Principles and Practice of Soil Science

The Soil as a Natural Resource

Fourth Edition

R O B E R T E . W H I T E

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of Soil Science

Dedication

This book is dedicated to my wife Esme Annette White without whose support and encouragement it would not have been completed.

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Contents

Preface to the Fourth Edition

Dr Samuel Johnson is reputed to have said 'what is written without effort is in general read without pleasure'. This edition of *Principles and Practice of Soil Science* has certainly taken much effort to complete, so I hope it will be enjoyed and provide valuable information to as wide an audience of interested readers as possible. The people I would expect to be interested in learning more about soils are not only soil scientists and others concerned with production systems, but also the various scientists and natural historians who are concerned about Earth's ecology in its broadest sense.

At the time of the third edition (1997) I wrote about the 'new generic concept' of ecologically sustainable development (ESD) that was being promoted by international agencies and appearing with increasing frequency in government policy documents. However, through the 1990s and into the early years of the 21st century, more has been *written* about ESD than has been achieved on the ground in implementation of the policy. I have expanded on the topic of 'sustainability' in Chapter 15, drawing particularly on examples in Australia where a relatively fragile landscape continues to be put under pressure from 'development'. The largest areas affected are rural areas, especially in the better watered coastal zone and the expanding irrigation regions, and areas of urban concentration (mainly along the coasts also). In this context, the quality and quantity of water have become key issues attracting much public and political attention. In recent years in Australia, these twin issues have become enmeshed

with the question of climate change – by how much is it changing and where, and what are the possible positive and negative effects – which is directly linked to the emission of greenhouse gases from natural and human-influenced systems. Underlying these issues is soil behaviour because virtually all the precipitation that falls on land interacts with soil in some way. Hence, knowledge of the spatial distribution of different soil types and the pathways of water, with their associated physical, chemical and biological processes, in these various soil types becomes a very important component of land and water management. We need to be aware that everyone lives in a catchment and that the quality of life in that catchment depends on individual and collective human activities in that catchment. I have expounded on this subject in my 2003 G. W. Leeper Memorial Lecture 'What has soil got to do with water?', which is available on the Australian Society of Soil Science Inc. website (<wwwc>http://www.asssi.asn.au/asssi/flash/). Important tools for use in unravelling the complexity of water, energy and nutrient fluxes in catchments are models of the biophysical processes, incorporating a digital elevation model (DEM) and digital soil map, dynamically coupled with a Geographic Information System (GIS). I refer to these tools in Chapters 14 and 15.

Apart from updating and revising each chapter and adding colour photographs, I have provided sets of illustrative problems and questions at the end of each chapter, based on my experience in teaching undergraduate classes on soil resources

and their management at The University of Melbourne. I have benefited from feedback from students and also from advice given by friends and colleagues, notably Dr Nick Uren and Dr Robert Edis. To all those who contributed I am most grateful, but the ultimate responsibility for any errors and omissions rests with me. I am also grateful to Debbie Seymour, Rosie Hayden and Hannah Berry at Blackwell Publishing who have been very tolerant and supportive while I was preparing this edition.

Robert E. White
Melbourne
13 December 2004

Units of Measurement and Abbreviations used in this Book

SI units

Basic unit	Abbreviation
metre	m
hectare	ha
gram	g
mole	mol
second	s
temperature	K
ampere	A
becquerel	Bq

Derived units

Unit	Abbreviation	Value
Celsius	°C	K-273
newton	N	kg.m/s
joule	J	N.m
pascal	P	N/m^2
volt	V	J/A/s
siemen	S	A/V
coulomb	C	A.s
litre	L	$m^3/1000$
tonne	t	kg.1000
bar	bar	$Pa.10^5$
Faraday's constant	F	96500 J/mol/V
Universal gas constant	R	8.3143 J/K/mol

Non-SI units used in soil science

Physical term	Unit	Abbreviation	Value
length	Angstrom	Å	10^{-10} m
concentration	moles/litre	M	mol/L
cation exchange capacity	meq/100 g	CEC	cmol charge (+)/kg
electrical conductivity	millimho/ cm	EC	dS/m

Prefixes and suffixes to units

Prefix/suffix	Abbreviation	Value
tera-	T	10^{12}
giga-	G	10^9
mega-	M	10^6
kilo-	k	10^3
deca-	da	10^1
deci-	d	10^{-1}
centi-	c	10^{-2}
milli-	m	10^{-3}
micro-	μ	10^{-6}
nano-	n	10^{-9}
pico-	p	10^{-12}

Miscellaneous symbols

( )	denotes 'activity'
[ ]	denotes 'concentration'
$\cong$	approximately equal to
~	of the order of
<	less than
>	greater than
$\leq$	less than or equal to
$\geq$	greater than or equal to
log	$\log_{10}$
ln	$\log_e$
exp	exponential of

Abbreviations

ACIAR	Australian Centre for International Agricultural Research
ACLEP	Australian Collaborative Land Evaluation Program
ADAS	Agricultural Development and Advisory Service
AEC	anion exchange capacity
AM	arbuscular mycorrhizas
AMO	ammonia mono-oxygenase
ANZECC	Australian and New Zealand Environment and Conservation Council
AR	activity ratio
ASC	Australian Soil Classification
ASRIS	Australian Soil Resources Information System
ASSSI	Australian Society of Soil Science Inc.
ATC	4-amino-1,2,4-triazole
ATP	adenosine triphosphate
AWC	available water capacity
BET	Brunauer, Emmet and Teller
BIO	microbial biomass
BMP	best management practice
BP	before present
CEC	cation exchange capacity
CFCs	chlorofluorocarbons
CPMAS	cross-polarization, magic angle spinning
CREAMS	Chemicals, Runoff and Erosion from Agricultural Management Systems
CRF	controlled-release fertilizer

CSIRO	Commonwealth Scientific and Industrial Research Organization
DAP	diammonium phosphate
DCD	dicyandiamide
DCP	dicalcium phosphate
DCPD	dicalcium phosphate dihydrate
DDL	diffuse double layer
DDT	dichlorodiphenyltrichloroethane
DEM	digital elevation model
DL	diffuse layer
DM	dry matter
DNA	desoxyribose nucleic acid
DOC	dissolved organic carbon
DPM	decomposable plant material
DTPA	diethylene triamine pentaacetic acid
E	evaporation
EC	electrical conductivity
ECEC	effective cation exchange capacity
EDDHA	ethylenediamine di (O-hydroxyphenylacetic acid)
EDTA	ethylenediamine tetraacetic acid
EMR	electromagnetic radiation
ENV	effective neutralizing value
EOC	extracted organic C
ESD	ecologically sustainable development
ESP	exchangeable sodium percentage
E_t	evapotranspiration
EU	European Union
FA	fulvic acid
FAO	Food and Agriculture Organization
FC	field capacity
FESLM	Framework for Sustainable Land Management
FTIR	Fourier Transform Infrared
FYM	farmyard manure
GIS	Geographic Information System
GLC	gas-liquid chromatography
GPS	Global Positioning System
GR	gypsum required
HA	humic acid
HAp	hydroxyapatite
HARM	hull acid rain model
HUM	humified organic matter
HYV	high-yielding variety
IBDU	isobutylidene urea
IOM	inert organic matter
IPCC	Intergovernmental Panel on Climate Change
IPM	integrated pest management
IR	infiltration rate

IS	inner sphere	Q/I	quantity/intensity
IUSS	International Union of Soil Sciences	RAW	readily available water
KE	kinetic energy	RH	relative humidity
LAI	leaf area index	RNA	ribose nucleic acid
LF	leaching fraction	RPM	resistant plant material
LR	leaching requirement	RPR	reactive phosphate rock
LRA	land resource assessment	RUSLE	Revised Universal Soil Loss Equation
LSI	Langelier saturation index	RWEQ	Revised Wind Erosion Equation
MAFF	Ministry of Agriculture, Fisheries and Food	SAR	sodium adsorption ratio
MAH	monocyclic aromatic hydrocarbons	SCU	sulphur-coated urea
MAP	monoammonium phosphate	SGS	Sustainable Grazing Systems
MCP	monocalcium phosphate	SI	Système International
MDB	Murray-Darling Basin	SIR	substrate-induced respiration
meq	milli-equivalent	SLM	sustainable land management
MPN	most probable number	SOM	soil organic matter
MWD	maximum potential soil water deficit	SOTER	World Soils and Terrain Database
		sp, spp.	species, singular and plural
NASIS	National Soil Information System	SRF	slow-release fertilizer
NCPISA	National Collaborative Project on Indicators for Sustainable Agriculture	SSP	single superphosphate
		ST	Soil Taxonomy
		SUNDIAL	Simulation of Nitrogen Dynamics in Arable Land
NDS	non-linear dynamic systems		
NHMRC	National Health and Medical Research Council	SWD	soil water deficit
		TCP	tricalcium phosphate
NMR	nuclear magnetic resonance	TDR	time domain reflectometer/reflectometry
NRCS	Natural Resources Conservation Service		
		TDS	total dissolved salts
NSESD	National Strategy for Ecologically Sustainable Development	TEC	threshold electrolyte concentration
		TSP	triple superphosphate
NV	neutralizing value	UF	urea formaldehyde
OCP	octacalcium phosphate	UN	United Nations
o.d.	oven-dry	UNEP	United Nations Environment Program
OS	outer sphere		
p, pp.	page, singular and plural	USDA	United States Department of Agriculture
P	precipitation		
PAH	polycyclic aromatic hydrocarbons	USLE	Universal Soil Loss Equation
PAM	polyacrylamide	VD	vapour density
PAPR	partially acidulated phosphate rock	VP	vapour pressure
PAW	plant available water	WCED	World Commission on Environment and Development
PBC	phosphate buffering capacity		
PEG	polyethyleneglycol	WEPP	Water Erosion Prediction Project
POM	particulate organic matter	WEPS	Wind Erosion Prediction System
PR	phosphate rock	WEQ	Wind Erosion Equation
PSCU	polymer-coated sulphur-coated urea	WHO	World Health Organization
PVA	polyvinyl alcohol	WRB	World Reference Base for Soil Resources
PVAc	polyvinylacetate		
PVC	polyvinyl chloride	VFA	volatile fatty acid
PWP	permanent wilting point	XRD	X-ray diffraction
PZC	point of zero charge		

Part I

The Soil Habitat

'Soils are the surface mineral and organic formations, always more or less coloured by humus, which constantly manifest themselves as a result of the combined activity of the following agencies; living and dead organisms (plants and animals) parent material, climate and relief.'

V. V. Dokuchaev (1879), quoted by J. S. Joffe in *Pedology*

'The soil is teeming with life. It is a world of darkness, of caverns, tunnels and crevices, inhabited by a bizarre assortment of living creatures . . .'

