
2.1 The Rock Cycle

The soil's position in the material cycle of the lithosphere (Fig. 2.1) shows that a large number of processes are involved in the formation of rocks, lithogenesis, in the form of a cycle. At the beginning of lithogenesis, rocks are formed through crystallization when the molten magma cools down. They are subject to further diverse changes through the processes of weathering, erosion, transport, deposition, diagenesis, metamorphism and anatexis, which are connected to one another in a cycle. Soils are a significant station in this cycle. On the one hand, they are the result of the transformation of rock in contact with the atmosphere, hydrosphere and biosphere (pedogenesis), and on the other, they deliver material for the formation of new rocks. For this reason, soils cannot be understood and classified without knowledge of the rocks; however, the same is true for many rocks without knowledge of the soils (Kittrick 1985).

2.2 Minerals

2.2.1 General

Minerals are homogeneous components of rocks. They are natural, predominantly inorganic and chemically uniform compounds, whose elemental components are arranged in a defined, regular-periodical manner; they are crystalline. The

smallest geometrical unit of these crystals, which have exactly the same chemism and symmetry properties as the mineral, is called **elementary cell** (Ramdohr and Strunz 1978).

The occurrence of the elements can be derived from the average chemism of the Earth's crust (Table 2.1): Half of the mass can be attributed to oxygen, one quarter to silicon, and the rest consists almost entirely of Al, Fe, Mg, Ca, Na and K cations.

The dominance of the O ion and its large diameter (Table 2.2) indicate that most minerals consist of more or less densely packed O^{2-} ions, whose negative charges are neutralized by the often much smaller cations in the gaps of the O-packing. In doing so, the smaller cations such as Si^{4+} have four O^{2-} ions (ligands) as their next neighbours (coordination no. = 4), the somewhat larger cations such as Al^{3+} have six (coordination no. = 6), and particularly large ones like K^+ can also have eight or twelve O^{2-} ions. In addition to O^{2-} , the equally large hydroxyl anion OH^- and S^{2-} anions also act as ligands. Due to the various sizes of the ions, their volume fractions in the lithosphere may deviate considerably from their mass fractions: Table 2.1 shows that oxygen takes up 88 % of the volume, while important cations like the comparatively large K^+ , Ca^{2+} and Na^+ ions only account for 1–3 % by volume.

The average chemical composition of the lithosphere also shows that compounds consisting of O and Si, i.e. salts of silicic acid and the pure oxide SiO_2 predominate. Corresponding to the cation occurrence, the first eight minerals are

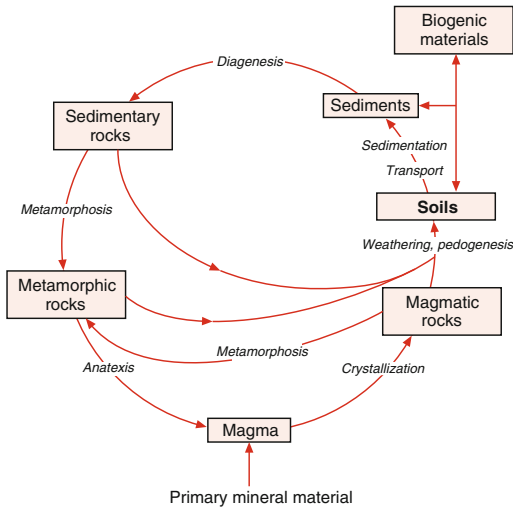


Fig. 2.1 The position of soils in the cycle of the lithosphere

Al, Fe, Mg, Ca, Na, and K silicates (Table 2.1). This is also true for most soils, which inherit the silicates not only from the parent material, but also form their own (pedogenic) silicates.

The conditions under which **primary** silicates crystallize out of the magma differ fundamentally in terms of temperature, pressure, oxygen and water content from the environmental conditions in the soil, where the crystal growth of the **secondary** minerals is usually strongly inhibited. **Lithogenic** minerals, originating from rocks, differ from **pedogenic** minerals, formed in the soil, not only in their grain size, but also in other properties, e.g. the sorption capacity. For this reason, the two groups will be discussed separately (Dixon and Weed 1989).

Table 2.1 Average chemism, mineral and rock constituents of the lithosphere (mass 2.85×10^{19} t)

Oxides	Mass (%) ^a		Elements	Mass (%)	Vol. (%)	Mineral constituents	Vol. (%)	Rock constituents ^b	Vol. (%)
SiO ₂	57.6	52.5	O	47.0	88.2	Plagioclases	39	Basalts, gabbros basic igneous rocks etc	42.6
Al ₂ O ₃	15.3	10.5	Si	26.9	0.32	Quartz	12	Gneisses	21.4
Fe ₂ O ₃	2.5	4.0	Al	8.1	0.55	K feldspars	12	Granodiorite, diorite and syenite	11.6
FeO	4.3		Fe ³⁺	1.8	0.32	Pyroxenes	11	Granites	10.4
MgO	3.9	3.3	Fe ²⁺	3.3	1.08	Micas	5	Crystalline schists	5.1
CaO	7.0	11.1	Ca	5.0	3.42	Amphiboles	5	Clays, clay schist	4.2
Na ₂ O	2.9	2.8	Mg	2.3	0.60	Clay minerals	4.6	Carbonate rocks	2.0
K ₂ O	2.3	4.6	Na	2.1	1.55	Olivines	3	Sands, sandstones	1.7
TiO ₂	0.8	—	K	1.9	3.49	Calcite, dolomite	2.0	Marble	0.9
CO ₂	1.4	—				Magnetite	1.5		
H ₂ O	1.4	—				Other minerals	4.9		
MnO	0.16	—							
P ₂ O ₅	0.22	—							

^aThe 2nd column shows the average composition of superficial rocks (Hudson 1995)

^bThe predominance of basic rocks is due to the surface area dominance of the oceanic crust

Table 2.2 Effective radii of various ions (pm) in crystals related to the coordination number IV or VI

^{VI} Na ⁺	102	^{IV} Al ³⁺	39	^{IV} C	15	P ⁵⁺	38
^{VI} K ⁺	138	^{VI} Al ³⁺	53.5	^{IV} Si	26	O ²⁻	140
^{VI} NH ⁴⁺	147	^{VI} Fe ²⁺	78.0	^{IV} Ti ⁴⁺	42	OH ⁻	137
^{VI} Mg ²⁺	72	^{VI} Fe ³⁺	64.5			S ⁶⁺	30
^{VI} Ca ²⁺	100	^{VI} Mn ²⁺	83			S ²⁻	182
		^{VI} Mn ⁴⁺	53			Cl ⁻	153

2.2.2 Silicate Structure

The structure of silicates helps to explain their diversity and properties, e.g. their weatherability. The basic building block of SiO₂ and silicates is a tetrahedron, in which the small tetravalent Si atom is surrounded by four large oxygen ions (Fig. 2.2 top). This creates a dense oxygen packing that fills the space and only allows cations to fill the gaps. If the centers of the O²⁻ ions are connected with each other, it creates a tetrahedron consisting of four triangles of the same size (Fig. 2.2). Every SiO₄ tetrahedron has four negative charges and is linked with other SiO₄ tetrahedra via oxygen bridges. The types and extents of the various cross-linking result in different silicate structures: The tetrahedra in

tectosilicates are completely cross-linked in all three spatial directions. Types of incomplete tetrahedron cross-linking include, **layered** or **phyllosilicates** with extensive 2-dimensional cross linking, as well as **band** and **chain silicates** with one-dimensional cross linking. If there is no cross-linking at all, they are called **nesosilicates** or **orthosilicates**. The tetrahedron basic units of this structure types are the tectosilicate-SiO₂⁰, phyllosilicate-Si₂O₅²⁻, band-Si₄O₁₁⁶⁻, chain-SiO₃²⁻ and the insular or nesosilicate SiO₄⁴⁻, characterized by an ascending O/Si ratio of 2.0, 2.5, 2.75, 3.0 and 4.0, and increasing demand for cations for the spatial connection of the tetrahedron units (Fig. 2.3).

Mainly K⁺, Na⁺, Al³⁺, Fe²⁺, Fe³⁺, Mg²⁺ and Ca²⁺ are involved, and together with the linking variations, they give rise to the chemical diversity of the silicates. Both the structure and the chemism have a significant effect on the weatherability of the various silicates (see Sect. 2.4).

Another variation of the silicates arises when, instead of the Si⁴⁺, the approx. 50 % larger Al³⁺ (Table 2.2) occupies the centre of the tetrahedron, without changing the ‘morph’ of the structure (therefore **isomorphic substitution**). However, it does change the charge conditions: The charge of Al³⁺ that is missing relative to Si⁴⁺ is compensated by the uptake of additional cations, e.g. K⁺, Na⁺ or Ca²⁺ into the structure.

With 80 % per volume (including quartz >90 %), silicates are the most frequently occurring minerals in igneous rocks. They are also the most important primary products for those minerals that are newly created by weathering and thus by pedogenesis. The ranges of variation in the chemical composition of the predominant igneous silicates fluctuate strongly (Table 2.3). The ranges show that silicates often do not

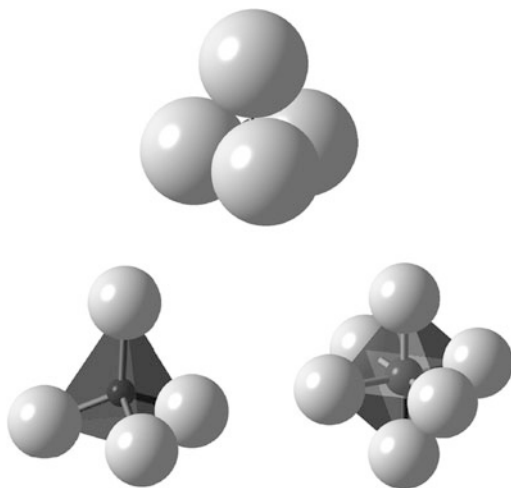


Fig. 2.2 Spherical model of a tetrahedron (top) and an octahedron (right) in combination with a polyhedral representation (left) to emphasize the coordination around the central ion (coordination polyhedron). Only the upper representation is to scale, the ions were drawn smaller in the other two representations to improve clarity

Fig. 2.3 Types of bonding in silicates: chain (*left*), band (*centre*) and layered structure (*right*)

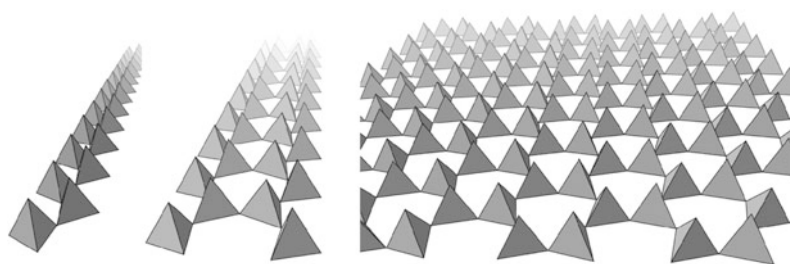


Table 2.3 Chemism (mass %) of important minerals of igneous and metamorphic origins

	Olivines	Pyroxenes ^a	Amphiboles ^b	Muscovites	Biotites	K-feldspars	Plagioclases
SiO ₂	38–47	47–53	39–54	39–53	33–45	63–66	43.5–69
TiO ₂	–	<4.4	–	<3.9	<10	–	–
Al ₂ O ₃	–	1–7	–	20–46	9–32	19–21	19–36
Fe ₂ O ₃	–	0.4–7.6	0.2–23	<8.3	0.1–21	<0.5	–
FeO	8–12	4–21	<9	–	3–28	–	–
MnO	–	–	–	<2.3	–	–	–
MgO	38–47	10–18	3–25	<2.4	0.3–28	–	–
CaO	–	13–22	10–14	<4.5	–	–	<19.5
Na ₂ O	–	–	0.5–2.3	<5.2	–	0.8–8.4	<12
K ₂ O	–	–	<1.7	7.3–13.9	6–11	3–16	–
H ₂ O	–	–	0.2–2.7	2–7	0.9–5	–	–

^aAugite

^bCommon hornblendes

correspond to the ideal formula. This is mainly due to isomorphic substitution.

2.2.3 Primary (Lithogenic, Pyrogenic) Silicates

2.2.3.1 Feldspars

Feldspars are pale or weakly colored Na–K–Ca–Al silicates with good cleavage and a hardness of 6. They belong to the tectosilicates, i.e., they consist of a three-dimensional tetrahedral framework. In the tetrahedra, $1/4$ (alkali feldspars) or $1/2$ (anorthite) of the tetrahedron centers are substituted by Al³⁺. To balance the charge, the relatively large K⁺, Na⁺ or Ca²⁺ ions are incorporated into the gaps in the silicate structure (Fig. 2.4).

