3. MECHANISMS CONTROLLING KIMBERLITE WEATHERING

This study suggests that kimberlite weathering is mainly due to the presence of swelling clays. In that case the cations present play a large role, as swelling clays can exchange especially interlayer cations to a large extent. Each cation influences the clay structure and properties in a unique way depending on the cation and clay properties as well as the mechanism of cation absorption.

3.1 Swelling as the weathering mechanism

Two types of distinctly different swelling mechanisms have been identified and are discussed by Madsen and Müller-Vonmoos (1989). According to this study the swelling is determined by the type of clay minerals, amount of clays, surface charge and valence of cations present in the double layer. The first phase termed crystalline swelling is due to the hydration of exchangeable cations of the initially dry clay. Phase two termed osmotic swelling occurs due to large differences in ion concentrations close to the surface and the pore water. Figure 14 shows the layer structure of the swelling smectite, montmorillonite. The adsorption of cations takes place for the structure to acquire charge balance. In the dry state the montmorillonite layers lie so close together (0.96 – 1 nm) that they are almost in contact (Madsen and Müller-Vonmoos, 1989). These negatively charged layers are held together strongly by coulombic forces but also weak van der Waals attraction. These cations hydrate upon contact with water (see table 3) and cause a widening of the spacing between the layers (as much as double the initial volume). Madsen and Müller-Vonmoos (1989) quote pressures of 100 MPa due to the crystalline swelling. They also show that this mechanism causes stepwise swelling (widening) where each step is associated with the addition of one more water layer up to a maximum water adsorption. This swelling mechanism is concluded the predominant of the two types.

Osmotic swelling is associated with a large concentration difference between the ions electrostatically bonded to the surface and the ions in the pore water of the rock. This excess negative charge must be corrected by positive ions close to the surface, giving very high concentrations of positive ions close to the surface. This negatively charged surface and cloud of positive ions form the diffuse electric double layer. Pressures associated with this type of swelling are normally less than 2 MPa (Madsen and Müller-Vonmoos, 1989).

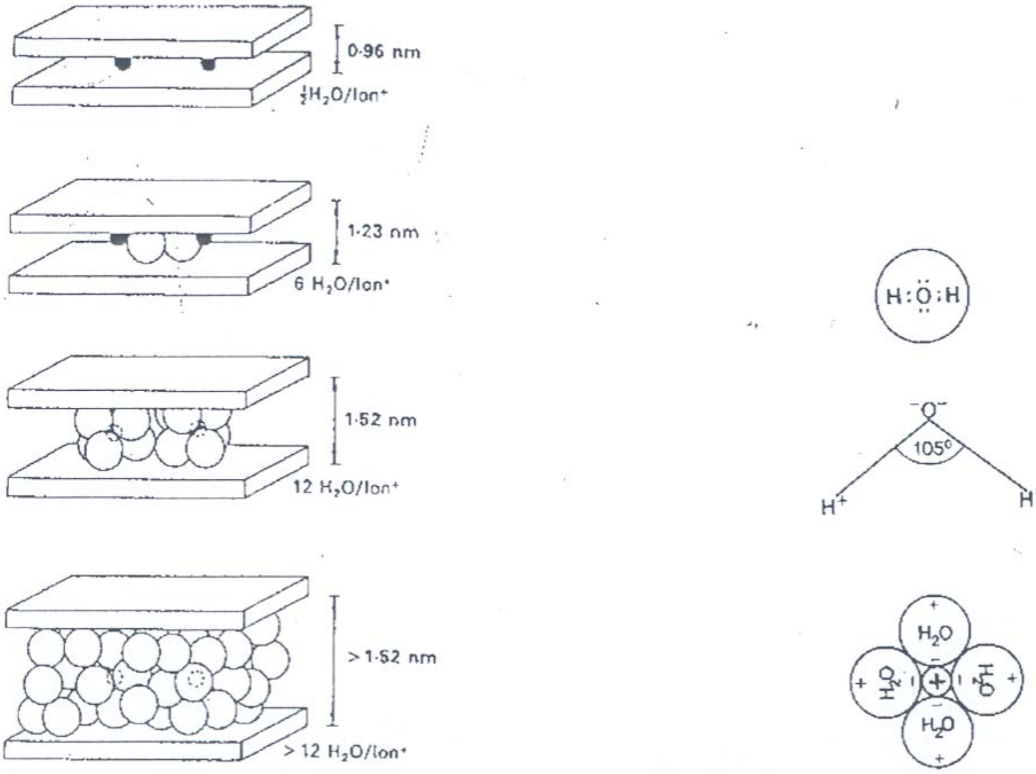

Figure 14. Innercrystalline swelling of montmorillonite (Madsen and Müller-Vonmoos, 1989).

3.2 The effect of cations on swelling behaviour

In the case where a kimberlite contains swelling clays (e.g. montmorillonite or saponite), it will also exhibit cation exchanging. The properties of the kimberlite can be altered by the type of cation/s present, because each cation has unique properties. One method used to indicate the extent of swelling taking place is the XRD interlayer spacing (see section 2.3.1.1.2), which is simply the d value of the smectite 001 peak on a XRD scan. An interlayer spacing below 10 Å is associated with 0 water layers, 12.6 Å with 1 water layer, 15.6 Å with 2 layers, 18.6 Å with 3 layers, 21.6 Å with 4 layers and above that with more water layers (Tessier *et al*, 2004). Ferrage *et al* (2005) show that the interlayer spacing under ambient conditions (approximately 25 °C and 35 % relative humidity) are very similar and rarely above two water layers. This study showed that the interlayer spacing of montmorillonite is correlated with the ionic potential of the cations (the effective cation radius and charge). This is investigated in section 6.6.

