Chapter 1

CLASTIC SEDIMENT AS A CHEMICAL AND PHYSICAL BREAKDOWN PRODUCT

Few ken to whom this muckle monument stands,
Some general or admiral I've nae doot,
On the hill-top whaur weather lang syne
Has blotted its inscribed palaver oot.

Hugh MacDiarmid, 'The Monument', 1936, *Complete Poems,* Vol. 1, Carcanet, 1993.

1.1 Introduction: clastic sediments— 'accidents' of weathering

Terrestrial clastic sedimentary rocks are usually quite different in their composition from the igneous and metamorphic rocks that sourced them. This is because they are derived from an altered *regolith* with a soil profile produced by chemical weathering of pristine bedrock and the source of mineral grains for such sediment. For example, feldspar is the commonest mineral in bedrock of the Earth's continental crust (about 60% of the total) but quartz is usually pre-dominant in clastic sediments and sedimentary rocks. Despite this difference the principle of conservation of mass tells us that for all elements present in the exposed crust and released by weathering, exactly the same levels of abundance must occur in the average total sedimentary mass. Thus the average *chemical* composition of *all* sediments is roughly that of the igneous rock, granodiorite, representing the mean composition of middle to upper continental crust.

It is traditional to divide rock weathering into physical and chemical components, but in reality the two are inextricably interlinked. Water is the chief reactant and plays a dual role since it also transports away both dissolved and solid weathering products. Earth is presently unique in its abundance of water and water vapour, yet Mars also had an earlier watery pre-history. It is easy to take water for granted, the deceptively simple molecule H_2O has remarkable properties of great importance for rock and mineral weathering (**Cookie 1**). These include its solvent and hydration properties, wetting effects due to high satu-ration and anomalous decrease of density at low liquid temperatures and after freezing. An outline of the near-surface terrestrial hydrological cycle is given in Fig. 1.1.

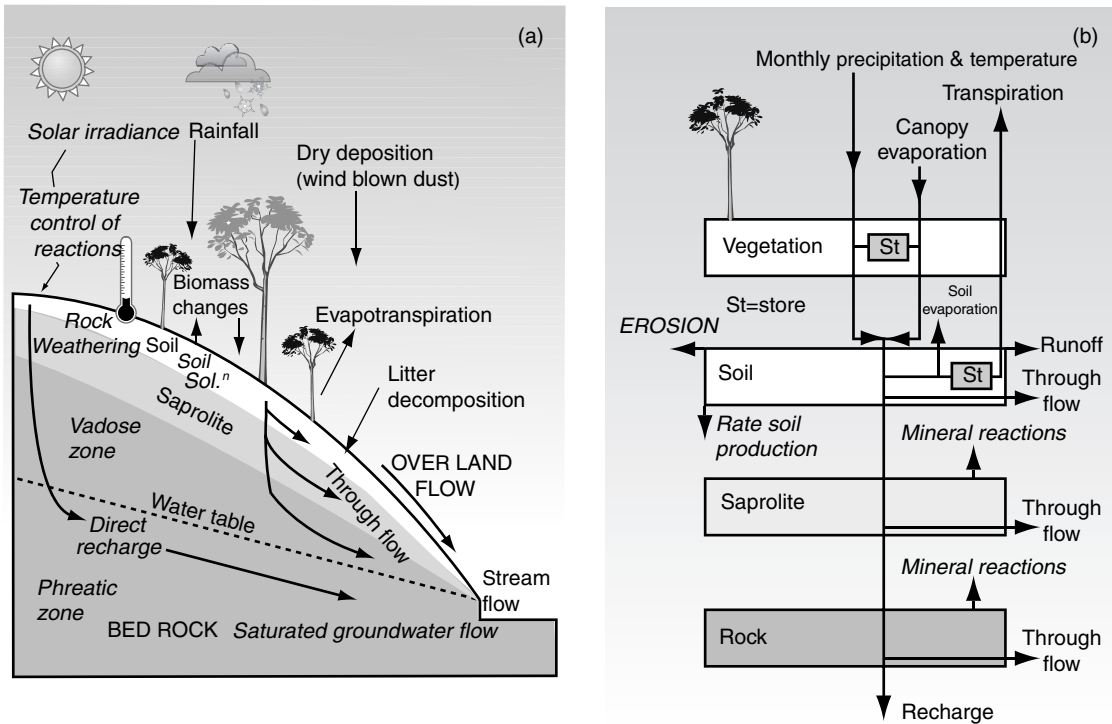Want to know more about the structure and properties of water? Turn to Cookie 1.

Fig. 1.1 (a) The main components of the terrestrial hillslope hydrological cycle. (b) Box model for water budget in the surface and near-surface weathering zones.

Chemical weathering involves aqueous reactions with a strong biochemical component since dissolved atmospheric gases are aided by soil-generated gases, dilute acids and organic ligands. Further, the reactions are complex since silicate minerals are involved, with their many constituent anions and cations; also the amount of water and dissolved ions varies in both time and space. Four main mechanisms contribute to chemical weathering: *dissolution*, *oxidation*, *hydrolysis* and *acid hydrolysis*. Reactions usually occur at mineral surfaces in the unsaturated (vadose) zone where, close to the local Earth's surface, rock pores contain atmospheric gases, water, living and dead vegetation and bacteria—all play an important role in weathering. The result is a regolith and soil profile whose characteristics depend upon climate and rock type.

Physical weathering involves the application of differential stresses to rock and mineral discontinuities in the unsaturated zone. These cause fragmenta-tion and are due to erosional unloading, gravity, wind shear, salt crystallization from groundwaters, freeze–thaw and differential thermal expansion.

The combined effects of biochemical and physical weathering produce a weathered regolith profile in bedrock that comprises:

- surface *soil* with significant living and dead organic content;
- chemically altered rock termed *saprolite* that never-theless preserves its framework coherency without volume loss (*isovolumetric weathering*);
- chemically unaltered but often physically fragmented (exfoliated) *bedrock*.

Interfaces between these layers are in a state of slow downward motion as the landscape reduces. In fact, landscape dating by *cosmogenic isotopes* and other means reveals that a steady-state system often exists, with the material mass removed by erosion being replaced by an equal volume made available from below for further decomposition.

Weathering acts on:
- mineral aggregates at or close to Earth's surface with their many intracrystalline pores and fracture networks;
- imperfect crystals with surface and lattice defects.

Weathering involves:
- bond *breaking*, physically by cracking and chemically by solution (see **Cookie 2**);
- broken bond (danglers) *adoption* by ionic predators;
- electron *removal* from the easily stripped transition metals like Fe and Mn (see **Cookie 3**).

Weathering depends on:
- H_2O *throughput* or hydraulic conductivity by laminar water flow in pore spaces between minerals, microporosity within minerals and cracks across minerals;
- H_2O *dissociation* into the reactive H and OH ions (see **Cookie 1**);
- CO_2*concentration* via atmospheric and soil processes;
- temperature, which controls both *reaction rates* (Fig. 1.2) in silicate minerals via the results of the *Arrhenius principle* (see **Cookie 3** and further

below) and the rate of aqueous throughput via its control on water's *dynamic viscosity*.

Want to know more about ions, electron transfer and Eh–pH diagrams? Turn to Cookie 2.

Want to know more about proton donors, pH, acid hydrolysis and calcium carbonate weathering? Turn to Cookie 3.

1.2 Silicate minerals and chemical weathering

The flux of dissolved elements and altered minerals from continent to ocean is largely controlled by the processes of chemical weathering. Global river sampling indicates that silicate weathering accounts for ~45% of total dissolved load, calcium carbonate weathering ~38% and evaporitic salts ~17%. The recharge of dissolved ions into rivers from the weathering zone (Fig. 1.3) is not only a function of source rock but also of the fluxes from atmospheric deposition, vegetation growth and respiration, and the net reaction of soil and other subsurface interstitial water with minerals in the unsaturated zone. Once liberated by weathering into the hydrological system, some elements behave *conservatively* in that they then proceed down-catchment with little further gain or loss. Other minerals behave in a decidely *non-conservative* way —Ca is a good example since it readily forms mineral precipitates in semiarid soils and in other terrestrial carbonate sinks (section 2.9).

Chemical weathering of silicate minerals plays a major role in the global hydrogeochemical cycle. Since the relative proportion of minerals in clastic sedimentary rocks is different from those in igneous and metamorphic rocks, it is clear that some are more stable than others in the weathering process and some are newly formed; this depends upon the thermodynamics of the reactions involved (**Cookie 4**). Reactions in natural waters include rapid dissolution of ionically bonded minerals like soluble salts (Cookie 1) and acid attack on carbonate minerals (Cookie 2). Both carbonates and evaporites usually dissolve *congruently*,
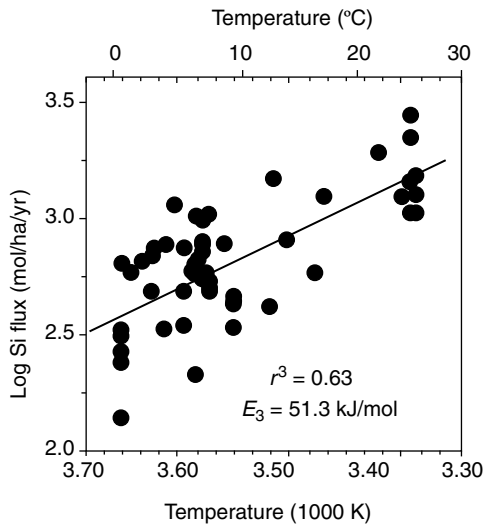

Temperature (°C)

Fig. 1.2 Arrhenius plot to show that the flux of Si from small, simple-geology granite catchments depends on temperature, once corrections are made to allow for rainfall amount. This is because the rate constant is determined by the Arrhenius effect discussed in the main text and **Cookie 3**. The solid diagonal line corresponds to the activation energy E_a. (After White *et al.*, 1999.)

