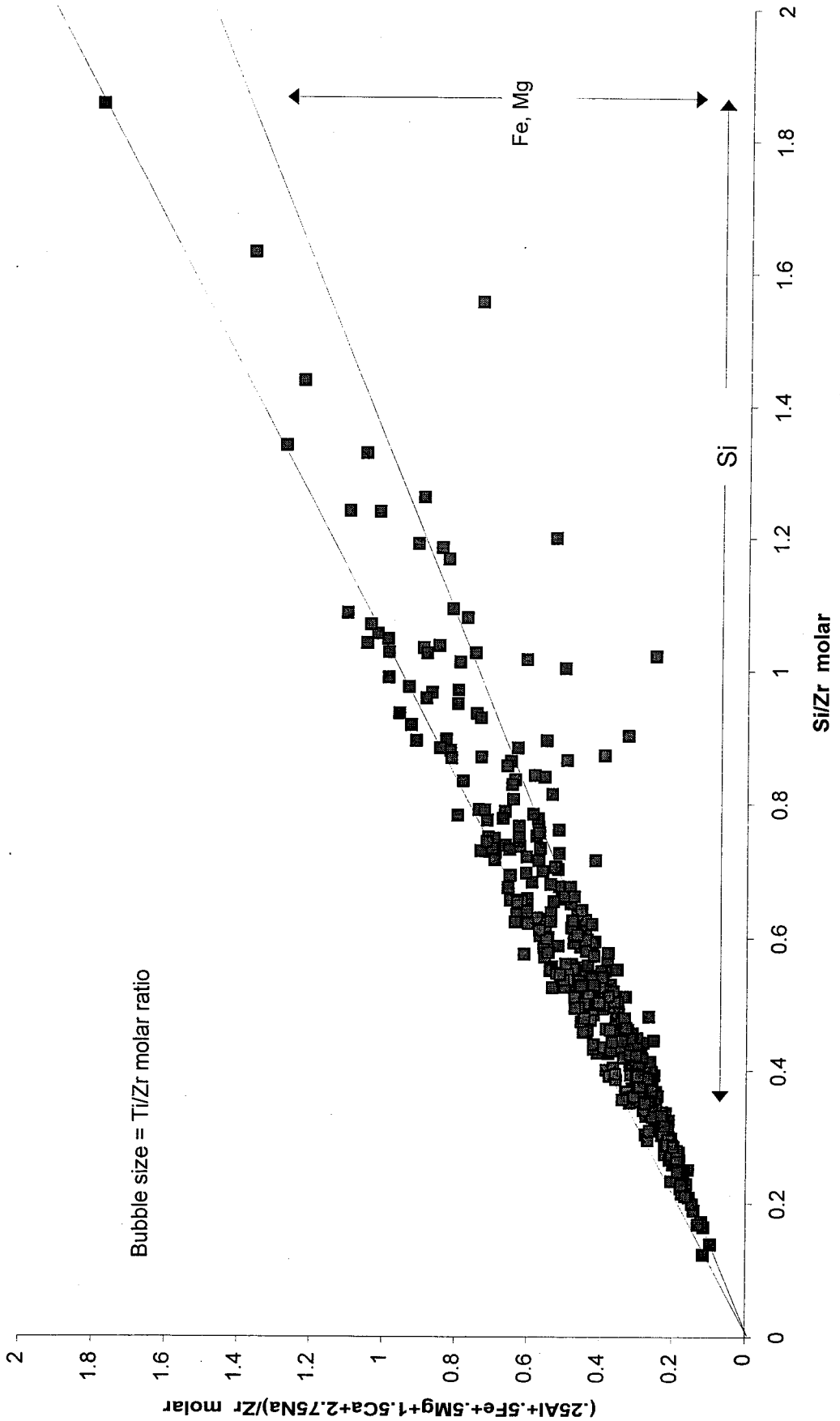
used. For rocks whose CO_2/Ca molar ratios are >1, the Y-axis term $(Na+K)/Zr$ is used instead, assuming that all of the Ca in the rock has been taken up by metasomatic carbonates.

Figure 5 is a plot showing alteration facies from unaltered to extremely altered felsic volcanics; here, a few samples plot along the model line, but most of the samples plot below this line, indicating that they have undergone alkali depletion. The mineralized samples, those which contain sulphides plot near the sericite line, while the fully alkali depleted samples plot along the X-axis; these are the samples which contain no alkalis, probably as a result of extreme acid leaching. Because all the mineralized samples are alkali-depleted, they are not likely to be good buffers for ARD reactions. The buffering capacity of these rocks is directly related to alteration facies, and decreases steadily from fresh to advanced argillic altered rock.

WEATHERING POTENTIAL INDEX

- $$WPI = \frac{100*mols(CaO+Na_2O+K_2O+MgO)}{mols(SiO_2+Al_2O_3+Fe_2O_3+CaO+Na_2O+K_2O+MgO)}$$

- Assessment of the manner and rate of deterioration of the rock matrix in the field.

- Abrasion pH is a function of a rock's modal mineralogy; OR indicator of the rock's weathering potential.

- WPI vs. initial pH scatterplot (Fig. 6) dataset shows that there is a functional relationship between the weathering potential of the samples and their initial pH. The basis of this relationship is the modal mineralogy of the rocks. As these rocks become more and more altered they lose progressively more alkalis, while their Al content remains approximately constant. Thus the bulk alkali/aluminum ratio of these rocks decreases, and the mineralogy of the altered rocks becomes dominated first by micas and then by clays. Since micas and clays behave like acids in water, the initial pH, as well as the abrasion pH of these rocks will decrease as the abundance of micas and clays increases.

CIPW NORMATIVE CALCULATIONS

- Predicted modal mineralogy, i.e., the mineral proportions calculated by the CIPW computer program, were found to differ markedly from the observed modal mineralogy.

- Calculation of CIPW norms and mesonorms is limited to modeling unaltered rocks, mesonorm can accommodate the presence of biotite and hornblende, neither procedure can deal with the presence of

