6

Weathering and associated landforms

6.1 The weathering system

Material carried to the sea by rivers, or transported by glaciers or the wind, experiences some degree of chemical decomposition or physical breakdown prior to being eroded. Weathering is therefore an appropriate place to begin our look at the operation and effects of exogenic geomorphic processes. Geomorphologists are concerned with the rates at which different weathering processes operate as a function of environmental conditions, and with the nature of the weathered material that is produced. But they are also especially interested in how weathering gives rise to specific landforms. This contrasts with, for instance, the soil scientist's interest in weathering which stems from a concern for the way it contributes to differences in soil characteristics and the release and movement of nutrients.

6.1.1 The nature of weathering

Weathering can be divided into those processes involving chemical reactions and the formation of new minerals (**chemical weathering**) and those that involve only physical changes (**physical weathering**). Although the differences between these two types of weathering are distinct in theory, in practice they rarely operate separately; rather, the effects of one aid the operation of the other. For instance, a rock shattered through physical weathering will be more liable to chemical weathering because of the increased surface area made available for chemical reactions. Conversely, chemical weathering along microfractures in a rock will weaken it and help physical processes break it down more rapidly.

Weathering can be defined as the adjustment of the chemical, mineralogical and physical properties of rocks in response to environmental conditions prevailing at the Earth's surface. For some igneous and metamorphic rocks formed at great depths and at high temperatures and pressures this adjustment can involve a complete transformation of their constituent minerals. Weathering occurs through complex interactions between the lithosphere, the atmosphere, the hydrosphere and the biosphere, and gives rise to three major types of product. Chemical processes lead to the release of compounds in solution and the creation of new mineral products, while physical processes cause the breakdown of the original rock into smaller particles. Dissolved material may subsequently be re-precipitated or be reincorporated into other minerals, but the great proportion is carried by rivers to the ocean.

6.1.2 Water in rocks and soils

Water plays a vital role in nearly all mechanisms of physical and chemical weathering. This arises in part from the fact that it is a polar solvent; that is, the covalently bonded H_2O molecule has a positive charge at each end balanced by a negative charge in the middle. The positive and negative parts of water molecules become attached, respectively, to the anions and cations of solids and free them by neutralizing their charge; water is thus a highly effective solvent. A second significant property of water is its ionized state. A proportion of H_2O molecules are always decomposed into **hydrogen ions** (H^+) and **hydroxyl ions** (OH^-) (a state known as **dissociation**), the concentration of H^+ ions being expressed as **pH**. This is defined as the negative logarithm to the base 10 of the H^+ concentration in grams per litre. At the standard temperature of 25 °C there are 10^{-7}g of H^+ ions per litre of pure water, giving a neutral pH of 7. Lower pH values indicate **acidity** (higher concentration of H^+ ions), and higher values represent **alkalinity** (lower concentration of H^+ ions). It is important to bear in mind that a change in pH of one unit represents a tenfold change in hydrogen ion concentration.

Water may enter the soil or bedrock simply through percolation through interconnected voids between particles under the force of gravity. But gravity is not the only factor controlling the distribution and movement of water in rock or soil, as is apparent from the ability of water to move laterally and upward as well as downward. The most important mechanism whereby horizontal and upward movements of moisture can occur is the **capillary suction** which affects the water films attached to soil and rock particles. This suction effect can be readily illustrated by imagining the rise of water in a thin (capillary) tube through surface tension effects. If such a tube is placed vertically into a tank of water the level of the water in the tube will rise above that in the tank. The rise is a result of the capillary suction which acts against the force of gravity. The suction is relatively more effective in comparison with the effects of gravity in a thin tube because the circumference of the tube (along which the suction effect operates) is large relative to its cross-sectional area (to which the effect of gravity is proportional). Interconnected pores in soils and rock possess a suction in a manner analogous to a capillary tube and this can be measured by the upward movement of water against the force of gravity. Water in fine-grained materials with small pores experiences a greater capillary suction in just the same way that the height to which water rises in a capillary tube increases as the diameter of the tube decreases.

Capillary suction, together with the force of gravity, therefore influence both the movement and distribution of water in soil and rock, and the interaction of these two factors gives rise to four zones of moisture storage (Fig. 6.1). Below the **water table** rock and soil pores are saturated; water movement is controlled by gravity and is subject to **hydrostatic pressure**, that is pressure exerted by the weight of overlying water. Above the water table capillary suction provides an additional control. A zone of **capillary saturation** exists immediately above in which the moisture content, which does not vary with depth, is present in the form of continuous films of water around particles with entrapped air between. Above this zone the moisture content decreases upward to a point where the continuous film of moisture eventually separates into discrete droplets. The two zones characterized by continuous moisture films are referred to collectively as the **capillary fringe**, the depth of which depends on pore size. In materials composed of sand-sized particles this depth is just a few millimetres, but in clay-sized materials in which the voids are 1 μm or less across it can be tens of metres. The rate of capillary movement in very fine pores is, however, so slow that the theoretical equilibrium height over which **capillary rise** should occur is rarely attained in such cases.

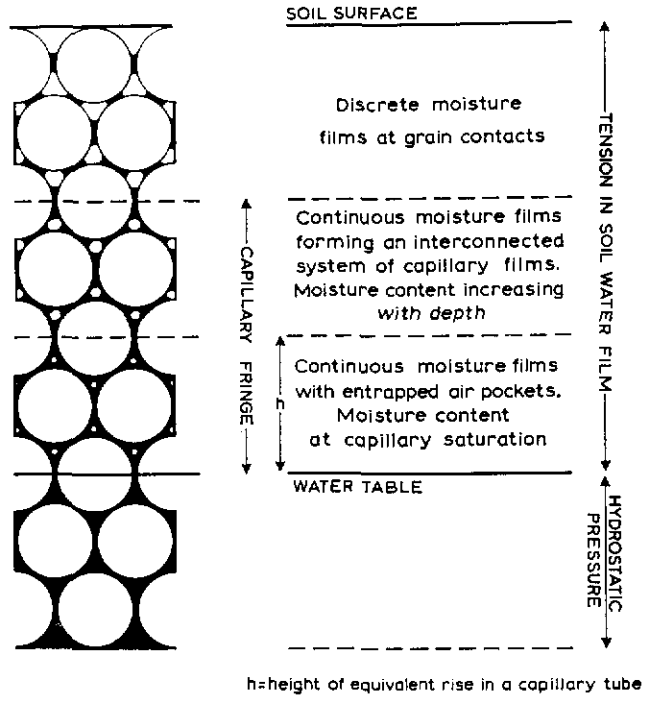


Fig. 6.1 The zones of capillary moisture in regolith and soils. (From M. A. Carson (1969) in R. J. Carson (ed.) Water, Earth and Man. *Methuen, London, Fig. 4.11.4, p. 100.)*

6.2 Chemical weathering

6.2.1 Chemical characteristics of rock-forming minerals

There are two main types of chemical bond existing between atoms contained in the compounds constituting the Earth's rock-forming minerals – **ionic bonds** and **covalent bonds**. Atoms with eight electrons in their outermost (valence) shell are chemically stable, but all the elements with which we are concerned have either more or less than this stable number. Those with one additional electron readily lose it and become positively charged ions (**cations**) (for instance, K^+, Na^+) and those with one less tend to gain an electron and become negatively charged ions (**anions**) (for example, F^-, Cl^-). For other elements the loss or gain of two electrons similarly creates ions with a double charge (for instance, Ca^{2+}, O^{2-}). Such ions are stable on their own but only form stable compounds when their electrostatic charge is neutralized by ionic bonding. In those elements which gain or lose three or more electrons in becoming ions, adjacent atoms can share electrons through covalent bonding. Some elements, such as oxygen, are able to form both covalent and ionic bonds.

This is a simplified picture because in reality most chemical bonds in the majority of rock-forming minerals are intermediate between ionic and covalent (Fig. 6.2). As the bonds with oxygen are particularly important in rock-forming minerals Table 6.1 gives estimates of the pro-

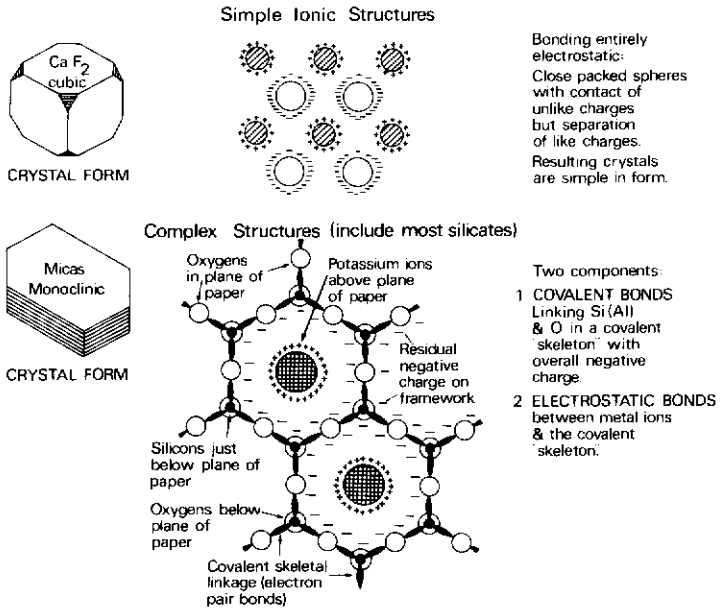


Fig. 6.2 *Ionic and covalent bonding in minerals. Silicate minerals have a basic structure consisting of silicon atoms covalently bonded between oxygen atoms to form tetrahedra with an overall negative charge. This is neutralized through electrostatic bonds with various cations, most commonly potassium, calcium, sodium and magnesium (from C. D. Curtis, (1976) in: E. Derbyshire (ed.)* Geomorphology and Climate. *Wiley, London, Fig. 2.2, p. 34.)*

Table 6.1 Bonding characteristics and ionic properties of some common elements

ELEMENT	ION	APPROXIMATE IONIC CHARACTER OF BOND WITH OXYGEN (%)	IONIC RADIUS (Å) (O^{2-} = 1.40)
Predominantly ionic bonding			
Potassium	K^+	87	1.60
Sodium	Na^+	83	1.16
Calcium	Ca^{2+}	79	1.12
Magnesium	Mg^{2+}	71	0.72
Iron (ferrous)	Fe^{2+}	69	0.77
Intermediate ionic-covalent bonding			
Aluminium	Al^{3+}	60	0.53
Iron (ferric)	Fe^{3+}	54	0.65
Titanium	Ti^{4+}	51	0.61
Predominantly covalent bonding			
Silicon	—	48	—
Phosphorus	—	35	—
Carbon	—	23	—
Sulphur	—	20	—

Source: Based on data in C.D. Curtis (1976) in: E. Derbyshire (ed.) *Geomorphology and Climate*. Wiley, London, Table 2.2, p. 33.

portion of bonding of an ionic type for a number of common elements. Although the relative dimensions of ions (indicated in Table 6.1 by ionic radius) can be used to predict the general form of crystalline compounds where the bonds are largely ionic (such as the cubic structure of fluorite (CaF^2, Fig. 6.2)), most rock-forming minerals are built from complicated silicate structures with complex charge patterns (Fig. 6.3).

6.2.2 Chemical reactions: thermodynamics and kinetics

Although chemical weathering reflects the tendency for new minerals to be formed which are stable under conditions prevailing at the Earth's surface, the rate at which these stable forms are produced is often very slow. This necessitates two complementary approaches to the study of chemical weathering: **thermodynamics** considers the ultimately stable forms by analysing the energy changes involved in chemical reactions, while **kinetics** focuses on rates and mechanisms of change.

The thermodynamic approach can be illustrated using a simple mechanical analogy (Fig. 6.4). All substances contain various amounts of energy within their chemical structures in rather the same way that the ball in Figure 6.4 possesses a potential energy proportional to its height above some datum. When chemical reactions occur energy is usually liberated as heat (although in some kinds of reactions heat is absorbed) just as the ball loses potential energy as it moves downslope. This liberation of heat represents a net release of free energy (ΔR) (more strictly referred to as **Gibbs free energy**). Whether a particular chemical reaction is likely to occur is related to the change in free energy involved. This can be calculated by subtracting the sum of all the free energies of the reacting

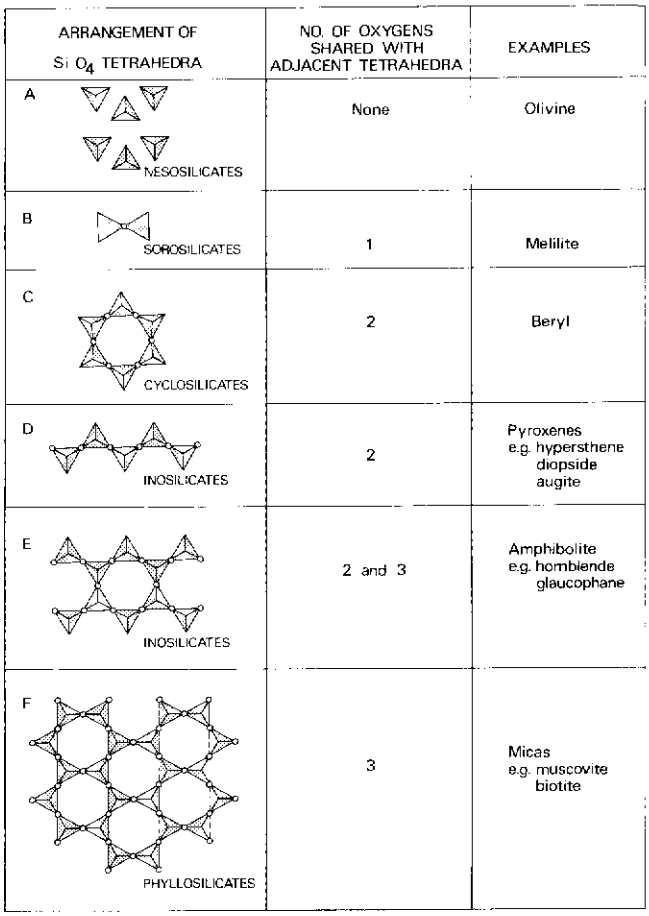


Fig. 6.3 *The primary structural forms of silicate minerals (shared oxygen atoms shown by open circles): (A) discrete tetrahedra; (B) a tetrahedra pair sharing one oxygen; (C) a ring of six tetrahedra each sharing two oxygens; (D) a single tetrahedra chain; (E) a double tetrahedra chain with the outward-facing tetrahedra sharing two oxygens, the inward-facing tetrahedra sharing three oxygens and the creation of hexagonal 'holes' between chains sufficiently large to accommodate ions such as OH^- (hydroxyl) or F^- (fluorine); (F) a tetrahedra sheet with a continuous network of hexagonal holes (this is the structure shown in Figure 6.2). A final structural type of great importance (tectosilicates) consists of a continuous three-dimensional framework of tetrahedra in which all four oxygens are shared; examples are quartz and feldspar). (Based partly on A. Holmes. (1978)* Principles of Physical Geology *(Nelson, Sunbury-on-Thames) Fig. 4.10, p. 52.)*

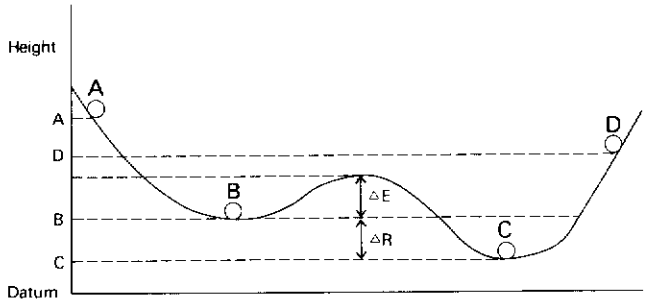


Fig. 6.4 *Types of stability illustrated by a ball on an undulating surface. The potential energy at each position is proportional to its height; the vertical axis is therefore an energy scale. The ball is stable at B and C since it has no spontaneous tendency to move, but A and D are unstable positions since the ball will spontaneously move down the slope towards the nearest trough losing potential energy (height) as it does so. Position B is not as stable as C (it is metastable) since with the addition of a small amount of energy (ΔE) it could roll over the hump to the right to position C where it would have a lower potential energy (height) (ΔR) than at its original position. In this model the most stable state is the one with the least potential energy (lowest height). (based on C. D. Curtis (1976) in: E. Derbyshire (ed.)* Geomorphology and Climate. *Wiley, London, Fig. 2.3, p.38, and Fig. 2.4, p.43.)*

substances from the sum of the free energies of the reaction products. If the calculated free energy change is negative this indicates that the reaction will occur spontaneously; the larger the negative value the more readily the reaction will occur and the more stable the reaction products will be in comparison with the original reactants.

Unfortunately, weathering processes and products cannot be understood simply in terms of the formation of stable mineral forms since many minerals are abundant on the Earth's surface even though thermodynamic considerations tell us that they are unstable. We therefore have to consider the kinetics of weathering by examining those factors which affect the *rate* of chemical reactions. A fundamental control is the degree of instability of the reacting system, or in our mechanical analogy (Fig. 6.4), how far up the slope our ball is located. Another crucial factor is the concentration of reactants; in the case of a solution (such as soil water) reacting with a solid (such as a rock) this will be related to the surface area of contact between the water and the constituent minerals of the rock. A fine-grained, permeable rock, for instance, will provide a much greater surface area than a densely cemented, massive rock. Temperature is another significant factor; this is expressed in the **Arrhenius equation** which indicates that reaction rates approximately double for each 10 °C rise in temperature. **Catalysts** can also greatly speed up chemical reactions, as is illustrated by the familiar oxidation of iron. In completely dry air this reaction proceeds very slowly, but with the addition of water as a catalyst the rate of oxidation increases dramatically. A further important control is the intensity of **leaching**, the downward movement of water through the weathering zone which leads to the removal of soluble products.

6.2.3 Chemical weathering processes

6.2.3.1 Solution

Solution (or **dissolution**) is the simplest process whereby minerals can be decomposed and involves water acting as a

solvent. The dissolution of quartz (a crystalline form of silica) provides an example:

SiO_2	+	$2H_2O$	→	$Si(OH)_4^0$
quartz		water		silica in solution (silicic acid)

The **equilibrium solubility** of a mineral represents the extent to which it will dissolve in water; it is usually expressed in ppm (parts per million by volume) or $mg\,l^{-1}$. Some minerals, such as halite (NaCl), are highly soluble in earth surface environments but others, such as quartz, have a very low equilibrium solubility and dissolve in pure water at an exceedingly slow rate. Equilibrium solubility is affected by the temperature and pH of the environment (Fig. 6.5) while the rate of throughput of water is important in controlling the rate of dissolution. This last variable is particularly significant as the film of water in direct contact with the mineral surface eventually becomes saturated with solutes, thereby hindering further dissolution. Consequently the saturated zone must be constantly flushed by under-saturated water if dissolution is to be an effective mechanism.