In plot: $r^3 = 0.63$, $E_3 = 51.3$ kJ/mol. Y-axis: Log Si flux (mol/ha/yr). X-axis: Temperature (1000 K).
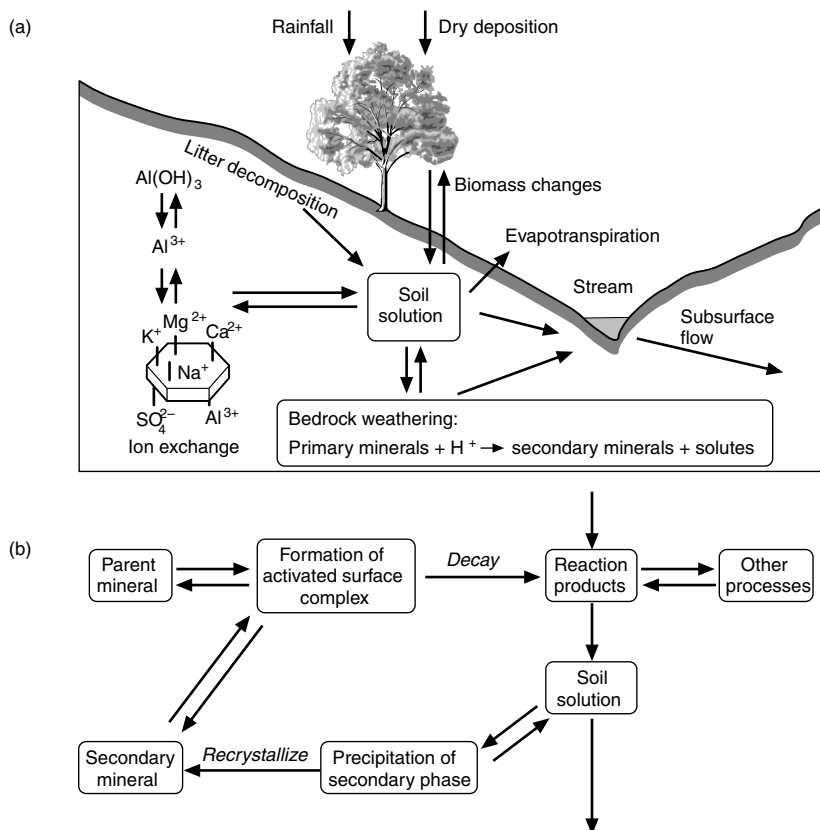
Fig. 1.3 (a) Some of the processes affecting solute fluxes in catchments. (After Drever & Clow, 1995.) (b) Flow diagram to show characteristics of surface mineral reactions. Note that incongruent behaviour involving mineral precipitation is characteristic of many weathering reactions. Also, non-conservative behaviour means that some dissolved ions may be precipitated *in situ* as other mineral phases, which therefore do not stay in solution to be exported by river water. (After Sverdrup & Warfvinge, 1995.)

i.e. the proportion of elements in solution is the same as the proportion in the former mineral(s). However, in the context of the whole catchment some of the dissolved ions may subsequently become involved in secondary mineral precipitation.

Want to know more about the thermodynamics of weathering reactions? Turn to Cookie 4.

Decomposition of silicate minerals is always *incongruent*—the reactions are very slow and temperature dependent, yielding other solid pro-

ducts in addition to dissolved ones. Reaction pathways vary according to local Eh–pH–temperature conditions. They proceed predominantly by *acid hydrolysis* in which activated surface complexes play a major role (Fig. 1.3) and where small, highly charged protons displace metallic cations in crystal silicate and oxide lattices. Silicic acid is produced from the intermediate metal-bonded silicate complexes and released to solution. OH^- or HCO_3^- ions finally combine with displaced cations to form solutions or local precipitates. Hydrolysis acts along lattice surfaces exposed by discontinuities such as joints, rock cleavage, crystal boundaries, mineral

cleavage planes and crystal surface defect sites. Once a dissolved ion is liberated from a crystal lattice by hydrolysis, it may link up with surrounding water molecules and thus stay in solution as a hydrated ion, or, if the force of attraction with water is insufficient to compete with that between the water molecules themselves, the ion will be 'ignored' by the water and will precipitate. Some elements will be exported from the weathering site, perhaps far away. Others will behave non-conservatively and precipitate locally, perhaps forming economic accumulations like in the concentration of Al and Fe in

bauxites and *laterites* respectively. The type of behaviour in solution is determined by the *ionic potential*, which is the ratio of ionic charge to ionic radius (Fig. 1.4). Cations (metals) whose potential is less than 3 are easily hydrated and highly mobile; anions of potential >12 form soluble complexes. Ions with potentials between 3 and 12 are mostly precipitated as hydroxides (in the absence of protons) and are thus immobile.

The proton concentration of soil water gives rise to pH values in the range 5–9, in which silicon is more soluble than aluminium. Thus prolonged chemical
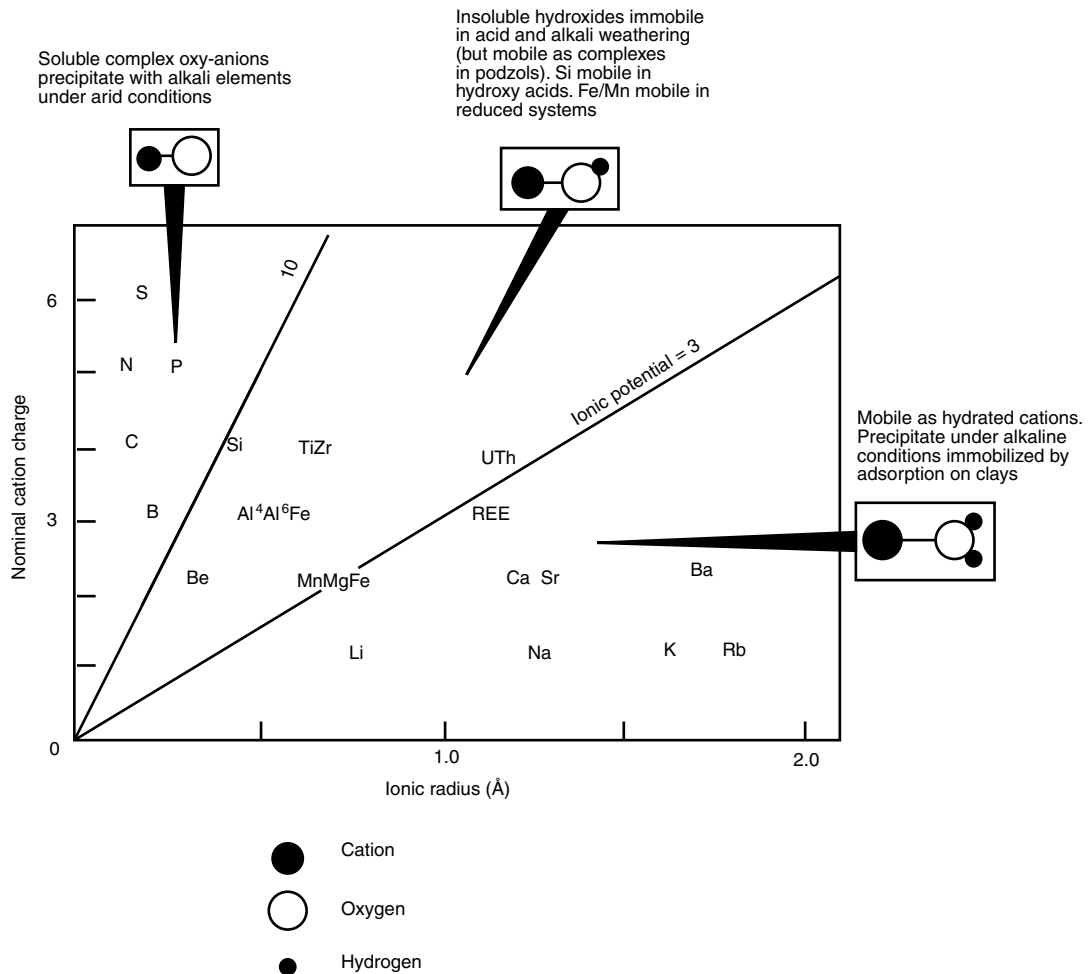

Fig. 1.4 The relationship between ionic charge and radius for various ions of importance in surface hydrogeochemical and weathering reactions. (After Gill, 1989).

weathering will leach Si from the soil profile, leaving behind a mixture of Al and Fe oxides and clays. These are *lateritic* (aka *ferralitic*) soils, common in well-drained tropical sites. By way of contrast, in highly acid soils Al and Fe are both leached to give a *podzol* with a characteristic light-coloured, silica-rich upper zone. Soils are discussed further in section 6.5.

Quartz, muscovite and K-feldspar dominate amongst clastic mineral components that survive chemical weathering from the weathered *regoliths* of igneous and metamorphic terrains (Fig. 1.5). However, the abundance of these and other primary minerals is highly variable, depending upon a number of factors including sourceland abundance, climate and type of weathering, original grain size, rapidity of sedimentation, and so on. As usual, sedimentology cannot be reduced to mere chemistry or physics. There are also important newly formed minerals produced by weathering.

Quartz

Quartz makes up ~20% by volume of the exposed continental crust. Its crystals comprise spiral networks of linked silicon–oxygen tetrahedra, making the lattice extremely resistant to chemical attack by aqueous solutions over the acidic and neutral pH range.
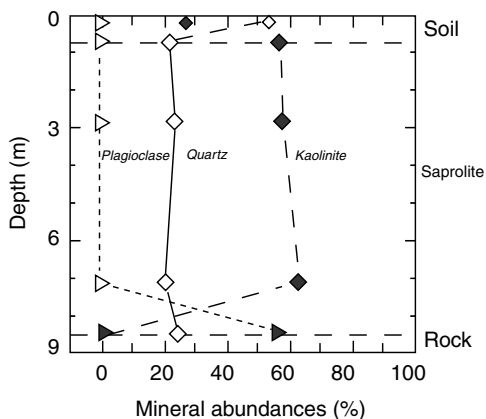

Fig. 1.5 Selected mineral abundance versus depth for the Rio Blanco Diorite, Costa Rica to illustrate the rapid changes observed in mineralogy at boundaries between bedrock/saprolite and saprolite/soil. (After Riebe *et al*., 2003.) Note dissolution of plagioclase and neoformation of kaolinite in the regolith.

Solubility increases at pH > 9 when crystal surfaces are subject to increasingly effective *hydroxylation*, particularly in the presence of alkali cations from NaCl and KCl. Hydroxylation is a process that introduces one or more hydroxyl groups (OH^-) into a compound or radical, thereby oxidizing it. Polymerization occurs in supersaturated solutions to form silica gels or sols. There is much evidence that quartz dissolution is greatly facilitated (perhaps by several orders of magnitude) by dissolved Al in the porewater environment. The main route by which quartz is made dissolvable, and also fragmentable, appears to be along microcracks and fractures.