J. A. Wallwork (1975) in *The Distribution and Diversity of Soil Fauna*
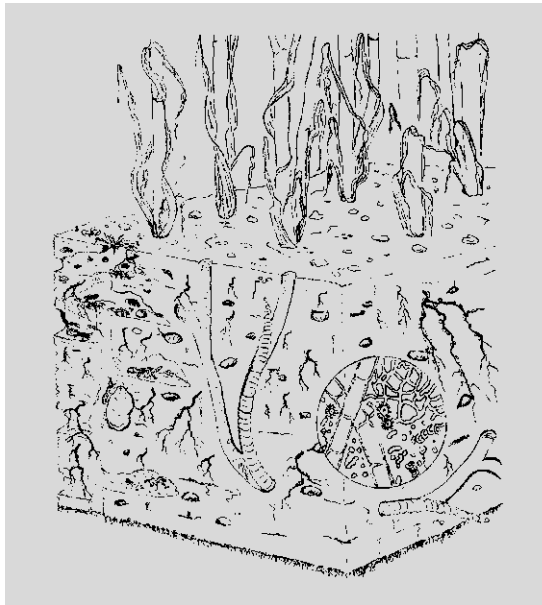
Redrawn from Reganold J. P., Papendick R. I. & Parr J. F. (1990) Sustainable agriculture. *Scientific American* **262**(6), 112–20.

Chapter 1

Introduction to the Soil

1.1 Soil in the making

With the exposure of rock to a new environment – following an outflow of lava, an uplift of sediments, recession of a water body, or the retreat of a glacier – a soil begins to form. Decomposition proceeds inexorably towards decreased free energy and increased entropy. The free energy of a closed system, such as a rock fragment, is that portion of its total energy that is available for work, other than work done in expanding its volume. Part of the energy released in a spontaneous reaction, such as rock weathering, appears as entropic energy, and the degree of disorder created in the system is measured by its entropy. For example, as the rock weathers, minerals of all kinds are converted into simpler molecules and ions, some of which are leached out by water or escape as gases.

Weathering is hastened by the appearance of primitive plants on rock surfaces. These plants – lichens, mosses and liverworts – can store radiant energy from the sun as chemical energy in the products of photosynthesis. Lichens, which are symbiotic associations of an alga and fungus, are able to 'fix' atmospheric nitrogen (N_2) and incorporate it into plant protein, and to extract elements from the weathering rock surface. On the death of each generation of these primitive plants, some of the rock elements and a variety of complex organic molecules are returned to the weathering surface where they nourish the succession of organisms gradually colonizing the embryonic soil.

A simple example is that of soil formation under the extensive deciduous forests of the cool humid areas of Europe, Asia and North America, on calcareous deposits exposed by the retreat of the Pleistocene ice cap (Table 1.1). The profile development is summarized in Fig. 1.1. The initial state is little more than a thin layer of weathered material stabilized by primitive plants. Within a century or so, as the organo-mineral material accumulates, more advanced species of sedge and grass appear, which are adapted to the harsh habitat. The developing soil is described as a Lithosol (Entisol or Rudosol*). Pioneering micro-organisms and animals feed on the dead plant remains and gradually increase in abundance and variety. The litter deposited on the surface is mixed into the soil by burrowing animals and insects, where its decomposition is hastened. The eventual appearance of larger plants – shrubs and trees – with their deeper roots, pushes the zone of rock weathering farther below the soil surface. After a few hundred more years, a Brown Forest Soil (Inceptisol or Tenosol) emerges. We shall return to the topic of soil formation, and the wide range of soils that occur in the landscape, in Chapters 5 and 9.

1.2 Concepts of soil

The soil is at the interface between the atmosphere and lithosphere (the mantle of rocks making up the Earth's crust). It also has an interface with bodies of fresh and salt water (collectively called the hydrosphere). The soil sustains the growth of many plants and animals, and so forms part of the biosphere.

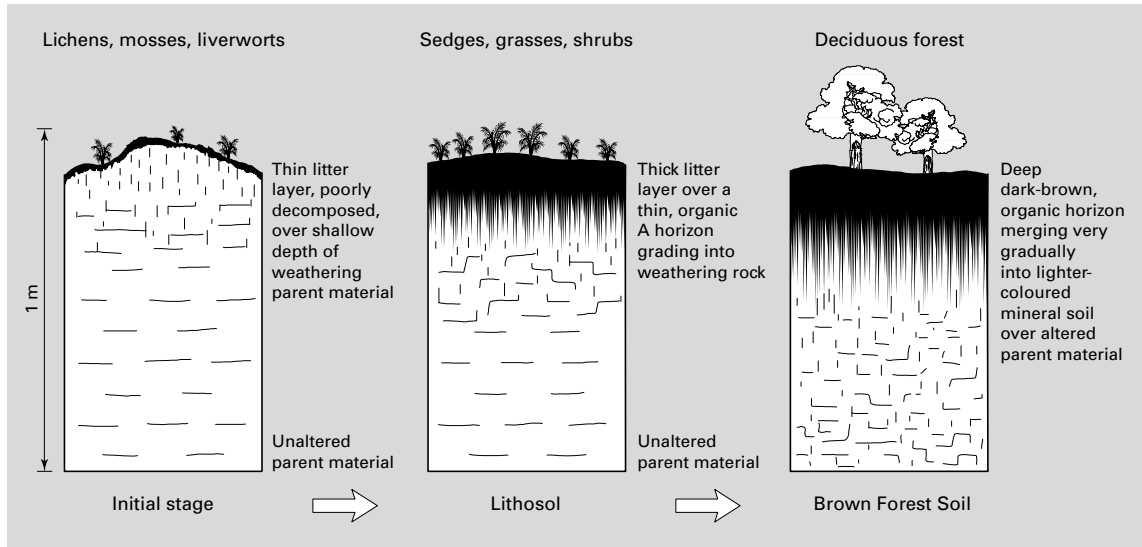* See Box 1.1 for a discussion of soil names.

Fig. 1.1 Stages in soil formation on a calcareous parent material in a humid temperate climate.

Box 1.1 Soil variability, description and classification.

The landscape displays a remarkable range of soil types, resulting from an almost infinite variation in geology, climate, vegetation and other organisms, topography, and the time for which these factors have combined to influence soil formation (human activity is included among the effects of organisms). To bring order to such variety and to disseminate knowledge about soils, soil scientists have developed ways of classifying soils. Individual soils are described in terms of their properties, and possibly their mode of formation, and similar soils are grouped into classes that are given distinctive names. However, unlike the plant and animal kingdoms, there are no soil 'individuals' – the boundaries between different soils in the landscape are not sharp. Partly because of the difficulty in setting class limits, and because of the evolving nature of soil science, no universally accepted system of classifying (and naming) soils exists. For many years, Great Soil Group names based on the United States Department of Agriculture (USDA) Classification of Baldwin *et al.* (1938) (Section 5.3) held sway. But in the last 30 years, new classifications and a plethora of new soil names have evolved (Chapter 14). Some of these classifications (e.g. *Soil Taxonomy*, Soil Survey Staff, 1999) and the *World Reference Base for Soil Resources* (FAO, 1998) purport to be international. Others such as *The Australian Soil Classification* (Isbell, 2002) and the *Soil Classification for England and Wales* (Avery, 1980) are national in focus. This diversity of classifications creates problems for non-specialists in naming soils and understanding the meaning conveyed by a particular soil name. In this book, the more descriptive and (to many) more familiar Great Soil Group names will be used. Where possible, the approximate equivalent at the Order or Suborder level in Soil Taxonomy (ST) and the Australian Soil Classification (ASC) will be given in parentheses.

There is little merit in attempting to give a rigorous definition of soil because of the complexity of its make-up, and of the physical, chemical and biological forces that act on it. Nor is it necessary to do so, for soil means different things to different users. For example, to the geologist and engineer, the soil is little more than finely divided rock material. The hydrologist may see the soil as
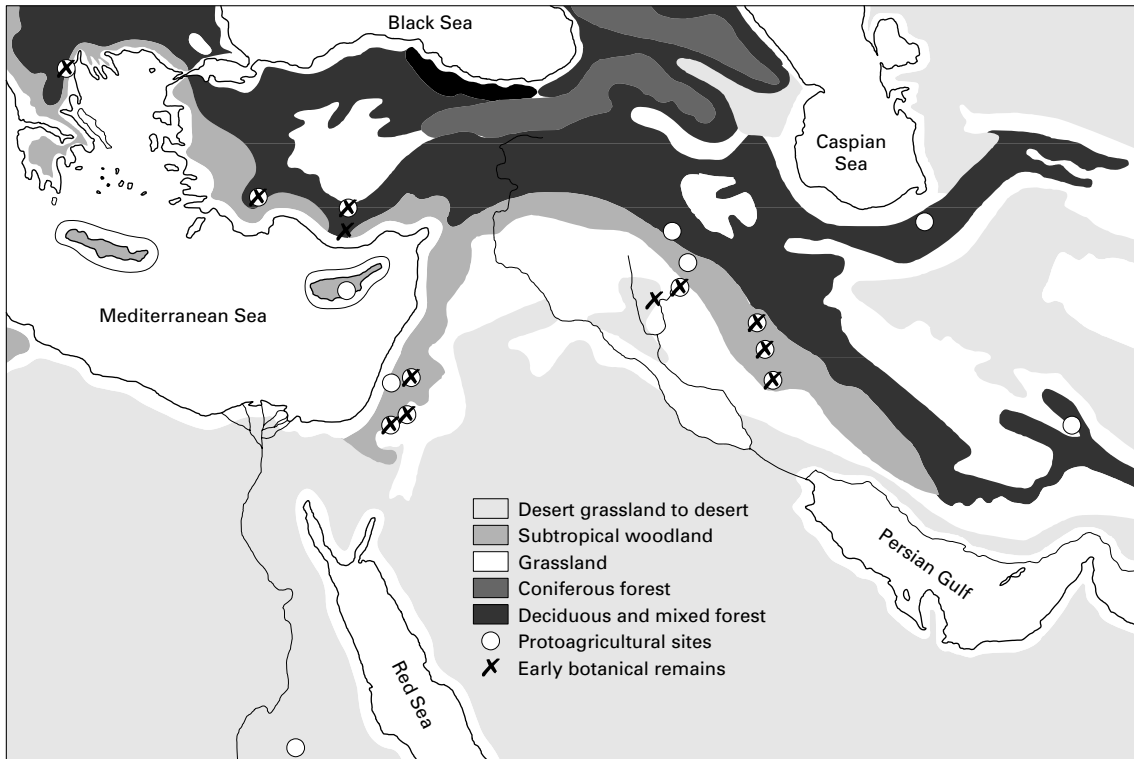
Fig. 1.2 Sites of primitive settlements in the Middle East (after Gates, 1976).

a storage reservoir affecting the water balance of a catchment, while the ecologist may be interested only in those soil properties that influence the growth and distribution of plants and animals. The farmer is naturally concerned about the many ways in which soil influences crop growth and the health of his livestock, although frequently his interest does not extend below the depth of soil disturbed by a plough (15–20 cm).

In view of this wide spectrum of potential user-interest, it is appropriate when introducing the topic of soil to readers, perhaps for the first time, to review briefly the evolution of our relationship with the soil and identify some of the past and present concepts of soil.

