The dissolution of naturally weathered feldspar and quartz

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Abstract—Surface area measurements and dissolution experiments were performed on subsamples from a naturally weathered mineral assemblage (100–1000 μm) consisting of feldspar and quartz. The subsamples were obtained by sieving the assemblage into four different ranges of grain density, each of which was sieved to three different size fractions. BET-krypton and geometric surface areas, combined with mineralogical data and average grain diameters, showed that (1) surface roughness factors of the subsamples are generally much higher than those of freshly created surfaces by grinding and (2) for individual density ranges (i.e., constant mineralogical composition), the surface roughness factor decreases linearly with decreasing grain diameter. Scanning electron microscopy and X-Ray diffraction showed that contributions to the surface roughness factors from secondary mineral coatings, macro pores (diameters >50 nm), and etch pits are insignificant. In contrast, krypton adsorption data indicated that by far most surface roughness is due to the presence of micropores and mesopores (diameters ≤50 nm). These findings strongly suggest that, during natural weathering, micropores/mesopores develop at sites whose density (cm−2 of geometric surface area) is approximately proportional to grain diameter. Multivariate linear regression showed that, at similar grain diameters, the micropore/mesopore density increases in the order: quartz < microcline < albite < oligoclase/andesine. This sequence is similar to the well-known sequence of relative weatherability of these minerals, suggesting a relationship between weatherability and micropore/mesopore density.

At pH 3 HCl and ambient temperature, dissolution rates of Na, K, Ca, Al, and Si from the subsamples, normalized to the BET-krypton surface area, were essentially independent of the grain diameter. Due to effects from surface roughness, dissolution rates normalized to the geometric surface area were essentially proportional to grain diameter. Comparison with micropore/mesopore and etch pit densities showed that the dissolution rates are determined by the pores, rather than by the etch pits. Furthermore, theoretical arguments indicate that the pore area perpendicular to the mineral surface (i.e., the pore “walls”) is essentially nonreactive, and that the dissolution rates are largely determined by the pore area parallel to the mineral surface (the pore “bottoms”). The pore area parallel to the mineral surface is equivalent to (1) the leached layer/fresh mineral interface, if the micropores/mesopores develop in leached layers or (2) the dislocation outcrops where strained mineral material is in contact with the solution, if the micropores/mesopores develop at crystal defects. Tentative calculations suggest that (1) as in the laboratory, dissolution during the previous natural weathering of the sample occurred from the micropore “bottoms” rather than from the etch pits, and (2) dissolution from the etch pits becomes more important with increasing exposure time to weathering conditions.

INTRODUCTION

The aqueous dissolution of minerals has been intensively studied over the past several decades, both in the laboratory (e.g., BUSenberg and CLEMENCY, 1976; CHOUL and WOLLAST, 1984; HOLDREN and SPIELER, 1985, 1987; BRANTLEY et al., 1986; KNAPP and WOLERY, 1986; CASEY et al., 1988, 1991) and in the field (e.g., APRIL and NEWTON, 1983; PACE, 1983; DELANY, 1985; FÖLSTER, 1985; HULTBERG, 1985; VELBEL, 1985; CLAYTON, 1986; OLSSON and MELKERUD, 1987). Experiments have shown that artificial and natural weathering of primary minerals such as feldspar and quartz proceeds as a nonuniform chemical attack of exposed surfaces, leading to the formation of etch pits (e.g., WILSON, 1975; BERNER and HOLDREN, 1977, 1979; ROBERT et al., 1980; HOCHELLA et al., 1987) and/or pores (e.g., PETT et al., 1987; CASEY et al., 1989; WALKER, 1990; WORDEN et al., 1990; ZHANG et al., 1993). Etch pits develop from enhanced dissolution at surface sites of high internal energy, such as crystal defects, if the dissolution rate is limited by the rate of a chemical reaction step at the mineral water interface (BERNER and HOLDREN, 1977, 1979; HELGESON et al., 1984; LASAGA and BLUM, 1986). Several models have been proposed to explain the formation of pores during mineral dissolution (1) like the etch pits, micropores (diameters ≤2 nm) and mesopores (2 nm < diameters ≤50 nm) may form at crystal defects if the dissolution rate is limited by the rate of a chemical reaction step at the mineral-water interface (VAN DER HOEK et al., 1982; LASAGA and BLUM, 1986); (2) a leached microporous surface layer may form if the dissolution rate is limited by the rate of a transport step, such as aqueous diffusion of reactants and products (DOREMUS, 1983; CHOUL and WOLLAST, 1984; CASEY and BUNKER, 1990); and (3) macropores (diameters >50 nm) may result from the formation of fluid inclusions during the initial cooling of the pluton, followed by leakage and weathering under Earth surface conditions (PARSONS et al., 1988).

Dissolution rates in the literature are normally expressed per unit of “average” mineral surface area (e.g., mol·cm−2·s−1). However, the etch pits, micro-
mesopores, and macropores, and possibly still other surface
details, may all dissolve at their own characteristic rate. Fur-
thermore, the formation of etch pits and pores during dis-
solution affects the amount of surface area—and thus, the
dissolution rate—in a way that may vary from sample to
sample (Helgeson et al., 1984; White and Peterson, 1990;
Anbeek, 1992a). This demonstrates that the relationship
between experimental dissolution rates, normalized to "aver-
age" surface area, and the nature, morphology, and relative
amounts of the various surface details is of great importance
to our understanding of the dissolution process.

The surface morphology of mineral grains can be quantified
by the surface roughness factor (λ). λ is defined as the ratio
of the actual surface area (S; cm²) to the geometric surface
area (s; cm²), which is the area of a hypothetical smooth
surface enveloping the actual surface (Jaycock and Parfit,
1981):

\[ \lambda = \frac{S}{s}. \]

Both the actual and the geometric surface area are in fact
scale dependent. The actual surface area may, for instance,
be approximated by the BET method (Brunauer et al.,
1938; Gregg and Sing, 1982). The specific geometric surface
area (s*; cm²·g⁻¹) may, for instance, be found from (Cart-
wright, 1962):

\[ s^* = \frac{K}{(p_d)}. \]

where \( K \) is a geometry factor related to the average shape
of the grains, \( p \) is the density (g·cm⁻³), and \( d \) is the average
grain diameter. For spherical grains, \( K \) equals 6 if \( d \) is in cm.
More accurate values of \( K \) may be found, for instance, from
microscopic observation of grains at low magnification (e.g.,
Fair and Hatch, 1933; Cartwright, 1962).

In this research, the results of surface area measurements
and dissolution experiments at pH 3 HCl are discussed for
feldspar and quartz in a naturally weathered mineral assem-
blage. The main objective of the research was to determine
the differences in nature, morphology, reactivity, and relative
amounts of the BET surfaces between feldspar and quartz
grains with similar hydrogeochemical history.