The most important types of feldspar are the **orthoclase** (potassium feldspar, KAlSi₃O₈),

albite (sodium feldspar, NaAlSi₃O₈) and **anorthite** (calcium feldspar, CaAl₂Si₂O₈). These pure types are rarely found in rocks. Thus, potash feldspars usually contain Na (e.g. sanidine, anorthoclase, microcline); in which case, together with albite, they are called alkali feldspars, whose K₂O content lie between 2.5 and 14.7 %. Between albite and anorthite, there is a continuous series of intermediates called **plagioclases** (Ca–Na feldspars), where Na and Ca are completely interchangeable due to their similar ionic radius (Na 102 pm; Ca 100 pm), contrary to Na and K (138 pm). For this reason, with decreasing albite and increasing anorthite fractions, Ca and Al contents increase, while the Na and Si content decreases. This also explains the variation in the chemical composition of plagioclases (Table 2.3). In basic igneous rocks, in addition to Ca-rich plagioclases, Si-poorer **feldspar representatives** (foids), nepheline (NaAlSiO₄) and

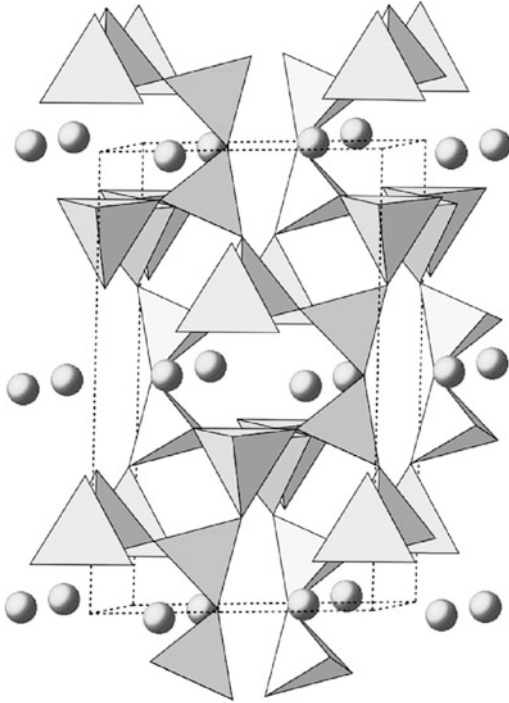


Fig. 2.4 Tetrahedral model of an albite. The *spheres* are the Na ions, the tetrahedra contain Si^{4+} and Al^{3+} at a ratio of 3:1. The *dotted lines* surround the elementary cell

leucite (KAlSi_2O_6) can occur, which are also tectosilicates.

2.2.3.2 Micas and Chlorites

Micas are K–Mg–Fe–Al phyllosilicates with extremely good cleavage, which is due to the laminar arrangement of their structure (sheet-like or phyllosilicates). The most common micas are the light-colored **muscovite** and the dark **biotite**. Muscovite is predominantly of metamorphic origin, but also igneous (only in intrusive rocks) and sedimentary. Biotite is usually igneous, and the darker it is in color, the higher its Fe content. The K content of both minerals lies between 6 and 14 % K_2O .

In the sheet-like structure of the micas, the SiO_4 tetrahedra are each linked with three (of 4) O^{2-} ions laying on one plane, i.e. two-dimensional (Figs. 2.3 and 2.5). The fourth O^{2-} ion that is not linked to the neighboring tetrahedron links the tetrahedral layer with the octahedral layer, in which Al^{3+} , Mg^{2+} or Fe^{2+} ions

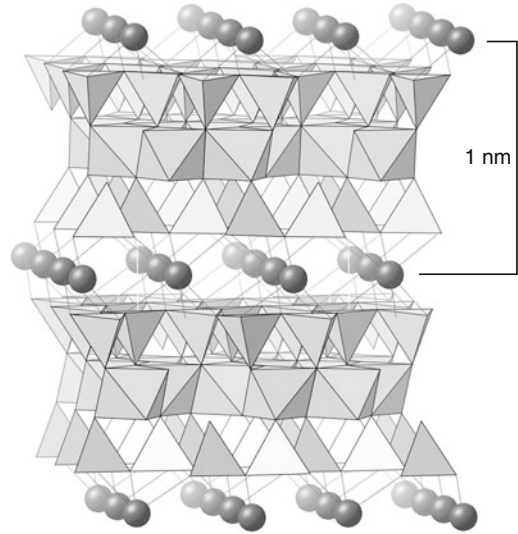


Fig. 2.5 Model of a mica structure. The *spheres* are K^+ ions. The *thickness* of one elementary layer is labeled

are six-fold coordinated. This octahedral layer is followed by another tetrahedral layer; however, it is rotated by 180° , so that the oxygen ions at the tips also point to the octahedral layer. Two of the six octahedrally coordinated oxygen ions from the octahedral layer bond with both the tetrahedral layers, and two form hydroxyl ions (OH^-) with H^+ . The remaining two oxygen ions link the octahedra via common edges to form sheets, which is why micas are also referred to as 2:1 or **three-layered minerals** (Fig. 2.5).

Three octahedron centers form one formula unit, and altogether, their central cations have six negative charges to be compensated. In **dioctahedral** muscovite, two of the three centers are occupied with Al^{3+} , and in **trioctahedral** biotite, in contrast, all three are occupied with variable proportions of Fe^{2+} and Mg^{2+} . For muscovite, this results in the idealized formula $\text{KAl}_2(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_2$, and accordingly for biotite $\text{K}(\text{Mg}, \text{Fe}^{2+})_3(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_2$.

In micas, the three-layered structural units are linked vertically to the layer planes by potassium ions, which penetrate into the central gaps of the 6-O rings of the outer oxygen layer of the tetrahedron (see Fig. 2.6), and thus hold the silicate layers together (=interlayer cations). Because 6

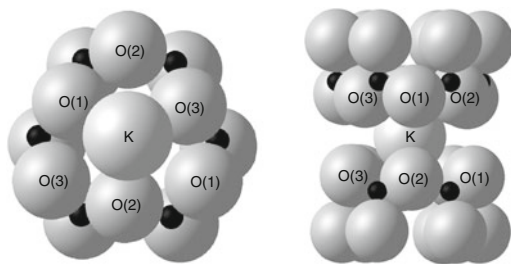


Fig. 2.6 Spherical model of the tetrahedral layer of mica seen from the front (*left*) and from the side (*right*) (true to scale). The oxygen and the potassium are labeled, the small black spheres are the Si^{4+} ions

oxygen ions on each side of the tetrahedral layer contribute to the bonding, K^+ with its O^{2-} ions has a coordination number of 12.

In a polyhedral model, the silicate sheets of micas are shown as a sequence of tetrahedral and octahedral layer at a ratio of 2:1 (Fig. 2.5), in a spherical model, as a package of two O and two (O, OH) layers. Together with the layer of K^+ ions between the silicate layers, these form the elementary layer with a thickness of 1 nm. The actual crystal sheet consists of a more or less large number of such elementary layers.

The so-called layer charge ζ determines whether there are interlayer cations or not: In micas, one of each of the four Si^{4+} ions is substituted by Al^{3+} . The lacking positive charge is therefore compensated by an interlayer K^+ . However, the layer charge can vary over a great range (see Sect. 2.2.4).

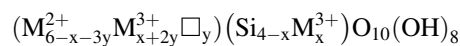
The strong cohesion of the silicate layers in micas is not only a result of the high layer charge, but is also due to the fact that the K^+ ion is only slightly larger than the gap at the center of the oxygen hexagonal rings, and therefore penetrates into these gaps (Fig. 2.6). Furthermore, K^+ is relatively easily polarized, so that its positive charge is slightly shifted under the influence of the negative excess charge, which can strengthen the bond.

The strength of the cohesion of the layers in trioctahedral biotite is lower than in dioctahedral muscovite, and therefore the availability of the K^+ ions for plant growth is higher in biotite than in

muscovite. Possible explanations are: (a) the K–O bond in trioctahedral minerals is somewhat longer and thus weaker than in dioctahedral minerals, (b) in trioctahedral three-layered minerals, the vector of the OH-bond is approximately perpendicular to the layer plane, while it forms an angle of $\sim 74^\circ$ in dioctahedral minerals. As a result, in trioctahedral micas, the distance between the H^+ and the K^+ ions is smaller, i.e., the repulsion between the two ions is stronger than in dioctahedral micas. This also explains why K^+ is much more difficult to liberate, as soon as the Fe^{2+} –OH groups are converted by oxidation to Fe^{3+} –O groups.

The vertical linking can also occur without interlayer cations only through the VAN DER WAAL forces, as is the case with pyrophyllite ($\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2$) or talc ($\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$). The interlayer distance is then only 0.9 nm. The bonding strength between the silicate layers mainly depends on the charge per area; this is demonstrated by the following sequence of scratch hardness H : Talc ($\zeta = 0$, $H = 1$), smectite-vermiculite group ($\zeta = 0.3$ – 0.9 , $H \sim 1^{1/2}$), muscovite ($\zeta = 1$, $H = 2$ – $2^{1/2}$), margarite ($\zeta = 2$, $H = 4$).

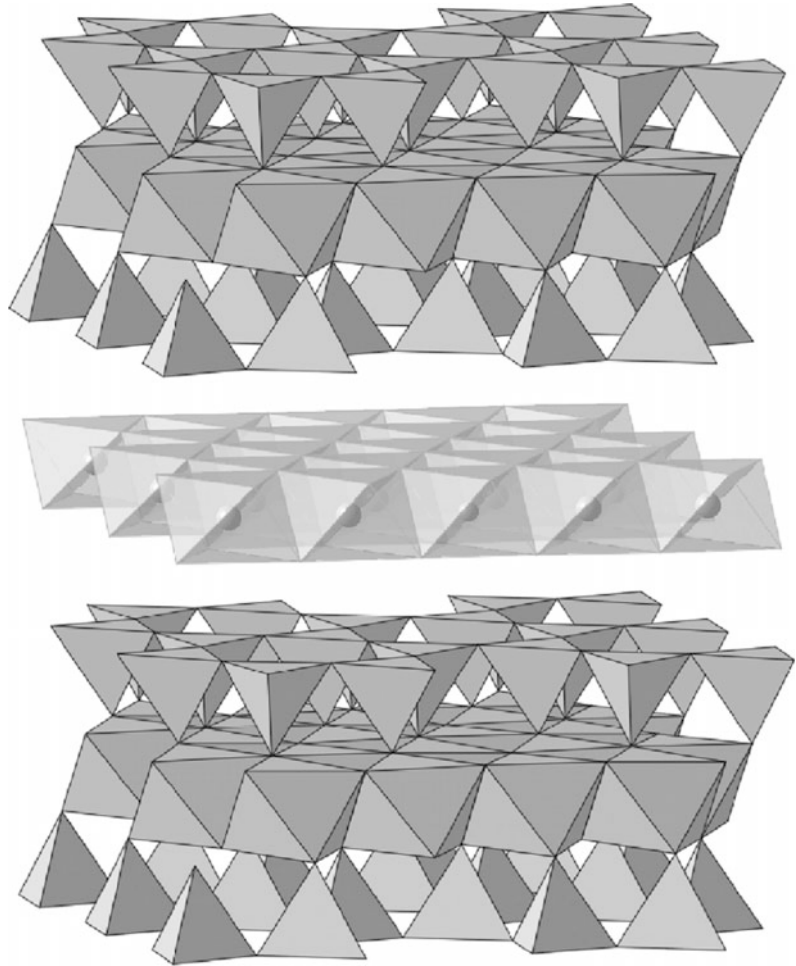
The phyllosilicates also include the generally green in color, Mg–Fe(II)-rich **chlorite** (gr. *chlorós* = green), which, like the micas, consist of trioctahedral 2:1-layers. However, contrary to the micas, it is not K^+ that is inserted between the layers, but rather an independent, mainly trioctahedral hydroxide layer with the molecular formula $(\text{Mg}^{2+}, \text{Fe}^{2+}, \text{Fe}^{3+}, \text{Al})_3(\text{OH})_6$ (Fig. 2.7). The substitution of M^{2+} by M^{3+} in both hydroxide layers generates a positive charge, which compensates for the negative charge of the tetrahedral layers. The latter comes from the partial substitution of Si^{4+} by Al^{3+} (Bailey 1991). Because the two octahedrally coordinated layers are similar in their structures and chemistry, chlorites can be grouped according to the general formula:



with $\text{M}^{2+} = \text{Mg}^{2+}$, Fe^{3+} and $\text{M}^{3+} = \text{Fe}^{3+}$, Al^{3+} .

\square represents an empty space, i.e. an unoccupied position in the structure. In addition to the purely

Fig. 2.7 Polyhedral model of the structure of chlorite. The *light octahedra* with the implied cation represent the hydroxide interlayer



electrostatic attraction, there are also H-bridge bonds between the OH-groups of the hydroxide layer and the O^{2-} ions of the two neighboring tetrahedral layers.

2.2.3.3 Pyroxenes, Amphiboles and Olivines

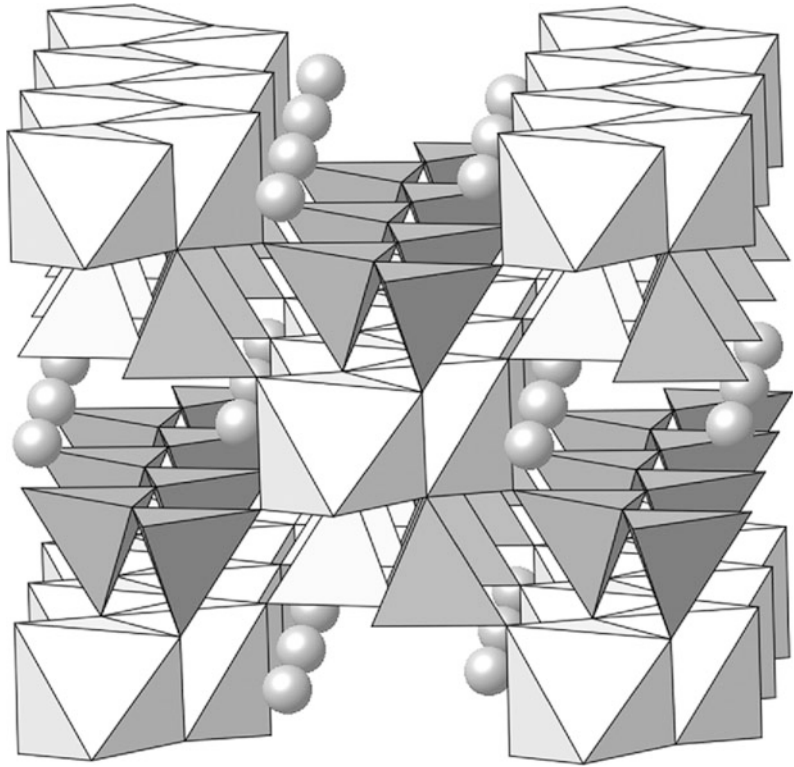
In contrast to the tecto- and phyllo-silicates, the generally dark **pyroxenes** and **amphiboles** are built with tetrahedral chains (Figs. 2.3 and 2.8) or bands (chain silicates arranged in parallel. In the tetrahedron centers, in turn, some of the Si^{4+} ions were substituted by Al^{3+} ions. The cations inserted to equalize the charge, mainly Ca^{2+} , Mg^{2+} and Fe^{2+} , link the chains and bands. Because this bond is weaker than the Si–O and Al–O bonds within the chains and bands, they

are cleaved and weathered parallel to the chains and bands.

