1 BACKGROUND

1.1 Project Definition

Weathering in the context of this study refers to the rapid breakdown of kimberlite material with a specific mineralogy when exposed to water. Kimberlite weathering/degradation is often neglected in process design, plant operation, maintenance, modelling and simulation. This can have serious process implications, since some kimberlites can be totally reduced to fines within minutes of contact with water while others are not prone to weathering degradation at all. These distinctly different types of material influence many plant operations, including crushing, desliming, dense medium separation and settling. If the behaviour of kimberlite material can be anticipated it will allow for preventative measures in managing and controlling the treatment plant. Understanding of the kimberlite weathering mechanism also creates opportunities of accelerating the weathering process and possibly developing new processing options.

The project initiated by De Beers firstly aimed to define the mineralogy of kimberlite, especially the clay systems which are present in kimberlite. The study then focused on identifying the critical parameters in the weathering process. With this understanding, new work on accelerating the weathering process can be suggested and feasibility of such processes investigated. On the other hand, weathering of kimberlite poses risks underground due to unstable tunnels and the knowledge on the weathering mechanism might provide means of decelerating or preventing weathering.

1.2 Diamond Processing

A generalised flow sheet for diamond extraction is shown as figure 1 (Hodgson, 1981). It consists of two groups of techniques namely liberation and concentration. The processing starts with the run of mine ore being crushed in two or three stages of primary comminution. The material is then fed to a scrubbing section where the fine material (< 1mm) is washed off and removed by screening. The fine material is thickened and dumped as tailings with the water being recovered and recycled. The washed ore is usually sized by screening and sent for further treatment in these size fractions. The primary concentration is usually by dense medium separation and then final concentration typically occurs by grease tables followed by X-ray sorting machines. The waste material of the fines processing stream is dumped as tailings whereas the waste material from the coarse stream is usually re-crushed to ensure that smaller diamonds are liberated before discarding the material.

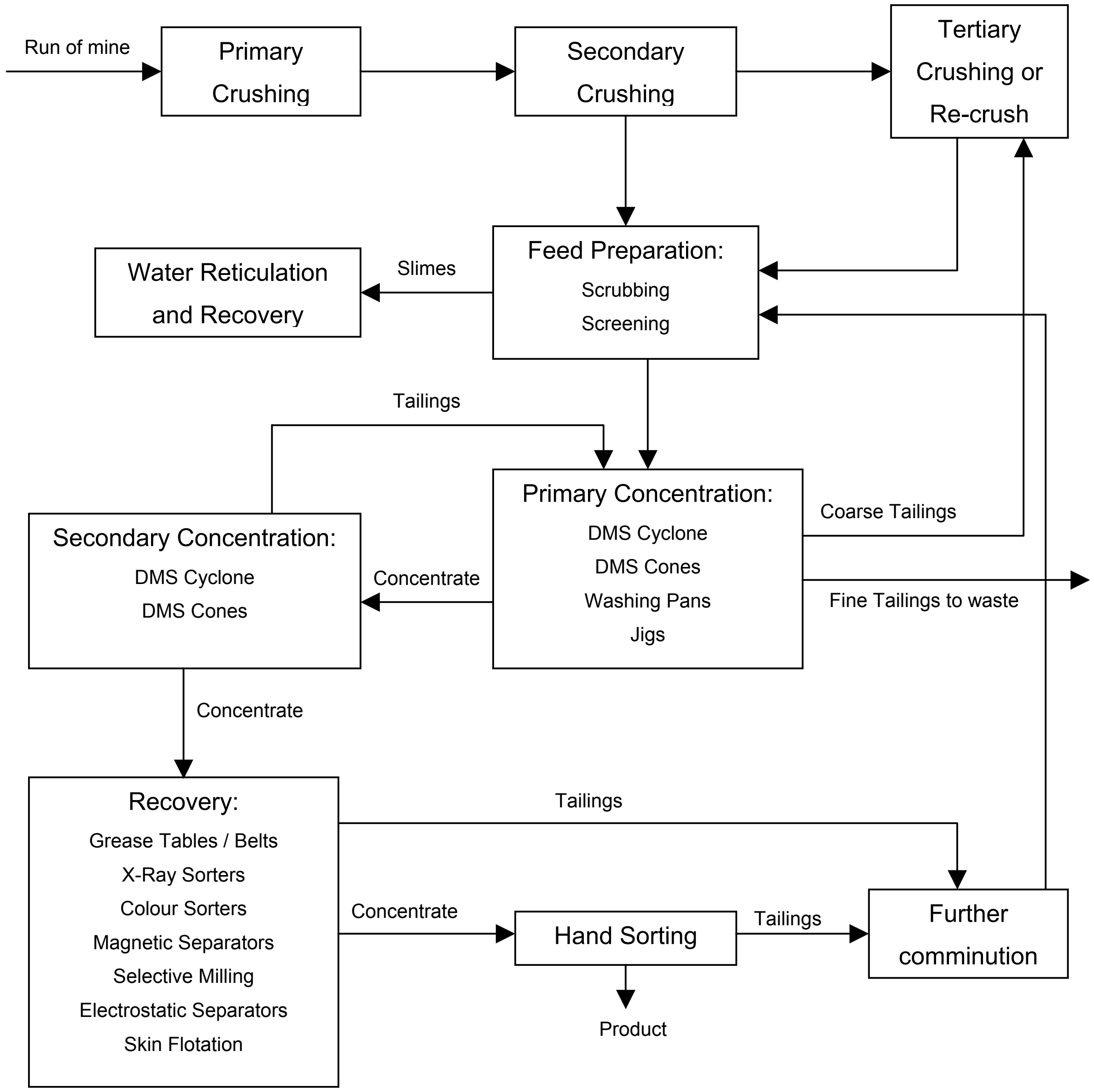

Figure 1. Generalised flowsheet for diamond extraction (Hodgson, 1981).

Weathering affects several aspects of diamond processing. Firstly because weathering causes decreased bulk strength the crushing requirement differs according to the mineralogy and state of weathering of the kimberlite. Therefore overcrushing of softer, more weathered material can occur and can also imply that diamond breakage can occur. Weathering on some ores can cause total failure with predominantly fine material as product. This increases the required capacity to handle slimes and influences the water regeneration and flocculation circuits. In terms of concentration, weathering can impact on the dense medium separation. There are also other implications for example the stockpiling and transport of material on conveyer belts can cause breakdown of ore after some weathering has taken place.

A map of the De Beers operations is shown in figure 2. It is shown here for reference, since kimberlite samples from different South African origins were tested.

Figure 2. De Beers Operations in Southern Africa (From the De Beers website: www.debeersgroup.com)

2 LITERATURE STUDY

2.1 KIMBERLITE MINERALOGY

The diamond bearing ore is referred to as kimberlite and is a rare type of volcanic rock. The kimberlite volcanoes are known as pipes due to their inverted-cone shape (Harlow, 1998). It is suggested that kimberlite pipes form by viscous magma travelling upward through cracks in the rock. The magma continues to dilate and fracture the crust whilst gases dissolved in the kimberlite dissociate from the matrix and expand, thus driving the magma and entrained rocks and diamonds up to the surface at ultrahigh velocities. The swirling fluid consisting of rock, mineral fragments and expanding gases breaks through the surface and forms the characteristic shape called a diatreme. At the top of the kimberlite pipe a crater zone is formed which is quickly stripped away by rain and weathering (Harlow, 1998).

Kimberlites are diverse and complex hybrid rocks consisting of crystals originating from mantle-derived xenoliths, the discrete nodule suite and primary phases crystallizing from the kimberlite magma as described by Mitchell (1986). These volatile rich (CO_2 predominantly) potassic ultrabasic igneous rocks can occur as small volcanic pipes, dykes and sills. Kimberlite is further defined by Mitchell (1986) as inequigranular alkalic peridotites containing rounded and corroded megacrysts, which can include olivine, phlogopite, magnesian ilmenite and pyrope. See table 1 for the chemical composition of these minerals. These macrocrysts (0.5 - 10 mm) are relatively large compared to the fine-grained groundmass and cause the inequigranular nature of kimberlites. These macrocrysts are set in a fine-grained matrix (groundmass) of second generation primary olivine and/or phlogopite together with serpentine, perovskite, calcite and/or dolomite (carbonates) and spinels. Other minerals include diopside, rutile, apatite, monticellite and nickeliferous sulphides. Weathering processes such as serpentization and carbonation commonly alters the early-formed matrix minerals as discussed under section 2.2. This causes replacement of early-formed olivine, phlogopite, monticellite and apatite by serpentine, calcite and chlorite as shown in figure 3. Highly weathered kimberlite can be composed of essentially calcite, serpentine, chlorite, smectite and magnetite together with minor phlogopite, apatite and perovskite. The changes in the crystal structure when clay minerals form, are discussed in section 2.2.5.

Clay minerals formed during the weathering process are classified under the phyllosilicates mineral group (see section 2.2.4.5) and consist of extended sheets of SiO_4^{4-} tetrahedra. The members of this mineralogical group are soft and flaky and have a relatively low specific gravity. Smectite (e.g. montmorillonite and saponite) and vermiculite are swelling clays commonly present in kimberlite. These clay minerals can generate internal pressures due to their swelling nature therefore decreasing the overall strength of the rock. The nature of clay minerals is discussed further in section 2.2.4.

Not all kimberlites contain diamond and if diamonds are present it is a very rare constituent at 5 - 140 carats per hundred tons (cpht) where 1 carat = 0.2 g (Wilson and Anhaeusser, 1998).

Mineralogical classification of kimberlites has been attempted by different authors and is reviewed below.

Wilson and Anhaeusser (1998) proposed classification into two groups. Group I is the olivine rich monticellite-serpentine-calcite kimberlites (< 5 % mica), which correspond to the basaltic kimberlites. Group II is the micaceous kimberlites (> 50 % mica) corresponding to the micaceous lamprophyric kimberlites.

Mitchell (1986) rather suggested three groups based upon the predominance of olivine, phlogopite and calcite e.g. kimberlite (equivalent to basaltic kimberlite), micaceous kimberlite (equivalent to lamprophyric kimberlite), and calcite or calcareous kimberlite.

Skinner and Clement (1979) derived five varieties of kimberlite based upon the predominance of diopside, monticellite, phlogopite, calcite and serpentine.

For this study the approach is to identify the mineralogy of kimberlites and relate it to the mechanism and rate of weathering in the simplest possible way. The mineralogy is therefore rather described in terms of the main mineral groups with little focus on subgroups, cation substitution ratios etc. The focus is also not on the lesser constituents of kimberlites (e.g. garnets, spinels etc.) and further reading, if required, is directed to the work of Mitchell (1986).

The mineral phases commonly present in kimberlites are discussed in the next section.

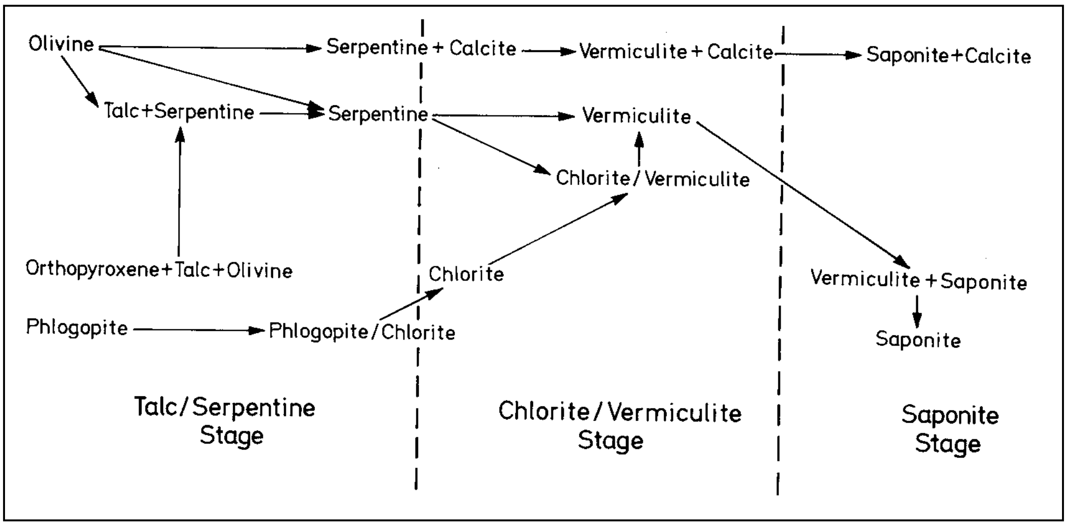

Figure 3. Schematic diagram showing the alteration of olivine, pyroxene and mica (Dawson, 1980).

Table 1. Kimberlite mineral phases (Composed from Klein and Hurlbut, 1993).