GLOSSARY OF SYMBOLS

a, b subscripts indicating conditions after and before sample
pretreatment, respectively

c, m, f subscripts indicating a coarse, medium, or fine size fraction,
respectively

C constant, indicating the BET surface area per cm² of sec-
ondary coating material

d, \( d_1 \) average grain diameter (µm)

\( d_i, d_m, d_f \) average grain diameter of a mineral species \( i \) (µm)

\( d_{w}, d_{n} \) average grain diameter of a naturally weathered sample (µm)

\( d_{n0} \) normalized to the average of grain diameters \( d_0 \) of a
number of samples (—)

\( \rho \) average (micro)pore density (cm⁻² of geometric surface area)

\( K \) geometry factor, related to the average shape of mineral
grains (—)

\( \rho_p \) average (micro)pore length (µm)

\( R_{w} \) dissolution rate of a naturally weathered sample, normalized
to BET surface (mol·cm⁻² of BET surface·s⁻¹)

\( R_{w0} \) normalized to the average of dissolution rates \( R_{w0} \) of a
number of samples (—)

\( \gamma \) dissolution rate of a naturally weathered sample, normalized
to geometric surface (mol·cm⁻² of geometric surface·s⁻¹)

\( \gamma_0 \) normalized to the average of dissolution rates \( \gamma_0 \) of a
number of samples (—)

\( S \) BET surface area (cm²)

\( S_w \) BET surface area of secondary mineral coating (cm²)

\( S_{a} \) geometric surface area (cm²)

\( s^* \) specific geometric surface area (cm²·g⁻¹)

\( t_{w} \) average thickness of a secondary mineral coating (µm)

\( t_{w0} \) volume of secondary coating material (cm³)

\( V_{w} \) volume fraction of mineral species \( i \) in sample \( w \) (—)

\( V_{p} \) volume fraction of (micro)pores (—)

\( \alpha_1, \beta_1 \) slope and intercept, respectively, of the (linear) relationship
between surface roughness factor and grain diameter for
mineral species \( i \) (µm⁻¹; µm; (—)

\( \lambda \) surface roughness factor (—)

\( \lambda_0 \) roughness factor of freshly created surfaces by grinding
(—)

\( \lambda_w \) surface roughness factor of mineral species \( i \) (—)

\( \lambda_w \) roughness factor of naturally weathered surfaces (—)

\( \rho \) density (g·cm⁻³)

MATERIALS AND METHODS

We wanted to relate unambiguously the mineralogy of exposed
surfaces in our samples to the bulk mineralogical composition.
Therefore, preliminary studies using optical microscopy, scat-
ning electron microscopy (SEM), and X-Ray diffraction were performed
on several naturally weathered samples to select material (1) free
from secondary mineral coatings and (2) with the constituent minerals
homogeneously distributed over the grains. The selected sample was a
mineral assemblage from Fiesch (Switzerland), collected 3 km south
of the Fiescher glacier. The sample consists of glacial deposits of low-
grade metamorphic Central Aar granite, and essentially contains only
feldspar and quartz. The material has been exposed to leaching for
at least 400 years (when the glacier retreated from the sampling site).
Grain diameters vary from approximately 100 to 1000 µm. Organic
matter and secondary minerals were not detected during sample
selection. The alkali feldspars in the Central Aar granites are generally
perthitic, consisting of low albite and low microcline (Bambauer
and Berndt, 1982). Berndt and Bambauer (1982). The Ca-
bearing plagioclases are generally oligoclase and andesine (Steck,
1976). During the period of Alpine metamorphism, temperature in
the Central Aar granites did not exceed 450°C (Schäfer and

The sample was given a mild (low intensity) ultrasonic cleaning
times for 10 min, each time followed by profuse washing with
deionized water. By sedimentation in bromoform/decaline mixtures
(Van Der Plas, 1966), the sample was fractionated to four ranges
of different grain density (2.56; 2.59; 2.60; 2.63; 2.67; 2.90; 2.88
g·cm⁻³). These were washed with ethanol to remove the bro-
moform and decaline, washed with deionized water to remove the
ethanol, oven-dried, and dried in vacuo to fractions 600–850, 300–425,
and 105–210 µm. All samples were analyzed by X-Ray fluorescence

Table 1: Elemental composition (μmol·g⁻¹) according to XRRS.

<table>
<thead>
<tr>
<th>sample</th>
<th>Na</th>
<th>K</th>
<th>Ca</th>
<th>Al</th>
<th>Si</th>
<th>Mg</th>
<th>Fe</th>
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<tr>
<td>Ac</td>
<td>705</td>
<td>270</td>
<td>≤5</td>
<td>3620</td>
<td>10100</td>
<td>27</td>
<td></td>
</tr>
<tr>
<td>Am</td>
<td>747</td>
<td>272</td>
<td>≤5</td>
<td>3680</td>
<td>10900</td>
<td>27</td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>984</td>
<td>240</td>
<td>≤5</td>
<td>3950</td>
<td>11000</td>
<td>36</td>
<td></td>
</tr>
<tr>
<td>Ba</td>
<td>1550</td>
<td>1650</td>
<td>23</td>
<td>3510</td>
<td>11400</td>
<td>76</td>
<td></td>
</tr>
<tr>
<td>Bm</td>
<td>2310</td>
<td>1000</td>
<td>39</td>
<td>3850</td>
<td>11400</td>
<td>74</td>
<td></td>
</tr>
<tr>
<td>Br</td>
<td>1600</td>
<td>500</td>
<td>≤5</td>
<td>3690</td>
<td>11000</td>
<td>56</td>
<td></td>
</tr>
<tr>
<td>Ce</td>
<td>1590</td>
<td>563</td>
<td>53</td>
<td>2290</td>
<td>13400</td>
<td>107</td>
<td></td>
</tr>
<tr>
<td>Cm</td>
<td>5600</td>
<td>256</td>
<td>99</td>
<td>2130</td>
<td>13700</td>
<td>78</td>
<td></td>
</tr>
<tr>
<td>Cr</td>
<td>982</td>
<td>99</td>
<td>≤5</td>
<td>1240</td>
<td>15000</td>
<td>62</td>
<td></td>
</tr>
<tr>
<td>Co</td>
<td>1600</td>
<td>355</td>
<td>452</td>
<td>3470</td>
<td>11700</td>
<td>525</td>
<td></td>
</tr>
<tr>
<td>Dm</td>
<td>2050</td>
<td>331</td>
<td>443</td>
<td>3570</td>
<td>11600</td>
<td>302</td>
<td></td>
</tr>
<tr>
<td>Dr</td>
<td>1940</td>
<td>395</td>
<td>570</td>
<td>3630</td>
<td>11300</td>
<td>417</td>
<td></td>
</tr>
</tbody>
</table>

