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Surface Cation Exchange Capacity Measurements on Solid and Pulverised Granitic Rock Samples

Ebong Fidelis Sameh[1,2]*, Asoba Gillian Nkeudem[1], Nick Evans[3]

[1]Department of Social Economy and Family Management, Higher Technical Teachers' Training College, University of Buea, Kumba, Cameroon
[2]Department of Chemistry, Loughborough University, England, UK
[3]School of Science and Technology, Clifton Campus Nottingham Trent University, Nottingham, UK
Email: *ebongf@yahoo.com

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Abstract

CEC, a major control on the distribution of mobile cationic species between the mineral phase and pore water or groundwater. It influences retention and release of essential nutrients in soil systems, or mobility, retardation, and migration of contaminants in the environment. Many analytical methods to estimate CEC have been developed using BET surface area measurement. This study aimed at determining the CEC of granitic samples in both the powdered and intact state. Two ways of measuring cation exchange capacity were studied, utilising rock beakers designed at the British Geological Survey using Biotite Mica, Muscovite Mica and Weardale Granite. The rock beakers together with the powered samples were used in cation exchange experiments. The Bascomb method buffered at pH of 8.1 was used. Granitic samples were used. 1 g of pulverised granitic samples using 50 cm^3 of buffered reagents (mixture of $BaCl_2$, triethanolamine, and 2 mol·dm^{-3} HCl) in a dual wash process, equilibrating for 24 h, followed by elemental analysis using ICP-AAS. K is the most leached element from the granitic rocks studied. After background reductions the effective metal concentration of metals leached was in the order K >> Ca > Fe, this is probably the case due to the high content of feldspars, which are rich in K. a relationship between the CEC of an intact sample and a crushed sample is established considering a unit surface area of both the crushed and intact samples. However, this relationship showed a vast difference between the CEC of the intact sample and the crushed sample.

Keywords

Exchange Capacity, Granitic Material, Leached Elements

1. Introduction

Cation Exchange Capacity, or CEC, is the maximum adsorption of readily exchangeable cation in solution (Weber & Quicker, 2018). It, thus, refers to a measure of the total ions exchanged between ions in the solid and those in solution. CEC is one of the most important properties of rocks, minerals, and soils, particularly important in materials that contain minerals such as some clay minerals and zeolites, which can have high concentrations of readily exchangeable sites within their structures. It is a major control on the distribution of mobile cationic species between the mineral phase and pore water or groundwater, and therefore influences such things as the retention and release of essential nutrients in soil systems, or mobility, retardation, and migration of contaminants in the environment. Consequently, many analytical methods to estimate CEC have been developed and have been reported in the published literature since the 19th century (Cecchin, 2008). The question as to which would be the most likely method to provide the best estimation of the CEC must necessarily be preceded by the answer to the question as to the chemical or physical conditions in which the chemical exchange occurs. It is evident that the pH during which cation exchange occurs should be considered, especially if the extractant cation is susceptible to change as a function of pH by condensation, or by partial neutralisation of the charge (Bergaya & Vayer, 1997). Most CEC measurements are performed on particulate matter. There are problems in the extrapolation and application of CEC values determined from powdered or crushed rock samples (using analytical methodologies that were originally intended for the analysis of loose materials). Thus, there is a difference in the CEC for loose material and that for intact samples. The methodologies used in the determination of CEC of disaggregated rock and mineral samples, generally over-estimate the true CEC of the rock (Cecchin, 2008) because the surface area of the powdered material is higher than the actual surface area of the undisturbed soil, and mineral surfaces that would not be in direct contact with the water are exposed. Therefore, the CEC properties of crushed material may be unrepresentative of the CEC of fracture surfaces.

1.1. Aims of the Study

This work was aimed at studying the cation exchange capacity of different granitic rock samples. The study involved studying the CEC of intact and powdered samples of rocks, and intact and powdered samples of main components of the granitic rocks as shown on **Figure 1** and **Table 1**. Most important was to determine a corelation between measurements made on powdered and intact samples.

1.2. Surface Cation Exchange Capacity for Granitic Rocks

CEC is an essential factor in the retardation of radionuclides in geomedia. It is an important sorption parameter by which radionuclides are retarded in the Geologic Barrier System (GBS) in geological disposal of nuclear waste. CEC is one of the most important chemical properties of rocks and soils, particularly important in materials that contain minerals such as clay minerals and zeolites, which can have high concentrations of readily exchangeable cationic sites within their crystal structures. It is a major control on the distribution of mobile cationic species between the mineral phase and porewater or groundwater, and therefore influences such things as the retention and release of essential nutrients in soil systems, or mobility, retardation, and migration of contaminants in the environment. Consequently, many analytical methods to estimate CEC have been developed and have been reported in the scientific literature since the nineteenth century (Cecchin, 2008).