Pyroxenes include mainly **augite** ($Ca, Mg, Fe, Al, Ti)_2(Si, Al)_2O_6$ and the minerals enstatite, hypersthene and diopside, and the amphiboles include the **hornblendes** ($Ca_2(Mg, Fe, Al)_5(Si, Al)_8O_{22}(OH)_2$) and actinolite, mainly found in metamorphic rocks. On average, hornblende contains more Al and less Ca than augite. It is greenish-black to black in color, similar to biotite, because it contains both Fe^{2+} and Fe^{3+} (given as FeO or Fe_2O_3 in Table 2.3).

The olive-green nesosilicate/orthosilicate **olivine**, $(Mg, Fe^{2+})_2SiO_4$, is often found in basic igneous rocks. Like the plagioclases, olivines form a completely isomorphic series of intermediates with the end members forsterite (Mg_2SiO_4)

Fig. 2.8 Polyhedral model of the pyroxene structure (diopside) with chain-like bonding of the SiO_4 tetrahedra. The *octahedra* contain Mg^{2+} , the *spheres* are the Ca^{2+}



and fayalite (Fe_2SiO_4). The SiO_4 tetrahedra are not linked by shared O^{2-} ions, but rather only by Mg^{2+} and Fe^{2+} ions. There is no isomorphic substitution with Al^{3+} . Olivines weather readily, leading to the formation of serpentine.

2.2.3.4 Rare Silicates

Almost all igneous rocks contain small fractions of several silicates, which belong to the so-called **heavy minerals**, i.e. minerals with a density $>2.9 \text{ g cm}^{-3}$. These include titanite (CaTiOSiO_4), zircon (ZrSiO_4) and tourmaline (idealized as $\text{MA}_3\text{X}_6[(\text{OH})_4](\text{BO}_3)_3[\text{Si}_6\text{O}_{18}]$ with $\text{M} = \text{Na}, \text{Ca}$; $\text{A} = \text{Mg}, \text{Fe}, \text{Li}, \text{Al}, \text{Ti}$; Cr ; $\text{X} = \text{Al}, \text{Mg}, \text{Fe}$). Tourmaline is an important supplier of boron for plants.

Typical silicates of metamorphic origins are: Garnet, $(\text{Ca}, \text{Mg}, \text{Fe}^{2+}, \text{Mn})_3(\text{Al}, \text{Fe}^{3+}, \text{Cr}^{3+})_2(\text{SiO}_4)_3$, andalusite and sillimanite, Al_2OSiO_4 , staurolite, $(\text{Fe}^{2+}, \text{Mg})_2(\text{Al}, \text{Fe}^{3+})_9\text{O}_6(\text{SiO}_4)_4 (\text{O}_9\text{OH}_2)$ and

epidote, $\text{Ca}_2(\text{Al}, \text{Fe}^{2+})\text{Al}_2[\text{O}/\text{OH}/\text{SiO}_4/\text{Si}_2\text{O}_7](\text{OH})$ and also serpentine, $\text{Mg}_3\text{Si}_2\text{O}_5 (\text{OH})_4$.

Igneous rocks that cooled very quickly contain large amounts of non-crystallized silicates, **volcanic glass**, the chemical composition of which varies in a wide range according to the magma.

In building materials such as concrete, poorly crystallized, hydrated calcium silicates with the composition $m\text{CaO} \cdot \text{SiO}_2 \cdot n\text{H}_2\text{O}$ occur as a reaction product from clinker phases with the mixing water, where m is $\sim 1.5\text{--}2$, depending on the water addition. Morphologically, they form needles and copings or bendings, and structurally, these silicates resemble the mineral **tobermorite**, in which the water molecules are embedded between the silicate layers. From the clinker phases containing Al, tetracalcium aluminate hydrates are formed when the concrete hardens, and in the presence of sulfate, analogous sulfates are also formed, such as ettringite, $\text{Ca}_6\text{Al}_2[(\text{OH})_4\text{SO}_4]_3 \cdot 24\text{H}_2\text{O}$.

2.2.4 Clay Minerals

2.2.4.1 General Properties

Clay minerals are defined here as silicate minerals occurring in the clay fraction ($<2\ \mu\text{m}$). Clay minerals formed from the weathering products of primary silicates are important constituents of many soils and sediments, which are lacking in igneous and metamorphic rocks. Structurally, they are related to the phyllosilicates, however, they have a very small particle size ($<2\ \mu\text{m}$), and therefore give mudstones, clayey rocks and clayey soils their plasticity, their swelling properties and their capacity to adsorb ions and molecules. Their chemical composition and their charge can vary even within the same mineral type (Table 2.4). Their nonstoichiometric chemical composition is expressed in the molecular formulas (see Table 2.5). They have “low” crystallinity, which, together with the layer charge, result in the reaction capacity of clay minerals in soils. All of these properties can be

attributed to the environmental conditions during formation in the earth surface: low temperatures, low pressure as well as the “impurity” and fluctuating compositions of the weathering solutions (Brindley and Brown 1984; Jasmund and Lagaly 1993).

2.2.4.2 Crystal Structure and Classification

In addition to the structural similarities with the micas, clay minerals have the following characteristics (Newman 1987).

1. Like with the micas, the basic building units of clay minerals are SiO_4 tetrahedral and octahedral layers. Among the octahedral layers, a distinction is made between dioctahedral (Al, muscovite type) and trioctahedral (Mg, Fe, biotite type).
2. The charge is highly variable and can range from almost 0 to >1 . The tetrahedral charge is always negative, the octahedral can be

Table 2.4 Variation ranges for the chemical composition of important clay mineral groups (in mass %)

Clay mineral	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	K_2O	Na_2O
Kaolinites	45–47	38–40	0–0.2	0–0.3	0	0	0	0
Smectites	42–55	0–28	0–30	0–0.5	0–3	0–2.5	0–0.5	0–3
Vermiculites	33–45	7–18	3–12	0–0.6	0–2	20–28	0–2	0–0.4
Illites	50–56	18–31	2–5	0–0.8	0–2	1–4	4–7	0–1
Chlorites	22–35	15–48	0–4	0–0.2	0–2	0–34	0–1	0–1

Table 2.5 Examples for chemical structures of common clay minerals

Clay mineral	Interlayer occupancy	Central cations octahedral layer	Central cations tetrahedral layer	Anions and water
Kaolinite	$X_{0.04}$	$(\text{Al}_{1.91}\text{Fe}_{0.04}^{3+}\text{Ti}_{0.04})$	$(\text{Al}_{0.05}\text{Si}_{1.95})$	$\text{O}_5(\text{OH})_4$
Halloysite	$x_{0.04}$	$(\text{Al}_{1.96})$	$(\text{Al}_{0.05}\text{Si}_{1.95})$	$\text{O}_5(\text{OH})_4 \cdot 2\text{H}_2\text{O}$
Illite (dioct.)	$\text{K}_{0.64}\text{X}_{0.10}$	$(\text{Al}_{1.46}\text{Fe}_{0.21}^{3+}\text{Fe}_{0.08}^{2+}\text{Mg}_{0.28})$	$(\text{Al}_{0.45}\text{Si}_{3.55})$	$\text{O}_{10}(\text{OH})_2$
Glauconite	$\text{K}_{0.72}\text{X}_{0.06}$	$(\text{Al}_{0.48}\text{Fe}_{0.96}^{3+}\text{Fe}_{0.17}^{2+}\text{Mg}_{0.41})_{2.05}$	$(\text{Al}_{0.26}\text{Si}_{3.74})$	$\text{O}_{10}(\text{OH})_2$
Vermiculite (trioct.)	$X_{0.71}$	$(\text{Al}_{0.14}\text{Fe}_{0.34}^{3+}\text{Fe}_{0.09}^{2+}\text{Mg}_{2.40})$	$(\text{Al}_{1.13}\text{Si}_{2.87})$	$\text{O}_{10}(\text{OH})_2$
Montmorillonite (dioct.)	$X_{0.39}$	$(\text{Al}_{1.50}\text{Fe}_{0.12}^{3+}\text{Fe}_{0.01}^{2+}\text{Mg}_{0.38})$	$(\text{Al}_{0.05}\text{Si}_{3.95})$	$\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}$
Palygorskite	–	$(\text{Al}_{0.34}\text{Fe}_{0.06}^{3+}\text{Mg}_{0.60})_4$	Si_4	$\text{O}_{10}(\text{OH})_2(\text{H}_2\text{O})_8$

X exchangeable cations in equivalents, K interlayer potassium, n changing proportions of H_2O , *dioct.* dioctahedral, *trioct.* trioctahedral

negative or positive. The total charge is then approx. 0.2–1.0.

3. In clay minerals, interlayers can occur between the silicate layers. These can consist of ions (K), hydrated ions ($\text{Mg} \cdot \text{H}_2\text{O}$) or octahedral layers.
4. Among platy clay minerals with “endless” silicate layers, a distinction is made between two-layer or 1:1, three-layer or 2:1, and four-layer or 2:1:1 minerals. In the latter, the interlayer consists of an octahedral layer. If the layers are not charged, they are connected by hydrogen bridges, dipole interactions or VAN-DER-WAALS forces.
5. A special type are band silicates, where five or eight octahedra form a band, which is then connected to other bands through Si–O–Si bridges, and thus results in tubular structures (palygorskite and sepiolite).
6. When there is a very rapid supply of Si and Al from the weathering solution, clay minerals can be formed that consist of one single tetrahedral-octahedral double layer. These double layers are then bent to form hollow spherules (allophane) or tubes (imogolite).

Clay minerals are classified according to the occurrence of these properties (Table 2.6).

2.2.4.3 Kaolinite and Halloysite

As virtually pure Al silicates, these two clay mineral groups are the most common dioctahedral two-layer minerals, $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$, while trioctahedral serpentine, $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$, occurs more rarely.

In kaolinite and halloysite, every silicate layer on the tetrahedron side is bordered by O^{2-} ions, and by OH^- ions on the octahedron side (Fig. 2.9). The silicate layers in kaolinite are held together by hydrogen bridges $\text{OH}-\text{O}$ between the OH^- ions of the octahedra and the O^{2-} ions of the tetrahedra in the neighboring silicate layer. The octahedron centers are occupied by Al^{3+} , and the tetrahedron centers by Si^{4+} . The layer distance is 0.7 nm. In halloysite, in contrast, there is a H_2O layer between the silicate layers; its layer distance is therefore larger by the thickness of one H_2O sheet (0.28 nm) and is of 1.0 nm. When heated, but sometimes also already when air drying, halloysite loses the interlayer of water and contracts to 0.7 nm to form metahalloysite. In kaolinite and halloysite, the amount of isomorphic substitution of Si by Al in the tetrahedra, and thus the charge of the silicate layers is very low. In the octahedra, there is usually a little substitution of Al^{3+} by Fe^{3+} (see formulas in Table 2.5).

Table 2.6 Classification of the most important clay minerals

Structure type	Example	Height of the negative layer charge per formula unit	Occupancy of the interlayer space
1:1 or two-layered-minerals	Kaolinite	0	–
	Halloysite	0	H_2O
	Serpentine	0	–
2:1 or three-layered-minerals	Illite	>0.6	K
	Vermiculite	0.6–0.9	Exchangeable cations
	Smectite	0.2–0.6	Exchangeable cations
	Chlorite	Variable	Hydroxide layer
Fibrous pyroxene-like	Palygorskite	0	–
Variable	Allophane	?	–
	Imogolite	?	–
	Hisingerite	?	–

Fig. 2.9 Polyhedral model of a two-layered silicate (kaolinite). The *spheres* symbolize the H^+ ions

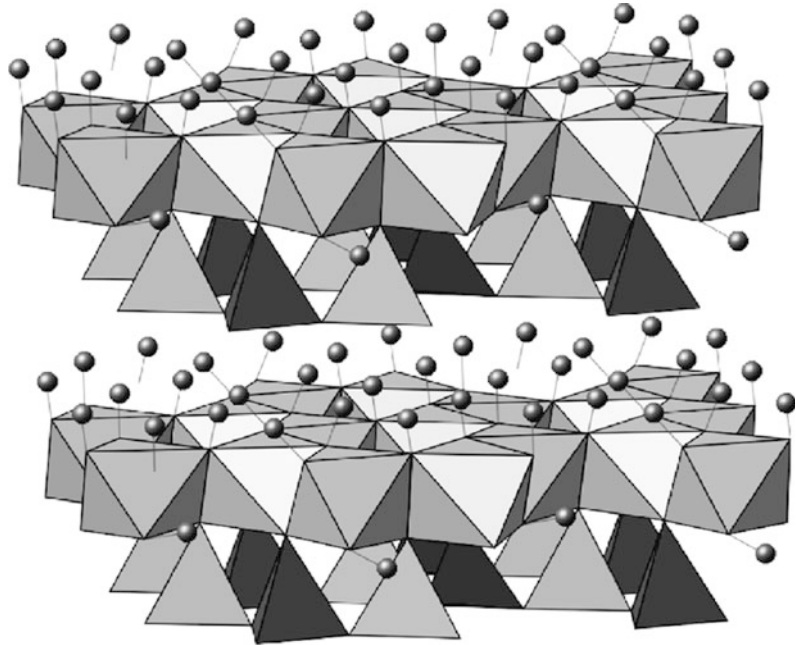
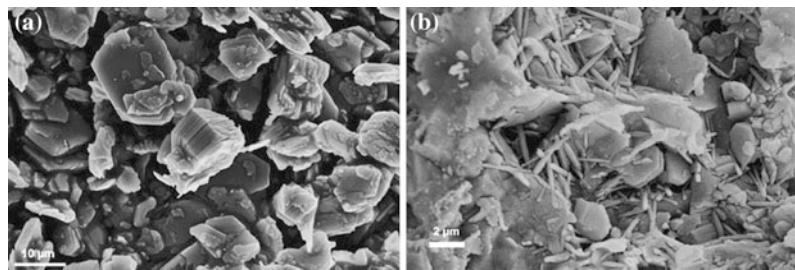


Fig. 2.10 **a** Pseudo hexagonal contour of kaolinite minerals (San Juanito, Chihuahua, Mexico). **b** Halloysite and kaolinite from the weathering of granite (Podzol, Bärhalde, Cv horizon) (image M. Zarei)



Kaolinite usually forms hexagonal μm -sized platelets, and halloysite forms tubes, rolled-up platelets (Fig. 2.10) or hollow spherules. Pedogenic kaolinite crystals are often smaller (several tenths of a μm) (Fig. 2.10a) and more rich in Fe than the many kaolin deposits. With increasing Fe incorporation, the crystal size and crystal arrangement (both combined in **crystallinity**) are decreasing. Kaolinite, as main component of the kaolins, is used to make high-quality ceramic and as filling material.