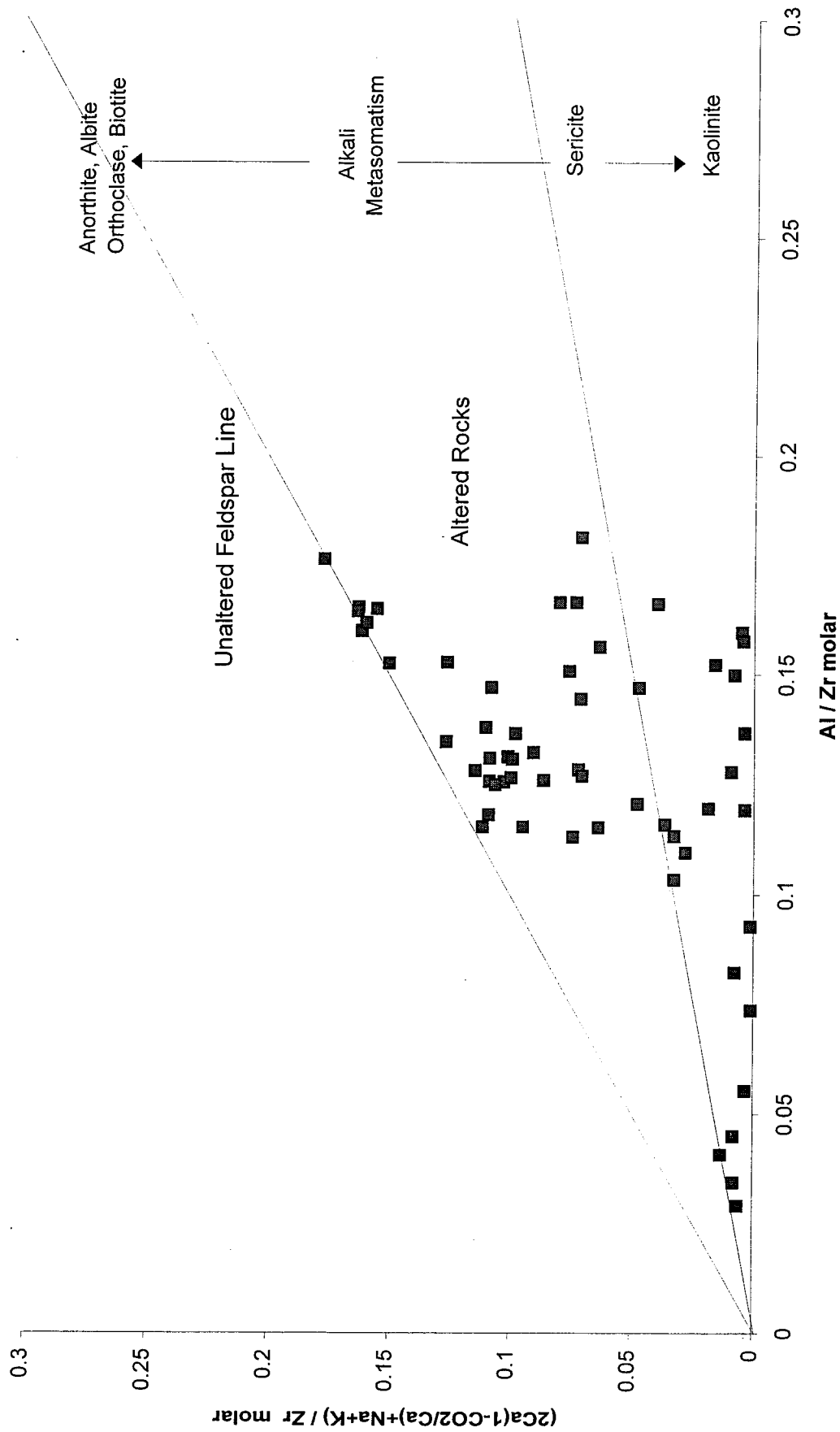Figure 5: Alteration Type Classification using the Feldspar - Biotite Model (SFV dataset)
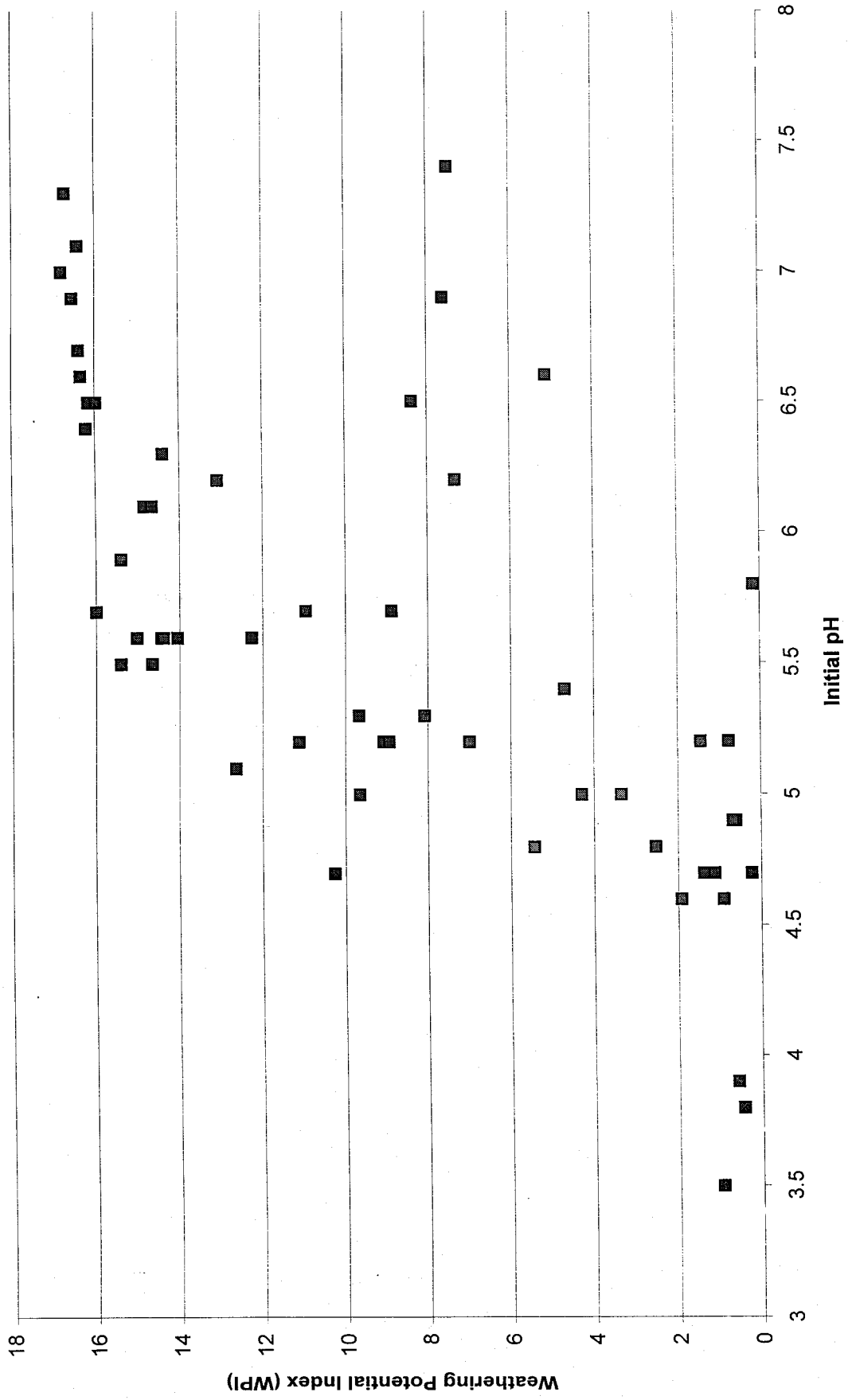
Figure 6 : Weathering Potential Index vs. Initial pH (SFV dataset)

alteration and sulphides. Normative and meso-normative calculation algorithms differ for saturated versus undersaturated rocks, thus the appropriate algorithm must be chosen for a specific lithology.

- When altered rocks are present, CIPW normative calculations cannot produce reliable estimates of mineral abundance, and thus cannot support meaningful NP estimates.

NEUTRALIZATION CAPACITY

- **REACTIVITY OF THE GANGUE MINERALS**
  - For ABA analyses, reaction rate is an important factor in assessing the results of acid-rock interaction over long periods of time. A plot of acid consumption vs. time for five samples is shown in Figure 9. This plot indicates that some rocks will be acid buffering much sooner than others, in other words, the plots show bulk reaction rates for each sample under laboratory conditions. The slope of each curve is a measure of the bulk reaction rate for that sample, and the inflection points on each curve probably indicate the influence of different mineral species on the buffering reactions. These curves can be classified by their slopes as to fast and slow rates of weathering and/or acid buffering. A plot of acid consumption (calculated NP) versus time typically shows a sharp initial rise as calcite is being consumed, then a lower rise due to Mg-Fe carbonates and/or Mg-Ca silicate dissolution, then another steeper rise when clays and phyllosilicates begin to break down and participate in the buffering reaction. NP tests should probably be run for a minimum of two to four weeks into order to properly estimate the actual NP of waste material. The buffering rates of individual samples (representing waste blocks) can be classified as slow, intermediate, and fast, using the minima, maxima, and inflection points of their respective curves (see Fig. 9). These rates can then be used to map the predicted buffering rates of waste blocks in a mining bench. A similar plot of NP versus time is shown for the NBM-1 standard, Figure 10. The net buffering capacity of a waste block is the product of the relative abundance and reaction rate of the neutralizing minerals calcite, Mg-Fe carbonates, Fe-Mg silicates, alkali silicates, phyllosilicates, and clay.