Soil as a medium for plant growth

Human's use of soil for food production began two or three thousand years after the close of the last Pleistocene ice age, which occurred about 11,000 years BP (before present). Neolithic people and their primitive agriculture spread outwards from settlements in the fertile crescent embracing the ancient lands of Mesopotamia, Canaan and southern Turkey (Fig. 1.2) and reached as far as China and the Americas within a few thousand years. In China, for example, the earliest records of soil survey (4000 years BP) show how soil fertility was used as a basis for levying taxes on landholders. To study the soil was a practical exercise of everyday life, and the knowledge of soil husbandry that had been acquired by Roman times was passed on by peasants and landlords, with little innovation, until the early 18th century.

From that time onwards, however, the rise in demand for agricultural products in Europe was dramatic. Conditions of comparative peace, and rising living standards as a result of the Industrial Revolution, further stimulated this demand throughout the 19th century. The period was also one of great discoveries in physics and chemistry,

Fig. 1.3 Soil development in relation to the landscape and underlying regolith.

the implications of which sometimes burst with shattering effect on the conservative world of agriculture. In 1840, von Liebig established that plants absorbed nutrients as inorganic compounds from 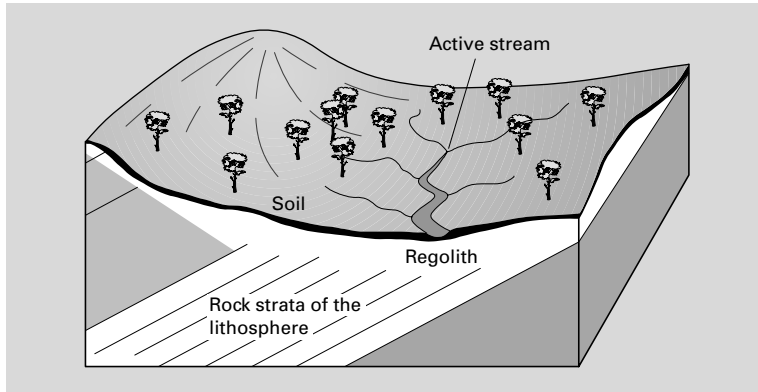the soil, although he insisted that plants obtained their nitrogen (N) from the atmosphere: Lawes and Gilbert at Rothamsted subsequently demonstrated that plants (except legumes) absorbed inorganic N from the soil. In the 1850s, Way discovered the process of cation exchange in soil. During the years from 1860 to 1890, eminent bacteriologists including Pasteur, Warington and Winogradsky elucidated the role of microorganisms in the decomposition of plant residues and the conversion of ammonia to nitrate.

Over the same period, botanists such as von Sachs and Knop, by careful experiments in water culture and analysis of plant ash, identified the major elements that were essential for healthy plant growth. Agricultural chemists drew up balance sheets of the quantities of these elements taken up by crops and, by inference, the quantities that should be returned to the soil in fertilizers or animal manure to sustain growth. This approach, whereby the soil was regarded as a relatively inert medium providing water, mineral* ions and physical support for plants, has been called the 'nutrient bin' concept.

* The term 'mineral' is used in two contexts: first, as an adjective referring to the inorganic constituents of the soil (ions, salts and particulate matter); second, as a noun referring to specific inorganic compounds found in rocks and soil, such as quartz and feldspars (Chapter 2).

Soil and the influence of geology

The pioneering chemists who investigated a soil's ability to supply nutrients to plants tended to see the soil as a chemical and biochemical reaction medium. They little appreciated soil as part of the landscape, moulded by natural forces acting on the land surface. In the late 19th century, great contributions were made to our knowledge of soil by geologists who defined the mantle of loose, weathered material on the Earth's surface as the regolith, of which only the upper 50–150 cm, superficially enriched with organic matter, could be called soil (Fig. 1.3). Below the soil was the subsoil that was largely devoid of organic matter. However, the mineral matter of both soil and subsoil was recognized as being derived from the weathering of underlying rocks, which led to an interest in the influence of rock type on the soils formed. As the science of geology developed, the history of the Earth's rocks was subdivided into a time scale consisting of eras, periods and epochs, going back some 550 million years BP. Periods within the eras are usually associated with prominent sequences of sedimentary rocks that were deposited in the region now known as Europe. But examples of these rocks are found elsewhere, so the European time divisions have gradually been accepted worldwide (although the European divisions are not necessarily as clear-cut in all cases outside Europe). Studies of the relationship between soil and the underlying geology led to the practice of classifying soils loosely in geological terms, such as granitic (from granite), marly (derived from a mixture of limestone and clay),

Table 1.1 The geological time scale.

Era	Period	Epoch	Start time (million years BP)
Cainozoic	Quaternary	Recent	0.011
		Pleistocene	2
	Tertiary	Pliocene	5
		Miocene	23
		Oligocene	36
		Eocene	53
		Palaeocene	65
Mesozoic		Cretaceous	145
		Jurassic	205
		Triassic	250
Palaeozoic		Permian	290
		Carboniferous	360
		Devonian	405
		Silurian	436
		Ordovician	510
		Cambrian	550
Pre-Cambrian			4600

loessial (derived from wind-blown silt-size particles), glacial (from glacial deposits) and alluvial (from river deposits).

A simplified version of the geological time scale from the pre-Cambrian period to the present is shown in Table 1.1.

The influence of Russian soil science

Russia is a vast country covering many climatic zones in which, at the end of the 19th century, crop production was limited not so much by soil fertility, but by primitive methods of agriculture. Early Russian soil science was therefore concerned not with soil fertility, but with observing soils in the field and studying relationships between soil properties and the environment in which the soil had formed. From 1870 onwards, Dokuchaev and his school emphasized the distinctive features of a soil that developed gradually and distinguished it from the undifferentiated weathering rock or parent material below. This was the beginning of the science of pedology*.

* From the Greek word for ground or earth.

Following the Russian lead, scientists in other countries began to appreciate that factors such as climate, parent material, vegetation, topography and time interacted in many ways to produce an almost infinite variety of soil types. For any particular combination of these soil-forming factors (Chapter 5), a unique physicochemical and biological environment was established that led to the development of a distinctive soil body – the process of pedogenesis. A set of new terms was developed to describe soil features, such as:

• Soil profile – constituting a vertical face exposed by excavating the soil from the surface to the parent material;
• soil horizons – layers in the profile distinguished by their colour, hardness, texture, the occurrence of included structures, and other visible or tangible properties. The upper layer, from which materials are generally washed downwards, is described as eluvial; lower layers in which these materials accumulate are called illuvial.

In 1932, an international meeting of soil scientists adopted the notation of A and B for the eluvial and illuvial horizons, respectively, and C horizon for the parent material. The A and B horizons comprise the solum. Unweathered rock below the parent material is called bedrock R. Organic litter on the surface, not incorporated in the soil, is designated as an L layer. A typical Alfisol (ST) or Chromosol (ASC) soil profile showing a well-developed A, B and C horizon is shown in Fig. 1.4.

Soil genesis is now known to be much more complex than this early work suggested. For example, many soils are polygenetic in origin; that is, they have undergone successive phases of development due to changes in climate and other environmental factors over time. In other cases, two or more layers of different parent material are found in one soil profile. Nevertheless, the Russian approach was a considerable advance on traditional thinking, and recognition of the relationship between a soil and its environment encouraged soil scientists to survey and map the distribution of soils. The wide range of soil morphology that was revealed in turn stimulated studies of pedogenesis, an understanding of which, it was believed, would enable the copious field data on soils to be collated more systematically. Thus, Russian soil science provided the inspiration for many of the early soil classifications.
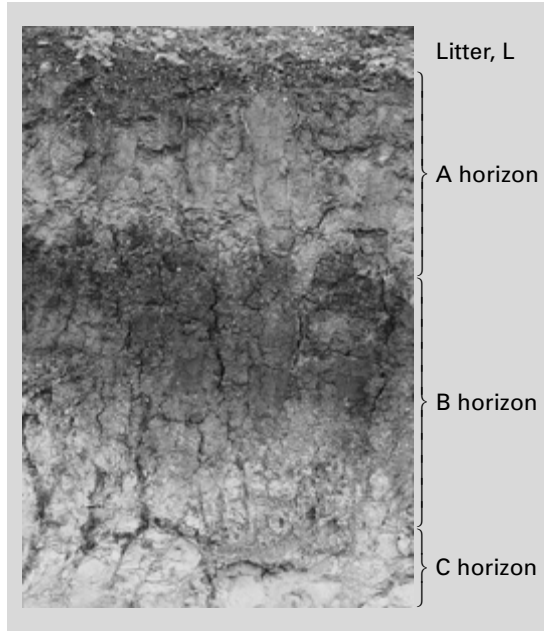
Fig. 1.4 Profile of an Alfisol (ST) or Chromosol (ASC) showing well-developed A, B and C horizons (see Plate 1.4).

A contemporary view of soil

Between the two World Wars of the 20th century, the philosophy of the soil as a 'nutrient bin' was prevalent, particularly in the western world. More and more land was brought into cultivation, much of which was marginal for crop production because of limitations of climate, soil and topography. With the balance between crop success and failure made even more precarious than in favourable areas, the age-old problems of wind and water erosion, encroachment by weeds, and the accumulation of salts in irrigated lands became more serious. Since 1945, demand for food, fibre and forest products from an escalating world population (now > 6 billion) has led to increased use of fertilizers to improve yields, and pesticides to control pests and diseases (Chapter 12). Such practices have resulted in some accumulation of undesirable pesticide residues in soil, and in increased losses of soluble constituents such as nitrate and phosphates to surface waters and groundwater. There has also been widespread dispersal of the very stable pesticides (e.g. organo-chlorines) in the biosphere, and their accumulation to concentrations potentially toxic to some species of birds and fish.

Box 1.2 Soil as a natural body.

A soil is clearly distinguished from inert rock material by:
• The presence of plant and animal life;
• a structural organization that reflects the action of pedogenic processes;
• a capacity to respond to environmental change that might alter the balance between gains and losses in the profile, and predetermine the formation of a different soil in equilibrium with a new set of environmental conditions.
The last point indicates that soil has no fixed inheritance, because it depends on the conditions prevailing during its formation. Nor is it possible to unambiguously define the boundaries of the soil body. The soil atmosphere is continuous with air above the ground, many soil organisms live as well on the surface as within the soil, the litter layer usually merges gradually with decomposed organic matter in the soil, and likewise the boundary between soil and parent material is difficult to demarcate. We therefore speak of the soil as *a three-dimensional body that is continuously variable in time and space.*

More recently, however, scientists, producers and planners have acknowledged the need to compromise between maximizing crop production and conserving a valuable natural resource. Emphasis is now placed on maintaining the soil's natural condition by minimizing the disturbance when crops are grown, matching fertilizer additions more closely to crop demand in order to reduce losses, using legumes to fix N_2 from the air, and returning plant residues and waste materials to the soil to supply some of a crop's nutrient requirements. In short, more emphasis is being placed on the soil as a natural body (Box 1.2) and on the concept of sustainable land management (Chapter 15).