Feldspar

As noted above, feldspar is the most abundant mineral in the Earth's crust and is most notable for being a major player in soil acidification and terrestrial inorganic CO_2 uptake (**Cookie 5**). It is an alumino-silicate in which Si–O and Al–O tetrahedra link to form an 'infinite' three-dimensional framework with variable proportions of the alkali cations Na, K and Ca in the interstices. The rate of dissolution is strongly temperature dependent and is also an interesting V-shaped function of pH (Fig. 1.6). At low pH the feldspar weathering reaction is simply a transformation by acid hydrolysis of the Al bonds. The main source of protons is dissolved CO_2, both from the atmosphere and the soil as a product of respiration. Such *acid dissolution* is probably the commonest form of soil weathering condition; it results in the precipitation of the white clay mineral, *kaolinite* and the liberation of the alkali and alkaline-earth elements in solution as hydrated ions, carbonate or bicarbonate ions with silica sometimes as byproduct (**Cookie 4,** Equation 4.1). Careful experiments show that the silica probably originates under slow-leach acidic conditions as a gel. Reaction rates are low at or about neutral pH, rising again because of hydroxylation at high pH when Si bonds are susceptible to dissolution in the presence of base cations. K-feldspar is also unstable under acid conditions and yields the products potassium carbonate, kaolinite and silica. There are several other possible products of the feldspar-weathering reaction depending upon local conditions of pH, which control the nature of the dissolved Al species—the most notable is *gibbsite*, ($Al(OH)_3$). At very low pH (< 3) reactions cause metallic cation leaching and the formation of a
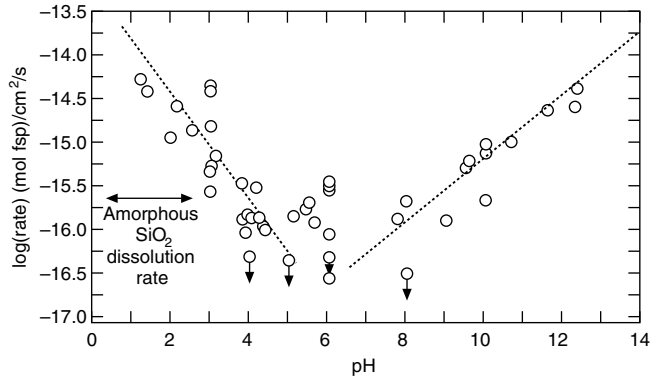
Fig. 1.6 Experimental sodium-rich feldspar (albite) dissolution rate as a function of weathering solution pH. Note the V-shaped curve common to many silicates. (After Blum & Stillings, 1995.)

thick surface layer rich in Si. Such surface layers do not form at other pH values and the dissolution process is dominated not by diffusion through a surface layer but by direct bond breaking and scavenging of 'danglers' (broken bonds).

Although there are a wide range of apparent activation energies and rate constants recorded in experiments, the generally observed field-weathering order for the various feldspar types is:

anorthite(Ca-plagioclase) > albite(Na-plagioclase)
    > orthoclase/microcline/sanidine(K-feldspars)

There is some evidence that the dissolution of K-feldspar is inhibited by the presence of Al in solution. Figure 1.7 shows spectacular etch pits and channels formed by Holocene weathering of a K-rich feldspar.

> Want to know more about chemical weathering as a geosink for global atmospheric CO_2? Turn to Cookie 5.

Micas

Micas have a distinctive sheet structure in which Mg, Al and Fe cations in octahedral arrangement lie between layers of $(Si, Al)O_5$ tetrahedral sheets. Cation substitutions give rise to negatively charged layers which are neutralized by an interlayer of K in both muscovite (K-rich mica) and biotite (Fe-rich mica) mica. This interlayer is released relatively quickly during weathering. Weathering reactions of the framework ions are slower and chiefly controlled by hydration and hydroxylation at broken metal–oxygen bonds, the process occuring progressively inwards from edge faces. Muscovite exhibits a typical V-shaped dissolution rate curve with respect to pH, with the lowest rates around pH 6. Biotite shows the same dissolution rate trend as muscovite at acid pH, but rates are usually very much higher (five times that of muscovite and up to eight times that of plagioclase) because of the dissolution effects of aqueous oxidation upon ferrous iron, Fe^2.

Chain silicates

These comprise the pyroxene and amphibole groups in which silica tetrahedra are linked in either single (pyroxene) or double (amphibole) staggered chains by oxygen sharing. The chains are linked and strongly held together by metallic cations like Ca, Mg and Fe. Amphiboles have additional OH^- in the rings between opposite chains. Weathering is chiefly by surface reactions that remove the metallic cations and acid hydrolysis by protonation to form surface species bonded as silicon oxide surface species. Rates of dissolution vary inversely with pH, with actual rates varying widely in these often chemically complex groups. As in biotite mica the occurrence of transition-group metals like Fe and Mn means that redox reactions with dissolved oxygen also occur, leading to generally faster rates of overall dissolution. Oxidation of liberated Fe^2 leads to surface crusting of
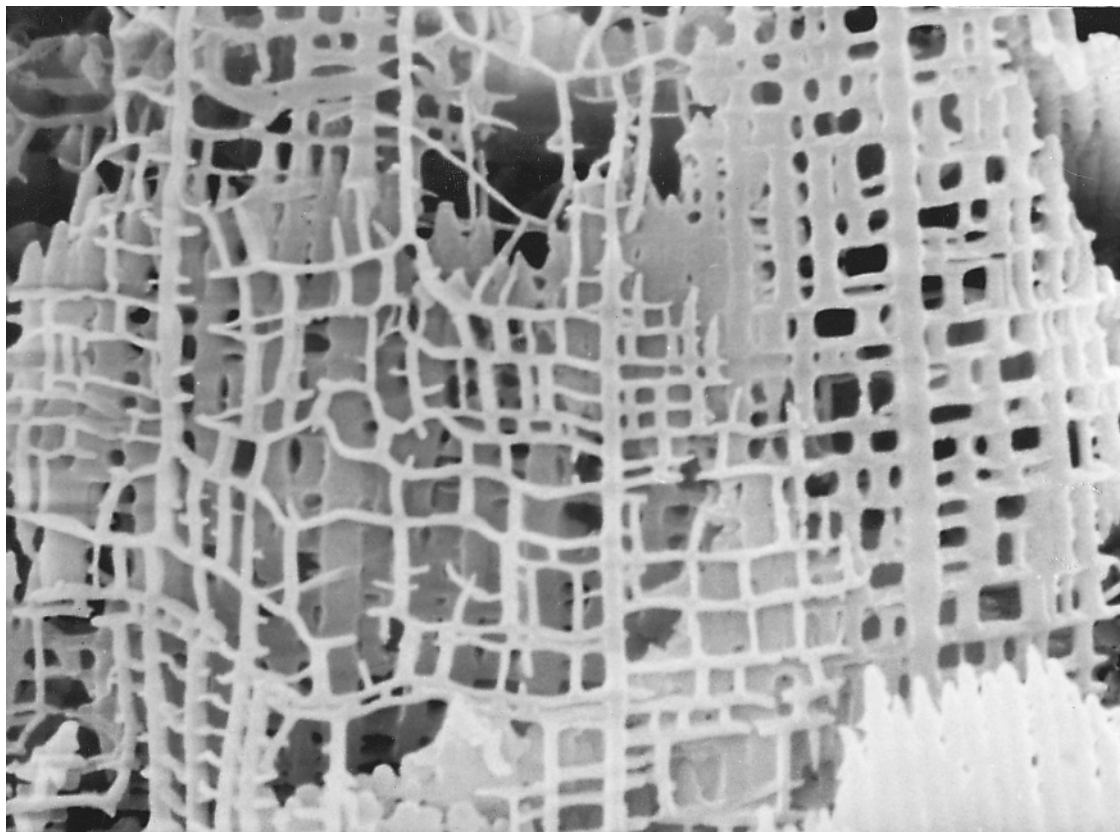
Fig. 1.7 Scanning electron microscope image of a resin cast of weathered feldspar. The former grain surface of the K-rich alkali feldspar is below the plane of the image and the weathered interior is in focus. The resin network has penetrated into the interior of the crystal along etch pits. Field of view 24 μm. (After Lee & Parsons, 1995, 1998; image courtesy of authors)

amorphous Fe^3 precipitates, but it is not thought that these adhere significantly enough to lead to diffusion-controlled reactions.

Olivine

Olivine has a simple structural arrangement of isolated SiO_4 tetrahedra linked by the divalent cations Mg^2 and Fe^2. It comprises the end-members fayalite (Fe-rich) and forsterite (Mg-rich), with a complete solid solution series in between. Mg is removed by surface leaching and complex formation after protonation. Fe-rich olivines are highly susceptible to oxidative weathering and the formation of hydrated clay minerals. Ferric crusts of *goethite* characterize humid saturated conditions whilst *haematite* occurs under subhumid to arid

unsaturated conditions. A major role for microbial oxidation of Fe^2 during acid-weathering is suggested by experiments that record lowering of mineral reaction due to surface adsorption of Fe^3.

Clay minerals

Clay minerals are the most important newly formed mineral group in the weathering zone since their eventual erosion and deposition produces copious mud-grade sediments that give valuable information about weathering conditions. We have already encountered *kaolinite*, formed under humid, acid weathering conditions from the alteration of feldspar-rich rocks. *Illite*, a potassium aluminium hydrated silicate, is formed by weathering of feldspars and micas under

alkaline weathering conditions where significant leaching of mobile cations such as potassium does not occur. *Smectites* are complex expandable sheet silicates with intracrystalline layers of water and exchangeable cations. They form from the weathering of igneous rocks under alkaline conditions. Gibbsite is simply aluminium hydroxide and forms under intense tropical weathering conditions with high annual precipitation (>2000 mm) when all other cations and silica present in bedrock are leached out.

Apatite and the P cycle

Apatite is either a stoichometric, fluorinated calcium phosphate (igneous fluorapatite, FAP) or a non-stoichometric sedimentary carbonate fluorapatite (CFA) with variable substitution of Mg^{2+}, Na^+ and CO_3^{2-}. The mineral is a common accessory mineral in granitic rocks and forms the majority of sedimentary phosphate rock. Both FAP and CFA define the primary exogenic phosporus sink and serve as the long-term weathering source of P to the biogeosphere where it is an essential nutrient element for cellular life and acts as a control upon net ecosystem production. Weathering is optimal under warm, acidic pH conditions, with FAP being the easiest to dissolve.

Rock weathering profiles: changes, age and depth

Data from studies of chemical, physical and mineralogical changes with depth in weathered granodiorite are shown in Figs. 1.8 & 1.9. The fresh granitodiorite comprises plagioclase feldspar (32%), quartz (28%), K-feldspar (21%), biotite (13%) and muscovite (7%) with rarer (<2%) amphibole. The main secondary minerals formed during weathering are kaolinite with lesser amounts of halloysite, goethite, haematite, gibbsite and amorphous Fe-hydroxides. Note the rapid loss of alkaline earth elements Na and Ca from fresh to plagioclase-weathered bedrock with K, Fe and Al showing slight relative enrichment. K subsequently declines in saprolite as K-feldspar is incongruently dissolved whilst Fe and Al enrich, the former due to Fe^{3+} precipitation in hydroxides, the latter due to kaolinite precipitation. Si usually behaves conservatively or slightly depletes throughout, apart from in the soil zone where it concentrates and Al/Fe strongly depletes. Cosmogenic isotope dating reveals mean rates of descent of the weathering fronts at speeds of
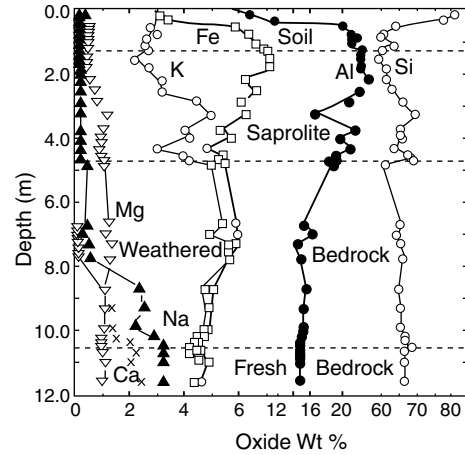

Fig. 1.8 Elemental distributions with depth in the Panola regolith developed over ~10^5 yr on a granodiorite bedrock, Georgia Piedmont province, USA. Weathering was essentially isovolumetric with preservation of primary granitic textures in the saprolite, average saprolite porosities of ~35%, presence of boxwork textures of secondary minerals surrounding primary remnants and etch-pit formation. (After White *et al.*, 2001.)