1 A = 2.56–2.59 g·cm⁻³; B = 2.59–2.60 g·cm⁻³; C = 2.63–2.67 g·cm⁻³; D = 2.67–2.88 g·cm⁻³; E = 300–850 µm; F = 105–210 µm; G = 0.304–0.455 µm; H = 0.165–0.210 µm.
spectrometry (XRF; Table 1), X-ray diffraction, and point counting with optical microscopy to estimate the bulk mineralogical composition from normative calculations (Brown and Skinner, 1974). Optical microscopy and X-ray data showed that the samples are mainly composed of microlite (assumed pure KAlSiO₃), albite (assumed pure NaAlSi₃O₈), microcline-perthite, consisting of a microcline and an albite component, plagoclase which according to the method by Thor (1963) consists of oligoclase and andesine (assumed pure Ab₃An₇Sis), and quartz (assumed pure SiO₂). Also, a few percent of muscovite (assumed pure KAl₂Si₂O₇(OH)₂) and biotite (assumed pure K(Mg, Fe⁺²⁺, Al)₂Si₂O₇(OH)₂), and traces of amphibole, epidote, and tourmaline are present in most samples. According to the XRF data, the summed mass fraction of oxides of other elements (Ba, Ti, and Mn) is invariably <0.2%. Optical microscopy and normative calculations showed that large differences in mineralogical composition exist between samples of different density range (Fig. 1). For size fractions of similar density range, however, variations in mineralogical composition are small, and deviations from average mass fractions seldom exceed 10% (Tables 2 and 3). The incomplete purification by density fractionation (Fig. 1) primarily results from the presence of the perithes and the rock fragments.

Using the method by De Kansel and Morrise (1979), the specific BET surface area (Sₐ, m²·g⁻¹) was estimated for all samples from a 3-point krypton adsorption isotherm. General equations were derived for seventeen different types of grain geometry (ellipsoids, prisms, pyramids, etc., and combinations) to calculate the volume and the geometric surface area of individual grains from variable linear grain dimensions. In this way, the average equivalent spherical grain diameter and the specific geometric surface area of samples can be estimated in terms of an almost infinitely large number of possible grain shapes. The linear dimensions of thirty individual grains were determined in all samples from observation by a dissecting microscope at 40X magnification. At this scale of surface detail, etch pits and pores are not observed and have no effect on the surface area estimate. Dimensions parallel to the microscope axis were obtained from measurement of shadows, cast by a rotatable light source at known angles. Essential data on all samples are given in Tables 2 and 3.

To determine the effect of ultrasonic cleaning on the surface roughness of the samples (Cremens et al., 1987), 10 g of untreated sample material was gently washed with deionized water for 3 min. and wet-sieved using a 600 and a 210 μm sieve. The mineral fragments >1000 μm were handpicked from the fraction >600 μm, and the grains < approximately 100 μm were decanted from the fraction <210 μm. The geometric and BET surface area of these minimally treated samples 600–1000 μm and 100–210 μm were determined as for the other samples.

The effect of etch pitting on surface morphology was investigated by SEM for the three samples of density range 2.67–2.88 g·cm⁻³ (Fig. 2a and hereinafter). The 600–850 μm, 2.67–2.88 g·cm⁻³ sample was used in three additional experiments to further evaluate the nature of the BET surfaces.

In the first experiment, a small amount of sample was immersed in commercial grade synolite lacquer. After hardening, the resulting stub was sawed and carefully polished, exposing cross sections of randomly oriented grains. The presence of macropores throughout the bulk of the grains (Woroben et al., 1990; Walker, 1990) was investigated using SEM (Woroben et al., 1990) at magnifications up to 20,000X (Fig. 2b and hereinafter).

In the second experiment, the krypton adsorption isotherm of the sample was compared to that of a reference sample. This technique gives an estimate of the difference in micropore volume (cm³·g⁻¹) of microlite = 0.55; abit = 0.26; Ab₆Al₂₋₃ = 0.46; quartz = 0.49; Muscovite = 0.26; Biotite = 0.25, freshly derived from the inner core material of a 10 cm large single crystal. The ground adularia was cleaned ultrasonically in ethanol three times for 10 min, each time followed by washing with ethanol. The ground, clean adularia fraction is similar to that used by Anbreck (1992b). Its BET surface area is 99% freshly created by grinding (Anbreck, 1992b), so etch pits, pores, secondary mineral coatings, etc., from natural weathering are virtually absent. The third experiment was to determine whether the BET surface area is near the surface of the grains or throughout the bulk of the grains. 2.0082 g of 600–850 μm, 2.67–2.88 g·cm⁻³ sample was mixed with 0.2410 g of 10 μm corundum powder in a 5 mL plastic container. 0.8 mL of deionized water was added, and the resulting slurry was vigorously shaken mechanically for about 7 h. The fine and coarse grains were then carefully separated by repeated sedimentation in deionized water until the supernatant was totally clear. Velocities of sedimentation showed that the mechanical treatment had not caused any significant fracturing of the coarse grains, so their numbers before and after treatment are essentially the same. The two size fractions were oven-dried, collected, cooled to room temperature, and reweighed. The coarse size fraction was again ultrasonically washed, dried, and reweighed. The densities of the samples were measured using the sink-float method and the results are given in Table 3.

<table>
<thead>
<tr>
<th>Table 2. Characterization of samples of grain density 9.8–9.85 g·cm⁻³</th>
<th>density (g·cm⁻³)</th>
<th>2.56–2.59</th>
<th>2.59–2.63</th>
<th>2.67–2.68</th>
<th>2.68–2.68</th>
</tr>
</thead>
<tbody>
<tr>
<td>fraction (μm)</td>
<td>600–850</td>
<td>300–425</td>
<td>105–210</td>
<td>600–850</td>
<td>300–425</td>
</tr>
<tr>
<td>dₐ (μm)</td>
<td>762</td>
<td>366</td>
<td>194</td>
<td>825</td>
<td>402</td>
</tr>
<tr>
<td>Sₐ (m²·g⁻¹)</td>
<td>1400</td>
<td>1690</td>
<td>1400</td>
<td>2200</td>
<td>1890</td>
</tr>
<tr>
<td>c₁ (μm²·g⁻¹)</td>
<td>38.9</td>
<td>88.8</td>
<td>151</td>
<td>34.8</td>
<td>73.9</td>
</tr>
<tr>
<td>microcline</td>
<td>0.73/1</td>
<td>0.27/1</td>
<td>0.94/1</td>
<td>0.28/1</td>
<td>0.21/1</td>
</tr>
<tr>
<td>albite</td>
<td>0.19/2</td>
<td>0.19/2</td>
<td>0.13/1</td>
<td>0.39/1</td>
<td>0.38/1</td>
</tr>
<tr>
<td>Ab₆Al₂₋₃</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.001</td>
<td>0.001</td>
</tr>
<tr>
<td>quartz</td>
<td>0.09/2</td>
<td>0.002/2</td>
<td>0.063/1</td>
<td>0.106/1</td>
<td>0.086/1</td>
</tr>
<tr>
<td>muscovite</td>
<td>0.031</td>
<td>0.041</td>
<td>0.042</td>
<td>0.054</td>
<td>0.051</td>
</tr>
<tr>
<td>biotite</td>
<td>0.004</td>
<td>0.004</td>
<td>0.006</td>
<td>0.012</td>
<td>0.011</td>
</tr>
<tr>
<td>K₂O (wt.%)</td>
<td>7.81</td>
<td>7.82</td>
<td>7.57</td>
<td>7.49</td>
<td>7.77</td>
</tr>
<tr>
<td>ξ (10⁻³)</td>
<td>36.1</td>
<td>19.8</td>
<td>9.8</td>
<td>47.4</td>
<td>27.5</td>
</tr>
</tbody>
</table>

1 dₐ is the average spherical grain diameter; Sₐ is the specific BET surface area; ξ is the specific geometric surface area; ξ is the surface roughness factor.