- **SURFACE AREA OF MINERALS AVAILABLE FOR REACTION.**
  - Particle size is very important. In a typical ABA test, samples are ground to approximately -150 mesh. At this particle size the reaction surface areas of most rock-forming silicates, and of carbonates are approximately the same, but the reaction surface areas of micas and clays can be several orders of magnitude greater. Clay minerals originally present in mine waste, along with the clays formed by acid-leaching the rock-forming silicates, will likely dominate the long-term water-rock interactions, and thus the long term neutralization potential and the adsorption of metals liberated by ARD process.

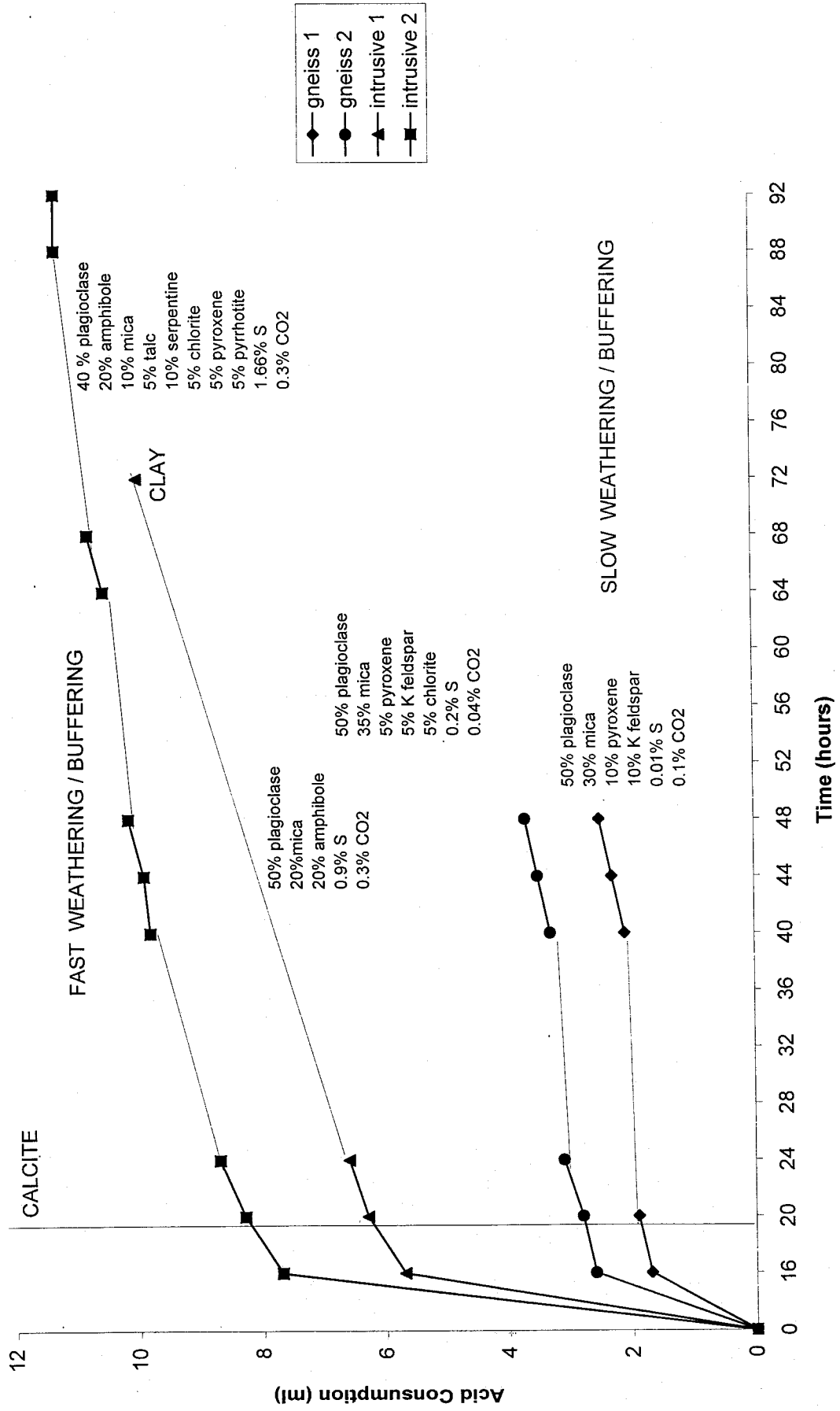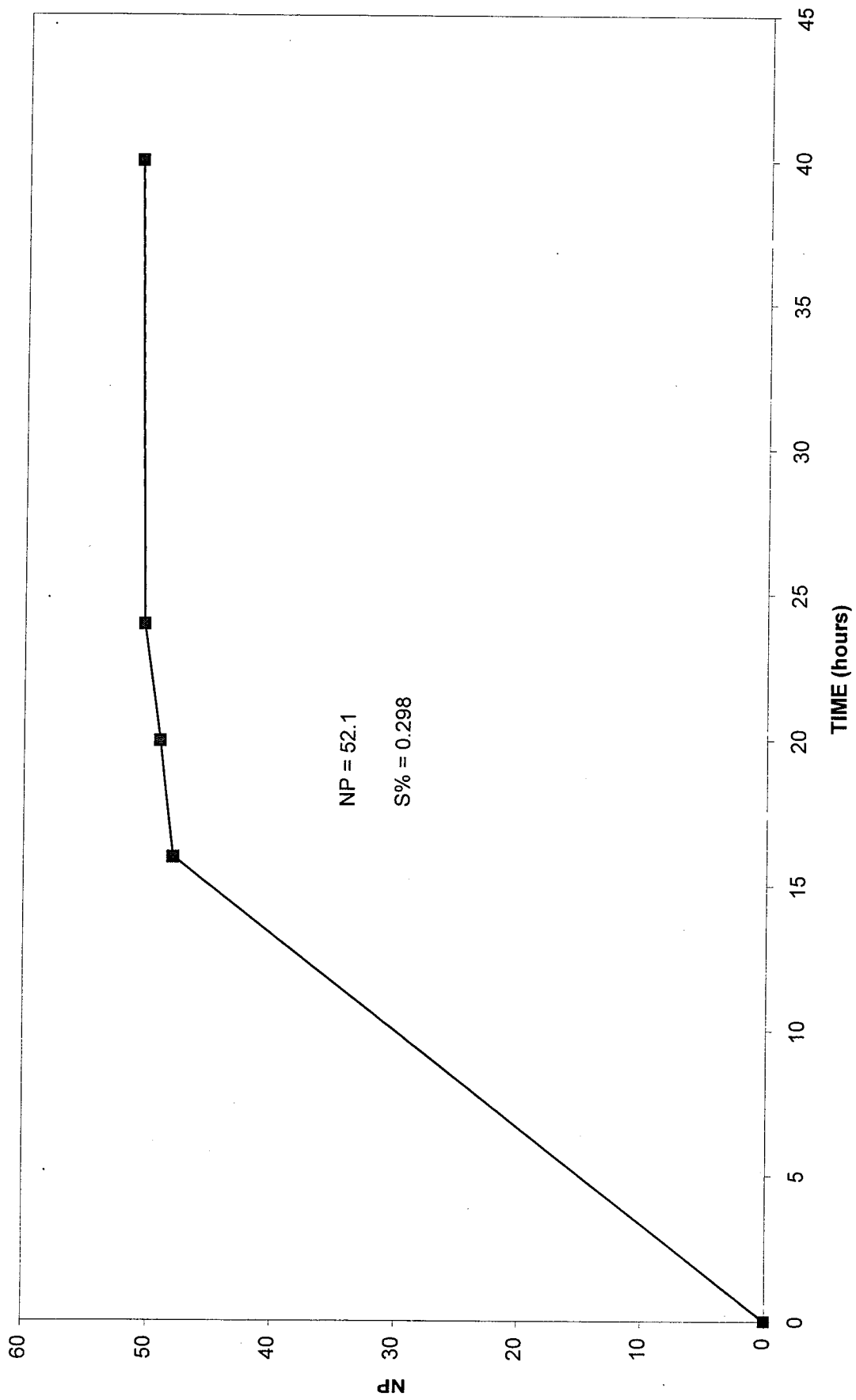# FIGURE 9 : Acid consumption vs. Time (MMS dataset)