1.3 Components of the soil

We have seen that a combination of physical, chemical and biotic forces acts on organic materials and weathered rock to produce a soil with a porous fabric that retains water and gases. The mineral matter derived from weathered rock
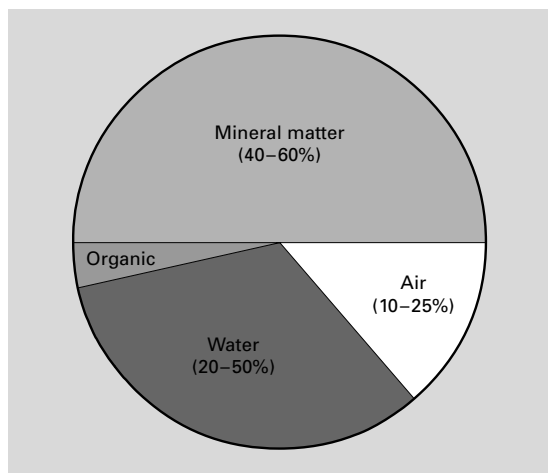
Fig. 1.5 Proportions of the main soil components by volume.

consists of particles of different size, ranging from clay (the smallest), to silt, sand, gravel, stones, and in some cases boulders (Section 2.1). The particle density ρ_p (rho p) varies according to the mineralogy (Section 2.3), but the average ρ_p is 2.65 Mg/m^3. Organic matter has a lower density of 1–1.3 Mg/m^3, depending on the extent of its decomposition. Water has a density of 1.0 Mg/m^3 at normal temperatures (c. 20°C)*.

Soil water contains dissolved organic and inorganic solutes and is called the soil solution. While the soil air consists primarily of N_2 and oxygen (O_2), it usually contains higher concentrations of carbon dioxide (CO_2) than the atmosphere, and traces of other gases that are by-products of microbial metabolism. The relative proportions of the four major components – *mineral matter, organic matter, water and air* – may vary widely, but generally lie within the ranges indicated in Fig. 1.5. These components are discussed in more detail in the subsequent chapters of Part 1.

1.4 Summary

Soil forms at the interface between the atmosphere and the weathering products of the regolith. Physical and chemical weathering, erosion and redeposition, combined with the activities of

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* The density of water is 1.000 Mg/m^3 at 4°C and 0.998 Mg/m^3 at 20°C, which is rounded to 1.0.

a succession of colonizing plants and animals, moulds a distinctive soil body from the milieu of rock minerals in the parent material. The process of soil formation, called pedogenesis, culminates in a remarkably variable differentiation of soil material into a series of horizons that constitute a soil profile. Soil horizons are distinguished by their visible and tangible properties such as colour, hardness, texture and structural organization. The intimate mixing of mineral and organic matter to form a porous fabric, permeated by water and air, creates a favourable habitat for a variety of plant and animal life. Soil is a fragile component of the environment. Its use for food and fibre production, and waste disposal, must be managed in a way that minimizes the off-site effects of these activities and preserves the soil for future generations. This is the basis of sustainable soil management.

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Example questions and problems

1 The upper-most horizon of a soil is generally enriched with organic matter, in varying states of decomposition. Where does most of this organic matter come from?

2 (a) Give the notation for the main horizons recognized in a soil profile.
   (b) What do the terms 'eluvial' and 'illuvial' mean in the context of soil profile description?

3 What are the main external factors that cause soil variation in the landscape?

4 Soil samples were taken from the 0–10 cm depth along two transects at right angles in a pasture grazed by cattle. The samples were spaced at 5 m intervals and analysed for organic carbon (C) content. The results, in percent organic C, were as follows.

Transect 1	2.5	1.6	1.1	1.7	1.5	2.1	2.7	2.2	3.0	1.3
Transect 2	1.6	1.9	1.5	2.9	2.5	2.2	1.5	1.0	1.4	2.7

   (a) Calculate the mean organic C content for each transect, and the coefficient of variation (CV) for each set of values

$$\left(CV = \frac{\text{standard deviation}}{\text{mean}} \times 100 \right).$$

   (b) Can you suggest a reason for the spatial variation in organic C content?

5 Suppose that the volume fraction of mineral matter in a field soil is 0.5, and the organic matter fraction is 0.025.
   (a) Calculate the remaining volume fraction and say what this volume fraction is called.
   (b) (i) Calculate the weight in tonnes (t) of 1 cubic metre (1 m^3) of completely dry soil, given that the particle densities (ρ_p) of the mineral and organic fractions are 2.65 and 1.2 Mg/m^3, respectively, and (ii) calculate the weight of 5 cm^3 of dry soil (roughly 1 teaspoon).
   (c) If the depth of ploughing in this soil is 15 cm, what is the weight of dry soil (Mg) per hectare to 15 cm depth?
   (d) Suppose the 50% mineral matter (by volume) of a field soil included 10% iron oxide ($\rho_p = 5.55$ Mg/m^3) and organic matter was negligible. (i) What would be the weight of 1 m^3 of soil, and (ii) the weight of 1 ha of dry soil to 15 cm depth?

Chapter 2

The Mineral Component of the Soil

2.1 The size range

Rock fragments and mineral particles in soil vary enormously in size from boulders and stones down to sand grains and very small particles that are beyond the resolving power of an optical microscope (< 0.2 μm in diameter). Particles smaller than *c*. 1 μm are classed as colloidal. Particles that do not settle quickly when mixed with water are said to form a colloidal solution or sol; if they settle within a few hours they form a suspension. Colloidal solutions are distinguished from true solutions (dispersions of ions and molecules) by the Tyndall effect. This occurs when the path of a beam of light passing through the solution can be seen from either side at right angles to the beam, indicating a scattering of the light rays.

An arbitrary division is made by size-grading soil into material:
• That passes through a sieve with 2 mm diameter holes – the *fine earth*, and
• that retained on the sieve (> 2 mm) – *the stones or gravel*, but smaller than
• fragments > 600 mm, which are called *boulders*.
The separation by sieving is carried out on air-dry soil that has been gently ground by mortar and pestle, or crushed between wooden rollers, to break up the aggregates. Air-dry soil is soil allowed to dry in air at ambient temperatures (between 20 and 40°C).

Particle-size distribution of the fine earth

The distribution of particle sizes determines the soil texture, which may be assessed subjectively in the field or more rigorously by particle-size analysis in the laboratory.

Size classes

All soils show a continuous range of particle sizes, called a frequency distribution, which is obtained by plotting the number (or mass) of particles of a given size against their actual size. When the number or mass in each size class is summed sequentially we obtain a cumulative distribution of soil particle sizes, some examples of which are given in Fig. 2.1. In practice, it is convenient to
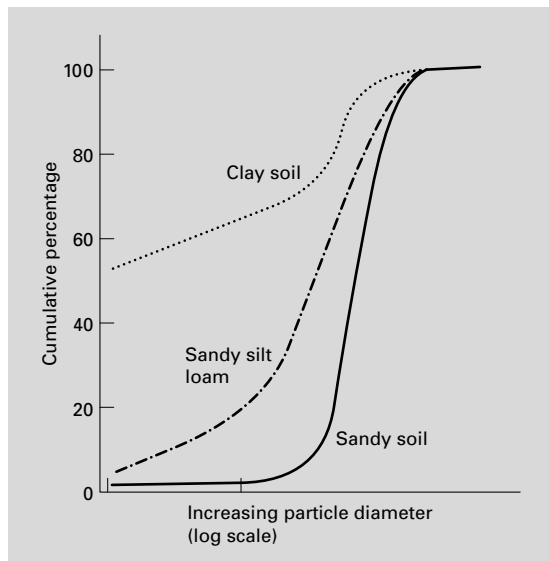

Fig. 2.1 Cumulative frequency distributions of soil particle sizes in a typical clay, sandy silt loam and sandy soil.

subdivide the continuous distribution into several class intervals that define the size limits of the *sand*, *silt* and *clay* fractions. The extent of this subdivision, and the class limits chosen, vary from country to country and even between institutions within countries. The major systems in use are those adopted by the Soil Survey Staff of the USDA, the British Standards Institution and the International Union of Soil Sciences (IUSS). These are illustrated in Fig. 2.2. All three systems set the upper limit for clay at 2 µm diameter, but differ in the upper limit chosen for silt and the way in which the sand fraction is subdivided.

Field texture

A soil surveyor assesses soil texture by moistening a sample with water until it glistens. It is then kneaded between fingers and thumb until the aggregates are broken down and the soil grains thoroughly wetted. The proportions of sand, silt and clay are estimated according to the following qualitative criteria:
• *Coarse sand* grains are large enough to grate against each other and can be detected individually by sight and feel;

• *fine sand* grains are much less obvious, but when they comprise more than about 10% of the sample they can be detected by biting the sample between the teeth;
• *silt* grains cannot be detected by feel, but their presence makes the soil feel smooth and silky and only slightly sticky;
• *clay* is characteristically sticky, although some dry clays, especially of the expanding type (Section 2.3), require much moistening and kneading before they develop their maximum stickiness.
High organic matter contents tend to reduce the stickiness of clay soils and to make sandy soils feel more silty. Finely divided calcium carbonate also gives a silt-like feeling to the soil.

Depending on the estimated proportions of sand, silt and clay, the soil is assigned to a textural class according to a triangular diagram (Fig. 2.3). The triangle in Fig. 2.3a is used by the Soil Survey of England and Wales and is based on the British Standards system of particle-size grading (Fig. 2.2); the one in Fig. 2.3b is used in Australia and is based on the International system (Fig. 2.2). The USDA system is very similar to the British Standards system. Note that in these systems there are 11 textural classes, but the Australian system has
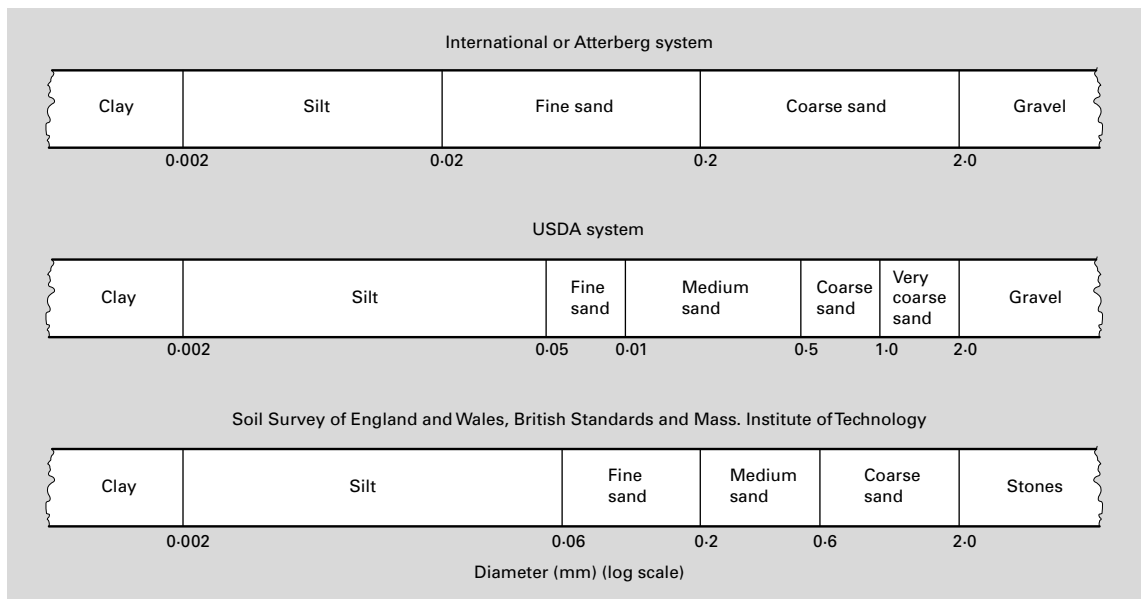

