Kimberlite degradation: The role of cation type


De Beers, Cullinan Diamond Mine, South Africa
De Beers, Debtech, South Africa
Department of Materials Science and Metallurgical Engineering, University of Pretoria, Lynnwood Drive, Pretoria 0002, South Africa

Abstract

It has been found that disintegration of kimberlite in contact with water is associated with the swelling of clays (such as smectite). This work investigates the possibility that cation exchange between kimberlite and the aqueous weathering medium could enhance or retard disintegration. A strong effect of cations has been found, with the extent of disintegration of kimberlite decreasing in the order

\[ \text{Cu}^{2+} > \text{Fe}^{3+} > \text{Fe}^{2+} > \text{Mg}^{2+} > \text{Li}^{+} > \text{Ni}^{2+} > \text{Ca}^{2+} > \text{Al}^{3+} > \text{Na}^{+} > \text{NH}_4^+ > \text{K}^+ \].

It was found that K\(^+\) retards disintegration. The concentration of cations and temperature have strong effects, whereas the identity of the anion (sulphate or chloride) has little effect. The relationship between the ionic potential (cation valence and effective radius) of each cation, and the observed extent of kimberlite disintegration, holds well for all cations except the trivalent species. Fe\(^{3+}\) and Al\(^{3+}\) have the tendency to form hydroxy species in the interlayer and therefore exhibit a very different mechanism of adsorption. The interlayer spacing of the basal planes of the clays (after exposure to solutions containing the different cations) does not have a clear relationship with the extent of disintegration.

It is suggested that it may not only be swelling that determines the weathering behaviour of kimberlite but that the cations possibly influence the surface energy.
1. Introduction

Diamonds are normally liberated from kimberlite through a series of mechanical size degradation processes such as crushing or milling before recovery. However, if kimberlite disintegration could be accelerated, this could be employed as an alternative to or in combination with crushing (for size reduction), especially at smaller kimberlite deposits. Therefore this subject has seen ongoing interest and research at De Beers. Retardation of kimberlite disintegration would also be useful in some circumstances, for example for improved tunnel wall stability and to maintain integrity of drill core samples. Previous work (Morkel and Vermaak, 2006) showed a strong link between disintegration behaviour and the smectite content of the kimberlite.