- *CATIONS THAT SWELL CLAY INTERLAYERS*

Absorption and desorption studies on the Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+} montmorillonite exchanged forms by Cases *et al* (1997) have shown that these cations have a swelling effect on montmorillonite. Other studies on Na^+, Ca^{2+} and Mg^{2+} exchanged swelling clays confirm the swelling capability of these cations. (Rytwo *et al*, 1996; Badreddine *et al*, 2002; Prost, 1981). Ferrage *et al* (2005) shows that for room temperature the relative humidity around 35% results in primarily 2 water layer spacings for Mg^{2+} and Ca^{2+}. Na^+ and Li^+ on the other hand will display primarily 1 water layer spacing, and K^+ predominantly 0 water layers.

- *CATIONS THAT COLLAPSE SWELLING CLAY INTERLAYERS*

Collapsing the interlayer of swelling clays has been shown to be possible with NH_4^+, Cs^+, K^+, Rb^+ (Czimerova *et al*, 2004). K^+, Cs^+ and Rb^+ clays were also investigated by Badreddine *et al* (2002). Grim (1968) show that vermiculite saturated with K^+, NH_4^+, Rb^+ and Cs^+ showed no expansion of the lattice. The selectivity of potassium in montmorillonite was studied by Carson and Dixon (1972). These cations are unique in their large ionic sizes K^+ (1.33 Å), NH_4^+ (1.43 Å), Cs^+ (1.69 Å).

The collapsing capability of potassium was studied by Malla and Douglas (1985). This study 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 with potassium. Ferrage *et al* (2005) showed that under ambient conditions K^+ exchanged montmorillonite results in predominantly 0 water layers. The possibility of slowing down weathering has merit within underground mines as it could be used to improve tunnel wall stability. This opportunity is discussed in section 7.2.

- *CATION EXCHANGE MECHANISM*

From literature it is also shown that cation exchange is influenced by a selectivity order which refers to the ease of replacing an existing cation in the interlayer spacing. Wu and Li (1998) show a selectivity order as follows: $Na^+ < K^+ < Cd^{2+} < Zn^{2+} < Mg^{2+} < Cu^{2+} < Ca^{2+} < Pb^{2+}$. Eberl (1980) include different cations and show a selectivity order of: $H^+ < Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$. The selectivity order of Wu and Li (1998) suggests that if the interlayer is collapsed by potassium, the potassium could easily be replaced by magnesium or calcium if available and energetically favourable. Grim (1968) show the replacement order of Ba saturated clays: $Li^+ < Na^+ < NH_4^+ < K^+ < Mg^{2+} < Rb^+ < Ca^{2+}$. The selectivity order is however determined by the type of smectite or vermiculite, the layer charge and also the type of replaceable cations.

Anderson *et al* (1989) suggest that cation selectivities are determined by the cation valence, hydrated radii, hydration energies and polarizability. The cation valence and hydrated radii has been combined in what is called the ionic potential (z/r_{eff}) as used by Ferrage *et al* (2005) to model the XRD interlayer spacing. The ionic potential is investigated further in section 6.2.5.

Cation exchange data can be expressed by the selectivity coefficient K_N also referred to as the cation exchange constant. Bruggenwert and Kamphorst (1982) report the cation exchange data as follows (equation 28):

$$K_N = \frac{N_B^{1/z_B}}{N_A^{1/z_A}} \frac{c_A^{1/z_A}}{c_B^{1/z_B}} \tag{28}$$

where N_i is the equivalent fraction adsorbed in the clay, c_i is the concentration in the solution, and z_i is the valence of cation *i*. *A* is the cation in the clay at the start of the reaction, and *B* is the exchanging cation.

For cations of equal valence (e.g. exchange of Na^+ in the clay with K^+ in the solution), the equation shows that there will be a preference for the exchanging cation (i.e. $c_A/c_B > N_A/N_B$) if $K_N>1$ (i.e. $\ln K_N > 0$).

For the exchange of cations where the valence is not equal, the situation is not so simple (because of the exponent 1/*z* in the equilibrium constant expression). In that case, the ratio c_A/c_B is given by:

$$\frac{c_A}{c_B} = K_N^{z_A} \frac{N_B^{z_A/z_B}}{N_A} c_B^{(z_A/z_B - 1)} \tag{29}$$

The "preference" of the clay for cation *B* hence depends on its concentration in the solution, and also the degree of loading of *B* onto the clay (N_B).

If one takes the arbitrary situation of $N_B=N_A=0.5$, we then find:

$$\frac{c_A}{c_B} = K_N^{z_A} \left(0.5 c_B\right)^{(z_A/z_B - 1)} \tag{30}$$

Hence $c_A/c_B>1$ if:

$$K_N\left(0.5c_B\right)^{(1/z_B-1/z_A)}>1 \tag{31}$$

The data from Bruggenwert and Kamphorst (1982) is compared with experimental work in section 6.5.

From studies on cation exchange it seems that the absorption mechanism differs for different cations. Strawn *et al* (2004) showed that copper tends to adsorb not only on the interlayer but also sorb on aluminol function groups. Adsorption at positions other than the interlayer – such as crystal edges - has also been shown true for Li^+ (Anderson *et al*, 1989) and Fe^{2+} (Hofstetter *et al*, 2003). On the other hand trivalent cations especially Al^{3+} and Fe^{3+} tend to form hydroxy species in the clay interlayer as utilised in pillared clay formation (Belver *et al*, 2004; Newman, 1987). It is clear that cation exchange in clays does not follow a simple mechanism but is rather unique for different clays, different cations and different environments.

4. PROBLEM STATEMENT

The main hypothesis states that the swelling clays present in the ore will determine whether a kimberlite will be prone to weathering. The reason is that the swelling action generates internal pressure and causes rapid breakdown of the material. The idea originated from initial observations on the Koffiefontein ore sample, which showed rapid breakdown in seconds compared to Wesselton ore, which could not be weathered under any reasonable conditions. The main difference between these ores was their swelling clay content; Koffiefontein contains ~ 50 – 60 % smectite compared to none detected in Wesselton. Smectite is the main swelling clay group present in kimberlite ores, being sub-classified as principally montmorillonite, nontronite and saponite. Swelling clays also allow for extensive cation exchange, which can enhance and accelerate the weathering process.