Mineral Name	G Specific Gravity	H Hardness	Composition	Comments
Apatite	3.15 - 3.2	5	$Ca_5(PO_4)_3(F,Cl,OH)$	-
Calcite	2.71	3	$CaCO_3$	-
Chlorite	2.6 – 3.3	2 – 2.5	$(Mg,Fe)_3(Si,Al)_4O_{10}(OH)_2\cdot(Mg,Fe)_3(OH)_6$	Green colour
Diopside	3.2	5 - 6	$CaMgSi_2O_6$	White to light green pyroxene
Dolomite	2.85	3.5 - 4	$CaMg(CO_3)_2$	-
Halloysite	2.0-2.2	1-2	$Al_2Si_2O_5(OH)_4\cdot 2H_2O$	
Ilmenite	4.7	5.5 - 6	$FeTiO_3$	-
Kaolinite	2.6	2	$Al_2Si_2O_5(OH)_4$	-
Magnetite	5.18	6	Fe_3O_4	Spinel group
Monticellite	3.2	5	$CaMgSiO_4$	Rare olivine alteration product
Montmorillonite	2.5	1 – 1.5	$(Al,Mg)_8(Si_4O_{10})_4(OH)_8\cdot 12H_2O$	Al rich - Smectite
Olivine	3.27 – 4.37	6.5 - 7	$(Mg,Fe)_2SiO_4$	Green ground-mass mineral
Perovskite	4.03	5.5	$CaTiO_3$	-
Phlogopite	2.86	2.5 - 3	$KMg_3(AlSi_3O_{10})(OH)_2$	Yellow brown Mica
Pyrope	3.58	7	$Mg_3Al_2Si_3O_{12}$	Garnet
Rutile	4.18 – 4.25	6 – 6.5	TiO_2	Reddish brown
Serpentine	2.3	3 - 5	$Mg_3Si_2O_5(OH)_4$	Green to yellow
Spinel	3.5 – 4.1	8	$MgAl_2O_4$	-
Talc	2.7 – 2.8	1	$Mg_3Si_4O_{10}(OH)_2$	-
Vermiculite	2.4	1.5	$(Mg,Ca)_{0.3}(Mg,Fe,Al)_{3.0}(Al,Si)_4O_{10}(OH)_4\cdot 8H_2O$	Altered (biotite) mica

2.1.1 Olivine

Olivine ($(Mg,Fe)_2SiO_4$) is originally the commonest and most characteristic mineral in kimberlite, according to Mitchell (1986). As groundmass constituent olivine occurs as single crystals smaller than 0.5 mm with the colour ranging from pale green to pale yellowish-brown with increasing iron (Mitchell, 1986). Magnesian ilmenite, chrome spinel and rutile can be present in some olivine groundmass as inclusions. Primary olivines richer in iron than Fo_{85} are not characteristic of kimberlites. Forsterite ("Fo") refers to the end member of olivine Mg_2SiO_4, thus Fo_{100} means no substitution of the Mg^{2+} by Fe^{2+} has occurred. Therefore in kimberlites the highest substitution of iron for magnesium in forsterite is 15 %, but is seldom this high.

Due to its high weatherability, olivine is commonly altered along margins and fractures to several varieties (pseudomorphs) of serpentine with or without magnetite (see figure 3). The formation of magnetite when olivine is weathered to serpentine is discussed in section 2.2.2.7. Secondary processes can locally form less prominent alteration minerals e.g. brucite, serpentine, chlorite, calcite, talc, pyrite and other clay minerals (Mitchell, 1986).

Megacrystal olivines, single crystals of 2 – 5 cm in diameter, are present in a few localities but are very rare. Macrocrystal olivines are 0.5 – 1 cm in diameter and occur as round to elliptical single crystals. The ratio of macrocrystal to groundmass olivines can vary widely. Macrocrysts (fragmented megacrysts) are commonly intergrown with enstatite, Cr-pyrope, ilmenite, diopside, chromite, phlogopite, Cu-Ni sulphides and rutile. Macrocrysts can commonly be identified by CO_2 fluid inclusions.

In this study very little olivine was identified suggesting that weathering has progressed past this point in these specific South African kimberlites.

2.1.2 Phlogopite / Micas

Phologopite ($KMg_3(AlSi_3O_{10})(OH)_2$) is a silvery bronze mineral consisting of single crystals around 5 mm – 10 cm in diameter. It is often replaced by calcite, chlorite and serpentine especially along cleavage planes. Micas are defined as the finer size fraction of phlogopite (- 5 mm). Micas are found in the groundmass as well as megacrysts / macrocrysts. Groundmass micas are usually 0.05 – 1 mm large rounded, corroded and distorted crystals. Intergrowth with diopside is found at an extremely fine grain size. Groundmass micas can contain inclusions of spinel and perovskite and can commonly be found within calcite-serpentine segregations. In some kimberlites megacrystal or macrocrystal micas can account for the bulk of the minerals present (> 50 %) and in other cases can be as low as 1%.

Dawson and Smith (1977) categorized South African micas into two types as given in table 2.

Table 2. The mica types present in South Africa according to Dawson and Smith (1977), (compositions are in mass percentage).

Mica Type	Mg / (Mg + Fe)	% Al_2O_3	% TiO_2
Type I (Fe rich)	0.45 - 0.65	14 - 16	3 - 6
Type II (Mg rich)	0.82 - 0.93	6.8 - 14.2	0.07 - 0.4

2.1.3 Serpentine

Serpentine ($Mg_3Si_2O_5(OH)_4$) can account for up to 50 % of the groundmass minerals. It is usually very fine grained and finely intergrown with other phases. Serpentine is usually classified according to different pseudomorphs of serpentine called lizardite, antigorite and chrysotile. These subgroups of serpentine have characteristic features of appearance e.g. antigorite is flaky and lamellar whilst chrysotile is fibrous. These subgroups of serpentine cannot be detected by conventional XRD due to the poor crystallinity of serpentine.

2.1.4 Monticellite

Monticellite ($CaMgSiO_4$) occurs as very fine particles (0.005 – 0.08 mm), from trace to 60 – 80 % of the groundmass of kimberlites. This mineral is very difficult to identify, as it is colourless and finely dispersed. It is very easily replaced by calcite in the weathering process, which could account for its absence in some kimberlites. The mineral is relatively pure in kimberlites (close to $CaMgSiO_4$ in composition) although in some cases a trend for solid solution towards forsterite (Mg_2SiO_4) can occur.

2.1.5 Perovskite

Perovskite ($CaTiO_3$) usually accounts for trace amounts up to 10 % in kimberlites. In rare occasions where perovskite and spinel have been concentrated in the kimberlite due to magmatic processes it can rise up to 25 %. The crystals range from 0.05 – 0.2 mm in size and can be scattered throughout the groundmass or concentrated together with spinel phases. The colour can range from yellow-brown through brown to reddish-brown. Perovskite in kimberlite is relatively pure $CaTiO_3$ and very little substitution takes place. Small amounts of rare earth elements (REE) can report in this mineral phase.

2.1.6 Carbonates (calcite and dolomite)

Calcite ($CaCO_3$) is the predominant carbonate in kimberlites and can report at trace levels to over 50 % in calcite rich kimberlites. It is usually pure with low MgO and FeO impurities. Dolomite is present as an accessory phase in small quantities. A few other carbonates can occur in minute quantities e.g. aragonite ($CaCO_3$) and strontianite ($SrCO_3$).

2.1.7 Chlorite

Chorite has been found in four parageneses according to Mitchell (1986):

1. *Replacing serpentinized olivine.* Olivines are initially transformed to serpentine, which is transformed to chlorite and ultimately to vermiculite as shown by figure 3.
2. *Discrete nodules of chlorite* are 1 – 4 cm in size and can be categorized according to the iron content into high, intermediate and low iron chlorites. In kimberlites it is typically the low iron chlorites that are predominant.
3. *Replacing phlogopites*. Chlorite readily replaces phlogopites along cleavage planes and grain boundaries. These chlorites vary from colourless to pale green to bright emerald green in highly weathered micaceous kimberlites.
4. *Primary groundmass chlorites* are identified by blue-green platelets of ~ 0.05 mm and are only found in calcite rich samples. It is very rare in phlogopite and serpentine rich kimberlites.

2.1.8 Clay minerals

A wide variety of clay minerals has been reported in kimberlites such as montmorillonite, halloysite, kaolinite, sepiolite, vermiculite, talc, saponite etc. (Mitchell, 1986). Classification of clay minerals is not consistent and differs from author to author. Predominant clay minerals in kimberlite are discussed further in section 2.2.5.

2.1.9 Spinel

Groundmass spinel (0.001 - 0.1 mm) can typically comprise 1 – 30 weight % of the kimberlite. The composition of most kimberlite spinels fall within the eight-component system: $MgCr_2O_4$ (magnesiochromite), $FeCr_2O_4$ (chromite), $MgAl_2O_4$ (spinel), $FeAl_2O_4$ (hercynite), Mg_2TiO_4 (maganoan ulvöspinel), Fe_2TiO_4 (ulvöspinel), $MgFe_2O_4$ (magnesioferrite), Fe_3O_4 (magnetite). For further information on the spinel groups the reader is referred to Mitchell (1986) for extensive coverage of these mineral phases.

2.1.10 Magnesian Ilmenite

Magnesian ilmenite is a solid solution combination of ilmenite ($FeTiO_3$) and geikielite ($MgTiO_3$). This mineral is relatively resistant to chemical and physical weathering and is easily recognizable by its bright metallic luster. It can account for trace to ~ 10 weight % of kimberlites. Some kimberlites e.g. Koffiefontein and Finsch seem to be devoid of this mineral. It can again occur as a groundmass constituent or as megacrysts/macrocrysts and is largely intergrown with other minerals e.g. olivine, phlogopite and spinel. It can occur in the groundmass as grains smaller than 0.5 mm and can be as large as 10 cm. The ilmenites in South Africa are quite enriched in magnesium with 4 – 20 % as MgO.

2.1.11 Pyroxene

Clinopyroxenes are common as megacrysts and groundmass phases compared to orthopyroxenes, which are relative rare due to high weatherability. Most of the clinopyroxenes in kimberlites are chromium poor according to the classification of Mitchell (1986). This specific group is distinguished by a grey-green to dark, bottle-green colour and is usually coated by a fine white alteration product consisting of serpentine, calcite and chlorite. Pyroxene minerals that have been identified are diopside, omphacite and hedenbergite.

2.1.12 Apatite

This phosphate mineral as groundmass constituent (< 0.01 mm grains) can account for as little as 1 % or as much as 10 weight % of the kimberlite. Apatites are usually found in carbonate or calcite rich kimberlites. It is not very stable and is often replaced by calcite. It is considered to be very pure fluoro-hydroxy apatite although significant replacement of the phosphor by silicon can occur.

2.1.13 Garnet

Garnet is a trace kimberlite mineral but characteristic of kimberlites. Its distinctive lilac or purple red pyrobes are easily distinguished and are very resistant to weathering. Therefore this mineral is central in the exploration process. In terms of weathering it is considered insignificant.

2.1.14 Conclusion

The aim of this project is to relate the mineralogy of kimberlites to the weathering process, which is accompanied by a decrease in mechanical properties of the kimberlite rock together with an increase in fines generation and increased stickiness. A simple relationship between the mineralogy and the weathering process is proposed and therefore the mineralogical focus of this study is on the predominant mineral groups rather than detailed, complex and very accurate geological description of the mineralogy. If detailed geological and mineralogical information is required, the reader is referred to Mitchell (1986).

2.2 WEATHERING PRINCIPLES

The weathering mechanisms present can be mechanical, chemical and / or biological. These different mechanisms will be discussed separately although the weathering mechanism in realistic terms is a combination of all the above.

2.2.1 Mechanical Weathering

Mechanical weathering, also termed physical weathering, involves the disintegration of rock without any chemical alteration, although chemical and mechanical weathering usually occur in parallel, enhancing the effects of weathering. Bland and Rolls (1998) suggest the following mechanisms of mechanical weathering:

2.2.1.1 Low temperature, water based weathering

- Freezing of in-place water

Freeze-thaw weathering represents the disintegration of rock when water freezes and expands within the rock. The volumetric expansion of ~ 9 % is due to the hexagonal arrangement that frozen water acquires. Associated with the expansion is internal pressure against walls where Bland and Rolls (1998) quote a pressure of 207 MPa at - 22 °C (under constraint). Even though these temperatures are rarely reached in South Africa, any force larger than 10 MPa can already exceed the tensile strength of some rocks and cause breakdown.

- Water migration and ice growth

This refers to the movement of water to a freezing zone rather than in-place freezing. At temperatures even below 0 °C water can coexist with ice, as the freezing point can be reduced by the presence of salts or by a thin adsorbed water layer or by capillary effects. Factors that modify the behaviour of freezing water include rock properties and environmental conditions. The migration of water is energetically driven by a free energy gradient, which is influenced by rock permeability, temperature and water availability.

2.2.1.2 Hydration shattering

Hydration is in fact a chemical process and discussed in section 2.2.2.1. However, this chemical process can imply mechanisms for mechanical weathering. Due to their polarity water molecules are attracted to charged mineral surfaces and an adsorbed layer is formed. The attraction occurs in a certain orientation, which decreases the ability of the water to freeze (even at subzero temperatures), as the energy required to re-orientate may be insufficient. This can also cause repulsion forces between molecules in small cracks. This mechanism of weathering is common for carbonates and schists and clay minerals may also be susceptible.

2.2.1.3 Salt weathering

Salts are chemical compounds which form from the reaction between acids and bases. Salts are important in the weathering process because of the expansionary forces upon thermal expansion, hydration and crystallisation.

Thermal expansion

The thermal expansion coefficient of the salt should exceed that of the surrounding rock for weathering to take place. For sodium chloride a volumetric expansion of 1 % occurs on a temperature rise of 50 °C, which is greater than any rock. The internal stresses produced by thermal expansion are less significant than hydration and crystallisation pressures.

Hydration pressure

When salts are hydrated, volumetric expansions of 100 - 300 % can occur generating pressures of 20 - 200 bar. Sulphates are of particular interest as they can pass through a full hydration - dehydration cycle in 24 hours, if the temperature reaches the transition point at which salts become fully hydrated and then the temperature falls for the dehydration cycle. The chemical process of hydration is discussed in section 2.2.2.1.

Crystallisation pressure

Crystallisation can occur when the concentration of a solution is increased at a constant temperature (usually by evaporation) or when the temperature of an almost saturated solution is decreased. Crystallisation is not possible if the solution does not reach saturation. After saturation the salt can crystallise slowly around nuclei or the solution can become super saturated and crystallisation is postponed, but the rate of crystallisation is much higher when it eventually starts. When crystals grow during crystallisation a pressure is generated which is well in excess of the tensile strength of rocks.

Experimental work

Salt weathering can be studied under controlled laboratory conditions where the most common method is to expose different rock types to a range of aqueous salt solutions. A climatic cabinet is usually used to simulate climatic conditions. Such a cabinet allows for the temperature and humidity to be artificially controlled. The weathering tests can thus be accelerated in order to produce results rapidly and to allow for monitoring of the process with a precision that is not possible in field investigations. Bland and Rolls (1998) discuss the weaknesses of the laboratory approach:

- Reproduction of natural climatic conditions is complex

Simulation of the natural heat and humidity as well as climatic cycles is difficult and can not be closely related due to the limitations of experimental equipment and the complexity of natural climatic conditions.