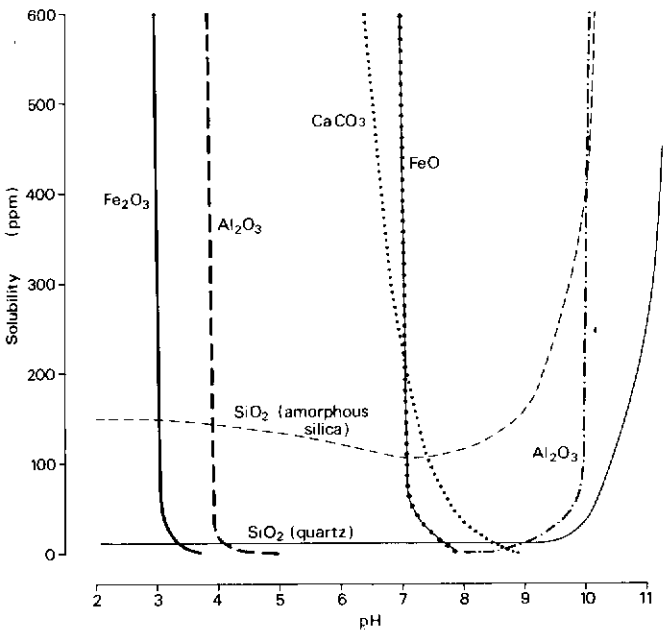


Fig. 6.5 *Equilibrium solubility (expressed in parts per million (ppm)) in water of some components involved in chemical weathering as a function of pH. Note that: (1) the equilibrium solubility of quartz (SiO_2) (crystalline silica) is only about one-tenth of that of amorphous silica; (2) ferrous iron (FeO) is soluble below a pH of about 7, whereas ferric iron (Fe_2O_3) is insoluble except under highly acidic conditions (pH<3.5); (3) alumina (Al_2O_3) is insoluble in the pH range 4–10; and (4) the solubilities of calcium carbonate ($CaCO_3$) and silica (SiO_2) are inversely related over the pH range 6.5–9. (Based on various sources including H. Blatt* et al. *(1972)* Origin of Sedimentary Rocks. *Prentice-Hall, Englewood Cliffs Fig. 10-12, p. 364; R. K. Iler (1979)* The Chemistry of Silica. *Wiley, New York, Fig. 1.6, p.42; and F. C. Loughnan (1969)* Chemical Weathering of the Silicate Minerals. *Elsevier, New York, Fig. 15, p.32.)*

Some minerals have a marked ability to absorb water into their crystal structure through a reversible reaction known as **hydration**. This can be illustrated by the hydration of iron oxide:

$2Fe_2O_3$	+	$3H_2O$	⇋	$2Fe_2O_3 . 3H_2O$
iron oxide		water		hydrated iron oxide

This reaction is significant in chemical weathering because it aids other chemical processes by introducing water molecules deep into crystal structures.

6.2.3.2 *Hydrolysis*

In addition to acting as a solvent, water may react directly with minerals through **hydrolysis**. This involves the replacement of metal cations (most commonly K^+, Na^+, Ca^{2+} and Mg^{2+}) in a mineral lattice by H^+ ions and the combining of these released cations with hydroxyl (OH^-) ions. The effects of this process can be illustrated by crushing different minerals in pure water. The resulting **abrasion pH** indicates the amount of exchange between H^+ ions in the water and cations in the mineral, the increase in pH being due to the abstraction of the H^+ ions from the water (Table 6.2).

The basic hydrolysis reaction can be illustrated by the weathering of the silicate mineral albite (a sodium-rich plagioclase feldspar) to the clay mineral kaolinite:

$4NaAlSi_3O_8$	+	$6H_2O$	→	$Al_4Si_4O_{10}(OH)_8$	+	$8SiO_2$	+	$4Na^+ + 4OH^-$
albite		water		kaolinite		silica		dissolved hydroxyl sodium ions

Note that some of the silicon is retained in kaolinite and that sodium is removed in solution. This reaction leads to the production of hydroxyl ions and would make pore and surface waters alkaline, yet in most environments these waters are neutral to slightly acid. Consequently, we can conclude that hydrolysis as such is not a realistic weathering reaction.

6.2.3.3 *Carbonation*

The **bicarbonate ion** (HCO_3^-) is invariably present in weathering solutions and is easily the most abundant anion in most surface waters. It is formed from the dissolution and dissociation of carbon dioxide in water in a reversible reaction:

H_2O	+	CO_2	⇋	H_2CO_3	⇋	H^+	+	HCO_3^-
water		carbon dioxide		carbonic acid		hydrogen ion		bicarbonate ion

Carbon dioxide is fixed from the atmosphere by photosynthesis and enters the weathering system through the intermediary of respiration by plant roots and the breakdown of plant debris by bacteria. Carbon dioxide is

Table 6.2 Abrasion pH of some common rock-forming minerals

MINERAL	GENERAL FORMULA	ABRASION pH
Olivine	$(Mg, Fe)_2 SiO_4$	10–11
Augite (pyroxene)	$Ca(Mg, Fe, Al)(AlSi)_2O_6$	10
Hornblende (amphibole)	$(Ca, Na)_2 (Mg, Fe, Al)_5 (AlSi)_8O_{22} (OH)_2$	10
Dolomite (carbonate)	$CaMg(CO_3)_2$	9–10
Albite (feldspar)	$NaAlSi_3O_8$	9–10
Biotite (mica)	$K(MgFe)_3 (AlSi_3) O_{10}(OH)_2$	8–9
Anorthite (feldspar)	$CaAl_2Si_2O_8$	8
Hypersthene (pyroxene)	$(Mg, Fe)_2 Si_2 O_6$	8
Orthoclase (feldspar)	$KAlSi_3O_8$	8
Calcite (carbonate)	$CaCO_3$	8
Muscovite (mica)	$K_2Al_4 (Si_6 Al_2 O_{20} (OH)_4$	7–8
Quartz	SiO_2	7

consequently abundant in the atmosphere of soils, especially those characterized by high rates of organic activity; it may reach a concentration of 10 per cent (in comparison with 0.035 per cent in the free atmosphere). The dissolution of carbon dioxide in precipitation provides an additional source of bicarbonate ions.

Surface waters are in fact weak carbonic acid solutions and we can write a more realistic reaction for the weathering of albite in which the release of metal cations (in this case sodium) is matched by the production of bicarbonate ions, a reaction termed **carbonation**:

$$\underset{\text{albite}}{4NaAlSi_3O_8} + \underset{\text{water}}{6H_2O} + \underset{\substack{\text{carbon}\\\text{dioxide}}}{4CO_2} \rightarrow \underset{\text{silica}}{8SiO_2} + \underset{\text{kaolinite}}{Al_4Si_4O_{10}(OH)_8}$$

$$+ \underset{\substack{\text{dissolved}\\\text{sodium}}}{4Na^+} + \underset{\substack{\text{bicarbonate}\\\text{ions}}}{4HCO_3^-}$$

In humid tropical environments, where organic activity is very high and leaching intense, we would expect silica to be removed in solution as silicic acid:

$$\underset{\text{albite}}{4NaAlSi_3O_8} + \underset{\text{water}}{22H_2O} + \underset{\substack{\text{carbon}\\\text{dioxide}}}{4CO_2} \rightarrow \underset{\text{kaolinite}}{Al_4Si_4O_{10}(OH)_8}$$

$$+ \underset{\substack{\text{dissolved}\\\text{sodium}}}{4Na^+} + \underset{\substack{\text{bicarbonate}\\\text{ions}}}{4HCO_3^-} + \underset{\substack{\text{silicic}\\\text{acid}}}{8Si(OH)_4^0}$$

In general it appears that the leaching of metal cations from silicate minerals is controlled by the supply of acids; this not only involves carbonic acid, although this is the most pervasive, but also sulphuric acid and, more significantly, a range of organic acids.

Carbonation plays a particularly important role in the weathering of calcareous rocks. Limestones contain a high proportion of calcium carbonate (nearly always in the form of the mineral calcite) and its weathering involves complex reversible reactions with carbon dioxide in the soil or subterranean atmosphere and carbonic acid in natural waters

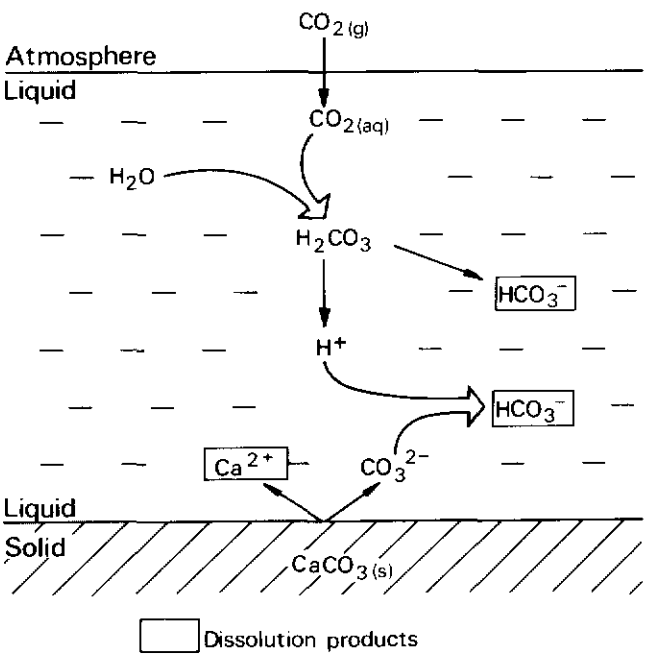


Fig. 6.6 General scheme of the reactions involved in the chemical weathering of calcium carbonate. (After S. Trudgill, 1985, Limestone Geomorphology. *Longman, London, Fig. 2.8, p.17.)*

(Fig. 6.6). In the weathering of calcite, half of the bicarbonate is derived from the calcite itself:

$$\underset{\text{calcite}}{CaCO_3} + \underset{\text{water}}{H_2O} \rightarrow \underset{\substack{\text{calcium}\\\text{ion}}}{Ca^{2+}} + \underset{\substack{\text{bicarbonate}\\\text{ions}}}{2HCO_3^-}$$

The factors controlling the efficacy of limestone solution are complex (Fig. 6.7) but the role of temperature is of particular interest. Whereas the rate of chemical reaction between carbonic acid and calcite increases, as we would expect, with temperature, the equilibrium solubility of carbon dioxide decreases with temperature (at 20 °C it is only half that at 0 °C). This has the effect that high

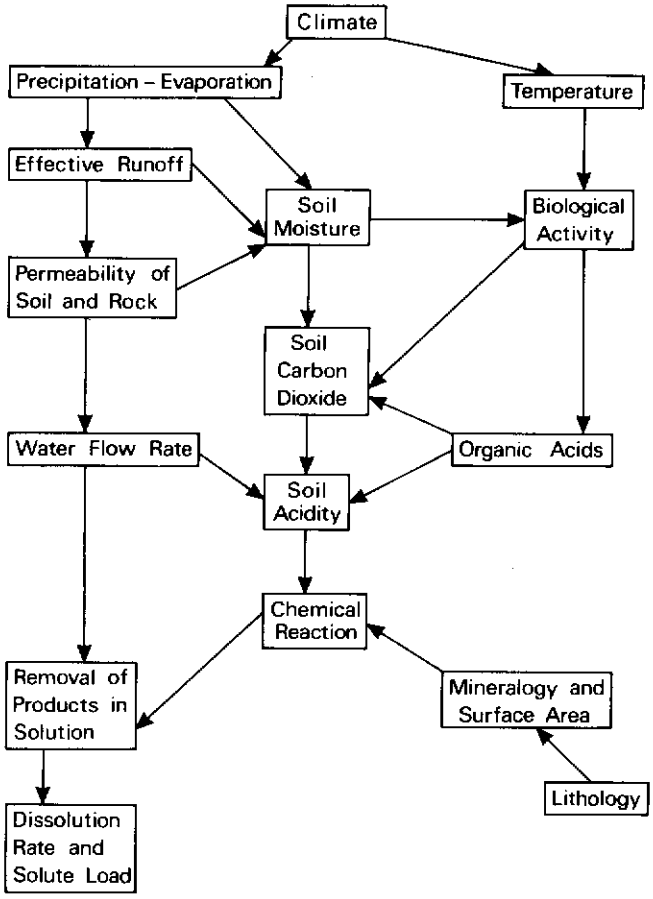


Fig. 6.7 *Key variables in the control of limestone solution. (After S. Trudgill (1985)* Limestone Geomorphology. *Longman, London, Fig. 3.1, p. 27.)*

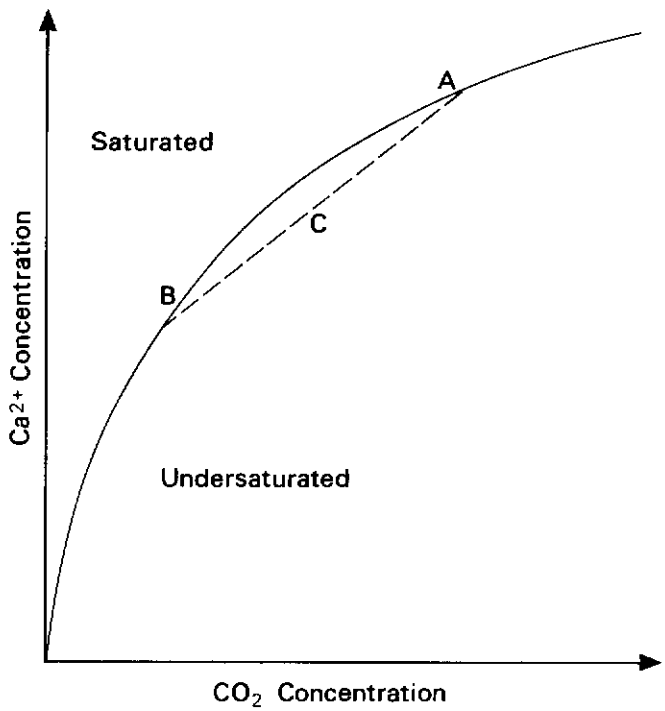


Fig. 6.8 *Schematic representation of the effect on the potential dissolution of calcite of mixing waters with different bicarbonate concentrations arising from the non-linear relationship between CO_2 and Ca^{2+}. The curve represents the equilibrium concentration of Ca^{2+} in solution at given CO_2 levels. Mixing of waters at A and B occurs along the dashed line C in the zone of undersaturation. (After S. Trudgill (1985)* Limestone Geomorphology. *Longman, London, Fig. 2.16, p. 21.)*

concentrations of carbonic acid can be attained in cold regions even though the rate of production of carbon dioxide by organic activity in such environments is relatively low. The mixing of saturated waters with different equilibrium solubility concentrations can also cause further decomposition of calcite (Fig. 6.8).

The concentration of dissolved $CaCO_3$ in surface waters varies considerably. Tropical waters are frequently found to be supersaturated with respect to the prevailing pH levels and the equilibrium concentration of dissolved carbon dioxide. This suggests that the solution of limestone in such areas must be controlled by components other than carbonic acid and it seems likely that organic acids play a major role.

6.2.3.4 Oxidation and reduction

Oxidation is the process whereby an atom or ion loses an electron and thus acquires an increase in its positive charge or decrease in its negative charge. Oxygen dissolved in water is by far the most common oxidizing agent. The reaction can be reversed by **reduction** which involves the gaining of an electron.

Oxidation acts as a weathering process in two distinct ways. Various elements, such as iron, titanium, manganese and sulphur can be oxidized to form oxides or hydroxides. For iron this reaction is written:

$$\underset{\text{iron}}{4Fe^{2+}} + \underset{\text{oxygen}}{3O_2} \rightarrow \underset{\text{iron oxide}}{2Fe_2O_3}$$

Iron usually exists in the bivalent ferrous state (Fe^{2+}) in most rock-forming minerals, but it can be converted by oxidation to the trivalent ferric form (Fe^{3+}) with the effect that the neutral charge of the crystal structure is upset and can only be regained by the loss of other cations. This mechanism can lead to the collapse of the mineral lattice (as in the formation of the clay mineral vermiculite from biotite) and it also renders a mineral more vulnerable to the operation of other weathering processes.

The tendency for oxidation or reduction to occur is indicated by the **redox potential** (**Eh**) of the environment. This is measured in units of millivolts (mV), with positive values registering an oxidizing potential and negative values a reducing potential. Abundant oxygen is dissolved in most surface waters and the Eh is predominantly positive in weathering environments; that is, oxidation occurs spon-

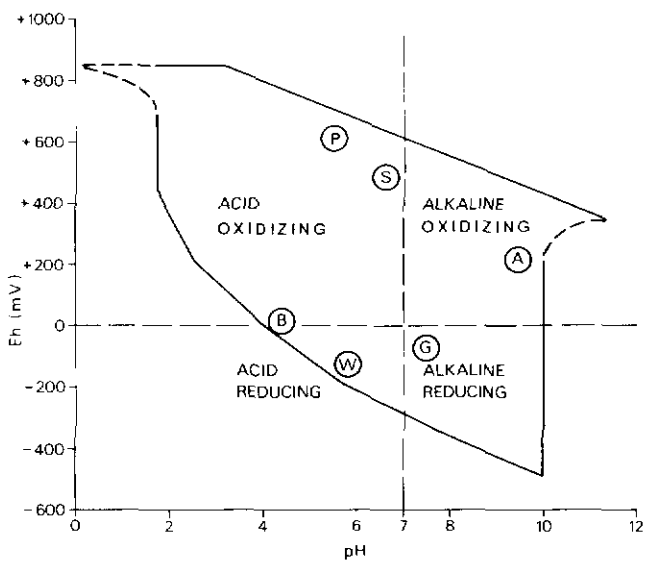


Fig. 6.9 Range of Eh–pH values encountered in the environment. The enclosed area represents the extreme limits of natural Eh–pH values as indicated by the extensive collation of data by Baas Becking et al. *(1960). The letters represent typical values for various types of environments: (P) precipitation, (S) stream water, (B) bog water, (W) waterlogged soils, (G) ground water and (A) aerated alkaline environments. (Based on R. M. Garrels and C. L. Christ (1965)* Solutions, Minerals, and Equilibria. *Freeman, Cooper, San Francisco, Fig. 11.1, p. 380 and Fig. 11.2, p. 381 after L. G. M. Baas Becking* et al. *(1960)* Journal of Geology ***68*** *Fig. 31, p. 276.)*

taneously, though not necessarily rapidly. However, in some localities, such as below the water table and in waterlogged soils, reducing conditions can prevail. Eh also varies with pH, becoming generally lower as alkalinity increases. This relationship can be seen clearly by plotting pH and Eh values measured in various Earth surface environments (Fig. 6.9). Where a particular environment is located on such an Eh–pH diagram provides a useful indication of the nature of chemical reactions that are likely to occur.