2.2.4.4 Illites and Glauconites

Illites show the closest similarity to the micas. They are like these three-layer minerals, however, their negative layer charge with 0.6–0.9 per formula unit is lower than that of the micas (1.0),

and other than through the Si–Al substitution in the tetrahedra, also originate from the substitution of Al^{3+} by Mg^{2+} and Fe^{2+} in the octahedra. Due to the lower layer charge, the K content of illites with 4–6 mass % is lower than that of mica. Like with the micas, the silicate layers are held together by K at approx. 1 nm layer distance. In soils, illites are formed through the physical and chemical weathering of micas. During the diagenesis of sediments, illites are mainly formed from smectites through recrystallization and chemical incorporation of potassium between the layers. If the conversion is incomplete, a portion of the layers inside the crystal remains smectitic and thus expandable. Due to this chemical heterogeneity, illite is not classified as a defined mineral in the strict sense.

Under the electron microscope, illites appear as irregularly shaped platelets. Their crystals often only consist of 100–300 silicate layers, i.e. they have a thickness of approx. 0.1–0.3 μm .

The green-colored glauconites are related to the illites. They are found in marine sediments and differ from the illites through a higher Fe content in the octahedral layers. The glauconites also contain generally K-depleted, partially expanding layers.

2.2.4.5 Vermiculites and Smectites

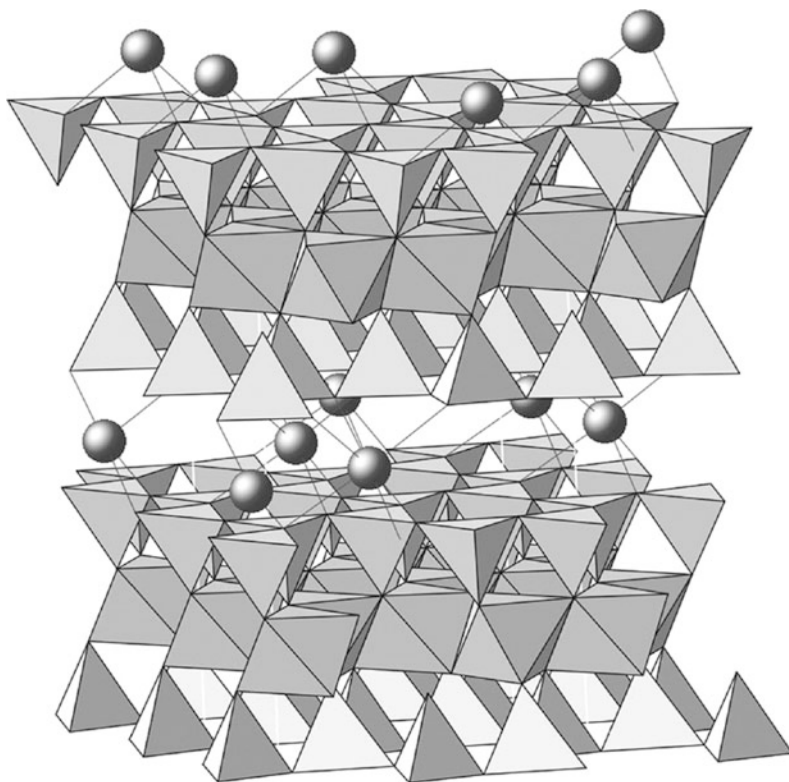
Vermiculites and smectites are expandable three-layer minerals, whose negative layer charge is compensated by various exchangeable cations in the interlayer space (Fig. 2.11). By definition, the two minerals are separated by their layer charges: Those with a charge of 0.6–0.9 per formula unit are classified as vermiculites, those with 0.2–0.6 as smectites. With the addition of potassium, vermiculites contract due to their high charge to an interlayer distance of 1 nm, and therefore turn

into illites and contribute to the so-called **K-fixation** of soils (Chap. 5), however, smectites do not.

Vermiculites generally originate from biotites through the **oxidation** of octahedral Fe^{2+} – Fe^{3+} . Due to the increase in the positive charge, the negative layer charge is reduced, the mineral expands and K is liberated from the interlayer space. Vermiculites also differ from smectites in the location of the isomorphic substitution and in the chemical composition. When heated, vermiculites expand to many times their original volume, and are used in this form as isolation and packaging material.

Due to their lower layer charge, smectites store more water and therefore expand more than vermiculites. The expansion height depends on the height of the layer charge and the type of interlayer cations. A smectite saturated with Ca^{2+} or Mg^{2+} stepwise stores up to four ~ 0.28 nm-thick water layers, so that its interlayer distance increases to approx. 2 nm. Sediments rich in

Fig. 2.11 Polyhedral model of a smectite. The *spheres* (not true to scale) between the silicate layers are the exchangeable cations



smectites and soils, such as Vertisols (Chap. 8), therefore swell and shrink strongly with fluctuating water contents. The swelling can trigger landslides and can lead to structural degradation in soils. The various smectites differ from one another in the height of the layer charge, the proportion of tetrahedral and octahedral charges, and the chemical composition. Mg^{2+} -rich forms with mainly octahedral charge are called montmorillonite, Al^{3+} -rich with mainly tetrahedral charge are beidellite, and Fe^{3+} -rich are nontronite. Pure smectite deposits are usually montmorillonite, while smectites in soils generally have higher Fe and lower Mg contents. Their charge is of 0.3–0.4 per formula unit and is 40–80 % tetrahedrally localized. Thus, they are Fe-rich, beidellitic smectites. Under the electron microscope, smectites appear as very thin and therefore flexible sheets that are often folded or rolled up at the edges, have an irregular boundary, and are riddled with many structural faults.

Smectites are the main minerals of the economically significant bentonites, as they occur e.g. in Lower Bavaria and in Wyoming and Mississippi, and have a multitude of technical applications (e.g. as adsorbents, binding agents for molding sands, additive for rinsing in deep drilling).

2.2.4.6 Pedogenic Chlorites

Soil chlorites (secondary chlorites) are similar to the ‘primary’ chlorites from rocks (Sect. 2.2.3.2) in that they both contain between the 2:1 layer a more or less complete hydroxide (Fig. 2.7) interlayer, and their stacking distance is therefore 1.4 nm. Their dioctahedral silicate layers are like those of vermiculite or smectite, and contrary to the primary chlorites from rocks, their layer interspace is sporadically occupied by an Al hydroxide octahedral sheet (also called Al chlorite) (Fig. 2.12). The Al hydroxides have a structure similar to gibbsite (Sect. 2.2.6.2).

Through the imperfect filling of the interlayer Al-hydroxy polymers, the properties of the formerly expandable three-layer minerals change: They lose their expandability and their capacity to contract with the addition of K. Already small amounts of Al-hydroxy polymers are sufficient

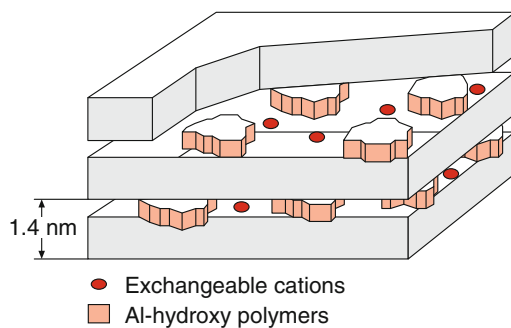


Fig. 2.12 Diagram of a pedogenic chlorite

(approx. $\frac{1}{6}$ of the possible interlayer sites) to cause this effect. The cation exchange capacity decreases with increasing filling.

Treatment with NaOH, NaF or Na citrate (100 °C) can dissolve the Al-hydroxy interlayer polymers and reverse the above-mentioned changes. Liming can cause a similar effect, if the clay particles are not too big and the degree of chloritization is not too high. The increase in pH neutralizes the positive charges of the Al-hydroxy polymer cations ($\text{OH}/\text{Al} = 3$; layer charge = 0), which can then no longer be held by the negatively charged silicate layers and exit the interlayer space.

Pedogenic chlorites only occur naturally in acidic soils, because only these release sufficient Al. Favorable conditions for deposition are a pH range of 4–5 and not too much organic matter, because SOM binds the Al complex and thus impedes deposition. If the pH drops even further, in the interlayers no more Al-hydroxy polymers are formed, and the soils can be “dechloritized” (podzolization).

2.2.4.7 Palygorskite and Sepiolite

The two Mg-rich, trioctahedral clay minerals palygorskite and sepiolite consist of bands of 2:1 silicate layers, which are staggered by one layer thickness vertical to the layer plane. Both minerals differ only in the width of the bands (palygorskite has 5 octahedra, sepiolite has 8 octahedra per band). This band structure is expressed physically in the fiber form of the crystals. There are channels between the bands that are filled with H_2O molecules. The octahedra are mostly

occupied with Mg, but sometimes also with Al, Fe and Ti. Their excess negative charge is low. Both minerals are formed in the alkaline range and/or in saline soils. For this reason, they are mainly found in semi-desert soils (Chap. 8).

2.2.4.8 Allophane, Imogolite and Hisingerite

Allophanes are hydrous secondary aluminum silicates with an Si/Al molar ratio of 0.5–1.0, in some cases up to 4, originating mainly from the weathering (Chap. 8) of volcanic glasses (Sect. 2.4.2) in humid climates. They consist of tiny hollow spherules with 3.5–5 nm outer diameter and walls with a thickness of approx. 0.7–1 nm (Fig. 2.13). The walls of the hollow spherules consist of a curved Al–O–OH octahedral layer, where incomplete Si–O–OH-tetrahedral layers are bound by O bridges on the inner surface. In contrast to the other clay minerals, the crystal arrangement only extends over the range of the very small hollow spherules (short range order), so that the allophanes were long considered to be amorphous. Due to their similarity to imogolite, Al-rich allophanes (Si/Al = 0.3–0.4) are called proto-imogolite allophane. The very rare hisingerite contains Fe in the octahedral layer instead of Al.

In contrast, imogolite has a one-dimensional long range order, since it consists of several μm -long, very fine tubes with 1 nm inner and 2 nm outer diameter. The outside of the tubes form a dioctahedral Al hydroxide layer, which is connected to an incomplete layer of Si–O₃OH tetrahedra on the inside via O bridges. Therefore, the outer surface of the tubes consists of Al–OH groups, and the inside of Si–OH groups (Fig. 2.14). This results in the chemical structure $(\text{HO})_3\text{Al}_2\text{O}_3\text{SiOH}$, according to the sequence from the outside to the inside, and an Si/Al ratio of approx. 0.5.

2.2.4.9 Interstratified Minerals

The clay mineral crystals in soils often have different elementary layers arranged in a regular or irregular sequence (Fig. 2.15). Such minerals are called interstratified minerals. With irregular mixed layers, which occur more frequently in

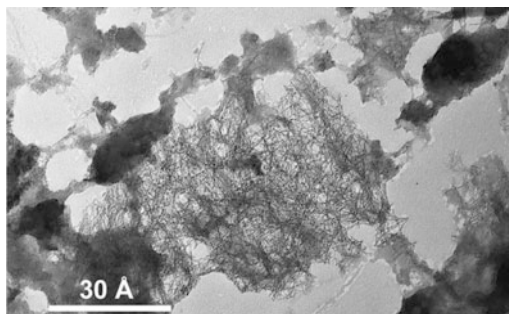


Fig. 2.13 Thread-like structures of imogolite, Bw horizon of an Andosol in Iceland (*image M. Zarei*)

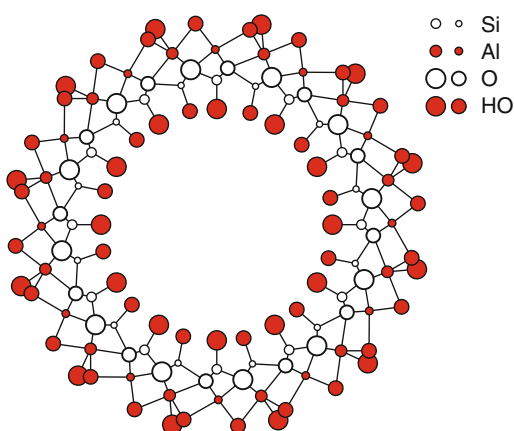


Fig. 2.14 Structure of imogolite: Cross section through an imogolite tube. The smaller structural elements lie somewhat underneath the plane of the drawing, and the larger ones above

soils than regular sequences, the relative proportions of the elementary layers can fluctuate across a wide range. This includes those between

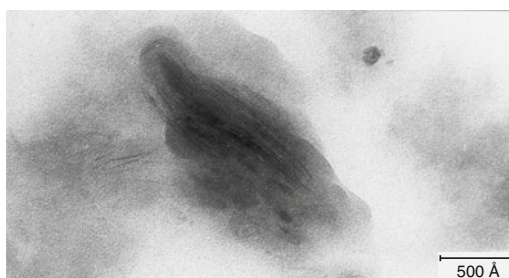


Fig. 2.15 Section through an expanded smectite with 1.0–1.8 nm layer sequence from the Bwk horizon of a Calcic Luvisol on Lanzarote (*image M. Zarei*)

chlorite and vermiculite, or between illite and smectite, generally originating from the partial weathering of chlorite or illite. There occur also mixed layers between kaolinite and smectite. The more rare, regular mixed layers—e.g. at a ratio of 1:1—are formed by the transformation of biotite to vermiculite (hydrobiotite) or from chlorite to smectite (corrensite) through the loss of the interlayer K or of the hydroxide layer in every second elementary layer. However, silicate layers with different charges can be combined to a crystal with mixed layers already during the formation of the clay minerals from the solution.