Swelling of kimberlite can occur because of the presence of specific layered silicates. Kimberlite is described as complex hybrid potassic, ultrabasic rocks which occur as pipes, dykes and sills (Mitchell, 1986). Kimberlite consists mainly of weathered products that are classified as phyllosilicates (sheet silicates). Of these phyllosilicates, smectite has a 2:1 structure (where an octahedral sheet is present between two tetrahedral sheets), and contains cations in the interlayers to balance the electrical charge. These cations can hydrate and so incorporate water in the interlayer space causing swelling. The degree of swelling can be quantified by measuring the interlayer spacing, which is the $d$ value of the smectite 0 0 1 peak on an XRD scan. An interlayer spacing below 10 Å is associated with 0 water layers, 12.6 Å with one water layer, 15.6 Å with two layers, 18.6 Å with three layers, 21.6 Å with four layers and above that with more water layers (Tessier et al.,
2004). Ferrage et al. (2005) showed that the interlayer spacing under ambient conditions (approximately 25 °C and 35% relative humidity) was rarely above two water layers. The degree of swelling of clay minerals depends on the type and amount of clay minerals present, surface charge and cation valence (Madsen and Müller-Vonmoos, 1989). Smectite clays also exhibit the property of exchanging cations, where the type of cation/s influence the smectite minerals and hence kimberlite properties when smectite is present. Adsorption and desorption studies on Na+, Mg2+, Ca2+, Sr2+ and Ba2+-containing smectites showed that these cations have a swelling effect on smectites ([Cases et al., 1997], [Rytwo et al., 1996], [Badreddine et al., 2002] and [Prost, 1981]). Ferrage et al. (2005) showed that, at room temperature and a relative humidity of 35%, interlayer spacings corresponding to mainly two water layers for smectites saturated with Mg2+ and Ca2+. Smectites saturated with Na+ and Li+ displayed primarily one water layer spacings, and K+ predominantly zero water layers. NH4+, Cs+, K+ and Rb+ have been shown to collapse the smectite interlayer spacing ([Badreddine et al., 2002] and [Czimerova et al., 2004]). Grim (1968) showed that vermiculite saturated with K+, NH4+, Rb+ and Cs+ showed no expansion of the interlayer spacing. The collapsing capability of potassium was studied by Malla and Douglas (1985), which showed that the smectite interlayer can be collapsed to 10.6–12.8 Å depending on the layer charge of the original smectite layer. Carson and Dixon (1972) showed collapse of calcium montmorillonite from 23 Å to 14 Å by K+. These collapsing cations are unique in their large ionic sizes: K+ (1.33 Å), NH4+ (1.43 Å) and Cs+ (1.69 Å). Newman (1987) showed that Mg2+ and Ca2+ hydrate to two layer complexes under controlled humidity whereas Sr2+ and Ba2+ tend to form single layer complexes. The cations Mg2+, Ca2+, Sr2+ and Ba2+ cause the clay to swell to 19 Å in water, but do not cause macroscopic swelling. Newman (1987) showed that K+ easily dehydrates in the interlayer spacing, tending towards spacings of 12–13 Å in water. NH4+ behaves similarly to K+ with the difference that it can dissociate into H+ and NH3, Cs+ and Rb+ are large enough to prevent swelling and both form 12 Å interlayer spacings independent of water content. Al3+ was shown by Newman (1987) to swell up to 19 Å but can increase to 22 Å at high pH values due to the formation of Al–OH polymers. In the present work, the effect of different cations on kimberlite swelling and weathering was investigated.
Crystalline swelling is the dominant smectite swelling mechanism and occurs by hydration of cations in the interlayers of the silicate sheet structure. The ionic potential \( (Z/r_{\text{eff}}) \) can be used as an indication of the strength of hydration of cations of valency \( Z \) and effective ionic radius \( r_{\text{eff}} \). This property is expected to correlate with kimberlite disintegration. Ferrage et al. (2005) showed a correlation between the interlayer spacing and the ionic potential of cations present in the interlayer, such a relationship was also investigated in this work.

2. Experimental work

Kimberlite from Dutoitspan (Lynn et al., 1998) in Kimberley, South Africa, was used for test work, since previous work (Morkel and Vermaak, 2006) showed that this kimberlite contains 30–40% smectite, rendering it susceptible to disintegration upon contact with water. The test work was done using 300 g batches of kimberlite which was screened to the size range 13.2–16 mm. The kimberlite was exposed to the “weathering” solutions (salt solutions containing the different cations) in 1 l containers utilising 800 ml of weathering solution. The kimberlite was exposed to the weathering solution for 6 days at room temperature (\( \approx 20 \) °C), the ore was then removed and air-dried for 1 day, after which the fines were filtered from the weathering solution. The sample was screened to obtain a particle size distribution.

Different cation-containing solutions were tested. The monovalent cations tested were potassium, sodium, ammonium and lithium, divalent cations were magnesium, calcium, ferrous and cupric, and the trivalent cations were aluminium and ferric; all of these were added to distilled water as the chlorides, to achieve a concentration of 0.5 M.

3. Results and discussion

The results of the investigation on the effect of monovalent cations are shown in Fig. 1, divalent cations in Fig. 2 and trivalent cations in Fig. 3. Some of these results are combined in Fig. 4 for comparison.
Fig. 1. Disintegration of kimberlite upon exposure to solutions containing the chlorides of different monovalent cations. Tests were done using 300 g 13.2–16 mm kimberlite weathered for 6 days in 0.5 M potassium-, sodium-, ammonium and lithium chloride solutions, and compared with distilled water (“H₂O” in the figure).
Fig. 2. Disintegration of kimberlite upon exposure to solutions containing the chlorides of different divalent cations. Tests were done using 300 g 13.2–16 mm kimberlite weathered for 6 days in 0.5 M calcium-, magnesium-, ferrous and cupric chloride solution, and compared with distilled water (“H₂O” in the figure).