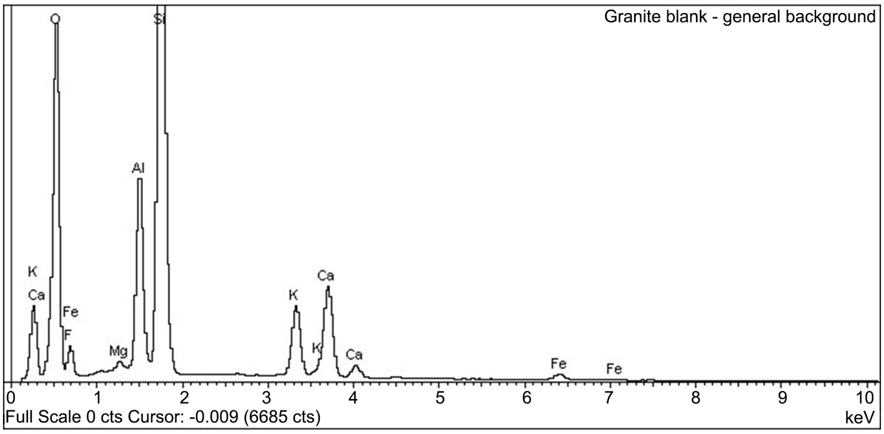


Figure 1. Energy dispersive spectrum of the elemental composition of granite sample with high concentration of Si and O from FIE QUANTA 600 Environmental scanning electron microscope, coupled with Oxford Instrument-INCA450 courtesy of the British Geological Survey Nottingham UK.

Table 1. Summary of quantitative whole-rock XRD analysis nd = not detected, "mica" = undifferentiated mica species including muscovite, biotite, illite and illite/smectite.

	Mineralogical percentage composition							
sample	**amphibole**	**smectite**	**chlorite**	**kaolinite**	**K-feldspar**	**"mica"**	**plagioclase**	**quartz**
Graphic Granite	nd	nd	nd	<0.5	49.4	0.5	21. 6	28.3
Granite Adamellite	nd	<0.5	<0.5	nd	32.9	3.1	25.7	38.1
Biotite Granite	2.9	<0.5	<0.5	nd	17.2	7.4	40	28.1
Grey Granite	nd	nd	<0.5	nd	22.6	4.3	34.4	38.6
Rapakivi Granite	3.5	<0.5	<0.5	<0.5	32.1	1.6	29.2	33.3

Ever since the pioneering work of Thompson (1850) on the absorbent power of soils, much work has been done on the chemical properties of natural porous media (Bergaya & Vayer, 1997). Despite the work done, CEC which is the basis of the retention phenomena is still not fully predictable. One of the reasons being that the CEC of a given sample may vary with the latter's chemical and thermal history (Bergaya & Vayer, 1997). The retention capacity of heavy metals and radionuclides in the far field is still not fully understood. In clay minerals the most common exchangeable cations, in order of usual relative abundance, are Ca^{2+}, Mg^{2+}, H^+, K^+, NH^{4+}, Na^+. It is commonly believed that cation exchange occurs due to the broken bonds around the crystal edges, the substitutions within the lattice, and the hydrogen of exposed surface hydroxyls that may be exchanged. The clay minerals are not the only components having CEC. All minerals of extremely small particle size have a small CEC because of broken bonds around their edges. This capacity increases as the particle size decreases, but even at the smallest size in non-clay minerals associated with clays, the exchange capacity due to broken bonds is relatively insignificant (Ma & Eggleton, 1999). It is evident that the pH which cation exchange occurs should be considered, especially if the extractant cation is susceptible to change as a function of the pH, by hydrolysis or by partial neutralisation of the charge (Bergaya & Vayer, 1997).

1.3. Point of Zero Charge

The Point Zero Charge (PZC) of a mineral is defined as the pH value at which a mineral with amphoteric surface functional groups has no net surface charge (Papelis, 2001). At this value, the anion and cation exchange capacities (adsorption of counter-ions from solution to balance the charge) are equal. When conditions are more acidic than the PZC, the oxide surface is positively charged, and the anions or the negative regions of a polarised molecule are attracted to, and electrostatically held to the surface. Under conditions more alkaline than the PZC, the same attraction applies to the cations or their equivalents (Sarah, 2004).

The free energy of adsorption on oxide surfaces can be composed of three components (Bergaya & Vayer, 1997). Firstly, pure electrostatic bonding which depends only on ionic charge. The second component arises from specificity in bonding of different ions due to their charges, size and polarizability; this attraction will be zero for uncharged surfaces. The third is due to specific interactions between an iron and the surface and can be positive, negative or zero depending on whether adsorption, repulsion or no interactions occurs **Table 2**. It arises from the electronic nature of the ions of the surface and the electrolyte, and is composed of coordination, van der Waals and polarisation forces, so that an ion may be adsorbed by an uncharged or even a similar charged surface (Bergaya & Vayer, 1997). Minerals with silanol sites tend to have low PZCs (e.g. quartz has a PZC of approximately 2 to 3); whereas minerals with aluminol sites have higher PZCs (gibbsite has a PZC of approximately 8 to 9). Minerals with a combination of aluminol and silanol sites tend to have intermediate PZCs (the PZC of kaolinite is 4 to 5). Because feldspars are composed of both silica tetrahedra and alumina octahedra they are expected to have a PZC of less than 7. pH values measured in the field are usually higher, probably due to the present of carbonate and/or other salts Charalambos 2001. Adsorption that results in shifts in PZC indicates that forces in addition to electrostatic attraction are involved in the adsorption mechanism. Typically, this means that inner-sphere complexes are formed, although outer-sphere complexes bound by strong hydrogen bonds cannot be ruled out. Adsorption that does not result in a shift in PZC may be due to either inner-sphere or outer-sphere surface complex formation (Goldberg et al., 2007).