Fig. 2.2 Particle-size classes most widely adopted internationally.
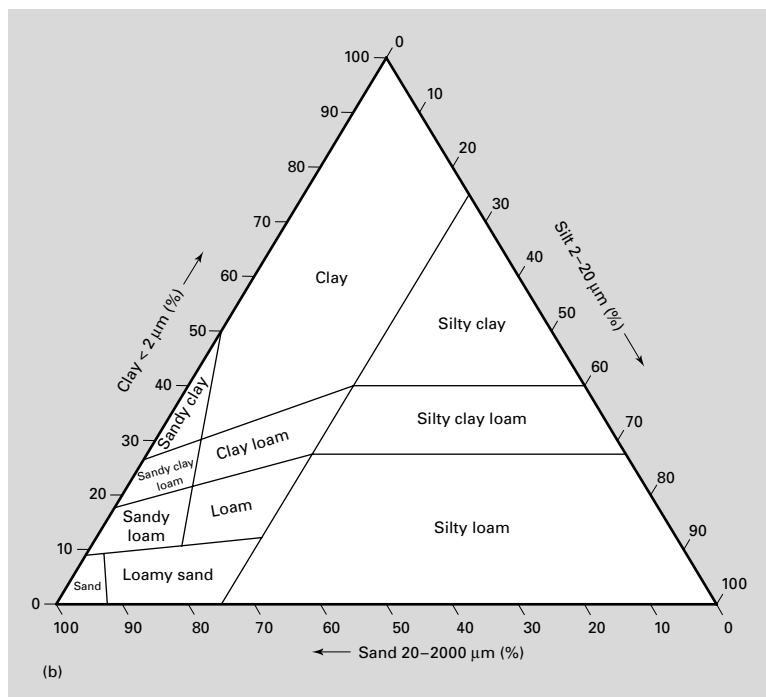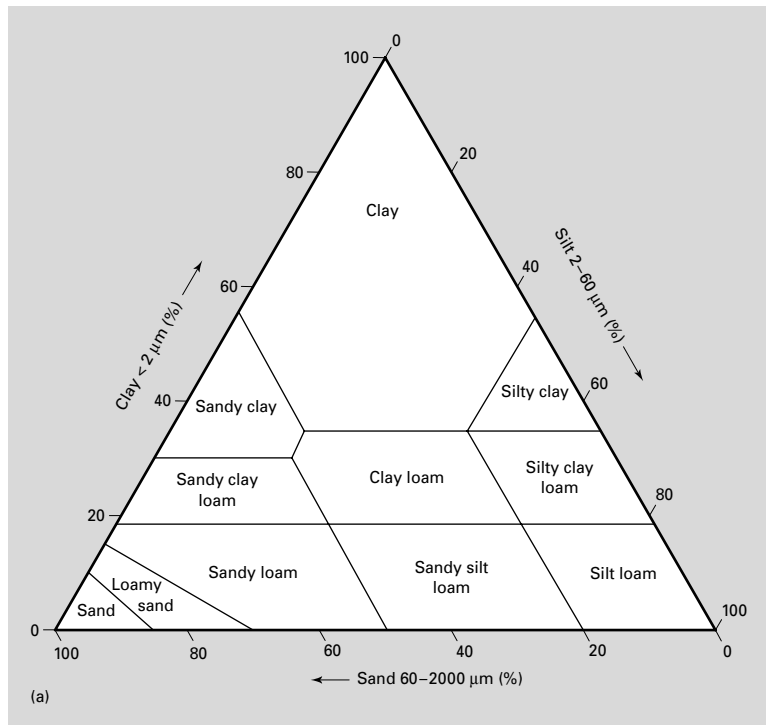
Fig. 2.3 (a) Triangular diagram of soil textural classes adopted in England and Wales (after Hodgson, 1974). (b) Triangular diagram of soil textural classes adopted in Australia (after McDonald *et al.*, 1998).

broader classes for the silty clays, silty clay loams and silty loams than the British or USDA systems.

Soil surveyors become expert at texturing after years of experience, which is gained by their checking field assessments of texture against a laboratory analysis of a soil's particle-size distribution.

Particle-size analysis in the laboratory

The success of the method relies on the complete disruption of soil aggregates and the addition of chemicals that ensure dispersion of the soil colloids in water. Full details of the methods employed are given in standard texts, for example Klute (1986) and Rayment and Higginson (1992). The sand particles are separated by sieving; silt and clay are separated using the differences in their settling velocities in suspension. The principle of the latter technique is outlined in Box 2.1.

The result of particle-size analysis is expressed as the mass of the individual fractions per 100 g of oven-dry (o.d.) soil (fine earth only). Oven-dry soil is soil dried to a constant weight at 105°C. When the coarse and fine sand fractions are combined, the soil may be represented by one point on the triangular diagrams of Fig. 2.3 (a, b). Alternatively, by stepwise addition of particle-size percentages, graphs of cumulative percentage against particle diameter of the kind shown in Fig. 2.1 are obtained.

2.2 The importance of soil texture

Soil scientists are primarily interested in the texture of the fine earth fraction. Nevertheless, in some soils the size and abundance of stones cannot be ignored because they can have a marked influence on the soil's suitability for agriculture. As the stone content increases, a soil holds less water than a stoneless soil of the same fine-earth texture, so that crops become more susceptible to drought. Conversely, such soils may be better drained and therefore warm up more quickly in spring in cool temperate regions. Large stones on the soil surface act as sinks during daytime for heat energy that is slowly released at night – this is of benefit in cool climate vineyards, such as in the Rhône Valley, France, where frost in spring and early summer can damage flowering and fruit

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Box 2.1 Measurement of silt and clay by sedimentation.

A rigid particle falling freely through a liquid of lower density will attain a constant velocity when the force opposing movement is equal and opposite to the force of gravity acting on the particle. The frictional force acting vertically upward on a spherical particle is calculated from Stoke's law. The net gravitational force acting downwards is equal to the weight of the submerged particle. At equilibrium, these expressions can be combined to give an equation for the terminal settling velocity v, as

$$v = \frac{2}{9}\frac{g}{\eta}\left(\rho_p - \rho_w\right)r^2, \qquad (B2.1.1)$$

where g is the acceleration due to gravity, η (eta) is the coefficient of viscosity of the liquid (water),

which varies with temperature, ρ_p is the particle density, ρ_w is the density of water, and r is the particle radius.

When all the constants in this equation are collected into one term A, we derive the simple relationship

$$v = Ar^2 = \frac{h}{t}, \qquad (B2.1.2)$$

where h is the depth, measured from the liquid surface, below which all particles of radius r will have fallen in time t. To illustrate the use of Equation B2.1.2, we can calculate that all particles > 2 µm in diameter settling in a suspension at 20°C will fall below a depth of 10 cm in 7.73 hours. Thus,

Box 2.1 *continued*

by sampling the mass per unit volume of the suspension at this depth after 7.73 hours, the amount of clay can be calculated. The suspension density at a particular depth can be measured in one of several ways:

• By withdrawing a sample volume of the suspension, evaporating to dryness, and weighing the mass of sediment – the pipette method;

• by using a Bouyoucos hydrometer in the suspension; or

• by calculating the loss in weight of a bulb of known volume when immersed in the suspension – the plummet balance method, illustrated in Fig. B2.1.1.

Note that constant temperature should be maintained (because of the temperature effect on the viscosity of water), and also that simplifying assumptions are made in the calculation of settling velocity by Equation B2.1.2. In particular, note that:

• Clay and silt particles are not smooth spheres, but have irregular plate-like shapes;

• the particle density varies with the mineral type (Section 2.3).

In practice, we take an average value for ρ_p of 2.65 Mg/m^3, and speak of the 'equivalent spherical diameter' of the particles being measured.
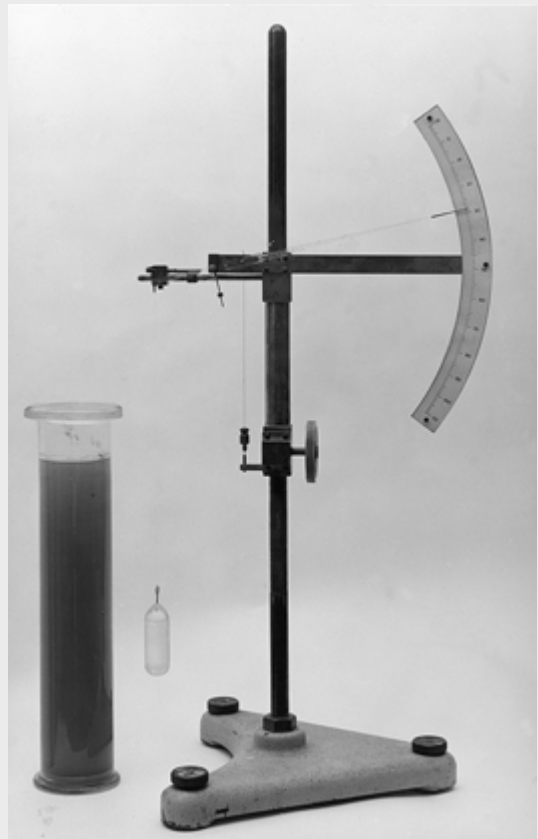

Fig. B2.1.1 A settling soil suspension and plummet balance (courtesy of J. Loveday).

set (Fig. 2.4). Stoniness also determines the ease, and to some extent the cost of cultivation, as well as the abrasive effect of the soil on tillage implements.

Texture is one of the most stable soil properties and is a useful index of several other properties that determine a soil's agricultural potential. Fine and medium-textured soils, such as clays, clay loams, silty clays and silty clay loams, are generally more desirable than coarse-textured soils because of their superior retention of nutrients and water. Conversely, where rapid infiltration and good drainage are required, as for irrigation or liquid waste disposal, sandy or coarse-textured soils are preferred. In farming terms, clay soils are described as 'heavy' and sandy soils as 'light', which does not refer to their mass per unit volume, but to the power required to draw a plough or other implements through the soil. Because it is easy to estimate, and is routinely measured in soil surveys, texture (and more specifically clay content) has been used as a 'surrogate' variable for other soil properties that are less easily measured, such as the cation exchange capacity (Section 2.5).

Texture has a pronounced effect on soil temperature. Clays hold more water than sandy soils, and the presence of water considerably modifies the heat required to change a soil's temperature because:

Fig. 2.4 Boulders and stones covering the soil surface in a vineyard in the central Rhône Valley, France (see also Plate 2.4).

• Its specific heat capacity is 3–4 times that of the soil solids;

• considerable latent heat is either absorbed or evolved during a change in the physical state of water, for example, from ice to liquid or *vice versa*. Thus, the temperature of wet clay soils responds more slowly than that of sandy soils to changes in air temperature in spring and autumn (Section 6.6).