Fig. 3. Disintegration of kimberlite upon exposure to solutions containing the chlorides of different trivalent cations. Tests were done using 300 g 13.2–16 mm kimberlite weathered for 6 days in 0.5 M aluminium- and ferric chloride solutions, and compared with distilled water (“H₂O” in the figure).
The results from Fig. 1 confirm that potassium is a decelerating agent in kimberlite weathering, decreasing the cumulative percentage passing 11.2 mm from 20% for distilled water to 8%. Ammonium caused the same effect, but to a smaller extent, with 11% passing 11.2 mm. Results for sodium is similar to water at 19% passing 11.2 mm and lithium displayed increased weathering behaviour at 49% passing 11.2 mm. All divalent cations tested increased the rate of disintegration of kimberlite. Calcium showed a 15% increase in cumulative percentage passing 11.2 mm, compared with distilled water. Magnesium showed a further 15% increase at 51% passing 11.2 mm. Ferrous cations reported 55% and cupric cations yielded the most effective disintegration at 93% passing 11.2 mm. The cupric cations have an exceptionally strong effect on kimberlite disintegration, decreasing the size of the rock fragments to 87% passing 4.8 mm.
Two trivalent cations were tested with aluminium yielding 24% passing 11.2 mm and ferric cations 60% compared to distilled water at 21% passing 11.2 mm.

Comparing the differently charged cations yields the disintegration series (from most effective to least effective) as Cu$^{2+}$ > Fe$^{3+}$ > Mg$^{2+}$ > Li$^{+}$ > Ca$^{2+}$. Based on these results, Cu$^{2+}$ is clearly the most effective cation; cupric salts are also readily available at reasonable cost. Further test work hence focused on copper-containing solutions, investigating the effect of the concentration and the time dependence of disintegration. A correlation of ionic potential ($Z/r_{\text{eff}}$) with the extent of kimberlite disintegration is demonstrated in Fig. 5. The $r_{\text{eff}}$ values were obtained from Shannon (1976), using the values for 6-fold coordination. Except for the trivalent cations (which tend to form hydroxy interlayers, rather than simply exchanging into the interlayer ([Newman, 1987] and [Belver et al., 2004])), the relationship between observed weathering behaviour and ionic potential is strong. The disintegration effects of Cu$^{2+}$, Fe$^{2+}$ and Li$^{+}$ lie above the trend formed by the other monovalent and divalent cations, suggesting that these may play another role in disintegration, in addition to the swelling effect. It has been reported that all three of these ions adsorb at other positions (such as crystal edges) in addition to exchanging into the interlayer ([Strawn et al., 2004] and [Anderson et al., 1989]). This might explain the strong effects of these three cations on weathering.
Fig. 5. Relationship between the extent of disintegration of kimberlite, and the ionic potential of the cations in the solution to which the kimberlite was exposed. Results from tests were with 300 g of $-16 + 13.2$ mm Dutoitspan kimberlite, exposed to a 0.5 M cation solution for 6 days.

For investigation of the effect of cation concentration, tests were done at 0.005, 0.025, 0.05, 0.1, 0.2 and 0.4 M using cupric sulphate as the chemical reagent. The test work was done using 1.5 kg batches of kimberlite which was sieved to the size range 22.4–26.5 mm. Weathering tests were done in 10 l containers ($0.7 \times 0.4 \times 0.2$ m) using 5 l of weathering solution ensuring that the ore was spread out, not touching and no stirring was used. The kimberlite was exposed to the weathering solution for 6 days at room temperature ($\sim 20$ °C), the ore was subsequently removed from solution and air-dried for 1 day, whereafter the fines were filtered from the weathering solution. The air-dried sample was subsequently milled in an autogeneous, 30 cm inner diameter, rubber lined laboratory mill (with no lifter bars) for 10 min at $\sim 60$ rpm. The milled sample was sieved to obtain a particle size distribution. The extent of weathering was found by comparing
this size distribution with that of an unweathered milled sample (referred to as zero days weathered).

The results of the concentration tests are reported in Fig. 6 and Fig. 7, and show a strong effect of reagent concentration. A very strong dependence is displayed up to 0.05 M, beyond which the effect is smaller but still significant.

