# Chapter 6. Evaluation of Particle Size and Surface Area Effects

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## Introduction

Hornberger and Brady (1998) surveyed some 90 different leach protocols that have been applied to AMD overburden rock analyses for which a prescription is usually presented on the geometry, frequency of sample collection, and amount of material to be leached, but no detailed accounting was made of these parameters nor was the data utilized in any analytical sense. In order to provide a common basis for comparison between different leach experiments following a protocol, account of the exposed surface of the solids to the solvent needs to be addressed. Otherwise the cross-laboratory experiments, although individually correct, cannot be compared with other results in the literature, and cannot be used to extract quantitative rate constants. The observed leach rates would be an accurate result of the individual experiment, but meaningless as a fundamental property of the material itself.

# Conceptual Background

## Effects of Surface Area

On an atomistic level, dissolution of solid materials involves the interaction of water molecules with the surface atoms of the solid. Ion-dipole attractions from water molecules break the bonds holding the surface ion in the solid which then move to the solvent. Solvation of these ions occurs in the solvent as water molecules attach themselves to the ions and the complex diffuses out into the solvent. Fundamentally, the more bonds that need to be broken, the slower a material is to dissolve. Conversely, the more bonds exposed to the interaction with water, the more ions will be taken into solution. We are all familiar with the dissolution behavior of sugar in iced-tea: sugar cubes, granular sugar and powdered sugar can easily be ranked by their exposed surface area.

## Effect of Leachate Volume

In a similar analogy, the volume of the iced-tea to which the powdered sugar is added will impact the rate of the dissolution of sugar. A small amount of solids will readily dissolve in a large volume of solvent; where as a large amount of solid will only slowly dissolve in the same large volume of solvent as saturation is approached. Figure 6.1 is a typical leach behavior which depicts rapid dissolution at short times resulting in low but steadily increasing concentration. As the concentration approaches the solubility controlling limit the early stage rapid dissolution rate decreases to the steady state condition at saturation.

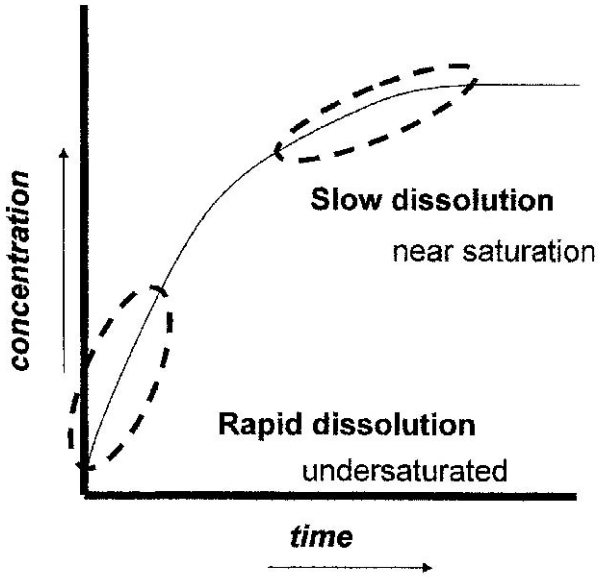


Figure 6.1. Schematic representation of dissolution as a function of time.

Machiels and Pescatore (1983) illustrate this effect of surface area to volume ratio with both laboratory leach data and computational modeling of the leach data; presented here in Fig. 6.2. In this example of the leaching of a borosilicate glass analog of a nuclear wasteform, the glass dissolution, as represented by a normalized mass loss, is an order of magnitude less in leaching solutions with a high SA/V versus a low SA/V.

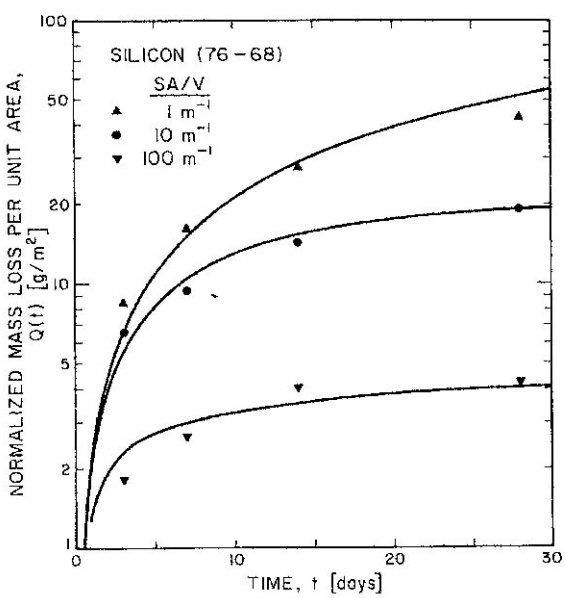


Figure 6.2. Effect of SA/V ratio on the release of silicon to leaching solutions for a borosilicate glass. [Machiels and Pescatore, 1983]