The properties of the interstratified minerals result from the type and the proportions of the components. In general, the interstratified minerals are transitions that are more reactive than pure clay minerals.

2.2.5 Clay Mineral Formation and Transformation

2.2.5.1 Changes in the Interlayer Filling

Among the phyllosilicates, the micas muscovite and biotite as well as the primary chlorites are most important for clay mineral formation (Niederbudde 1996). Typical for these transformations is the preservation of the silicate layers, even if they do not remain unaltered, while the occupancy in the interlayer space changes. Supported by mechanical crushing, K^+ ions (Sect. 7.2) are extracted from the edges of the micas and substituted by other cations such as Ca^{2+} and Mg^{2+} , which, as hydrated interlayer cations, are not pulled into the bowl-shaped depressions in the O hexagonal ring like the K^+ ions, but rather remain substitutable with other cations. This initially leads to partly expanded layers at the edges of the crystals, and with increasing K-loss, to completely expanded layers (Fig. 2.16).

The decrease in the negative layer charge facilitates or even enables the expansion. In the

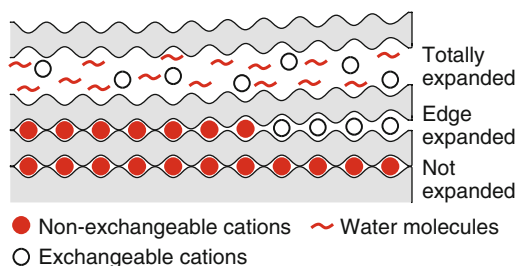


Fig. 2.16 Diagram of mica with a vermiculite or smectite layer that is not expanded, expanded at the edges, and completely expanded

micas containing Fe^{2+} (biotite), this is a result of the oxidation from Fe^{2+} to Fe^{3+} , i.e. through an increase in the positive charge. However, the decrease in the negative charge is generally lower than the extent of the $Fe^{2+} \rightarrow Fe^{3+}$ oxidation, because some of the Fe^{2+} -OH groups are transformed into Fe^{3+} -O groups by releasing H^+ , so not only the positive, but also the negative charge increases and/or part of the octahedral Fe^{3+} and Mg^{2+} is released (Fe) or bound but still exchangeable (Mg). With the dioctahedral micas, the negative charge probably decreases through $O \rightarrow OH$ transformation.

This process ultimately results in a completely K-free and expanded clay mineral, which, depending on the layer charge, is a vermiculite or smectite. In the same way, primary chlorites are transformed into vermiculite or smectite when their (Mg, Fe, Al) hydroxide layer is dissolved by protonation.

The transformation of micas into expandable three-layer minerals takes place in the soil faster the more the pH values drops and the K concentration in the soil solution decreases; the equilibrium solution for biotite is of 10–15 mg K L^{-1} , for muscovite approx. 0.01 mg K L^{-1} . This demonstrates that biotite weathers much more easily than muscovite. Plant roots and K-fixing clay minerals can lower the K concentration so much that biotite turns into vermiculite within a relatively short time (Nahon 1991).

2.2.5.2 New Formation from the Weathering (Decay) Products of Silicates

During chemical weathering, feldspars, pyroxenes, amphiboles, olivines and also phyllosilicates break down into their individual ionic components. The new minerals can form either inside (pseudomorphosis) or in the immediate vicinity of the original mineral, but also after transport of the weathering products to other soils or waters (rivers, lakes, oceans).

Close spatial contact between weathered and newly formed mineral demonstrate that structurally related parts can be adopted. Such a process is improbable for feldspars as tectosilicates, because during their transformation, e.g. to kaolinite, tetrahedral Al is transformed to octahedral Al and therefore the (Si, Al) tetrahedral bond structure must be broken; thus, in contrast to the primary phyllosilicates (mica, chlorite), the structural relationship is minor.

The type of clay mineral that is formed under a given set of conditions can be derived from the pH and the composition of the solution as well as the solubility products of the individual minerals using stability diagrams (Fig. 2.25). They indicate that smectite is formed in neutral to slightly alkaline environments and with high concentrations of Si and Mg, illite with higher K concentrations, kaolinite in the acidic range with moderate Si concentrations, and at very low Si concentrations ($<10^{-5}$ mol L⁻¹), no more silicate is formed, only gibbsite. Smectite and gibbsite are therefore mutually exclusive. This concurs with observations in nature (see Sect. 2.4.4).

With the formation of new clay minerals, Fe is generally precipitated separately as an oxide, because these are very poorly soluble.

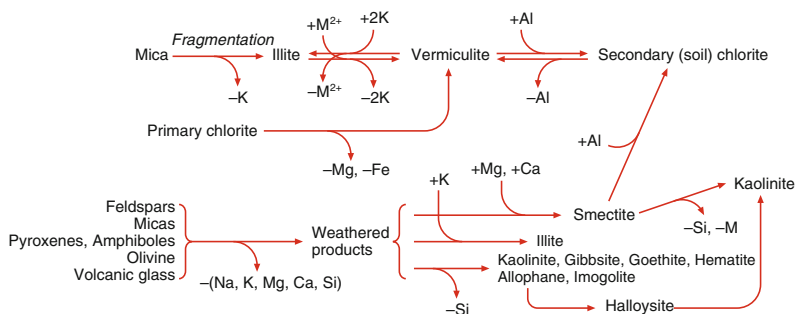
2.2.5.3 Clay Mineral Transformation

Clay minerals develop from the weathering of rock to form soil. They may originate from rocks and can be further transformed because the conditions change in a particular direction with progressive weathering. For example, the degree of acidification increases with time in soils of humid areas. As a result of this, aluminum can be liberated from various minerals and embedded between the layers of expanded three-layered minerals, and they become pedogenic chlorites. If the parent material contains vermiculite in addition to biotite, they can absorb K⁺ from the potassium-releasing biotite and turn into illite (**illitization**). With long-term tropical weathering, the Si concentration decreases so much that the initially formed smectite, as can be read from the stability diagram (Fig. 2.25), is transformed into kaolinite, and in extreme cases, even into gibbsite (**desilification**, Chap. 8). Allophane and imogolite are transformed over the course of time into the better crystallized minerals kaolinite and halloysite. Figure 2.17 summarizes the described formation and transformation pathways of clay minerals.

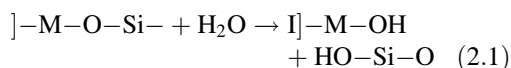
2.2.6 Oxides and Hydroxides

Minerals in this group can be both of primary and secondary origin. The most common oxide

Fig. 2.17 Formation and transformation paths of clay minerals (M = metal cation)



in rocks and soils is quartz. In contrast, Al, Fe and Mn oxides and hydroxides, as well as some Si and Ti oxides, are generally characteristic new formations of weathering, i.e. of secondary origin, and are therefore present in most soils and sediments. In primary minerals, metals are mainly bound in silicates, and are liberated during weathering by hydrolysis and protolysis (Stanjek 1997, 1998; Waychunas 1991). In doing so, their silicate (SiO_4) ligands are substituted by O and OH ligands (M = metal):



The affinity to the new ligands increases with increasing charge and decreasing size of the metal cation. If metals are oxidized when they are liberated from the silicate bond, e.g. Fe^{2+} and Mn^{2+} , their tendency towards oxide formation increases, while the tendency to form clay minerals decreases. The list of oxide minerals that are found in rocks and soils reflects a great diversity (Table 2.7).

2.2.6.1 Silica Oxides

The most important Si oxide by far in the Earth's crust is **quartz** (SiO_2). Most quartzes are of igneous and metamorphic origins (primary

Table 2.7 The oxide, oxihydroxide and hydroxide minerals of Si, Al, Fe, Mn and Ti in rocks and soils

Element	Name	Formula	Color
Si	[Quartz] ^a	SiO_2	Colorless
	Opal	$\text{SiO}_2 \cdot n\text{H}_2\text{O}$	Colorless
	[Cristobalite]	SiO_2	Colorless
Al	Gibbsite	$\gamma\text{-Al(OH)}_3$	Colorless
	(Boehmite) ^b	$\gamma\text{-AlOOH}$	Colorless
	(Diaspore)	$\alpha\text{-AlOOH}$	Colorless
	(Corundum)	$\alpha\text{-Al}_2\text{O}_3$	Colorless
Fe	Goethite	$\alpha\text{-FeOOH}$	Yellowish-brown (7.3–1.6Y)
	Lepidocrocite	$\gamma\text{-FeOOH}$	Orange (4.9YR–7.9YR)
	Hematite	$\alpha\text{-Fe}_2\text{O}_3$	Red (3.5R–4.1YR)
	Maghemite	$\gamma\text{-Fe}_2\text{O}_3$	Brownish-red (6.2YR–9.4YR)
	[Magnetite]	Fe_3O_4	Black
	Ferrihydrite	$5 \text{ Fe}_2\text{O}_3 \cdot 9\text{H}_2\text{O}$	Reddish-brown (2.8YR–9.2YR)
	{Schwertmannite} ^c	$\text{Fe}_8\text{O}_8(\text{OH})_6\text{SO}_4$	Orange (6.2YR–0.3Y)
Mn	Vernadite	$\gamma\text{-MnO}_2 \cdot n\text{H}_2\text{O}$	Blackish-brown
	Birnessite ^d	$(\text{Mn}_2^{3+}\text{Mn}_7^{4+})\text{O}_{18} \cdot \text{R}(\text{H}_2\text{O})_n$	Blackish-brown
	Lithiophorite ^e	$[\text{Al}_2\text{Li}(\text{OH})_6] [\text{Mn}_5^{4+}\text{Mn}^{3+}\text{O}_{12}]$	Blackish-brown
	(Pyrolusite)	MnO_2	Blackish-brown
Ti	Anatase	TiO_2	Light black
	[Rutile]	TiO_2	
Fe + Ti	[Ilmenite]	FeTiO_3	Black?
	Pseudorutile	$\text{Fe}_{2-x}\text{Ti}_3\text{O}_{9-x}(\text{OH})_{3x}$	

^a[] Usually only lithogenic

^b() Rare in soils

^c{ } More common in mine piles

^dThe interlayer cation R(=Na, K, Ca) is surrounded by water molecules

^eLi/Al < 0.5 in soils

quartz), a smaller fraction is formed in the soil. It accounts for 12 % vol. of the composition of the lithosphere (Table 2.1). It has a density of 2.65 g cm^{-3} , conchoidal fracture and is usually transparent/clear to white. Quartz consists exclusively of SiO_4 tetrahedra forming a continuous 3-dimensional network. Therefore, there are 4 half O^{2-} ions for each Si^{4+} ion; this results in the formula SiO_2 . The framework structure contributes greatly to the high hardness (scratch hardness 7 on the Mohs scale from 1 to 10) and weathering resistance, so that quartz is accumulated during weathering and transport processes (Headnay et al. 1994; Dixon and Weed 1989).

As a second SiO_2 modification, **cristobalite** is found in volcanic rocks and their soils. Often found in soils and sediments, **opal**, $\text{SiO}_2 \cdot n\text{H}_2\text{O}$, is a mixture of amorphous SiO_2 , poorly crystallized cristobalite and **tridymite**, another SiO_2 modification. The H_2O content of opal, depending on its degree of aging, usually ranges from 4 to 9 %, its density from 2.1 to 2.2 g cm^{-3} .

In the tropics and subtropics, Si originating from weathering can accumulate in depressions as quartz or opal. Si indurations are called **silcrete** (Chap. 8). In many other soils, opal is of biogenic origin. Topsoils contain up to several percent opal in many different shapes. This so-called **bio-opal** either comes from the supporting tissues of plants (phytoliths), especially from grasses, or the needles of siliceous sponges. Straw from cereals contains 1–1.5 % and grasses ~5 % SiO_2 by weight. The plant-specific form of the bio-opal/phytolith particles (e.g. strips or needles) often provides information on the history of the origin of the soil.

The majority of the Si liberated by weathering is used in the formation of secondary silicates. Only a small portion is precipitated as pedogenic Si oxide. It is formed from the dissolved Si that is present in the solution as orthosilicic acid H_4SiO_4 (also formulated as $\text{Si}(\text{OH})_4$). With higher concentrations and in the pH range from 5 to 7, the silicic acid tends towards polymerization and its solubility decreases. Finally, a hydrous, amorphous Si oxide is formed, which, passing through opal, slowly turns into more or less well arranged cristobalite, tridymite or quartz. In doing so, the

solubility decreases from approx. 60 to $1.4\text{--}3.3$ (quartz) mg Si L^{-1} . The solubility of bio-opal is of $2\text{--}9 \text{ mg Si L}^{-1}$. Polymerization can be inhibited by adsorption of Si on other minerals, e.g. Fe and Al oxides. In the range of pH 2–8, the solubility of Si oxides is almost independent of the pH. Above pH 8–9, they depolymerize to form silicate anions and the solubility increases.

The Si concentration of the soil solution generally lies between the solubility of the amorphous SiO_2 and of quartz. Its formation is therefore thermodynamically possible, however, it is kinetically inhibited because of the high crystallization energy. This is why quartz is only seldom found as a newly formed mineral in soils.