2 Oligoclase and andesine.

3 ξ is the geometric factor, calculated assuming densities (g·cm⁻³) of microlite = 2.55; albite = 2.61; Ab₆Al₂₋₃ = 2.69; quartz = 2.65; muscovite = 2.62; biotite = 2.64.

FIG. 1. Average mineralogical composition of the four density ranges (Tables 2 and 3). "Others" includes muscovite and biotite, and traces of amphibole, epidote, and tourmaline.
showed that analytic errors in leachate concentrations are in the order of 5% for Al and Si, 10% for Ca and Na, and 20% for K.

SURFACE AREA MEASUREMENTS

Using the data in Tables 2 and 3, the surface roughness factor of the naturally weathered samples (\( \lambda_w \)) was plotted vs. their average spherical grain diameter (\( d_g \); Fig. 3). The results show that the surface roughness factor of samples of comparable mineralogical composition decreases approximately linearly with decreasing grain diameter. We can think of three reasonable ways to explain these findings: (1) effects from the presence of unobserved secondary mineral coatings, (2) effects from the sample pretreatment (ultrasonic cleaning and dry-sieving), or (3) effects from the primary phases. These are discussed in greater detail hereafter.

Secondary Mineral Coatings

Secondary mineral coatings can be highly porous and may contribute to the BET surface area of naturally weathered samples (White and Peterson, 1980). At constant composition of a secondary coating, its porous character can be quantified by a constant (\( C; \text{cm}^{-1} \)) denoting the equivalent BET surface area of the gas absorbed per cm\(^2\) of coating material. The BET surface area of secondary coating material (\( S_w; \text{cm}^2 \)) in a sample is then given by

\[
S_w = V_w C.
\]

where \( V_w \) is the volume of coating material. Equation 3 can be used to quantify the effect of secondary coatings on the surface roughness factor of a naturally weathered sample as follows. If, during natural weathering, the surface roughness factor changes only as a result of formation of secondary coatings, the surface roughness factor of the primary phases does not change and equals that of their freshly created counterparts. For freshly created spherical primary grains, covered...
by secondary coating material, it follows from Eqn. 3 and from simple geometry that

$$\lambda_w = \lambda_f + C[t_c - 2d_w/3]^{1/3} + 4t_c^2/(3d_w^3),$$  \hspace{1cm} (4)

where $\lambda_f$ is the surface roughness factor of the freshly created primary grains, $t_c$ is the average thickness of the coating, and $d_w$ is the average grain diameter including the coating. In the samples used here (grain diameters $\geq 100$ $\mu$m), secondary coatings in the order of nanometers thickness may have remained unobserved during sample selection. For such coatings ($t_c \ll d_w$), Eqn. 4 simplifies to

$$\lambda_w \approx \lambda_f + Ct_c.$$  \hspace{1cm} (5)

At constant composition of the primary phases, $\lambda_f$ is independent of the grain diameter (Anbæk, 1992a). Thus, Eqn. 5 indicates that the actual relationships in Fig. 3 can be explained from the presence of secondary coatings only if, far from reason, the increase in coating thickness would be proportional to the increase in grain diameter of the primary phases. Furthermore, the value of C for secondary iron (hydr)oxide in Tahoe Granite is in the order of 0.004 $\mu$m (White and Peterson, 1990). An increase in the coating thickness of 0.25 $\mu$m would then increase $\lambda_w$ by one unit (Eqn 5). Thus, iron (hydr)oxide coatings on the 650–800 $\mu$m grains in these samples should be approximately 10 $\mu$m thick over the entire geometric surface (Fig. 3). Both from SEM and from X-Ray diffraction, such coatings would have been easily observed during sample selection.

Sample Pretreatment

In general, abrasion of grains during ultrasonic cleaning and/or dry-sieving gives higher (or lower) $\lambda$ only if the surface details which are destroyed have lower (or higher) $\lambda$ than those which are created. For instance, Creemens et al. (1987) found that abrasion of fresh mineral surfaces by grinding created additional surface roughness at the scale of observation by SEM. In contrast, we found a decrease in surface roughness from BET analysis in the corundum experiment (see hereafter). This suggests that $\lambda$ of surface details created by abrasion is intermediate between $\lambda_f$ from SEM analysis and $\lambda_w$ from the BET method. The vigorous treatment in the corundum experiment abraded 32% of the BET surface area of the 600–850 $\mu$m, 2.67–2.88 $g \cdot cm^{-3}$ sample (see hereafter). Therefore, the much less vigorous and much shorter ultrasonic treatment could not have abraded, for instance, 63% of the BET surface area of the 105–210 $\mu$m, 2.67–2.88 $g \cdot cm^{-3}$ sample needed to decrease its $\lambda_w$ from 69.9 to 26.1 (Table 3). The specific surface areas from the experiment using minimal sample pretreatment were (cm$^2$ g$^{-1}$): 37.3 (geometric; 600–1000 $\mu$m), 172 (geometric; 100–200 $\mu$m), 1910 (BET; 600–1000 $\mu$m), and 3270 (BET; 100–200 $\mu$m), respectively. Thus, the surface roughness factor was 51.3 (600–1000 $\mu$m) and 19.0 (100–200 $\mu$m), respectively. Realizing that both samples cover the entire range of grain densities, these values are in good agreement with the data in Fig. 3.

In conclusion, we are confident that most or all of the differences in the surface roughness of these samples are inherent to the primary phases and not to secondary coatings or to the sample pretreatment.

Primary Phases

In the samples of density 2.67–2.88 $g \cdot cm^{-3}$, $\lambda_w$ from scanning electron microscopy at 1000$\times$ magnification was approximately 2.0, including effects from etch pitting (Fig. 2a for the 600–850 $\mu$m fraction). From analysis of representative SEM images, etch pit densities (cm$^{-2}$ of geometric surface) were approximately 3600 ± 1200 (105–210 $\mu$m), 2800 ± 1000 (300–425 $\mu$m), and 4000 ± 1400 (600–850 $\mu$m), respectively. The average etch pit diameter was approximately 1.3 $\mu$m in all three samples. If the average depth of the etch pits is, for instance, 1 $\mu$m, the proportion of the SEM area occupied by etch pits is approximately 0.01% for all three samples. However, surface roughness factors from BET analysis (Table 3) are much higher than those from SEM observation (Fig. 2a). This demonstrates that the formation of etch pits during natural weathering does not explain the high $\lambda_w$ from BET analysis in these samples.