This concept was more widely recognized by researchers [e.g. Ethridge et al., (1979); Hench et al., (1980); Buckwalter et al., (1982); Oversby (1982); Pederson et al., (1983); Machiels and Pescatore (1983)] that the particle size of the leached materials and the volume of fluid that was available for the leaching process had a significant impact on the experimental results. Figure 6.3 demonstrates this dependence. Shown is the release of silica form a nuclear waste form as a function of time with control of the surface area to volume ratio.

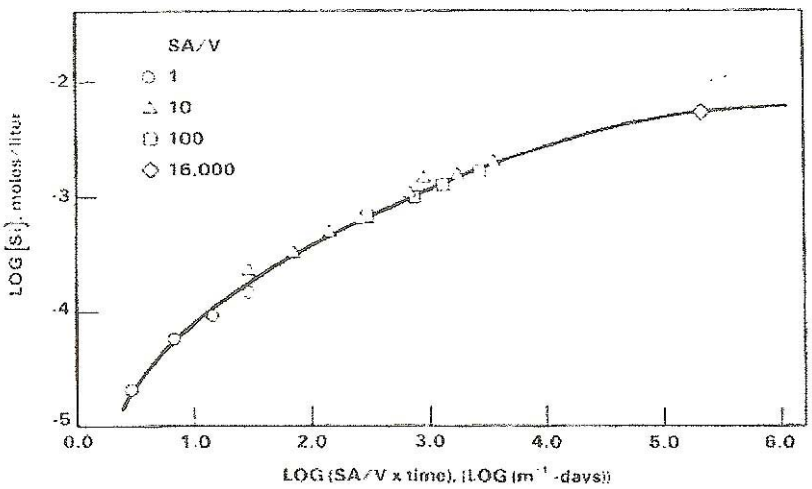


Figure 6.3. Log [Si] vs Log SA/V x t for a glassy nuclear waste form (after Pederson et al., 1983).

What is important in this figure is that by specifically including the surface area/volume parameter, leaching rates varying over 3 orders of magnitude can be scaled onto the same plot.

**Measurement of Surface Area**

The well established method for determining the surface area of a solid material is BET [Brunauer et al., (1938); Yates (1992)]. This method is a routine analytical approach to measure the accessible surface of the rock to $N_2$ gas molecules. In the analytical procedure, the rock specimen is heated to degas the surface in a heated vacuum cell. This step is followed by the introduction of gas back into the cell. The final step is to drive off the newly adsorbed gas and measure the quantity released. Knowing the volume of the gas and the molecular diameter of the particular gas, an accurate surface area can be calculated. Gases other than $N_2$ can be used but they would possess a different molecular size and thus a different quantity of gas would be needed to cover the same surface area. Therefore, it becomes necessary to specify the gas used in the measurement. Additional discussion of surface area measurements and their relationships to porosity and reaction kinetics is given by Brantley and Mellott (2000).

Although the technique is well established, instrumentation may not be readily available to most laboratories. To address this issue, some researchers have used a geometric surface area in place of the BET surface. If the solid materials being tested are glass, this approach may be acceptable, however, if the materials are rocks with irregular surface areas, this approach will significantly under estimate the areas.

Machiels and Pescatore (1983) also illustrated this phenomenon by taking a glass and polishing its surface to roughness of 7 microns. They used this surface roughness as a reference to which they compared the enhanced roughness of the same material polished to a 600 and 100 grit finish (Fig. 6.4).