Table 2. Chemical composition of different minerals found in granite, adapted from (Mukai et al., 2020; Allard et al., 1980).

Mineral	Chemical composition
Quartz	SiO_2
Muscovite	$K(Mg, Fe)_3(AlSi_3O_{10})(OH)_2$
Orthoclase Feldspar	$KAlSi_3O_8$
Plagioclase Feldspar	$NaAlSi_3O_8$ / $CaAl_2Si_2O_8$

Electrostatically bound cations can exchange with other cations in solution in reactions which are fast, stoichiometric, and reversible. In principle, the sorption due to cation exchange is independent of pH, except sometimes at low pH, and where dissolution of the mineral may lead to the release of competing cations (Berry, 1992). Ionic substitution in the tetrahedral/octahedral structural layer leads to a permanent negative charge, which is compensated through exchangeable cations, e.g. in montmorillonite. The permanent negative charge (at its equilibrium pH) on mineral surfaces arising from isomorphous substitution is compensated for by an excess of aqueous cations held closely by electrostatic attraction around the outside of the Si-Al-Si units. The ion exchange process has two contributions, the first of which is non-pH dependent and is due to the isomorphous substitution of one atom by another of lower valency e.g. aluminium for silicon. This has the effect of creating a negative overall charge on the lattice structure, which is compensated by the presence of compensating cations (Huber, 2003). The second and pH-dependent contribution arises from the existence of broken bonds at the edge of mineral layers which are balanced by adsorbing H^+ or OH^- ions to achieve full coordination of the surface atoms (Huber, 2003). Considering the cation exchange reaction in which Na is being replaced by M^{2+} (Arcos, 2008).

The ability of a mineral to partake in an ion exchange process with a cationic radionuclide is referred to as the cation exchange capacity (Bradbury & Baeyens, 1993). This is the total exchangeable equivalent of cationic charge (in milli equivalent (meq) g^{-1}) under experimental conditions. The ion-exchange properties of a particular solid material are represented by its Cation-Exchange Capacity (CEC) or Anion-Exchange Capacity (AEC), relative to a reference electrolyte and by its ion-exchange isotherms. Ion exchange isotherms are plots of equilibrium concentrations of ions in the exchanger (solid) phase versus equilibrium concentrations of ions in the solution phase for a particular pair of exchangeable ions in an aqueous suspension at fixed temperature and pressure (Bradbury & Baeyens, 1993). For very small edges (<2 μm), on minerals, the areas might be too small so that the net charge on the lattice is determined mainly by the degree of isomorphous substitution that has occurred. Knowledge of the CEC of a geologic medium gives a strong indication to the extent to which radionuclides may be retarded.

2. Experimental

Two ways of measuring cation exchange capacity were studied, utilising rock beakers. The rock beakers were designed at the British Geological Survey using Biotite Mica, Muscovite Mica and Weardale Granite. The beakers were designed to prevent any solution leaks from the sides. This was done by cutting the granite based to fit in the base of the cylinder followed by further sealing with silicone (**Figure 2**). The design was made such that the silicone sealant did not come in contact with the solution in the beaker to avoid sorbing the solution inside the beakers. Thus, there was no need to do a control to check if the sealant interfered with the concentration of the solution in the beakers. The geometrical diameter of the surface of the rock was 7.0 cm. The rock beakers together with the powered samples were used in cation exchange experiments. There are several methods used in the study of CEC, however, the Bascomb method is the preferred method by the BGS (Cecchin, 2008). This method is used because it avoids the variation of pH which can lead to dissolution of the solid. In recognition of this, the solution is buffered at pH of 8.1 as described below. Graphic Granite (GG), Granite Adamellite (GA), Grey Granite (GrG), Weardale Granite, Plagioclase Feldspar (PF), Milky Quartz (MQ), and Muscovite Mica (MM) have been used as crushed samples. Weardale Granite, biotite and Muscovite Mica were used to form the rock beakers.

The Reagents

1) 2N barium chloride solution: 488 g of $BaCl_2 \cdot 2H_2O$ were weighed diluted to 2000 cm^3 with additional MQ water (obtained from Milli-Q Purification System)

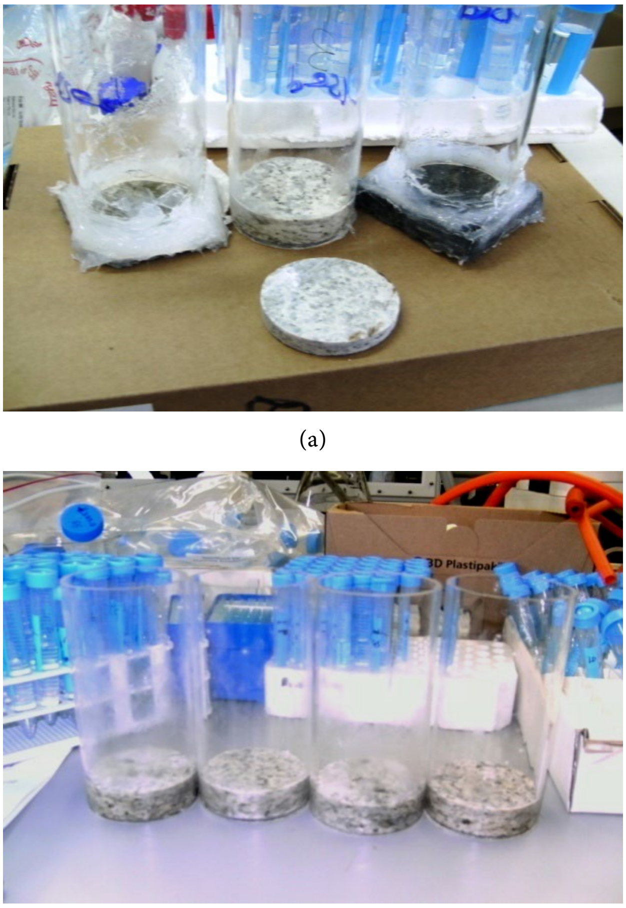
2) 90 cm^3 triethanolamine solution were dissolved in a beaker in 1000 cm^3 of distilled water. Approximately 130 to 140 cm^3 of 2 $mol \cdot dm^{-3}$ HCl were added to the solution while a pH probe was immersed in it. The pH is carefully adjusted to 8.10 and then the solution is diluted to 2000 cm^3 with additional MQ water.