CALCITE

FAST WEATHERING / BUFFERING

CLAY

SLOW WEATHERING / BUFFERING

40 % plagioclase
20% amphibole
10% mica
5% talc
10% serpentine
5% chlorite
5% pyroxene
5% pyrrhotite
1.66% S
0.3% CO2

50% plagioclase
20%mica
20% amphibole
0.9% S
0.3% CO2

50% plagioclase
35% mica
5% pyroxene
5% K feldspar
5% chlorite
0.2% S
0.04% CO2

50% plagioclase
30% mica
10% pyroxene
10% K feldspar
0.01% S
0.1% CO2

gneiss 1
gneiss 2
intrusive 1
intrusive 2

Acid Consumption (ml)

Time (hours)

Figure 10: Neutralization Potential vs. Time for NBM-1 STANDARD

NP = 52.1

S% = 0.298

TIME (hours)

NP

- **FLOW RATE OF ACIDIC IRON-BEARING SOLUTIONS**
  - This essentially deals with the retention time that an acidic solution is in contact with various minerals.

- The *effective* neutralizing power of a gangue or rock is the product of these factors, distinguishing it from the theoretically *total* neutralizing power which the gangue or rock would possess if the acid remained in contact with a given unit area long enough for the gangue to react fully.

- Neutralizing power which has been calculated via BCR method is only a measure of the initial neutralization power.

LITHOGEOCHEMICAL MODELS OF NEUTRALIZATION POTENTIAL

AND

NET NEUTRALIZATION POTENTIAL

- **SULPHIDE – SULPHATE MODEL**

- **NET NEUTRALIZING POTENTIAL MODEL**

SULPHIDE – SULPHATE MODEL

- To model the ARD buffering capacity of rocks, consider which sulphate minerals are likely to be formed by the reaction of sulphuric acid (H_2SO_4) with the minerals present in these rocks. Given the abundance of Ca- and K-bearing silicates in rocks, the minerals most likely to form are gypsum ($CaSO_4 2H_2O$), anhydrite ($CaSO_4$), and alunite ($KAl_3(SO_4)_2(OH)_6$), or the intermediate product jarosite ($KFe_3(SO_4)_2(OH)_6$). The ability of Mg to buffer ARD is also important, especially in Mg-rich rocks such as ultramafics. The end products of ARD buffering in most other rocks (gypsum, anhydrite and alunite) can be modelled by plotting the molar ratios S_{total}/Zr vs. $(Ca+.5K)/Zr$. Because Zr is a conserved element, it can be used in the denominator to normalize the data. The molar ratio $S_{total}/(Ca+.5K)$ describes the theoretical buffering capacity of these rocks, based on balanced molar quantities of S, Ca and K in the sulphate minerals.

- $S_{total}/(Ca+.5K)$ can be considered equivalent to AP/NP in a theoretical sense, however, this buffering model is based on bulk chemistry, irrespective of the abundance or reactivity of neutralizing minerals present in the rock, whereas NP is an empirical (titration) measurement of the contribution soluble neutralizing minerals make to ARD buffering in the test tube. Therefore, the empirical measurements are typically much lower than the theoretical predictions

On this linear covariation model (Fig. 11), sulphide minerals plot along the Y-axis, the sulphate minerals gypsum, anhydrite, and alunite plot along the model line of slope 1, and Ca- and K- bearing silicate minerals plot along the X-axis. Samples plotting along the sulphate model line, $S_{total}/(Ca+.5K) = 1$, should be ARD neutral, samples plotting above the model line, $S_{total}/(Ca+.5K) > 1$, should be acid generating, and samples plotting below the model line, $S_{total}/(Ca+.5K) < 1$, should be acid buffering. This ratio can be considered equivalent to AP/NP in a theoretical sense, however, this buffering model is based on bulk chemistry, irrespective of the abundance or reactivity of neutralizing minerals present in the rock, whereas NP is an empirical (titration) measurement of the contribution soluble neutralizing minerals make to ARD buffering in the test tube. Therefore, the empirical measurements are typically much lower than the theoretical predictions.

NET NEUTRALIZING POTENTIAL MODEL

Theoretical NNP vs Measured NNP

- The maximum theoretical NNP can be stated by the equation
$$NNP = (Ca + .5K) - S.$$

- Short term NBC(s) which considers ARD buffering by carbonate minerals with high reaction rates, and a long term NBC(l) which considers buffering by silicate minerals with much slower reaction rates.

- Difference in slope and intercept of the trend observed in the data and the predicted trendline (intercept 0,0 and slope = 1) is a measure of the factor (or amount) by which the neutralizing potential (NP) actually available in these rocks is overstated.

- Theoretical capacity far exceeds the actual ability of these rocks to buffer the ARD reactions as simulated by the ABA tests.

- Unaltered rocks which have significant amounts of Ca and K to contribute to buffering ARD, contain feldspars which do not break down rapidly enough to react with and buffer the H_2SO_4 being generated by the oxidizing sulphides, and the altered rocks which contain micas and clays which may break down quickly enough, do not contain sufficient Ca and K to buffer the ARD reaction.

NNP graphs of theoretical and model NNP can be developed whereby short term and long term buffering effects are accounted for by using major oxide data. These graphs are based on the premise that the bulk oxide data is representative of the bulk mineralogy of a rock, and that NP determinations are a result of mineralogical buffering. The theoretical NNP expresses the maximum capacity of a rock to buffer an ARD reaction given its bulk chemistry, and as such is independent of pH-dependent titration analyses such as