- Representativeness of rock samples

Does the sample used for testing relate to the field conditions in terms of composition, size and shape? The natural stress conditions present in the environment are developed by several mechanisms and are therefore difficult to reproduce.

- Nature of the solutions used in the laboratory experiments

In laboratory experiments single salt-hydrate solutions are usually used whereas complex mixtures are most common in nature.

2.2.1.4 Wetting and drying

When wetting and drying occur in cycles e.g. rain followed by evaporation, weathering can occur. When a crack or exposed rock surface is wetted, an adsorbed water layer is formed. The addition of more water may cause swelling pressure. If evaporation now occurs the water not adsorbed will be removed which will now cause attractive forces between residual water molecules on opposing wall surfaces. These expansion and contraction forces give rise to cracking and flaking of rocks. Shale is particularly susceptible to this process as are other rocks such as sandstone, limestone, granite, basalt and schist. The following rock properties cause vulnerability to wetting and drying weathering, as defined by Bland and Rolls (1998).

- the presence of clay minerals with water adsorption ability
- structural weaknesses which encourage water entry e.g. cleavage planes
- low tensile strength
- pore size and distribution

2.2.1.5 Insolation weathering

This mechanism refers to the influence of temperature change on the physical breakdown of rocks. Rock surfaces expand when exposed to the sun or other heat sources and contract when the heat source is removed. The expansion and contraction cause stresses, which can cause breakage if these exceed the elastic limit of the rock. Infrequent bush fires cause temperatures as high as 800 °C, with subsequent cooling within 10 minutes, which expose rocks to extreme thermal shock with destructive results. The rock properties play a large role in this mechanism of weathering such as albedo (reflection of heat, thus a measure of the ability to absorb heat), thermal conductivity (ability to conduct heat) and the coefficient of thermal expansion. The thermal conductivity of rocks is usually low and causes marked temperature gradients, which cause steep stress gradients in the upper layers because of the changes in the amount of expansion. The coefficient of thermal expansion is an important characteristic as far as weathering is concerned, as expansion can generate very high stresses.

2.2.1.6 Pressure release weathering

The presence of sheet joints parallel to the local land surface weakens the bulk strength of the rock. Such joints are usually formed by land erosion. Due to the weight of the overlying rocks, the rocks just below the surface experience high compressive stress. Erosion now occurs by removing overlying rock, which reduces the compressive stress on the rock and expansion in the direction of the stress reduction occurs. Failure usually begins with the extension of an initial crack and continues with the development of sheet jointing parallel to the unloading surface. This type of weathering is most effective in brittle, crystalline rocks of high elasticity e.g. granites and massive sandstones. The Griffith theory can be used as guidance to crack propagation (Bland and Rolls, 1998).

2.2.2 Chemical weathering

Agents that can cause chemical weathering are water, carbon dioxide and oxygen. Carbon dioxide will alter the pH when dissolved in water and can drastically influence the dissolution of calcite and silica as well as minerals containing iron and aluminium. Oxygen plays an important role especially in oxidation processes.

The mechanisms of chemical weathering are hydration, solution, oxidation (redox reactions), hydrolysis and complex formation (chelation).

2.2.2.1 Hydration

All ions, whether positively or negatively charged, are hydrated to varying extents in water. Ionic hydration is an exothermic process releasing energy defined as the hydration energy (enthalpy). The degree of hydration is dependent on the ionic size and charge density, with the relationship of a direct increase in hydration enthalpy exothermicity with decreasing size and increasing charge density as shown in figure 5 (Greenwood and Earnshaw, 1997). In figure 5 the effective ionic radius of the cation plus a constant value of 85 pm is used (r_{eff}). The hydration of cations is of particular interest in the kimberlite weathering process due to the swelling process that takes place in kimberlite. Figure 4 shows the effect of hydration size for monovalent cations Li, Na and K. The hydration enthalpy (exothermicity) decreases with increasing cation hydration size. From figure 5 it is concluded that trivalent cations are the highest in hydration enthalpy, then divalent cations and lastly monovalent cations. Hydration data for some mono-, di- and trivalent cations are given in table 3. Latimer derived an equation for the hydration energy (equation 1), which is a function of the charge of the cation (Z) and the cationic radius (r in pm). This equation holds when the electronegativity of the metal is not too great (< 1.5). Cations with electronegativies >1.5 have substantially higher hydration energies than more electropositive cations of comparable radius and charge. These electronegative metals have some degree of covalent bonding in their interaction with the oxygen atom of the water molecule, i.e., oxygen's unshared pair of electrons is shared with the metal atom. As the interaction between the metal ion and the coordinated water molecules increases, the oxygen further polarises the oxygen, hydrogen bond. This increases the acidity of the complex ultimately leading to hydrolysis. Z^2/r is used as an indication of the acidity. $Z^2/r < 0.01$, with r in pm, is non acidic e.g. Cs^+ and Rb^+. Li^+, Ba^{2+} and Ca^{2+} are defined as feebly acidic, falling in the range $0.01 < Z^2/r < 0.04$. Mg^{2+} is weakly acidic, lying in the range $0.04 < Z^2/r < 0.1$, and Al^{3+} lies in the moderately acidic range of $0.1 < Z^2/r < 0.16$. Strongly acidic cations ($Z^2/r > 0.22$) are not able to exist in water. (Note that the hydration enthalpy data in figure 5 are plotted against Z^2/r_{eff}, where $r_{eff} = r + 50$ pm, and hence these do not correspond to the Z^2/r values quoted above.)

$$\Delta H_{hyd} = -\frac{60900Z^2}{r+50} \text{ [kJ/mol]} \tag{1}$$

Where Z is the charge of the cation and r is the cationic radius in pm.

Table 3. Metal and ionic radii from Greenwood and Earnshaw (1997) and hydration bond size from Richens (1997).

Element	Cation Charge	Metal radius	Ionic radius	M-OH bond size	Hydration Enthalpy
		pm	pm	pm	kJ/mol
Ag	+ 1	144	115	240	-475.3
Li	+ 1	152	76	195-228	-514.1
Na	+ 1	186	102	240-250	-405.4
K	+ 1	227	138	260-295	-320.9
Ca	+ 2	197	100	241-246	-1592.4
Cr	+ 2	128	80	230	-1849.7
Cu	+ 2	128	77	196-200	-2100.4
Fe	+ 2	124	78	213	-1920
Mg	+ 2	112	27[a]	200-215	-1922.1
Mn	+ 2	118	83	218	-1845.6
Al	+ 3	143	53.5[b]	187-190	-4659.7
Cr	+ 3	128	80	196	-4401.6
Fe	+ 3	124	78	200	-4376.5
Ga	+ 3	135	62	215	-4684.8

[a] For a coordination of 4, [b] For a coordination of 6

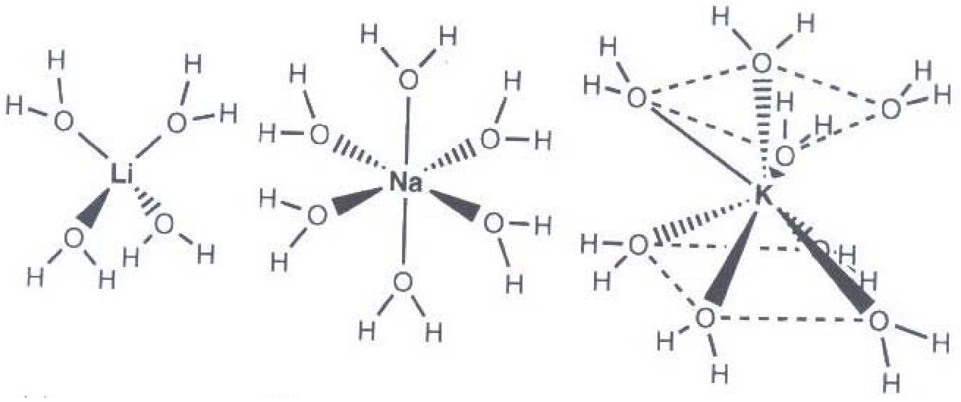

Figure 4. Hydration structures of lithium, sodium and potassium (Richens, 1997).

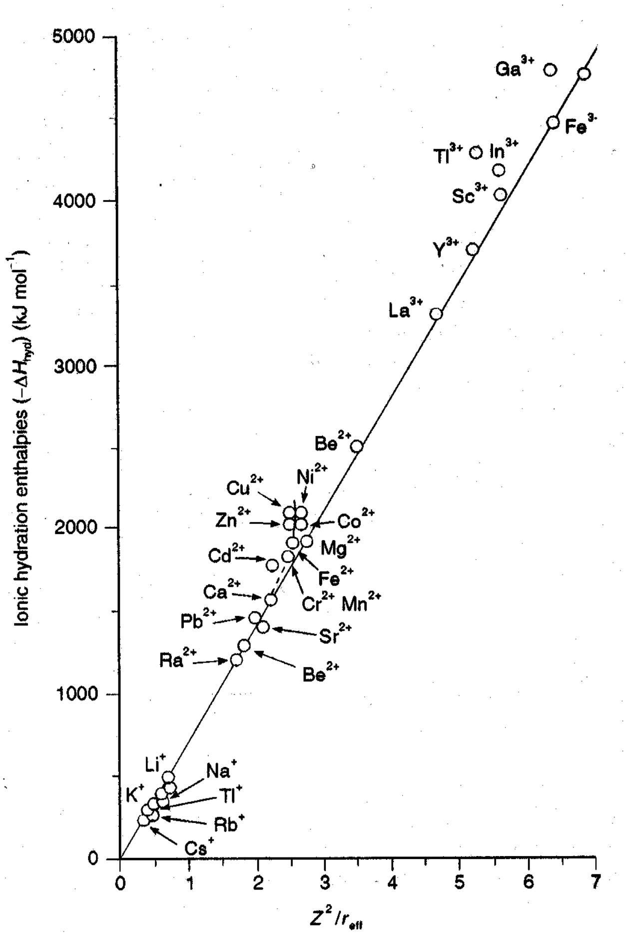

Figure 5. Hydration energy as a function of size and charge of the cation (Greenwood and Earnshaw, 1997).

2.2.2.2 *Water exchange rates on hydrated ions*

The rate of water exchange on aqua ions gives an indication of the stability of ion–water complexes. Figure 6 gives water exchange rate constants and mean residence times for aqua metal ions at 25 °C (Richens, 1997). These water exchange rates may give an indication of ion exchange rates between the interlayer cations in swelling clays and hydrated cations in the bulk solution.

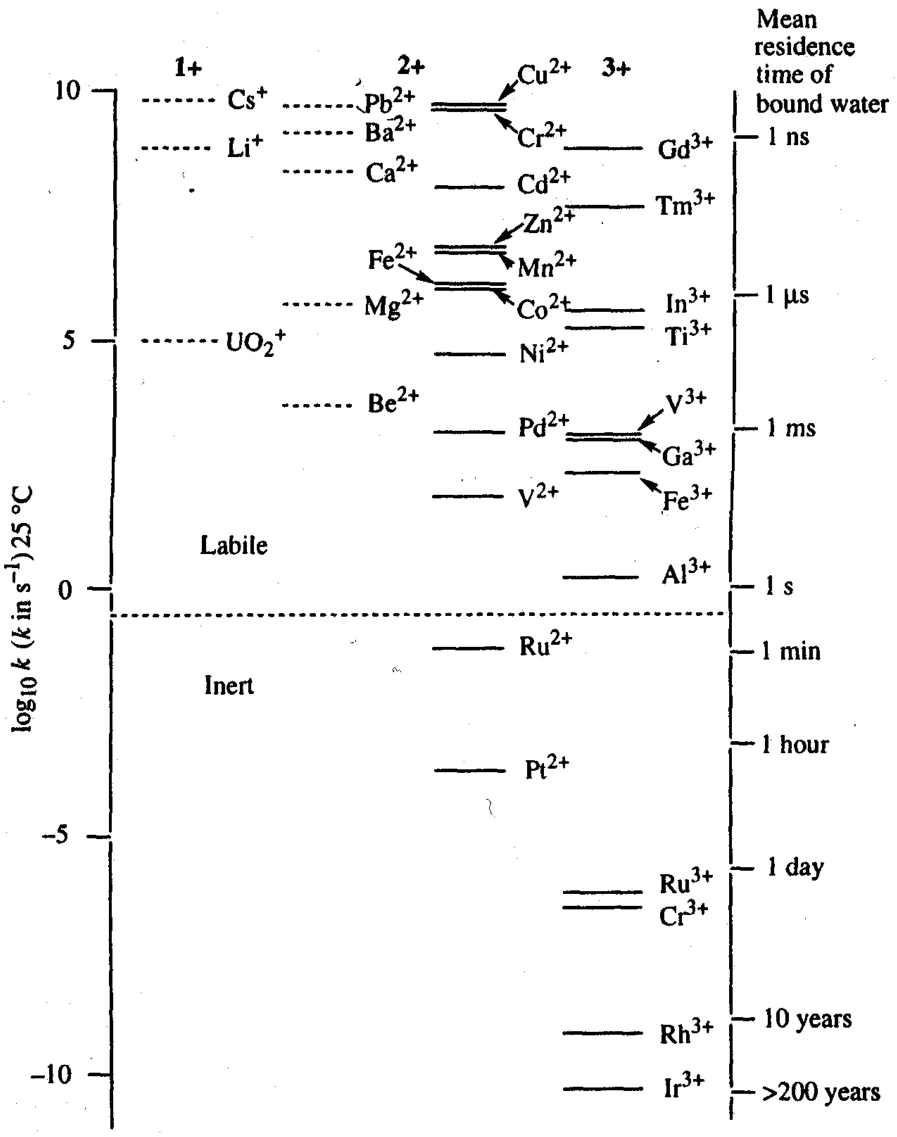

Figure 6. Water exchange rate constants and mean residence times for aqua metal ions at 25 °C (Richens, 1997).

2.2.2.3 Solution

Ionic salt added to a solution will initially dissolve until the solution becomes saturated. Super saturation can occur, usually when the conditions change, and if there are no nucleation sites available for crystallization to start. As mentioned previously the rate of crystallization when it finally starts will be much greater than for saturated-solution crystallization.