6.2.3.5 Cation exchange

Cation exchange is the substitution of one cation for another of a different element in a mineral structure. This can occur with any mineral, but it is by far the most common in clay minerals which typically have rather loosely bonded cations on their surfaces which can be readily exchanged for cations in solution. Each type of clay mineral has a different propensity for the exchange of cations which can be measured by its **cation exchange capacity** (**c.e.c.**) in units of milliequivalents per 100 g (meq 100 g^{-1}) of clay. The mechanism is extremely important in the alteration of one clay mineral to another. The two cations most readily absorbed on to clay minerals are H^+ and Ca^{2+}, and the cation most easily released is Na^{2+}. Cation exchange capacity is affected by the pH of the surrounding solution since under acidic conditions H^+ readily replaces metal cations. Where the environment is alkaline, however, metal cations are less easily detached and may even replace H^+ adsorbed on to a mineral surface.

6.2.3.6 Organic processes

We have already referred to the role of organic acids in chemical weathering, the anions of which may be important in the removal of metal cations from silicate minerals and in the dissolution of carbonates. However, it is the formation of **chelating agents** by organic processes that is of particular significance in weathering. These are able to mobilize metal cations, such as Fe^{3+} and Al^{3+}, which are virtually insoluble under normal Eh–pH conditions, a process known as **chelation**. Chelating agents can come from various sources, but most are organic compounds either secreted directly by organisms such as lichen, or formed through the decomposition of humus in the soil. Although the effects of chelation are well known its detailed mechanisms are not. It appears that a stable ring structure is formed between complexing agents and metal cations. The structure may be subsequently broken down by microbial activity and the complexed cation precipitated.

The dark staining characteristic of rock surfaces in arid regions, which is also observed to a limited extent in more humid environments, appears to be primarily a result of biogenic processes. **Desert varnish** (alternatively **rock varnish**), as it is termed, is composed of clay minerals, oxides and hydroxides of manganese and/or iron, together with detrital particles, which form a layer typically around 10–30 μm thick. It probably takes many thousands of years for a characteristic black to brown desert varnish to develop, apparently through the action of bacteria which preferentially oxidize and concentrate certain elements (especially manganese) supplied from dust and surface water.

6.2.4 Products of chemical weathering

6.2.4.1 The weathering mantle

Chemical processes assisted by the physical disintegration of the bedrock combine to produce a **weathering mantle** or **regolith** which, if differentiated into identifiable horizons, constitutes a **weathering profile**. The interface between weathered material and unweathered bedrock is known as the **weathering front**. The thickness of a weathering mantle at a particular locality represents a balance between the rate of bedrock weathering and the rate of removal of weathered material by denudational agents (Fig. 6.10). Depths of weathering may exceed 100 m and exceptionally reach 300 m or more.

Thick weathering mantles will only form in regions of

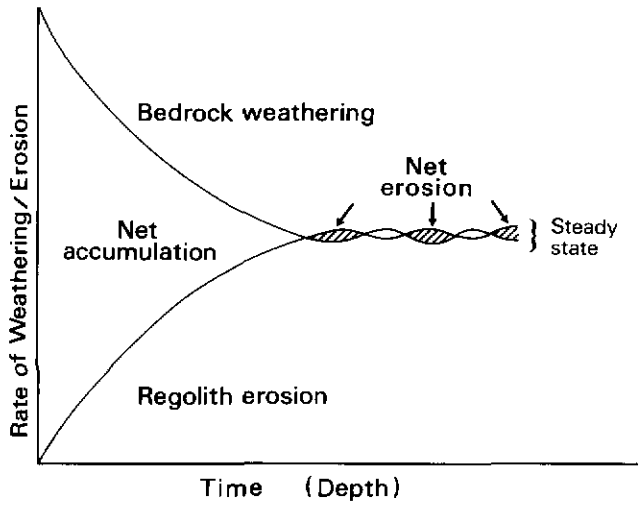


Fig. 6.10 *Schematic representation of the achievement of a steady-state weathering profile thickness dependent upon the rate of weathering and rate of erosion. (After M. J. Crozier (1986)* Landslides: causes consequences and Environment. *Croom Helm, London, Fig. 4.8, p. 138.)*

minimal local relief where rates of erosion have been low for a prolonged period. High rates of weathering are not a prerequisite for the formation of deep weathering profiles if the rate of removal of weathered material is sufficiently slow. This observation is well supported by the presence of very great depths of weathering on the Russian Platform. The general absence of deep weathering mantles in many regions of low relief in the mid-latitudes of the northern hemisphere can probably be attributed to the effects of glacial scouring during the repeated ice-sheet advances of the Pleistocene.

Deep weathering profiles are widespread in the humid tropics, where high temperatures and abundant rainfall create conditions in which the potential for chemical weathering is great. However, when the weathering mantle has developed to a depth of several metres the rate of water movement at the weathering front becomes very slow. Consequently, under these conditions the rate of chemical decomposition at the weathering front is minimal, an effect which is clearly evident in the typically very low concentrations of solutes recorded in streams draining highly leached deep weathering profiles in lowland humid tropical regions (see Section 15.3).

The situation on mountain slopes in the humid tropics is, however, quite different as here high erosion rates lead to the rapid removal of weathered material. Deep weathering mantles cannot develop even though the actual rate of weathering is probably very high as a result of the proximity of the weathering front to the surface and the associated rapid downslope movement of soil water. We need, therefore, to distinguish carefully between *potential* rates of weathering related to climatic parameters, and *actual* rates of weathering related to conditions at the weathering front.

A further complication in the interpretation of regolith thickness is climatic change. In presently arid central Australia, for instance, deep weathering profiles are to be found which have clearly been inherited from a previously more humid climatic regime. Their partial preservation has been aided by the presence of siliceous crusts which are themselves highly resistant to weathering and erosion (see Section 6.5).

The physical characteristics of weathering profiles depend upon the rock type and its structural properties and mineralogy as well as the intensity and nature of the chemical weathering processes. A number of geomorphic studies have focused on weathering profiles developed on granite under humid tropical and subtropical climates. Although considerable differences exist in profile characteristics on other rock types and under different climatic regimes, deep weathering profiles on granite exhibit features which are common to many (Fig. 6.11). There is typically a gradation over tens of metres from fresh bedrock, through weathering material incorporating **corestones** of relatively unweathered rock, to clay-rich horizons capped by a soil.

The mineralogical composition of the various horizons will be influenced by the mineralogy of the bedrock, the hydrological regime and, related to this, the intensity of leaching. For instance, ferrous iron taken into solution below the water table where reducing conditions prevail may be drawn upwards by capillary suction and precipitated as ferric iron in the upper part of the profile. Under a seasonally dry climate this leads to the formation of a characteristically red-coloured, iron-rich horizon overlying a bleached **pallid zone** which has been effectively leached of ferric iron.

In some weathering mantles original bedrock structures are preserved. The term **saprolite** is given to this type of regolith and it reflects the operation of **isovolumetric weathering**, that is, weathering accomplished without any change in volume. This is probably a very common phenomenon, but in many cases its occurrence cannot be proved either because the original bedrock lacked well-defined structures or because any such structures have been destroyed by organic activity.

6.2.4.2 *Mineral stability and the formation of secondary minerals*

The types and proportions of the various minerals in a weathering profile are usually quite different from the original bedrock. Some minerals seem to survive more or less unaltered even after being subject to prolonged weathering, whereas others decompose very rapidly. A classic study by S. S. Goldich published in 1938 showed a consistent variation in the stability in the weathering environment of common silicate minerals occurring in a range of igneous and metamorphic rocks (Fig. 6.12). Goldich pointed

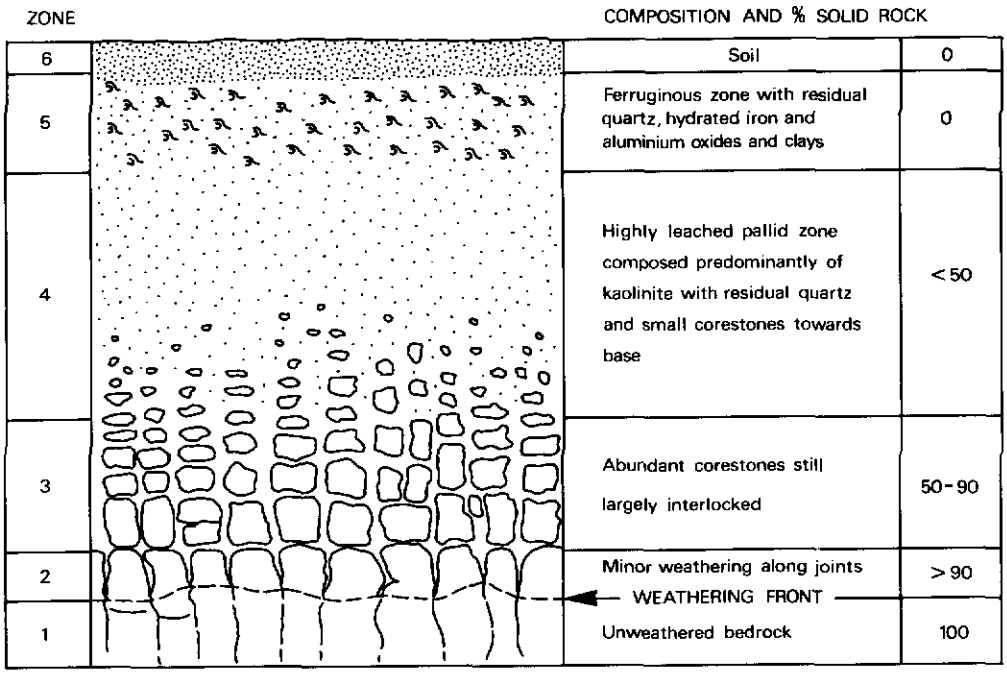


Fig. 6.11 *Features occurring in a fully developed weathering profile on granitic rocks. Based on B. P. Ruxton and L. Berry, 1957,* Bulletin of the Geological Society of America *68, Fig. 2, p. 1266.)*

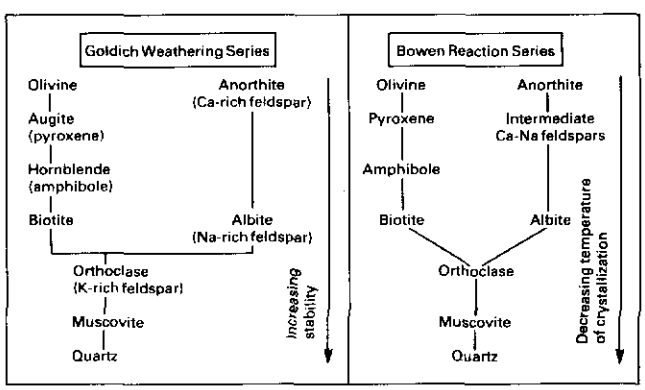


Fig. 6.12 *The weathering series of Goldich and the reaction series of Bowen.*

out that this weathering series closely matched Bowen's reaction series which listed various silicate minerals in terms of their order of crystallization from a silicate melt. Olivine, for instance, is the most unstable mineral in the weathering series and crystallizes at the highest temperature in the reaction series. Quartz, on the other hand, is the most stable and crystallizes at the lowest temperature.

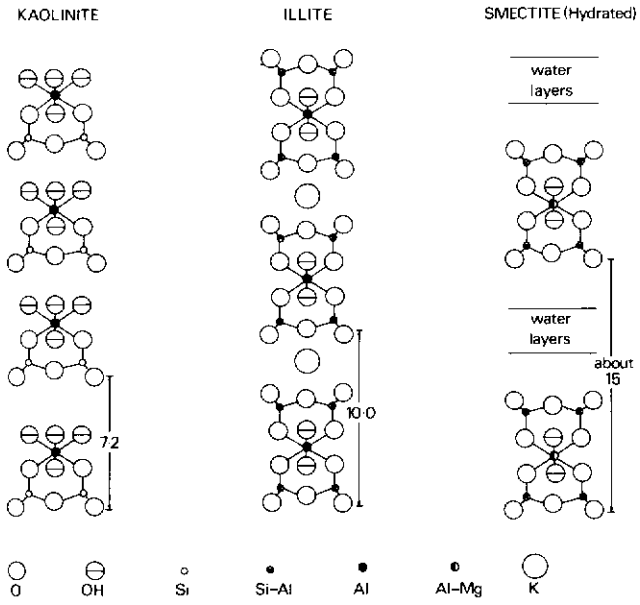
Part of the reason for this relationship between susceptibility to weathering and temperature of crystallization appears to lie in the relative strength of the bonds between oxygen and the cations in each mineral. But the structure of the bonding also seems to be significant, with minerals having few silicon–oxygen bonds (such as the neosilicates and inosilicates) generally being less stable than those with more bonds (such as the phyllosilicates and tectosilicates) (Fig. 6.3). The relationship can also be viewed thermodynamically, there being a larger change in free energy accompanying the decomposition of an unstable mineral like olivine than a comparatively stable mineral like muscovite.

In addition to quartz, which can at least partially survive prolonged weathering in most environments, the mineralogical composition of the weathering mantle includes a range of **secondary minerals** (Table 6.3). These form by the decomposition of primary minerals and the incorporation of dissolved constituents into new mineral forms, by far the most important of which are **clay minerals**. Clay minerals occur in a bewildering variety of forms; only the major groups are listed in Table 6.3. In most cases they are formed through the recombination of silica, alumina and metal cations released during weathering into layered phyllosilicate-type structures (Fig. 6.13). Other secondary minerals formed during weathering include those composed of oxides and hydroxides of iron and aluminium and, less significantly, of titanium oxide, as well as amorphous or finely crystalline silica.

The type of clay mineral produced during weathering depends on the composition of the circulating pore waters (specifically the concentration of dissolved silica and the type and concentration of cations), the mineralogy of the

Table 6.3 Major secondary minerals formed in weathering environments

MINERAL GROUP	COMPOSITION	GENERAL FORMULA	MAJOR VARIETIES	COMMENTS
Oxides and hydroxides				
Oxides of silicon	Silicon dioxide	SiO_2 SiO_2 $SiO_2 \cdot nH_2O$	Quartz Amorphous silica Opaline silica	Water content usually < 10%
Hydroxides of aluminium	Hydrous alumina	$Al_2(OH)_6$ $AlO(OH)$	Gibbsite Boehmite	Has a clay-like layered structure
Oxides and hydroxides of iron	Iron oxide and hydrous iron oxide	Fe_2O_3 $FeO \cdot OH$	Hematite Goethite	
Oxide of titanium	Titanium dioxide	TiO_2	Anatase	
Clay minerals				
Kaolinite group	Hydrous aluminium silicate	$Al_2Si_2O_5(OH)_4$		Kaolinite is the most common variety
Illite group	Hydrous potassium silicate	$KAl_2(AlSi_3)O_{10}(OH)_2$ (K content varies and there is partial substitution of Al by Mg and Fe)		Layered structure similar to mica. Occurs in 1-, 2- and 3-layer forms
Smectite group	Complex hydrous magnesium aluminium silicate	$Al_4Si_8O_{20}(OH)_4 \cdot nH_2O$ (variable replacement of Mg for Al and Al for Si with attachment of Ca and Na)		Readily hydrated with expansion of up to 10 times: montmorillonite is a common variety.
Chlorite group	Hydrous silicate of aluminium iron and magnesium	$(Mg, Fe)_5Al(AlSi_3)O_{10}(OH)_9$		
Vermiculite group	Hydrous magnesium silicate	$Mg_3[Si_4O_{10}](OH)_2 \cdot nH_2O$ (some Al replacement of Si and introduction of Mg, Fe and Al may occur)		Structure intermediate between smectite and chlorite
Mixed-layered group	Hydrous silicate			Regular or irregular interstratification of two clay minerals. Illite–smectite and chlorite-vermiculite mixed layers are the most common
Palygorskite and sepiolite group	Hydrous magnesium silicate	$Mg_4[Si_6O_{15}](OH)_2 \cdot 6H_2O$		Modified amphibole-type double-chain structure rather than layered phyllosilicate structure of other clay minerals



bedrock, the intensity of leaching and the prevailing Eh–pH conditions (Table 6.4). Primary minerals with an existing layered structure, such as biotite, can be fairly readily altered into a clay mineral (often illite which is similarly potassium-rich), whereas most other silicate minerals require a more fundamental reorganization of their crystal structure.