2.2.6.2 Aluminum Oxides

Among the crystallized Al hydroxides found in soils, **gibbsite** ($\text{Al}(\text{OH})_3$) is by far the most common. The Al^{3+} ions form octahedra with six OH^- ions that are connected via shared OH^- ions to form layers, in which $2/3$ of the octahedral centers are occupied with Al. The crystals consist of stacks of such Al–OH octahedron layers and often form hexagonal platelets or columns of clay or silt size (Fig. 2.18).

Furthermore, weathering produces two AlOOH forms, **diaspore** and **boehmite**, which mainly occur in bauxites (aluminum ore) and have the same crystal structure (isotypic) as the two Fe oxides goethite and lepidocrocite (see Sect. 2.2.6.3).

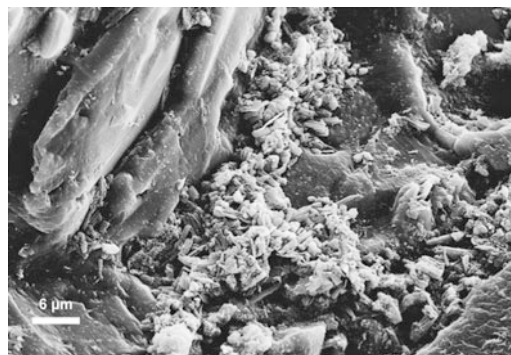


Fig. 2.18 Gibbsite crystals on quartz (Ferralsol in Northern Thailand, image M. ZAREI)

Corundum (Al_2O_3) is generally of lithogenic origin, and was also formed in tropical soils, probably during fires.

Gibbsite is formed through slow hydrolysis of the Al liberated during the weathering of silicates containing Al (feldspars, micas, clay minerals, etc.); however, this only occurs if, as is the case in some tropical soils, the Si concentration drops below 0.5 mg Si L^{-1} due to strong desilification, and is therefore no longer sufficient for clay mineral formation (Fig. 2.26). Here, for example, plagioclases can be directly transformed into gibbsite. Similarly, gibbsite results from the progressive desilification from clay minerals.

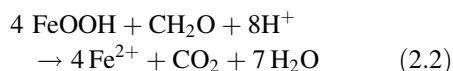
In acidic soils under temperate humid climates, no gibbsite is formed from the liberated Al, because apparently the formation of Al silicates (clay minerals) or Al sulfates, of hydroxy-Al polymers in the interlayer of expandable three-layered clay minerals, of Al complexes with humic matter, or of amorphous Al hydroxide seems to be preferred. The composition of soil solutions and the solubilities of these compounds often imply the presence of amorphous Al hydroxide or Al-hydroxy-sulfates (e.g. alunite, $\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6$ or jurbanite, $\text{AlSO}_4(\text{OH}) \cdot 5\text{H}_2\text{O}$); direct identification of these compounds has not yet been possible.

At a pH of 5, the solubility product $K_{\text{sp}} = a_{\text{Al}} \cdot a_{\text{OH}}$ (a = activity) of gibbsite (approx. 10^{-34}) results in an Al concentration of only approx. 3 mg Al L^{-1} . The amorphous form is 1–2 orders of magnitude more soluble ($K_{\text{sp}} \sim 10^{-32}$). However, because the solubility increases with decreasing pH by three powers of ten per pH-unit, gibbsite is no longer stable in the highly acidic range.

2.2.6.3 Iron Oxides

The greatest portion of iron liberated from minerals by weathering is bound in Fe^{3+} oxides and not, as with Al, in clay minerals. Because the iron in primary minerals (biotite, amphibole, pyroxene, olivine, magnetite) is usually divalent, it is oxidized by oxygen from the atmosphere in the presence of water and liberated from the silicate bond. The Fe^{3+} hydrolyzes to Fe(III) oxides already at the weathering site (see Eq. 2.12 in

Sect. 2.4.2.3), giving the soil a uniform brown or red color (Cornell and Schwertmann 1996). The ratio of the oxidized to the total iron (corrected by the Fe oxides in the rock) is therefore an indicator of the soil's degree of weathering. The ratio is 0.2–0.3 in young soils from Pleistocene sediments, and of 0.8–0.9 in old soils in the humid tropics. As very stable weathering products (see Sect. 2.4.4), the Fe hydroxides remain in the soil as long as aerobic conditions exist. Under anaerobic conditions, they are reduced with the microbial oxidation of biomass (simplified to CH_2O), i.e. they serve as an electron acceptor (Chap. 4). In doing so, they are dissolved:



The Fe^{2+} moves along a redox gradient on a cm to km scale, until it reaches aerobic areas, where it is oxidized again and precipitated as Fe(III) oxide. This results in local, sometimes hardened Fe oxide accumulations in the form of mottles, concretions and horizons (**ferricrete**, Sect. 8.2.6.2).

In soils where the Fe oxides are evenly distributed, the Fe oxide contents generally range from 0.2 to 20 %; it especially depends on the texture (sand < clay), on the parent material and on the stage of pedogenesis. In accumulation zones, like rust mottles, concretions and ferri-cretes, it can increase up to 80–90 %.

On the one hand, the significance of iron oxides for the matter balance of soils and landscapes lies in their capacity to incorporate trace elements during their formation, such as chromium and vanadium, and on the other, they bind anions such as phosphate, arsenate, chromate, selenite, but also heavy metals, firmly on their surface and reduce its mobility in soils (see Chaps. 5 and 9).

(a) Forms and properties

The two most common Fe(III) oxides in soils and rocks (Table 2.7) are the generally needle-shaped **goethite** ($\alpha\text{-FeOOH}$), and the hexagonal platelet crystals of **hematite** ($\alpha\text{-Fe}_2\text{O}_3$). Less common, but by no means rare, are **lepidocrocite** ($\gamma\text{-FeOOH}$), which

usually forms strongly lobed or toothed platelets or ledges, **maghemite**, the ferri-magnetic form of Fe_2O_3 , and the very poorly crystallized, hydrous **ferrihydrite** (formerly: amorphous Fe(III) hydroxide), which mostly occurs as aggregates with small crystals 2–5 nm in size. Small amounts of lithogenic **magnetite** (Fe_3O_4) are found in many rocks, which weathers relatively slowly. There are also bluish-green colored Fe(II,III) hydroxides, the so-called green rusts, which are formed under anaerobic conditions and can contribute to the bluish-green color of reduced horizons in groundwater (Gleysol) soils.

The only structural element of the most common Fe(III) oxide is an octahedron, where the central Fe^{3+} is surrounded by six O^{2-} or by three O^{2-} and three OH^- ions. The individual minerals differ only in the spatial arrangement of the octahedra (Fig. 2.19). The basic pattern of the hematite structure are two FeO_6 octahedra that share three oxygen ions. These double octahedra are connected to each other at the edges (i.e. two shared O^{2-} ions respectively) and form a three-dimensional framework. In goethite, $\text{FeO}_3(\text{OH})_3$ octahedra are connected at the edges to form double chains and these are linked at octahedral corners (i.e. via one shared O^{2-} ion and H^+ bridges). In lepidocrocite, the double chains form zigzag layers due to octahedral edges that are held together by H^+ bridges. In pedogenic or soilborne goethites and hematites, some of the Fe^{3+} ions are isomorphically substituted by Al^{3+} ions (in goethite up to $1/3$,

in hematite up to $1/6$ of the Fe^{3+}). Because the Al^{3+} ions are smaller than the Fe^{3+} ions (Table 2.2), the elementary cell of the Al-substituted Fe(III) oxides is somewhat smaller than that of the pure minerals.

All Fe(III) oxides are poorly soluble compounds. The solubility products $a_{\text{Fe}^{3+}} \cdot (a_{\text{OH}^-})^3$ of goethite and hematite are of 10^{-42} – 10^{-44} , that of lepidocrocite is of about 10^{-40} , and of ferrihydrite 10^{-37} – 10^{-39} . A typical characteristic of Fe oxides in soils is that, because of the very low solubility and crystallization-inhibiting substances in the soil solution, they only form very small crystals (nanoparticles) (goethite and hematite 10–100 nm, ferrihydrite 2–5 nm). Therefore, they have a very large specific surface (50 – $200 \text{ m}^2 \text{ g}^{-1}$), and can contribute significantly to the total surface area of the soil substance even at low contents.

(b) Occurrence and formation

The mineral form and the properties of iron oxides reflect the conditions of pedogenesis in many ways. Because of its high stability, **goethite** is found in soils of all climate regions and is thus the most common pedogenic Fe oxide. In the absence of hematite, it gives the soil the typical yellow to rusty-brown color. The conditions under which the Fe oxides were formed in soils can be deduced both from field observations and from synthesis trials in the laboratory. Both Fe^{2+} and Fe^{3+} are possible initial forms of iron, both of which do not exist as naked ions, but rather are initially surrounded by six water molecules. In the first step, one of these water molecules dissociates

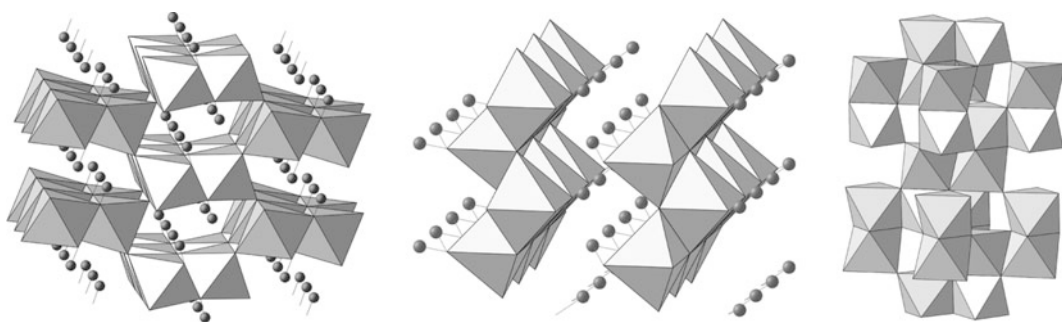
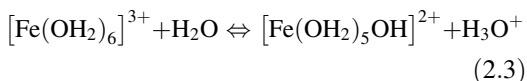
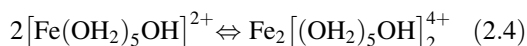


Fig. 2.19 Octahedral model of goethite (left), lepidocrocite (centre) and hematite (right). The smaller spheres are H^+ ions

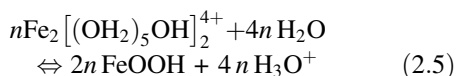
a proton and thus reduces the charge of the dissolved species. This (reversible) reaction step, which takes place both with Fe^{2+} and Fe^{3+} , is called **hydrolysis**:



The now lower-charged monomers dimerize according to:



and then polymerize, forming $-\text{Fe}-\text{OH}-\text{Fe}-$ and $-\text{Fe}-\text{O}-\text{Fe}$ bonds, resulting in crystalline iron oxides:



Which oxide is formed by this reaction depends, among other things, on the rate with which the low-molecular components are supplied, and whether the crystallization is disturbed by other components in the solution. If there is a rapid supply and/or strong disturbances, the poorly crystallized **ferrihydrite** is formed, e.g. with rapid oxidation of waters containing Fe^{2+} or in the presence of organic compounds, as in the B horizons of Podzols. The oxidation of Fe^{2+} by chemolithotrophic bacteria (e.g. species from the *Leptothrix*, *Crenothrix* or *Gallionella* genera) also often leads to ferrihydrite, which can fully incrustate the dead cells or be slimy in texture. Ferrihydrite is found in lake ores, bog irons and in the B horizons of Podzols. In general, ferrihydrite can be called a young Fe oxide; it is lacking in older, more strongly developed soils.

Orange-colored schwertmannite, $\text{Fe}_8\text{O}_8(\text{OH})_6\text{SO}_4$, occurs in acid sulfate mine waters and soils (*acid sulfate soils*) as a bacterial oxidation product of pyrite. It is structurally related to akaganeite, $\beta\text{-FeOOH}$, but probably contains sulfate in the tunnel instead of chloride.

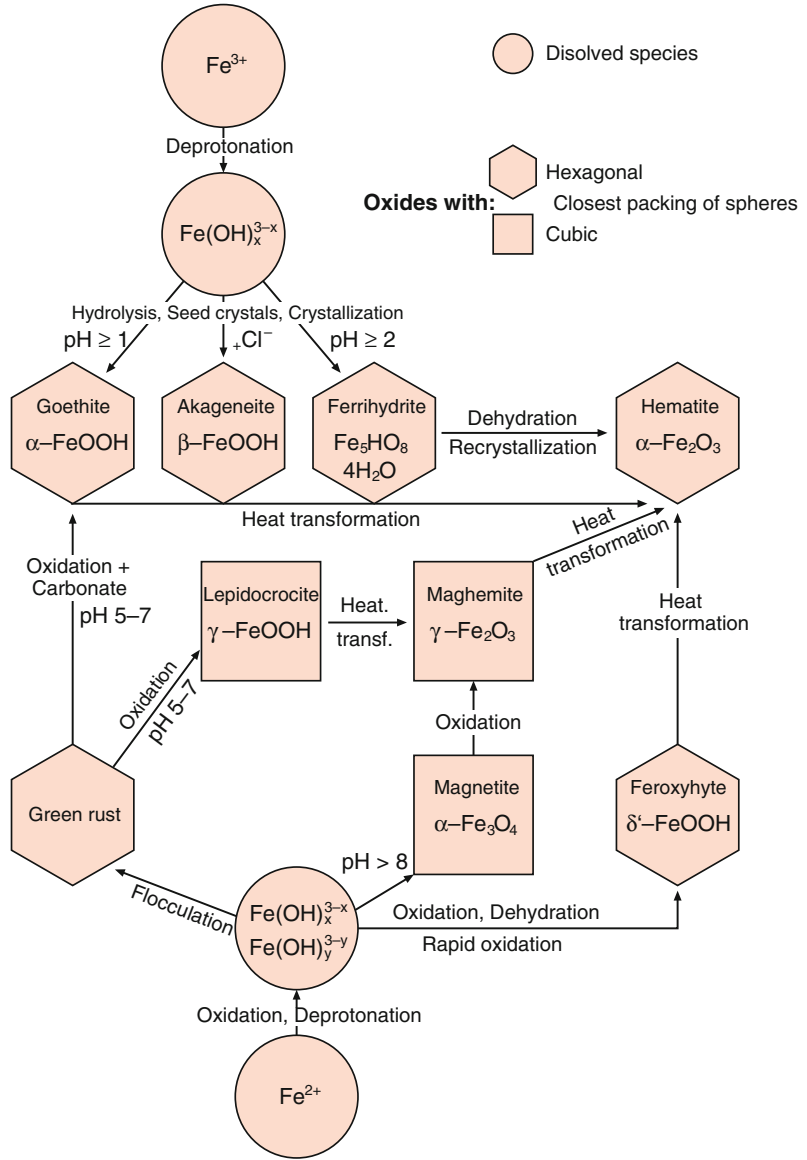
When Fe is supplied at a slower rate, like e.g. with the weathering of silicates containing Fe^{2+} (mafic), the better crystallized mineral goethite is formed. Goethite is promoted by carbonate ions when present during the oxidation of Fe^{2+} . Because there are transitions between all formation environments in soils, ferrihydrite and goethite are often associated in temperate climates; this is also because ferrihydrite is a less stable oxide that transforms into goethite through solution in the course of time. This is also delayed by substances such as silicate and organic molecules that are sorbed on the ferrihydrite.