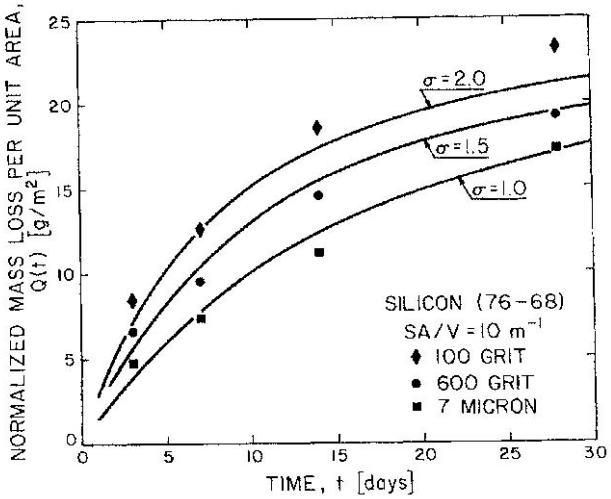


Figure 6.4. Comparison of the normalized release of silicon from a borosilicate glass as a function of surface roughness. [Machiels and Pescatore, 1983]

# Results

## Measurement Method for Surface Area of Column Materials

Surface areas were measured on the sieve fractions of starting material. At the completion of the testing; the contents of the columns were again sieved and remeasured. The bulk surface areas for each column could be determined for the post-leaching rock by taking the individual masses of the sieve fractions specified in the protocol above, multiplying each mass by the surface area (SA), and combining their fractional percent of the total as a weighted linear average:

$$A \times SA_{sieve1} + B \times SA_{sieve2} + C \times SA_{sieve3} + \quad = \quad SA_{bulk}$$

Where: A + B + C = 1

A = fraction of total sieve 1 size
B = fraction of total sieve 2 size
C = fraction of total sieve 3 size

## Surface Area Data

Duplicate leaching columns were run for each of the shales in this study and only a single column for the sandstone. Tables 6.1 through 6.5 summarize the surface area data. Each contains the weight fraction of retained on the individual sieves, the BET surface area for each fraction and the modeled ‘effective’ surface area for the materials before the testing protocol.

Table 6.1 Surface area measurements, sieve analysis and calculation of effective surface areas before and after weathering testing in duplicate for the Kawanaha Black Flint Shale.

**Kawanwha Black Flint Shale**

| | surface area | % retained | normalized surface area |
|---|---|---|---|
| 3/8 | 8.94 | | 0 |
| #4 | 7.5 | 0.4 | 3 |
| #10 | 12.98 | 0.25 | 3.2 |
| #16 | 9.8 | 0.1 | 1 |
| #40 | 9.91 | 0.1 | 1 |
| #60 | 10.68 | 0.05 | 0.5 |
| pan | 7.61 | 0.1 | 0.8 |
| | | | 9.5 m^2/g |

**Kawanwha Black Flint Shale**

| | **column 3** | | |
|---|---|---|---|
| | surface area | % retained | normalized surface area |
| 3/8 | 8.32 | | 0 |
| #4 | 9.31 | 0.4 | 3.72 |
| #16 | 8.34 | 0.35 | 2.92 |
| #40 | 10.17 | 0.1 | 1.02 |
| #60 | 10.1 | 0.05 | 0.51 |
| pan | 9.57 | 0.1 | 0.96 |
| | | | 9.12 m^2/g |

| | **column 4** | | |
|---|---|---|---|
| | surface area | % retained | normalized surface area |
| 3/8 | 10.76 | | 0 |
| #4 | 7.9 | 0.4 | 3.2 |
| #16 | 9.69 | 0.35 | 3.4 |
| #40 | 10.59 | 0.1 | 1.1 |
| #60 | 13.65 | 0.05 | 0.7 |
| pan | 7.73 | 0.1 | 0.8 |
| | | | 9.07 m^2/g |

Table 6.2. Surface area measurements, sieve analysis and calculation of effective surface areas before and after weathering testing in duplicate for the lower Kittanning Shale.