Thermodynamics can indicate which mineral species will be in equilibrium with conditions prevailing in the weathering environment; but the rate at which this equilibrium is achieved is often extremely slow and consequently it is

Fig. 6.13 *Basic structures of some major clay mineral groups. All the clay minerals illustrated have a layered phyllosilicate structure comprising successions of tetrahedral (Si–O) and octahedral (Al–O or Al–OH) layers with, in some cases, intervening layers of absorbed water. The various clay minerals have a characteristic spacing of these layers (shown in the diagram in ångstroms (Å) (10^{-10} m). (Modified from C. Ollier, (1984)* Weathering. *(2nd edn) Longman, London, Fig. 6.5, p. 73.)*

Table 6.4 Mineralogy of weathering products in relation to environmental controls

ENVIRONMENT	pH	Eh	BEHAVIOUR OF MAJOR ELEMENTS	MINERALOGY OF WEATHERING PRODUCTS
Non-leaching. Mean annual precipitation 0–300 mm. Hot	Alkaline	Oxidizing	Some loss of Na^+ and K^+. Iron present in ferric state	Partly decomposed parent minerals. Illite, chlorite, smectite and mixed-layered clay minerals. Hematite, carbonates, secondary silica and salts. Organic matter absent or sparse
Non-leaching below water table	Alkaline to neutral	Reducing	Some loss of Na^+ and K^+. Iron present in ferrous state	Partly decomposed parent materials. Illite, chlorite, smectite and mixed-layered clay minerals. Siderite (iron carbonate) and pyrite (iron sulphide). Organic matter present
Moderate leaching mean annual precipitation 600–1300 mm. Temperate	Acid	Oxidizing to reducing	Loss of Na^+, K^+, Ca^{2+} and Mg^{2+}. Some loss of SiO_2. Concentration of Al_2O_3, Fe_2O_3 and TiO_2	Kaolinite with or without degraded (K-deficient) illite. Some hematite present. Organic matter generally present
Intense leaching. Mean annual precipitation > 1300 mm. Hot	Acid	Oxidizing	Loss of Na^+, K^+, Ca^{2+}, Mg^{2+} and SiO_2. Concentration of Al_2O_3, Fe_2O_3 and TiO_2	Hematite, goethite, gibbsite and boehmite with some kaolinite. Organic matter absent or sparse
Intense leaching. Mean annual precipitation > 1300 mm. Cool	Very acid	Reducing	Loss of Na^+, K^+, Ca^{2+}, Mg^{2+} and some iron and Al_2O_3. SiO_2 and TiO_2 retained	Kaolinite, possibly with some gibbsite or degraded illite. Organic matter abundant

Source: Modified from F. C. Loughnan (1969) *Chemical Weathering of the Silicate Minerals*. Elsevier, Amsterdam, Table 21, p. 73.

important to know what factors control the rate at which more stable weathering products are created. The intensity of leaching is probably the major such kinetic control in most weathering environments (Fig. 6.14). Clay minerals such as kaolinite, which have been stripped of metal cations together with iron and aluminium oxides and hydroxides, are prevalent in environments characterized by intense leaching since here the large throughput of water removes cations in solution and prevents their concentration in pore waters within the regolith. Conditions of extreme leaching can even lead to a significant removal of iron and silicon to leave an aluminium-rich residue in the form of the mineral gibbsite.

Where leaching is of only moderate intensity, cations released during weathering can build up in the solutions moving through the weathering mantle and the formation of cation-bearing clays such as illite and smectite is favoured.

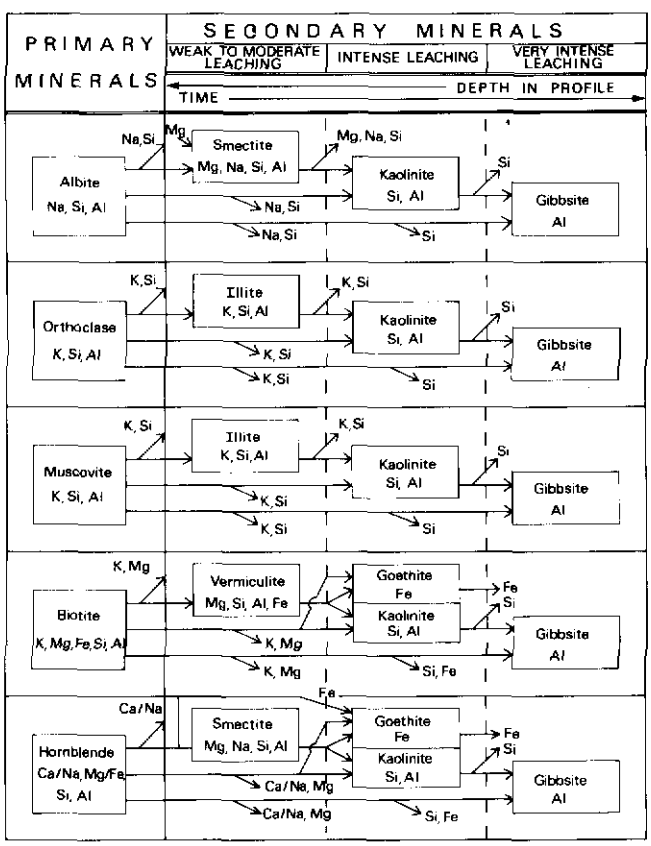


Fig. 6.14 *Schematic representation of the relationship between leaching intensity and types of clay minerals formed. The main constituent elements of each mineral are indicated together with the progressive loss in solution of soluble components at each stage of weathering. A range of primary rock-forming minerals are shown in order to illustrate the role of bedrock mineralogy in controlling the types of clay minerals produced under conditions of weak leaching. Under intense leaching such differences are gradually eliminated. Since the weathering of a unit of bedrock and the leaching of soluble constituents will be progressive the sequences of clay minerals may, in some cases, represent a temporal succession. However, irrespective of the duration of weathering, gibbsite is only likely to form where there is free drainage and intense weathering. Similarly, leaching intensity is likely to vary down profile and this may be reflected in the changing proportions of various secondary minerals*

In arid and semi-arid regions leaching may be minimal and solutions in the weathering mantle can attain high concentrations of dissolved constituents. This condition commonly leads to the accumulation of calcium carbonate at, or near, the surface, while under more extreme conditions of aridity soluble salts such as gypsum ($CaSO_4 \cdot 2H_2O$), halite (NaCl) and thenardite (Na_2SO_4) may be precipitated.

The intensity of leaching is never uniform throughout an entire weathering profile since the throughput of water normally decreases with depth due to compaction and the downward translocation of fine particles which reduces the size of voids. The resulting reduction in the intensity of leaching is usually reflected in mineralogical changes with depth (Fig. 6.15). Clay minerals such as illite and smectite, which are readily altered in the zone of active leaching towards the top of a profile, may be relatively stable at lower levels where leaching is less intense. Vertical differentiation in mineralogy in weathering profiles may also reflect the stage-by-stage alteration of primary rock minerals. Smectite and illite may form preferentially near the weathering front only to be eventually altered to kaolinite, and perhaps gibbsite, as gradual lowering of the weathering front and erosion at the top of the profile effectively causes individual clay mineral particles to move up through the profile.

The relative abundance of dissolved constituents released through weathering reactions into surface waters can be compared to their relative abundance in the bedrock in order to provide information on the types of chemical reactions that are occurring. A number of studies have attempted to rank the relative mobilities of the major constituents released during weathering, and although the precise order varies depending on the environmental conditions the generally agreed sequence is

$$Ca^{2+} > Mg^{2+} > Na^{+} > K^{+} > Fe^{2+} > Si^{4+} > Fe^{3+} > Al^{3+}$$

6.2.5 Factors influencing chemical weathering

It has long been recognized that five factors control the nature of soil development: climate, parent material, topography, organic activity and time. The factors controlling chemical weathering, and indeed weathering as a whole, can be viewed in a similar way. Figure 6.16 illustrates the way in which the four environmental factors influence both the thermodynamics and kinetics of weathering reactions by indicating the conditions required for maximum rates of weathering to be attained.

These factors clearly operate at different scales. Apart from montane environments, where climatic gradients are typically sharp, the effects of climatic differences on weathering tend to be most apparent at the continental and global scale. Indeed attempts have been made to produce world maps indicating the distribution of different weathering products (Fig. 6.17). Although there is a reasonably good correlation between the major climatic regions and particular weathering zones, the correspondence becomes very weak in more mountainous areas where topographic factors can become predominant. This is

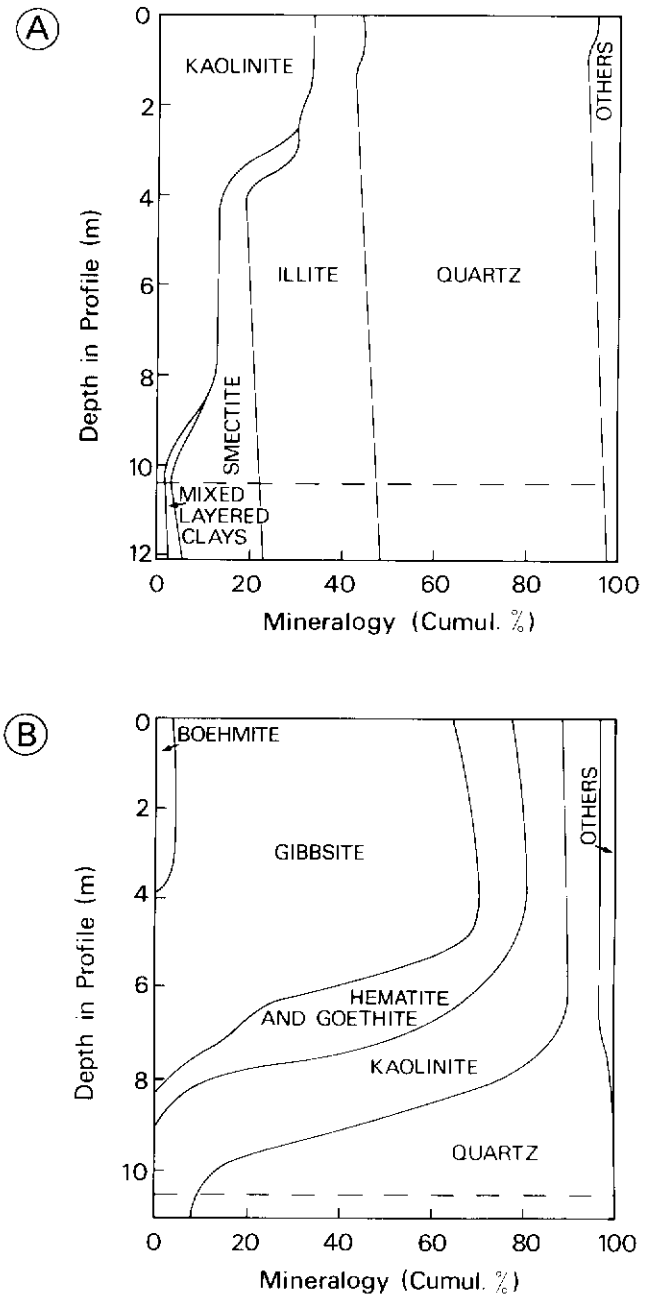


Fig. 6.15 *Variation in mineralogy for weathering profiles developed on clay slates at Goulburn, New South Wales, Australia, under a humid, warm temperate climate (A) and on a sandstone at Weipa, Queensland, Australia, under a hot, monsoonal climate (B). The approximate transition between bedrock and weathered material is indicated by a dashed line. (Adapted from P. S. Bayliss and F. C. Loughnan, (1964),* Clay Mineral Bulletin **5**, *Fig. 3, p. 358, and F. C. Loughnan and P. Bayliss, 1961,* American Mineralogist **46**, *Fig. 4, p. 212.)*

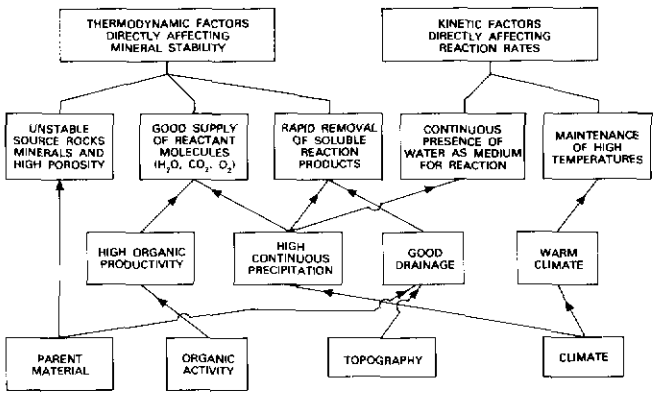
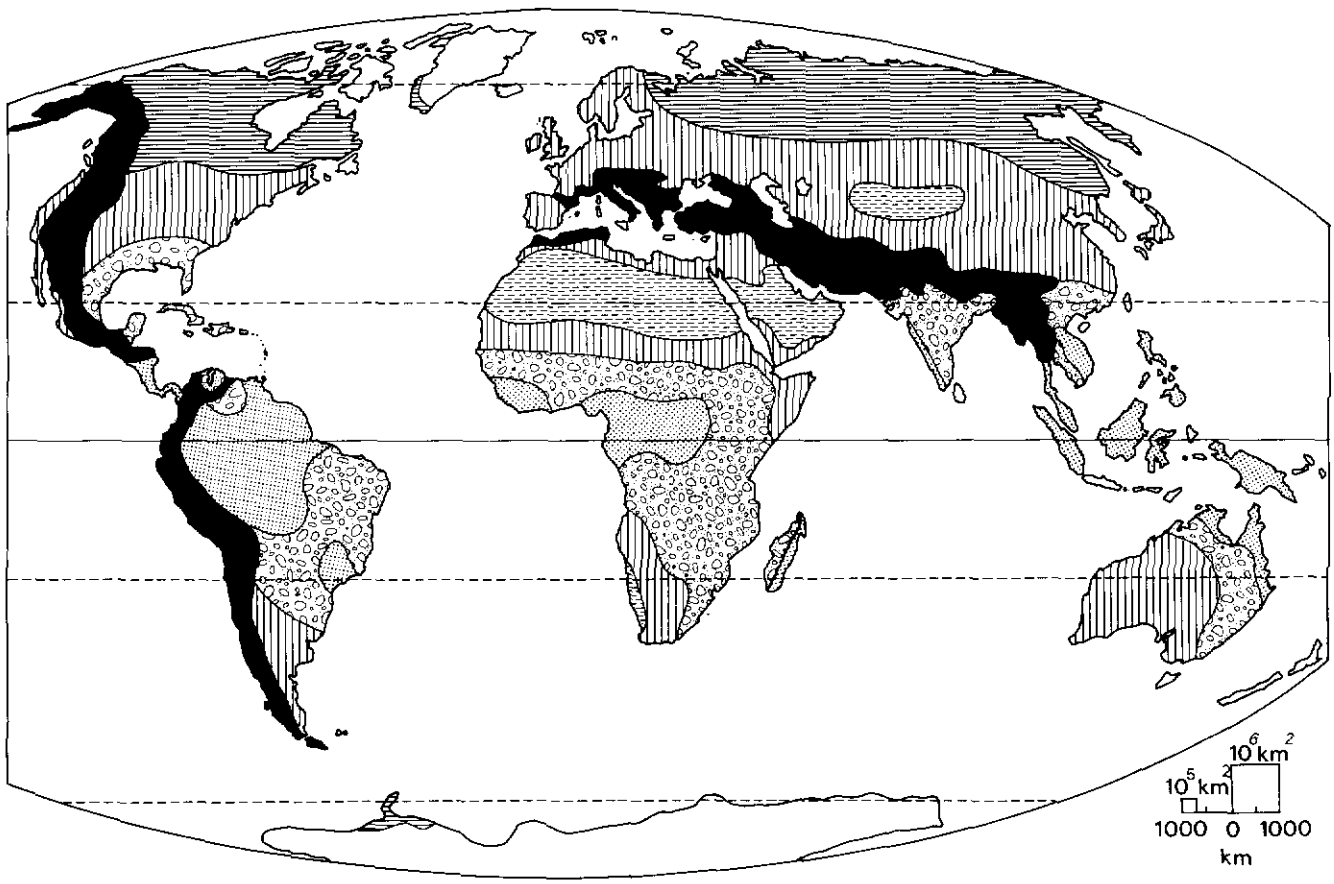


Fig. 6.16 *Schematic representation of the way in which environmental factors can contribute to high rates of chemical weathering. (Modified from C. D. Curtis (1976) in: E. Derbyshire (ed.)* Geomorphology and Climate. *Wiley, London, Fig. 2.5, p. 50.)*

especially the case when the depth of weathering is considered; although a fairly systematic relationship with climate and vegetation is evident as a consequence of variation in precipitation and temperature (Fig. 6.18), this only applies in the absence of marked relief.



Zone of very intense weathering characterized by kaólinite, gibbsite and aluminium oxides and hydroxides

Zone of intense weathering characterized by kaolinite and *iron oxides and hydroxides*

Zone of moderate weathering characterized by illite and smectite

Arid regions with low rates *of chemical weathering and little* accumulation of weathering products

Zone of low temperatures and low rates of chemical weathering. Deep weathering possible in regions of minimal local relief

Ice-covered areas

Mountainous regions of highly variable weathering with little accumulation of weathering products

Fig. 6.17 *Global distribution of major weathering zones. Modified from N. M. Strakhov (1967)* Principles of Lithogenesis *Vol. 1. Oliver and Boyd, Edinburgh, Fig. 1, p. 5.)*

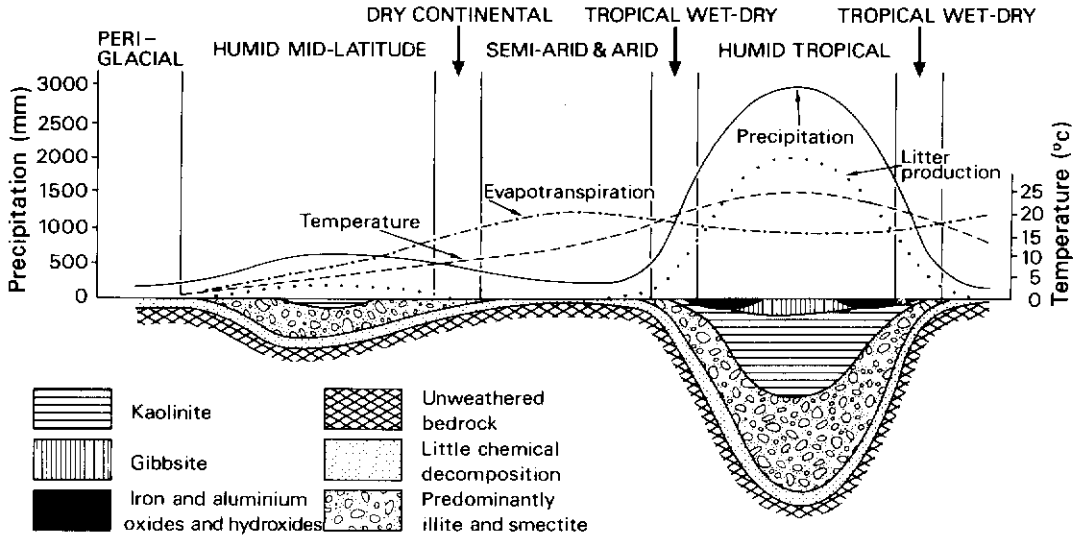


Fig. 6.18 *Variation in weathering mantle depth and composition in relation to climatic and biotic variables. (Modified from N. M. Strakhov, (1967)* Principles of Lithogenesis *Vol. 1. Oliver and Boyd, Edinburgh, Fig. 2, p. 6).*

Temperature is an important factor in rates of chemical weathering, both through the direct effect it has on the rate of chemical reactions (see Section 6.2.2), and indirectly through its influence on rates of organic activity and hence the production of both soil carbon dioxide and organic acids – both critical components in chemical weathering. As long as there is an abundant supply of water high temperatures tend to be associated with high rates of weathering, although this does not necessarily result in deep weathering profiles for, as we have already noted, where slope gradients are steep the products of weathering may be removed almost as soon as they are created.