The ionic potential can be an indication of weathering as it reflects the measure of ease with which an ion can be removed from a mineral in solution. Ions with low ionic potential are the main components of weathering solutions as they are more mobile (easily dissolved and carried away). The ionic potential can be calculated by dividing the charge of the ion by its radius in angstrom units. Tabulated values are available in (Richens, 1997). The solubility product (K_{SP}) can also be used as an indication of weathering for solids. The higher the solubility product, the higher the tendency for the rock to dissolve and the greater is the likelihood of weathering. For an exothermic dissolution a higher temperature will lower the solubility, whereas a higher temperature will increase the solubility for an endothermic process.

2.2.2.4 Acids and Bases

Silica is a mineral of interest as far as weathering is concerned as it can form silicic acid in the presence of water by equation 2. The extent to which this reaction can occur however depends on the stable form of silica, where quartz is slow to react with water while amorphous silica is more reactive. The weathering of aluminosilicates, e.g. feldspars and micas, can form silica. Water becomes acidic with dissolved CO_2, which can cause the solubility of SiO_2 to be exceeded, resulting in the precipitation of amorphous silica. The amorphous silica can slowly expel water by the ageing process to first form opal or cristobalite (~10 % water), then chalcedony (~ 1 % water) and lastly quartz, with an associated increase in density from 2.1 - 2.7 g/cm^3.

$$SiO_2\,(s) + 2H_2O = Si(OH)_4\,(aq) \qquad (2)$$

2.2.2.5 Hydrolysis

Hydrolysis in contrast with hydration involves a chemical reaction with water causing one O-H bond of H_2O to be broken. Hydrolysis can occur under acidic, neutral or basic conditions and occurs with compounds in which either the cations or anions or both give rise to the formation of a weak acid or base. The resulting pH (see table 4) is of interest when weathering is concerned. Different methods of determining the hydrolysis potential and hydrolysis constant values for ions are discussed in Richens (1997).

Table 4. Hydrolysis of salts as in Bland and Rolls (1998).

Type of salt	Example	pH of resulting solution
Strong acid - strong base	$CaSO_4$, Na_2SO_4	7
Weak acid - strong base	$CaCO_3$, Na_2CO_3	> 7 (basic)
Strong acid - weak base	$(NH_4)_2SO_4$	< 7 (acidic)
Weak acid - weak base	$(NH_4)_2CO_3$	Close to 7 depending on strength of the acid and base

2.2.2.6 *Carbonation*

The weathering effects of CO_2 in aqueous solutions are described as the Earth's commonest weathering mechanism. As previously discussed dissolved CO_2 causes water to become acidic (equation 3) due to the formation of carbonic acid. The pH of water in equilibrium with the atmosphere (containing 0.03 - 0.04 % CO_2 by volume) is ~ 5.6, but the concentration of CO_2 can be up to 20 % higher in groundwater because of biological activity that generates CO_2 (Bland and Rolls, 1998).

$$CO_2\,(g) + H_2O\,(l) = H_2CO_3\,(aq) \tag{3}$$

This weak acid can dissociate further:

$$H_2CO_3\,(aq) = H^+\,(aq) + HCO_3^-\,(aq) \tag{4}$$

The interaction of calcium carbonate (limestone) is also of interest under the carbonation subject. Calcium carbonate is soluble to a limited extent in water according to equation 5 whereafter hydrolysis can occur (equation 6) to alter the water to a calcium rich basic solution. The dissolution of calcium carbonate increases as the pH decreases. The weathering of pyrite (FeS_2) causes the production of sulphuric acid, which can cause the breakdown of limestone as shown in equation 7. Limestone can also be weathered by carbonic acid, which is formed when CO_2 is dissolved in water as shown by equation 8.

$$CaCO_3\,(s) = Ca^{2+}\,(aq) + CO_3^{2-}\,(aq) \tag{5}$$

$$CO_3^{2-}\,(aq) + H_2O(l) = HCO_3^-\,(aq) + OH^-\,(aq) \tag{6}$$

$$CaCO_3\,(s) + 2\,H^+\,(aq) = Ca^{2+}\,(aq) + H_2O\,(l) + CO_2\,(g) \tag{7}$$

$$CaCO_3\,(s) + H_2CO_3\,(aq) = Ca^{2+}\,(aq) + 2\,HCO_3^-\,(aq) \tag{8}$$

2.2.2.7 Redox reactions

- Oxidation

Dissolved oxygen acts as oxidising agent, and can also affect ions in solution with iron as the most commonly oxidised material. Ferrous iron [Fe(II)] with a yellowish colour is oxidised to ferric iron [Fe(III)] which has a reddish colour. An example of direct oxidation from the mineral and the influence on weathering is, for example, comparison of the micas, biotite [$K(Mg,Fe)_3(AlSi_3O_{10})(OH)_2$] and muscovite [$KAl_2(AlSi_3O_{10})(OH)_2$]. Biotite is much more easily weathered due to the oxidation of iron that can occur. Another mechanism of iron oxidation is where the Fe^{2+} is first released from the mineral and then oxidised e.g. the release of ferrous oxide upon hydrolysis of olivine to serpentine shown by equation 9. Oxidation then occurs and forms goethite (equation 10). The oxidation can also produce ferric iron in the hematite form (Fe_2O_3). Manganese is also a susceptible element for oxidation due to the Mn^{2+} and Mn^{4+} oxidation states.

$$3\ MgFeSiO_4 + 2\ H_2O \rightarrow H_4Mg_3Si_2O_9 + SiO_2 + 3\ FeO \qquad (9)$$

$$2\ FeO + \tfrac{1}{2}\ O_2 + H_2O \rightarrow 2\ FeOOH \qquad (10)$$

- Reduction

Weathering products due to reduction reactions are less prominent, although reduction can occur in oxygen free environments e.g. waterlogged soils. Such soils are characteristically green/grey due to the reduced form of iron that is stable. Organic matter commonly functions as reducing agents.

2.2.2.8 Cation Exchange

Fine soil particles (< 0.2 μm diameter clay or humus colloidal particles) produced by weathering can provide a reservoir of exchangeable cations and anions, which may be involved in further weathering processes. Exchangeable cations are more common than exchangeable anions and include H^+, K^+, Na^+, Mg^{2+} and Al^{3+}. Of particular interest in clays is that the replacement of Si^{4+} with Al^{3+} in tetrahedral sheets causes a negative charge of one, attracting monovalent cations to be adsorbed onto the surface. The octahedral sheet, in the way it links with other layers, also causes a –2 negative charge allowing for cations to be absorbed in the structure. The ability of an ore or soil to absorb cations is described by the cation exchange capacity (CEC), which can be as high as 60 [cmol/kg] for clay soils according to Bland and Rolls (1998). The units describe the number of centimoles (0.01 Mol) of cations replaced per kilogram of ore or soil. Therefore if a soil has a CEC of 10 cmol/kg, 1 kg of this soil can absorb 10 cmol of H^+ (for example) and can exchange it for 10 cmol of another cation. The focus is on the charge exchanged rather than number of ions or molecules (Brady and Weil, 1999). Vermiculite is the clay mineral with the highest CEC with values of 100-180 while smectites vary from 80 – 140.

The CEC can be determined at ARC (Agricultural Research Council, South Africa) using the standard method as described by the Soil Science Society of South Africa (1990). The method uses 1 M of ammonium acetate as extractant measuring the extracted calcium, magnesium, potassium and sodium. Brady and Weil (1999) give general information on determining the CEC and the different methods that can be used.

In the case where a kimberlite or clay mineral has a tendency to exchange cations, the properties of the ore can be altered by the type of cation present. Each cation will alter the clay structure and properties differently due to its unique properties e.g. valence, effective radius and absorption mechanism. A considerable amount of work has been done on the influence of cations on swelling clays and their properties e.g. Cases *et al* (1997); Rytwo *et al* (1996); Badreddine *et al* (2002); Prost (1981); Czimerova *et al* (2004). This subject is discussed in more detail in section 3.2.

2.2.3 Biological weathering

Living organisms are not usually part of the immediate causes of breakdown but are agents of the physical and chemical weathering mechanisms. The zone of activity of these organisms is called the biosphere and includes biological agents such as bacteria, lichens, algae, fungi, plant roots and organic matter in a state of decay. These organisms contribute to weathering by either exerting a physical stress or by emitting substances e.g. carbon dioxide, as part of their life processes.

2.2.3.1 Production of organic and inorganic acids

The production of acid is perhaps the biggest contribution that biological agents can make to weathering. The inorganic acid largely arises from oxidation processes e.g. sulphuric acid is produced when bacterial oxidation of sulphur compounds occurs. Organic acids can be produced as by-products of organic decomposition or by biological agents as part of their existence. The influence of organic acids depends on specific materials e.g. olivine responds more rapidly to organic acid attack than to weathering under sterile conditions.

The main biological agents are:

Bacteria

Bacteria contribute to weathering in a number of ways as listed below.

- Releasing carbon dioxide

The increase in the proportion of carbon dioxide due to the activity of microorganisms has been estimated at 0.5 - 20 % compared to the atmosphere average of 0.03 %. As mentioned previously this can give rise to weakly acid solutions with pH ~ 5 - 6, which enhance chemical weathering.

- Nitrification process

The nitrobacteria are involved in the nitrification process, which is the term for conversion of ammonium ions (products of the bacterial processing of dead plant and animal matter) to nitrates (NO_3^-, process of nitratation) and nitrites (NO_2^-, process of nitritation). This process is of importance to weathering as it entails the release of protons as shown by equation 11, and particularly 2 hydrogen ions are produced for every ammonium ion resulting in acidic conditions.

$$NH_4^+ + 2\ O_2 \rightarrow NO_3^- + 2\ H^+ + H_2O \qquad (11)$$

Experimental tests on vermiculite clay as quoted in Bland and Rolls (1998) show the removal of Mg^{2+} from this mineral in a bacterial environment compared to a sterile environment. In the bacterial environment the removal of the magnesium ions was twice as much as for the sterile environment, confirming that weathering mechanisms interact and cannot be evaluated as separate entities.

- Oxidation of metals

Many bacteria are capable of oxidising metals, which can then be removed from the host structure and subsequently precipitated. This microbial alteration is most effective under acidic conditions. At pH values of 2 - 4.5, these bacteria can raise oxidation rates by factors of 10^5 - 10^6 compared to non-biological environments.

Lichens

Lichens are compound organisms, which are capable of carrying out biophysical and biochemical weathering.

Biophysical weathering can be brought about by penetration of hyphae (fungal ligaments) along microcracks, which may generate considerable tensile stresses in excess of rock tensile strength and cause breakdown. Another form of biophysical breakdown is due to the expansion of thalli (plant bodies) and hyphae due to water absorption. Bland and Rolls (1998) discuss that lichens can increase their water content by 150 - 300 % under specific conditions, with enormous associated stresses due to the expansion that takes place.

Biochemical weathering of lichens again refers to the emission of organic acids, which contribute to chemical weathering as discussed under section 2.2.3.

Algae and cyanobacteria as biological weathering agents

These agents can also produce biophysical weathering due to the ability to absorb water, which generates expansion forces. Algae contribute to biochemical weathering through their ability to dislocate and precipitate metals at rock surfaces. Manganese-oxidising cyanobacteria can remove manganese from wind-blown dust by oxidation; the manganese is almost immediately precipitated under damp conditions to form a varnish on desert rocks.

Plant roots

The upper zone of the regolith dominated by plant roots is called the rhizosphere and in this region chemical breakdown can occur by plant roots. The substances emitted from plant roots as part of their life cycle are organic acids, protons and electrons (Bland and Rolls, 1998). These substances contribute mostly to chelation (complex formation) as weathering mechanism.

Decaying plant and animal matter

Humus acts as contributor to weathering through essentially oxidation which yields large amounts of carbon dioxide and humic and fulvic organic acids. These acids operate through proton and complexation reactions. These chelates that are formed are soluble and are removed from the weathering environment.

2.2.4 Silicate weathering

Silicates make up over 90 % of the earth's crust and about 75 % of the exposed surface rocks (Bland and Rolls, 1998). The weathering of minerals by aqueous solutions can be influenced by the compositions and lattice structure of the mineral and also the nature and behaviour of the weathering process. Silicates occur in numerous structural orientations, which allow for categorising of these minerals (see table 5). This mineralogical group is of particular importance in the study of kimberlite weathering as it includes the clay and mica groups, which is the focus point of this study.

Table 5. Types of silicates from Bland and Rolls (1998).

Name of Silicate	Structural Group	General formula	Number of oxygen atoms shared
Nesosilicates (Orthosilicates)	Tetrahedra	SiO_4^{4-}	0
Sorosilicates	Double tetrahedra	$Si_2O_7^{2-}$	1
Cyclosilicates	Closed rings of tetrahedra	$(SiO_3^{2-})_n$ n = 3, 4, 6	2
Inosilicates	(1) Chains of tetrahedra (2) Double chains of tetrahedra	$(SiO_3^{2-})_n$ $(Si_4O_{11}^{2-})_n$	2 2 and 3
Phyllosilicates	Sheets of tetrahedra	$(Si_2O_5^{2-})_n$	3
Tectosilicates	3 D framework of tetrahedra	SiO_2	4

2.2.4.1 Nesosilicates

Nesosilicates are typically ionic solids which are hard and brittle e.g. zircon and garnet ($Ca_3Al_2(SiO_4)_3$). The olivine group of this category contains divalent cations, e.g. Mg^{2+}, Fe^{2+}, Mn^{2+} and Ca^{2+} with the general formula M_2SiO_4. The olivine group is easily weathered due to the simple structure and low lattice energy. Zircon ($ZrSiO_4$) has a very high lattice energy and is one of the most inert silicates. It has been used as a standard to rate the weathering of other silicates against.