Figure 11: Theoretical Buffering Capacity (SFV dataset)
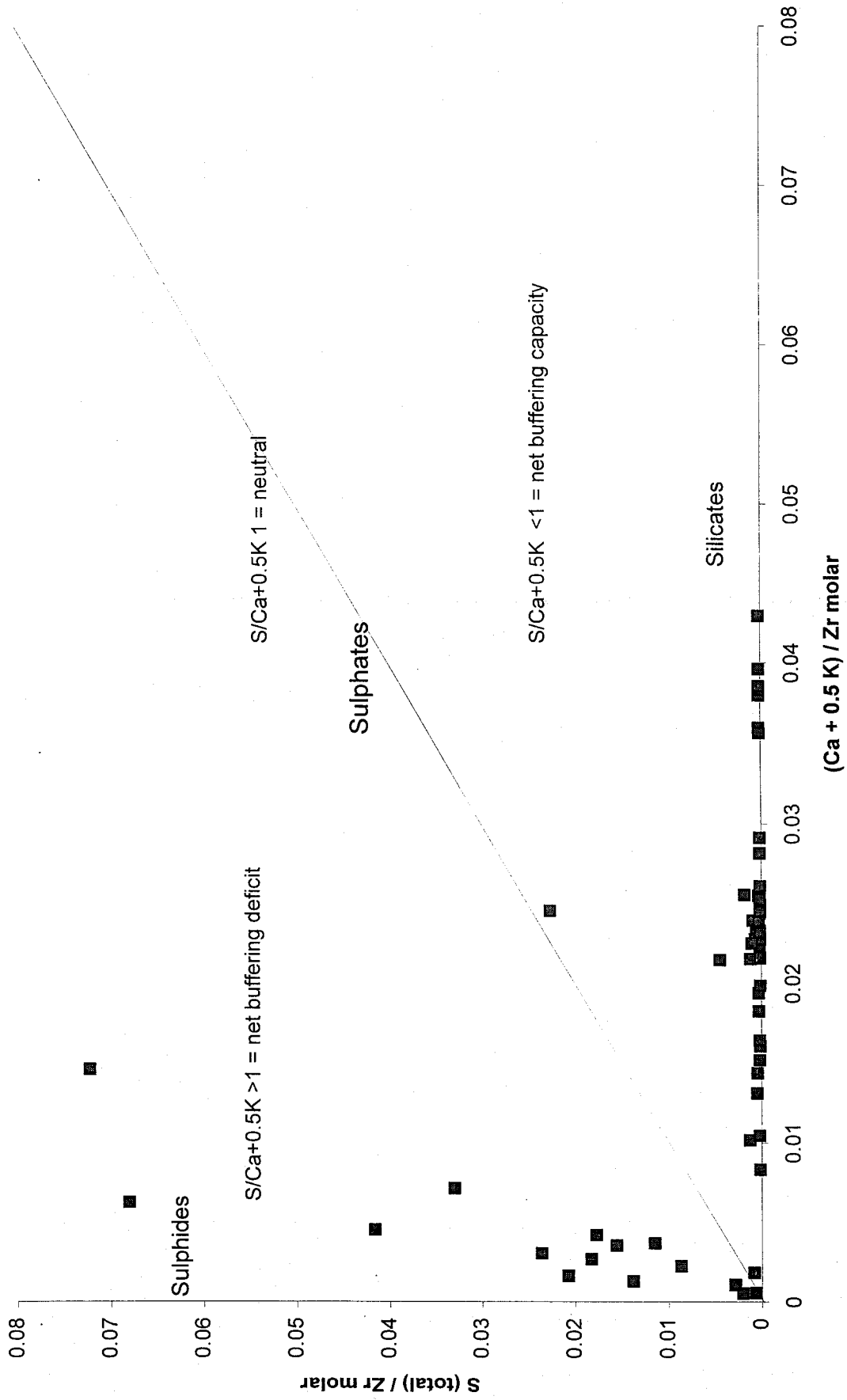
NP. Because conventional NP measurements are conducted over relatively short time periods, and because these measurements tend to be biased in favour of the nearly instantaneous reaction of H_2SO_4 with Ca-bearing carbonates, such as calcite ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$) , when they are present, two net buffering capacities (NBC) should to be considered. A short term NBC(s) which considers ARD buffering by carbonate minerals with high reaction rates, and a long term NBC(l) which considers buffering by silicate minerals with much slower reaction rates. In the laboratory, buffering by carbonates is obvious enough by the liberation of CO_2 from the test tube (fizzing), whereas evidence of the role of silicate minerals in buffering in the form of alkali depleted alumino-silicate minerals (hydrous micas and clays) must be confirmed by mineralogical (XRD) analysis of the solid residue remaining in the test tube. The maximum theoretical NNP can be stated by the equation NNP = (Ca + .5K) – S. A plot of the theoretical NNP vs. measured NNP (Fig. 12) shows a strong linear trend , and suggests a link between the theoretical and empirical data. The difference in slope and intercept of the trend observed in the data and the predicted trendline (intercept 0,0 and slope = 1) is a measure of the factor (or amount) by which the neutralizing potential (NP) actually available in these rocks is overstated. The distribution of data indicates that there is a correlation but that data points at or near the origin show some scatter, as would be expected, as the Ca+.5K represents total buffering (neutralizing) capacity, while NP represents only partial buffering capacity by soluble minerals measured over a very short time. However, when comparing the theoretical buffering capacity with the measured net neutralization potential (NNP) of rocks it becomes quite clear that the theoretical capacity far exceeds the actual ability of these rocks to buffer the ARD reactions as simulated by the ABA bench tests. The problem is that the unaltered rocks which have significant amounts of Ca and K to contribute to buffering ARD, contain feldspars which do not break down rapidly enough to react with and buffer the H_2SO_4 being generated by the oxidizing sulphides, and the altered rocks which contain micas and clays which may break down quickly enough, do not contain sufficient Ca and K to buffer the ARD reaction.

- Theoretical NNP can be further refined by modeling the data after examination of petrographic data, and by plotting CO_2 vs. NP. If there is a significant amount of carbonate minerals present, and the CO_2 vs. NP data show a strong correlation, then CO_2 must be taken into account in the equation. The data from Figure 12, when modelled (i.e. when carbonate minerals are taken into account) produce a very good correlation as indicated by the data points fitting a line of slope 1 (see Fig. 13).

REFINEMENT OF NNP MODEL

Examine relationship of initial pH and alteration, using alkali depletion index

- Once a functional relationship between alkali/aluminum ratios and initial pH has been established (Figure 14 & 15), an equation relating alkali/aluminum molar ratios to initial pH can be substituted for the initial pH measurements in the lithogeochemical NNP model. This means that all of the data necessary for calculating the model can now be obtained directly from whole-rock analyses

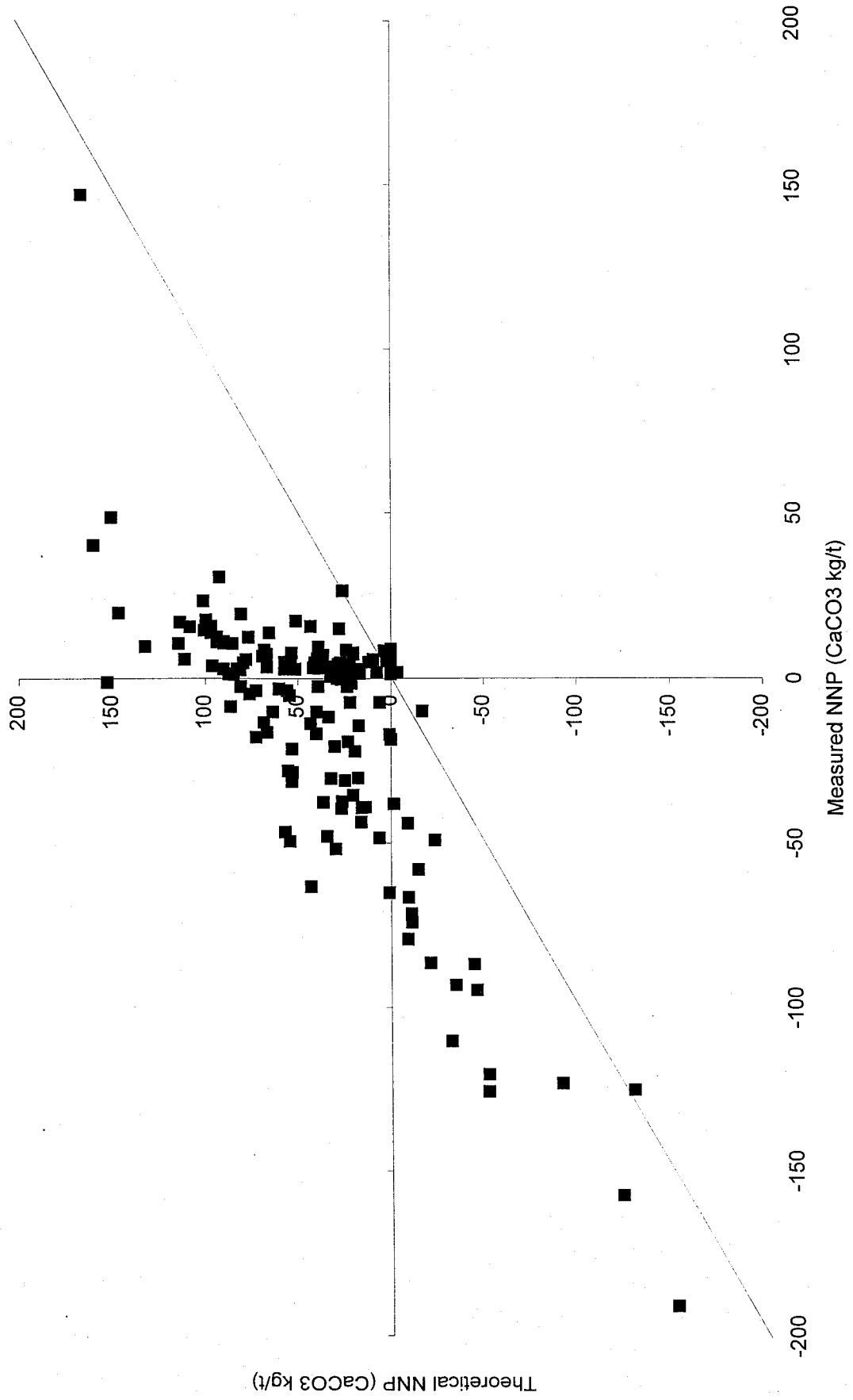Figure 12: Theoretical NNP vs. Measured NNP (PCG dataset)