~4–7 m/10^6 yr. These rates are very much slower then experimental feldspar weathering rates and suggest that in old regoliths surface mineral reactivity decreases significantly with time.

Chemical index of alteration

Although chemical weathering is complex there exists a simple Chemical Index of Alteration (CIA) that is useful to assess its extent. It involves simplifying weathering of the upper crust to a combination of feldspar and volcanic glass, involving only the commonest oxides in the silicate fraction, Al_2O_3, CaO, Na_2O and K_2O. The CIA is given by $100.Al_2O_3/(Al_2O_3 + CaO + Na_2O + K_2O)$ and varies between 100 and 47. The pristine upper crust has a mean CIA of 47, with 100 signifying wholesale removal of all alkaline earths. CIA values calculated for the suspended load of the major rivers of the world define a chemical weathering path (Fig. 1.10; section 23.3). Rivers draining tectonically active catchments have low CIA values since physical weathering and high mechanical erosion rates predominate here.
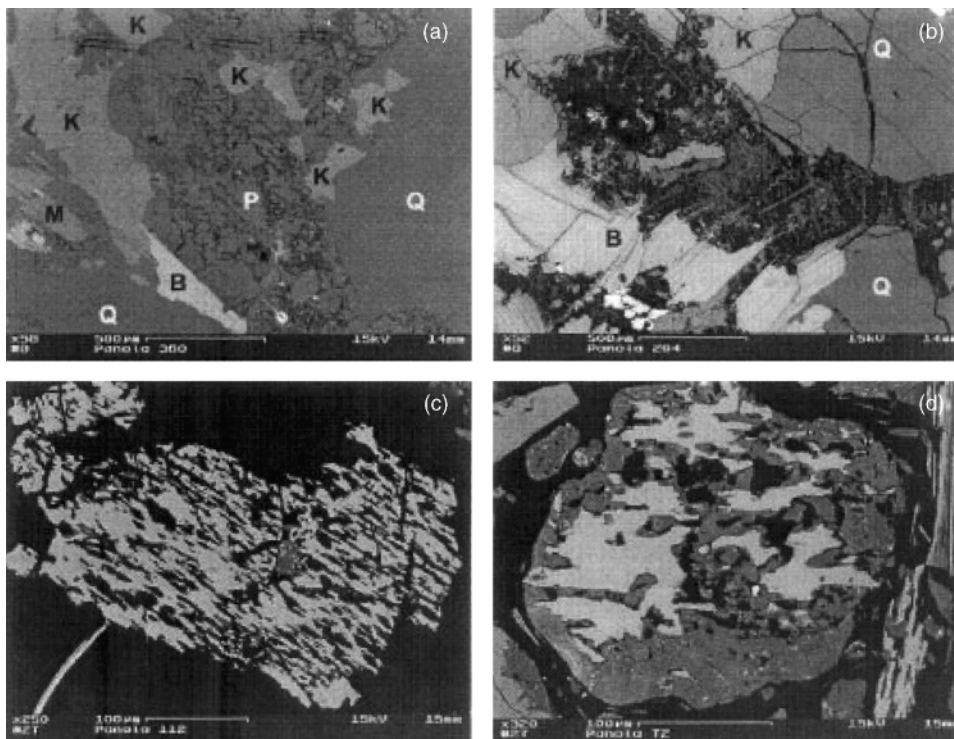
Fig. 1.9   Scanning electron microscope backscatter-mode images of rock sample thin-sections from various depths in the Panola regolith (P, plagioclase feldspar; K, −potassium feldspar; B, biotite mica; M, muscovite mica; Q, quartz). (a) 9.1 m depth; initial incongruent weathering of plagioclase feldspar in bedrock. Dark areas within the crystal are the clay mineral kaolinite. Note the pristine K-feldspar. (b) 7.5 m depth; the plagioclase crystal (centre) has virtually gone, leaving clay-filled vugs (black areas). The adjacent biotite mica is starting to weather along cleavage planes (dark areas within the biotite). The K-feldspar is again pristine. (c) 2.8 m depth. In this saprolite zone the K-feldspar has dissolved, gaining a skeletal appearance with open vugs (black areas) that originally may have been partially filled with clay. (d) 1.8 m depth just below the soil–saprolite interface. The K-feldspar is partially replaced by clay. Note the relatively unreacted muscovite mica to the right of the image. (After White *et al*., 2001.)

Al-release from silicates by acid hydrolysis ('acid rain' problem)

Acid hydrolysis reactions in soil zones with base cations (especially Ca^2) usually lead to effective neutralization of rainwater, which in unpolluted areas has a pH of around 5.0. However, in many temperate zones with high rainfall and thin soils on Ca-poor substrates, the acidity is not neutralized, leading to formation of characteristic podzol soils (see section 6.6) with leached Al-poor surface horizons. Vastly increased industrial pollutants and emissions (CO_2, SO_2, NO) have accelerated these processes in many areas, including exports of gases to 'innocent' countries (e.g. Scandinavia), leading to extensive Al-release in acidic waters and widespread environmental damage. The very steep increase of Al solubility in waters of low pH is illustrated by the data of Fig. 1.11. Assessments of acidification depend heavily upon estimations of cation fluxes, sources and sinks through the water–soil–bedrock system.

1.3   Solute flux: rates and mechanisms of silicate chemical weathering

In these times of rapid environmental change it is essential to truly understand and to be able to predict the rates and mechanisms of chemical weathering of
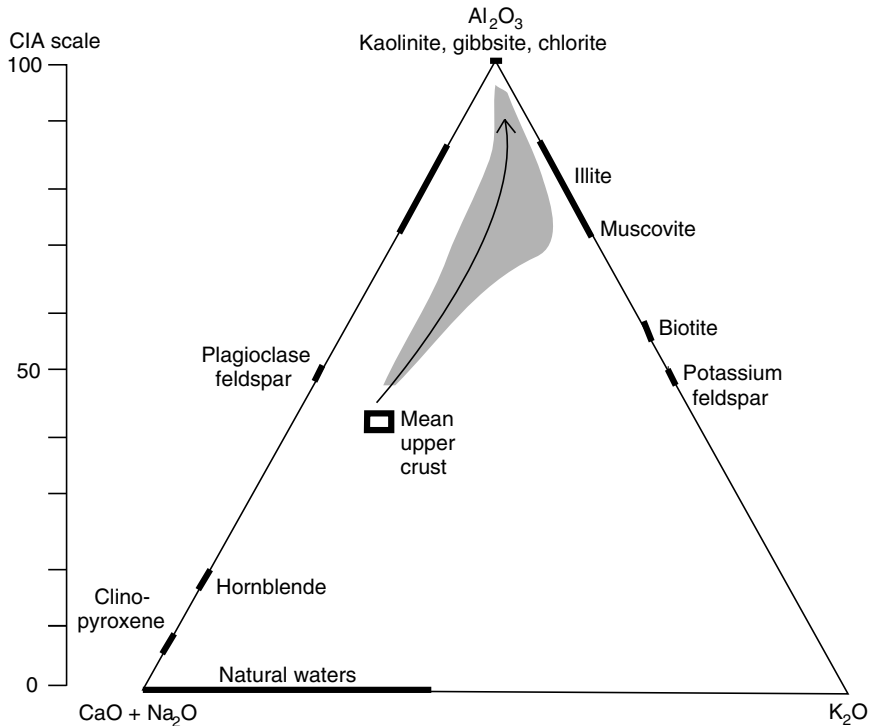
Fig. 1.10 Triangular diagram Al_2O_3–$(CaO + Na_2O)$–K_2O, with approximate compositional ranges of natural waters, common silicate minerals and Chemical Index of Alteration scale. (After McClennan, 1993.)

silicate-rich bedrock in response to water through-flow. Very generally the *solute flux* approach to catchment weathering seeks to draw up a balance sheet of all inputs and outputs to the catchment chemical system—it is basically a *conservation of mass* exercise. Its simplest expression states that:

cation weathering rate = leaching +

   uptake−deposition−base saturation decrease

It is usual to define weathering reactions in terms of a *rate constant*, the amount of mass lost from unit surface of a mineral over unit time. It is defined by *Arrhenius's law* (**Cookie 6**), controlled both by the energy needed to make a reaction happen, the *activation energy*, and by the *temperature* of reaction conditions. The law is easiest to understand kinetically, since any reaction needs sufficiently energetic collisions between reactant ions to cause it to happen; an *energy threshold* must be surmounted. In the case of silicate mineral surfaces in contact with natural waters, the warmer the aqueous

phase the more energetic will be the attacking protons and therefore the faster the reaction will be. Not only that, but the energetics increase exponentially as temperature increases. This means that there is a considerable (25-fold) disparity between the energy available for weathering at the poles compared to the tropics.

Want to know more about the rates and mechanisms of chemical weathering? Turn to Cookie 6.

Flow rate of water through the weathering zone is important because much rainfall is recycled back to the atmosphere by evapotranspiration; the amount available for throughflow is dependent on vegetation type and density. Most silicate reactions proceed to a point where the products have concentrations as predicted by the relevant *equilibrium constant*, which for silicates are *very* low (**Cookie 6**). When the rates of forward and backward reactions become equal, no
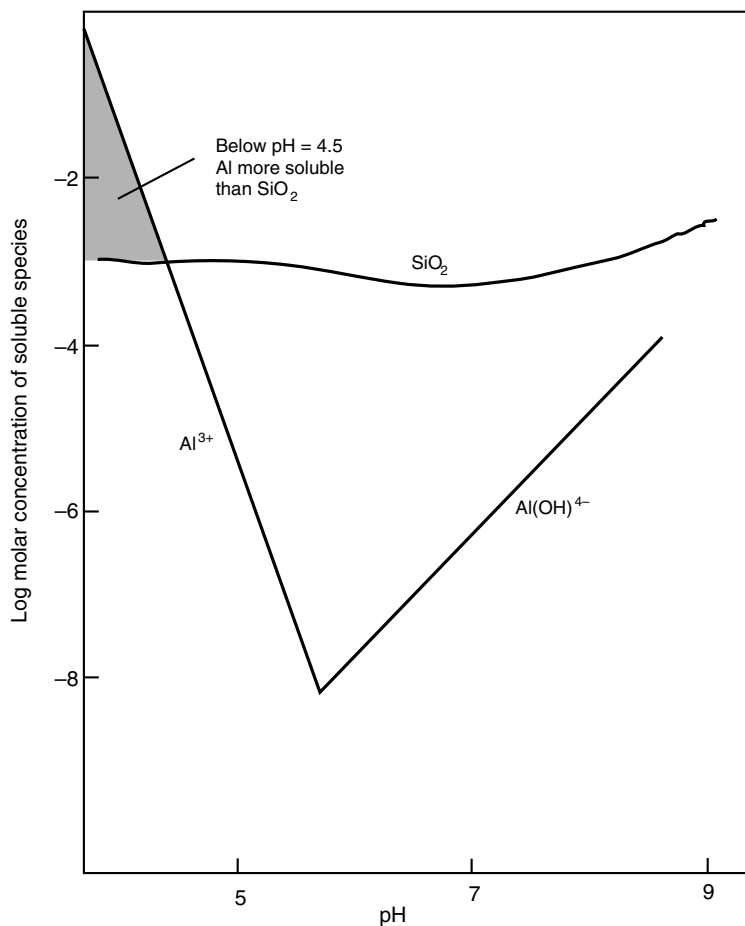
Fig. 1.11 The solubility of aluminium and silicon as a function of pH. (After Raiswell *et al*., 1980.)

further weathering occurs. Only by removing saturated porewaters and replacing them with new water can more weathering reactions occur. Optimal conditions for chemical weathering occur in forested orogenic highland areas of the humid tropics, where very thick soil and chemically altered bedrock zones have formed in the Holocene and where soil instability due to slope failure enables periodic exposure of fresh saprolite or bedrock. Lack of physical weathering and erosion on continental plateaux lead to thick residual soils and a marked decrease in total export of ions. Such catchment slope conditions are known as *transport-limited*, for there is always an abundance of weathered product to transport.