3) Equal volumes of reagent from the previous two solutions were mixed in a polythene bottle.

4) 6.20 g of $MgSO_4 \cdot 7H_2O$ were dissolved into 1000 cm^3 with deionised water a 1000 cm^3.

5) 1 ± 0.01 g of every sample (powder) was measured into 50 cm^3 centrifuge tubes (centrifuged tubes were used to minimise solute and solution losses if experiments were carried in volumetric flasks). Masses of the tubes before and after samples were placed, were recorded. 20 cm^3 of the buffered reagent were added to each tube. All the bottles were shaken for 10 minutes. Centrifugation was performed for 10 min at 3000 x g. The supernatant was collected (Ba wash 1). 40 cm^3 ± 1 cm^3 of the buffered reagent was measured and added to the filtrate in each centrifuge tube. The tubes were shaken for 2 hours and allowed to stand overnight. The supernatant after centrifugation was collected and this formed Ba wash 2. The supernatants were analysed for cations displaced by the barium. A small quantity

of the buffered reagent was collected as a blank for the first part of the experiment. 40 cm^3 of deionised water were added to each tube and shaken for 10 minutes to remove any free $BaCl_2$ in the filtrate and the supernatant was discarded. 45 cm^3 of $MgSO_4$ solution were pipetted into each centrifuge tube. Tubes were shaken for 2h and centrifuged at 3000 x g for 10 minutes. The supernatant was collected for analysis of the displaced barium. A small quantity of $MgSO_4$ solution was collected as a blank for the second part of the experiment. Three replicates of each sample were made. The same procedure was carried out with experiments with the rock beakers.



(a)

(b)

Figure 2. (a) and (b) show rock beakers with surface area of 3.8×10^{-3} m^2 for Muscovite Mica, Biotite Mica, and Weardale Granite. The inner surface area assumed to be equal to the net surface area involved in cation exchange reactions with the solution.

3. Results and Discussions

Energy dispersive spectrum of the elemental composition of granite sample with high concentration of Si and O also showed the presence of other leachable cations as shown by **Figure 1**. Results are presented in the form of leached elemental analysis displaced in solution. Energy dispersive spectrum of the elemental composition of granite sample with high concentration of Si and O.

3.1. Elemental Analysis

Normally, a layered silicate contains several cations in different concentrations depending on the origin and geological history of the sample. Therefore, the determination of its CEC is mostly based on saturating the surface with a defined cation (index cation), which is then displaced and its concentration in the leachate measured. When the cations involved in the exchange reaction are inorganic, the method of choice for their analysis is by displacing the inorganic cations with Ba^{2+} (Ma & Eggleton, 1999). The Bascomb method (Cecchin, 2008) relies on the washing of the rock samples with excess $BaCl_2$ to displace all exchangeable cations in the samples. This process can be repeated several times as desired; however, for this work just two washes with $BaCl_2$ were carried out to avoid loss of sample mass that can result from experimental process, such as filtration and centrifugation. Background corrections for any analysed cations that might be present in the $BaCl_2$ solution were made since the original $BaCl_2$ was not 100% pure.

Inductively coupled plasma-atomic absorption spectroscopy was used in analysing the samples. The calibration equations are shown in **Table 3** below (The concentration of the standards varied from 0.005 to 20 ppm). Three replicates of each sample were measured.

Table 3. Calibration parameters for ICP-AAS showing root mean square values close to unity. Operation conditions: Plasma view was set at auto, with a flush time of 30 s and 3 repeats for each measurement. Nebuliser flow was 0.5 $dm^3 \cdot min^{-1}$ and auxiliary gas flow at 0.5 $dm^3 \cdot min^{-1}$. Wavelength selection was done automatically, while checking for the degree of interference from other elements.