Rates of weathering are potentially highest where temperatures are high and rainfall is abundant. As indicated in Table 6.4 intensity of leaching, and hence the mineralogy of weathering deposits, is largely a function of temperature, precipitation and drainage. Although the precise mineralogical composition of weathering mantles is influenced by bedrock mineralogy, the effects of variations in precipitation are often evident with the relative abundance of kaolinite, gibbsite and iron and aluminium hydroxides showing a positive correlation with mean annual precipitation (Fig. 6.19).

Vegetation influences weathering, as we have already indicated, through the release of organic acids and in the supply of carbon dioxide to soil waters. Important to both these factors is the production of litter. This varies enormously not only between desert and forest ecosystems but also between temperate forests with a typical range of 0.1–0.3 $\times$ 10^6 kg km^{-2} a^{-1} and tropical rain forests which produce 0.4–1.3 $\times$ 10^6 kg km^{-2} a^{-1}. Organic activity is closely related to climatic controls, but vegetation type also varies at a local scale as a result of topographic factors and soil properites.

Topography affects weathering largely through the way it influences the movement of water through the regolith. Weathering rates and the intensity of leaching depend critically on the total throughput of water and this is likely to be far higher on a steep, well-drained slope than in flat terrain with poor drainage. If drainage is too efficient, however, little water may be present in the regolith for much of the time and rates of weathering will consequently be reduced.

Parent material influences the nature and rate of weathering in two major ways. Its mineralogical composition, particularly in terms of the proportion of unstable mineral phases present, will affect both the rate of chemical decomposition and the kinds of secondary minerals that are most likely to form. Although we might expect bedrock mineralogy to exert a pervasive control over the products of chemical weathering this is not the case, at least at the broad scale, both because the rocks and minerals exposed at the Earth's surface are dominated by just two or three types (Table 6.5), and because prolonged weathering tends to lead to a convergence of secondary mineral types irrespective of parent material mineralogy. The second factor is the physical nature of the parent material, especially its particle size and permeability, which influences the rate of weathering though not the weathering products.

The final factor of time is important because of the slowness of most chemical reactions at the Earth's surface. There is always a significant lag between the establishment of a particular set of conditions in the weathering environ-

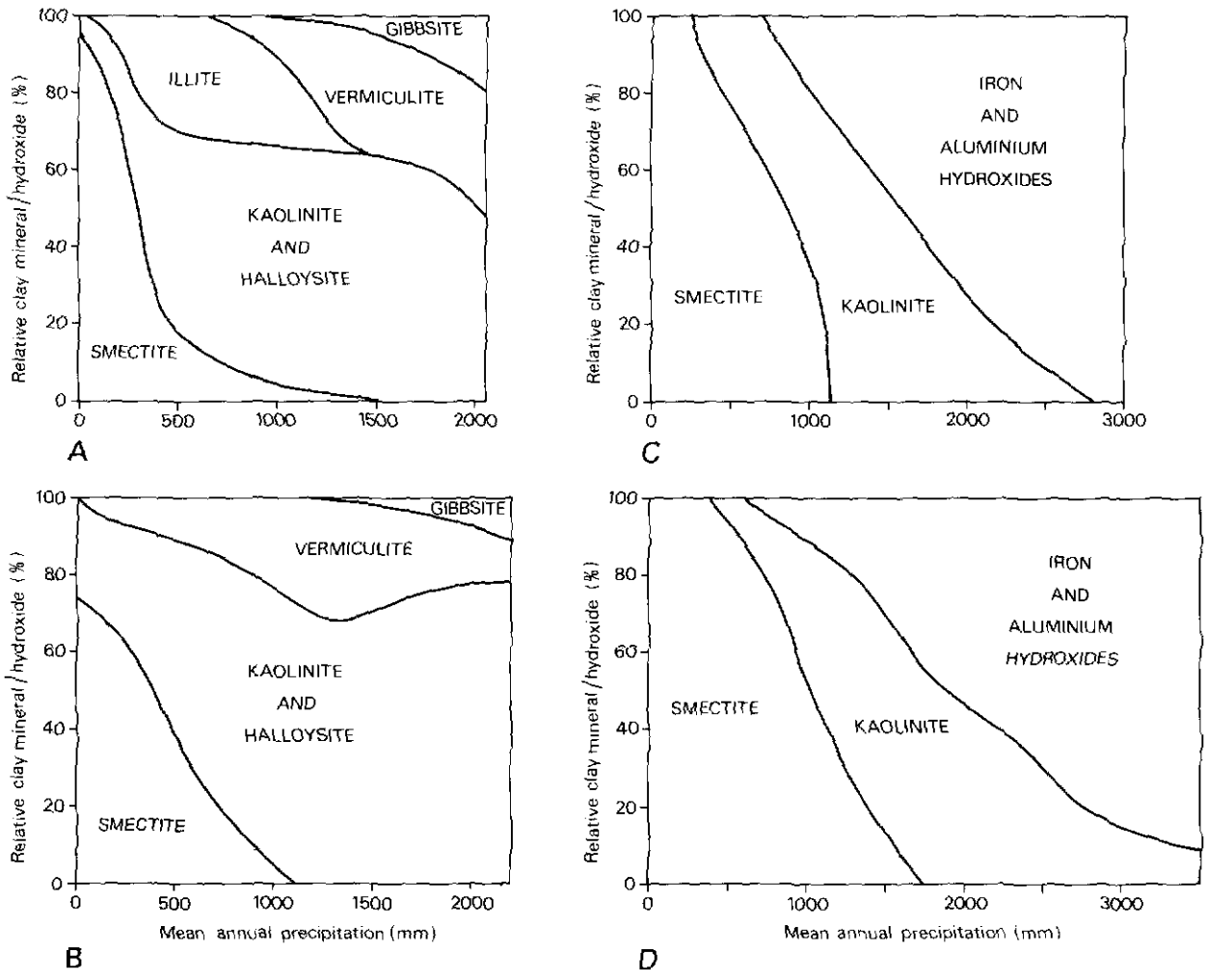


Fig. 6.19 *Variations in the clay mineral and residual hydroxide composition of soils in relation to mean annual precipitation: surface soil samples on feldspar and quartz rich igneous rocks (A) and an olivine, amphibole and pyroxene-rich igneous rocks* (B) *(both from California); soils developed on basalt under an alternating wet and dry climate (C) and a continuously humid climate (D) (both from Hawaii). (Constructed from data and figures in I. Barshad (1966)* International Clay Conference Proceedings *I, Figs 1 and 2, p. 167 and G. D. Sherman (1962)* Problems of Clay and Laterite Genesis, *American Institute of Mining and Metallurgical Engineering, New York, Fig. 2, p. 158 and Fig. 3, p. 159.)*

ment and the adjustment of the mineralogical and physical properties of the regolith to these conditions. Consequently, weathering profiles are rarely in full equilibrium with environmental conditions; in most cases the weathering mantle adjusts to long-term average conditions rather than to conditions at a specific time. We always have to be aware of the kinetics of weathering reactions when looking at the mineralogical composition of weathering profiles. As we shall see in Section 6.5, some weathering products show a remarkable resilience to changing environmental conditions to the extent that in some circumstances they can persist in the landscape essentially unaltered for tens of millions of years.

6.3 Physical weathering

Physical weathering encompasses a range of mechanisms, the relative effectiveness of which are not accurately known but clearly vary significantly as a function of environmental conditions. The physical breakdown of rock is always associated with some kind of volume change and it is useful to categorize the various processes into those involving an overall volumetric change in the rock mass and those related to changes in volume of material introduced into voids or fissures in the rock.

6.3.1 Volumetric changes of the rock mass

As noted in Chapter 5 in the context of granite intrusions (Section 5.5), rocks formed at depth or located beneath a

Table 6.5 Relative abundance of rock types and minerals exposed to weathering at the Earth's surface

Proportion of area covered by major rock types (%)	
Shale	52
Sandstone	15
Granite and granodiorite	15
Limestone and dolomite	7
Basalt	3
Others	8
Total sedimentary	~ 75
Total igneous and metamorphic	~ 25
Proportion of common minerals in bedrock exposed to weathering at the Earth's surface (%)	
Feldspars	30
Quartz	28
Clay minerals and micas	18
Calcite and dolomite	9
Iron oxide minerals	4
Pyroxenes and amphiboles	1
Others	10

Source: Data from L. B. Leopold *et al.* (1964) *Fluvial Processes in Geomorphology*. W. H. Freeman, San Francisco, p. 100.

thick overburden are under considerable internal stress. As the overlying strata are gradually removed by erosion and these rocks reach the surface they undergo expansion or dilation – a process known as **pressure release** – which promotes the development of joints. At the smaller scale micro-fissures and incipient joints related to the original pattern of mineral crystallization in the rock provide lines of weakness along which **exfoliation** (the spalling off of thin sheets of rock) (Fig. 6.20) and **granular disintegration** (the disaggregation of individual crystals or particles) can occur. In some kinds of rock, such as granite, the creation of steep, bare rock faces can lead to significant lateral expansion into the valley side as well as vertical dilation and this may give rise to **exfoliation domes** (Fig. 6.21).

Fig. 6.20 *Exfoliation in granite-gneiss in north-western Cape Province, South Africa. The hat towards the right-hand edge of the photograph indicates the scale.*

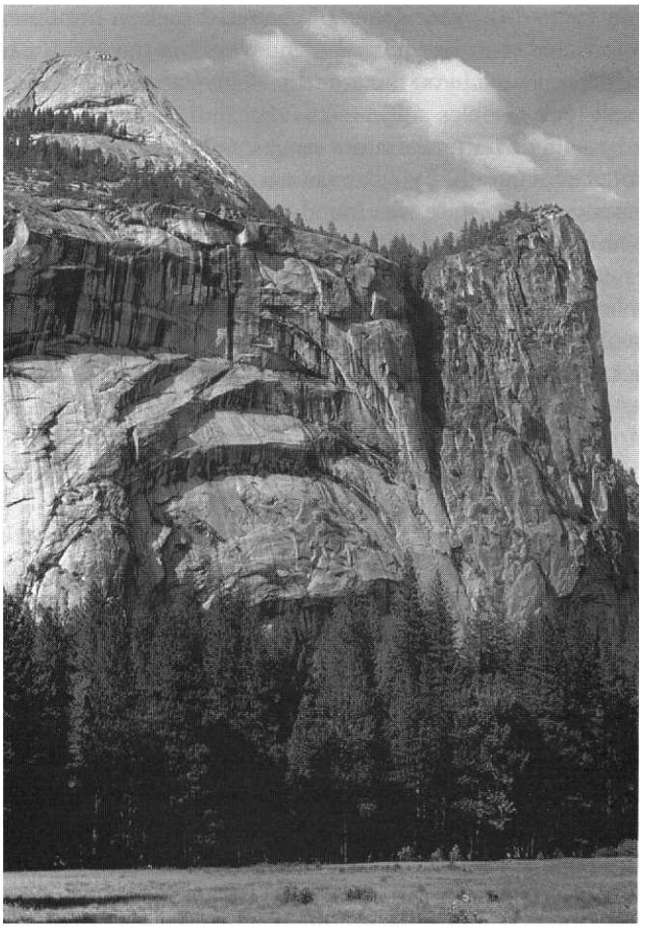


Fig. 6.21 *An exfoliation dome formed in granite in the Yosemite Valley, Sierra Nevada, USA.*

Insolation weathering, that is, the breakdown of rock as a result of volume changes arising from thermal expansion and contraction, is another potentially important physical weathering process. Fluctuations in temperature experienced by rocks at the Earth's surface due to day-time heating and night-time cooling certainly cause them to expand and contract. Nevertheless it has proved difficult to establish whether the resulting volume changes are sufficient to shatter rock, even in desert environments where diurnal temperature ranges on rock surfaces can easily exceed 30 °C. Since rock is a poor conductor of heat a thermal gradient is created when the surface is warmed. The exterior of the rock consequently expands more than the interior and stresses are set up. Data on bedrock surfaces in desert regions show that on dark rocks temperatures of 80 °C can be attained by solar radiation and diurnal ranges of 50 °C are not uncommon. Further (intergranular) stress might be expected to arise from the differential thermal expansion of individual minerals in a rock related to differences in colour, specific heat and coefficient of thermal expansion.

In spite of the abundance of shattered rock in hot desert regions and elsewhere, experimental work in the 1930s cast considerable doubt on the efficacy of insolation weathering. Small rock samples subjected to repeated cycles of heating and cooling over temperature ranges well in excess of those produced naturally by solar radiation failed to shatter. The presence of moisture was found to be necessary to promote chemical weathering and weaken the rock sufficiently for disintegration to occur. Subsequently these conclusions have been challenged, it being pointed out that experiments involving the rapid heating and cooling of small individual rocks do not accurately re-create field conditions. In particular, stresses set up in such samples can be relieved in all directions whereas stresses in bedrock are much more concentrated since the rock is confined both laterally and vertically.

The occurrence of scrub and forest fires provides another mechanism whereby rocks can be subjected to significant thermal expansion and contraction. It is certainly important in semi-arid regions characterized by vegetation communities, such as chaparral (North America) and eucalyptus (Australia), which require fires for regeneration. Such areas are frequently seen to be characterized by spalling rock outcrops and shattered boulders.

Chemical weathering frequently gives rise to minerals which are less dense than their precursors. The associated volume increase can exert pressure on the surrounding rock and the weathering rinds produced peel off to expose fresh rock to further weathering. The chemical processes involved are usually associated with hydration (see Section 6.2.3.1) and the addition of water plays a significant role in the physical breakdown of rock. Such **hydration weathering** can occur simply through wetting and drying which causes expansion and contraction. The process is most active in some clay minerals, notably those of the smectite group, which are capable of absorbing large quantities of water into their crystal structures.

A further hydration weathering mechanism, restricted to environments in which freezing occurs, is **hydration shattering**. This can occur in very fine-grained materials such as clays which are capable of retaining significant quantities of unfrozen water at temperatures well below 0 °C. At these low temperatures the dipolar molecules of this supercooled water become ordered in such a way that a repulsive force is set up across voids. It is thought that while this force is insignificant in large voids it can be sufficiently strong in the small pores in very fine-grained material to cause rock fracture. Chemical weathering is also probably associated with the mechanism which so far has only been investigated on clay-rich rocks, and it may be restricted to such lithologies.

6.3.2 Volumetric changes within rock voids and fissures

Under this heading we need to consider two main sets of processes: the effects of crystal growth and expansion, primarily of ice and salt, and the stresses induced by biological activity. The latter are induced by both fauna and flora. Earthworms, for instance, ingest and excrete huge volumes of soil, as so graphically reported in a classic study by Charles Darwin in the last century. The resulting mixing of the soil, or **bioturbation**, probably averages about a 5 mm depth annually over the more humid parts of the continents. Other soil fauna contribute to this effect, with termites being particularly significant in moving large quantities of soil in the tropics and subtropics.

The growth of tree roots and their penetration and enlargement of incipient rock fractures can contribute significantly to the break-up of rock which may have experienced relatively little weakening through chemical alteration. Large tap roots can penetrate rock to a depth of several metres and the process commonly works in association with other mechanisms, particularly ice crystal growth. It is also likely that chemical weathering is enhanced in the vicinity of roots where carbon dioxide concentrations are likely to be higher and where the extraction of metal cations is occurring. Although such organic activity can be significant, especially locally, it is the physical processes of crystal formation and expansion that are of more fundamental importance in rock weathering.

6.3.2.1 Frost weathering

In arctic and alpine environments the surface is often seen to be composed of a layer of angular rock fragments commonly described by the term **felsenmeer** and attributed to the operation of **frost weathering**. This process, which is also referred to as ***frost shattering*** and ***frost wedging***, involves the breakdown of rock or other solid materials as a result of stresses induced by the freezing of water.

Early explanations of frost weathering alighted on the simple and seemingly obvious effect of the 9 per cent volume expansion which accompanies the phase change from water to ice. Under ideal conditions it was estimated that ice formation could exert a maximum pressure of around 200 MPa (at which point the freezing temperature is −22 °C), but it was appreciated that this theoretical maximum pressure could never be attained under natural conditions, not the least because it far exceeded the tensile strength of most rocks (around 25 MPa). Even to build up moderately high pressures sufficient to shatter rock it was realized that a closed system was required in order for the pressure not to be relieved by the expulsion of water into adjacent voids. Such a closed system might be produced if freezing proceeds rapidly from the surface downwards since initial ice formation at the surface can then seal in water contained within pores in the rock.

Subsequent experimental work has failed both to clarify fully the exact mechanisms involved in frost weathering and to define precisely the climatic conditions under which the process is likely be most effective. It has been suggested that a freezing rate of at least 0.1 °C per minute and temperatures of –5 to –10 °C are required for rock shattering to occur. Most experimental studies have emphasized the importance of rapid freezing, a minimum temperature of –5 °C, the frequency of freeze–thaw cycles and the overriding significance of the moisture content of the rock. This last factor is crucial since if a rock is not saturated ice formation will simply cause the expulsion of water into air-filled cavities, thereby inhibiting a build-up of pressure. Some theoretical work, however, has questioned the importance of water freezing in sealed cracks and the frequency of freezing events, suggesting instead that crack growth will be greatest when the temperature ranges from approximately –4 to –15 °C. Other experimental studies have supported the idea that frost weathering is likely to be more effective in alpine and marine arctic environments, where freeze–thaw may occur diurnally, than in polar regions where freezing and thawing are predominantly seasonal phenomena.

Uncertainties about the efficacy of volume expansion on freezing in rock shattering has encouraged the examination of other possibilities. One of these is the pressure exerted by ice-crystal growth, the idea being that this is directional and that if the direction of growth is resisted by the wall of a void or crack then pressure will be exerted which may be sufficient to wedge the crack apart. As applied to the crystallization of ice this mechanism is largely conjectural at present since little experimental work has been undertaken to estimate the pressures likely to be generated. A further possibly important mechanism in rock breakdown associated with freezing, at least in very fine-grained lithologies, is hydration shattering (see Section 6.3.1) and it is likely that some of the effects of physical weathering previously attributed to frost weathering in fact result from this process.

