

## Measurements of internal and external surface area in feldspars — implications for mineral dissolution studies

M. E. Hodson

Soils and Soil Microbiology Division, Macaulay Land Use  
Research Institute, Craigiebuckler, Aberdeen, AB15 8QH,  
Scotland

Mineral dissolution plays an important role in the neutralisation of acid rain, the supply of nutrients to soils, water quality and climate control. Mineral dissolution is studied both in the field and in the laboratory. Typically, field dissolution rates are up to several orders of magnitude less than those measured in the laboratory. One of the most important parameters in determining laboratory dissolution rates, and also one of the least well understood, is mineral surface area. Surface area is typically measured using gas adsorption isotherms and the BET equation (Brunauer *et al.*, 1938) and can be considered to comprise an internal and external component. Hochella and Banfield (1995) state that 'definitions of external and internal surface remain mathematically precise, but physically approximate'. In this contribution we follow the definitions of White (1995), thus:

$$A_{\text{BET}} = [(6\lambda_p)/(\rho \cdot D)] + A_{\text{INT}}$$

(modified from White, 1995)

where  $A_{\text{BET}}$  = BET surface area ( $\text{m}^2\text{g}^{-1}$ ),  $\lambda_p$  = roughness factor accounting for departure of external surface area from that of a completely smooth particle,  $\rho$  = density ( $\text{gm}^{-3}$ ),  $D$  = grain diameter (m) and  $A_{\text{INT}}$  = internal surface area associated with walls of pores and cracks ( $\text{m}^2\text{g}^{-1}$ ). To further our understanding of mineral dissolution, and as a possible means of accounting for at least some of the discrepancy between laboratory and field dissolution rates, it is desirable to have information on the distribution of the surface area of experimental materials between the internal and external components. Here we present information on the values of internal and external surface area for different size fractions of four different unweathered alkali feldspars using gas adsorption, the BET equation, the t-plot method and SEM observations.

### Results

BET surface area increases with decreasing grain

size. The rate of increase varies between feldspar types. Adsorption isotherms indicate that all the samples are either non-porous or contain pores with diameters greater than 2 nm. SEM observations indicate that three of the samples, all perthites, are porous whilst the fourth, Eifel sanidine (structurally homogeneous), is not. Hysteresis loops indicate the presence of pores in some samples but not others. The geometry of pores predicted by the shape of hysteresis loops (open ended cylindrical or slit shaped pores) does not agree with SEM observations. t-plots indicate the presence of micropores in all samples. Calculations indicate that if smooth walled cylindrical micropores were present their diameters would be a similar size to alkali feldspar cell dimensions. Such pores would only just be accessible to the  $\text{N}_2$  molecules used to measure surface area. For rough walled micropores with an irregular, but roughly circular, cross section, pore diameters would be even smaller. It therefore seems likely that the microporosity is not due to naturally occurring pores, but rather to microcracks produced during the grinding involved in sample preparation. Internal surface area due to micropores is far more significant than that due to meso- and macro-pores. Micropore surface areas vary between the grain size fractions of individual feldspar types as does grain habit and meso- and macroporosity. It seems likely that surface roughness will also vary between grain size fractions. This means that it is not possible to predict the relative magnitudes of surface area due to the exterior grain surface (external surface area) and that due to the surfaces of pores and cracks (internal surface area) from equations which assume constant internal surface area and surface roughness. There is no consistent trend in the relative importance of internal and external surface area. It is concluded that the magnitude of internal surface area is a function of varying crack surface area due to intensity and duration of grinding. External grain surface area is greater than can be explained by SEM resolvable features. These conclusions should apply equally to