Element	Calibration	R^2	LOD (CPS)	LOQ (CPS)
Al	$y = 998x + 90.4$	0.99	2.2×10^{-3}	7.3×10^{-3}
Ba	$y = 42,900x + 1590$	0.99	$9.4\ 10^{-4}$	$3..2\ 10^{-3}$
Ca	$y = 151,000x - 10,700$	0.99	$1.1 \times 10^{-\ 2}$	$3..7 \times 10^{-2}$
Fe	$y = 1590x - 49.3$	0.99	2.2×10^{-3}	$7..3 \times 10^{-3}$
K	$y = 652x - 1.80$	1	6.7×10^{-2}	$2..2 \times 10^{-1}$
Mg	$y = 51,000x + 995$	0.99	3.1×10^{-3}	1.0×10^{-2}
Mn	$y = 6570x + 153$	0.99	3.0×10^{-4}	$1..0 \times 10^{-3}$
Sr	$y = 90,000x + 2260$	0.99	1.7×10^{-4}	$5..6 \times 10^{-4}$

LOD-Limit of detection in counts per second: LOD (limit of detection), is the lowest quantity of a substance that can be distinguished from the absence of that substance *(a blank value)* (Huber, 2003).

LOD = 3^*STD of counts of blanks/Average of gradients of the calibration curve

LOD-Limit of quantification in counts per second: LOQ is the lowest amount of analyte in a sample that can be quantitatively determined with suitable precision and accuracy.

LOQ = 10^*STD of counts of blacks/average of gradients of calibration curves.

The results for the elemental analysis for the leached elements are shown in the following figures. Results are analysed for each granitic sample studied. The results show which cationic species are the most likely to be exchanged in a cation exchange process. Due to the similarity of granitic rocks, the results do not show significant difference in terms of the different elements leached. To make comparisons between the CEC of intact and powdered samples the calculations and analysis will be interpreted in terms of surface area of the samples. BET surface area measurements calculated were used in calculating the CEC as shown in Table 5. using the effective surface area of the samples.

As seen in Figure 3, K is the most leached element from the granitic rocks studied. After background reductions the effective metal concentration of metals leached was in the order K >> Ca > Fe, this is probably the case due to the high content of feldspars, which are rich in K, in granitic rocks. Weardale Granite gave the most leached K, Ca, and Fe, compared to the other granites studied. Table 4 shows the relative concentrations of leached elements per gram of sample and per m^2 of effective surface area. The concentration of leached Sr is almost the same for all the granitic rocks studied as crushed samples. For granitic minerals such as Milky Quartz, Plagioclase Feldspar and Muscovite Mica, the results (Figure 4) are shown in Table 4. Elemental analysis for Al gave negative values, probably because values are below the limit of detection. However, the low concentrations of Al in the crushed granitic samples indicate that there is a general low presence of Al in granitic rock samples studied. The exchange kinetics of the accessible cations on muscovite can be quite different depending on the relative affinities of the cations involved to mica (McKinley & Hadermann, 1984). As reported earlier, it was important to do the analysis in terms of surface area because it made it easier to compare the CEC for intact solids and that of powdered samples. The results below show the elemental analysis per m^2 of reactive surface area of the rock beakers. As shown in Figure 5, the concentration of the leached elements for the rock beakers is exceedingly high with Ca and K the dominant species for Weardale Granite and Ba and F being the dominant species for both Biotite and Muscovite Mica.

Table 4. Concentration (ppm) of leached metals after 2 washes with $BaCl_2$, corrected for background elemental concentrations and for surface area effects. All values are calculated per m^2 of surface area.

	Al	Ca	Fe	K	Mg	Mn	Sr
Graphic Granite GG	0.39	0.50	0.22	6.2	0.09	0.04	0.71
Granite Adamellite GA	0.06	1.0	0.59	11	0.19	0.05	0.71
Grey Granite GrG	0.11	1.6	0.97	16	0.30	0.06	0.71
Weardale Granite WG	0.15	2.1	1.3	21	0.40	0.06	0.70
Milky Quartz MQ	0.45	19	4.4	52	1.1	0.47	2.3
Plagioclase Feldspar PF		18	2.5	20	0.47	0.41	1.3
Muscovite Mica MM		22	2.4	10	0.31	0.51	1.7
Weardale Granite beaker		6700	760	3900	110	160	510
Biotite Mica beaker		1800	101	4900	180	25	480
Muscovite Mica beaker		389	61	2600	100	19	470