Figure 13: Modelled NNP vs. Measured NNP (PCG dataset)
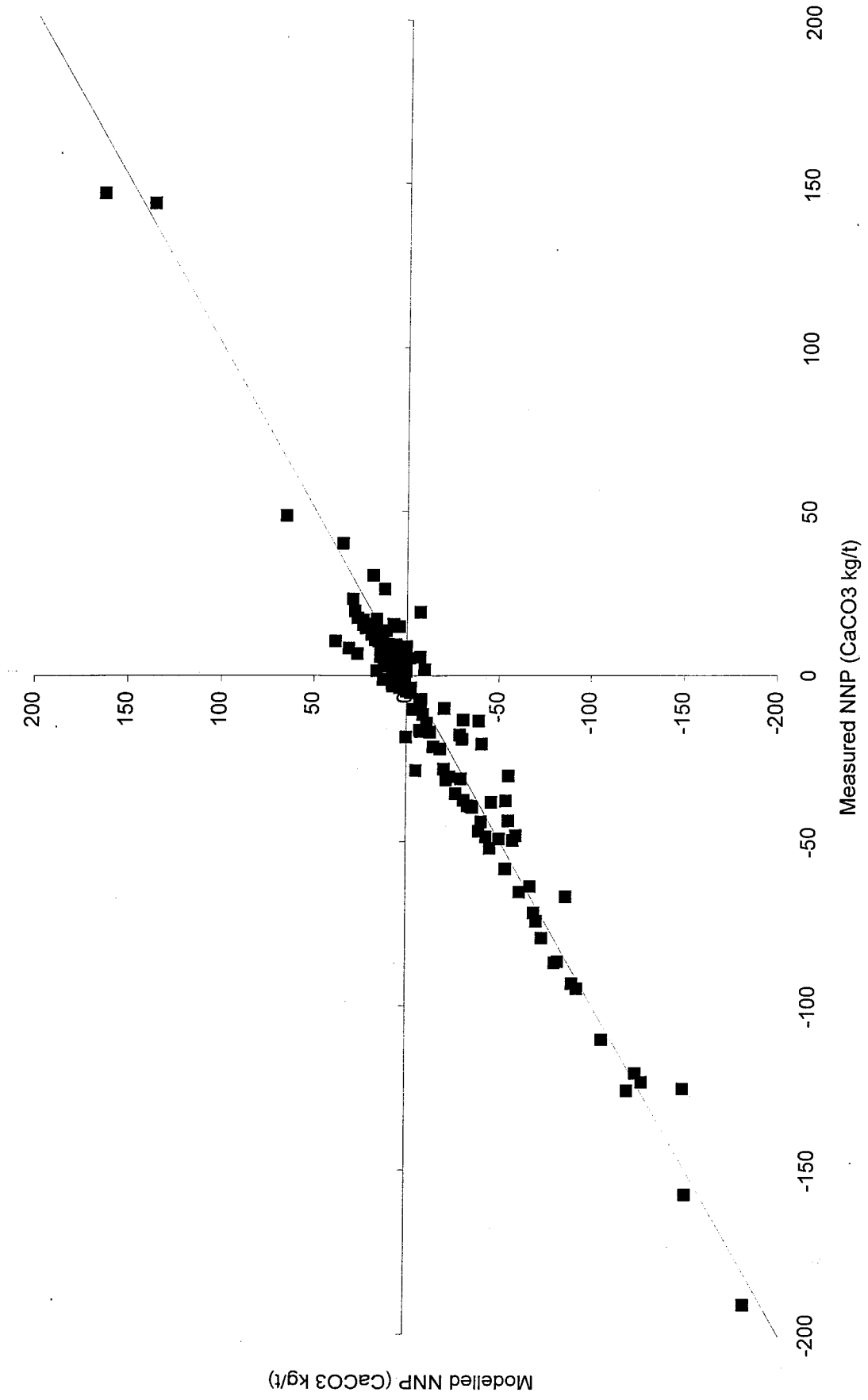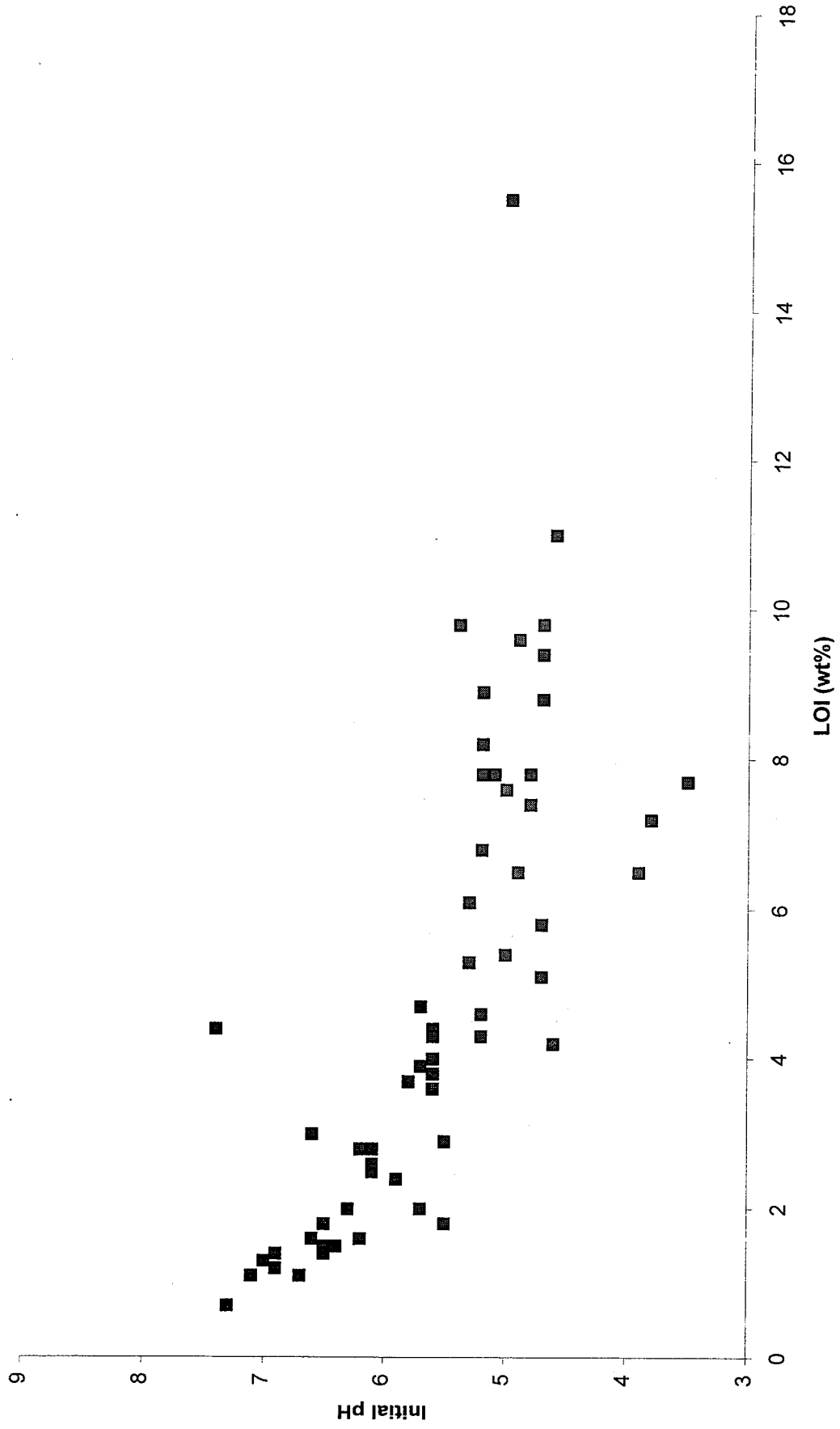
Figure 14: Initial pH vs. S (total)
(SFV dataset)