Hematite is widespread and is closely associated with goethite in tropical and subtropical soils, giving them their red color (see Table 2.7). Synthesis trials under simulated soil conditions show that ferrihydrite is transformed into hematite and goethite in two parallel reactions. Isotope trials also show that the two reactions take place in the solution, i.e., water is required. Compared to goethite, hematite is promoted by lower moisture contents and higher temperatures. The formation of goethite, in contrast, is promoted with increasing distance from the solubility minimum of the ferrihydrite, which is in the neutral range (pH 6–8) and coincides with the zero charge point.

Because of their high stability, goethite and hematite in soils do not directly transform into each other through dehydroxylation or rehydroxylation. Hematite is not formed from goethite through the loss of water (except for fires), and goethite is also not formed when hematite absorbs water. This is not contradicted by the observation that red tropical soils containing hematite turn into yellowish-brown soils from top to bottom (Xanthization), because under more humid conditions today, hematite is preferentially dissolved by reduction or complexing with the participation of microorganisms and organic substances, and goethite remains behind.

Lepidocrocite is mainly formed through slow oxidation of Fe^{2+} at low carbonate ion concentrations. Although it is metastable compared to

Fig. 2.20 Formation and transformation paths of iron oxide minerals (after U. SCHWERTMANN)



goethite, it only transforms into goethite very slowly, so that it is persistent over a longer period of time. It mainly occurs in clayey, carbonate-free, waterlogged soils in the form of orange mottles or bands (Chap. 7).

Bacterially formed **magnetite** has been found in soils influenced by groundwater. **Maghemite** is either formed through the oxidation von lithogenic magnetite especially in basic volcanic rock, or through the effect of heat (fires) on other Fe(III) oxides in the presence of organic

substances. The association with charcoal and corundum suggests the effect of fire. Maghemite and Feroxyhyte are mainly finely distributed in tropical and subtropical soils or widely spread in concretions, because the frequency of forest fires here is high. Figure 2.20 shows a sketch of the explained formation and transformation paths for the different iron oxides.

Thus, Fe oxides reflect the pedogenic conditions in many ways. This is especially true for the goethite-hematite ratio in soils. Soils in temperate

and cool climates are usually free of hematite, while many (sub)tropical soils also contain hematite in addition to goethite. The soil hydro-sequences in these regions contain less hematite with increasing water saturation. At the same time, they are topequences where the upper, drier soils are red, and the lower, more humid soils are yellow. Even within the profile itself, yellow topsoils are often observed above red subsoils, which is a sign that hematite is not formed or is not stable in the humic topsoil of such soils. Lepidocrocite in soils of temperate zones usually indicates a reducing, CaCO_3 -free environment, ferrihydrite the presence of crystallization inhibitors (see above) or rapid oxidation of Fe^{2+} in reductomorphic soils.

The extent of Fe substitution by Al also depends on the pedogenic environment. In acidic, strongly weathered soils (e.g. Ferralsols), the Al substitution of goethite is generally high (up to $1/3$ of the Fe), in neutral or reduced soils, in contrast, it is much lower ($<1/6$). The spatial proximity to a source of Al (e.g. clay minerals) also plays a role. Finally, the crystallinity also reflects the pedogenic environment. Thus, humic soils in cool-humid climates contain more poorly crystallized goethite associated with ferrihydrite, while humus-free, strongly desilified, oxide-rich tropical soils contain more well-crystallized goethite.

2.2.6.4 Titanium Oxides

Rocks contain Ti in silicates and oxides; among the latter, **rutile** (TiO_2), **ilmenite** (FeTiO_3) and **titanomagnetite** ($\approx \text{Fe}_{2.4}\text{Ti}_{0.6}\text{O}_4$) dominate. The Ti liberated by weathering is derived from primary, easily weathered silicates (biotite, amphiboles and pyroxenes), while the poorly weatherable oxides are relatively accumulated in the soil. Titanium is not only subordinately incorporated into clay minerals during weathering, but is rather mainly precipitated as **anatase** (TiO_2), in which the Ti is partly substituted by Fe^{3+} . Anatase can also be synthesized at room temperature. **Pseudorutile** is an Fe–Ti oxide of variable composition that is formed from the weathering of ilmenite. Titanomagnetites weather (oxidize) to titanomaghemites.

The Ti content in strongly weathered soils can increase to more than 1 %, in some tropical soils on Ti-rich rocks to even more than 10 %, while in younger soils of temperate climate zones, it is usually only of 0.1–0.6 %.

2.2.6.5 Manganese Oxides

During the weathering of silicates containing Mn (e.g. biotite, amphiboles and pyroxenes), the Mn^{2+} is precipitated under aerobic conditions mainly as blackish-brown to black colored, poorly soluble Mn(IV) oxide. Mn oxides occur in soils, like the Fe(III) oxides, as mottles, particle coatings (Mangans), concretions and crusts.

The mineralogy and chemism of Mn oxides (Table 2.7) are more diverse than those of Al and Fe oxides, because in addition to the tetravalent Mn, they may also contain Mn^{3+} and Mn^{2+} , and absorb cations such as Li, Na, K, Ca, Ba, Al and Fe for charge compensation. For this reason, like the clay minerals, Mn oxides are often non-stoichiometrically composed.

Only a few of the oxides have been reliably identified in soils until now. They belong to the **phylломanganates**, consisting of MnO_6 octahedral layers with an interlayer distance of 0.7 or 1.0 nm. The 0.7 nm mineral with an H_2O layer is called **birnessite**, and the form that is expanded to 1 nm due to the embedding of a second H_2O layer is called **buserite**. The substitution of Mn^{4+} by Mn^{3+} and Mn^{2+} creates a negative charge in the MnO_6 layers, which is compensated by cations like Na^+ , K^+ , Mg^{2+} and Ca^{2+} between the layers. In **lithiophorite**, a Li–Al hydroxide layer is incorporated between the MnO_2 layers. Poorly crystallized forms of the layer types are called Vernadite ($\partial\text{-MnO}_2$).

Tunnel manganates occur more rarely in soils, in which the MnO_6 octahedral chains form tunnels of variable size that absorb exchangeable cations and water. These include the MnO_2 forms **todorokite**, K-containing **cryptomelane**, Ba-containing **hollandite**, and rarely found in soils **pyrolusite**.

The Mn oxides, like the Fe oxides, have a low solubility, but can be subject to microbial reduction and thus dissolved. Because Mn(IV) oxides are more easily reduced than Fe(III)

oxides (Sect. 4.3) and Mn^{2+} is only reoxidized with the help of bacteria, manganese is more mobile in a reducing environment. For this reason, manganese oxides are more likely to occur in soils as separate accumulations and are less likely to be associated with iron oxides. Manganese oxides have a high affinity to many heavy metals, especially to Co, Ni, Pb and Zn, and therefore co-accumulate these metals.

2.2.7 Carbonates, Sulfates, Sulfides and Phosphates

The most common carbonate is CaCO_3 , which occurs as calcite, more rarely as aragonite. Carbonates with several cations are also widespread, such as **dolomite** ($\text{CaMg}(\text{CO}_3)_2$, 13.1 % Mg) and **ankerite**, $\text{CaFe}(\text{CO}_3)_2$, which usually also contains Mg and Mn. Calcite and dolomite are the main minerals of carbonatic rocks: limestone and dolomite (Alaily 1996, 1998 and 2000).

In soils, calcite and dolomite are generally inherited from the rocks. In the lower part of soils in temperate humid regions, calcite is formed from dissolved $\text{Ca}(\text{HCO}_3)_2$ that was eluviated from the upper profile sections. It coats the inside of the pores, or often occurs in loess soils as lime concretion (loess puppet). Calcitic precipitations from CaCO_3 -rich groundwater are called meadow, spring or floodplain lime. In semi-arid regions, lime crusts are formed, called **calcretes**. The formation of dolomite (dolocretes) in soils has only been observed in isolated cases. **Siderite** (FeCO_3) is formed both in sediments and in soils under predominantly anaerobic conditions, e.g. in fens and in association with goethite in bog iron.

Anhydrite (CaSO_4) and **gypsum** ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, hardness 2) are the main components of gypsum rocks. Gypsum occurs in small amounts in many sediments and soils, especially in arid areas. Furthermore, it is formed as an oxidation product from sulfides.

For example, a K-Fe hydroxysulfate, the light yellow **jarosite**, $\text{KFe}_3(\text{OH})_6(\text{SO}_4)_2$, is found as an oxidation product of sulfides, in addition to gypsum, in acid sulfate soils at pH 2–3.

The occurrence of **baryte** (BaSO_4) is more rare. Other salts, especially soluble sulfates and chlorides, and to a lesser extent also nitrates and borates of Na, K and Mg, are sometimes found in large quantities in marine and continental deposits (salt deposits), but also in soils of arid regions.

Among the sulfides, the two forms of iron disulfide (FeS_2), **pyrite** and **marcasite**, are the most common representatives. Finely-grained and therefore black FeS_2 is widely distributed in clayey sediments that were formed under anaerobic conditions, but also in reduced soils, coloring them dark. Iron monosulfide with variable composition (Fe_{1-x}S) and low crystallinity is usually a young formation in anaerobic sediments and soils, and could be the instable precursor of pyrite ($\text{FeS} + \text{S} \rightarrow \text{FeS}_2$). Sulfides such as **greigite** (Fe_3S_4) can also be directly formed by bacteria in sediments and soils. The forms of heavy metal sulfides (e.g. those of Cu, Pb, Zn etc.) are particularly diverse.

Apatite, $\text{Ca}_5(\text{PO}_4)_3(\text{OH}, \text{F}, \text{CO}_3)$ is the most important phosphate mineral that primarily supplies the nutrient phosphorous to the pedosphere and biosphere. It has both igneous and pedogenic origins. Another, frequently occurring pedogenic Fe^{2+} phosphate, e.g. in fens (ground water peat), is **vivianite**, $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$, which is white oxidizes at the surface when exposed to air and turns bright blue.

2.3 Rocks

Rocks are solid or unconsolidated, natural mineral mixtures of the crust of the Earth. Their mineralogical composition must be uniform over a certain spatial, geologically significant extent. The most important or highest classification criterion of rocks is their genesis. The three main types of origin are: hardening or cooling down of magma (magmatism), sedimentation in the ocean or on land (sedimentation), and transformation under the effect pressure and heat (metamorphism). Classifications at lower levels and designations of the types of rocks are based on the

mineralogical composition (e.g. mica schist), the chemism (e.g. acidic, intermediary, basic igneous rock), the texture and structure (e.g. coarse-grained/fine-grained granite), the formation site (e.g. plutonite, vulcanite), the fossil content (e.g. Bryozoan limestone) and the type locality (adamellite, tonalite) (Wedepohl 1969; Wimmenauer 1985).

2.3.1 Igneous Rocks

Igneous rocks are formed from the hardening of molten magma either deep in the Earth's crust (plutonites or intrusive rocks) or at the Earth's surface (vulcanite or extrusive rocks). In both groups, the rocks are classified according to their chemical SiO_2 contents into acidic, intermediate, basic and ultrabasic igneous rocks. The designation "acidic" or "basic" refers to the silicic acid content. The mineral constituents essentially depend on the SiO_2 content, which is used to define the various igneous rocks. Figure 2.21 shows this for the most important representatives of the plutonites (top row) and vulcanites (bottom row), and Table 2.8 summarizes their chemism. In Si-rich 'acidic' rocks, quartz, alkali feldspars, Na-rich plagioclases and micas dominate, and Si-poor 'basic' rocks are dominated by Ca-rich plagioclases and dark, Fe-containing pyroxenes, amphiboles and olivines. Therefore, acidic igneous rocks are usually light in color,

and the basic igneous rocks are dark (Carmichel et al. 1974).

The chemism of igneous rocks varies according to the mineralogical constituents. As can be seen in Table 2.8, the Ca, Mg, Fe, Mn and initially also the P content increase when the Si content decreases, while the K content decreases. The corresponding intrusive and extrusive rocks concur largely in their chemical composition, however, they differ significantly in their structure (Fig. 2.21). In plutonites, the slow cooling results in relatively coarse grained minerals (e.g. with granites; from the Latin *granum* = grain), while the fast cooling of vulcanites results in a fine crystalline or even glassy matrix, in which individual coarser crystals (inclusions) can be embedded that were formed as early crystallisations out of the liquid magma (e.g. porphyritic structure).