6.3.2.2 Salt weathering

Salt weathering involves three major processes: the precipitation of salt in voids and the expansion of salt crystals through either hydration or heating. It is most active in arid environments where rates of evaporation are high relative to precipitation, and consequently surface and soil waters can become saturated with respect to a variety of salts. Although frequently associated with hot desert regions, the effects of salt weathering have also been observed in high-latitude arid regions such as Antarctica. Moreover, the high salinity of sea water makes it likely that salt is an active weathering agent in coastal environments (see Section 13.3.1.1). In inland areas salt is derived from a number of sources. These include surface and soil waters containing cations released during bedrock weathering which have subsequently been concentrated by evaporation, precipitation with a high salt content (especially in regions near coasts), saline ground waters and saline deposits blown inland from the coast or originating in inland saline basins. A number of salts are found in the soils of arid regions but only a few are generally quantitatively significant – $CaSO_4(.2H_2O)$, NaCl, Na_2SO_4, Na_2CO_3, K_2SO_4, $MgSO_4$ and KCl.

When saline solutions in rock pores become saturated as a result of a temperature change or evaporation, salt crystals begin to form and considerable pressures are generated. Whether these lead to rock fracture will depend on both the stresses produced by crystal growth and the tensile strength of the rock. Salt crystal growth in unconsolidated sediments can cause considerable ground heave, and where salt solutions enter desiccation cracks various types of **patterned ground** may be formed (Fig. 6.22). A second cause of stress arises from the capacity of several common salts to absorb significant quantities of water into their crystal structure. Such hydration expansion commonly occurs in response to changes in relative humidity which, since they are closely related to temperature, may be diurnal. The importance of thermal expansion, the third mechanism of salt weathering, has yet to be fully evaluated. Its possible significance derives from the observation that the coefficients of thermal expansion of many salts are greater than that of most rocks. Sodium chloride (common salt), for instance, can expand by up to 1 per cent under the very large diurnal temperature ranges typical of continental deserts.

The rather specific environmental requirements of salt weathering mean that its action is spatially highly variable. It is likely to be intense in west coast deserts, such as the Atacama (Chile/Peru) and Namib (Namibia), where frequent fogs supply both salt and moisture. It is also active in areas adjacent to nearly enclosed seas in hot deserts, for example the Red Sea, where both humidity and salinity are high. Other favourable environments include the margins of salt-covered basins, along river channels and in other areas of low-lying topography where shallow saline ground waters can be drawn to the surface by capillary action.

Different salts also vary significantly in their efficacy as weathering agents, and several laboratory investigations have indicated the particular effectiveness of sodium sulphate. This can be attributed to its various physical properties. First, it experiences a large increase in volume when hydrated (from Na_2SO_4 to $Na_2SO_4.10H_2O$). Secondly, it has a high equilibrium solubility so that large quantities can be precipitated from a given volume of solution. Thirdly, its equilibrium solubility is particularly sensitive to temperature, reaching a maximum at 32.3 °C. This is within the range of diurnal temperature change in many hot deserts and precipitation will occur as the temperature rises

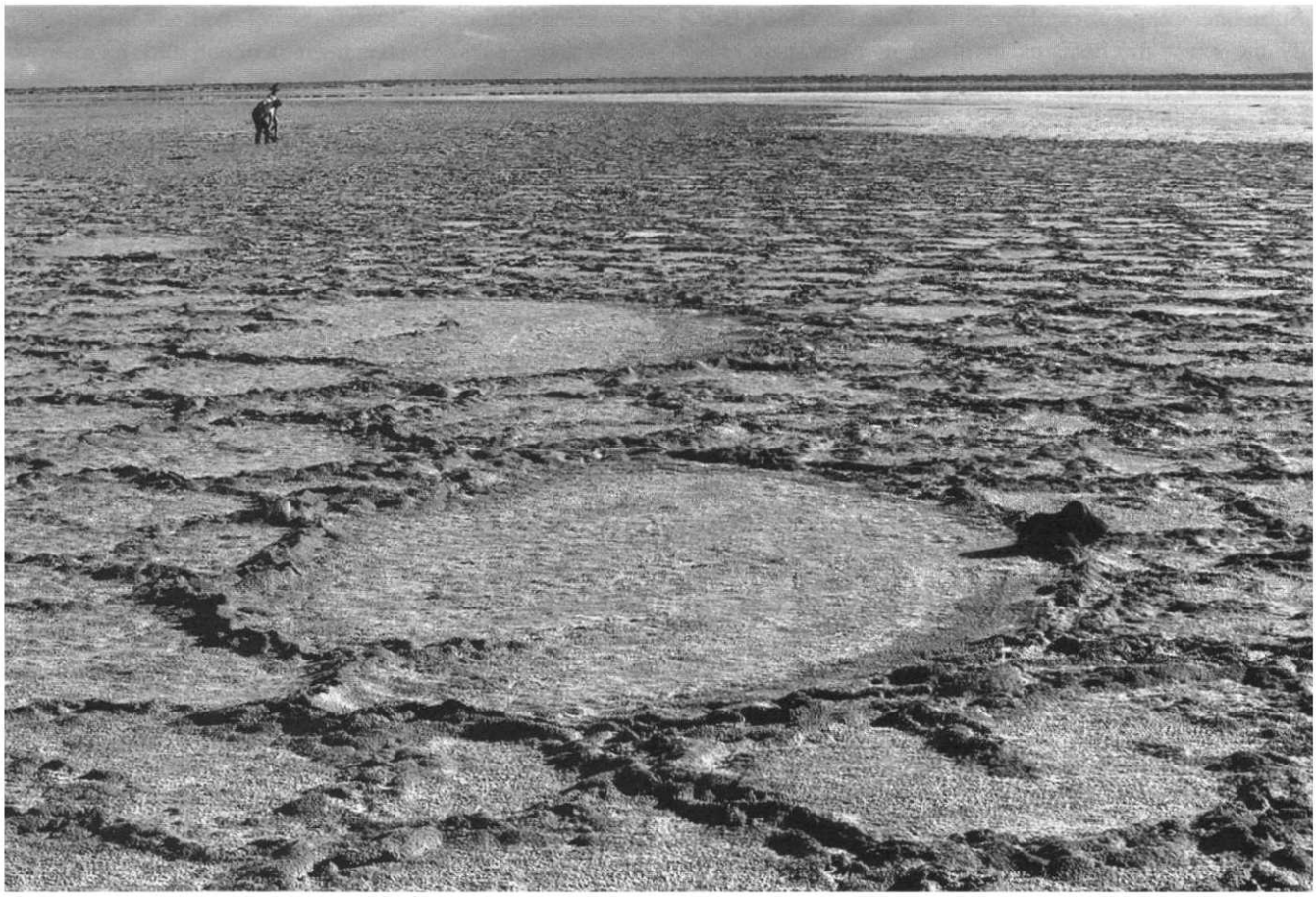


Fig. 6.22 *Polygonal patterned ground developed in the saline bed of the southern margin of Lake Eyre, South Australia.*

or falls across this value. Finally, crystallization occurs preferentially along a single crystal axis and large pressures can be generated within rock fractures.

6.4 Lithology and weathering forms

Just as variations in the physical and mineralogical properties of bedrock can influence the mineralogical products of weathering so different lithologies give rise to a range of weathering forms. On most lithologies landforms related directly to weathering tend to be minor features, but on rock types such as limestones, in which a large proportion of the products of chemical weathering processes are removed in solution, major landforms can be produced. In this section we will focus on weathering forms in limestone, although it should be pointed out that similar weathering forms can develop on other lithologies.

6.4.1 Karst weathering forms

Karst is the German form of a Slovene word meaning 'bare stony ground' and is used to describe limestone terrain characterized by a lack of surface drainage, a discontinuous or thin soil cover, abundant enclosed depressions and a well-developed system of underground drainage including caves, all features attributable to the solubility of limestone. Limestone is defined as a rock which contains at least 50 per cent $CaCO_3$, which nearly always occurs as the mineral calcite. Other carbonate minerals include aragonite (a rare form of $CaCO_3$) and dolomite ($CaMg(CO_3)_2$). Rocks in which more than 50 per cent of the carbonate content occurs as the mineral dolomite are given the rock name dolomite. The term ***karstification*** is used to refer to the process of karst landscape development. Karst landforms are classically exemplified by the landscape of northern Yugoslavia and a number of terms used to describe karst landforms originate from this region.

The term **pseudokarst** is applied to landforms in non-carbonate rocks which are morphologically similar to those characteristic of limestone terrains. In most cases pseudokarst develops as a result of processes analogous to those operating on true karst; such is the case on some pure siliceous rocks subject to prolonged weathering where the slow dissolution of quartz creates karst-like forms. In other cases quite different processes can give rise to topography

superficially resembling true karst, an example being the creation of 'underground drainage' through the formation of lava tunnels in volcanic terrains.

Karst scenery is not entirely, or in many cases even primarily, a product of weathering since fluvial processes play a crucial role in its development. Nevertheless, it is appropriate to consider here those components of karst topography that owe much of their origin to weathering processes. Karst landforms related more specifically to fluvial activity are discussed in Chapter 9.

The fullest development of karst scenery is attained where the limestone is relatively pure (in excess of 80 per cent $CaCO_3$), very thick, mechanically strong and massively jointed (so that water flow is concentrated along joints rather than passing through the mass of the rock). In addition a humid climate is required together with sufficient relief for extensive vertical water flow down to a regional water table deep below the surface. In the karst region of Yugoslavia there are pure limestones up to 4000 m thick and part of the area is more than 2000 m above sea level. Although chalk is a very pure limestone it is mechanically too weak to allow the development of large underground cavities. Similarly, thin beds of limestone do not permit the development of underground drainage while in arid regions there is insufficient water for significant limestone weathering to occur. There is an extensive vocabulary of special terms to describe karst landforms which can be confusing to the uninitiated, and even to the expert.

6.4.1.1 *Minor forms*

The German term **karren** and the French term **lapies** refer to the small-scale solutional forms developed on limestone. (Note that the terms 'solution' and 'dissolution' are used widely in discussions of karst landforms, but this is just a form of shorthand since, as was discussed in Section 6.2.3.3, limestone weathering involves complex chemical reactions.) There is no English equivalent for these terms although some specific forms have acquired local names. A

Table 6.6 Classification of solutional microforms developed on limestone

	FORM	TYPICAL DIMENSIONS	COMMENTS
Forms developed on bare limestone — *Developed through areal wetting*	**Rainpit**	<30 mm across, <20 mm deep	Produced by rain falling on bare rock. Occurs in fields on gentle rather than steep slopes. Can coalesce to give irregular, carious appearance
	Solution ripples	20–30 mm high; may extend horizontally for >100 mm	Wave-like form transverse to downward water movement under gravity. Rhythmic form implies that periodic flows or chemical reactions are important in their development
	Solution flutes (rillenkarren)	20–40 mm across, 10–20 mm deep	Develop due to channelled flow down steep slopes. Cross-sectional form ranges from semi-circular to V-shaped but is constant along flute
	Solution bevels	0.2–1 m long, 30–50 mm high	Flat, smooth elements usually found below flutes. Flow over them occurs as a thin sheet
	Solution runnels (rinnenkarren)	400–500 mm across, 300–400 mm deep, 10–20 m long	Down runnel increase in water flow leads to increase in cross-sectional area. May have meandering form. Ribs between runnels may be covered with solution flutes
Forms developed on bare limestone — *Developed through concentration of runoff*	**Grikes** (kluftkarren)	500 mm across, up to several metres deep	Formed through the solutional widening of joints or, if bedding is nearly vertical, of bedding planes
	Clints (flackkarren)	Up to several metres across	Tabular blocks detached through the concentration of solution along near-surface bedding planes in horizontally bedded limestone
	Solution spikes (spitzkarren)	Up to several metres	Sharply pointed projections between grikes
Forms developed on partly covered limestone	**Solution pans**	10–500 mm deep, 0.03–3 m wide	Dish-shaped depressions usually floored by a thin layer of soil, vegetation or algal remains. CO_2 contributed to water from organic decay enhances dissolution.
	Undercut solution runnels (hohlkarren)	400–500 mm across, 300–400 mm deep 10–20 m long	Like runnels but become larger with depth. Recession at depth probably associated with accumulation of humus or soil which keeps sides at base constantly wet
	Solution notches (korrosionkehlen)	1 m high and wide, 10 m long	Produced by active solution where soil abuts against projecting rock giving rise to curved incuts
Forms developed on covered limestone	**Rounded solution runnels** (rundkarren)	400–500 mm across, 300–400 mm deep 10–20 m long	Runnels developed beneath a soil cover which become smoothed by the more active corrosion associated with acid soil waters.
	Solution pipes	1 m cross, 2–5 m deep	Usually become narrower with depth. Found on soft limestones such as chalk as well as mechanically stronger and less permeable varieties

Note: The commonly encountered German terms are given in parentheses

Source: Based largely on discussion in J. N. Jennings (1985), *Karst Geomorphology*. Blackwell, Oxford, pp. 73–82.

bewildering variety of karren have been described and the most important of these are classified and described in Table 6.6

Several factors influence the form of karren. Probably of most importance is the presence or absence of a cover of soil or vegetation during its formation. This is probably because the solution process operates differently on covered and bare surfaces. On covered surfaces soil and vegetation maintains a continuous presence of moisture on the rock surface while organic decay increases the quantity of organic acids and the abundance of carbon dioxide; both increase the aggressiveness of the water percolating on to the rock surface. (**Aggressivity** refers to the propensity of water to dissolve calcium carbonate.) The resulting solutional forms tend to be rounded and less sharp-edged than those formed on bare rock.

A second factor is lithology. Karren are best developed on relatively massive and uniform, mechanically strong and impermeable limestones in which there is a sharp contact between soil and rock. Chalk, for instance, is too porous and mechanically weak for karren development. Climate is also important since adequate moisture must be present for effective solution. In arid climates there is generally insufficient surface water, whereas in periglacial regimes frost action may be so effective that solutional forms have little time to develop. Snow patches, with their enhanced concentrations of CO_2, which experience seasonal melting may, nevertheless, be favourable environments for karren development. Time is the final significant factor since karren developed under a relatively humid climate may survive for a period after a change to a more arid climatic regime. Moreover, forms developed under a soil cover may subsequently be exposed by erosion, in some cases promoted by human activities such as forest clearance.

The role of organisms in directly creating both erosional and depositional microforms on limestone has probably been underestimated. Micro-organisms may be instrumental in many commonly observed microforms in limestones, but the precise nature of their role is as yet poorly known. The terms **biokarst** and **phytokarst** are used to describe forms attributable in large part to organic processes.

6.4.1.2 Major forms

If one landform can be regarded as typifying karst scenery it is the **doline.** A doline is a closed depression which may range in shape from bowl-shaped to cylindrical and in size up to 100 m deep and 1 km across. In some limestone terrains the surface is pitted with large numbers of dolines which each provide separate foci for surface drainage, in contrast to the integrated valley systems of fluvially eroded landscapes. In fact it is likely that doline formation may be a kind of contagious process whereby the establishment of an initial depression will tend, through its effect on lowering the water table in its immediate vicinity, to promote the development of further depressions near by.

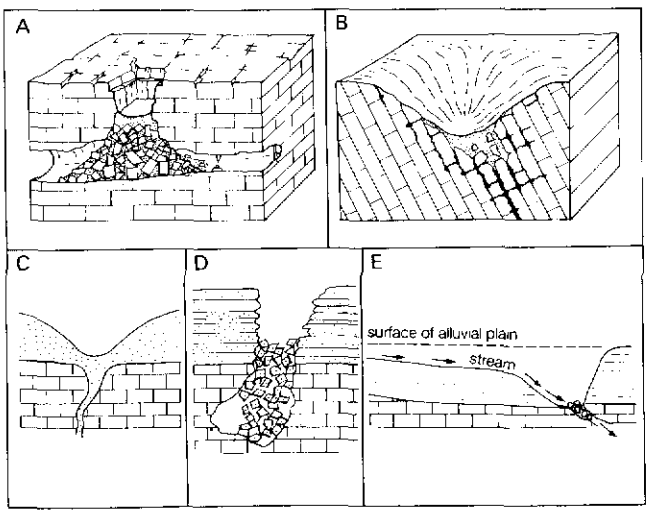


Fig. 6.23 Major types of doline: (A) collapse doline; (B) solution doline; (C) subsidence doline; (D) subjacent karst collapse doline; (E) alluvial stream sink doline. (From J. N. Jennings (1985) Karst Geomorphology. *Blackwell, Oxford, Fig. 37, p. 107).*

Various types of doline are recognized in terms of their mode of formation (Fig. 6.23). A **collapse doline** is created through the fall of the roof of a cave to leave a steep-walled cavity. These steep walls are, however, likely to be subject to rapid degradation through dissolution and physical weathering processes in all but arid climates, and their gradients may be consequently reduced in a short period of time to the extent that a collpase doline may be indistinguishable in form from other types. Collapse into a water-filled cave or a subsequent rise in the local water table can lead to the formation of a lake, such as in the case of the **cenotes** which are common in the Yucatan Peninsula, southern Mexico.

Solution dolines are formed when localized dissolution usually concentrated at the intersection of major joints lowers the bedrock surface. The initial development of the depression leads to the capture of more surface drainage and this in turn promotes further doline enlargement. Solution dolines are one of the few karst landforms which are capable of forming in relatively soft limestones such as chalk. **Subsidence dolines** form in a similar manner, but in this case there is a covering of superficial deposits which collapse either suddenly or progressively into the cavity developing in the underlying limestone. More dramatic collapse characterizes **subjacent karst collapse dolines** in which a covering non-calcareous rock unit collapses into a void in the underlying limestone. The final generally recognized type is the **alluvial stream sink doline** which consists of a stream flowing into a doline before disappearing underground.