Macropore porosities from leakage and weathering of fluid inclusions may reach several percent by volume within parts of selected crystals, the higher values being found in rocks judged to be "wetter" on petrographic grounds (Montgomery and Brac, 1975; Worden et al., 1990). If the surface roughness factor of a naturally weathered sample results only from the formation of macropores, the roughness at an atomic level, both inside and outside the macropores, does not change during natural weathering and equals that of freshly created surfaces. For cylindrically shaped pores of identical diameter, distributed homogeneously throughout the bulk of spherical grains, it follows from simple geometry that

$$\lambda_w = \lambda_f[1 + 2d_p/v_p/(3d_w)],$$  \hspace{1cm} (6)

where $v_p$ is the volume fraction of pores in the grains and $d_p$ is the pore diameter. From point counting and scale measurements on representative SEM images up to 20,000$\times$, the 600–850 $\mu$m, 2.67–2.88 $g \cdot cm^{-3}$ sample has an average macropore volume fraction of approximately 0.5% maximum, and the average macro pore diameter is approximately 2 $\mu$m (Fig. 2b). The 0.5% is a maximum because it is not clear from the SEM observations if all cavities in the polished cross sections are internally connected to the surface of the grains. Values of $\lambda_f$ for microcline, albite, oligoclase, and andesine are approximately 3.4, 2.5, 5.2, and 6.3, respectively (Anbæk, 1992a). Given its crystal structure, $\lambda_f$ of quartz is probably even lower (see Anbæk, 1992a). Assuming $\lambda_f = 4$ for the 600–850 $\mu$m, 2.67–2.88 $g \cdot cm^{-3}$ sample, its maximum $\lambda_w$ equals 6.3 (Eqn. 6). Thus, the formation of macropores during natural weathering does not explain the actual $\lambda_w$ of 69.9 for this sample.

The krypton adsorption isotherms of the dolastrol reference and of the 600–850 $\mu$m, 2.67–2.88 $g \cdot cm^{-3}$ test sample are shown in Fig. 4a. Comparison of the two isotherms (Lippens and De Boer, 1965; Fig. 4b) indicates (3.1 ± 0.2) $10^{-3} cm^2 \cdot g^{-1}$ more micropore volume for the test sample than for the reference sample. If the micropore volume of the reference sample equals zero, and if the micropores in the test sample are cylindrically shaped and internally smooth, this explains 620 $cm^2$ of BET surface $g^{-1}$ sample at maximum average micropore diameter (2 nm). However, this estimate is a minimum. For instance, if the surface roughness factor
at an atomic level inside the micropores equals that of freshly created surfaces (say, $\lambda_s = 4$), a micropore diameter of 1.7 nm would explain all BET surface area of the sample. Additionally, the adsorption-desorption hysteresis for the test sample (Fig. 4a) indicates the presence of mesopores (Gregg and Sing, 1982). These findings strongly suggest that the BET surface area of these samples can be largely explained from the formation of micropores and mesopores in the primary phases during natural weathering.

Reweighing the corundum-treated fractions gave 1.8117 g of coarse grains, and 0.4317 g of fine grains. Thus, the unexplained loss in total weight of solids is 0.0058 g, and the shift in mass from coarse to fine grains is 0.1936 ± 0.0029 g. For spherical grains of 338 µm radius (Table 3), this can be explained from the abrasion of a 11 µm thick surficial layer. The BET surface area of the coarse grains after treatment is 2030 cm²·g⁻¹, compared to the original 2990 cm²·g⁻¹. If the BET surface area of the 600-850 µm, 2.67-2.88 g·cm⁻³ sample is homogeneously distributed over the bulk of the grains, Eqn. 6 also applies to the data from the corundum experiment. In that case, the change in specific geometric surface area and in surface roughness of the treated sample, due to the diminution in average grain diameter, follows from Eqns. 2 and 6:

$$\lambda_{sa} = \frac{K_a d_b}{K_b d_a} \lambda_s,$$

and, because $\nu_b$ and $d_b$ do not change during the corundum treatment:

$$\lambda_a = \lambda_f + (\lambda_b - \lambda_f) d_a / d_b,$$

where the subscripts a and b refer to after and before treatment, respectively. Application of Eqns. 1, 7, and 8 to the data from the corundum experiment, assuming $\lambda_f = 4$, indicates that the specific BET surface area of the treated sample is 3000 cm²·g⁻¹ if $K_b = K_a$ (minimal gain of BET surface, compared to the untreated sample, if the average shape of the grains does not change). Even if the corundum treatment resulted in a perfect spherical shape for all grains ($K_b = 6$), the specific BET surface area after treatment would still be 2340 cm²·g⁻¹ ($K_b = 7.69$; Table 3). Thus, the actual BET area of 2030 cm²·g⁻¹ indicates that the micropores/mesopores in the sample were, at least partly, localized near the surface of the grains. Due to the irregular shape of the grains, the actual layer thickness removed by the corundum probably varied from 0 µm at some places to more than 20 µm at others. Therefore, the actual thickness of the layer where the BET surface area of the sample is located could not be determined and may be any value between almost zero and several tens of micrometers.

**DISSOLUTION EXPERIMENTS**

Dissolution data for the samples of density ranges 2.56, 2.59 and 2.59-2.63 g·cm⁻³ were obtained at pH 3 HCl (days 0 to 156) and at pH 5 HCl (days 156 to 186), respectively. Dissolution data for the samples of density ranges 2.63-2.67 and 2.67-2.88 g·cm⁻³ were obtained at pH 3 HCl (days 0 to 115 and 157 to 183) and at pH 5 HCl (days 115 to 157), respectively. Typical dissolution runs are shown in Fig. 5. Normally, dissolution rates showed high initial values in the first few months and leveled off to lower, more or less constant values over the next few months. After switching from pH 3 to pH 5, concentrations of Na, K, Ca, and Al generally dropped quickly to much lower levels (sometimes within the range of the blanks), while concentrations of Si generally stayed relatively high. The results at pH 5 may not be similar to those without prior dissolution at pH 3. Results from similar dissolution experiments (Anbeek, 1993a) suggest that concentrations of Na, K, Ca, and Al remain low at pH 5, while concentrations of Si take several months to reach new steady state values. Therefore, the pH 5 experiments were not continued any further, and results at pH 5 are ignored hereinafter.

Average steady state dissolution rates at pH 3, normalized to geometric and to BET surface area, were estimated from the ten last data before switching to pH 5. The average steady state rates were further normalized to a reference sample composition for each density range (Tables 4 and 5). This eliminates differences in dissolution rate, due to differences
in mineralogical composition for samples of similar density range. The average composition of all samples in a density range was used as the reference composition. For instance, the 600–850 μm, 2.56–2.59 g cm⁻³ sample contains 735 μmol Na g⁻¹ sample, and a reference sample of 2.56–2.59 g cm⁻³ contains 815 μmol Na g⁻¹ sample (Table 1). The estimated pH 3 steady state dissolution rate of Na in the 600–850 μm, 2.56–2.59 g cm⁻³ sample is \((6.41 \pm 1.12) \times 10^{-16}\) mol cm⁻² of geometric surface area s⁻¹ (Fig. 5a). Thus, a 600–850 μm, 2.56–2.59 g cm⁻³ sample of reference composition has a Na dissolution rate of \((855/735) \times (6.41 \pm 1.12) \times 10^{-16} = (7.11 \pm 1.39) \times 10^{-16}\) mol cm⁻² of geometric surface area s⁻¹ (Table 5).