Fig. 6. Effect of cupric ion concentration on kimberlite disintegration. Tests were done using 1.5 kg 22.4–26.5 mm kimberlite exposed to 0.005, 0.025, 0.05, 0.1, 0.2 and 0.4 M copper(II) sulphate solutions for 6 days.
Fig. 7. Effect of copper concentration on kimberlite disintegration, shown as the cumulative percentage passing 14.2 mm (drawn from the results of Fig. 6).

The time dependence of the disintegration process was investigated by exposing the kimberlite to a 0.2 M copper sulphate solution for 6 h, 12 h, 24 h and 6 days. A lower concentration was used so that the reaction rate is lower and the effect of time can be evaluated more readily. The test results are shown in Fig. 8; the results are also summarised as the cumulative percentage passing at 17.5 mm, in Fig. 9. Disintegration is rapid during the first 24 h of exposure; the process slows down, but appears to continue up to 6 days or longer. At this concentration of 0.2 M, 83% of the disintegration that took place over 6 days occurred within the first 24 h. A kinetic study of the adsorption of Cu$^{2+}$ and K$^+$ has been conducted and submitted for publication (Morkel et al., 2007).
Fig. 8. Time dependence of kimberlite disintegration. Tests were done using 1.5 kg 22.4–26.5 mm kimberlite exposed for 6 h, 12 h, 24 h and 6 days to a 0.2 M copper(II) sulphate solution.
Fig. 9. Time dependence of kimberlite disintegration, shown as the cumulative percentage passing 17.5 mm (drawn from the results of Fig. 8, for 0.2 M copper sulphate).

The effect of the anion on weathering was evaluated by comparing kimberlite disintegration in a cupric chloride and in a cupric sulphate solution, both at 0.3 M, and for 6 days’ exposure to the solution. The results (Fig. 10) show that the anion plays no significant role in the weathering process.

![Graph showing cumulative percentage passing](image)

**Fig. 10.** Results of tests to determine the influence of the anion on kimberlite disintegration. Tests conducted on a 1.5 kg, 22.4–26.5 mm kimberlite sample at 0.3 M cupric chloride and cupric sulphate concentration.

The influence of temperature was tested by comparing the effects of kimberlite exposure to distilled water and a 0.1 M magnesium chloride solution (both of which cause limited disintegration) at room temperature and 40 °C. The effect of increased temperature is shown in Fig. 11; at the higher temperature (40 °C), kimberlite disintegration in distilled water increased by 25% passing 13.2 mm, and in the magnesium solution an increase of
27% is observed at the higher temperature. The influence of temperature is strong and comparable with that of cations.

Fig. 11. Effect of temperature on kimberlite disintegration, in distilled water ("H2O") and 0.1 M MgCl₂, at room temperature ("RT") and 40 °C.

Possible effects of cation identity on the interlayer spacing as measured by X-ray diffraction (d spacing) were investigated. A XRD study of various kimberlites was previously conducted and is published in Morkel et al. (2006). This paper addresses some of the difficulties in utilising XRD when clay minerals are present.

Dutoitspan kimberlite was exposed to 0.5 M cation solutions (sulphate and chloride anion) for 6 days. The air-dried samples were milled to −75 μm in a swing mill and submitted for XRD analysis. Note that the order of the effect of the cations on kimberlite disintegration was Cu²⁺ > Mg²⁺ > Li⁺ > Ca²⁺ > Al³⁺ > Na⁺ > NH⁴⁺ > K⁺. The final d spacings are shown in Table 1, which shows that there is no correlation between the interlayer spacing and the severity of weathering; the order of d spacings is quite different from the order of the disintegration effects. For example, the differences between the
interlayer spacing following Ca$^{2+}$, Mg$^{2+}$ and Cu$^{2+}$ exchange were very small whilst the weathering results were very different. For K$^+$ the interlayer spacing relates to the collapsed form, as expected. Ferrage et al. (2005) showed that, for ambient conditions (room temperature and around 35% relative humidity) montmorillonite with Mg$^{2+}$ and Ca$^{2+}$ in the interlayer had primarily two water layers in the interlayer. Na$^+$ and Li$^+$ on the other hand will display primarily one water layer spacings and K$^+$ predominantly zero water layers. The results for Ca$^{2+}$, Mg$^{2+}$, Li$^+$ and K$^+$ (in Table 1) agree well with this. Cu$^{2+}$ agrees with the Mg$^{2+}$ and Ca$^{2+}$ exchanged forms, indicating a two water layer system under ambient relative temperature and humidity conditions.