In this category of silicates the minerals containing iron e.g. forsterite ($MgFeSiO_4$) are important when discussing weathering, as oxidation of the Fe^{2+} takes place readily. The weathering of these minerals is modified by environmental conditions. Under tropical conditions with good drainage the silicon and magnesium are lost while the Fe^{2+} is oxidised and the iron redistributed as goethite or hematite along fractures. Under less extreme conditions only magnesium is initially removed resulting in an iron-silicon rich framework. The silicon will eventually be removed and the iron rich network remains. Forsterite (Mg_2SiO_4) is an example of a mineral that is first weathered by hydrolysis and the oxygen atoms are protonated resulting in the release of silicic acid by equation 12.

$$Mg_2SiO_4 + 4\,H^+ \rightarrow 2\,Mg^{2+} + H_4SiO_4 \qquad (12)$$

2.2.4.2 Sorosilicates

These ionic solids are very rare minerals and are of little significance in the weathering processes.

2.2.4.3 Cyclosilicates

In this structure SiO_4 tetrahedra are shared to form a closed ring. Cyclic metasilicates occur with three, four, six or eight shared tetrahedra. An example is benitoite ($BaTiSi_3O_9$). This group is again rare and not very important in terms of kimberlite and weathering.

2.2.4.4 Inosilicates

Inosilicates are characterised by tetrahedra joined to form chains. Minerals included in this group are pyroxenes and amphiboles and their weathering is aided by their good cleavage. When slow leaching takes place, weathering produces smectites along cleavage planes and fissures. Stronger leaching of pyroxenes and amphiboles dissolves residues congruently, resulting in iron rich smectites as weathering product. Tropical weathering with good drainage totally removes Ca^{2+}, Mg^{2+} and Si^{4+} leaving mainly oxohydroxides e.g. goethite.

2.2.4.5 Phyllosilicates

These sheet structure minerals are of utmost importance to weathering as these include most of the clay minerals e.g. kaolinite, montmorillonite, vermiculite. Mica is included under this category as the commonest phyllosilicate. In the mica structure, Al^{3+} can replace the Si^{4+} at the centre of some of the tetrahedra to give a layered structure. This mineral is hard but has pronounced cleavage planes making it mechanically weak as it can be split into sheets. Mica minerals include biotite, muscovite, phlogopite and annite. The cleavage planes allow for effective weathering e.g. in the case of biotite, which goes through several alterations during weathering in that it can be converted to chlorite or vermiculite and other clay minerals. Conversion of biotite to clay minerals can for example form kaolinite and gibbsite as shown in equation 13.

$$2\ KAl_3Si_3O_{10}(OH)_2 + 18\ H_2O + 2\ H^+ \rightarrow 3\ Al_2O_3{\cdot}3\ H_2O + 6\ H_4SiO_4 + 2\ K^+ \qquad (13)$$

2.2.4.6 *Tectosilicates*

Tectosilicates have a characteristic framework structure such as silica and aluminosilicates, of which the most important group is the feldspars. Feldspars are also the most important single group of rock-forming silicate minerals. In these groups up to 50 % of the Si^{4+} ions have been replaced by Al^{3+}, causing extra cations to be added to maintain the charge balance. The feldspars are divided into alkali feldspars (replacement by monovalent cations) and plagioclase feldspars (replacement by divalent cations). In for example albite, the Na^+ can be replaced by K^+ (monovalent cation, thus alkali feldspars) ending up as orthoclase, as illustrated in equation 14. Alternatively the Na^+ in albite can be replaced by Ca^{2+} (divalent cation thus plagioclase feldspars) ending up as anorthite, as shown by equation 15.

$$NaAlSi_3O_8 \rightarrow Na_xK_{1-x}AlSi_3O_8 \rightarrow KAlSi_3O_8 \qquad (14)$$

$$NaAlSi_3O_8 \rightarrow Na_xCa_{1-x}Al_{2-x}Si_{2+x}O_8 \rightarrow CaAlSi_2O_8 \qquad (15)$$

The ternary phase diagram, shown as figure 7, illustrates the variation in make up of feldspars.

Feldspars show very good cleavage planes and weathering typically takes place along fracture surfaces. The main weathering alteration reactions (equations 16 and 17) transform orthoclase to kaolinite and mica as the weathered products (Bland and Rolls, 1998).

$$\underbrace{4\ KAlSi_3O_8}_{\text{orthoclase}} + 22\ H_2O \rightarrow \underbrace{Al_4Si_4O_{10}(OH)_8}_{\text{kaolinite}} + 8\ H_4SiO_4 + 4\ K^+ + 4\ OH^- \qquad (16)$$

$$\underbrace{4\ KAlSi_3O_8}_{\text{orthoclase}} + 12\ H_2O + 2\ H^+ \rightarrow \underbrace{KAl_3Si_3O_{10}(OH)_2}_{\text{mica}} + 6\ H_4SiO_4 + 2\ K^+ \qquad (17)$$

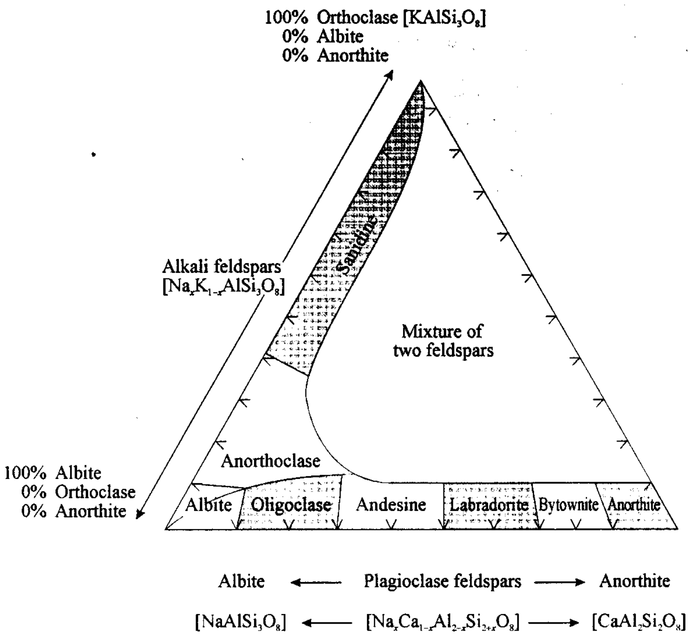

Figure 7. Ternary phase diagram showing the make up of feldspars (Bland and Rolls, 1998).

2.2.5 Products of weathering

2.2.5.1 Crystalline phyllosilicate clays

Clay minerals are the largest group of alteration products. The alteration sequence (Dawson, 1980) from olivine, pyroxene and mica is shown as figure 3 (section 2.1), to illustrate the formation of some clays. Clays are characterized by their small size and crystalline nature i.e. platelike structure. These minerals can be classified by the structure of the sheets or by the linkage between sheets.

2.2.5.1.1 Structure of the sheets

These minerals are formed from linked SiO_4^{4-} tetrahedra or octahedra.

- The tetrahedral sheet

Figure 8 illustrates the tetrahedral sheets where each tetrahedron is linked with its neighbours by sharing its basal oxygens. The enclosed ion of each tetrahedron is normally Si^{4+}, but this can be replaced by Al^{3+} or Fe^{3+}.

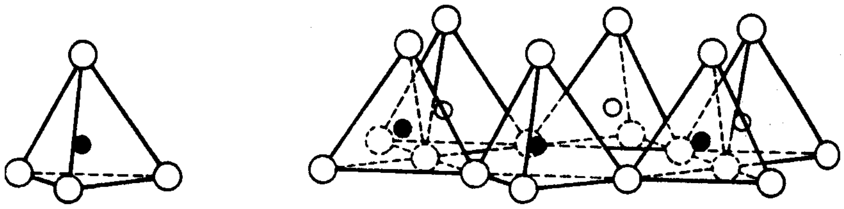

Figure 8. Illustration of a single SiO_4 tetrahedron and the sheet structure of SiO_4 tetrahedra (Bland and Rolls, 1998).

- The octahedral sheet

Figure 9 illustrates that each octahedron consists of six oxygen or hydroxyl ions which link by sharing the octahedral edges resulting in a nett charge of -2. In the basic form of the structure, two out of every three cation positions are filled by Al^{3+}, giving a (gibbsite) dioctahedral sheet. In some cases, all cation positions are filled by divalent cations such as Mg^{2+}, to give a trioctahedral sheet (brucite, if the cation is Mg^{2+}).

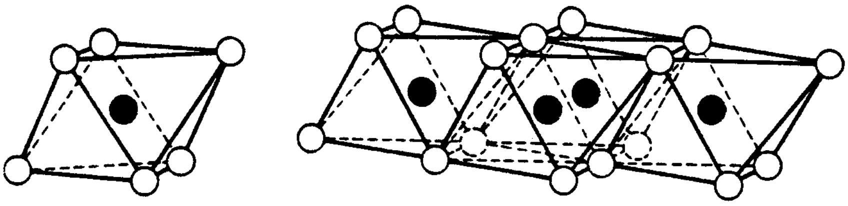

Figure 9. Illustrating a single octahedron and the sheet structure of linked octahedral (Bland and Rolls, 1998).

2.2.5.1.2 Linkage between sheets

Sheets are linked to form layers and how these are combined to form unit structures is of importance.

- Linkage to form 1:1 layers

A 1:1 layer refers to the linkage of a single octahedral sheet and a single tetrahedral sheet by weak intermolecular forces (induced dipole-dipole forces). This paired structure is about 7 Å thick (Bland and Rolls, 1998). The oxygens at the tips of the tetrahedra project into a plane of hydroxyls in the octahedral sheet, thus the oxygens replace two-thirds of the hydroxyls. Kaolinite ($Al_2Si_2O_5(OH)_4$) is considered the most important 1:1 clay type, shown in figure 10. Water cannot enter between these layers and therefore kaolinite is non-swelling. The other clay mineral categorised in this group is serpentine ($Mg_3Si_2O_5(OH)_4$), which is very similar to kaolinite except that a sheet of brucite ($Mg(OH)_2$) is present rather than the gibbsite layer ($Al(OH)_3$). Serpentine is also non-swelling due to its similar structure. Halloysite on the other hand has a single layer of water molecules between the structural sheets to form hydrogen bonds and is therefore a swelling clay (see figure 10).

- Linkage to form 2:1 layers

This structure typically consists of three sheets, an octahedral sheet between two silica tetrahedral sheets on both sides. This layer is about 10 Å thick. The oxygens of the tetrahedral sheet point towards the central octahedral sheet and replace two-thirds of the hydroxyls of the octahedral. The layers are bonded by cations e.g. illite and vermiculite or by a brucite sheet in chlorite. The 2:1 clay group is divided into 4 groups namely illite, smectite, vermiculite and chlorite as is shown in figure 10.

Illite

In this mineral about one-sixth of the Si^{4+} in the tetrahedral layer is substituted by Al^{3+}, resulting in a high silicon to aluminium ratio and a reduced net charge deficiency. The interlayer cations (K^+, Ca^{2+}, Mg^{2+} or H^+) are relatively few thus the forces between layers are weaker. If potassium cations are present these will prevent the entrance of water and other cations, therefore illite generally has a low cation exchange capacity.

Smectite group

The central sheet of gibbsite is altered in this mineral group, in that oxygens replace two of every three hydroxide ions. Substitution by low valence cations in the octahedral (Al^{3+} replaced by Fe^{2+}, Mg^{2+} replaced by Zn^{2+}) and tetrahedral sites (Si^{4+} by Al^{3+}) causes electronic imbalance, which is usually corrected by the presence of interlayer cations e.g. Na^+, Ca^{2+}, Mg^{2+}. For montmorillonite the replacement of Al^{3+} by Mg^{2+} in the octahedral sheet is common with the occurrence of Na^+ as the interlayer cation. This group is called 'swelling clays' because water is readily absorbed between the layers therefore the basal spacing varies between 10 – 21 Å. The swelling of smectites is due to their small layer charge. It is suggested that the primary cause is because there is not a large enough attraction from the interlayer cations to keep the layers together (Moore and Reynolds, 1989).

Vermiculite

Vermiculite consists of a central sheet of brucite with octahedrally coordinated Mg^{2+} and Fe^{2+}. Extensive substitution of Si^{4+} by Al^{3+} and Fe^{3+} occurs. The charge imbalance is compensated by the introduction of Mg^{2+} interlayer cations. Water is also present between the layers thus making it a swelling clay. It is the clay mineral with the highest cation exchange capacity.

Chlorite minerals

An extra brucite-like layer is introduced as an octahedral sheet, which is electrostatically bonded. Due to the strong bond no hydration or swelling of this mineral can take place.

Figure 10 and table 6 illustrates the structural groups with examples.

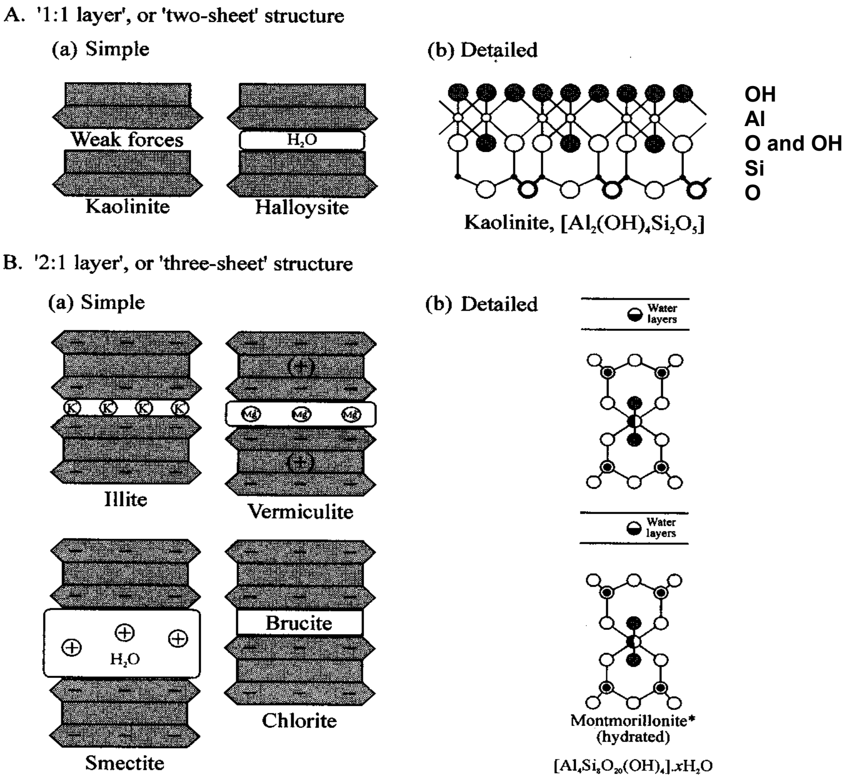

Figure 10. Structures of the clay minerals (Bland and Rolls, 1998).