Texture should not be confused with tilth, of which it is said that a good farmer can recognize it with his boot, but no soil scientist can describe it. Tilth refers to the condition of the surface of ploughed soil prepared for seed sowing: how sticky it is when wet and how hard it sets when dry. The action of frost in cold climates breaks down the massive clods left on the surface of a heavy clay soil after autumn ploughing, producing a mellow 'frost tilth' of numerous small granules (Section 4.2).

2.3 Mineralogy of the sand and silt fractions

Simple crystalline structures

Sand and silt consist almost entirely of the resistant residues of primary rock minerals, although small amounts of secondary minerals (salts, oxides and hydroxides) formed by weathering also occur. The primary rock minerals are predominantly silicates, which have a crystalline structure based upon a simple unit – the silicon tetrahedron, SiO_4^{4-} (Fig. 2.5). An electrically neutral crystal is formed when cations, such as Al^{3+}, Fe^{3+}, Fe^{2+}, Ca^{2+}, Mg^{2+}, K^+ and Na^+, become covalently bonded to the O atoms in the tetrahedron and the surplus valencies of the O^{2-} ions in the SiO_4^{4-} group are satisfied. An example of this kind of structure is the primary mineral olivine, which has the composition $(Mg, Fe)_2SiO_4$.

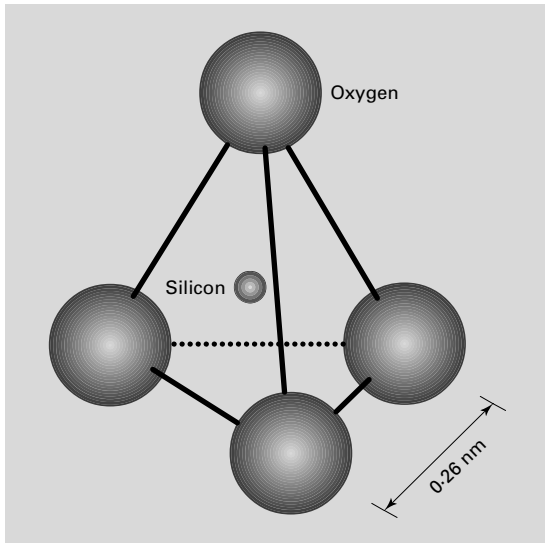**Fig. 2.5** Diagram of a Si tetrahedron (interatomic distances not to scale).

Table 2.1 Cation to oxygen radius ratios and coordination numbers for common elements in the silicate minerals. After Schulze, 1989.

Coordination no. 4		Coordination no. 6		Coordination no. 8 or greater	
Si^{4+}	0.28	Al^{3+}	0.36	Na^+	0.69
Al^{3+}	0.36	Ti^{4+}	0.49	Ca^{2+}	0.71
		Fe^{3+}	0.46	K^+	0.95
		Mg^{2+}	0.47	Ba^{2+}	0.96
		Fe^{2+}	0.53	Rb^+	1.05
		Mn^{2+}	0.57		

Isomorphous substitution

Elements of the same valency and coordination number frequently substitute for one another in a silicate structure – a process called isomorphous substitution. The structure remains electrically neutral. However, when elements of the same coordination number but different valency are exchanged, there is an imbalance of charge. The most common substitutions are Mg^{2+}, Fe^{2+} or Fe^{3+} for Al^{3+} in octahedral coordination, and Al^{3+} for Si^{4+} in tetrahedral coordination. The excess negative charge is neutralized by the incorporation of additional cations, such as unhydrated K^+, Na^+, Mg^{2+} or Ca^{2+} into the crystal structure, or by structural arrangements that allow an internal compensation of charge (see the chlorites).

Coordination number

The packing of the O atoms, which are the largest of the more abundant elements in the silicates, determines the crystalline dimensions. In quartz, for example, O occupies 98.7% and Si only 1.3% of the mineral volume. The size ratio of Si to O is such that four O atoms can be packed around one Si, and larger cations such as iron (Fe) can accommodate more O atoms. The cation to oxygen radius ratio determines the coordination number of the cation (Table 2.1). Many of the common metal cations have radius ratios between 0.41 and 0.73, which means that an octahedral arrangement of six O atoms around the cation (coordination number 6) is possible. Larger alkali and alkaline earth cations, such as K^+ and Ba^{2+}, that have radius ratios > 0.73 form complexes of coordination number 8 or greater. Aluminium, which has a cation to oxygen radius ratio close to the maximum for coordination number 4 and the minimum for coordination number 6 (0.41), can exist in either fourfold (IV) or sixfold (VI) coordination.

More complex crystalline structures

Chain structures

These are represented by the pyroxene and amphibole groups of minerals, which collectively make up the ferromagnesian minerals. In the pyroxenes, each Si tetrahedron is linked to adjacent tetrahedra by the sharing of two out of three basal O atoms to form a single extended chain (Fig. 2.6). In the amphiboles, two parallel pyroxene chains are linked by the sharing of an O atom in every alternate tetrahedron (Fig. 2.7). Cations such as Mg^{2+}, Ca^{2+}, Al^{3+} and Fe^{2+} are ionic-covalently bonded to the O^{2-} ions to neutralize the surplus negative charge.
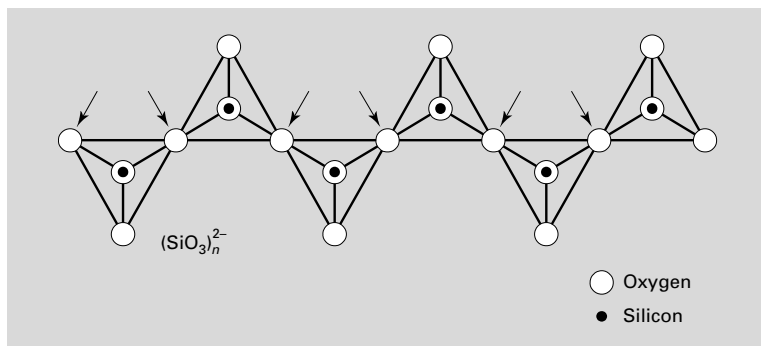
Fig. 2.6 Single chain structure of Si tetrahedra as in a pyroxene. The arrows indicate O atoms shared between adjacent tetrahedra (after Bennett and Hulbert, 1986).
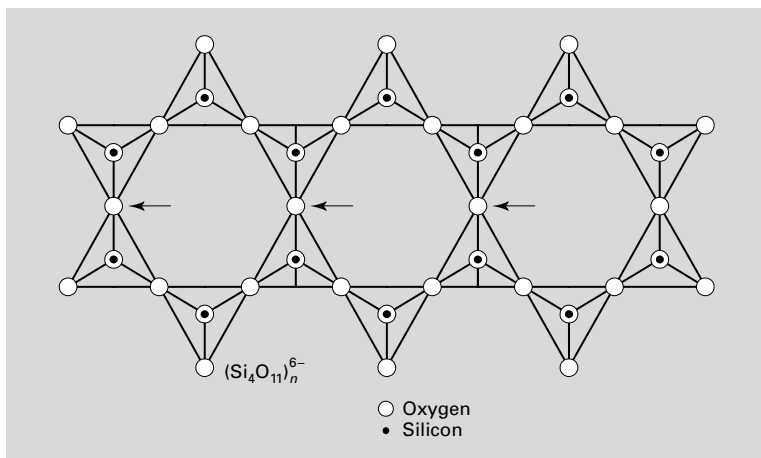

Fig. 2.7 Double chain structure of Si tetrahedra as in an amphibole. The arrows indicate O atoms shared between chains (after Bennett and Hulbert, 1986).

Sheet structures

It is easy to visualize an essentially one-dimensional chain structure being extended in two dimensions to form a sheet of Si tetrahedra linked by the sharing of all the basal O atoms. When viewed from above the sheet, the bases of the linked tetrahedra form a network of hexagonal holes (Fig. 2.8). The apical O atoms (superimposed on the Si atoms in Fig. 2.8) form ionic–covalent bonds with other metal cations by, for example, displacing OH groups from their coordination positions around a trivalent Al^{3+} ion. (Because the unhydrated proton is so small, OH occupies virtually the same space as O.) When Al octahedral units (one is shown diagrammatically in Fig. 2.9) are linked by the sharing of edge OH groups, they form an alumina sheet. Aluminium atoms normally occupy only two-thirds of the available

octahedral positions – this is a dioctahedral structure, characteristic of the mineral gibbsite, $[Al_2OH_6]_n$. If Mg is present instead of Al, however, all the available octahedral positions are filled – this is a trioctahedral structure, characteristic of the mineral brucite $[Mg_3(OH)_6]_n$.

The bonding together of silica and alumina sheets through the apical O atoms of the Si tetrahedra causes the bases of the tetrahedra to twist slightly so that the cavities in the sheet become trigonal rather than hexagonal in shape. When two silica sheets sandwich one alumina sheet, the result is a 2 : 1 layer structure characteristic of the micas, chlorites and many soil clay minerals (Section 2.4). Two-dimensional layer crystal structures such as these are typical of the phyllosilicates, some characteristics of which are given in Box 2.2.

Additional structural complexity is introduced by isomorphous substitution. In the dioctahedral
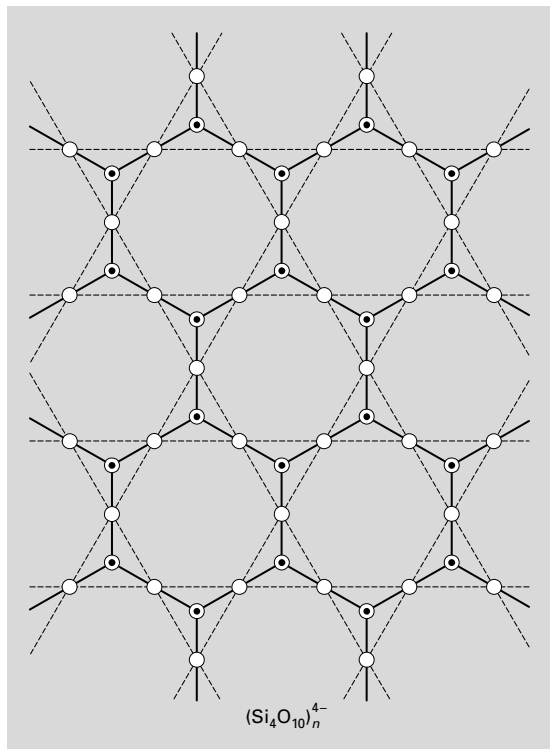
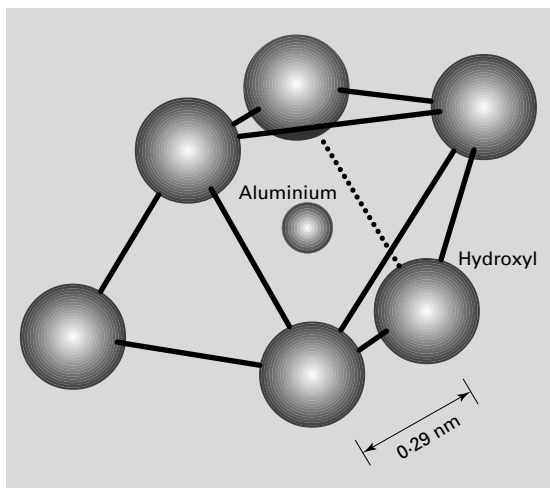**Fig. 2.8** A silica sheet in plan view showing the pattern of hexagonal holes (after Fitzpatrick, 1971).