There is much experimental work to suggest that weathering rates are linear, controlled by surface reactions between mineral and aqueous phases. Surface in this case refers to fractured and cleaved mineral faces. There is also sound evidence from electron microscopy studies that weathering can occur along uncracked and uncleaved areas of minerals, the process occurring along submicroscopic diffusion paths at sites of lattice dislocations. The chemical attack is seen in the form of etch pits (Fig. 1.7). Rates of surface reactions are usually very slow compared to diffusion rates, and the concentration of products adjacent to the reacting mineral surface are comparable to that of the weathering solution.

(a)

(b)

Fig. 1.12 (a) Granodiorite corestones showing exfoliated 'onion-skin' morphology in a tropical weathering zone of saprolite. (b) The hand-inserted shear vane is measuring the strength of a saprolite that was once solid granite—testament to the reality of rapid tropical chemical weathering. (Images from Tai Po, Hong Kong, courtesy of Steve Hencher.)

Although experimental and some field studies indicate a constancy of dissolution rates over time, there is also evidence from naturally weathered materials that rates decrease as a result of elemental exhaustion and/or the build-up of a thickening surface layer of weathered material that slows aqueous access during diffusion. A steady state may be set up by removal of the weathered material by erosion (see further below). The local rate of chemical weathering by diffusion will determine the thickness of *weathered rinds*, defined as discoloured and permeable crusts enriched in immobile oxides (e.g. Fe_2O_3, TiO_2 and Al_2O_3) relative to unweathered cores. With calibration to features of known age, it is possible to use weathering rind thicknesses to determine weathering ages. The ultimate signature of progressive chemical weathering of rock masses comes from *corestones*, where rounded remnant nucleii of more pristine rock are surrounded by saprolite (Fig. 1.12).

The rate of chemical alteration of glacial-sourced debris in moraines and soils also shows a well-defined decrease with age, probably because the finely ground carbonate and sulphide mineral components dissolve first and easiest. Silicate weathering increases with distance from an active glacier in the older outwash sediments, particularly if vegetation becomes established. It is thought by some that chemical weathering rates have risen and fallen globally in tune with glacial and interglacial development over the last million or so years, although it should be stressed that there is no *direct* evidence for this. This idea is based upon the greatly increased availability of glacier-ground fine sediments (loess, tills, outwash) that cover higher latitudes and mountain belts at deglaciation. The fresh
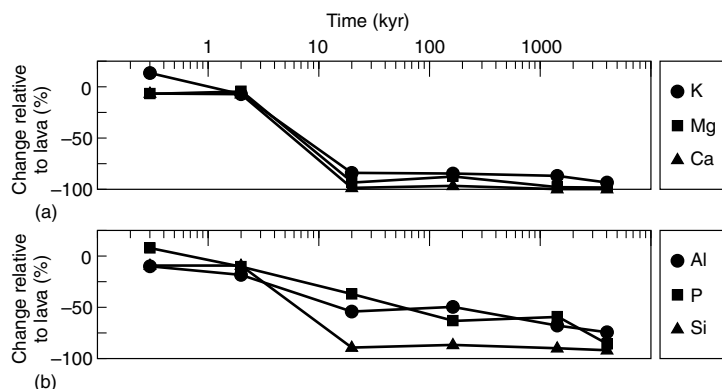
Fig. 1.13 The time change of elemental proportions in soils developed on Hawaiian basalts of various ages. Note the most rapid rate of change in K, Mg, Ca and Si between 2 and 10 kyr. (From Vitousek *et al.*, 1997; see also Chadwick *et al.*, 1999; Sak *et al.*, 2004.)

mineral surfaces in these are expected to weather very rapidly at first, declining over millenial times scales—we return to this topic in connection with strontium isotope studies relating to global denudation trends (Chapter 10).

Studies spanning 3.5×10^6 yr on soils atop dated basalt lava flows in Hawaii (humid subtropical forested environment) indicate that the easily weatherable base elements K, Mg and Ca, together with Si, are reduced to less than 10% of their initial values in the top 1 m of the soil profiles within 20 kyr (Fig. 1.13). More resistant Al, present in residual kaolinite, declines much more slowly, reaching such low levels only after 3 Myr. Tables 1.1 & 1.2 summarize work

done on the relative rates of dissolution of common catchment rocks and minerals.

It is noteworthy that the relative rates of pure, single-mineral dissolution in laboratory experiments show far greater ranges than those determined from natural rocks in catchments underlain by single lithologies. One problem is that many igneous rocks contain small but chemically significant ammounts of carbonate minerals which may dominate the flux of base cations like Ca. Natural weathering is also more complex, particularly in the flow, concentration and fluxes of both aqueous and solute phases. This is nicely

Table 1.1 Relative rates of CO_2 consumption and solute fluxes in runoff from various catchments based on rock type groups shown. (After Amiotte-Suchet & Probst, 1993.)

Rock type	Relative rate CO_2 consumption	Relative rate solute flux
Plutonic/metamorphic (granite, gneiss, schist)	1.0	1.0
Felsic volcanics (rhyolite, andesite, trachyte)	2.3	?
Basic volcanics (basalt)	5.0	?
Sandstones	1.5	1.3
Mudrocks	6.6	2.5
Carbonate rocks	16.7	12.0
Evaporites	3.1	40–80

Table 1.2 Relative rates of dissolution of various minerals in laboratory experiments at pH 5 far from equilibrium. (After Drever & Clow, 1995, and sources cited therein; see also Sverdrup & Warfvinge, 1995, Table 20.)

Mineral	Normalized rate (mineral rate/ albite rate)
Quartz	0.02
Mica (muscovite)	0.22
Mica (biotite)	0.6
K-feldspar (microcline)	0.6
K-feldspar (sanidine)	2
Na-plagioclase feldspar (albite)	1
Na/Ca feldspar (bytownite)	15
Orthopyroxene (enstatite)	57
Clinopyroxene (diopside)	85
Mg-olivine (forsterite)	250
Dolomite	360 000
Calcite	6000 000

(a)

Concentration µmol/l

2002 monsoon

2003 monsoon

Ca

Mg

Na   K

Apr May Jun Jul Aug Sep Oct Nov Dec Jan Feb Mar Apr May Jun Jul Aug

(b)

discharge m³/s

monsoon

monsoon

Apr May Jun Jul Aug Sep Oct Nov Dec Jan Feb Mar Apr May Jun Jul Aug

(c) Silicate

weathering flux [kg/day/km²]

RO

GW

slope = 0.65±0.05
Intercept= 9.24±9.74
R^2 = 0.88
P<0.0001

runoff mm/day

(d) Carbonate

weathering flux [kg/day/km²]

RO

GW

slope = 2.45±0.17
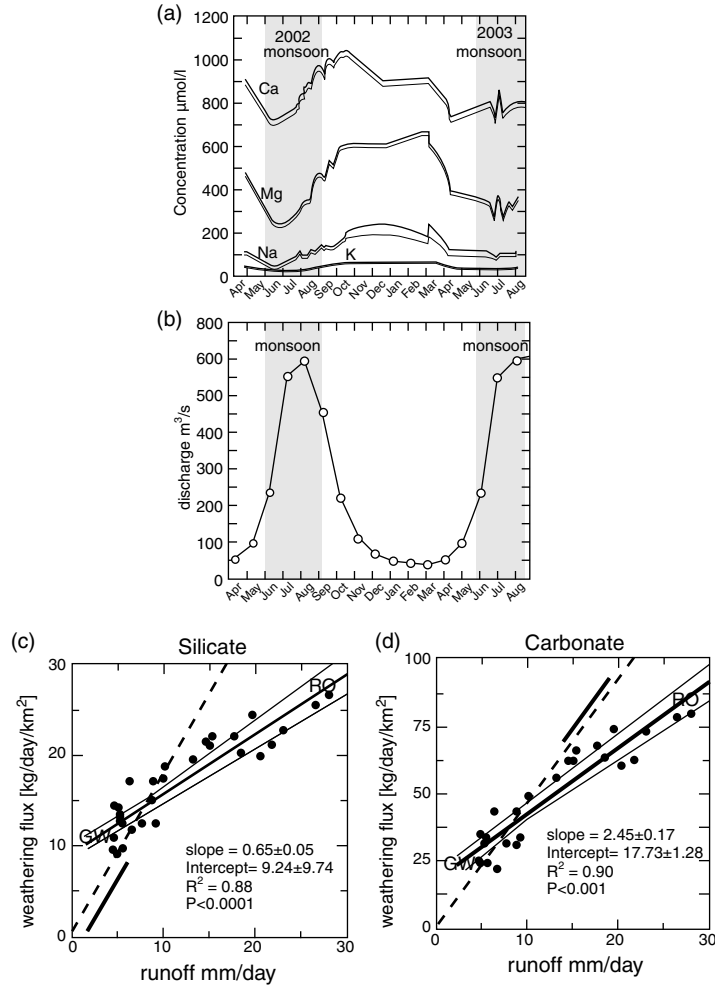Intercept= 17.73±1.28
R^2 = 0.90
P<0.001

runoff mm/day

Fig. 1.14 (a) Selected ionic concentrations through the annual hydrological cycle of the Marsyandi River, Nepal Himalaya. Note highest concentrations occur during dry seasons (b) Monthly discharge of the Marsyandi River averaged over a 10-year period. (c) and (d) The positive dependence of weathering ionic flux on runoff for carbonate and silicate bedrock for a subcatchment of the Marsyandi River system. Note highest fluxes occur during rainy seasons. (After Tipper *et al.*, 2006.)

illustrated by large-magnitude seasonal variations in river-water chemistry and elemental fluxes from Himalayan catchments whose bedrock includes igneous, metasilicate, metacarbonate and sedimentary limestones (Fig. 1.14).