The driving force behind the exchange of cations was explained by Madsen and Müller-Vonmoos (1989). As discussed, clay minerals are part of the phyllosilicate group (layered silicates) and consist of SiO_4^{4-} tetrahedra and octahedra. In the tetrahedral arrangement a trioctahedral cation (e.g. Fe^{3+} or Al^{3+}) can replace Si^{4+} and cause negatively charged layers. The octahedral layers consist of six oxygens or six hydroxyl ions and are linked with the other layers by sharing the octahedral edges resulting in a –2 negative charge. These negatively charged layers cause the incorporation of an interlayer of cations between two negatively charged surfaces bonded by coulombic forces. Upon water contact the cations become hydrated (some cations have a higher tendency towards hydration than others), incorporate water into the structure and cause widening of the interlayer. This mechanism causes the breakdown during weathering but also allows for enhanced and accelerated weathering by exchanging some of the existing cations with more ‘aggressive’ cations. This study suggests that the effect of a cation is determined by its valence and effective ionic radius, also called the ionic potential as discussed by Ferrage *et al* (2005), although other factors such as the type of clay, layer charge and absorption properties also influence the clay behaviour. This is discussed further in section 6.2.5.2.

The property of ores to exchange cations is reported as the CEC (cation exchange capacity) and is an inherent property of each ore. This property was found to complement the swelling clay hypothesis as ores with a high CEC show high weathering and ores with a very low CEC show no signs of degradation.

In summary the hypothesis is that a kimberlite is rendered weatherable if swelling clay is present in the ore. The rate of weathering will depend on the amount of swelling clay present and the type of cations present in the ore and in the weathering medium, as these will determine the extent of swelling, the cation adsorption mechanism and rate of cation exchange. The effect of different cations on weathering behaviour is investigated in this study to aim at defining this exchange process better for kimberlite.

5. EXPERIMENTAL PROCEDURE

Thirteen different types of kimberlite samples were received and labelled according to their origin. These samples were Geluk Wes (Tuffisitic Wesselton ore), Koffiefontein, Wesselton (Hypabyssal kimberlite ore), Cullinan TKB (Tuffisitic Kimberlite Breccia), Dutoitspan and eight samples from Venetia named: K1 Hypabyssal North East, K1 Hypabyssal South, K1 TKB East, K2 South, K2 West, K2 North East, K8 and Red Kimberlite. See figure 2 for a map of the South African De Beers mines. For more information on Venetia kimberlites see Doorgapershad *et al* (2003).

These ores were in the nominal size range of 50 – 100 mm. The ore was subsequently crushed in a laboratory jaw crusher to – 26 mm. The sample sizes ranged from 80 – 300 kg per sample.

5.1 Mineralogy

Ore in the – 9 + 8 mm size fraction was riffled to a ± 500 g sample and milled fine in a swingmill to around 50 μm for XRF and XRD analysis.

5.1.1 XRF ANALYSIS

XRF analysis was done at Mintek Analytical Services, South Africa. They use a X-lab 2000 instrument by Spectro. All the samples were analysed as powder briquettes. The briquettes were made with a wax binder and pressed under 10 tons of pressure. Except for milling in a WC bowl on rare occasions, the samples were analysed as received.

5.1.2 XRD ANALYSIS

The theory behind XRD analysis is discussed in section 2.3.1.1.2. It was mentioned that clay minerals can produce overlapping peaks on the XRD scan and therefore can require more work for accurate analysis. Therefore, the sub-treatment of clay minerals as discussed in this section was used in some cases to obtain more accurate results. To ensure the validity of the results, the samples were analysed at three different institutions as discussed below.

Agricultural Research Council

ARC (Agricultural Research Council) uses a Philips 1840 XRD instrument with a Co lamp over a range of 2 – 45 ° 2θ. Their procedure involves the removal of the –2 μm fraction and performing clay treatments on this fraction. The clay treatments involve glycol, glycerol and thermal treatments followed by the XRD scan. The % of -2 μm material is also determined by particle settling. An air-dry scan of the total sample was also done compared to other work only on the clay fraction.

One drawback of this procedure is that the clay minerals are not accurately determined on the whole sample. The typical sub -2 micron fraction of these kimberlite samples is less than 30 %, so the clay XRD analysis could not represent the total mineralogy of the ore. Mineral identification results showed incorrect identification of minerals on some samples especially on overlapping clays e.g. smectite and chlorite both with lattice spacings at 14 Å. All De Beers' samples had previously been analysed at ARC and it is suggested that their procedure should be re-evaluated.

University of Pretoria

University of Pretoria XRD analysis was done on a Siemens D501 instrument utilising a copper lamp and a 4 – 70 ° 2θ range. The other specifications are given in Appendix A. The treatment of the sample included an air-dry, glycol and temperature treatment on selected samples. For quantification purposes the software program Topaz was used.

Mintek

Mintek XRD analysis is done on a Siemens D500 instrument with a Cu lamp and a 5 – 80 ° 2θ range. The other specifications on the instrument are given in Appendix A.

The kimberlite samples as received were milled for ten minutes in a McCrone micronizing mill with the purpose to reduce all mineral particles to a relatively small size (~ 50 μm). Size differences may have an influence on the XRD peak intensities of the different mineral components of this rock type. The samples were also side-mounted to minimise the effect of preferred orientation (Moore and Reynolds, 1989).

From the micronized material three representative sub-fractions were obtained for the following purposes:

1] XRD on the first fraction was done on the material after micronizing and labelled "untreated".

2] The second fraction was treated with ethylene glycol — this is used as an auxiliary treatment to expand swelling clays if present. Swelling clays include smectites (e.g. montmorillonite, nontronite), and some mixed-layer clays, and vermiculite. The sample was directly loaded into the XRD sample holder and placed in a desiccator where it was exposed to ethylene glycol fumes for 12 hours at 60°C. Thereafter XRD analysis was carried out on the sample.

3] The third fraction was loaded into a porcelain crucible and heated for 2 hours in a muffle furnace at 550°C in air. XRD analysis was carried out on the product. This was followed by a consecutive session of another two hours heat treatment under the same conditions and XRD analysis repeated.