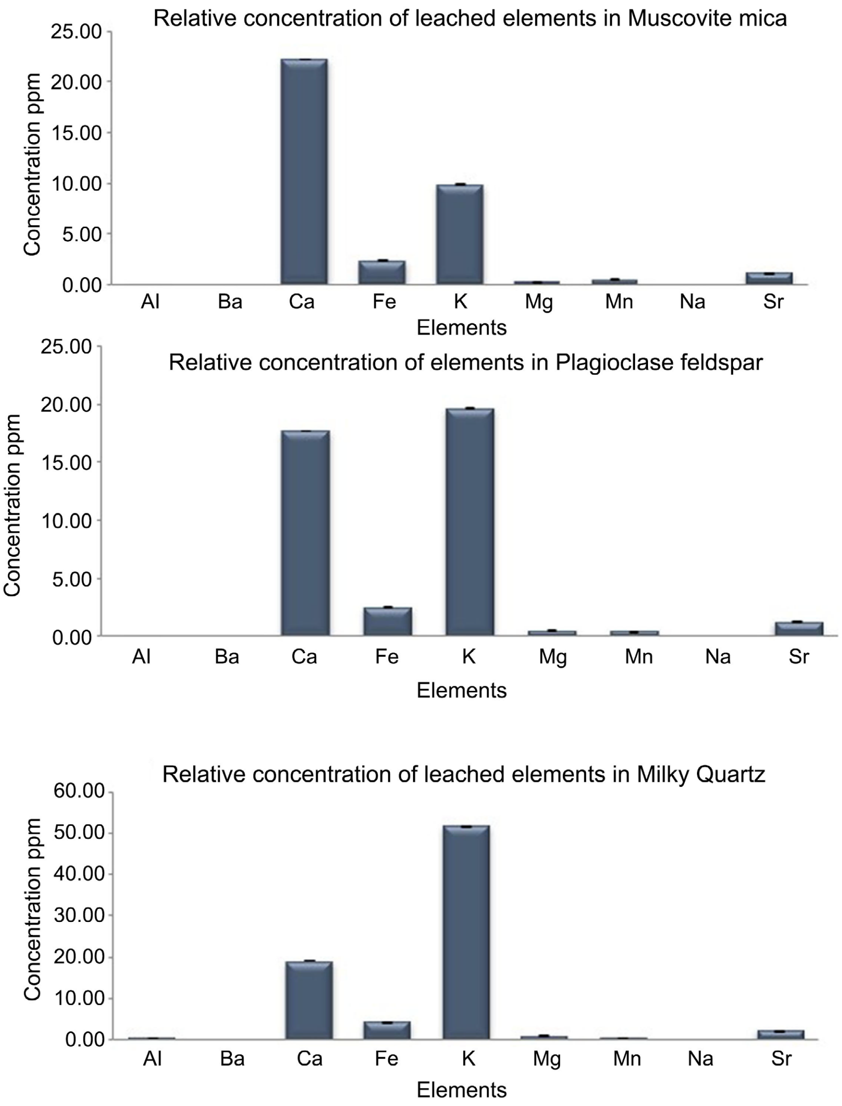


Figure 3. Concentration of leached elements from 1 g of pulverised Granitic mineral (Plagioclase Feldspar, Muscovite Mica, and Milky Quartz respectively) using 50 cm^3 of buffered reagents (mixture of $BaCl_2$, triethanolamine, and 2 mol·dm^{-3} HCl) in a dual wash process, equilibrating for 24 h, followed by elemental analysis using ICP-AAS.

3.2. Magnesium Wash Analysis

This section reports on the analysis of the effective cation exchange capacity of the different powdered and rock beakers (which is a measure of the total exchangeable cations). The cation exchange capacity is calculated per unit surface area of the solid. The assumption is that the effective surface area is that due to the radius of the rock beaker (7.00 ± 0.1 cm as measured at BGS). However, based on the porous nature of granitic rocks, the net reactive surface area is bound to be different as results will show. The concentration of Mg used to displace Ba is calculated by taking the difference in the initial and final concentrations of Mg. Analysis of decreased concentration of Mg used in the Mg wash gave the effective cationic exchange capacity of the sample. Just one wash was carried out with three replicates of each sample used. The concentration of displaced Ba^{2+} is equal to the concentration decrease of Mg^{2+} since wall sorption was negligible.

$$\left[\mathrm{Ba}^{2+}\right]_{\text{displaced}} = \left[\mathrm{Mg}^{2+}\right]_{\text{bound}} = \left[\mathrm{Mg}^{2+}\right]_{\text{initial}} - [\mathrm{Mg}^{2+}]_{\text{solution}} \tag{1}$$

For a known mass of powered sample, the CEC is calculated as shown below (Simsek, 2007).