$(Si_4O_{10})_n^{4-}$

Fig. 2.9 Diagram of an Al octahedron (interatomic distances not to scale).

Box 2.2 Generalized phyllosilicate structures.

Phyllosilicates are silicate minerals composed of two-dimensional tetrahedral or octahedral sheets, or covalently bonded combinations of these, stacked in regular array in the Z direction (Fig. B2.2.1). As shown in this figure, the directions of the crystal axes are X, Y and Z, and the repeat distances for atoms of the same element to occur along these axes are respectively a, b and c. The following terminology is used:

- A single *plane* of atoms (such as linked O or OH);
- a *sheet* is a combination of planes of atoms (such as a silica tetrahedral sheet);
- a *layer* is a combination of sheets (such as two silica sheets combined with one alumina sheet in mica);
- a *crystal* is made up of one or more layers;
- planes of atoms are repeated at regular intervals in multilayer crystals, which gives rise to a characteristic d spacing, or basal spacing, in the phyllosilicates;
- between the layers is interlayer space that may be occupied by water, organic or inorganic ions and molecules, and precipitated hydroxides;
- phyllosilicates generally have large planar surfaces and small edge faces.
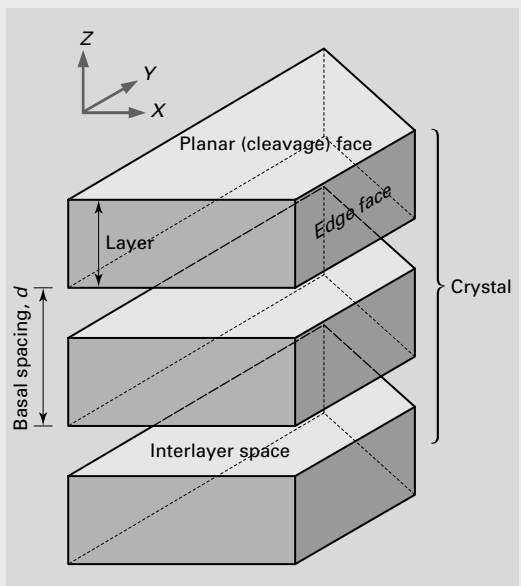

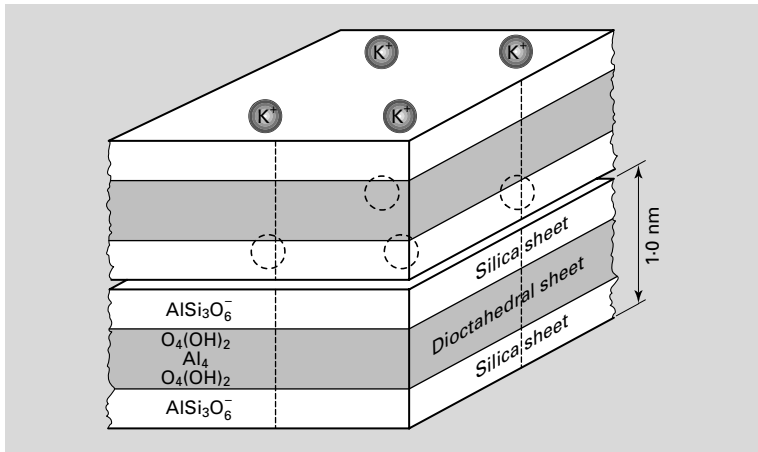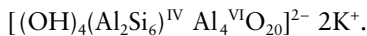**Fig. B2.2.1** General structure of a phyllosilicate crystal.

Fig. 2.10 Structure of muscovite mica − a 2 : 1 non-expanding phyllosilicate mineral.

mica muscovite, for example, one-quarter of the tetrahedral Si^{4+} is replaced by Al^{3+} resulting in a net 2 moles of negative charge per unit cell (Box 2.3). Muscovite has the structural composition:

$$[(OH)_4(Al_2Si_6)^{IV} \, Al_4^{VI}O_{20}]^{2-} \, 2K^+.$$

Note that the negative charge is neutralized by K^+ ions held in the spaces formed by the juxtaposition of the trigonal cavities of adjacent silica sheets (Fig. 2.10). Because the isomorphous substitution in muscovite occurs in the tetrahedral sheet, the negative charge is distributed over only three surface O atoms. The magnitude of the layer charge and its localization are sufficient to cause cations of relatively small ionic potential*, such as K^+, to lose their water of hydration. The unhydrated K^+ ions have a diameter comparable to that of the ditrigonal cavity formed between opposing siloxane surfaces and their presence provides very strong bonding between the layers. Such complexes, where an unhydrated ion forms an ionic-covalent bond with atoms of the crystal surface, are called inner-sphere (IS) complexes.

Biotite is a trioctahedral mica which has Al^{3+} substituted for Si^{4+} in the tetrahedral sheet and contains Fe^{2+} and Mg^{2+} in the octahedral sheet. Again, because of the localization of charge in the tetrahedral sheet, unhydrated K^+ ions are retained in the interlayer spaces to give a unit cell formula of:

* Determined by the charge to radius ratio. As this ratio increases, the ionic potential of the cation increases.

$$[(OH)_4(Al_2Si_6)^{IV} \, (Mg,Fe)_6^{VI}O_{20}]^{2-} \, 2K^+.$$
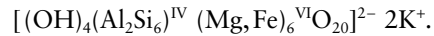
The most complex of the two-dimensional structures belongs to the chlorites, which have a brucite layer sandwiched between two mica layers. In the type mineral chlorite, the negative charge of the two biotite layers is neutralized by a positive charge in the brucite, developed due to the replacement of two-thirds of the Mg^{2+} cations by Al^{3+} (Fig. 2.11). Chlorite is an example of a regular mixed-layer mineral. Predictably, the bonding between layers is strong, but the high content of Mg renders this mineral susceptible to weathering in acidic solutions. For the same reason, and also because of its ferrous (Fe^{2+}) iron content, biotite is much less stable than muscovite. Micas and chlorites weather to form vermiculites and smectites in soil (Section 2.4).

Three-dimensional structures

The most important silicates in this group are silica and the feldspars. Silica minerals consist entirely of polymerized Si tetrahedra of general composition $(SiO_2)_n$. Silica occurs as the residual mineral quartz, which is very inert, and as a secondary mineral precipitated after the hydrolysis of more complex silicates. Secondary silica initially exists as amorphous opal that dehydrates over time to form microcrystalline quartz, known as flint or chert. Silica also occurs as amorphous or microcrystalline silica of biological origin. For
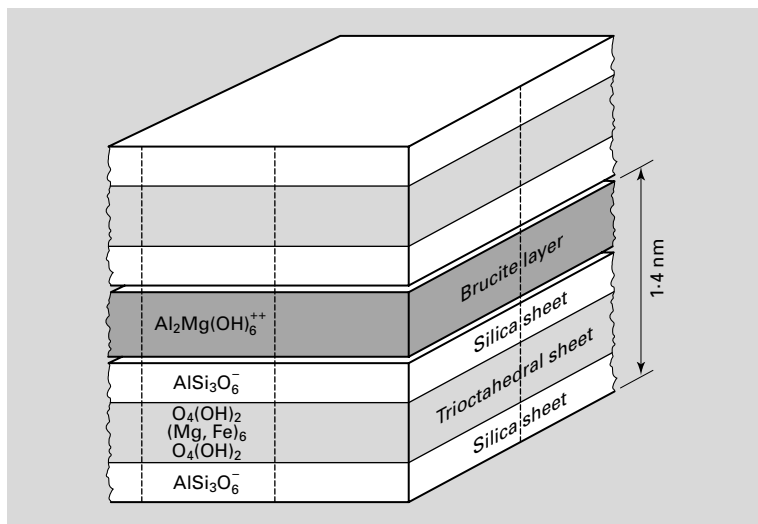
Fig. 2.11 Structure of chlorite – a 2 : 2 or mixed layer mineral.

Box 2.3 Moles of charge and equivalents.

The molar mass of an element is defined as the number of grams weight per mole (abbreviated to mol) of the element. The standard is the stable C-12 isotope of carbon. On this scale, H has a molar mass of 1 g, K a mass of 39 g, and Ca a mass of 40 g. The recommended unit of charged mass for cations, anions and charged surfaces is the mole of charge, which is equal to the molar mass divided by the ionic charge. Thus, the mass in grams of one mole of charge for the elements H, K and Ca is as follows:

- For H^+, $1/1 = 1$;
- for K^+, $39/1 = 39$;
- for Ca^{2+}, $40/2 = 20$.

For clay minerals and soils, the most appropriate unit of measurement is the centimole of charge (+) or (−) per kg (abbreviated to cmol charge/kg). For example, the cation exchange capacity (CEC) is expressed in cmol charge (+)/kg since it is measured by the moles of cation charge adsorbed (Section 2.5). In the older soil science literature, the charge on ions and soil minerals was expressed in terms of an equivalent weight, which is the atomic mass (g) divided by the valency (and identical to a mole of charge). The CEC of a mineral was expressed in milli-equivalents (meq) per 100 g, which is numerically equal to cmol charge/kg.

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example, the diatom, a minute aquatic organism, has a skeleton of almost pure silica. Silica absorbed from the soil by terrestrial plants (grasses and hardwood trees in particular) forms opaline structures called phytoliths, which are returned to the soil when the plant dies.

Quartz or flint fragments of greater than colloidal size are very insoluble, and hence are abundant in the sand and silt fractions of many soils. The feldspars, on the other hand, are chemically more reactive and rarely comprise more than *c*. 10% of the sand fraction of mature soils. Of these, the potassium feldspars are more resistant to weathering than the Ca and Na feldspars. Their structure consists of a three-dimensional framework of polymerized Si tetrahedra in which some Si^{4+} is replaced by Al^{3+}. The cations balancing the excess negative charge are all of high coordination number, such as K^+, Na^+ and Ca^{2+}, and less commonly, Ba^{2+} and Sr^{2+}. The range of composition encountered is shown in Fig. 2.12. Details of the structure, composition and chemical stability of the feldspars are given in specialist texts by Loughnan (1969) and Nahon (1991).
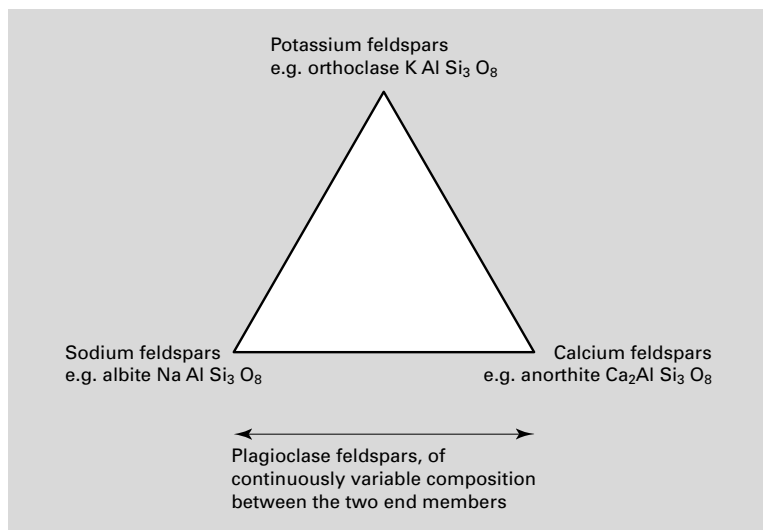
Fig. 2.12 Type minerals of the feldspar group.