In the untreated XRD scan the mineral groups / minerals were identified. Certain minerals could only be identified with certainty within the broad basis of their mineral groups (e.g. smectite, mica, chlorite, amphibole, and pyroxene), while other minerals could be identified with certainty (e.g. talc and quartz). The mineral species identified in the untreated sample and their measured 2θ and d-values are presented in table 13. Table 14 contains the literature 2θ and d-values of these minerals (Bühmann, 1998; Moore and Reynolds, 1989). The measured d spacings of the minerals compare well with literature, although the smectite d value falls within a range depending on the type of interlayer cations (dioctahedral vs. trioctahedral) and the swelling condition. For this reason the sample was glycolated and the scan repeated. The expected changes in diffraction characteristics of smectite and chlorite upon glycolation and heat treatment are given in table 15.

Table 13. Minerals identified by X-ray diffraction in the Cullinan TKB sample.

Mineral name (Mineral group name and probable identity)	Formula	d-values (Å) of most prominent peaks (range 3 – 30° 2θ)	2θ values of most prominent peaks (degrees 2θ)	Symbol used
CHLORITE (Clinochlore)	$Mg_5Al(Si_3Al)O_{10}(OH)_8$	14.1 7.2 4.8 3.6	6.3 12.3 18.5 24.7	C
Smectite	$(NaCaK)(MgAl_2Si_4O_{10})(OH)_2{\cdot}nH_2O$	14.1 12.3	6.3 7.2	S
MICA (Phlogopite ?)	$KMg_3Al\ Si_3O_{10}(OH)_2$	10.1	8.8	M
Talc	$Mg_3Si_4O_{10}(OH)_2$	9.3	9.5	T
AMPHIBOLE (Tremolite)	$Ca_2\ Mg\ _5Si_8O_{22}(OH)_2$	8.4 3.2	10.5 27.9	A
PYROXENE (Diopside)	$Ca(Mg,Al)(Si,Al)_2O_6$	3.0	29.8	P
Quartz	SiO_2	3.3	27.0	Q

Table 14. Literature information on minerals in the Cullinan TKB sample in the 3 - 30 ° 2θ range.

Mineral name (Mineral group name and probable identity)	Formula	d-values (Å) of most prominent peaks (range 3 – 30° 2θ)	2θ values of most prominent peaks (degrees 2θ)	Symbol used
CHLORITE (Clinochlore)	$Mg_5Al(Si_3Al)O_{10}(OH)_8$	14.1 7.1 4.6 3.6	6.3 12.5 19.3 24.7	C
Smectite	$(NaCaK)(MgAl_2Si_4O_{10})(OH)_2{\cdot}nH_2O$	13 - 18	6.8 – 4.9	S
MICA (Phlogopite ?)	$KMg_3Al\ Si_3O_{10}(OH)_2$	10.1	8.8	M
Talc	$Mg_3Si_4O_{10}(OH)_2$	9.3	9.5	T
AMPHIBOLE (Tremolite)	$Ca_2Mg\ _5Si_8O_{22}(OH)_2$	8.4 3.2	10.5 27.9	A
PYROXENE (Diopside)	$Ca(Mg,Al)(Si,Al)_2O_6$	3.0	29.8	P
Quartz	SiO_2	3.3	27.0	Q

Table 15. Changes recorded in diffraction characteristics of untreated and treated clay minerals. Numbers in the table refer to d-spacings in Å.

Clay mineral	Peak position at specific d-value and effect of treatment			
	Untreated	Ethylene glycol	2h heat treatment	4h heat treatment
CHLORITE (Clinochlore)	14.1 7.2 4.8 3.6	14.1 7.2 4.8 3.6	14.1 increases in RPH* 7.2 4.8 and 3.6 decrease in RPH*	14.1 increase further in RPH* 4.8 and 3.6 collapse
SMECTITE (Swelling clay)	14.1 12.3	~ 16.5	-	~ 10 Å

* RPH - Relative peak height

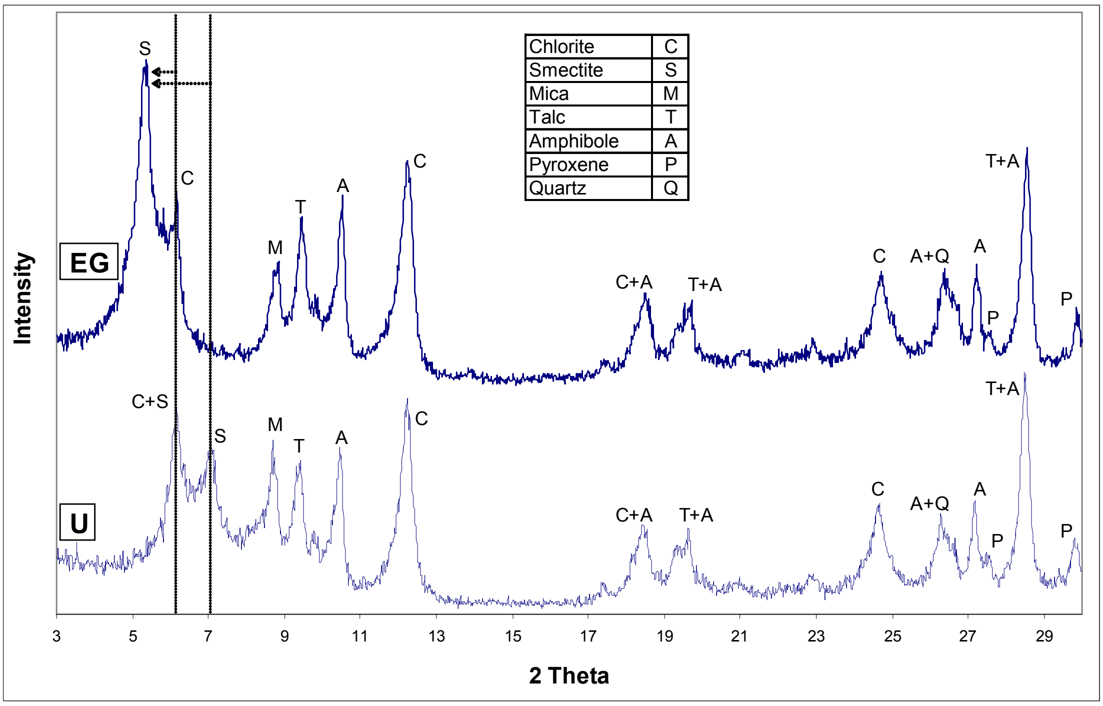

Figure 15. XRD scans of untreated (U) and ethylene glycol treated Cullinan TKB (EG), displaying the peak shift that characterizes smectite (swelling clay).