Figure 15: Initial pH vs. Loss-on-ignition (LOI)
(SFV dataset)

- A comparison of modelled NNP values with measured NNP values (Fig. 17) shows very good correlation

It is widely believed that initial pH of a water-rock slurry is controlled by the sulphide mineral content of the rocks. The measurements and analytical data from the high-sulphidation epithermal silver deposit provide an excellent demonstration that, at least in this case, this is not so. A plot of the initial pH vs. S_{total} content (Fig.14) shows that in these rocks there is no correlation between initial pH and S_{total}. What is evident, however, is that only rocks with initial pH's lower than 5.5 contain any S at all, and that in these rocks S_{total} concentrations vary from 0.0 to nearly 5.0 wt%. What controls the initial pH of these rocks can be observed on the plot of initial pH vs. loss-on-ignition (Fig. 15). In these rocks, because they contain little or no CO_2, loss-on-ignition is a reasonably good approximation of their degree of hydrolysis, the substitution of H^+ for Ca, Na, and K cations in feldspars, which results in a mica and clay dominated modal mineralogy. The reason that the initial pH is low in rock-water slurries containing abundant of clays and/or micas is that in water these minerals tend to behave as acids (Grant, 1969). Whether or not these altered rocks also contain sulphides is of no consequence in terms of their initial pH's (see Fig. 14). The relationship between the sulphur content and initial pH of rocks is that although altered rocks have low initial pH's and sulphides are only present in altered rocks, not all altered rocks contain sulphides. Therefore, while initial pH cannot predict the presence or abundance of sulphide minerals, it is a reasonable predictor of alteration facies, e.g., alkali depletion (see Fig. 16).

It appears that the initial pH of these rocks is, more or less, inversely proportional to the capacity of these rocks to contribute Ca and K to buffer the ARD reaction (see Fig. 16). In other words, the reaction rate of the Ca- and K-bearing minerals in these rocks can be expressed in terms of their initial pH, and/or in terms of their degree of hydrolysis. Thus, initial pH can be used as a factor in a lithogeochemical model of the NNP of these rocks, which can be calculated as follows:
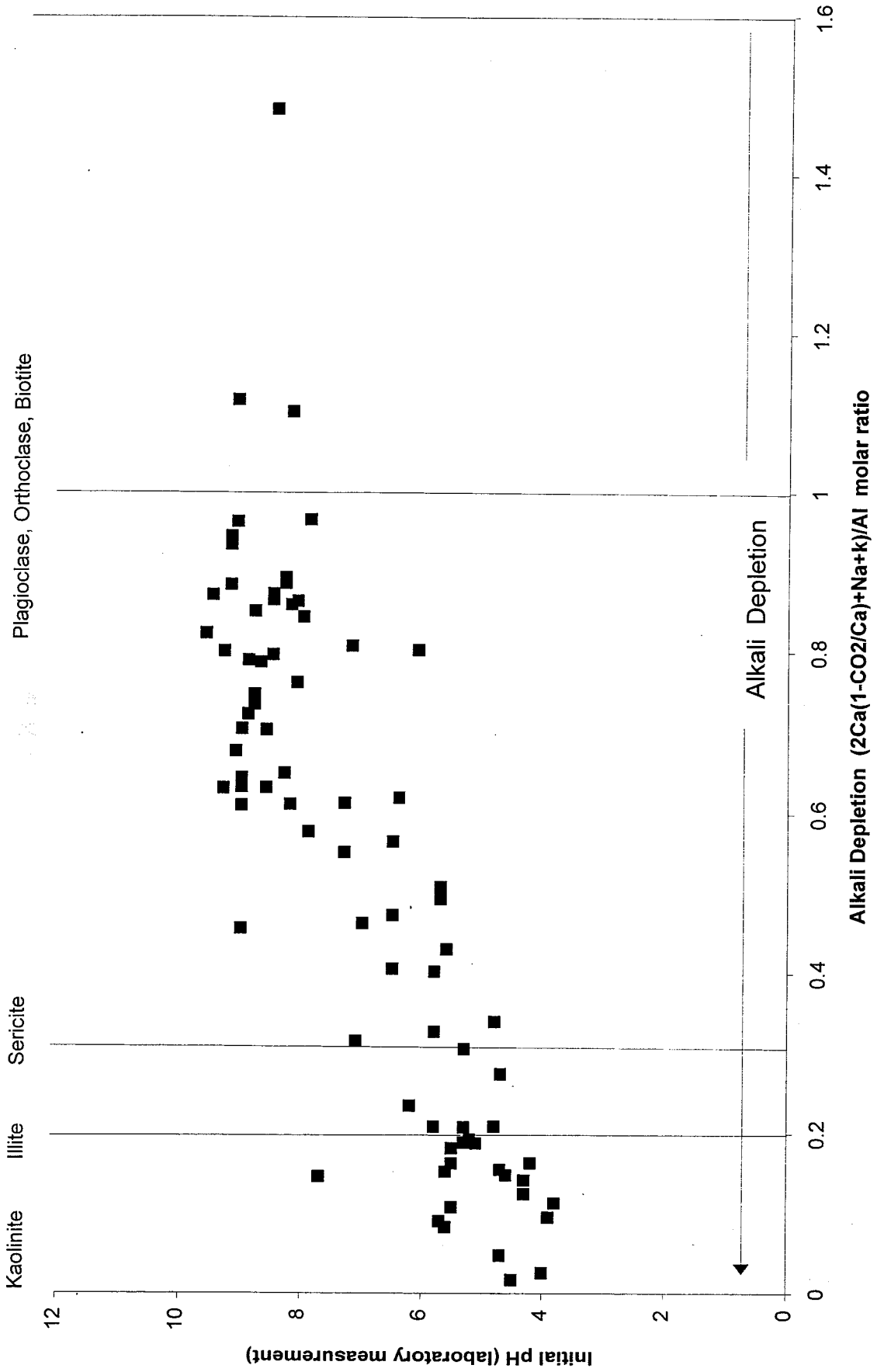
$$NNP(CaCO_3\, kg/t) = 1000.9 \left(\frac{1}{initial\ pH} \left(\frac{CaO}{56.08} + \frac{0.25\, K_2O}{94.20} \right) - \frac{S_{total}}{32.06} \right) \qquad (1)$$