2.4 Mineralogy of the clay fraction

A large assortment of minerals of varying degrees of crystallinity occurs in the clay fraction of soils. Broadly, these minerals may be divided into the crystalline clay minerals – predominantly phyllosilicates – and other minerals (oxides, hydroxides and salts). Because of their large specific surface areas and surface charges, these minerals are very important sites for physical and chemical reactions in soil (Chapters 6 and 7).

For many years the small size of clay particles prevented scientists from elucidating their mineral structure. It was thought that the clay fraction consisted of inert mineral fragments enveloped in an amorphous gel of hydrated sesquioxides ($Fe_2O_3.nH_2O$ and $Al_2O_3.nH_2O$)* and silicic acid ($Si(OH)_4$). The surface gel was amphoteric, the balance between acidity and basicity being dependent on the soil pH. Between pH 5 and 8, the surface was usually negatively charged (proton-deficient), which could account for the observed cation exchange properties of soil. During the 1930s, however, the crystalline nature of the clay minerals was established unequivocally by X-ray diffraction (XRD) (Box 2.4). Most of the

* Fe and Al oxides are collectively called sesquioxides (prefix 'sesqui' meaning one and a half), because the ratio of oxygen to metal cation is 1.5.

Box 2.4 Identification of minerals in the clay fraction.

The technique of X-ray diffraction involves directing a beam of X-rays (electromagnetic radiation of wavelength from 0.1 to 10 nm) at a clay sample (particles < 50 μm diameter). Monochromatic X-rays whose wavelength is of the same order as the spacings of atomic planes in the crystals (0.1–0.2 nm) are the most useful. The clay sample can be a powder or a suspension dried on to a glass slide, which gives a preferred orientation of the plate-like crystals. As the X-rays penetrate a crystal, a small amount of their energy is absorbed by the atoms which become 'excited' and emit radiation in all directions. Radiation from atomic planes that is in phase will form a coherent reflected beam that can be detected by X-ray sensitive film. For a beam of parallel X-rays of wavelength λ (lambda), striking a crystal at an angle θ (theta), the necessary condition for the reflected radiation from atomic planes to be in phase is

$$n\,\lambda = 2\,d\sin\theta, \qquad\qquad (B2.4.1)$$

where n is an integer and d is the characteristic spacing of the atomic planes. Equation B2.4.1 is a mathematical statement of Bragg's Law.

minerals were found to have a phyllosilicate structure similar to the micas and chlorite. The various mineral groups were identified from their characteristic d spacings (Fig. B2.2.1), as measured by XRD, and their unit cell compositions deduced from elemental analyses. Subsequent studies using scanning and transmission electron microscopes have confirmed the conclusions of the early work.

In addition, within the accessory minerals there are the weathered residues of resistant primary minerals that have been comminuted to colloidal size, and soil minerals synthesized during pedogenesis. The latter mainly comprise Al and Fe hydroxides and oxyhydroxides, which occur as discrete particles or as thin coatings on the clay minerals. The crystallinity of these minerals varies markedly depending on their mode of formation, the presence of other elements as inclusions, and their age. Some, such as the iron hydroxide ferrihydrite, were previously thought to be amorphous, but are now known to form extremely small crystals and to possess short-range order: that is, their structure is regular over distances of a few nanometres, but disordered over larger distances (tens of nanometres).

The crystalline clay minerals

Most clay minerals have a phyllosilicate structure, but a small group – the sepiolite-palygorskite series – has chain structures and another group – the allophanes – forms hollow spherical crystals. Palygorskite and sepiolite are unusual in having very high Si : Al ratios, with Mg occupying most of the octahedral positions. Sepiolite is very rare in soil and palygorskite survives only in soils of semi-arid and arid regions. They are not discussed further.

Under mild (generally physical) weathering conditions, clay minerals may be inherited as colloidal fragments of primary phyllosilicates, such as muscovite mica. Under more intense weathering, the primary minerals may be transformed to secondary clay minerals, as when soil illites, vermiculites and smectites are formed by the leaching of interlayer K from primary micas, or from the weathering of chlorites. Neoformation of clay minerals is a feature of intense weathering, or of diagenesis in sedimentary deposits (Section 5.2),

when minerals completely different from the original primary minerals are formed. When the soluble silica concentration in the weathering environment is high, 2 : 1 layer minerals such as smectites are likely to form. Leaching and removal of silica, however, can produce kaolinite and aluminium hydroxide. Increased negative charge in the crystal due to isomorphous substitution of Al^{3+} for Si^{4+} in the smectites leads to K^+ being the favoured interlayer cation, with the resultant formation of illite.

Minerals with a Si : Al mole ratio ≤ 1

Three groups of clay minerals – *imogolite*, *allophanes*, and *kaolinites* – have Si : Al ratios ≤ 1.

Imogolite and allophane are most commonly found in young soils (< 1000 years) formed on volcanic ash and pumice (order Andisol (ST)). Imogolite has also been identified in the B horizon of podzols (order Spodosol (ST) or Podosol (ASC)). Both minerals appear amorphous by XRD, but high-resolution electron microscopy has revealed their crystalline nature, so they are properly called short-range order minerals. Because of their hollow crystal structures, they have very large specific surfaces (Table 2.2) and are highly reactive, especially towards organic anions and phosphate.

Imogolite has the structural formula:

$$(OH)_6Al_4^{VI}O_6Si_2^{IV}(OH)_2$$

and occurs in 'threads' 10–30 nm in diameter and several μm long. Each thread consists of several tubular crystals with inner and outer diameters c. 1 and 2.5 nm, respectively. They are curved to permit a reduced number of Si tetrahedra to bond to the Al octahedral sheet, as shown in Fig. 2.13.

Allophane exists as hollow, spherical particles of diameter 3.5–5 nm. One kind of allophane, which has a Si : Al ratio of 0.5 and the structural formula:

$$(H_2O)_2,(OH)_4Al_3^{VI}O_2(OH)_4(Si_2,Al)^{IV}O_3,(OH)_2,H_2O$$
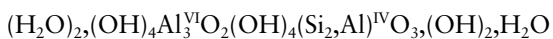
contains most of its Al in sixfold coordination and has charge properties very similar to imogolite, that is, very little permanent negative charge due
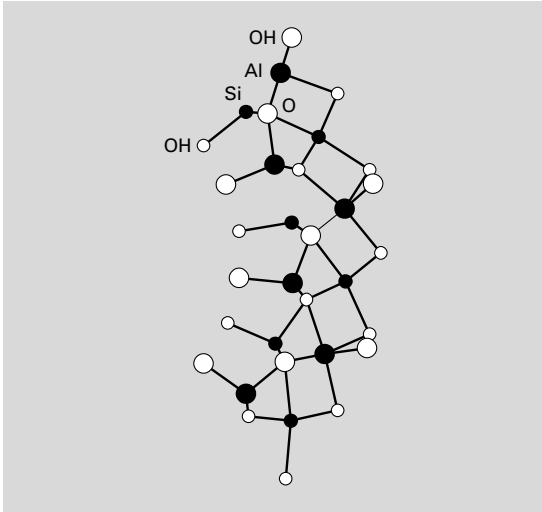
Fig. 2.13 Projection along the imogolite *c* axis showing the curvature produced as the Al octahedral sheet distorts to accommodate the Si tetrahedra (after Wada, 1980).

to isomorphous substitution, but variable positive and negative charge due to H^+ association or dissociation at surface OH groups (Section 7.1). At the other extreme, allophane with a Si : Al ratio of 1 and the structural formula:

$$H_2O,(OH)_2 \, Al^{VI}O,(OH)_2 \, H_2O(Si_2,Al)^{IV}O_3, (OH)_2,H_2O$$
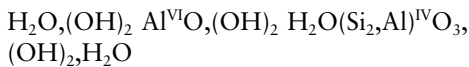
contains half its Al in the tetrahedral sheet and half in the octahedral sheet. Although a large layer charge arises because of the substitution of Al^{3+}

for Si^{4+}, it is neutralized to a variable extent, depending on the ambient pH, by the association of H^+ ions with surface OH groups. Thus, the allophanes and imogolite have pH-dependent surface charges at pH > 4.5.

Minerals of the kaolinite group have a well-defined 1 : 1 layer structure formed by the sharing of O atoms between one Si tetrahedral sheet and one dioctahedral alumina sheet. The unit cell composition is:

$$Si_2^{IV}O_5Al_2^{VI}OH_4$$

The common mineral of the group is kaolinite, the dominant clay mineral in many weathered tropical soils such as Oxisols (ST) or Ferrosols (ASC). Halloysite is found in weathered soils formed on volcanic ash, but is less stable than kaolinite.

Kaolinite has a *d* spacing fixed at 0.71 nm because of hydrogen-bonding between the H and O atoms of adjacent layers (Fig. 2.14). The layers are stacked fairly regularly in the Z direction to form crystals from 0.05 to 2 μm thick, the larger crystals occurring in relatively pure deposits of China Clay that is used for pottery. The crystals are hexagonal in plan view and usually larger than 0.2 μm in diameter, as shown in the electron micrograph of Fig. 2.15. Halloysite has the same structure as kaolinite, with the addition of two layers of water molecules between the crystal layers, which increases the *d* spacing of the mineral to 1 nm. The presence of this hydrogen-bonded water alters the distribution of stresses within the crystal so that the layers curve to form a tubular structure.
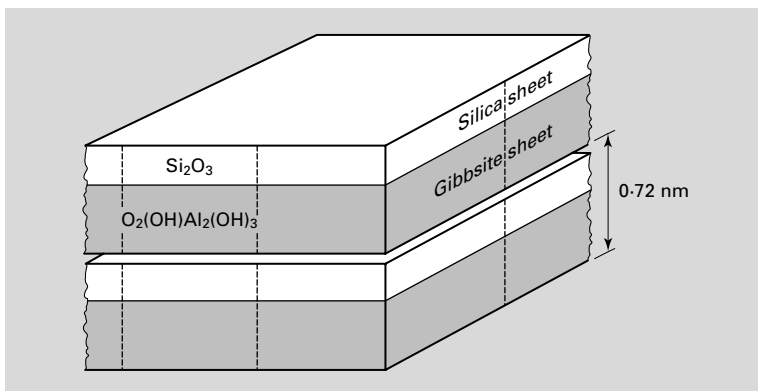

Fig. 2.14 Structure of kaolinite – a 1 : 1 phyllosilicate mineral with H-bonding between layers.