Figure 15 illustrates a peak shift after ethylene glycol treatment from 14.1 to 16.5 Å (with 2θ changing from 6.3° to 5.3°) and 12.3 to 16.5 Å (with 2θ changing from 7.2 to 5.3°), indicating the presence of a swelling clay (see table 16). For this study it was assumed that smectite as the swelling clay, as Cullinan brown or Type 2 TKB has been shown to be primarily saponite rich (Bartlett, 1994). The presence of two peaks could indicate the presence of two different types of smectite or otherwise two different swelling conditions. The peak at 12.3 Å (untreated sample) indicates the smectite has a monolayer of H_2O. More information, especially on the chemical composition of the clays, could be useful for a positive identification.

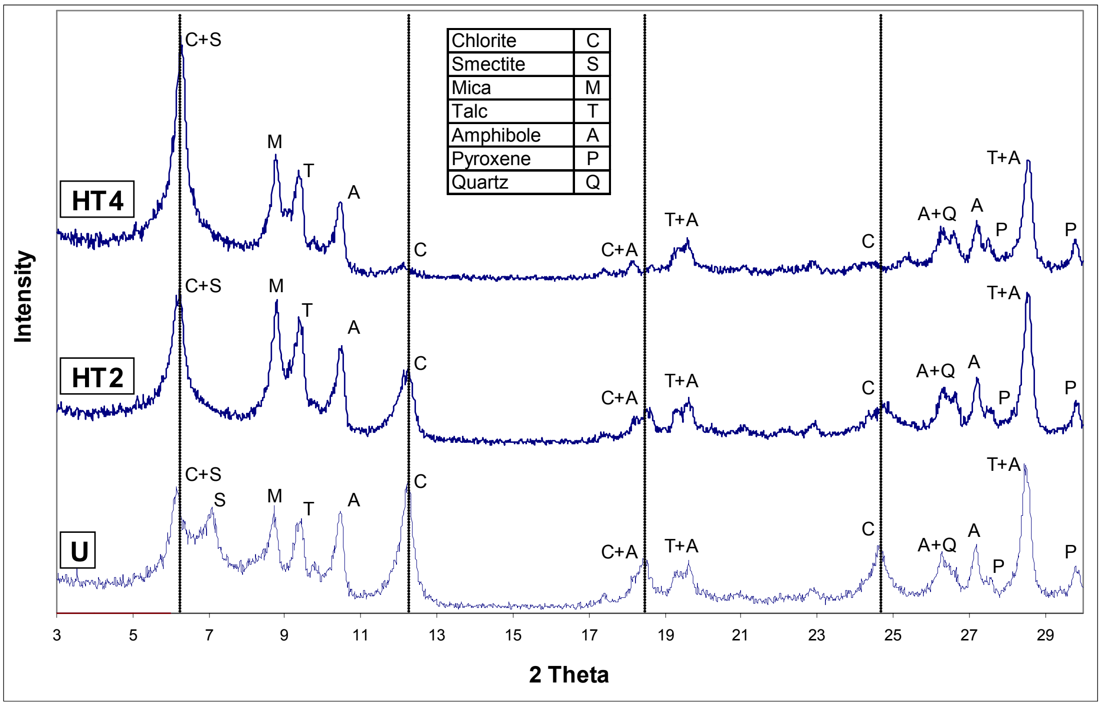

Figure 16. XRD-scans of Cullinan TKB for untreated (U), two-hour (HT2), and four-hour heat-treated (HT4) samples, displaying the effect on chlorite peaks (550 °C heat treatment temperature).

Chlorite was positively identified on the basis of the 14.1 Å (2θ=6.3°) and 7.2 Å (2θ=12.3°) peaks (figure 15), but not the specific mineral. The peak at 14.1 Å is positioned within a larger broad-based peak with uncertain identification. After the four-hour heat treatment, the 14.1 Å peak had increased in size whereas the other peaks collapsed (shown in figure 16). Table 15 summarizes the observed changes in diffraction characteristics of clay minerals. Note that the smectite peak at 12.3 Å (2θ = 7.2°) also collapsed after the heat treatment. It is however possible that the heat treatment caused a structural change (loss of interlayer water) and could result in this behaviour.

During the experimental work it also became evident that the time allowed for the heat treatment is significant, as shown in figure 16. With the two hour heat treatment the chlorite peak at 14.1 Å increased in relative intensity while all the other chlorite peaks diminished to approximately half of their original size. With the four-hour heat treatment the 14.1 Å peak increased further in size while the other chlorite peaks disappeared, as expected. In addition to the changes to the clay minerals the mica and talc peaks also appeared to be affected by the heat treatment. This can possibly be explained by an increase in crystallinity of these two mineral species after heating.

A summary of the experimental d-values (measured at maximum peak height) as well as reference d-values (Thorez, 1975) obtained for smectite and chlorite with treatments is presented in tables 16 and 17. (The d-spacing scale in the table is only approximate).

Table 16. Basal spacings (Å) for smectite minerals.

Condition / treatment	Individual d-values measured experimentally or referred to in literature				
Air dried - experimental			14.2		12.3
Air dried – reference*					
Ethylene Glycol treated - experimental	16.5				
Ethylene Glycol treated - reference	17				
d-spacing scale	←17	←16	←15	←14	←13

* Depending on the type of smectite the d value can fall anywhere within this range

Table 17. d- spacings (Å) for chlorite minerals.