$$NNP(CaCO_3\, kg/t) = 1000.9 \left(\frac{1}{initial\ pH} \left(\frac{Ca}{40.07} + \frac{0.5\, K}{39.09} \right) - \frac{S_{total}}{32.06} \right) \qquad (2)$$
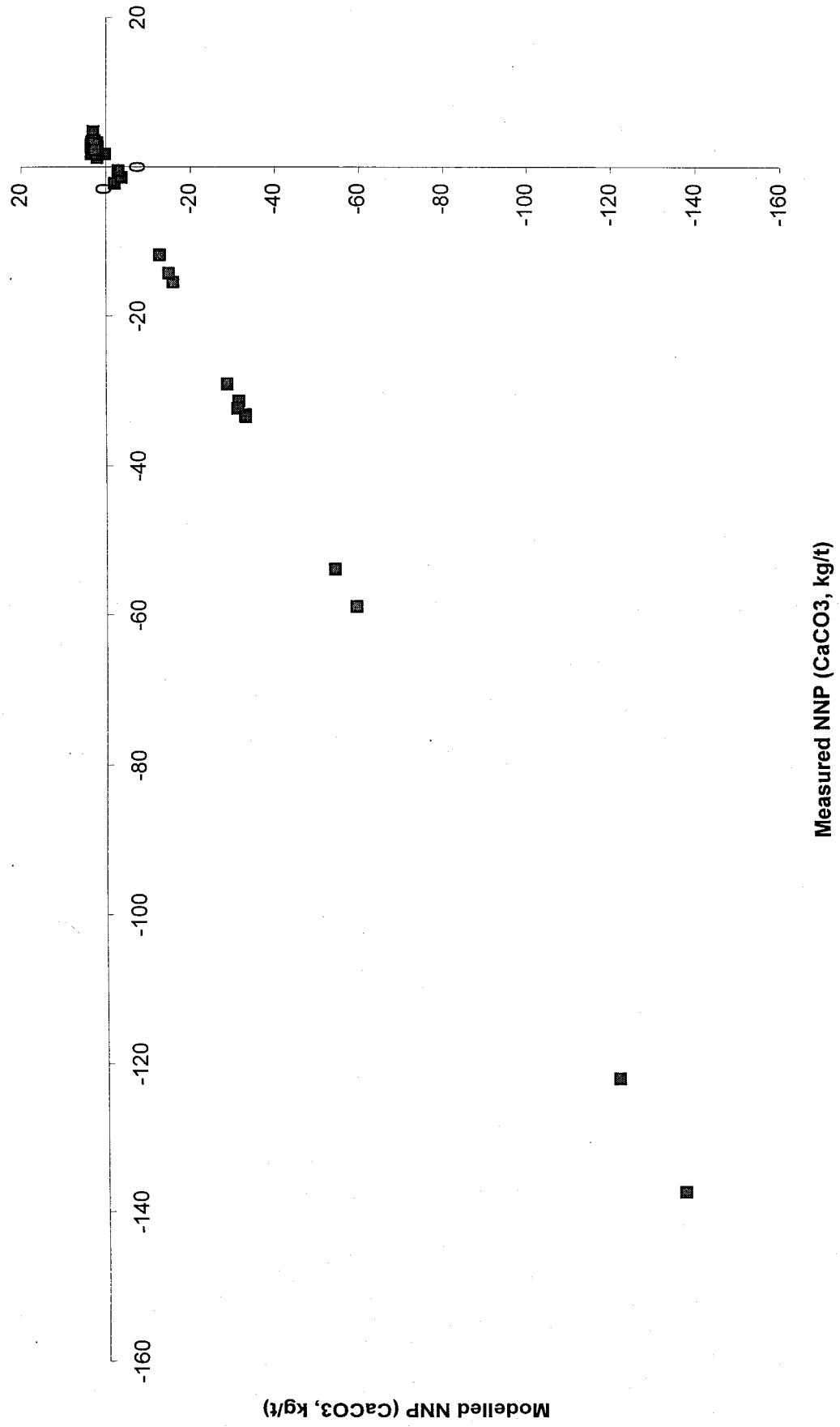
Depending on whether analyses are reported as oxide or elemental concentrations, formula (1) or (2) is used, respectively. These calculations depend on Ca, K and S analyses, and on initial pH measurements. Concentrations of these three elements could, for example, be obtained in the field or at a mine site from an XRF analyzer. But the initial pH measurement must still be made in a laboratory, although abrasion pH measurements, as described in Stevens and Carron (1948), may prove to be an adequate substitute.

Once a functional relationship between alkali/aluminum ratios and initial pH has been established, an equation relating alkali/aluminum molar ratios to initial pH can be substituted for the initial pH measurements in the lithogeochemical NNP model. This means that all of the data necessary for

Figure 16: Initial pH vs. Alkali Depletion (PCG dataset)

Plagioclase, Orthoclase, Biotite

Figure 17: Modelled NNP vs. Measured NNP (SFV dataset)

calculating the model can now be obtained directly from whole-rock analyses. Depending on whether these analyses are reported as oxide or elemental concentrations, formula (3) or (4) is used, respectively.

$$NNP(CaCO_3\,kg/t) = 1000.9\left(\frac{0.15}{2(Alk/Al)+5}\left(\frac{CaO}{56.08}+\frac{0.25\,K_2O}{94.20}\right)-\frac{S_{total}}{32.06}-0.0025\right) \quad (3)$$

$$NNP(CaCO_3\,kg/t) = 1000.9\left(\frac{0.15}{2(Alk/Al)+5}\left(\frac{Ca}{40.07}+\frac{0.5\,K}{39.09}\right)-\frac{S_{total}}{32.06}-0.0025\right) \quad (4)$$

The molar alkali/aluminum ratio used in the modified lithogeochemical NNP models above, and depending on whether major oxide or elemental analyses are used, is calculated as follows:

$$Alk/Al\ molar\ ratio = \frac{\left(\dfrac{2CaO}{56.08}+\dfrac{2\,Na_2O}{61.98}+\dfrac{2\,K_2O}{94.20}\right)}{\dfrac{2\,Al_2O_3}{102.96}} = \frac{\left(\dfrac{2Ca}{40.07}+\dfrac{Na}{22.98}+\dfrac{K}{39.09}\right)}{\dfrac{Al}{26.98}}$$

A comparison of modelled NNP values with measured NNP values (Fig. 17) show very good correlation. This demonstrates that the calculations above provide a reasonable approximation of the NNP values calculated by BC Research method using S_{total} and SO_4 determinations, and NP titration measurements.

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CONCLUSIONS

- Acid rock drainage (ARD) buffering capacity of mine waste is governed by its bulk chemistry and its mineral assemblage. Samples of different rock types, or of different alteration facies of the same rock type will have different ARD characteristics.

- Conventional acid base accounting (ABA) tests can be used to predict short-term buffering, but should be used with caution to model or predict the long-term ARD buffering capacity.

- Conventional ABA reports the net results of acid-rock interaction tests, but make no attempt to explain the geological, mineralogical, and geochemical factors that influence these results.

- Main problem with conventional ABA tests is that they are biased toward the rapid ARD buffering by Ca- and Mg-bearing acid-soluble minerals in the waste rocks.

- It would be useful to conduct both short-term and long term tests, examine the modal mineralogy before, during, and after the buffering tests, and then devise a model of the processes involved in ARD buffering. Once the mineralogical parameters of ARD buffering processes have been recognized, lithogeochemical models using bulk chemistry might be devised.

- Examine petrographic data together with lithogeochemical data in order to better understand acid rock drainage parameters on a site by site basis. Theoretical (i.e., modelled) NNP will indicate buffering capacity over "geological" time, whereas the laboratory measured NNP indicates buffering over "run of mine life".

POTENTIAL USES

- Costs of analyzing major oxides, CO_2 and S(total) are far lower than conducting NP tests for every sample.

- Transportable x-ray fluoresence equipment:
analytical data from blast holes is now available for real time determination of potential acid and non-acid generating waste material.

- WPI measure of weatherability of material
  - Construction purposes
  - Blending
  - Kinetic testwork

- NP vs Time Curves measure of buffering potential

- Graphical method to test for clays

- Rapid lithological and alteration classifications

- Lithogeochemical data will help in understanding water quality data

- The use of lithogeochemical methods should be used in any study for which BLENDING may be considered.

- The use of lithogeochemical methods should be used in any study for which KINETIC TESTWORK may be considered.

THIS IS A LITHOGEOCHEMICAL TOOL TO CHARACTERIZE THE GEOCHEMISTRY OF GEOLOGICAL MATERIALS WHICH HAVE A HIGH DEGREE OF VARIABILITY