**DISCUSSION**

If the linear relations in Fig. 3 hold, and if the micropores/mesopores in these samples are cylindrically shaped and perpendicular to the surface, the average pore density (\(D_p\)) follows from simple geometry:

\[
P_p = \frac{\pi d_p^2 L_p}{\alpha a_d},
\]

where \(D_p\) is the number of micropores/mesopores per unit of geometric surface area, \(\alpha\) is the slope of the linear relation between surface roughness and grain diameter (Fig. 3), and \(L_p\) is the average length of the pores. Thus, at constant diameter and length, the micro/mesopore density in these samples is proportional to grain diameter. Consequently, at infinitely small grain diameter their density is essentially zero. Extrapolated values of \(\lambda_m\) in Fig. 3 are in good general agreement with those reported for nonporous, freshly created feldspar surfaces (2.5 to 11: ANBECK, 1992a).

As discussed in the introduction, micropores and/or mesopores may form from enhanced dissolution at crystal defects, or from selective leaching of surficial layers. The density, depth, and diameter of pores in leached layers primarily depend on crystal structure, mineral composition, temperature, pH, and reaction time (CASEY and BUNKER, 1990). For the Fiesch samples of similar density range, these are all essentially independent of the grain diameter. Thus, the actual relations between surface roughness and grain diameter (Fig. 3) suggest that leached layers, whether present or not, did not contribute significantly to the BET surface area. For instance, if density and diameter of selectively leached pores are independent of grain diameter, the leached layer thickness would, far from reason, be proportional to grain diameter. Furthermore, for the nine different naturally weathered feldspars by HOLDRÉN and SPEYER (1985, 1987), ANBECK (1992a) concluded that the surface roughness factor of Grass Valley Anorthite was high (average 2.600). However, contrary to microcline and albite, Al-depleted leached layers in anorthite can exist only if condensation of silanol groups (≡Si—OH) into a linked structure (for instance, ≡Si—O—Si≡) occurs (CASEY and BUNKER, 1990).

### Table 5. Dissolution rates \((r_m)\) at pH 3 HCl (average ± standard deviation in \(10^{-16}\) mol cm⁻² of geometric surface area s⁻¹), normalized to reference sample composition for each density range (see text).

<table>
<thead>
<tr>
<th>sample</th>
<th>Na</th>
<th>K</th>
<th>Ca</th>
<th>Al</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ac</td>
<td>7.14 ± 1.39</td>
<td>25.4 ± 10.6</td>
<td>8.11 ± 1.78</td>
<td>70.5 ± 7.7</td>
<td>200 ± 32</td>
</tr>
<tr>
<td>Am</td>
<td>4.60 ± 1.25</td>
<td>14.5 ± 5.8</td>
<td>3.70 ± 0.76</td>
<td>37.2 ± 3.8</td>
<td>118 ± 22</td>
</tr>
<tr>
<td>Al</td>
<td>2.77 ± 0.60</td>
<td>10.3 ± 4.1</td>
<td>1.30 ± 0.29</td>
<td>25.1 ± 2.3</td>
<td>75.3 ± 14.4</td>
</tr>
<tr>
<td>Bm</td>
<td>10.3 ± 1.7</td>
<td>24.0 ± 10.0</td>
<td>14.0 ± 3.2</td>
<td>92.0 ± 9.2</td>
<td>296 ± 92</td>
</tr>
<tr>
<td>Br</td>
<td>6.77 ± 0.92</td>
<td>16.4 ± 6.7</td>
<td>3.54 ± 0.76</td>
<td>43.2 ± 4.3</td>
<td>145 ± 25</td>
</tr>
<tr>
<td>Bl</td>
<td>4.19 ± 0.70</td>
<td>8.25 ± 3.5</td>
<td>2.49 ± 1.32</td>
<td>28.1 ± 3.9</td>
<td>61.3 ± 11.5</td>
</tr>
<tr>
<td>Cc</td>
<td>21.8 ± 2.7</td>
<td>30.7 ± 7.4</td>
<td>11.0 ± 2.4</td>
<td>251 ± 14.5</td>
<td>358 ± 44</td>
</tr>
<tr>
<td>Cr</td>
<td>8.71 ± 1.40</td>
<td>16.1 ± 7.0</td>
<td>3.77 ± 1.76</td>
<td>217 ± 1.8</td>
<td>109 ± 14</td>
</tr>
<tr>
<td>Cl</td>
<td>2.77 ± 0.60</td>
<td>13.6 ± 3.1</td>
<td>1.22 ± 0.52</td>
<td>21.4 ± 2.4</td>
<td>223 ± 4.7</td>
</tr>
<tr>
<td>Dc</td>
<td>30.3 ± 2.7</td>
<td>105 ± 26</td>
<td>54.7 ± 16.2</td>
<td>367 ± 52</td>
<td>873 ± 74</td>
</tr>
<tr>
<td>Dm</td>
<td>24.3 ± 3.4</td>
<td>88.8 ± 38.8</td>
<td>17.6 ± 3.9</td>
<td>149 ± 19</td>
<td>430 ± 46</td>
</tr>
<tr>
<td>Df</td>
<td>14.7 ± 2.6</td>
<td>46.4 ± 11.5</td>
<td>7.91 ± 1.18</td>
<td>104 ± 15</td>
<td>320 ± 27</td>
</tr>
</tbody>
</table>

1 see note Table 1.
of silanol groups occurred in the Grass Valley Anorthosite during natural weathering, its high $\lambda_s$ cannot be explained from the formation of Al-depleted leached layers.

The observed dependence of surface roughness on grain diameter can be explained if preferential fracture planes have relatively high densities of dissolution reactive sites (i.e., sites where BET surface area is created during dissolution). A similar mechanism was proposed by Anbuek (1992b) to explain the dissolution behaviour of freshly created feldspar surfaces by Holdren and Speyer (1985, 1987). Under such conditions, artificial grinding in the laboratory and grinding in the field (for instance, by the mechanical action of rivers, glaciers, etc.) exposes freshly created surfaces with increasingly lower density of dissolution reactive sites, thereby decreasing the average density at all grain diameters. If, during subsequent natural weathering, BET surface area develops at such sites, smaller grains have lower surface roughness factors. This may also explain the observation that the surface roughness factor of the naturally weathered Nova Scotia sample (612 $\mu$m; Anbuek, 1993a) is much smaller than that of the naturally weathered feldspar fragments by Holdren and Speyer (1 cm; Anbuek, 1992a).