TABLE 1. Experimental results

Sample	Size range <sup>1</sup> ( $\mu\text{m}$ )	Mean grain diameter <sup>2</sup> ( $\mu\text{m}$ )	$A_{\text{GEOM}}$ <sup>3</sup> ( $\text{m}^2/\text{g}$ )	Surface roughness <sup>4</sup>	$A_{\text{EXT}}$ <sup>5</sup> ( $\text{m}^2/\text{g}$ )	$A_{\text{BET}}$ ( $\text{m}^2/\text{g}$ )	Total surface area <sup>6</sup> ( $\text{m}^2/\text{g}$ )	Micropore surface area <sup>7</sup> ( $\text{m}^2/\text{g}$ )	Micropore surface area <sup>8</sup> ( $\text{m}^2/\text{g}$ )	Micropore volume ( $\text{mm}^3/\text{g}$ )
KB14	150–106	165	0.014	17	0.241	0.375	0.367	0.130	0.138	0.093
	106–75	115	0.020	24	0.484	0.586	0.601	0.110	0.095	0.066
	75–63	82	0.029	13	0.374	0.546	0.561	0.179	0.164	0.119
	63–53	70	0.033	7	0.215	0.756	0.703	0.514	0.568	0.344
	53–43	57	0.041	9	0.381	0.897	0.932	0.534	0.499	0.314
	43–20	41	0.057	13	0.735	1.404	1.148	0.541	0.797	0.390
Perth perthite	150–106	164	0.014	1	0.018	0.111	0.115	0.095	0.091	0.043
	106–75	105	0.022	5	0.109	0.178	0.178	0.069	0.069	0.044
	75–63	68	0.035	5	0.168	0.226	0.232	0.061	0.056	0.037
	63–53	58	0.041	4	0.161	0.374	0.386	0.220	0.207	0.113
	53–43	49	0.048	6	0.280	0.602	0.599	0.320	0.324	0.201
	43–20	34	0.068	5	0.369	0.507	0.523	0.147	0.130	0.093
Keystone microcline	150–106	157	0.015	5	0.070	0.148	0.149	0.079	0.078	0.037
	106–75	105	0.022	7	0.155	0.188	0.186	0.032	0.034	0.014
	75–63	72	0.032	7	0.224	0.269	0.269	0.045	0.045	0.024
	63–53	54	0.043	2	0.104	0.293	0.282	0.183	0.195	0.096
	53–43*	51	0.046	—	—	0.351	—	—	—	—
	43–20	36	0.065	5	0.331	0.471	0.466	0.138	0.143	0.083
Eifel sanidine	106–75	109	0.022	4	0.090	0.116	0.118	0.027	0.025	0.018
	75–63	78	0.030	3	0.083	0.222	0.207	0.132	0.147	0.087
	63–53	59	0.040	2	0.087	0.337	0.302	0.233	0.268	0.141
	53–35	47	0.050	5	0.247	0.510	0.509	0.263	0.264	0.161
	35–20	33	0.070	5	0.343	0.765	0.755	0.417	0.427	0.316

\* Adsorption run terminated after relative pressure of 0.5 was reached. <sup>1</sup> Based on sieve sizes, <sup>2</sup> From Coulter laser particle size analyser, <sup>3</sup> Geometric surface area =  $6 / \rho D$  assuming cubic geometry, <sup>4</sup> Surface roughness =  $(A_{\text{BET}} - A_{\text{INT}} (\text{due to micropores})) \cdot \rho D / 6$ , <sup>5</sup> External surface area from calculated surface roughness  $\times A_{\text{GEOM}}$ , <sup>6</sup> From lower slope on t-plot,

<sup>7</sup> From difference between upper and lower slopes on t-plot, <sup>8</sup> From difference between  $A_{\text{BET}}$  and upper slope on t-plot.

laboratory and naturally ground grains.

### Implications for dissolution studies

Dissolved species may be advected away from exterior grain surfaces whereas at the bottom of cracks, where fluid may be stagnant, dissolved species are likely to be removed by diffusion. This difference in removal process will have an effect on dissolution rates. Dissolution in cracks is likely to be less rapid than at the exterior of the grain. Therefore the increase in BET surface area during the crushing of experimental material, which is a function of both grain size reduction and the generation of micro-cracks, does not necessarily cause a proportional

increase in dissolution rate. Thus, as suggested by Hochella and Banfield (1995) the comparison of BET surface area normalised mineral dissolution rates from different experiments must be carried out with extreme care.

### References

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