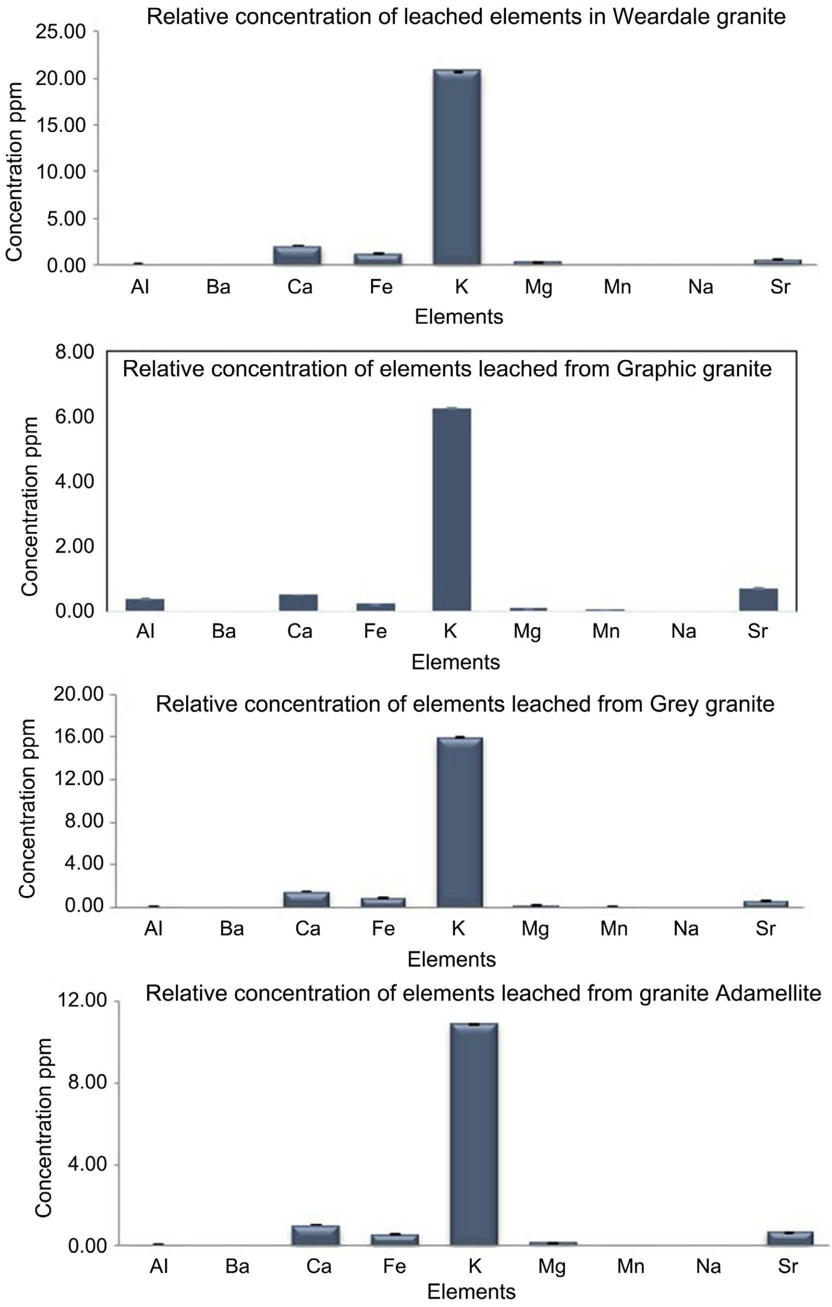


Figure 4. Concentration of leached elements from 1 g of pulverised Granitic rock (Grey Granite, Weardale Granite, Granite Adamellite, and Graphic Granite) using 50 cm^3 of buffered reagents (mixture of $BaCl_2$, triethanolamine, and 2 $mol \cdot dm^{-3}$ HCl) in a dual wash process, equilibrating for 24 h, followed by elemental analysis using ICP-AAS.

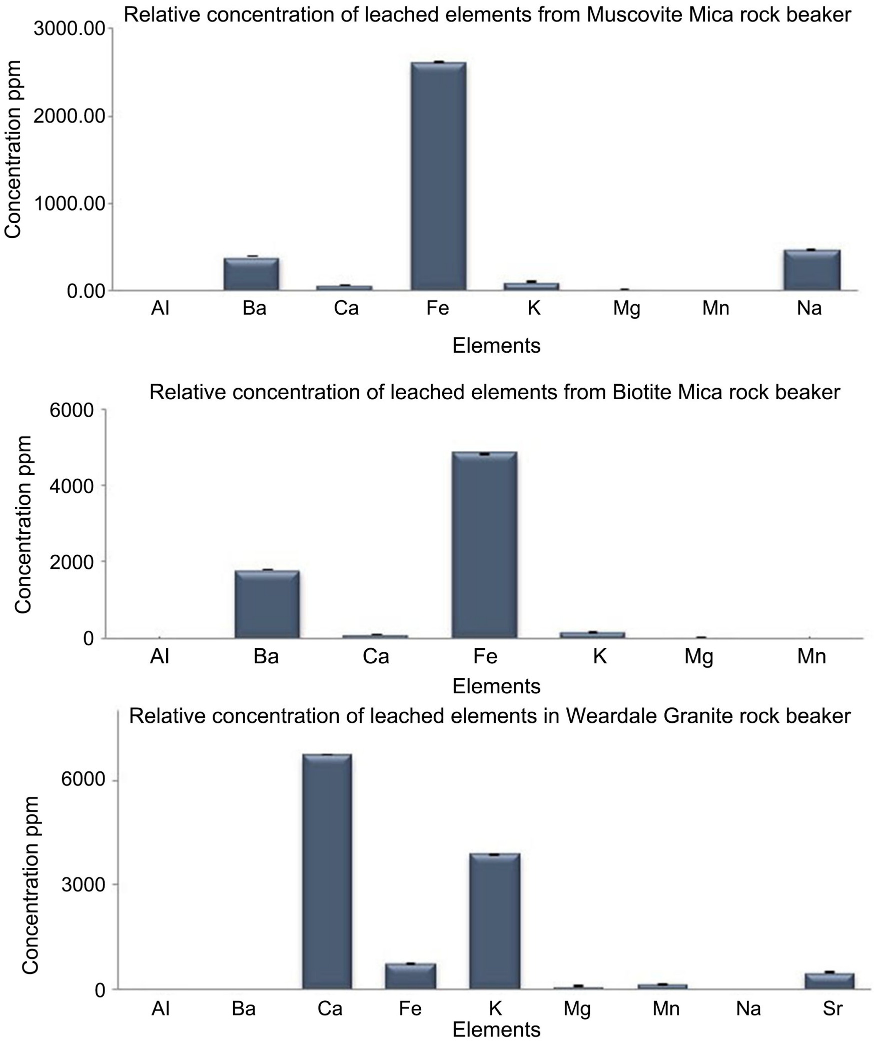


Figure 5. Concentration of leached elements from 3.8×10^{-3} m^2 of Biotite Mica, Muscovite Mica, and rock beaker surface, using 50 cm^3 of buffered reagents (mixture of $BaCl_2$, triethanolamine, and 2 $mol \cdot dm^{-3}$ HCl) in a dual wash process, equilibrating for 24 h, followed by elemental analysis using ICP-AAS.