The surface roughness factors of these samples are in fact weighted averages of the surface roughness factors of the constituent minerals. Because, at constant mineralogical composition, surface roughness in Fig. 3 is linearly related to grain diameter, similar relationships will hold for the pure constituent minerals $i$ according to

$$\lambda_i = \alpha_i d_i + \beta_i,$$

where $\lambda_i$ is the surface roughness factor of mineral $i$, $\alpha_i$ and $\beta_i$ are the slope and intercept, respectively, and $d_i$ is the average grain diameter of mineral $i$. If the constituent minerals are homogeneously distributed over the grains in a sample, and if all grains in the sample are of similar size and shape, the weighting factors are the volume fractions of the minerals $i$ (Anbuek, 1993b), which can be obtained from mass fractions (Tables 2 and 3) and densities $\lambda_s$ is then given by (Anbuek, 1993b)

$$\lambda_s = \Sigma_i (v_i \lambda_i (\alpha_i d_i + \beta_i)), \tag{11}$$

where $v_{si}$ is the volume fraction of mineral $i$ in sample $w$ ($\Sigma_i v_{si} = 1$), and where the expression between parentheses is the surface roughness factor of mineral $i$ in sample $w$. In Eqn. 11, $\alpha_i$ and $\beta_i$ are the unknowns, so the resulting multivariate linear regression model can be solved if the number of samples $w \geq 2l$. Using the data in Tables 2 and 3 for microcline, albite, oligoclase/andesine, and quartz only (no muscovite or biotite considered), the model indicates that quartz has the lowest surface roughness factor in these samples and oligoclase/andesine the highest. Based on the high $\lambda_s$ of biotite (White and Peterson, 1990) and the low $\lambda_s$ of muscovite (Nokak, 1954), we assumed in the final analysis that $\alpha_i$ and $\beta_i$ equal those of quartz for muscovite, and those of oligoclase/andesine for biotite. The results of the final regression analysis are shown in Fig. 6. At a given grain diameter, values of $\lambda_s$ in these samples increase in the order: quartz < microcline < albite < oligoclase/andesine. This sequence is similar to the well-known sequence of relative weatherability of these minerals (Goldich, 1938). That the same sequence can be derived from surface roughness data strongly supports the validity of our approach. The results indicate a relationship between the weatherability of minerals and the density of micropores/mesopores after natural weathering. This is true, for instance, if the micropores/mesopores develop at highly reactive dissolution sites. Moreover, the relations in Fig. 6 suggest that sequences of relative weatherability hold only at similar grain diameter of the minerals considered.

The molar ratio of Al to Si in the leachates follows from the data in Table 4. If Al and Si dissolve stoichiometrically, the ratio of Al to Si is 0 for the quartz, 0.33 for the albite.
the microcline, and the trace mineral biotite, 0.48 for the oligoclase/andesine of assumed average composition Ab$_{40}$An$_{30}$, and 1.00 for the trace mineral muscovite. The experimental ratios at pH 3 steady state vary between 0.3 and 0.5 (Table 4), indicating that dissolution rates were largely determined by the feldspars, and possibly the trace mineral biotite. Similar results were found for dissolution from the Nova Scotia feldspar-quartz assemblage (Ansbek, 1993a).

For the purpose of graphic presentation, the relative grain diameter of a sample with $d_w$ is defined as the ratio of the grain diameter of that sample ($d_w$) to the average grain diameter over all (three) samples in that density range:

$$d_w' = \frac{d_w}{d_{w_c} + d_{w_m} + d_{w_f}}. \tag{12}$$

where the subscripts c, m, and f refer to the coarse (600–850 μm), medium (300–425 μm), and fine (105–210 μm) fractions in that density range, respectively. In analogy, the relative dissolution rate normalized to the BET surface area ($R_w'$) is defined as

$$R_w' = \frac{3R_w}{R_c + R_m + R_f}. \tag{13}$$
and the relative dissolution rate normalized to the geometric surface area \((r'_w)\) is defined as

\[
r'_w = \frac{3w}{(r_e + r_w + r_f)},
\]

(14)

It follows from Eqns. 12, 13, and 14 that the relative grain diameters and dissolution rates \((d_e, R_e, r_e)\) differ from the actual grain diameters and dissolution rates \((d_a, R_a, r_a)\) only by a constant factor for samples of similar density range.

In the literature, dissolution rates normalized to the BET surface area are frequently implied to be independent of grain diameter. However, for freshly created surfaces of nine different feldspars by Holdren and Speyer (1985, 1987), dissolution rates normalized to the BET surface area are approximately proportional to grain diameter instead (Anbeek, 1992b; see also Fig. 7). To determine the relationship between dissolution rates normalized to BET surface and grain diameter in these naturally weathered samples, \(R'_a\) (calculated from the data in Table 4) was plotted vs. \(d'_a\) (calculated from the data in Tables 2 and 3) for all elements analyzed (Fig. 8). Square sums were calculated for the data in Fig. 8, assuming (1) dissolution rates normalized to the BET surface area are independent of grain diameter or (2) dissolution rates normalized to the BET surface area are proportional to grain diameter (Table 6). The results show that, except for Ca, model predictions based on dissolution rates independent of grain diameter explain the actual data better than those based on dissolution rates proportional to grain diameter. Thus, dissolution rates of these samples normalized to BET area largely conform to literature assumptions.

As discussed in the introduction, dissolution rates normalized to BET surface area hold for the “average” BET surface and would hold for individual surface sites only if all BET surface area dissolves equally fast. To determine the reactivity of the micropores/mesopores relative to that of the etch pits, dissolution rates normalized to the geometric surface area \((r'_w\); calculated from the data in Table 5) were plotted vs. \(d'_a\) (Fig. 9). Square sums were calculated for the data in Fig. 9, assuming (1) dissolution rates normalized to the geometric surface area are independent of grain diameter or (2) dissolution rates normalized to the geometric surface area are proportional to grain diameter (Table 6). The results show that model predictions based on dissolution rates proportional to grain diameter explain the actual data better than those based on dissolution rates independent of grain diameter. Because the density of etch pits (cm\(^{-2}\) of geometric surface) in these samples is essentially independent of grain diameter, and because the density of micropores/mesopores (cm\(^{-2}\) of geometric surface) is essentially proportional to grain diameter, the results in Fig. 9 indicate that the micropores/mesopores are the reactive sites, rather than the etch pits. Note that the independence on grain diameter of dissolution rates normalized to BET surface area (Fig. 8) cannot be explained from the independence on grain diameter of etch pit densities normalized to geometric surface area.

Micropores may form from the development of leached layers (Chou and Wollast, 1984; Ngobiti and Muir, 1988; Casey and Bunker, 1990), and micropores/mesopores may form from enhanced dissolution at crystal defects (Van der Hooek et al., 1982; Lasaga and Blum, 1986). If the micropores in these feldspars formed from the development of leached layers during natural weathering, the BET surface area of the leached material (i.e., the micropore “walls” in Fig. 7) must be essentially nonreactive, at least for the leached substances (Casey et al., 1989; Muir et al., 1989, 1990; Hellmann et al., 1990). If, alternatively, the micropores (and mesopores) formed from enhanced dissolution at crystal defects, the BET surface area of the pore “walls” is essentially nonreactive too, because micropores/mesopores at crystal defects develop by increasing their depth rather than their diameter (Van der Hooek et al., 1987; Lasaga and Blum, 1986).