1.4 Physical weathering

Erosion causes subsurface rock to be exposed at the surface. During such *exhumation*, elastic volumes are increased by the unloading: deep conditions of higher, but balanced, triaxial stresses are replaced by *in situ* biaxial compressive stresses of order of magnitude (hereafter [O]) 35 MPa, a value in excess of most rocks' strength at the surface. These stresses are vividly illustrated by geologically sudden unloading produced by quarrying or mining with resultant sudden sheeting, arching or catastrophic rock bursting. Together with slow unloading brought about by surface erosion a variety of rock *joints* are produced. These are linear

fractures and curvilinear exfoliations parallel to buttressed rock outcrops or valley surfaces. It is now considered impossible for diurnal temperature changes in deserts to cause rock exfoliation since many experiments have failed to reproduce the effects in the laboratory. The effect is ascribed to the spalling-off of partly chemically weathered rock skins from bedrock surfaces, either in saprolite (Fig. 1.12) or on shady parts of rock surfaces. Here, the effects of surface moisture upon minerals is greatest and acts for longer periods.

The various physical imperfections in rock are acted upon by chemical weathering solutions, by biogenic attack and by other physical processes, chief of which are freeze–thaw (frost) and salt weathering. Both of the latter involve the production of stresses through crystallization of solids from solution in tiny rock fractures or near-isolated pores. The net effect, in combination with slow gravity creep down hillslopes (*soil creep*), frost shattering, salt growth and near-surface chemical weathering, is the production of *colluvial mantle* overlying saprolite and bedrock. In this way the landscape reduces, almost by auto-destruction.

Frost weathering is particularly important in high mountainous catchments not under permafrost. Up to 165 freeze–thaw cycles per year have been recorded in the French Alps at altitudes of just 2.5 km. A certain amount, sometimes a significant amount, of daily freeze–thaw also occurs in low-latitude and/or high-plateau deserts, where winter rains and dews may provide enough moisture for the freeze–thaw process to be effective. It is partly due to anomalous expansion and decreasing density as water freezes. The accompanying increase in volume of up to 13.5% (at $22\,°C$) generates up to about 200 MPa of pressure in confined situations. However, the story is inevitably more complicated because of the effect of ice whisker crystal growth, liquid film transfer and stress gradients in tiny to small isolated or tortuous cracks ($<0.5\,mm$) and pores. Additional stresses—as much as 10 times those arising from simple expansion above—may arise from ice growth as clusters of parallel ice crystal needles grow normal to the freezing surface. Provided the small crack is supplied with a net input of water, then the stresses arising from crystal growth are limited only by the tensile strength of water, which is drawing water molecules to the ends of the growing crystals through capillary films. This process carries on below normal freezing point in the thin films, being most

effective between 4 and $15\,°C$. It seems that frost weathering is most effective in tiny cracks and crevices of irregular shape in temperate to subarctic climates where repeated thawing and freezing occur on a daily basis, the water moving around by capillary attraction. Between 0.02 and 0.8% by mass of shattered material was generated in experimental 40-yr shatter cycles with a variety of 'hard rocks'. Porous and permeable rocks, where drainage is freer, are not so prone to shattering, but do so nevertheless.

Salt weathering has often been greatly underestimated as a weathering type. It occurs in semiarid to arid climates and in coastal areas of all latitudes where salts are concentrated and where dews, coastal mists, sea spray and ordinary rainfall provide the necessary liquid phases. It would seem to have been particularly important at some stage on the surface of Mars (Chapter 23). There seem to be three ways in which salt expansion may give rise to stresses that lead to rock disintegration: (i) periodic hydration and dehydration, (ii) periodic heating and cooling, and (iii) crystal growth. The last mechanism is probably the most important. As we have seen, crystal-growth stresses are particularly dependent upon rock porosity and the mechanism is most effective in porous sedimentary hosts. Salts vary in their ability to disintegrate rocks by crystal growth, sodium and magnesium sulphates being most effective. Crystal growth stresses occur in tortuous cracks under pressure. They arise at the crystal–rock interface via aqueous films as the crystallizing salts occlude the available space. Open systems, where salts crystallize due to evaporation, cannot give rise to changes of volume and hence cannot give stresses. Finally, a neglected form of salt weathering occurs when sedimentary pyrite is oxidized in fissile calcareous mudrock. The resulting crystal growth of ferrous sulphate and gypsum is highly efficient in disaggregating rock.

1.5 Soils as valves and filters for the natural landscape

Soil is usefully envisioned as a valve or filter for the landscape. Imagine it as a graduated semipermeable skin or carapace through which the atmosphere and hydrosphere communicate with the lithosphere. It is graduated in the sense that it divides into more-or-less distinct layers. It is a valve in that it allows some proportion of precipitation to pass through it and

hence into saprolite to further the weathering process of bedrock. It is a filter in that the usually well-drained, aerated and oxygenated surface soil layers are the site of a myriad of chemical reactions, many of them biologically mediated, that modify intercepted precipitation. Biological mediation in this case includes:

- elemental uptake and pH-modifying activities due to higher-plant root systems and their adjacent soil volumes (the *rhizosphere*). Rhizosphere pH-diminution is caused by both CO_2 production by root respiration and H-ion release to compensate for the excess of cations over anions taken up for plant growth;
- ingestive and metabolic activities of worms;
- metabolizing aerobic soil microbe populations of bacteria (actinomycetes) and symbiotic mycorrhizal fungi on plant roots, algae, protozoa, slime moulds;
- surface encrustation by lichens that cause a substantial increase in silicate mineral dissolution compared to control sites undergoing abiotic weathering.

Concerning the many different soil types, it is the nature of the various constituent layers that forms the basis for soil classifications. There is often an upper accumulation of organic litter of dark hue. Below is a depletive horizon due to mineral alteration, weathering and physical washing-out of materials (*eluviation*). Finally there may be a lower accumulative horizon that represents the deposition of materials from above or the site of deposition of clay-grade material from the throughflowing waters (*illuviation*). In older classifications these three layers are given the codes A, B and C respectively. Below these horizons is saprolite.

An important point is that natural soils develop progressively with time, leading to changes in chemistry and physical characteristics. Residual soils, particularly *duricrusts*, occur in landscapes from which only small amounts of soil breakdown products are removed physically. Such soils are extremely useful to geologists in assessing the nature of past climates and of climate change (Chapters 10 & 23) since they may take many millions of years to form. They are indicative of tectonic stability and frequently occur on ancient erosion surfaces.

In eroding landscapes the extent and age of the soil will depend on the balance between formation and erosion. Studies in landscapes like those of Scandinavia and northern North America, whose young soils were initiated on ground-up mineral grains as

Quaternary glaciers retreated in the early Holocene, enable estimates of rates of elemental depletion and soil textural development with time.

We may simplify chemical weathering and soil environments into acid, alkaline and reduced trends (Figs. 1.15 & 1.16). These occur in humid and arid climates and in wetland systems, respectively. We may also simplify soil types into four major groups, ignoring the distinctive but ephemeral character of soil developed upon unconsolidated, glass-rich volcanic ashes.

Acid weathering occurs with high rainfall and a well-developed rhizosphere. This causes hydrolysis and leaching, and results in *ferralitic* and *podzolic* soils.

1 Ferralitic weathering involves Fe–Al enrichment during soil formation and is characteristic of stable, well-drained landscapes in seasonally humid tropical climates encouraging deep, high-pH dissolution of silicate minerals. It has been estimated that such soils cover almost 30% of the continents. Mature soils ($>10^4$ yr old) are dominated by aluminium (defining bauxites) and/or iron oxides and hydroxides (defining ferricretes/laterites), with the minerals goethite, haematite, kaolinite and gibbsite variably present in often very thick weathering profiles. Bauxites form under humid tropical conditions and contain gibbsite and goethite whilst ferricretes/laterites contain haematite and kaolinite formed under subhumid climates. Detailed studies of laterite profiles reveal evidence for both leaching of other cations under alkaline conditions, leading to relative Fe-enrichment, and absolute enrichment of Fe by ionic migration under alternating oxidizing and reducing conditions. The very old ages of some profiles (10^1–10^2 Ma) leads to opportunities in interpreting past versus present conditions of formation, since climate change has often occurred during their interval of development.

2 Podzolic weathering and *podzol* soil formation (aka *spodosols*) occur in cool, humid-temperate climates under coniferous vegetation that provides acidic leaf litter and also widely in high mountains. Humus accumulates rapidly in an upper horizon since under cool conditions the rate of metabolic breakdown is slow. Moderately to highly acidic conditions ensue as organic breakdown occurs giving *fulvic acids*, which causes Al, Fe and Mn
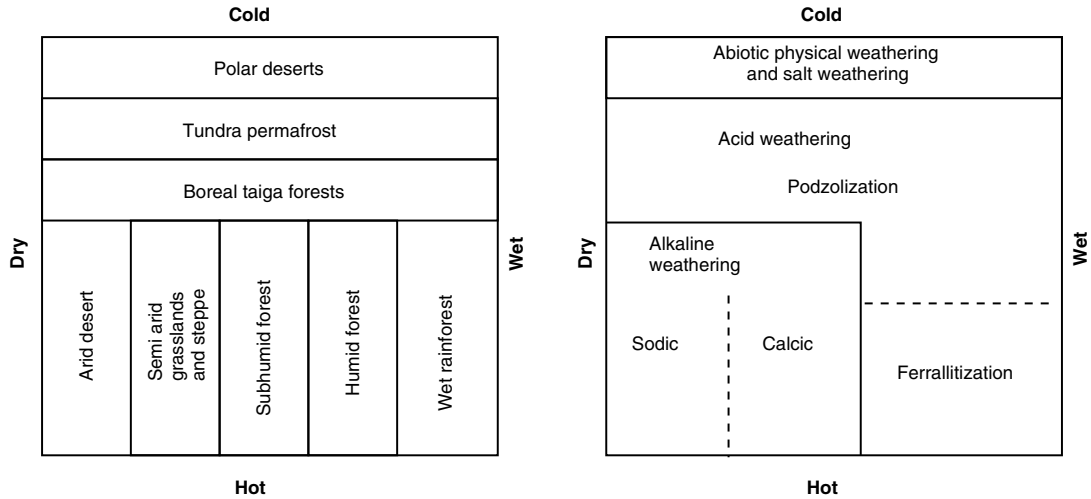
Fig. 1.15 Simple box classification of climate, vegetation, weathering and soil types developed on well-drained (i.e. oxidising) substrates. This scheme ignores local (sometimes crucial) control by particular lithologies. (Simplified after Chesworth, 1992, and sources therein.)

leaching from a pale middle-depth Si-rich layer and their subsequent eluviation and ultimate reprecipitation in lower soil layers.

Alkali weathering trends occur in arid, semiarid and Mediterranean areas with annual water deficit, and include calcic and sodic soil types.