Condition / treatment	Individual d-values measured experimentally or referred to in literature											
Air dried - experimental	14.1							7.2			4.8	3.6
Air dried - reference	14.1							7.1			4.8	3.5
Ethylene Glycol treated -experimental	14.1							7.2			4.8	3.6
Heat-treated - reference	14.1							—			—	—
d-spacing scale	←15	←14	←13	←12	←11	←10	←9	←8	←7	←6	←5	←4

Clay minerals generally give intrinsically broad lines (peaks) because of small scattering domains, structural disorder, mixed layering, or some combination of these factors. Smectite minerals occur only as extremely small particles so that detailed diffraction data are difficult to obtain. The d-values as presented in the tables 16 and 17 were given at maximum peak value to be compared with data from literature. From this data saponite appears to be the best general fit when individual smectite minerals are considered to match the XRD-data. The basal peaks are broad and the d-values for certain saponite peaks (width at half height) are given in table 18. A more definitive chemical composition of the clay minerals in the Cullinan TKB could be very informative to make a more precise mineral identification. Electron microprobe determinations on these clay minerals could be very useful but it could also be difficult to locate a suitable specimen for analysis due to the small size of clay minerals in general.

Table 18. d-value ranges for saponite after treatment (Thorez, 1975)

Smectite mineral	d-value range of basal reflection	Remarks
Saponite (13-0086)	17.5 to 15.5 Å	After EG-treatment
Saponite (13-0086)	14.5 to ~ 10 Å	After heat treatment

Comparison of XRD results from the three different institutions on Cullinan TKB is shown in table 19. The work by the University of Pretoria compares well with the results obtained by Mintek as the mineral groups and specific minerals identified correlate well. It is however a concern that the quantities are expressed as accurate numbers when in fact the error range is around 10 %. However, the semi-quantitative results also compare well with the work by Mintek. The only concern is the absence of serpentine from the University of Pretoria results. Mineral identification by Agricultural Research Council shows correlation with the other institutions but the quantitative results do not correlate with their results. Reporting of 50 % quartz in this sample shows the extent of errors that can occur during mineralogical characterization if critical evaluation of results is neglected. However, the presence of xenoliths and poor sampling techniques can cause misleading results. The point is that results like these should be cautiously evaluated and re-analysed.

The final results of Mintek were used although these were compared with the minerals identified at the University of Pretoria to ensure accurate peak identification. The results from Mintek were used as the mineralogist who did the interpretation was readily available and spent hours to ensure the quality of results. The mineralogist at the University of Pretoria did not have the time to discuss and continually work on the results. Mintek also provided semi-quantitative results using the combined methods of peak ratios and Topaz software. These results on all the kimberlites tested are given later in tables 21 and 22 (section 6.1.2).

Table 19. Comparison of XRD results from three different institutions, Mintek, Agricultural Research Council and University of Pretoria.

Mintek		Agricultural Research Council		University of Pretoria	
Mineral name (Mineral group name and probable identity)	Quantity	Mineral name (Mineral group name and probable identity)	Quantity	Mineral name (Mineral group name and probable identity)	Quantity
Chlorite (Clinochlore)	> 20	Quartz	50	Chlorite	34
Swelling Clay	10 - 20	Serpentine	16	Talc	16
Mica (Annite)	5 - 10	Smectite	11	Smectite (Montmorillonite)	13
Talc	10 - 20	Amphibole	9	Amphibole (Tremolite)	11
Amphibole (Tremolite)	10 - 15	Talc	8	Mica	8
Serpentine (Antigorite)	10 - 15	Mica	6	Quartz	6
Olivine (Forsterite)	< 10			Pyroxene	5
Pyroxene (Diopside)	~ 5			Dolomite	3
Magnetite	< 10			Calcite	2
Quartz	< 5			Orthoclase	1
Dolomite	< 5				

These results highlight the importance to evaluate mineralogical results critically and to ensure that interpretation is done by an experienced and professional individual or institution. In kimberlite the overlapping peaks of swelling clay and chlorites require further work to distinguish the one from the other (as shown in figures 15 and 16). The presence of quartz in predominance is very unlikely and should be further investigated if reported as such. Preferred orientation is a concern with clay rich samples, therefore micronizing of the sample is suggested. Preparation of the sample is very important e.g. the milling procedure and type of mounting used (see Schoen *et al*, 1973). Comparing the mineralogy and weathering behaviour could also show possible errors in mineralogical characterization, for example a hypabyssal kimberlite consisting mostly of minerals like mica, calcite and serpentine should not show any signs of degradation during weathering. Incorrect sampling could also cause unreliable results.

5.2 Weathering tests and conditions

5.2.1 Standard test

The kimberlite samples tested were all crushed in a laboratory jaw crusher to a size of –26.5 mm. The material was then screened into size fractions of –26.5 + 22.4, -22.4 + 19, -19 + 16, -16 + 13.2, -13.2 + 11.2, -11.2 + 9, – 9 + 8, -8 + 5.4 and –5.4 mm. Tests were done in size fractions so that if the size of the particles played a role in the weathering the effect could be eliminated. For the standard test 1.5 kg of the –26 + 22.4, -22.4 + 19 or –19 + 16 mm material was weathered in distilled water (pH 5.5) by immersion for 6 days and in some cases up to 15 days. Tests were performed at room temperature in 10 L flat bottomed plastic containers using 5 L solution. The particles were spread as a single layer, not touching. No dispersion took place. This was compared to the 0 days test which was a 1.5 kg sample that was milled in the unweathered state. The weathered samples were removed from the water after the specific weathering period and left to air dry for 1 day. The fine particles were filtered from the solution and added to the weathered sample after milling. The autogeneous batch mill test was used on the weathered sample. This involved autogeneous dry milling of the ore sample for 10 minutes in a 30 cm inner diameter, 30 cm in length stainless steel, rubber lined lab mill at around 60 rpm. The ore was subsequently removed from the mill and sized. The laboratory mill did not have lifter bars, unlike the autogeneous mill test discussed in the literature study. The weathering tests were performed in close proximity to the laboratory mill so that handling of the ore could be minimised. Some of the later test work did not utilise milling, as the degree of weathering was substantial enough and the size distribution after drying the sample was simply used as the output.