Although the micropore/mesopore “walls” were most likely nonreactive, dissolution may have occurred at the pore “bottoms” (i.e., the leached layer/fresh mineral interface or the dissolution outcrops where strained mineral material is in contact with the solution). If so, the proportion of the geometric surface area occupied by reactive surface area is proportional to grain diameter, because the density of micropores/mesopores (cm\(^{-2}\) of geometric surface area) is proportional to grain diameter (Eqn. 9; see also Fig. 7). Thus, dissolution at micropore/mesopore “bottoms” explains the relationships between dissolution rates normalized to geometric surface area and grain diameter (Fig. 9). Note that the proportion of the BET area inside the pores which is occupied by the pore “bottoms” is independent of grain diameter if the pore length and pore diameter are independent of grain diameter (Fig. 7). Because the BET area of the samples essentially equals that of the micropores/mesopores, this explains why dissolution rates normalized to the BET surface area are independent of the grain diameter (Fig. 8).

Because micropores/mesopores are absent in the quartz, its dissolution rate may be determined by the etch pits instead. If so, dissolution rates of quartz, normalized to the geometric surface area, should be independent of grain diameter (because the density of etch pits is independent of grain diameter). Due to the absence of micropores/mesopores, the surface roughness factor of quartz in these samples is essentially independent of grain diameter (Fig. 6). Because dissolution rates normalized to BET surface area are by definition a factor surface roughness smaller than those normalized to geometric surface area, quartz dissolution rates, normalized to BET surface area, should be independent of grain diameter too.

Discrepancies up to several orders of magnitude between field- and laboratory-derived dissolution rates have been reported for feldspar (Paes, 1983; Velbel, 1985). Part of this discrepancy may be related to the fact that most surface area of naturally weathered feldspar grains is present as nonreactive micropore/mesopore “walls,” which are absent on freshly

Table 6. Square sums for the data in Figs. 8 and 9, assuming dissolution rates normalized to BET surface area (Fig. 8) and to geometric surface area (Fig. 9) to be independent of (dashed horizontal line) or proportional to (dashed diagonal line) grain diameter.

<table>
<thead>
<tr>
<th></th>
<th>Na</th>
<th>K</th>
<th>Ca</th>
<th>Al</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fig. 8, hor. lines</td>
<td>0.19</td>
<td>0.79</td>
<td>1.30</td>
<td>0.32</td>
<td>0.78</td>
</tr>
<tr>
<td>Fig. 8, diag. lines</td>
<td>3.47</td>
<td>3.22</td>
<td>0.91</td>
<td>2.79</td>
<td>2.33</td>
</tr>
<tr>
<td>Fig. 9, hor. lines</td>
<td>2.00</td>
<td>2.23</td>
<td>8.81</td>
<td>3.07</td>
<td>4.39</td>
</tr>
<tr>
<td>Fig. 9, diag. lines</td>
<td>0.29</td>
<td>0.33</td>
<td>0.78</td>
<td>0.24</td>
<td>0.43</td>
</tr>
</tbody>
</table>
created feldspar surfaces in the laboratory. Because micro-
opores/mesopores are absent both on freshly created and nat-
urally weathered quartz surfaces, the discrepancy between field- and laboratory-derived dissolution rates for quartz should be small relative to that for feldspar.

In the 600–850 μm, 2.67–2.88 g·cm⁻³ sample, the micro-
opore volume is approximately 3.1 · 10⁻³ cm³·g⁻¹, the etch
pit density is approximately 4000 cm⁻² of geometric surface
area, and the average etch pit diameter is approximately 1.5
μm. The volume of mesopores is not well known and is is-
nored hereinafter. If the etch pits and micropores are cylin-
drically shaped and internally smooth, if the micropore
“walls” are nonreactive, and if the average depth of the etch
pits and micropores is, for instance, 1 μm, the volume amount
dissolved during natural weathering (cm³·cm⁻³ of reactive
surface area) is 2.7 · 10⁻³ for the etch pits, and 1.0 · 10⁻⁴ for
the micropores. This suggests that the field weathering rates,
normalized to reactive surface area, were of approximately
the same order of magnitude for the etch pits and the mi-
cropores. However, the reactive surface areas (cm²·g⁻¹ sam-

tured by the network.
ple) are 0.011 for the etch pits, and 0.313 for the micro pores. Furthermore, the reactive surface area of the etch pits was smaller than 0.011 during the initial stages of natural weathering (because the etch pits were smaller), while the reactive surface area of the micro pores was probably constant throughout the exposure time (because micropore growth increases only the amount of nonreactive surface area). These tentative calculations suggest that—as in the laboratory—dissolution rates during the previous natural weathering of the sample material were determined by the micropore “bottoms,” rather than by the etch pits. The calculations also suggest that the contribution of etch pits to the dissolution of feldspar, relative to the contribution of micropores, increases with increasing exposure time to natural weathering.

CONCLUSIONS

Surface area measurements and dissolution experiments were performed on subsamples from a naturally weathered assemblage consisting of feldspar and quartz. The subsamples were obtained from density fractionation and sieving. Roughness factors of the naturally weathered surfaces were much higher than could be explained from sample pretreatment, secondary mineral coatings, etch pits, or macropores. Krypton adsorption/desorption data showed that the high surface roughness factors can be explained from the presence of micropores and mesopores, concentrated near the mineral surface. Because freshly created surfaces by grinding are nonporous, these findings indicate that, during natural weathering, micropores/mesopores develop at dissolution reactive sites. The data also indicate that, at constant mineralogical composition, the micropore/mesopore density is approximately proportional to grain diameter. This suggests that leached layers, whether present or not, do not contribute significantly to the BE'1 surface area. The data can be explained, however, if preferential fracture planes have relatively high densities of dissolution reactive sites. A similar mechanism was proposed earlier to explain the dissolution behaviour of freshly created feldspar surfaces by grinding (Anbeek, 1992b). Multivariate linear regression showed that the micropores/mesopores develop in the feldspar grains but not in the quartz grains during natural weathering. At similar grain diameters, surface roughness factors increase in the order: quartz < microcline < albite < oligoclase/andesine. This sequence is similar to the well-known sequence of relative mineral weatherability. The findings strongly suggest a relationship between the weatherability of minerals and the density of micropores/mesopores.

Steady state dissolution rates of Na, K, Ca, Al, and Si were determined at pH 3 HCl. The data indicate that the micropores/mesopores are the dissolution reactive sites, rather than the etch pits. Theoretical arguments indicate that the pore area perpendicular to the grain surface (i.e., the pore “walls”) is essentially nonreactive. This strongly suggests that dissolution rates in these samples are largely determined by the area of the micropore/mesopore “bottoms” in the feldspar, which is equivalent to (1) the leached layer/fresh mineral interface if the pores develop from selective leaching or (2) the dislocation outcrops where strained mineral material is in contact with the solution if the pores develop at crystal defects. Tentative calculations suggest that dissolution during natural weathering prior to the experiments was determined—as in the laboratory—by the pore “bottoms” in the feldspar.

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