1 Sodic soils occur in arid climates where there is an upward movement of porewaters leading to evaporative concentration of alkali and alkaline-earth elements such as sulphates, bicarbonates and chlorides. They often occur in interior drainage catchments and reflect ions translocated to the soil profile from considerable distances in through-flowing groundwaters. They are a major problem in irrigated farmlands with poorly planned drainage.
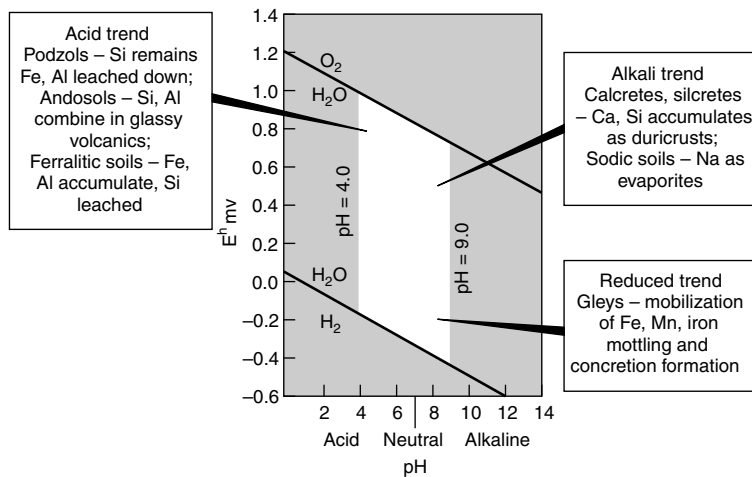

Fig. 1.16 Broad classification of soil chemical processes in terms of Eh (redox potential) and pH. (After Chesworth, 1992.)

2 Calcic soils (section 2.9) occur widely in semiarid and Mediterranean climates where they result from a balance between downward leaching of $CaCO_3$ and its reprecipitation as calcite in lower soil layers. Stable isotope analysis ($\delta^{13}C$, $\delta^{18}O$) of calcic soils gives valuable evidence for palaeoclimate regime.

Gley soils are poorly drained soils that form where the water table is close to the surface and where reducing conditions occur below it. The diagnostic gley horizon has red/brown mottles in a paler matrix. The mottles are coloured by oxidation that occurs when the water table lowers and reduced Fe^{2+} species in the pale horizon can oxidize to Fe^{3+} (**Cookie 2**).

A final point concerns classification and field description of ancient soils (palaeosols) in the sedimentary rock record (Fig. 1.17). Here it is important to be able to assess soil type independently of degree of secondary alteration during burial of what were once primary soil features. Thus physical attributes such as soil agglomerations (*peds*) and expansion/contraction cracks are easily destroyed by compaction (unless mineralized or otherwise infilled) during burial.

1.6 Links between soil age, chemical weathering and weathered-rock removal

Chemical weathering and soil formation have been considered separate from physical processes of sediment removal so far in this text; they are in fact strongly coupled. As noted above, it is widely recognized that the rate of chemical weathering from any given soil volume decreases with time. Thickening of soil profiles into saprolite replenishes the supply of fresher mineral surfaces available for chemical reaction. Because of soil-thickening most soils are very much older than the residence times of the minerals within them. However, as soils thicken so their hydraulic conductivity and aqueous throughflow lessens and so the *rate* of thickening decreases. It is the periodic or constant removal of weathered material (both soil and saprolite) by physical transport processes such as *colluvium* (by mass gravity flow) and *alluvium* (by aqueous transport) that provides *new* bedrock material for chemistry to get to work on and produce new soil and saprolite. Chemical erosion rates are thus coupled to physical erosion rates (Fig. 1.18), a topic further considered in Chapter 10.
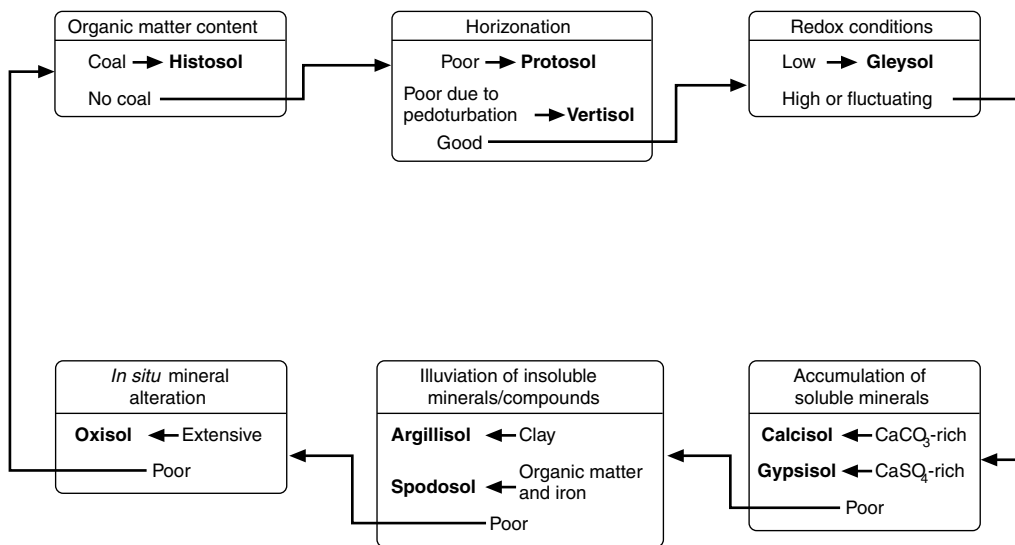

Fig. 1.17 Simplified flowchart of palaeosol orders to be defined for ancient terrestrial environments by systematic application of six key attributes. (After Mack *et al.*, 1993.)
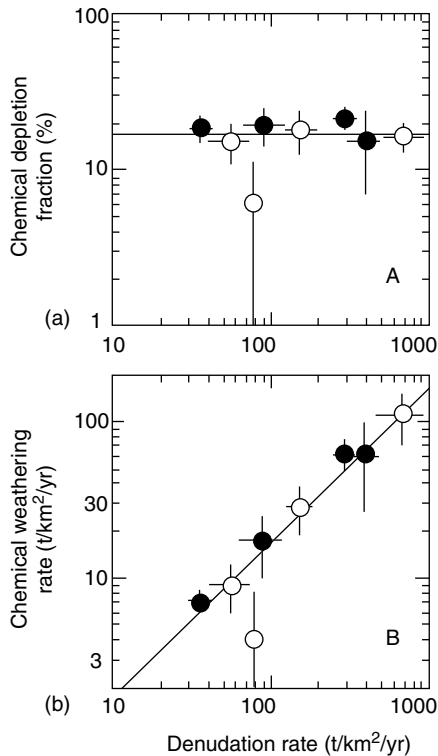
Fig. 1.18 Chemical depletion fractions and weathering rates from two sites in the Sierra Nevada, California where denudation rates vary substantially. (After Riebe *et al.*, 2003.) (a) The fraction of chemically depleted rock is similar from catchment to catchment. (b) The rate of chemical weathering increases systematically with denudation rate. Lines correspond to relationships based on average chemical depletion fractions of 18%. The coupling shown in (b) suggests weathering rates are supply-limited, i.e. dependant upon fresh exposure of mineral surfaces due to physical denudation processes.

1.7 Provenance: siliciclastic sediment-sourcing

In general, provenance means the particular source of something and takes it ultimate meaning from conjunction of the common Latin preposition *pro-*, meaning before and the verb *venire*, to come, i.e. literally, to come before. In sedimentary geology the term denotes the ultimate source of sediment. Thus for the geologist working in the ancient stratigraphic record of uplifted and eroded sedimentary basins (Chapters 22 & 23), siliciclastic sediment may contain the key evidence for

crustal evolution in deep geological time. In this section we briefly consider the evidence for sediment-sourcing from the sediment grains themselves; it is vital to recognize that other attributes of sedimentary deposits are equally important, including palaeoenvironmental and palaeocurrent analysis. Major advances in large-scale provenance studies and crustal evolution have come with the measurement of immobile rare-earth elemental concentrations and isotopic compositions of fine sediment fractions (e.g. Sm–Nd (*samarium–neodymium*); Os (*osmium*). Sm–Nd systems behave conservatively during weathering processes and are now widely used to establish mean age and composition of large catchments and to infer rates of continental growth and changing tectonic regimes. For example, a major reorganization of regional drainages in eastern Tibet and southwestern China took place in the Cenozoic as deformation from the growing Himalayas and Tibetan Plateau affected an increasingly wider area. Geochemical and Nd signatures of sedimentary rocks on the northern margin of the South China Sea reveal a major change during the Oligocene when the centre of rifting transferred south and basins on the north margin of the South China Sea experienced rapid subsidence. Further uplift and erosion then exposed Mesozoic and Cenozoic granites that supplied large amounts of granitic detritus. A mid-Miocene change occurred at ca 13 Ma, resulting in less input from local sources (i.e. the fault blocks formed by Mesozoic–Cenozoic tectonics and magmatism) to an increasing contribution of older continental material, mostly from Indochina to the west (see also section 23.3).

Regarding the rock-specific geology of palaeocatchments we must ask, given the destruction visited upon original source rocks by weathering processes, whether an assemblage of coarser sediment grains can tell us anything at all about catchment lithology? The answer is a surprising but qualified yes, particularly when certain mineral grains, properly chemically analysed, may be directly dated by radiogenic techniques. This is despite post-depositional alteration by subsurface waters during burial and diagenesis. The task becomes more difficult though with each tectonically induced cycle of uplift, weathering, erosion and deposition. First-cycle deposits are those derived directly from igneous or metamorphic rocks and are clearly easiest to assess in terms of their provenance. To mix many metaphors, sedimentary geologists can see ancient worlds in their grains of sand, but more darkly further
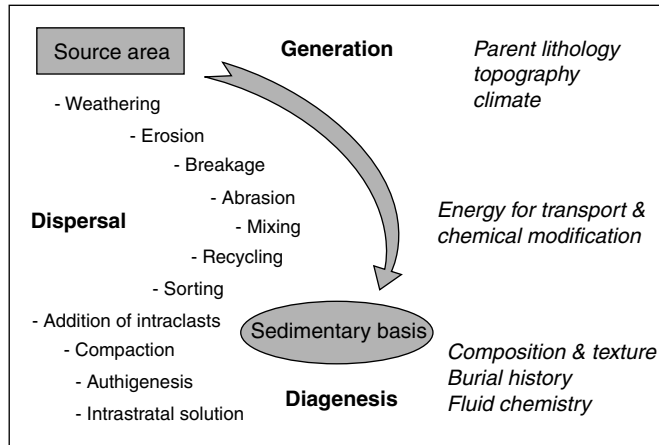
Fig. 1.19 To illustrate the main pathways in sediment grain evolution (bold) and the principal processes whereby sediment grains might be altered in their journey from sediment source to sediment sink by the main controlling variables (italics). From Weltje & von Eynatten, 2004.)

back in time. A scheme to illustrate the main steps involved in sediment evolution from the point of view of provenance studies is given in Fig. 1.19.