Sieving to determine the particle size distribution was done dry with manual shaking, utilising a single sieve at a time. The particle size distribution curves were plotted using the arithmetic mean sieve size and not the upper size limit as is the convention.

The other variables tested were:

- Time dependence of weathering
- Effect of cation species on weathering
- Effect of cation concentration on weathering
- Effect of temperature on the weathering process
- The influence of particle size
- The influence of anions

5.2.2 Koffiefontein

The standard test (6 or 15 days' weathering) was attempted on Koffiefontein ore but due to an inherently fast weathering rate, complete disintegration of the ore occurred and it could not be compared with the other samples. Instead a –26.5 + 22.4 mm sample was weathered for 1 and 3 hours to obtain results on the weathering rate.

5.2.3 Wesselton

On the Wesselton ore almost no weathering took place with the standard test utilising – 19 + 16 mm ore weathered for 6 and 15 days. More severe test conditions included immersion in acidified water at a pH ~ 3. The solution was prepared by adding sulphuric acid to the distilled water. A sodium chloride solution was also used for weathering tests at a concentration of 0.2 M. Cyclic wetting tests were performed by wetting the ore daily with 500 ml of distilled water. After further test results showed copper to be a very good accelerator for weatherable kimberlite, this was also used as a weathering solution at a concentration of 0.2 M, to test whether this ore maintains its non-weatherability under all the tested conditions. These weathering tests were done on – 26.5 + 22.4 mm particles for 6 days.

5.2.4 Cullinan TKB

The standard test was performed on Cullinan TKB utilising – 19 + 16 mm particles and further testing included using a sodium chloride solution (0.2 M).

5.2.5 Geluk Wes

The standard water test was done on the –19 + 16 mm fraction for 0 and 15 days. Further test work was done on the –22 + 19 mm fraction in sodium-, aluminium- and lithium-chloride solutions (all at 0.2 M concentration) for 6 days. This was done to test the effect of cations on the weathering process. It was specifically tested on this ore because although it has a slow weathering rate in water it does contain swelling clays and is therefore amenable to accelerated weathering by cations. A single test was done to test the effect of low pH (pH ~ 2.5) and cations by adding sulphuric acid to a sodium chloride solution. These tests showed interesting results. Due to limited availability of Geluk Wes ore, the effect of cations was then further investigated on the Dutoitspan sample.

5.2.6 Dutoitspan

The Dutoitspan sample was a large ore sample allowing more tests, specifically on the accelerated weathering of kimberlite by cations.

The standard test was performed on a 1.5 kg, – 26.5 + 22.4 mm sample for 6 days.

5.2.6.1 Influence of Mono-, Di- and Trivalent cations on weathering

This ore was used to finalise the test work to determine the effect of cations on an ore which is known to be weatherable. For monovalent cations the effect of lithium, sodium, potassium and ammonium on the weatherability was tested. Divalent cations included cupric, calcium, magnesium and ferrous. In the trivalent cation group the tests included aluminium and ferric. All these tests were done at 0.4 M cation concentration with kimberlite particles in the -26.5 + 22.4 mm size fraction.

5.2.6.2 Time dependence of weathering

Tests were done on 1.5 kg -26.5 + 22.4 mm Dutoitspan kimberlite samples in a 0.2 M magnesium chloride solution at 2, 6 and 15 days.

The tests were repeated in a 0.2 M copper sulphate solution for 6, 12, 24 and 144 hours, thus up to 6 days.

Another test with a copper sulphate solution was conducted at 0.5 M utilising 200 - 250 g of - 16 + 13.2 mm Dutoitspan kimberlite. This test was done at 4, 8, 24, 48, 168 hours (7 days), 360 hours (15 days) and 720 hours (30 days) to evaluate equilibrium conditions.

5.2.6.3 Influence of cation concentration on weathering

The effect of concentration of cations was tested in a copper solution as this was the most aggressive cation from the previous test work. Test work was done at 0.005, 0.025, 0.05, 0.1, 0.2 and 0.4 M concentrations for 6 days utilising particles sized – 26.5 + 22.4 mm.

5.2.6.4 Influence of temperature on weathering

Temperature tests were done to investigate the mechanism of cation weathering. The tests were performed in a water bath, which allows for temperature regulation. Containers with the ore spread out in the weathering media were placed in the bath and covered to limit the loss of water by evaporation. These tests were done on a 1.5 kg (size fraction – 19 + 16 mm) ore sample weathered in a distilled water and 0.2 M $MgCl_2$ solution at 40 °C for 6 days. The results were compared to room temperature tests.

5.2.6.5 Influence of anions on weathering

The influence of the type of anion was tested by comparing a 0.3 M cupric chloride and cupric sulphate solution weathered for 6 days using a 1.5 kg -26.5 + 22.4 mm sample.

5.2.6.6 Influence of particle size on weathering

The effect of particle size was tested with – 26.5 + 22.4, - 22.4 + 19, - 19 + 16 and - 16 + 13.2 mm size fractions in a 0.2 M $MgCl_2$ solution for 6 days. Magnesium chloride was chosen as the weathering medium because the test work on the influence of cations showed it to be a medium strength accelerator of the weathering process. Therefore the extent of weathering is limited and would enable clear determination of the effect of particle size on weathering.

5.2.6.7 Influence of milling on weathering results

The influence of employing an autogeneous milling test after the weathering procedure was investigated. The weathering tests were done in a 0.2 M copper sulphate solution (- 26.5 +

22.4 mm) for 12 hours with one sample milled and compared to the particle size distribution of the unmilled sample.

5.2.6.8 The effect of a stabilising cation vs. swelling cation

The effect of a stabilising cation (potassium) vs. a swelling cation (copper) and their effect on weathering was investigated. The test utilised 200 - 250 g of Dutoitspan kimberlite (- 16 + 13.2 mm) weathered in a 0.5 M potassium solution for 8, 48 and 144 hours. The tests were repeated in a 0.5 M copper solution at 4, 8, 24, 48, 168 (7 days) and 360 hours (15 days).