Table 6. The layered silicates (Bland and Rolls, 1998).

Main group	Subgroup	Examples
Two layers (1:1)		
Kaolinite	Kaolinite	Kaolinite, halloysite
Kaolinite	Serpentine	Chrysotile, greenalite
Three layers (2:1)		
Pyrophyllite	Pyrophyllite, talc	Pyrophyllite, talc
Smectite	Dioctahedral	Montmorillonite, beidelite
	Trioctahedral	Saponite, saucinite
Vermiculite	Dioctahedral	Vermiculite
	Trioctahedral	Vermiculite
Mica	Dioctahedral	Illite, muscovite, sericite
	Trioctahedral	Biotite
Chlorite	Trioctahedral	Corundophite, pseudothuringite, talc-chlorite

Information on the unit layer formulas, octahedral and tetrahedral cations, charge per unit formula and exchangeable cations are shown in table 7 (from Brady and Weil, 1999).

Table 7. Unit layer formula, octahedral and tetrahedral cations, charge per unit formula and fixed and exchangeable interlayer components (Brady and Weil, 1999).

Mineral	Octahedral sheet	Tetrahedral Sheet	Coordinating Anions	Charge per unit formula	Interlayer components	
					Fixed	Exchangeable
1:1 Type						
Kaolinite	Al_2	Si_2	$O_5(OH)_4$	0	None	None
Serpentine	Mg_3	Si_2	$O_5(OH)_4$	0	None	None
2:1 Type Dioctahedral						
Pyrophyllite	Al_2	Si_4	$O_{10}(OH)_2$	0	None	None
Montmorillonite	$Al_{1.7}Mg_{0.3}$	$Si_{3.9}Al_{0.1}$	$O_{10}(OH)_2$	-0.4	None	$M^+_{0.4}$
Beidellite	Al_2	$Si_{3.6}Al_{0.4}$	$O_{10}(OH)_2$	-0.4	None	$M^+_{0.4}$
Nontronite	Fe_2	$Si_{3.6}Al_{0.4}$	$O_{10}(OH)_2$	-0.4	None	$M^+_{0.4}$
Vermiculite	$Al_{1.7}Mg_{0.3}$	$Si_{3.6}Al_{0.4}$	$O_{10}(OH)_2$	-0.7	xH_2O	$M^+_{0.7}$
Fine mica (Illite)	Al_2	$Si_{3.2}Al_{0.8}$	$O_{10}(OH)_2$	-0.8	$K^+_{0.7}$	$M^+_{0.1}$
Muscovite	Al_2	Si_3Al	$O_{10}(OH)_2$	-1.0	K^+	None
2:1 Type Trioctahedral						
Talc	Mg_3	Si_4	$O_{10}OH)_2$	0	None	None
Vermiculite	$Mg_{2.7}Fe^{3+}_{0.3}$	Si_3 Al	$O_{10}(OH)_2$	-0.7	xH_2O	$M^+_{0.7}$
Chlorite	$Mg_{2.6}Fe^{3+}_{0.4}$	$Si_{2.5}(Al,Fe)_{1.5}$	$O_{10}(OH)_2$	-1.1	$Mg_2Al(OH)_6^+$	$M^+_{0.1}$

2.2.6 Intensity of weathering

Intensity refers to the degree of weathering or decomposition at a specific point in time, whilst the rate refers to the amount of change per unit time.

2.2.6.1 Controls of intensity

The controlling factors are categorised according to intrinsic and extrinsic factors. The intrinsic factors are the properties related to the parent material.

Intrinsic factors

- Pores and fractures

These physical properties guide the entry of weathering fluids and therefore also the intensity of weathering. Weathering targets the fractures, cracks, fissures, cleavage planes and other surface weaknesses.

- Mineralogy

An arrangement of minerals in their order of stability is shown by Bland and Rolls (1998) where the method to determine the stability was to arrange them by the frequency of their occurrence in sedimentary rocks of increasing age, therefore an arrangement by their order of persistence. The version of Pettijohn (1941) is shown as table 8. However, the version published by Goldich (1938) is the more accepted version (figure 11). However this only includes the igneous rock-forming minerals. Some conflicting data has been reported especially in considering the environmental conditions when interpreting the mineral stability.

Table 8. Sequence of mineral persistence or Bowen's reaction series (Pettijohn, 1941).

Mineral	Persistence
Anatase	-3*
Muscovite	-2*
Rutile	-1*
Zircon	1
Tourmaline	2
Monazite	3
Garnet	4
Biotite	5
Apatite	6
Ilmenite	7
Magnetite	8
Staurolite	9
Kyanite	10
Epidote	11
Hornblende	12
Andalusite	13
Topaz	14
Sphene	15
Zoisite	16
Augite	17
Sillimanite	18
Hypersthene	19
Diopside	20
Actinolite	21
Olivine	22

Decreasing
Stability

* Negative numbers indicate a tendency to formation rather than disappearance during long periods of burial.

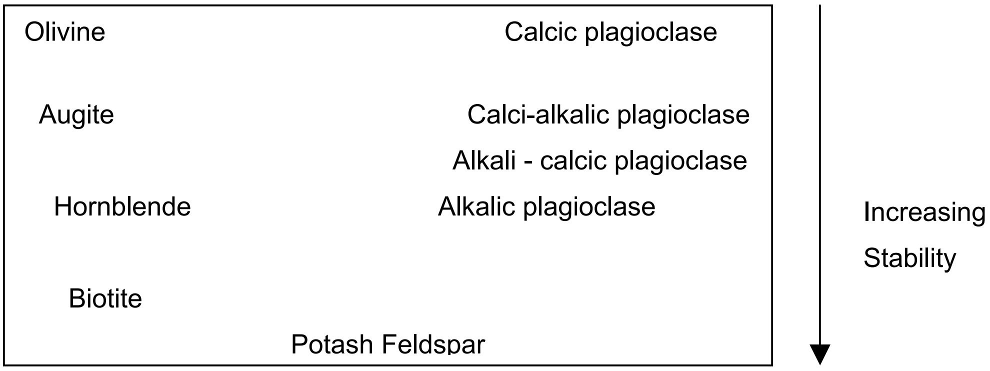

Figure 11. Sequence of mineral stability (Goldich, 1938).

Extrinsic factors (Environmental)

- Temperature

Temperature greatly influences the weathering rate because it influences the rates of chemical reactions. Bland and Rolls (1998) generalise it to an increase of 10 °C, which doubles the rate of the reaction. Changes in temperature can also cause the mechanism of weathering to change. Temperature will play a big role if the reaction is activation controlled. Temperature can be used to determine whether mass transfer of the reagent or product species is controlling the rate of the reaction or whether it is the rate of the chemical reaction itself. A very strong dependence on temperature indicates a chemically controlled reaction.

- Chemistry of weathering solutions

The characteristics of the weathering solution that determine the weathering activity are ion concentration, pH and temperature. As discussed previously, the content of CO_2 and biological agents largely influence the pH. The influence of specific ions on weathering is discussed in section 3.2.

- Hydrodynamics

Igneous rocks are highly permeable allowing for efficient water circulation and therefore high weathering possibilities compared to sedimentary rocks, which are slightly permeable and therefore higher in resistance. At mineral scale, water can enter at fractures and cleavage planes, whilst at a larger scale the joints, bedding planes and faults are weaknesses exploited by the weathering solution. Therefore the density and patterns of these fractures determine the efficiency of weathering.

In the regolith region the pathway of water is generalised to three distribution methods:

- Groundwater flow
- Shallow, saturated flow in soil.
- Saturation overland flow, which occurs where subsurface water returns to the land surface or where precipitation falls onto saturated areas, usually near surface channels.

The organised flow of water through rocks and the regolith contribute to weathering in that the fresh water comes into contact with minerals, which may accelerate weathering. Flushing carries the products of weathering away relating to the rate of weathering. Usually flushing speeds up the dissolution of minerals up to a limiting point after which dissolution is controlled by the solubility of the minerals.

2.2.6.2 Verbally descriptive approach to the intensity of weathering

Usually this appraisal is based on observation leading to verbal description for example as shown in table 9, which was obtained from Bland and Rolls (1998).

Table 9. Scheme of weathering grades for engineering purposes (Bland and Rolls, 1998).

Term	Grade	Description of weathering intensity
Fresh	I	No visible sign of rock material weathering; perhaps slight discolouration of major discontinuity surfaces
Slightly weathered	II	Discoloration indicates weathering of rock material and discontinuity surfaces. Weathering may discolour some of the rock material; yet it is not noticeably weakened.
Moderately weathered	III	Less than half of the rock material is decomposed or fragmented. Discoloured but unweakened rock is present either as a continuous framework or as corestones.
Highly weathered	IV	More than half of the rock material is decomposed or disintegrated. Fresh or discoloured or weakened rock is present either as a discontinuous framework or as corestones within the soil
Completely weathered	V	All rock material is decomposed and/or disintegrated to soil. The original mass structure and material fabric are still largely intact.
Residual soil	VI	All rock material is converted to soil. The mass structure and material fabric are destroyed. There is a large change of volume, but the soil has not been significantly transported. Can be divided into an upper A horizon of eluviated soil and a lower B-horizon of illuviated soil.

A five-point scale of friability is shown as table 10, which utilises simple equipment such as a boot or hammer to make an easy assessment of the strength or friability of the rock. This is mostly used where an assessment is made on site.

Table 10. A five-point scale of friability (Ollier, 1965).

1. Fresh: a hammer tends to bounce off the rock
2. Easily broken with a hammer
3. The rock can be broken by a kick (with boots) but not by hand
4. The rock can be broken apart in the hands, but does not disintegrate in water
5. Soft rock that disintegrates when immersed in water.

2.2.7 Rate of weathering

Weathering rates can be described in different units of volume, of distance per unit time or mass per unit time, etc. The major problem in describing weathering is the difficulty of arriving at an accurate number due to the complexity concerning the different mechanisms and variables that influence weathering.

2.2.7.1 Units for measuring weathering rates

Units for measuring alteration by ionic loss:

- meq / m^2 (milliequivalents per square metre)
- mol / ha or mol/cm^2 (moles per hectare, or per square centimeter)
- mol / g (moles per gram)

Units for expressing loss/change:

- μm (micrometer)
- mm (millimeter)

Units for weathering rates where alteration is *__uniform__* *(linear over time)*:

- meq / ($m^2 \times a$) (milliequivalents per square metre per year)
- mol / (ha × a) (moles per hectare (or square centimeter) per year (or per second)))
- µm / ka (micrometers per 1000 years)
- mol / (g × h) (moles per gram per hour)
- t / ($km^2 \times a$) (tonnes per square kilometer per year)

Units for weathering rates where alteration over time is *__non-uniform__* *and may be expressed as a regression equation*:

For example the rate of accumulation of clay in the B-horizon of an Antarctic soil has been expressed as:

$$Y = a + (b \log X) \tag{18}$$

where Y is the clay present as a percentage, a and b are regression coefficients and X is the time in years.

2.2.7.2 Experimental determination of weathering rates

This allows for research of the influence of time, mineralogy, temperature, solution concentration, surface area of substance etc. It does however involve simplification of this complex subject and care should be taken to ensure representation of the true conditions to be simulated. Laboratory testing is usually time limiting and the active agents in weathering solutions are usually present in much higher concentrations than in the environment. Bland and Rolls (1998) discuss that experimentally determined rates are usually one to three times higher than weathering rates in the field. This can be due to differences in temperatures and reduced contact between water and minerals in field situations.

The following variables have been identified to influence the weathering rate:

- The mineral composition

Specified weathering rates are given by Bland and Rolls (1998) e.g. the weathering rate of olivine was determined by two methods. The first used the release rate of Mg from forsterite and calculated a rate of 3.98×10^{-15} mol/cm^{2}s, the second was calculated from the Si release rate and resulted in a rate of 5.01×10^{-16} mol/cm^{2}s.

- The mineral structure

The original and developing structure have been found to influence weathering. Weathering is most rapid at reactive sites such as crystal defects, dislocations, twin boundaries and micro fractures. As weathering develops, these weaknesses can become enlarged (weathering rate maintained or increased) or blocked with secondary products, causing the weathering rate to drop rapidly. Diffusion paths have been found to block if the structures of the weathered material and the secondary product are similar. For example Bland and Rolls (1998) discuss the formation of clays when olivine weathers, where the structural units of the clays are too large to occupy diffusion avenues, therefore resulting in a high weathering rate. On the other hand the hydration of pyroxene results in a talc-like silicate product of which the lattice dimensions almost perfectly fit pyroxene resulting in blocking of the diffusion channels.

- Time

The weathering rate is usually found to decrease over time. This can be explained by either a precipitated layer at the mineral surface or due to preparation of the sample where grinding leaves a fine powder at the mineral surface, which will react rapidly with weathering fluids until it is dissolved. The high initial rate of mineral dissolution will fall away as the fine particles are dissolved.

- Weathering solution

The pH of the solution can largely influence the weathering rate of especially aluminium, magnesium and silicon. The presence of chelating agents for example fulvic acid can also influence the weathering rate. The concentration of salts in solution will also influence the weathering rate mechanically as discussed in section 2.2.1.3. Specifically the presence of certain cations should influence the weathering as discussed in section 3.2. The test work incorporated this property.

2.3 QUANTIFICATION / MEASUREMENT OF KIMBERLITE WEATHERING

2.3.1 Expressing kimberlite weathering

A few possibilities of expressing kimberlite weathering were considered:

- The mineral phases in the kimberlite could give an indication of the weatherability e.g. different clay minerals present.
- The chemical properties of the ore change e.g. the release of Fe or Na from the ore and uptake of other cations in the clay structures.
- The chemical properties of the weathering solution change as ions are released and used for clay formation.
- If swelling clays form, water uptake during absorption can be measured.
- Bulk strength of the ore decreases which can be determined by mechanical rock tests.
- Clays tend to form fines (slime), which can be determined by the weight loss of the sample.
- The slake durability test is a test mainly used in the mining industry and measures the weight loss of sample as a function of cyclic wetting (Saydam *et al*, 2003).