$$\mathrm{CECMg} = \frac{[\mathrm{Mg}]\mathrm{mg}}{L} * \frac{\mathrm{g}}{1000\ \mathrm{mg}} * \frac{\mathrm{mol}}{24\mathrm{g}} * \frac{100\ \mathrm{cmol}}{\mathrm{mol}} * \frac{2\ \mathrm{cmolc}}{\mathrm{cmol}} * \frac{\mathrm{Vol}(\mathrm{L})}{\mathrm{Mass}(\mathrm{kg})} \tag{2}$$

In terms of surface area exposed to solution the CEC is given by:

$$\mathrm{CECMg} = \frac{[\mathrm{Mg}]\mathrm{mg}}{\mathrm{L}} * \frac{\mathrm{g}}{1000\ \mathrm{mg}} * \frac{\mathrm{mol}}{24\ \mathrm{g}} * \frac{100\ \mathrm{cmol}}{\mathrm{mol}} * \frac{2\ \mathrm{cmolc}}{\mathrm{cmol}} * \frac{\mathrm{Vol}(\mathrm{L})}{\mathrm{Area}(\mathrm{m}^2)} \tag{3}$$

- CECMg is the CEC determined from magnesium used in displacing Ba^{2+} ions as determined from Equation (3).
- [Mg] is the total concentration of Mg used to displace Ba^{2+} in $mg \cdot L^{-1}$.
- 24 is the relative atomic mass of Mg.
- V (L) is the volume of Mg solution.
- Mass (kg) is the mass of sample used the exchange process.

- A is the net surface area (m^2) of the sample used.
- 2 cmolc is the mol equivalent for Mg.

Table 5. Cation exchange capacity calculated in terms of the mass and net surface area in contact with Ba^{2+}/Mg^{2+}. Surface area of powered samples determined by BET N_2 and that of rock beaker as πr^2. Table shows the effect of surface area on the cation exchange capacity.

Sample	Concentration of Mg used (ppm)	CEC ($cmol\cdot kg^{-1}$)	CEC ($cmol\cdot m^{-2}$)
Pulverised samples			
Graphic Granite GG	138	52	18
Granite Adamellite GA	139	52	18
Grey Granite GrG	137	52	18
Weardale Granite WG	141	53	18
Milky Quartz MQ	138	52	61
Muscovite Mica MM	139	52	31
Plagioclase Feldspar PF	137	51	32
Rock beakers			
Weardale Granite WG	135		1.58×10^6
Biotite Mica BM	139		1.62×10^6
Muscovite Mica MM	137		1.61×10^6

Calculated cation exchange capacities for rock beakers and pulverised samples are shown in Table 5. The CEC calculated in terms of the net surface area of the samples is shown in the far-right column of Table 5. For pulverised granitic rocks the CEC 18 $cmol\cdot m^{-2}$, while for the granitic minerals (MQ, PF and MM) the range was in the range 30 to 62 $cmol\cdot m^{-2}$, with MQ having the highest CEC because of the small surface area (0.85 $m^2\cdot g^{-1}$), this was not expected, because the results imply that the CEC decreased with increased surface area. Normally the CEC is expected to increase because of increased surface area in contact with the exchanging solution. The explanation for the above observation could be faulty measurements of the BET surface area of the samples since measurements were conducted from a different laboratory, by other workers. Results showed that MQ, PF and MM have a greater ability to exchange cations compared to GG, GA, GrG and WG. Table 5 also shows the CEC for the rock beakers calculated in terms of the surface area. The results showed very high values about 1.0 × 10 raised to the power 6 $cmol\cdot m^{-2}$ for a surface area of 3.8×10^{-3} m^2 of surface area. The high values are can be expected because the net surface area is pitted (higher than calculated). The results obtained from the rock beakers and pulverised samples showed a difference when the effect of surface area is considered. The results show that the CEC for the rock beaker is 6 orders of magnitude higher than that of crushed samples. Since CEC depends on the net surface area of the sample exposed to the cationic solution it is expected that for the same surface area the CEC should not vary very much. However, this is not the case as seen above. The reason for the disparity of results can be due to the penetration of $BaCl_2$ solution into the bulk of the granite base thereby, exchanging cations with the rest of the granite base of the rock beaker. It is impossible to hold all the Ba^{2+} ions at the surface of the rock beaker; as such the overall cationic species displaced are due to the bulk mass of the rock beaker. Several reasons can be attributed to observed differences in the results, such as:

- The equilibration method, samples must be shaken fully to allow the exchange of cations between the solid and the solution.
- Errors resulting from BET N_2 adsorption, resulting to faulty surface area of the powered samples.
- Also, attainment of equilibrium in the rock beaker-solution, and crushed solid-solution are important factors that can affect the results.

4. Conclusion

From the results shown above, a relationship between the CEC of an intact sample and a crushed sample is established considering a unit surface area of both the crushed and intact samples. However, this relationship showed a vast difference between the CEC of the intact sample and the crushed sample. The results highlight the difficulties associated with the determination of the CEC of an intact sample and that of a crushed sample of the same material, as there is always a possibility of diffusion of the exchanging cation into the bulk material. It may be possible that the exchanging cations are strongly bound to the surface of the intact solid. Any attempts to make the intact solid completely impervious will lead to physico-chemical changes which will also result in deviation of results.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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