**Lower Kittanning Shale**

| | surface area | % retained | normalized surface area |
|---|---|---|---|
| 3/8 | | | 0 |
| #4 | 11.71 | 0.4 | 4.7 |
| #10 | 12.78 | 0.25 | 3.2 |
| #16 | 12.78 | 0.1 | 1.3 |
| #40 | 14.71 | 0.1 | 1.5 |
| #60 | 13.68 | 0.05 | 0.7 |
| pan | 10.63 | 0.1 | 1.1 |
| | | | 12.4 m^2/g |

**Lower Kittanning Shale**

| | **column 7** | | | | **column 8** | | |
|---|---|---|---|---|---|---|---|
| | surface area | % retained | normalized surface area | | surface area | % retained | normalized surface area |
| 3/8 | | | 0 | 3/8 | 11.71 | | 0 |
| #4 | 13.44 | 0.4 | 5.38 | #4 | 13.44 | 0.4 | 5.38 |
| #16 | 14.04 | 0.35 | 4.91 | #16 | 12.83 | 0.35 | 4.49 |
| #40 | 15.95 | 0.1 | 1.6 | #40 | 15.67 | 0.1 | 1.57 |
| #60 | 12.3 | 0.05 | 0.62 | #60 | 16.15 | 0.05 | 0.81 |
| pan | 15.54 | 0.1 | 1.55 | pan | 15.36 | 0.1 | 1.54 |
| | | | 14.05 m^2/g | | | | 13.78 m^2/g |

Table 6.3. Surface area measurements, sieve analysis and calculation of effective surface areas before and after weathering testing in duplicate for the Houchin Creek Shale.

**Houchin Creek Shale**

| | surface area | % retained | normalized surface area |
|---|---|---|---|
| 3/8 | 13.03 | | 0 |
| #4 | 15.77 | 0.4 | 6.3 |
| #10 | 12.15 | 0.25 | 3 |
| #16 | 17.8 | 0.1 | 1.8 |
| #40 | 18.5 | 0.1 | 1.9 |
| #60 | 17.06 | 0.05 | 0.9 |
| pan | 11.39 | 0.1 | 1.1 |
| | | | 15 m^2/g |

**Houchin Creek Shale**

| | **column 5** | | |
|---|---|---|---|
| | surface area | % retained | normalized surface area |
| 3/8 | 13.09 | | 0 |
| #4 | 10.98 | 0.4 | 4.39 |
| #16 | 13.78 | 0.35 | 4.82 |
| #40 | 14.02 | 0.1 | 1.4 |
| #60 | 16.58 | 0.05 | 0.83 |
| pan | 12.75 | 0.1 | 1.28 |
| | | | 12.72 m^2/g |

| | **column 6** | | |
|---|---|---|---|
| | surface area | % retained | normalized surface area |
| 3/8 | 11.59 | | 0 |
| #4 | 10.31 | 0.4 | 4.12 |
| #16 | 8.68 | 0.35 | 3.04 |
| #40 | 9.08 | 0.1 | 0.91 |
| #60 | 11.55 | 0.05 | 0.58 |
| pan | 12.2 | 0.1 | 1.22 |
| | | | 9.87 m^2/g |

Table 6.4. Surface area measurements, sieve analysis and calculation of effective surface areas before and after weathering testing in duplicate for the Middle Kittanning Sandstone.

**Middle Kittanning Sandstone**

| | surface area | % retained | normalized surface area |
|---|---|---|---|
| 3/8 | 2.65 | | 0 |
| #4 | 2.55 | 0.4 | 1 |
| #10 | 2.79 | 0.25 | 0.7 |
| #16 | 2.82 | 0.1 | 0.3 |
| #40 | 2.79 | 0.1 | 0.3 |
| #60 | 2.69 | 0.05 | 0.1 |
| pan | 3.23 | 0.1 | 0.3 |
| | | | 2.7 m^2/g |

**Middle Kittanning Sandstone**

| | surface area | % retained | normalized surface area |
|---|---|---|---|
| 3/8 | 2.7 | | 0 |
| #4 | 2.74 | 0.4 | 1.1 |
| #16 | 3.05 | 0.35 | 1.07 |
| #40 | 2.91 | 0.1 | 0.29 |
| #60 | 2.53 | 0.05 | 0.13 |
| pan | 2.91 | 0.1 | 0.29 |
| | | | 2.87 m^2/g |

Table 6.5. Surface area measurements, sieve analysis and calculation of effective surface areas before and after weathering testing in duplicate for the Brush Creek Shale.