2.3.1.1 Changes in chemical or mineralogical properties of the ore

2.3.1.1.1 X-Ray Fluorescence analysis

The chemical composition of the ore can be determined by XRF (X-Ray Fluorescence) analysis. This analysis method is also called X-ray emission spectrography. The material is ground into a powder and compressed into a pellet using a binder. In the analysis procedure the pellet is irradiated with X-rays, which are generated in a high-intensity X-ray tube. The X-ray energy that is absorbed in the sample results in the generation of an X-ray emission spectrum that is characteristic for each element in the sample. This spectrum is then resolved into spectral lines, which can be identified by wavelengths that are specific to the element that is producing the spectral line. This is then compared to standards to enable quantification. For more information on the analysis method and equipment the reader is referred to Klein and Hurlbut (1993). This analysis method allows for accurate determination of the chemical composition of inorganic matter. It is however very important to notice that this method cannot give any information on the mineral phases present or quantification thereof. Therefore this analysis method is optimally useful when used in conjunction with X-Ray Diffraction (XRD) analysis, which determines the minerals present.

In theory, XRF can be used as in section 2.2.7.2 to calculate the weathering rate by the release rate of Mg or Si from the ore. This approach will however be invalid if Mg is redeposited in another mineral e.g. a clay mineral. Therefore the approach is rather to follow the alteration to clay minerals (mineral phase analysis).

2.3.1.1.2 X-Ray Diffraction analysis

X-ray diffraction is a useful technique in identifying the minerals present. It is only applicable to crystals as they consist of an ordered three-dimensional structure with characteristic identity periods along crystallographic axes. When an X-ray beam strikes such a three-dimensional arrangement it causes the electrons in its path to vibrate with a frequency of the incident X-radiation. These electrons absorb some of the X-ray energy and emit (scatter) this energy as X-radiation of the same frequency and wavelength. Usually these scattered waves interfere destructively but in some conditions (when the Bragg law is fulfilled), these waves reinforce one another producing a cooperative scattering effect known as diffraction. Again more detailed discussions can be obtained from Klein and Hurlbut (1993). Quantitative analysis using XRD analysis is limited and only minerals in excess of ~ 5 % can be reported.

X-Ray Diffraction of clay minerals

The work by Bühmann (1998) and Moore and Reynolds (1989) discuss in detail the XRD analysis of clay minerals and how to determine the clay minerals accurately. Other authors on the X Ray Diffraction of clays are Brindly (1955) and Thorez (1975). Identification of clay minerals can become a cumbersome process due to overlapping reflections. This can be overcome by treating the ore. Firstly concentration of the clay mineral fraction (< 2 μm) is suggested for optimal XRD results. This will however not give an indication of the total sample mineralogy. A normal air-dry scan is then recorded. The ore can subsequently be treated firstly with ethylene glycol and / or glycerol to aid identification of the smectites and vermiculites (the procedure is discussed in Bühmann, 1998 and Moore and Reynolds, 1989). The XRD scan is again recorded before the sample is further treated with hydrazine and formamide which helps in identification of kaolinites. The sample is lastly treated at 500 °C to collapse the swelling clays and this destroys or transforms minerals such as kaolinites and chlorites respectively. The XRD scans from the different treatments can now be compared and will allow identification of the main clay groups. Further treatments like saturation with Na, K, Ca and Mg can be considered if more accurate identification of the swelling clays is required. Other more specific applications are discussed by Bühmann (1998) and Moore and Reynolds (1989) if more information is required. From these treatments, comparison of the XRD scans will allow for identification of the clay groups.

For example the minerals in the kaolinite/serpentine group are both characterised by a 7 Å reflection in the normal scan but koalinite will collapse in the 500 °C treated scan whereas serpentine will be unaffected. Hydrazine treatment will expand kaolinites to 10.4 Å.

Smectite and vermiculite can both have a first basal spacing at 14 Å. The smectite spacing will expand to ~ 17 Å after glycol treatment whilst the vermiculite will show a peak at 14.2 Å after glycerol treatments. Heat treatment will shift smectite and vermiculite to 10 Å. The swelling clays are distinguished with certainty by saturation with K and Mg. Chlorite minerals will remain at 14 Å with glycol, glycerol and heat treatment.

For more information the reader is referred to Bühmann (1998), Moore and Reynolds (1989), Weaver (1989) and Poppe *et al* (2001).

The document by Bühmann (1998) also discusses optimal usage of the XRD equipment when working with clay minerals, to achieve the best results.

The smectite lattice parameter (the d value of the smectite 001 peak on a XRD scan) is called the interlayer spacing; i.e. the c axis spacing between the clay interlayers. It therefore gives an indication of the amount of swelling that has taken place. 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). Some authors have used this property to relate to the swelling. This is discussed further in section 3.2.

2.3.1.1.3 Chemical indices as an indication of the intensity

Combining XRD and XRF analysis, a few possibilities arise of quantifying weathering. The degree of alteration can be determined by either comparing the constitution of the parent material (if known) with the weathered material, or another approach is to work out the ratio between a highly resistant material e.g. quartz and other more easily weathered materials, which can then be used as an index.

- Absolute methods

Absolute methods are based on the approach that a quantifiable relationship exists between the unweathered and weathered material.

Isovolumetric method

This simple method is based on the assumption that no rock volume change occurs during the weathering process, and therefore the mass loss is an indication of the weathering that took place. This assumption is valid if the original petrographic textures and geological structure are still intact, which can be valid in some cases of low weathering rates. Kimberlite weathering however does not fit this assumption.

Benchmark mineral method

A resistant mineral is selected as benchmark and other minerals compared to it. Alumina is sometimes used because it is quite insoluble at pH values down to ~ 5.5 and is still retained in clay mineral weathered products. The approach is that the ratio between the alumina content of the parent rock and of the regolith is used to calculate the loss of the other compounds. This approach may prove useful if the material contains a highly weathering resistant mineral at relative high concentrations.

- Relative methods

In some cases the composition of the parent material is unknown or uncertain. In these cases the degree of weathering can be assessed by calculating the ratio between more stable and the less stable oxides, which is again expressed as an index. Two main groups exist, where the first one is based on alumina as the immobile mineral (the more general approach) and the other assumes that tourmaline is the most resistant mineral. For the second approach two weathering ratios (WR) are used, for heavy (h) and light (l) minerals:

$$WR(h) = \frac{zircon + tourmaline}{amphiboles + pyroxenes} \qquad (19)$$

$$WR(l) = \frac{quartz}{feldspars} \qquad (20)$$

These relative methods do however have the shortcoming that the various elements are assumed to be oxides, which is not entirely reliable as for example sodium oxide will rapidly react to form sodium hydroxide.

Table 11 below shows weathering indices that rely on the assumption that aluminium remains immobile during weathering and each ratio is suited for specific conditions (Bland and Rolls, 1998). This assumption is that Al is in the alumina form and does not take into account Al in other minerals e.g. feldspars. These indices again assume all elements as oxides, which are not necessary valid.

Table 11. Weathering indices as published by Bland and Rolls (1998).

Chemical index of weathering (Harnois, 1988):

$$CIW = [Al_2O_3 / (Al_2O_3 + CaO + Na_2O)] \times 100 \qquad (21)$$

Chemical index of alteration (Nesbitt and Young, 1982):

$$CIA = [Al_2O_3 / (Al_2O_3 + CaO + Na_2O + K_2O)] \times 100 \qquad (22)$$

Weathering Index (Parker, 1970):

$$WI = [(2\ Na_2O / 0.35 + (MgO / 0.9) + 2\ K_2O / 0.25) + CaO / 0.7)] \times 100 \qquad (23)$$

Weathering index Vogel (1973):

$$MWPI = [(Na_2O + K_2O + CaO + MgO) / (Na_2O + K_2O + CaO + MgO + SiO_2 + Al_2O_3 + Fe_2O_3)] \times 100 \qquad (24)$$

2.3.1.1.4 Changes in chemical properties of the weathering solution

Ca, Mg and Fe release into the weathering solution was evaluated as functions of time by Hodgson (1981). The tests were done on Cullinan kimberlites in a 9 M sulphuric acid solution at 70 ˚C. All three cation concentrations were found to increase with time and reached constant levels around 24 hours. The highest concentration was for Mg, although Mg and Fe in solution were found to be very similar, in concentrations twice as high as Ca. Specific values are not quoted as this is very much determined by the type of ore and specific testing conditions, but this method could be used to evaluate the changes taking place during weathering.

2.3.1.1.5 Adsorption of water to form swelling clays

An extensive study by Erguler and Ulusay (2003) explored the methods that have been developed to determine swelling. This includes the free swell index, modified free swell index, methylene blue, $Wmax_{24,72}$ and direct measurement of volume change by the odometer. The free swell test as suggested by Holtz and Gibbs (1956) uses a 100 cm^3 water filled beaker. 10 cm^3 dry soil is sieved through a 0.42 mm aperture size and the undersize poured into the water. The swollen volume of the soil after it comes to rest is noted. The free swell is given as %. Holtz and Gibbs also discuss the modified free swell index which is a non-dimensional index developed from the free swell test to overcome its limitations, for example a negative swell percentage for kaolinite clay and measurement errors in reading off the volume. The methylene blue test gives a relative measure of the CEC as methylene blue is preferentially adsorbed on the negatively charged sites. The $Wmax_{24,72}$ parameter suggested by Erguler and Ulusay uses 400 g of ore adding water up to 300 mL. The slurry is stirred for ~ 5 minutes and then left for 24 and 72 hours respectively. After 24 hours the beaker is laid down for 15 minutes for the water to flow out. The water content of the sample is now determined and reported as W_{24} or W_{72}.

The results from these authors did not show good correlation between the free swell, modified free swell or methylene blue tests. They therefore introduced the new parameter $Wmax_{24,\ 72}$, which showed better predictive ability.

Stephens (1975) also did experimental work on the swelling characteristics of clays. This study included drying of weathered material at 150, 750 and 800 °C. All the dehydration and dehydroxylation in clays will be complete at 800 °C, thus higher temperature tests should not prove useful. The amount of water was evaluated by the mass loss of the sample. This investigation concluded that the water loss (in mass unit) from clays was too small for sufficient differentiation. This study did not take into account the type of kimberlite or any mineralogical properties and whether swelling clay was present is not known.

2.3.1.2 Assessment based on the mechanical properties of the ore

2.3.1.2.1 Single particle breakage tests

Napier Munn *et al* (1996) discussed the different single particle breakage tests and concluded slow compression, drop weight and pendulum tests to be very similar. The disadvantage of single particle breakage tests is the large number of particles that needs to be assessed for a statistically representative analysis. These methods are discussed below.

- Schmidt hammer

More advanced equipment such as the Schmidt hammer measures the changes in the mechanical strength of the material, but avoids possible operator bias (Bland and Rolls, 1998). This test does however yield questionable results when applied to clay bearing rocks.

- Pendulum test

This apparatus is constructed in such a way that the input pendulum is released from a known height to swing down and break a particle attached to the rebound pendulum. It allows for study of the effect of velocity on the single particle, determination of the size distribution and new surface of the comminuted products. A correlation can be made of the specific fracture energy with the new surface area created. Bond (1954) used the pendulum under controlled crushing conditions on specific sized particles, which became known as the crushability test. Napier-Munn *et al* (1996) consider irregular specimens better than spherical particles for a wide range of input energy.

A technological twin pendulum test was developed by the JKMRC institute. This specific development of the twin pendulum test consists of an input and rebound pendulum suspended from a rigid frame. The single particle is fixed to the rebound pendulum and the input pendulum is released from a known height to swing down and collide with the particle. The rebound pendulum swings between a laser source and detector. The detector is mounted at right angles to the plane of swing on an optical bench and a computer records the motion (Napier-Munn *et al*, 1996).

The pendulum test was used by Stephens (1975) as a possible kimberlite weathering output but this produced severely scattered results. It was also suggested that the particles break on weakened planes and therefore the measurement does not reflect the reduced bulk strength due to weathering.

- Drop weight test

This test is considered the most suited for characterizing the breakage of soft materials e.g. simulating of the handling of ores. The test works on the principle that a particle is dropped from a known height and the size distribution of the broken product is measured. The energy can be calculated simply as the potential energy in Joules (equation 25), with m the mass of the particle in kg, g is the gravitational acceleration equal to 9.81 m/s^2 and h is the drop height in m. Conversion gives 1 kWh/t = 3600 J/kg resulting in a height of 367 m required to apply 1kWh/t, which is the typical crushing energy. Therefore this test was altered for a more convenient but similar test where a suitable weight is dropped on to the particle, where distances of less than 1 m are required.

$$E = mgh \tag{25}$$

The altered test can be used to establish the relationship between surface area produced and the input energy. The size distribution of the resulting particles can be described by the Schuhmann linear equation (equation 26).

$$Eis = Ak^{(1-n)} \tag{26}$$

Eis is the specific energy input [Joules / kg], A and n are constants and k is the size modulus.

Further modifications have been made to this test to fit the specific application as discussed by Napier-Munn *et al* (1996). Again a more technological version of this test was developed by the JKMRC. This test allows for drop weights of 20 – 50 kg to be released by a pneumatic switch at drop heights of 0.05 – 1 m. The particles used are 10 – 50 mm in diameter and the test was designed for ores with specific gravities of 2.8 – 4 g/cm^3. These conditions represent operating energy ranges of 0.01 – 50 kWh/t. For softer material it is suggested that smaller breakage heads ~ 2 kg be used at a height of ~ 0.35 m (0.001 kWh/t). During the test the rebound of the breakage head should be minimized as this allows for loss of energy that is not measured.

The JKMRC comminution handbook by Napier-Munn *et al* (1996) regards the drop weight test to be superior to the pendulum test as it allows for extended input energy ranges, requires shorter testing times, can use an extended particle range and has greater precision.