Table 1.
Interlayer spacing for Dutoitspan kimberlite exposed to solutions containing different cations

<table>
<thead>
<tr>
<th>Cation type</th>
<th>Measured $d$ spacing (Å)</th>
<th>Predicted spacing (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca$^{2+}$</td>
<td>15.1</td>
<td>15.06</td>
</tr>
<tr>
<td>Mg$^{2+}$</td>
<td>14.6</td>
<td>14.70</td>
</tr>
<tr>
<td>Cu$^{2+}$</td>
<td>14.9</td>
<td>14.72</td>
</tr>
<tr>
<td>Al$^{3+}$</td>
<td>14.6</td>
<td>14.47</td>
</tr>
<tr>
<td>K$^+$</td>
<td>10.1</td>
<td>10.00</td>
</tr>
<tr>
<td>NH$_4^+$</td>
<td>12.5</td>
<td>12.47</td>
</tr>
<tr>
<td>Na$^+$</td>
<td>13.3</td>
<td>12.40</td>
</tr>
<tr>
<td>Li$^+$</td>
<td>12.9</td>
<td>12.30</td>
</tr>
</tbody>
</table>

Predicted spacings are based on the correlation of Ferrage et al. (2005).

From these results it is concluded that the interlayer spacing (swelling) cannot in itself explain the disintegration behaviour of kimberlite. The absence of an effect of cation type...
on the extent of smectite swelling is in apparent contradiction with the central role of swelling clay in kimberlite disintegration, which is proposed in this paper. To state the apparent contradiction simply: swelling causes kimberlite disintegration; kimberlite disintegration is strongly affected by the identity of cations in the solution; yet cation identity has little effect on swelling.

This apparent contradiction can be resolved by invoking other elements of the failure process. Griffith-style fracture of brittle materials depends on defect length, applied stress and surface tension. Of these, the defect length is expected to depend on the kimberlite structure, and this does not change if the weathering solution is changed. The stress is applied by swelling; this can be seen to be little affected by cation identity. By elimination, this leaves an effect of cation identity on the surface energy of the crack; such an effect could arise from cation adsorption on the crack surface. A study of Cu$^{2+}$ sorption on montmorillonite (Stadler and Schindler, 1993) suggested that for $3 < \text{pH} < 5$ the Cu$^{2+}$ sorbs in the interlayer of montmorillonite through ion exchange, but for $\text{pH} > 5$ forms surface complexes with surface hydroxyl groups, which could influence the crack surface energy. This effect was not explored further in this study (careful study of fracture behaviour is severely impeded by the rapid disintegration of the kimberlite).

However, it would be a worthwhile direction for future work, especially where solutions with more than one cation are used (perhaps the solution could be designed to contain one cation which exchanges with interlayer cations to cause swelling and another cation/s which changes the crack surface energy).

Further work could also include X-ray photoelectron spectroscopy (XPS) which can provide information on the binding energy and changes in binding energy when cations are adsorbed. This information could contribute to a better understanding of the mechanism of cation weathering of kimberlite.

4. Conclusion

This work has demonstrated that the cation-exchanging ability of smectite can be used to affect kimberlite disintegration strongly. Cupric ions show the strongest disintegration
effect, but other cations can also be used for accelerated disintegration. The interlayer spacing, which is established by exposure to the different cations does not correlate generally with kimberlite disintegration – although collapse of the interlayer spacing (for potassium and ammonium ions) is associated with decreased disintegration. This means that the fundamental effect of cation exchange on kimberlite disintegration does not only involve swelling. An effect on the surface energy of crack surfaces is a likely second role of the exchanged cations.

References


Corresponding author. Address: Department of Materials Science and Metallurgical Engineering, University of Pretoria, Lynnwood Drive, Pretoria 0002, South Africa. Tel.: +27 124203191; fax: +27 123625305.