**Brush Creek Shale**

| | surface area | % retained | normalized surface area |
|---|---|---|---|
| 3/8 | 20.43 | | 0 |
| #4 | 9.59 | 0.4 | 3.8 |
| #10 | 13.06 | 0.25 | 3.3 |
| #16 | 11.77 | 0.1 | 1.2 |
| #40 | 11.76 | 0.1 | 1.2 |
| #60 | 11.49 | 0.05 | 0.6 |
| pan | 11.02 | 0.1 | 1.1 |
| | | | 11.1 m^2/g |

**Brush Creek Shale**

| | **column 1** | | |
|---|---|---|---|
| | surface area | % retained | normalized surface area |
| 3/8 | | | 0 |
| #4 | 17.45 | 0.4 | 6.98 |
| #16 | 17.79 | 0.35 | 6.23 |
| #40 | 18.73 | 0.1 | 1.87 |
| #60 | 18.61 | 0.05 | 0.93 |
| pan | 11.41 | 0.1 | 1.14 |
| | | | 17.15 m^2/g |

| | **column 2** | | |
|---|---|---|---|
| | surface area | % retained | normalized surface area |
| 3/8 | 15.67 | | |
| #4 | 17.98 | 0.4 | 7.19 |
| #16 | 16.4 | 0.35 | 5.74 |
| #40 | 18.42 | 0.1 | 1.84 |
| #60 | 17.77 | 0.05 | 0.89 |
| pan | 17.78 | 0.1 | 1.78 |
| | | | 17.44 m^2/g |

Unlike the Hornberger (2003) study, two of the shales exhibited an increase in surface area after the leaching experiment and two show a reduction as would be anticipated by the preferential dissolution of small high surface energy particles. These data are summarized in Table 6.6.

Table 6.6 Summary of the before and after changes in the observed BET surfaces areas.

| | starting surface area | post leaching surface area A | B | percent change |
|---|---|---|---|---|
| **Kawanwha Black Flint Shale** | 9.5 | 9.12 | 9.07 | -4.3 |
| **Lower Kittanning Shal**e | 12.4 | 14.05 | 13.78 | 12.2 |
| **Houchin Creek Shale** | 15 | 12.72 | 9.87 | -24.7 |
| **Middle Kittanning Sandstone** | 2.7 | 2.87 | | 6.3 |
| **Brush Creek Shale** | 11.1 | 17.15 | 17.44 | 55.8 |

Shales are mixtures of quartz, feldspars, clays and chlorite plus or minus calcite or dolomite and minor amounts of accessory minerals. They are fine grained with a large, but variable, volume fraction of its constituents made up of phyllosilicates, all of which contribute to themeasured BET surface area which is about a factor of 3 to 10 times larger than limestone or sandstone. Because of the variability in the mineralogical composition of the shales in general, a wider variability in BET surface areas would be anticipated. Shales that have more soluble, fine-grained components will in general present a larger measured surface area after leaching primarily because of the layered structure of the phyllosilicates. In contrast, both sandstone and limestone are more nearly monomineraloic, quartz or dolomite/calcite, respectively. Neither of these minerals have structures that contribute to enhanced surface area.

Previous phases of this program (Hornberger et al., 2003) have looked at other rock types. Figure 6.5 summarized the BET surface areas of all of the rock types tested to date.

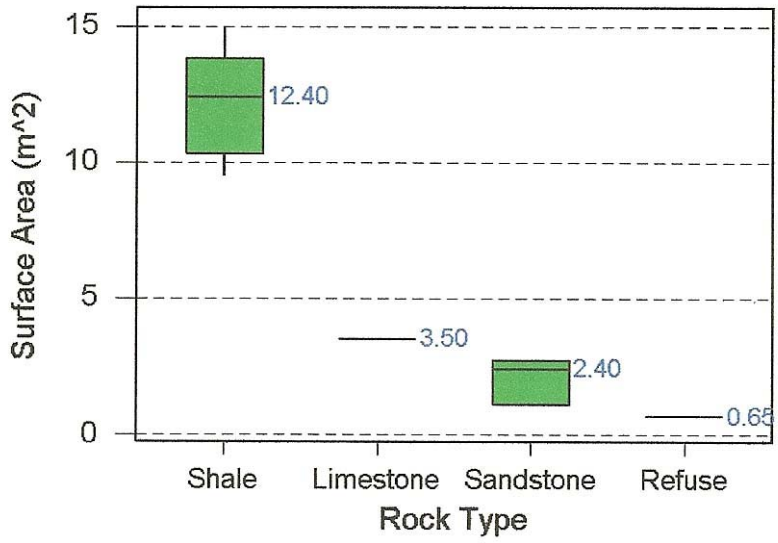


Figure 6.5. Box and whisker plot for BET of different rock types used in this program to date. [Brady, personnel communication]