The outputs of a pendulum/drop weight or any other breakage test will have to accommodate the product size distribution. To relate this to the mineralogy or rate of weathering will require the reduction of the size distribution to a single breakage ratio or index. JKMRC has developed the characteristic breakage index (t_{10}) for this reason. This index simply refers to the cumulative % passing at 10 % of the original ore particle size (See figure 12). Y is the geometric mean of the size interval for the test particles.

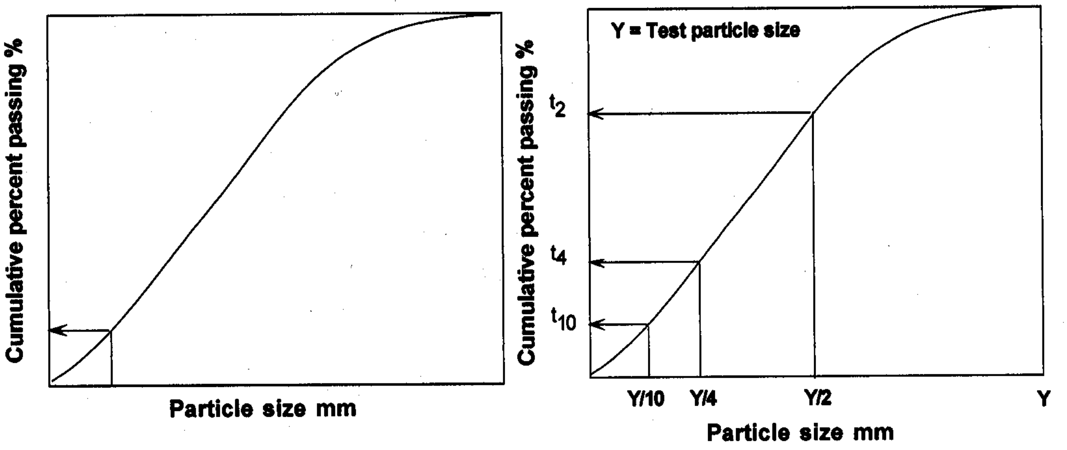

Figure 12. Normal size distribution curve illustrating the t_{10} from Napier-Munn *et al* (1996).

Another index rather than t_{10} can be used in a similar way from the size distribution curve e.g. t_4 and t_2 as shown in figure 12.

- Compression test

Compression testing was done by Stephens (1975) in a vice as a possible kimberlite weathering evaluation. As with the pendulum test it was found that consistent results could not be found due to irregularities of the testing specimen [i.e. weakened planes, mineralogy, surface characteristics (machining), size of the specimen etc.]

2.3.1.2.2 Batch tests

- Autogeneous milling

Autogeneous milling tests as indicator of the reduced bulk strength of the material were applied by Stephens (1975) and Hopwood and Webb (1975); both found this method very suitable. Hopwood and Webb (1975) used an 8-inch batch mill at 50 % critical speed for 30 minutes. The size distribution of the product can be used as a weathering index or a specific point on the curve e.g. t_{10}, d_{10} (particle size where 10 % of the cumulative % of ore passed) or d_{80} (particle size where 80 % of the cumulative % of ore passed) as a function of time.

The major advantage of this test is that it can accommodate larger samples, which increases representativeness and the ease of obtaining a representative sample. It is not as sensitive to mineralogical and physical properties of the ore as single particle breakage tests. This type of test should require fewer tests for repeatability due to the increased size of the sample.

Both of the investigations mentioned above used the median size (d_{50}) as the output parameter, as a meaningful difference could be reported for small variation in the weathering. The difference between the reports is that Stephens (1975) found the product size distribution to be a normal distribution for fully weathered material but found that unweathered material lacked intermediate sizes (milling rounded the unweathered rock leaving large and fine particles). Hopwood and Webb (1975) on the other hand found weathered kimberlite material to lack intermediate sizes and concluded the weathering process to be surface limited. For these investigations the geology or mineralogy of the kimberlite material was not at all considered and it is suggested that the mineralogy of the kimberlites for the two studies might have been very different. The study by Hopwood and Webb (1975) was done on Cullinan kimberlite whilst the study by Stephens (1975) was done on Kimberley kimberlites. The type of milling (energy applied) will also have an influence on the product size distribution. The present study showed that the type of ore would determine this parameter. An ore like Koffiefontein, which is highly weatherable, generates a lot of fines in a very short time whereas a medium weatherable ore will not really generate fines but the size distribution curve will move to smaller sizes.

t_{10} as an output parameter seemed very suitable as it is already used in De Beers for modelling and simulation of crushing units. This model can then determine the influence of weathering on t_{10} and on the product size distribution. The t_{10} for crusher breakage is usually 10 – 20 % and can range between 20 – 50 % for tumbling mills.

Using an ore abrasion test (Napier-Munn *et al*, 1996) might also prove useful in terms of the fines generation during weathering and clay formation. The output parameter is now defined as t_a. t_a is defined as one tenth of t_{10} and therefore is one tenth of the cumulative percentage passing at Y/10 (see figure 12). t_a can be as low as 0.2 for very hard ores to above 2 for very soft ores and gives an indication of the resistance to abrasion that a specific ore has. This abrasion test uses a 300 mm diameter x 300 mm long tumbling mill with four 10 mm lifter bars. A 3 kg sample of size – 55 + 38 mm is then ground for 10 minutes at 70 % critical speed (~ 53 rpm).

Ultimately the choice of parameter depends on whether much fines would be generated after weathering (greater part of the size distribution curve similar to unweathered state) or whether the whole size distribution curve would shift to smaller sizes. Based on this, the output parameter could be chosen.

- Comminution Energy

The parameter t_{10} as discussed under the drop weight test was adapted for autogeneous or semi-autogeneous milling, to incorporate the comminution energy (Napier Munn *et al*, 1996). This adaptation included fitting of a function, given as equation 27.

$$t_{10} = A\left[1 - e^{(-b \times E_{CS})}\right] \tag{27}$$

t_{10}: The percent passing 1/10 th of the initial mean particle size
E_{CS}: The specific comminution energy (kWh/t)
A,b: The ore impact breakage parameters

The influence of comminution energy can therefore be determined by plotting t_{10} vs. E_{CS}.

2.3.1.3 Fines generation or mass loss of the sample

Some form of fines generation or mass loss of the sample due to fines generation was used as a quantitative measure by Stephens (1975), Hodgson (1981) and Clark (1982). Stephens (1975) concluded that too little fines generation took place for quantitative analysis without attrition or without accelerated weathering tests. He concluded that this might be a useful parameter if the tests could be altered to produce ~ 50 % slimes. Clark (1982) simply used the % slimes defined as the % -1 mm material, which was a useful tool to compare weathering at different times of 1, 2, 4 and 6 months where a maximum of 20 % of the feed material reported to the fines. Hodgson (1981) used the % - 75 μm material after weathering (which was in the order of 20 % after one day) but at increased temperatures around 70 °C. Again the mineralogy of these ores can not be compared to link the fines generation to the mineralogical properties. Fines generation could be a useful parameter on highly weatherable ores.

2.3.1.4 The slake durability test

Towards the end of this study the slake durability test (figure 13) which is mainly utilised in the mining industry was recognised as an alternative weathering test. This test combines the effect of cyclic swelling and abrasion to accelerate the rate of weathering. This test was standardized by the American Society for testing and materials (ASTM D4644-04). The test uses ~ 10 pieces of rock weighing 40 – 60 g each. The sample is rotated in a steel mesh drum partially immersed in water for 10 minute cycles with oven drying between cycles at ~ 80 °C for 8 – 12 hours. The steel drums are made of sieve mesh at 2 mm allowing all particles smaller than this to pass into the water bath. The slake durability index (see table 12) is then used as the output which is defined as the percentage of the final weight to initial dry weight after each cycle. Usually at least four cycles are required for characterisation of a clay rich material (Gökceoğlu *et al*, 2000).

Table 12. Weathering Description of the Slake durability index.

Amount of slaking / Weatherability of the ore	Slake durability index (%)
Very low	0 – 25
Low	25 – 50
Medium	50 - 75
High	75 – 95
Very High	95 - 100

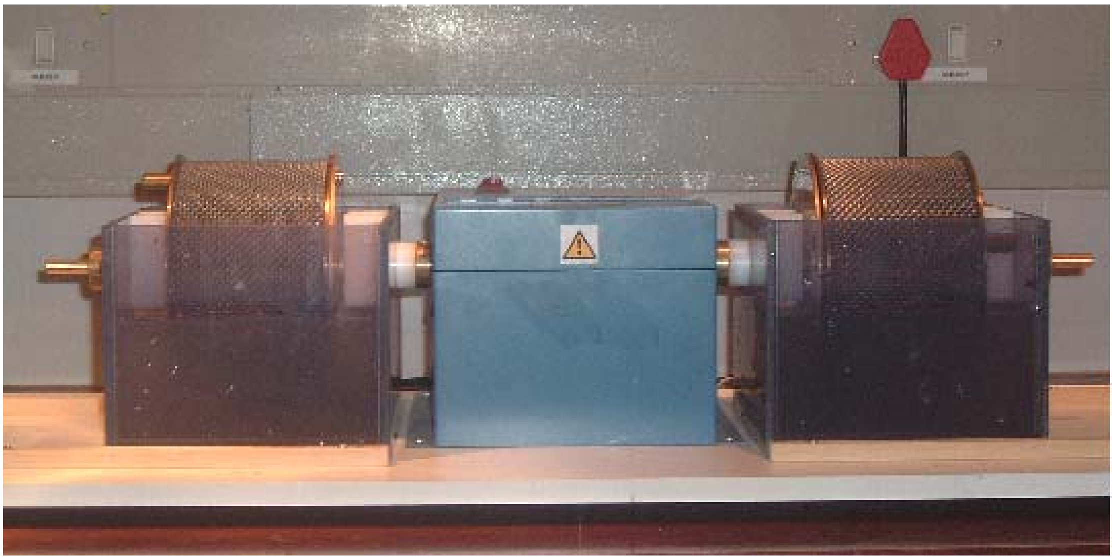

Figure 13. Slake durability test equipment.

2.3.1.5 Conclusion

From the discussion above it was concluded that one single parameter could not sufficiently describe weathering. It was decided to use a combination of chemical and mineralogical properties of the ore together with a mechanical test to represent the reduced bulk strength after weathering.

XRF analysis was used to obtain the chemical composition of the ore. XRD with the clay sub treatments as discussed in section 2.3.1.1.2 was used to identify the mineral phases present on a semi-quantitative basis. The interlayer spacing (d) from XRD was used as an indication of the amount of swelling.

For the mechanical test the autogeneous batch mill test was initially used, as the applicability of this test with South African kimberlites has been proven and repeatability should be better with batch tests than single particle breakage tests. The output parameter of weathering tests was therefore chosen as the size distribution of the weathered and milled ore as compared to the non-weathered milled ore (base case). For reduction of the size distribution graph to a single output t_{80} was mostly used. t_{10} was found not to be suitable as the most significant changes in the size distribution graphs took place at 70 – 80 % of the starting size. Later on the slake durability test was also used.

2.4 PARAMETERS THAT INFLUENCE KIMBERLITE WEATHERING

2.4.1 Accelerated weathering

Weathering can occur in as little as a few seconds but can sometimes take months or even years before it becomes visible. The controlling variables that can cause these differences in kimberlite ores need to be studied and how the weathering environment can impact on this process need to be defined and understood. Previous work on accelerated kimberlite weathering is summarised below.

2.4.2 Ion concentration

Accelerated weathering tests by Hopwood and Webb (1975) concluded that the presence of aluminium in solution led visually to the breakdown of a Cullinan kimberlite. The mineralogy of the sample used is unknown.

Hodgson (1981) did a study on the hydrothermal alteration of kimberlite. He found the combination of H^+, Al^{3+} and temperature determined the clay minerals that will form.

No other literature utilising cations as accelerator for the weathering process was found. Other literature on the influence of cations on the smectite structure and swelling is however available and discussed in section 3.2.

2.4.3 Acid concentration

As discussed under section 2.4.2 above, Hodgson (1981) found that the temperature, acid and aluminium concentration determine the type of clays formed as alteration products. Hodgson also tested the influence of different acids at different concentrations (1-16 M) and temperatures (70 and 100 °C) separately. He found sulphuric acid a little more aggressive than hydrochloric acid.

In practice the weathering solution pH can be as low as 5 as discussed under section 2.2.3.1 depending on the dissolved CO_2 and bacteria present. Mine recycle water on the other hand can be as high as pH 9 – 10.

2.4.4 Temperature

Hopwood and Webb (1975) tested the effect of temperature on weathering between 50 and 900 °C and also used heating and cooling/quenching cycles. The conclusions were that above 800 °C the kimberlite became brown and very tough and would not weather under any conditions. They found no other effect of temperature on the weathering process under normal heating and cooling, heating and quenching and cyclic variation. Again the mineralogy of the sample used is unknown.

In contrast to the findings of Hopwood and Webb (1975), Hodgson (1981) found that temperature definitely influenced weathering. He concluded that the combination of temperature, acid and aluminium concentration determines the clay product and cannot be studied separately. The influence of the type of clay product on the rate and degree of weathering has not been tested.

With South African diamond mines the temperature limits in different geological areas can be between - 5 and 40 °C.

2.4.5 Wetting and drying cycles

Cyclical wetting and drying is important for mechanical weathering as discussed in section 2.2.1.4. Swelling clays especially should be vulnerable to cyclic wetting and drying and this could be a parameter utilised when accelerated weathering is required. Cyclic wetting and drying is utilised by the slake durability test discussed in section 2.3.1.4.

2.4.6 Other parameters

Hopwood and Webb (1975) tested microwave heating as a possible weathering accelerator but found that the kimberlite exploded without any prior softening. It was concluded that breakage occurred by differential expansion and not chemical weathering of the material. The same investigation tested ultrasonic breaking as a possible influential factor but found no physical degradation of the kimberlite even at very high ultrasonic sound intensity. It was however found that the ultrasonic breaking could break down products that formed on the surface and in this regard improve weathering. They also tested ultraviolet and infrared light and found no influence on kimberlite weatherability.