Dolines, especially of the solution type, may be so numerous that they merge into each other to form **uvalas**. Where dissolution is significantly controlled by joint systems uvalas may be elongated forms, but in other cases they are irregular depressions. In the humid tropics dolines characteristically have an irregular to star-shaped plan form due to their mutual interference as they have grown and completely consumed the original surface. This produces a polygonal pattern of ridges surrounding individual dolines which are sometimes described as **cockpits** following the local name given to them in Jamaica. Residual hills are often present on the divides separating depressions. They are usually rounded in form and are termed **cones** or **kegel**, and the whole landscape assemblage is called **cockpit karst** (or alternatively **cone karst** or **kegelkarst**). Many cockpits contain stream sinks and the morphology of cockpits is probably attributable to the abundance of surface runoff in humid tropical environments which leads to the creation of minor valley-like solutional forms on their slopes. In some localities in the humid tropics the residual hills on doline divides have a remarkable sharp-edged, pinnacle form and this has given rise to the term **pinnacle karst** (Fig. 6.24).

Large flat-floored depressions ranging in size up to 200 km^2 or more are found in some karst terrains and are termed **poljes**. Polje floors are commonly covered by alluvium and one or more sides of the depression has a steep angle in excess of 30°. Water flows on to the polje floor via springs along its edge or from impermeable strata which commonly form one side and leaves the polje either through stream sinks called **ponors** or via gorges penetrating one of the polje walls. Early attempts to explain the formation of poljes regarded them as a late stage in a developmental sequence of depression enlargement beginning with dolines, but current ideas now focus on structural controls. Many poljes appear to be aligned with structural trends represented by fold axes, faults or junctions between limestone and non-calcareous rocks; some may indeed be graben but in the majority of cases it appears that structure controls the location of lateral planation necessary for polje development. Most poljes are located at the junction of limestone and impermeable beds, and runoff from the latter will be undersaturated with calcium carbonate and will therefore be aggressive when entering the limestone terrain.

In humid tropical and subtropical environments some limestone landscapes are dominated by spectacular tower-like hills, or **mogotes**, up to 100 m or more high separated by broad, alluvial valley floors (Fig. 6.25). This type of terrain is described as **tower karst** and has been thought to represent the effects of enhanced limestone dissolution in regions of high precipitation. Acid waters in the alluvial valleys cause rapid lateral planation and undercutting of rock faces while high temperatures promote the evaporation of water flowing across the exposed rock leading to the deposition of a protective layer of calcite. This climatic interpretation of tower karst, however, has been revised in the light of the recognition of tower karst in the far from tropical environment of the Mackenzie Mountains in north-west Canada. In this region the limestone is massive and very thick with widely spaced joints and the tower karst appears to represent the last stage of karst landscape development. This apparently began with the formation of deep, joint-controlled dolines and progressed through the creation of long, narrow gorges called **karst streets** and then the development of a rectilinear network of deep gorges forming **labyrinth karst** to a final phase of lateral planation of the gorge rock walls to form towers.

Fig. 6.24 Pinnacle karst in the Mulu area of Sarawak. The development of this extraordinary topography is probably attributable to preferential dissolution focused along joints or bedding planes in steeply dipping metamorphosed limestone. The apparently rapid rate of limestone dissolution is related to high rainfall totals (in excess of 5000 mm a^{-1}), frequent mists and high rates of organic activity. (Interpretation by M. J. Day, and photo courtesy of the Royal Geographical Society and M. J. Day.)

6.4.2 Other weathering forms

Exposures of bare rock are found in many environments and result from differential weathering of bedrock and the removal of the weathered debris by slope processes. Rock outcrops which stand out on all sides from surrounding slopes are known as **tors**. They are particularly common on crystalline rocks, but also occur on other resistant lithologies such as quartzites and some sandstones. Some researchers have regarded deep weathering as a prerequisite for the development of tors, with a phase of intense chemical weathering preferentially focused along joints being followed by stripping of the weathered material in response to a change in conditions more favourable to erosion. Other workers, however, have argued that tors can develop in the absence of deep weathering where weathering and stripping operate simultaneously on rocks of variable resistance.

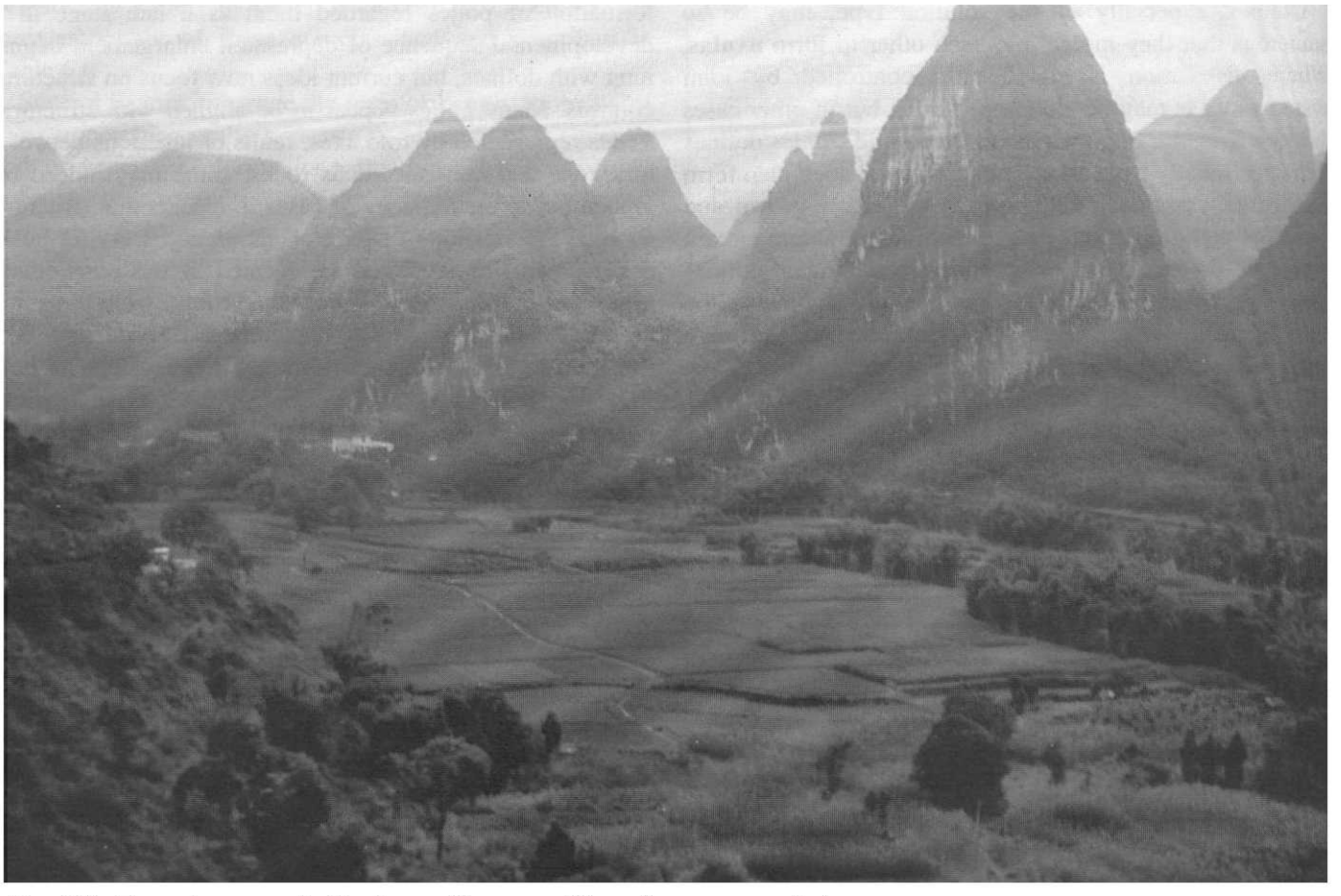


Fig. 6.25 *Tower karst near Guilin, Guangxi Province, China. (Photo courtesy D. Munro.)*

Nearly all exposed rock outcrops have irregular surfaces which appear to be related to the effects of weathering. These include rills, pits and cavernous forms. They are found on essentially all rock types and in all climates, but in view of the extent of exposed bedrock they are most apparent in arid and semi-arid environments. The origin of the wide range of forms that occurs is poorly understood; suggested mechanisms include salt weathering, hydration shattering, insolation weathering and frost action.

Two forms which have attracted particular attention are **honeycomb weathering** and **tafoni**. Honeycomb weathering consists of numerous small pits a few millimetres or centimetres in width and depth and the honeycomb form is produced when they coalesce to create a network structure. Tafoni are larger features ranging up to several metres in size and are cut into steep, bare rock faces (Fig. 6.26). In some cases selective chemical disintegration of the rock is apparent but in others evidence of chemical decomposition seems to be quite absent and mechanical processes such as salt weathering appear to be more probable processes. Organic activity may also be instrumental through the localized enhancement of acidity.

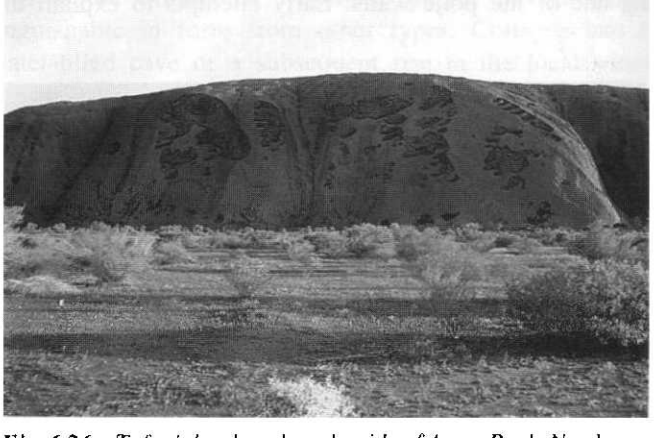


Fig. 6.26 *Tafoni developed on the side of Ayers Rock, Northern Territory, Australia.*

Case-hardening and core softening may also be important. **Case-hardening** appears to result from the localized mobilization and reprecipitation of minerals on the rock surface, thereby strengthening it and rendering it generally less permeable. Areas of the rock surface less effectively case-hardened would then be susceptible to weathering processes which could then selectively penetrate into the

rock interior producing cavities. Similarly, there is evidence that the cores of boulders may be weathered more rapidly than the surface and again this could lead to the selective development of cavities.

Differential heave in unconsolidated deposits arising from changes in volume can create a range of patterned ground phenomena (Fig. 6.22). Such changes in volume are most commonly associated with wetting and drying and freeze–thaw cycles and patterned ground is most evident in arid and periglacial regions (see Chapter 12).

6.5 Duricrusts

Duricrusts are hard layers formed in the weathering zone at, or near, the landsurface as a consequence of the absolute or relative accumulation of particular components through the replacement or cementation of pre-existing rock, soil, weathering materials or other unconsolidated deposits. The most important components in duricrust formation are iron and aluminium oxides and hydroxides, silica, calcium carbonate and gypsum. They are of interest not only in terms of their origin but also because of their role in landscape development and the evidence they provide of past climates. Duricrusts may reach thicknesses in excess of 50 m although 1–10 m is a more usual range. The ferruginous, calcareous and especially siliceous forms can be exceedingly hard, and particularly where they cap less resistant materials they form prominent and highly resistant elements of the landscape. Duricrusts may form several metres below the landsurface but they can be subsequently exposed by erosion of less resistant overlying materials.

Iron- and aluminium-rich duricrusts are known as, respectively, **ferricrete** and **alcrete**. Both occur in association with deep weathering profiles in the humid to subhumid tropics although alcretes are more prevalent where rainfall totals are particularly high. The term **laterite** has long been used to describe iron- and aluminium-rich weathering deposits while the term **bauxite** refers to deposits containing economically extractable concentrations of aluminium. Many laterites and bauxites are, however, relatively weak materials and the terms ferricrete and alcrete are reserved for the indurated forms.

Siliceous duricrusts, or **silcretes**, are commonly composed of more than 95 per cent SiO_2 and are found in both humid and arid tropical environments. They are particularly prominent in central Australia and parts of southern and northern Africa. In some cases they occur in weathering profiles in close association with ferricretes, while in more arid regions they are found in conjunction with calcium carbonate crusts or **calcretes**. Calcretes have an average $CaCO_3$ content of around 80 per cent and their distribution in general broadly coincides with areas with a current mean annual precipitation of between 200 and 600 mm (Fig. 6.27).

Fig. 6.27 A calcrete profile more than 10 m thick exposed in the Molopo gorge in the southern Kalahari Basin on the border between Botswana and South Africa. The calcrete has formed through the replacement of quartzites and tillites.

They cover a significant proportion of the world's semi-arid environments and they possibly underlie up to 13 per cent of the global landsurface area. Gypsum crusts, or **gypcretes**, by contrast have a much more limited distribution and appear to be largely confined to very arid regions where the mean annual precipitation is below 250 mm. The gypsum ($CaSO_4 \cdot 2H_2O$) content is highly variable but may exceptionally reach 95 per cent. Gypcrete reaches a maximum thickness of about 5 m, somewhat less than other duricrust types.

6.5.1 Models of duricrust formation

The formation of the different types of duricrust can be largely understood in terms of the relative mobility of different elements in the weathering environment. Ferricretes and alcretes in most cases represent the relative accumulation of iron and aluminium oxides and hydroxides as more mobile components are removed from the weathering mantle (Fig. 6.28). Such relative accumulation occurs under conditions of intense leaching under climates where rainfall is abundant for a significant part of the year. Locally absolute accumulation may occur as iron and aluminium are mobilized to a limited extent within the weathering mantle or are transported either mechanically or in solution from high to low topographic positions.

Silcrete, calcrete and gypcrete form through absolute accumulation of silica, calcium carbonate and gypsum respectively. Their formation requires a source for these constituents, a means of transferring them to the site of formation and a mechanism for precipitation. Possible sources include the weathering of bedrock or sediments, inputs from rainfall or dust, plant residues and solutes in ground water. Translocation of solid or dissolved source materials can be either lateral or vertical, and in the latter

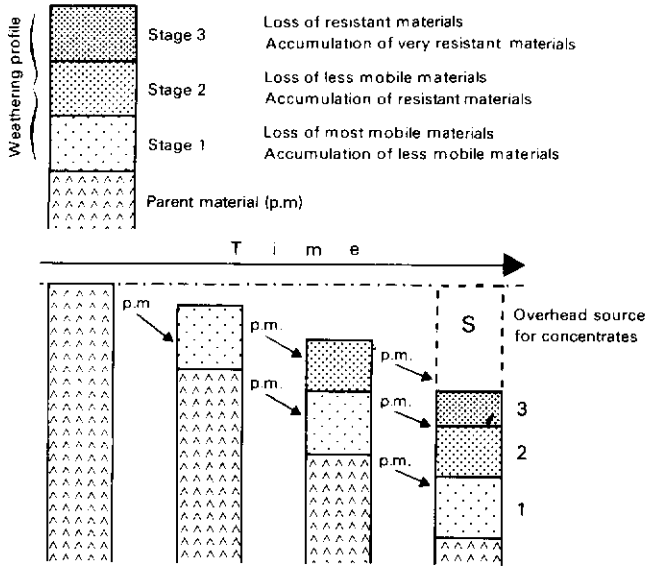


Fig. 6.28 *Stages of weathering leading to the relative accumulation of iron or aluminium to form ferricrete or alcrete. The profile in which the iron and aluminium accumulates experiences a continuous development whereby stage 1 weathering effectively occurs at progressively lower levels as the weathering front moves downward. Similarly, the landsurface experiences a progressive lowering and the iron and aluminium gradually becomes concentrated in the zone of stage 3 weathering. (From M. J. McFarlane (1983) in A. S. Goudie and K. Pye (eds)* Chemical Sediments and Geomorphology: Precipitates and Residua in the Near-Surface Environment. *Academic Press, London, Fig. 2.3, p. 22.)*

case may be either upward as a result of capillary rise (*per ascensum* model), or downward through percolation (*per descensum*) model (Fig. 6.29). Downward movements are probably more important in most cases since capillary rise will lead to a concentration of precipitation close to the surface and this will reduce the efficiency of surface evaporation and thus reduce the rate of subsequent capillary rise.

Precipitation can arise from a variety of factors in addition to the evaporation of weathering solutions: these include pH changes, reactions with other cations in solution and organic activity. Changes in pH appear to be of particular importance in the case of silcrete and may explain why this type of duricrust is found in both predominantly alkaline arid and semi-arid environments, and in acidic humid tropical weathering profiles (Fig. 6.30). The solubility of silica is more or less constant up to a pH of around 9, but above this point its solubility increases dramatically (Fig. 6.5). In alkaline environments, such as those commonly found around ephemeral lake beds in semi-arid and arid regions, pH may vary between 8 and 10 over short distances. Silica in solution moving from a locality where the pH is above 9 to one where it is below 9 will therefore be precipitated. In such circumstances silcrete can develop within calcrete while under different conditions calcrete can be seen replacing silcrete. A contrasting situation exists in the highly acidic conditions associated with abundant organic activity in humid tropical regions. At a pH of below 4 aluminium becomes more mobile than silica so clay minerals can be silicified as they lose aluminium, even though the concentration of silica in solution is invariably very low.

There are few firm data on how quickly duricrusts can form although it is clear that gypcrete and calcrete generally develop much more quickly than the other types. The rapid formation of some calcretes is demonstrated by the cementation of human artefacts, such as gravestones and even Coca-Cola tins! The slow development of silcretes, ferricretes and alcretes is probably in part explained by the very low concentrations of silica, iron and aluminium in most surface and regolith waters.

6.5.2 Environmental controls

As with other weathering products the factors important in the development of the different types of duricrust are scale dependent. At the broadest scale climate (and vegetation in so far as it affects pH) is the predominant control; but the overlap in the climatic conditions under which different types of duricrust develop (Fig. 6.30) demonstrates that other factors operate at the regional and local scale. Topography is of considerable significance. Low local relief is an essential requirement for virtually all duricrust formation since the rate of development must exceed the rate of denudation for a duricrust to be created. Secondly, topography is the key factor in determining local drainage conditions. Silica will not be retained in weathering profiles to form silcrete unless the drainage is very poor whereas alcrete develops preferentially where efficient drainage encourages intense leaching. Bedrock also plays a role since it influences the availability of source constituents – silica, iron, aluminium, calcium carbonate, gypsum – but, as with the development of other weathering products, lithological variations tend to become progressively masked after prolonged duricrust development.

Although the climatic parameters for calcrete and gypcrete genesis are known fairly well, the same is not true for other types of duricrust. This is because ferricretes, alcretes and silcretes are chemically and mechanically resistant so that once formed under a certain set of climatic conditions they can persist in the landscape for long periods even though the prevailing climate may have changed dramatically. Consequently, these types of duricrust may frequently not be in equilibrium with prevailing environmental conditions; indeed, they are likely to reflect in their chemical, mineralogical and physical characteristics a history of changes in climate and other variables affecting their development rather than a single equilibrium state.