**Calculation of Surface Area to Volume Ratios**

The design of the leaching column experiments allows a direct calculation of the surface area to volume ratio. The surface area for the reconstituted rock mass in the column is calculated as shown in the equation for $SA_{bulk}$ shown above. This quantity is then scaled to the total rock mass in the column. The volume is simply the volume of water drained from the column after each weekly 24-hour fill-and-drain cycle.

$$\frac{SA}{V} = \frac{1000\ m\ SA_{bulk}}{V}$$

Where: SA/V = surface area to volume ratio (meters $^{-1}$)
m = mass of solids inn column (grams)
$SA_{bulk}$ = BET surface area of solids (meter-squared/gram)
V = volume of leachate from each drain cycle (liters)

Using this formula, the range of SA/V for the shale samples is 36.1 x $10.^{6}$ m $^{-1}$ to 41.8 x 10 $^{6}$ m $^{-1}$ and the sandstone is 10.4 x 10- $^{6}$ m $^{-1}$. Hence, the SA/V for the shales is about 3 to 4 times greater than the sandstone. On Figure 6.5 there is a similar difference between surface areas of shales and sandstones, wherein the median shale of 12.4 is about 5 time greater than the median sandstone. The greater numbers for the shale is probably attributed to the number of bedding plans and the friability of these types of rocks. Figure 6.5 and Tables 6.1 through 6.6 show that the variation between rock types is greater than the variations within a rock type.

According to Pederson et al., (1982) "Thus, short-term tests at a high SA/V value can be used to predict leachate solution concentrations for long-term tests at lower values of SA/V."

The surface area data have been very useful in this study, however, it is not likely that most of the commercial labs using the leaching column method will have the BET surface area measuring equipment. However, the labs will have the sieves to do the particle size distributions, and some of that data can be related to the surface area data. Ideally the surface area data should be gathered on a greater range of rock types and more rock samples of each type. Then, some positive statements of surface area, given a certain rock type, could be made.

The range of concentrations of alkalinity, acidity, sulfates and metals in the present study are representative of the concentrations of those analytes found in the mine environment. Therefore, the writers believe that the SA/V ratios for the ADTI-WP2 leaching column method are appropriate for future use.

**Implementation of Surface Area to Volume Ratio**

A way of quantifying the release of ions into a leaching solvent is to represent it as a *normalized elemental mass loss* (ASTM C 1220, (1998)). The normalized mass loss $[NL]_i$ for an element is determined by:

$$[NL]_i = C_{ij} \times V_j/[f_i \times SA]$$

Where: $[NL]_i$ = normalized mass loss of element ***i***

$C_{ij}$ = concentration of element ***i*** in specimen ***j*** leachate that was filtered through a 0.45 micron filter

$V_j$ = the initial volume of leachate containing specimen ***j***

$f_i$ = the mass fraction of element ***i*** in the unleached specimen

SA = specimen surface area.

The observant reader will recognize that the normalized mass loss actually normalizes against only the quantity of materials that has been removed from the specimen; effectively compensating for the intrinsic solubility of that element in the solid materials being investigated. Just because an element may be present in a leach specimen, doesn't mean that it is labile.

**Conclusions**

If a useful leaching protocol is to be implemented which can be used to compare samples for a wide range of laboratories and a range of potential lithologies and ultimately will be used to predict long-term performance, then more of a realistic surface area than a geometric surface area needs to be utilized. Hornberger et al., (2003) illustrated this point by showing that the shale overburden in that study had a ten-fold larger surface area than a sandstone overburden.

For a leaching protocol to realistically represent the release of constituents from a solid into solution during dissolution, the methodology must take into account the entire surface of the materials to be tested. Determination of the surface areas of four shales and a sand stone using the nitrogen sorption pioneered by Brunauer et al., (1938) and now standardized as the BET method showed that the measured surface of the test shales is about a factor of five greater than rock which are composed of non-phyllosilicate mineral. Further, before and after comparison of the surface areas of the shales varied in response to their bulk mineralogy.