Quartz

This mineral comprises the most abundant sand- and silt-sized grains in clastic sediments due to a combination of original abundance, hardness, lack of cleavage planes and general chemical durability under normal earth-surface pH conditions. Sections of single crystals may show normal or undulose extinction under the crossed polars of a petrological microscope. Undeformed quartz from volcanic rocks shows normal extinction, but plutonic igneous and metamorphic rocks show either normal or undulose extinction, the latter due to lattice strain. It has been found that metamorphic quartz grains show mean extinction values of $>5°$, whereas plutonic grains show $<5°$, although the overall distributions overlap considerably. Quartz grains may also be single crystals or polycrystalline. Almost all quartz of volcanic origins is of single crystal type. The amount of polycrystalline quartz is least in plutonic igneous rocks, increasing in high-grade metamorphic rocks and is highest in low-grade metamorphic rocks. Also, the average number of crystal units in polycrystalline quartz is greatest in low-grade metamorphic rocks and least in high-grade examples.

The origin of angular quartz silt (4–64 μm size) in ancient marine sedimentary mudrocks is more varied than previously thought. Whilst much sediment of this grade has been considered to have originated as wind-blown dust, detailed imaging and stable oxygen isotope measurements indicate much of it is in fact biogenic, originating as precipitates in algal cysts. It therefore records organic productivity (radiolarian, diatoms, etc., see Chapter 2) of oceanic waters rather than sourceland weathering and detrital sedimentation as silt from planetary wind systems.

Feldspar

Feldspar also occurs widely in some sedimentary deposits, though its liability to destruction by acid hydrolysis and then break-up during transport along well-developed cleavage planes eventually eliminates many survivors. They are best and most voluminously preserved as first-cycle deposits derived from igneous or metamorphic rocks under limited chemical weathering in semiarid climates. In decreasing order of abundance they include alkali feldspars rich in potassium (orthoclase, microcline), perthite (intergrowths of K-rich and Na-rich feldspars) and the plagioclase series (albite to anorthite) rich in mixtures of sodium and calcium. This ordering follows the stability order of feldspars to chemical weathering discussed previously. Their tendency to dissolve in the subsurface

makes further preservation less probable; the stability of alkali feldspars in particular depends on their exact crystal microstructure. Microcline and orthoclase are widely distributed in both metamorphic and acidic plutonic igneous rocks. Plagioclase also occurs widely in metamorphic rocks; in igneous rocks it is increasingly calcic with decreasing silica content of the parent rock. Importantly, sanidine, the high-temperature alkali feldspar rich in K may be radiogenically dated (sometimes as single crystals or as tiny aliquots) by the ratio of its K and/or Ar isotopes, the technique being particularly successful in sediments containing sanidine-bearing volcanic ash.

Rock (lithic) fragments

These are some of the most useful grains to come across in a sedimentary deposit since they provide direct samples of catchment bedrock. Many igneous rocks have characteristic tectonic modes of origin along active plate margins; good examples would be subduction-related volcanic-arc lavas like andesites and dacites. Volcanic clasts and ash layers are particularly valuable for both provenance and for age-dating the sedimentary sequences in which they lie. The coarser plutonic igneous and schistose/gneissic metamorphic rocks are usually rarer in anything other than first-cycle deposits, breaking down during chemical weathering into individual minerals or breakdown products and fragmenting during sediment transport. Notable exceptions are in glacial lodgement till and oceanic *dropstone* deposits where, enclosed and plucked by ice from their frigid catchments, they often provide extraordinary evidence for glacier ice-provenance and iceberg dispersal paths (Chapters 15 & 21). Fine-grained sedimentary rock fragments in multicycle deposits are dominated by long-lived chert and quartzite lithologies which have extreme mechanical and chemical durability, properties that also encourage their longevity through many sedimentary cycles of uplift, erosion and renewed sedimentation, thus muddying the waters of their provenance.

Heavy minerals

This large group of non-quartz/feldspar minerals rarely make up more than 1% of a sedimentary deposit. They tend to be concentrated by density during transport and deposition, with the denser forms concen-trated in higher energy deposits called *placers*. For study they are separated out magnetically or by density using various high-density liquids to filter them, though since the advent of high-powered microscopy the separation process by hand-picking has become somewhat less laborious and healthier. Opaque heavy mineral grains are usually most abundant, but generally of little use in provenance. They include the iron oxides *haematite* and *magnetite*, titanium-rich *ilmenite* and tin-rich *cassiterite*. The iron sulphide, *pyrite*, is of particular interest in some Archaean sediments since it has lent support to theories for non-oxygenated weathering environments in deep geological time. Non-opaque forms include the hard and ultraresistant *zircon* (Part 1 Fig. 1), with *muscovite* mica, *rutile*, *garnet*, *monazite*, *rutile*, *tourmaline*, *staurolite*, *kyanite* and *sillimanite* common locally. Muscovite, zircon, tourmaline, monazite and garnet may all be radiogenically dated, often nowadays as single crystals by laser ablation. Extremely rarely and locally, provenance studies are enriched by spectacular occurrences of heavy mineral and metal placer deposits of *diamond* and *gold*.

Phyllosilicates

Amongst these platy minerals, muscovite mica is the most resistant to chemical weathering and is a fine provenance indicator since its high K content means it can be directly dated by Ar-isotope analysis. Clay minerals are generally of little use in provenance studies because of their common origin as weathering products; yet for this reason they are much-loved indicators of palaeoclimate and soil type.

Organic grains

Charcoal (fusinite) fragments may have an absolutely key role in palaeocatchment studies, for they record the occurrence of wildfires and associated sediment flushing. According to some authors it is the only direct evidence in the geological record for assessing whether levels of oxygen in past atmospheres approximated to those of the present day.

Wind-blown dust

In Earth's arid regions and on Mars a major sediment production mechanism is by impact-induced abrasion

during atmospheric transport. Studies have found that natural dust particles on Earth are more likely to be produced by wind abrasion of weathered sands that have acquired a superficial clay coating, instead of grains with clean surfaces. This coating is removed by the abrasion process and the dust produced by this mechanism in experimental runs has a modal size of 2–5 µm and material < 10 µm comprises up to 90% of the particles produced.

Further reading

General

A standard chemistry text, with material relevant to some of the chemical principles used in the study of silicate weathering, is by Atkins (1992). Readers lacking college-level chemistry and wanting texts with real geological and environmental relevance would do well to consult the sadly out-of-print Gill (1989), the commendably succinct Andrews *et al.* (2004b) and Chapter 6 of Albarède (2003). The all-time classic on Eh–pH controls is by Garrels & Christ (1965). Stumm (1992) is the fundamental book on chemical weathering and is made of sterner stuff. Drever (1988) discusses a wide range of natural water geochemistry. The collection of papers on the chemistry of rock weathering edited by White & Brantley (1995a) is invaluable, and a bargain. Selby (1993) is very good on physical weathering from a landscape perspective.

Specific

The Jack Hills' zircon discovery paper is Wilde *et al.* (2001), see also Hopkins *et al.* (2008). Plummer (1977) discusses Florida aquifer soil CO_2. Estimates for dissolved load to the oceans are by Holland (1978) and Wollast & Mackenzie (1983). Factors controlling detrital mineral abundances are discussed by Suttner *et al.* (1981) and Nesbitt & Young (1989).

References for weathering and dissolution of various minerals are: quartz (Dove, 1995; Hochella & Banfield, 1995), feldspar (Velbel, 1993; Blum & Stillings, 1995; Teng *et al.*, 2001; I. Parsons *et al.*, 2005; Hellmann & Tisserand, 2006), micas (Nagy, 1995; Malmström & Banwart, 1997), chain silicates (Brantley & Chen, 1995; Zakaznova-Herzog *et al.*, 2008), olivine (Hochella & Banfield, 1995; Welch &

Banfield, 2002; Zakaznova-Herzog *et al.*, 2008), apatite by Guidry & MacKenzie (2003).

Rates of chemical weathering are in White & Brantley (1995a) and White *et al.* 1999, 2001). For the effects of physical erosion on chemical denudation see Ferrier & Kirchner (2008). There are many experimental studies of chemical weathering rates and mechanisms, notably by Schott & Berner (1985), Furrer & Stumm (1986), Holdren & Speyer (1986), Muir *et al.* (1990), Stumm & Wollast (1990), Casey & Bunker (1991), Dove & Elston (1992) and Shotyk & Metson (1994). Field studies of granitic weathering profiles are by White *et al.* (2001) and of basalt weathering by Stewart *et al.* (2001). Time and space trends in the chemical weathering of glacial outwash sediment are discussed by Anderson *et al.* (2000). The influence of temperature on chemical weathering rates of silicate minerals is discussed by White *et al.* (1999), Dalai *et al.* (2002) and Richards and Kump (2003). Comparative lichen- versus abiotic-weathering studies from Hawaii are in Brady *et al.* (1999), whilst Hinsinger *et al.* (2001) present data on enhanced basalt weathering under higher-plant cover, in the realm of the rhizosphere, a concept due to Darrah (1993).

Weathering rind studies are by Colman & Pierce (1981), Knuepfer (1988), Taylor & Blum (1995), Sak *et al.* (2004). CIA studies are by Nesbitt & Young (1982), McClennan (1993) and Dalai *et al.* (2002). Rates of granitic weathering are by White *et al.* (1999) and basalt weathering by Vitousek *et al.* (1997), Chadwick *et al.* (1999) and Das *et al.* (2005).

Whole catchment studies of chemical fluxes in seasonal rivers draining mixed bedrock types are exemplified by Tipper *et al.* (2006) in the Nepal Himalaya. Problems with modelling chemical weathering processes without a priori knowledge of rock type and mineral precipitation in soil profiles (non-conservative elemental behaviour) are by Goddéris *et al.* (2006) and for the common calcite phases present in many granitoids by White *et al.* (2005). The critical link between rates of chemical weathering and physical erosion is explored by Riebe *et al.* (2003) and the concept of mineral residence time in soil profiles is discussed by Yoo & Mudd (2008). Henderson *et al.* (1994), Foster & Vance (2006), Vance *et al.* (2009) present contradictory views on likely trends in global interglacial/glacial weathering rates. Regolith controls on glaciation and weathering fluxes are by Millot *et al.* (2002) and Roy *et al.* (2004)

Fe–Al-rich palaeosols and their controversial development under changing climatic conditions are discussed by Beavais (1999) and Brown *et al.* (2003), and with the aid of O isotopes by Girard *et al.* (2000). Calcic palaeosols are discussed by Mack *et al.* (1994) and Andrews *et al.* (1998). The contribution of dust to basalt soils is by Kurtz *et al.* (2001).

Interesting experiments on frost weathering are by Lautridou and Seppala (1986). Salt weathering is reviewed by Cooke *et al.* (1993). Molnar *et al.* (2007) discuss active tectonics and fracture formation.

An excellent review of grain provenance is by Weltje & Eynatten (2004), with information on rapid provenancing on the AutoGeoSEM by Paine *et al.* (2005). Ingersoll & Eastmond (2007) give an illuminating case history and a comparison of methodologies. DeCelles *et al.* (1991) is a fine study of progressive source-rock denudation. For K-feldspar stability use in provenance, see Parsons *et al.* (2005). On the algal origin of marine quartz silt see Schieber *et al.* (2000). Nd provenancing is by Yan *et al.* (2007).