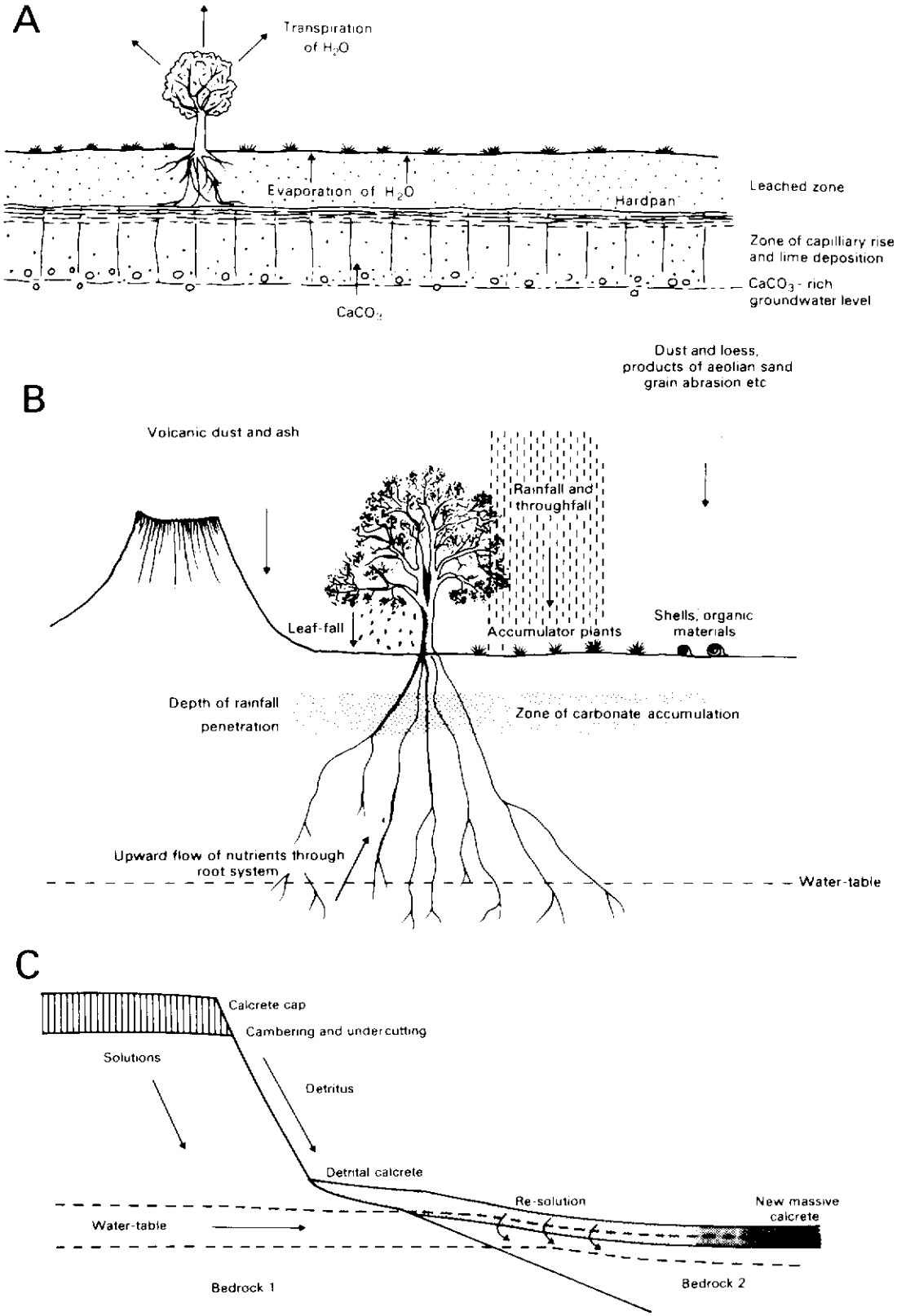


Fig. 6.29 *Models of the formation of calcrete: (A) the capillary rise* (per ascensum) *model; (B) the percolation* (per descensum) *model with inputs of carbonate from above; (C) the detrital model in which a secondary calcrete is formed through the solution and disintegration of an existing calcrete horizon at a higher level in the landscape. Calcium carbonate as well as silica may also be translocated in river waters, eventually being precipitated at some distance from the original source. (From A. S. Goudie (1983) in: A. S. Goudie and Pye, K. (eds)* Chemical Sediments and Geomorphology: Precipitates and Residua in the Near-Surface Environment. *Academic Press, London, Fig. 4.4, p. 113 and Figs. 4.5 and 4.6, p. 115.)*

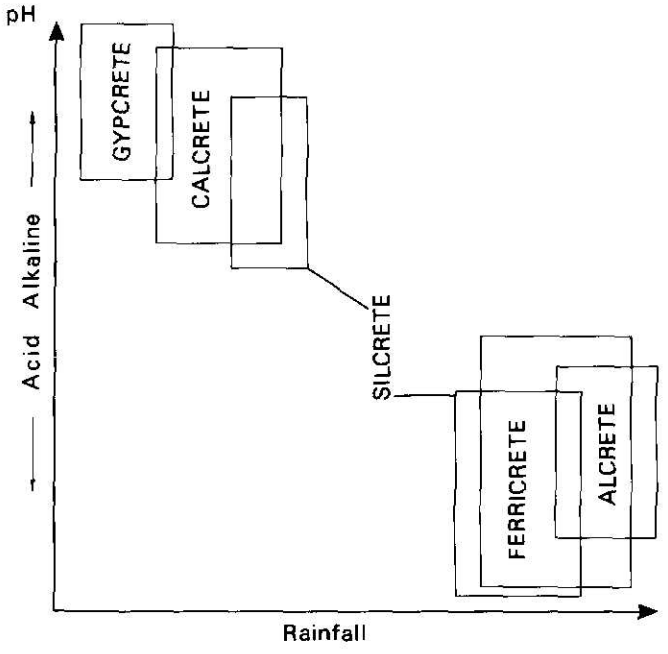


Fig. 6.30 *A schematic representation of the relationship between the formation of different types of duricrust and prevailing conditions of climate and pH. Note that the chemical and physical resistance of some kinds of duricrust mean that many occurrences may now exist outside the climatic and pH zones in which they were formed. In many instances local factors such as topography and drainage outweigh broad climatic controls.*

Calcretes and especially gypcretes are by contrast much more responsive to changing conditions; the relatively high solubility of gypsum, for instance, would lead to the rapid destruction of a gypcrete should the climate become humid. This contrasting 'survivability' in the face of environmental changes is largely responsible for the fact that few gypcretes and calcretes which have been continuously exposed at the surface are older than Late Cenozoic while some ferricretes and many silcretes date back to the Early Cenozoic, and even beyond.

Duricrusts are normally significantly harder and more resistant to erosion than the materials which they overlie. Consequently they tend to armour, or protect, landsurfaces from denudational processes (Fig. 6.31). Although some

Fig. 6.31 *Flat-topped hills (koppies) capped by silcrete near Riversdale, in southern Cape Province, South Africa. It is likely that the silcrete originally formed at a low elevation in the landscape and that subsequently topographic inversion has occurred (see Figure 6.32).*

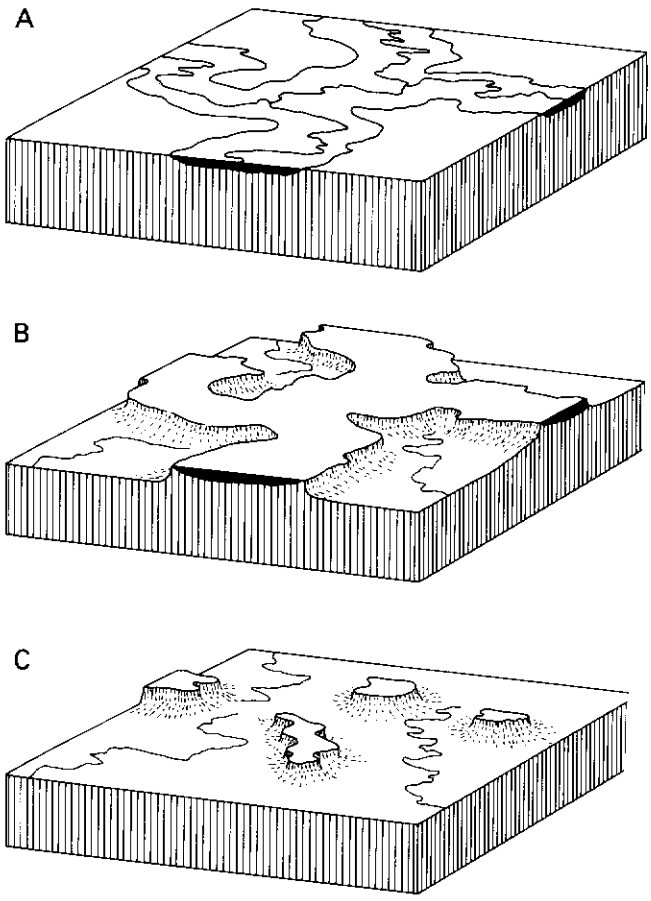


Fig. 6.32 *Schematic representation of stages in the development of inverted topography. A resistant duricrust, such as silcrete, is initially formed preferentially at low points in the landscape (A). Subsequently, differential erosion lowers the surrounding, less resistant, terrain (B) to leave the duricrust capping residual hills (C).*

types of duricrust seem to preferentially develop at low points in the landscape where ground water flows and surface runoff converge, this armouring can subsequently lead to the more rapid lowering of surrounding areas and the creation of **inverted topography** (Fig. 6.32). Even where a duricrust horizon has been broken up by prolonged erosion the duricrust fragments produced may still remain on the surface and perform a protective role for a long period of time. This is the case in the **gibber plains** which cover extensive areas of central Australia and which consist of silcrete boulders scattered on the surface (Fig. 6.33).

Further reading

There is an extensive literature on weathering though not all of it is written from a specifically geomorphic perspective. The books by Birkeland (1984) and Ollier (1984) provide good introductions to the processes and products of weathering in the context of landforms, while the reviews by Whalley and McGreevy (1985, 1987, 1988) are excellent sources for references, especially on physical weathering processes. The book by Gerrard (1988) is a valuable summary of the role of lithology in weathering and landscape development. The behaviour of water in the soil and regolith which is so important to an understanding of both physical and chemical weathering processes is discussed in detail by Williams (1982).

The best introduction to chemical weathering for the geomorphologist is probably still the short book by Loughnan (1969) although it is confined to silicate minerals. Drever (1985) provides a more detailed treatment of processes while Colman and Dether (1986) consider various aspects of chemical weathering rates. Curtis (1976a) and Ross (1987) provide brief and accessible introductions to energy considerations in chemical weathering while the complex sequence of reactions involved in the weathering of limestone is discussed by Gunn (1986) and Trudgill (1985). The pH and Eh conditions in natural environments are assessed by Baas Becking *et al.* (1960). The role of earthworms in bioturbation is examined in the classic study by Darwin (1881) and Goudie (1988) looks at the important role played by both earthworms and termites in the tropics. The probable role of organic processes in the formation of desert varnish is discussed by Dorn and Oberlander (1982) and Whalley (1983).

Weathering products are covered in the book by Ollier (1984) and in the volumes edited by Goudie and Pye (1983) and Wilson (1983). The deep weathering profiles of the humid tropics are discussed by Thomas (1974) and in the classic paper by Ruxton and Berry (1957). Mineral stability is treated from a thermodynamic perspective by Curtis (1976b), while Williams *et al.* (1986) look in detail at the chemical weathering of granite in terms of mineral stability and element mobility. The classic study of granite weathering by Goldich (1938) is still worth consulting. The formation of secondary minerals is examined in general terms by Loughnan (1969) and with specific reference to clays by Millot (1979). Loughnan (1969) also provides an excellent discussion of the environmental factors controlling chemical weathering, while Pye *et al.* (1986) show how apparently minor differences in bedrock chemistry can influence weathering rates.

Turning to physical processes Rice (1976) reassesses the importance of insolation weathering while McGreevy (1985) looks at the implications of the thermal properties of rock for physical weathering. Valuable field data on temperatures attained by rocks in the field are presented by Kerr *et al.* (1984), Peel (1974) and Smith (1977), while Ollier and Ash (1983) look at the role of fire in rock weathering. The importance of cracks within rocks for the effective operation of frost and salt weathering is emphasized by Whalley *et al.* (1982), while McGreevy and Whalley (1985) assess the importance of rock moisture to frost weathering both in

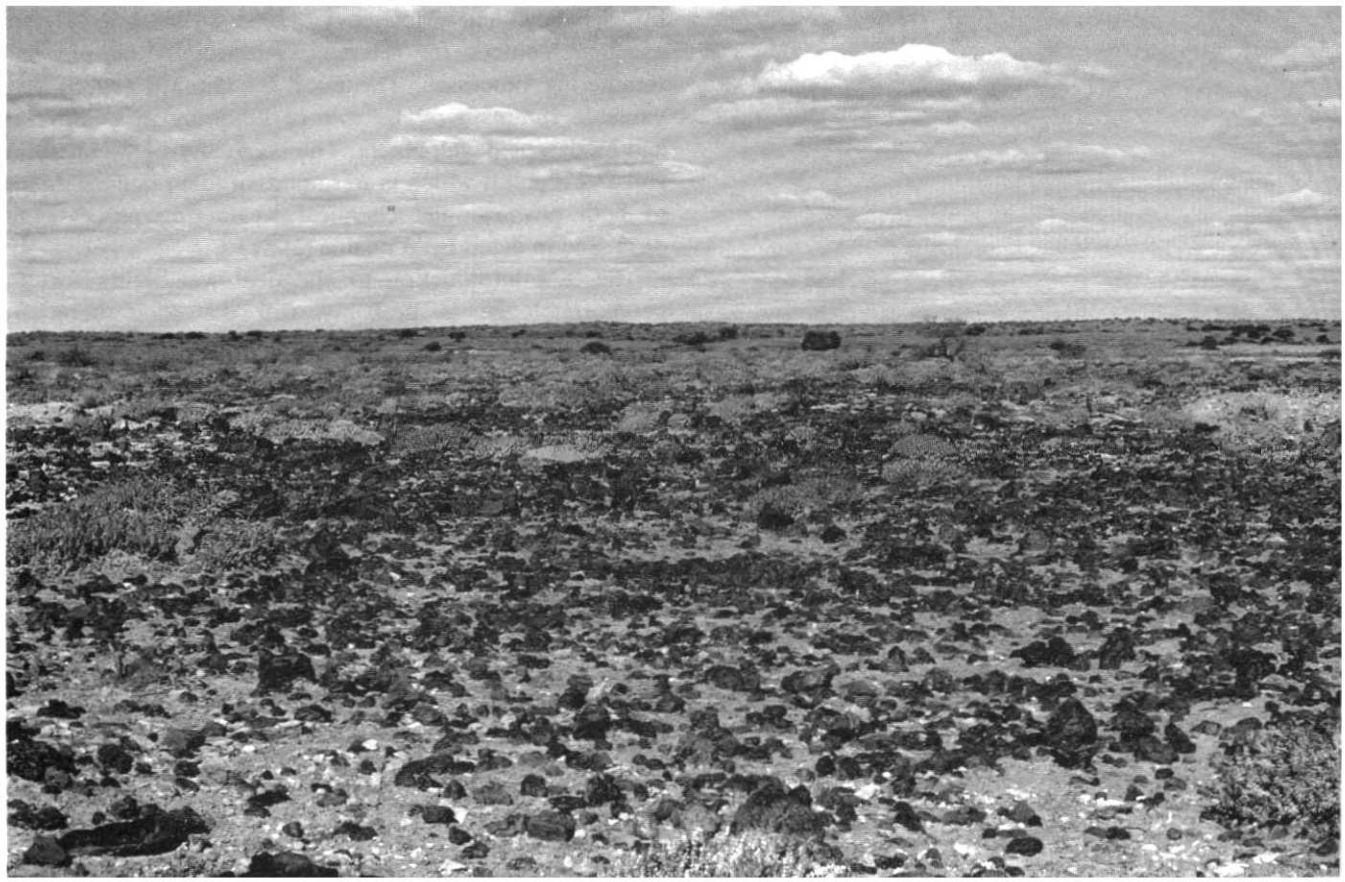


Fig. 6.33 *A gibber plain east of Lake Eyre, South Australia.*

the laboratory and under field conditions. Fifteen years of experimental work on frost weathering is summarized in Lautridou and Ozouf (1982), and Thorn (1979) reassesses the efficacy of freeze–thaw action in alpine environments. An important recent trend has been the greater application of basic physical principles to studies of frost weathering and this approach is exemplified by Walder and Hallet (1985). Salt weathering has attracted increasing attention from geomorphologists as its importance, especially in arid environments, has become appreciated. Sperling and Cooke (1985) and Smith and McGreevy (1983) report experimental and simulation studies of salt weathering, while Goudie and Day (1980) and Goudie and Watson (1984) provide evidence of its potency in the field.

There is a very large literature on weathering forms developed on bedrock, especially in the case of limestone. Both minor and major karst forms are comprehensively treated in Jennings (1985), Sweeting (1972), Trudgill (1985) and White (1988), while Viles (1988) provides a useful review of biokarst. Kemmerly (1986) presents a general model for the development of closed depressions, while Williams (1972) shows the value of applying morphometric techniques to karst terrains and Brook and Ford (1978) and Williams (1987) consider the long-standing problem of the development of tower karst. A variety of cavernous weathering forms, including tafoni and honeycomb weathering, occur on non-calcareous rocks and the origin of these features is considered by Conca and Rossman (1985) and Mustoe (1982, 1983). Pseudokarst microforms on granite are recorded by Watson and Pye (1985) while Young (1986) reports karst-like tower forms developed in sandstone.

Good summaries of the characteristics and origin of the various forms of duricrust are given in the volume edited by Goudie and Pye (1983). Of particular relevance are the chapters by Goudie (1983), McFarlane (1983), Summerfield (1983a) and Watson (1983). Other useful articles on particular duricrust occurrences are contained in Wilson (1983). Additional information can be found in Watson (1985) on gypsum crusts in Tunisia and Namibia, in Summerfield (1983b) and Young (1985) on contrasting interpretations of the climatic conditions under which different types of silcrete form and in Goudie (1985) on the role of duricrusts in landscape development.

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