5.2.7 Venetia

The Venetia ores were obtained to validate the weathering mechanism. This ore was received as big lumps (~ 20 – 30 cm) and in limited amounts. Smaller lumps were broken from the bigger pieces and crushed to obtain a workable sample. The final tests were conducted on a 1 kg sample of the – 26.5 + 19 mm size fraction. The weathering was done in a copper sulphate solution (concentration 0.05 M) for a six days weathering period.

Venetia samples were labelled according to their sample position in the Venetia pit and the type of ore (see Doorgapershad *et al*, 2003). These include K1 Hypabyssal North East (K1 HYP NE), K1 Hypabyssal South (K1 HYP S), K1 Tuffisitic Kimberlite Breccia East (K1 TKB E), K2 North East (K2 NE), K2 South (K2 S), K2 West (K2 W), Red Kimberlite and K8.

Because weathering was performed in a copper solution, which caused significant breakdown of the ore, the mechanical test was not required. Therefore the output is just reported as the size distribution after weathering (unmilled).

5.3 Repeatability of results

Triplicate tests were done on Dutoitspan kimberlite to investigate repeatability of the results. 300 g of kimberlite (-16 + 13 mm) was weathered at 0.025, 0.1 and 0.5 M copper concentration for 2 days and the typical error range established. No milling was performed of these samples.

5.4 Kinetic evaluation of cation exchange

In trying to understand the cation exchange mechanism, the kinetics of this exchange reaction was investigated. The experimental work utilised 300 g of Dutoitspan kimberlite (-16 + 13 mm) weathered in 0.025, 0.1 and 0.5 M cupric chloride solutions at room temperature (20 °C). Solution samples (~ 40 ml) were removed at 0, 4 hours, 24 hours, 48 hours, 72 hours, 168 hours (7 days), 360 hours (15 days) and 720 hours (30 days) for ICP analysis.

The kinetic test was repeated on a 300 g Venetia Red kimberlite sample (-16 + 13 mm) weathered in 0.1, 0.5 and 1 M potassium chloride solutions at room temperature (20 °C). Solution samples were removed at 0, 4 hours, 8 hours, 24 hours, 48 hours, 72 hours and 216 hours (9 days) for ICP analysis.

5.5 Cation exchange behaviour

Cation exchange behaviour was investigated utilising 15 g of finely milled Venetia Red kimberlite. The cation solutions were prepared with 200 ml distilled water adding cation sulphate or chloride salts at 0.05 M concentration. The cations utilised included K^+, Li^+, NH_4^+, Ca^{2+}, Mg^{2+}, Ni^{2+}, Fe^{2+}, Cu^{2+}, Fe^{3+} and Al^{3+}. The solutions were sent for ICP analysis after 48 hours.

5.6 Correlation between cation weathering and interlayer spacing (from XRD)

The smectite interlayer spacing was investigated as a function of time to relate the swelling of smectite with the kinetics. Tests utilised 250 - 300 g of -16 + 13 mm Dutoitspan kimberlite, weathered in a 0.5 M solution of cupric chloride for 4 hours, 8 hours, 24 hours (1 day), 168 hours (7 days) and 720 hours (30 days). The kimberlite was removed, air dried for one day, milled to powder and sent for XRD analysis.

The collapsing of the interlayer spacing was investigated utilising 250 – 300 g of – 16 + 13.2 mm Venetia Red kimberlite treated in a 1.5 M potassium chloride solution for 4 hours. The treated and untreated kimberlite was sent for XRD analysis.

The smectite interlayer spacing was investigated with different cation species at 0.5 M concentration weathered for 6 days utilising Dutoitspan kimberlite sized – 16 + 13.2 mm. The cations included Ca^{2+}, Mg^{2+}, Cu^{2+}, Al^{3+}, K^+, NH_4^+, Na^+ and Li^+.

5.7 Mechanical test

As stated in section 2.3.1.5 the autogeneous batch-milling test was chosen to quantify the reduced bulk strength. The laboratory mill used was a 30 cm inner diameter, 30 cm in length stainless steel, rubber lined mill (figure 17). This mill did not have lifter bars. All samples were milled for 10 minutes before being removed and sized. The milling speed was fixed at ~ 60 rpm. The material was subsequently screened and a product size distribution determined. The sieve size of the milled unweathered product is the base case (termed 0 days weathering) and compared to the weathered milled product after a specific treatment. The sieve series used can be seen in Appendix C.

The mechanical test was incorporated to simulate typical mechanical forces to which kimberlite ore particles might be exposed to under plant conditions during or after weathering. This includes transport e.g. conveyers, stockpiling, scrubbing etc.

With hindsight it is clear that the mechanical test after weathering might not be required under relatively aggressive weathering conditions. When small differences in weathering behaviour are investigated milling is a useful tool (e.g. for weathering in water or other slow weathering media). However in more aggressive media and with highly weatherable ore, the weathering can be so rapid that a simple sieve analysis of the weathered product, without milling, is sufficient to characterise weathering.

Figure 17. Autogeneous batch mill used.

5.8 Agglomeration test

In order to investigate the stickiness of the kimberlite ore (the extent to which the ore becomes “claylike” and sticks to objects) a possible test for evaluating this property was developed. The test was done by employing a laboratory swing mill (Figure 18). A 200 g dry ore sample (- 9 + 8 mm) was milled for 3 minutes. The sample added to the swing mill container is shown in figure 19. The powder that agglomerated on the grinding surfaces of the metal milling units inside the container and the side walls of the container itself (which could not be removed by light brushing) was then weighed and expressed as a percentage of the total initial mass. The mass of the outer metal ring is 1407.2 g and the inner ring is 1505.6 g.

Figure 18. Swing mill used for agglomeration tests.

Figure 19. Ore added to the swing mill container for the agglomeration test showing the grinding metal pieces inside the container.