Among the igneous rocks in the crust (mass $\sim 2.85 \times 10^{19}$ t), the granites and granodiorites account for 22 % vol., the basalts and gabbros for about 43 % vol. The rest are sedimentary and metamorphic rocks (Table 2.8). However, igneous rocks are only found to a limited extent at the surface of the earth, and are often restricted to mountainous terrain (Fig. 2.22). Granites are widely distributed in the Bohemian Massif with its bounding ranges (Riesengebirge, Erzgebirge, Fichtelgebirge, Bavarian Forest and Bohemian Forest), in the Black Forest and in the Harz, while continuous basalt masses are only found in the regions of the Vogelsberg and the Rhön, as well as in Bohemia. Larger areas of acidic igneous rocks are found in Scandinavia, the Central Alps, the Carpathians, in China, Canada, West Africa and the Pacific Cordillera of North and South America. Large areas of terrestrial basalts ('plateau basalts') and andesite as well as their glass-rich equivalents are found e.g. in East Africa, Central India, Asia (China, Japan, Indonesia, Philippines), South Brazil (Paraná basin) and again in the Cordillera of North and South America. Basic plutonites (gabbro, norite) are known in Germany from the Odenwald and Harz, much larger occurrences lie in Greenland, Scandinavia, Russia, Canada and Africa (South Africa, Zimbabwe).

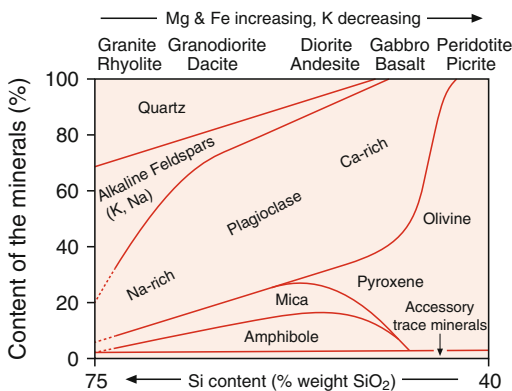


Fig. 2.21 The most common igneous rocks and their mineral constituents (after E. Murad)

Table 2.8 Average chemism (mass %, acc. to Nockolds in Wedepohl 1969) and mineral constituents (vol. %, acc. to Wedepohl 1969 and Wimmenauer 1985) of common igneous rocks

	Plutonites				Vulcanites		
	Granites	Grano-diorites	Gabbros	Peridotites	Rhyolites	Andesites	Tholeiitic basalts
SiO ₂	72.8	66.9	48.4	45.5	73.7	54.2	50.8
TiO ₂	0.37	0.57	1.3	0.81	0.22	1.3	2.0
Al ₂ O ₃	13.9	15.7	16.8	4.0	13.5	17.2	14.1
Fe ₂ O ₃	0.86	1.3	2.6	2.51	1.3	3.5	2.9
FeO	1.7	2.6	7.9	9.8	0.75	5.5	9.0
MnO	0.06	0.07	0.18	0.21	0.03	0.15	0.18
MgO	0.52	1.6	8.1	34.0	0.32	4.4	6.3
CaO	1.3	3.6	11.1	3.5	1.1	7.9	10.4
Na ₂ O	3.1	3.8	2.3	0.56	3.0	3.7	2.2
K ₂ O	5.5	3.1	0.56	0.25	5.4	1.1	0.82
H ₂ O	0.53	0.65	0.64	0.76	0.78	0.86	0.91
P ₂ O ₅	0.18	0.21	0.24	0.05	0.07	0.28	0.23
Quartz	27	21	–	–	30	5	–
K feldspar	35	15	–	–	40	11	–
Plagioclase	30	46	56	–	25	55	40
Biotite	5	3	–	–	2	–	–
Amphiboles	1	13	1		2	15	–
Pyroxenes	–	–	32	26	–	10	40
Olivine	–	–	++ ^a	70	–	–	5
Magnetite and Ilmenite	+	+	2	3	+	2	6
Apatite	+	+	+	+	+	++	+

^a+ and ++ indicate contents below the percent range

2.3.2 Sediments and Sedimentary Rocks

2.3.2.1 General

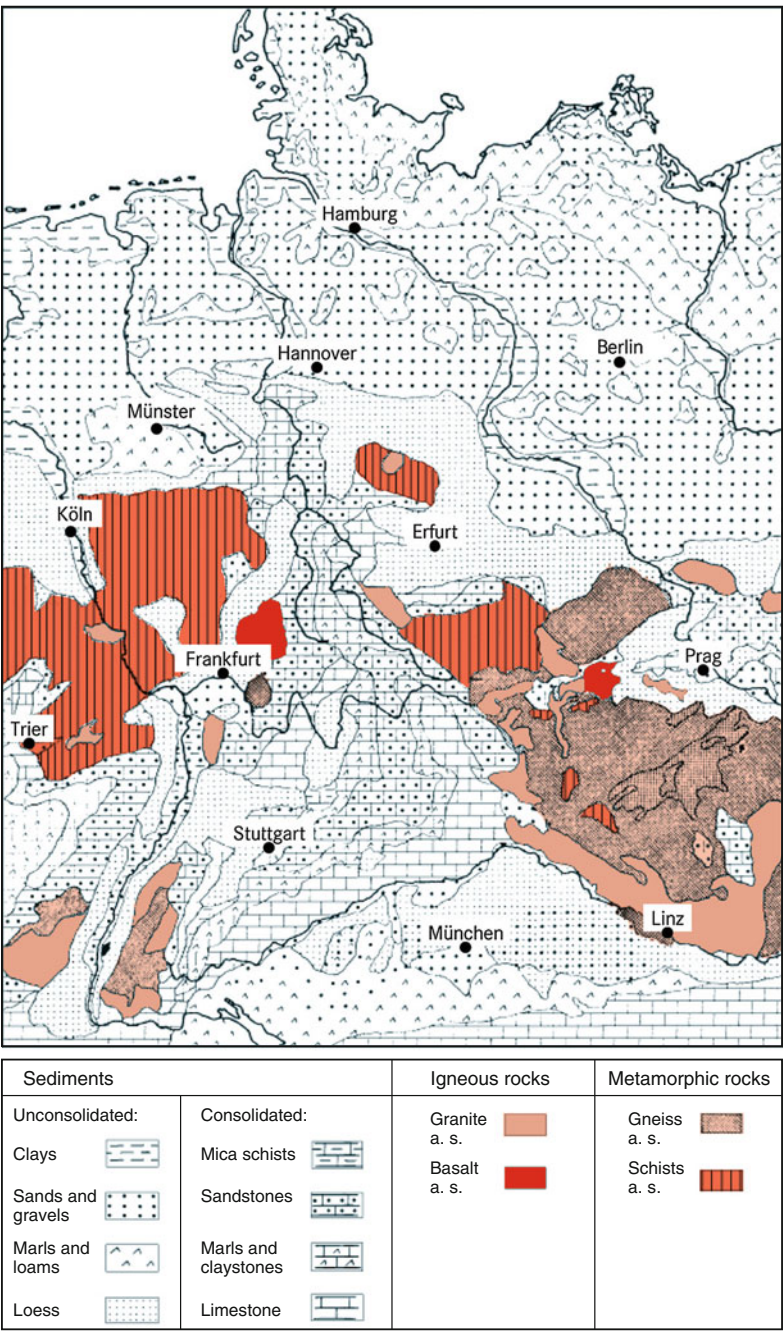
The rocks on land are exposed to the ‘weather’, i.e., they are weathered. As explained in Sect. 2.4, this results in solid and dissolved degradation products and new minerals, which form soils together with the transformation products from the vegetation (Fig. 2.1). Solid and dissolved products are eroded or eluviated by ice, water, wind and gravity, and deposited or precipitated (sedimented) at other, generally lower sites (valleys, lakes and oceans); unconsolidated sediments are formed. These consist of more or less unaltered minerals (detritus) as well as newly

formed minerals (Füchtbauer 1988; Tucker 1996).

The formation of sediment is therefore based on the process sequence weathering → erosion → transport → deposition and is often caused by soil formation (Fig. 2.1). This process sequence varied during the course of Earth history, e.g. due to climate change, fluctuations in the sea level, glaciation or tectonics. As a result of this, periods of soil formation on stable land surfaces with weathering and vegetation-friendly climate alternated with periods of soil degradation and sediment formation under vegetation-hostile climates.

If the sediments consist mainly of mechanically transported, largely unchanged rock

Fig. 2.22 Distribution of igneous rocks, metamorphic rocks and sediments in Central Europe (adapted by E. SCHLICHTING) (a.s. = and similar rocks)



material, they are referred to as **clastic** sediments. Their grain size depends on the mobility of the grains in the transport medium (wind, water, ice) and the length of the transport path, i.e. unsorted (e.g. in moraines) or relatively homogeneous, i.e. sorted (e.g. in eolian sands). In contrast, if the

sediments owe their mineral composition mainly to precipitation from the solution or biological processes (biomineralization), they are called **chemical** or **biogenic** sediments. Furthermore, sediments can be designated according to the transport medium (e.g. ice: glacial; wind: eolian)

and the deposition site (mainland: terrestrial; river: fluvial; lake: lacustrine; ocean: marine).

For clastic sediments, the different grain sizes are sorted according to the transport strength of the transport medium depending on their weight, and are thus predominantly sorted by size. Fine-grained sediments are formed with low transport forces, coarse grained with high transport forces. Rapid changes in the transport force, e.g. in river valleys, river deltas, basins and coasts, therefore lead to mixed layers between clays, silts, sands and gravels. Such mixed layers are found e.g. in the pre-alpine Molasse basin, where the erosion material from the forming Alps and the surrounding continents accumulated with alternating depositional environments (partly marine, partly fluvial and lacustrine).

All sedimentary rocks are initially deposited in loose beds, but can be consolidated over the course of time through cementation and/or the load from overlying sediments through the process of **diagenesis** to form **sedimentary rocks**. Cementation is caused by clays, Ca–Mg carbonates as well as Si and Fe oxides, which are precipitated out of correspondingly composed aqueous solution in the pore space. The load increasingly presses water out of the sediments, beds them more densely and arranges parallel sheet-formed structure of sediments. These processes both increase the contact area between the mineral grains and also the strength of the rock. In general, more and more consolidated sedimentary rocks are found with increasing geological age; Quaternary sedimentary minerals are therefore predominantly (unconsolidated) sediments, while Mesozoic and Paleozoic deposits are sedimentary rocks. These can be weathered, eroded and transported again (Fig. 2.1), so that in some cases, sediment can be subject to repeated cycles of weathering, transport and redeposition (see Sect. 2.1). Sediments can be usually recognized because they are layered and typically contain minerals in sedimentary environments such as clay minerals, carbonates, and fossils, and they accumulate stable primary minerals (e.g. quartz, rutile, zircon, heavy minerals).

The chemical and mineralogical composition of sediments varies greatly, even among those with the same name. In general, the quartz content increases and the silicate content decreases with increasing Si content (Table 2.9). Higher K contents usually indicate rocks with higher contents of potassium feldspars, micas or illites (graywackes, claystones, loess), higher Mg contents indicate rocks rich in chlorite and clay mineral (graywackes, claystones) or dolomite (dolomite), and higher Ca contents indicate calcite-rich rocks (carbonate rocks, loess).

Sediments and sedimentary rocks only account for approx. 8 % of the earth's crust, and about half of these are claystones, the rest are sand and carbonate rocks in about equal proportions (Table 2.1). However, sediments and sedimentary rocks cover about 75 % of the surface of the planet, and are therefore very significant for soils. Therefore, the average chemical composition of surface-near rocks sometimes differs greatly from that of the earth's crust (Table 2.1). The (consolidated) sedimentary rocks mostly form mountainous landscapes, while plains and valleys are filled with loose sediments.

The distribution of the individual types of sediment is generally on a smaller scale than that of igneous and metamorphic rocks, so that only a few large-scale occurrences are mentioned in the following.

2.3.2.2 Coarse Grained Sediments (Psephites)

Coarse-grained (>2 mm) sediments include scree (angular rock fragments) and pebble or gravel (rounded rock fragments). The predominant particle sizes >2 mm in angular rock fragments are called grit, and in rounded rock fragments, correspondingly, are called gravel/pebbles. Angular rock fragments indicate a high transport force, and are found in mountainous areas near the erosion site and in the valleys, where they are mainly glaciofluvial. Angular rock fragments are consolidated to form breccia, and pebbles form conglomerate (e.g. Nagelfluh). Sediments containing very coarse components in a fine-grained

Table 2.9 Average chemism (mass %) and mineral constituents (vol. %) of sediments (from WEDEPOHL)

	Sand-stones ^c	Gray-wackes	Claystones Pelites	Carbonate rocks	Eolian sand ^a	Loess ^a	Marly glacial till ^a
SiO ₂	70.0	66.7	58.9	8.2	96.8	72.8	64.2
TiO ₂	0.58	0.6	0.78	n.d. ^f	n.d.	0.77	0.48
Al ₂ O ₃	8.2	13.5	16.7	2.2	1.3	8.6	6.3
Fe ₂ O ₃	2.5	1.6	2.8	1.0	0.2	2.4	n.d.
FeO	1.5	3.5	3.7	0.68	n.d.	n.d.	3.2
MnO	0.06	0.1	0.09	0.07	n.d.	n.d.	0.06
MgO	1.9	2.1	2.6	7.7	0.1	0.85	1.0
CaO	4.3	2.5	2.2	40.5	0.1	5.1	9.7
Na ₂ O	0.58	2.9	1.6	n.d.	n.d.	n.d.	0.7
K ₂ O	2.1	2.0	3.6	n.d.	1.1	2.6	2.1
H ₂ O	3.0	2.4	5.0	n.d.	~0.5 ^c	n.d.	2.4 ^c
P ₂ O ₅	0.1	0.2	0.16	0.07	n.d.	n.d.	0.11
CO ₂	3.9	1.2	1.3	35.5	n.d.	3.4	7.7
Quartz	82	37	20	–	85	40– 45 ^d	38
K feldspars	5	28	10–15	12	13	10–15	16
Mica ^b	8	29	45–55	12	2	20	22.5
Chlorite	–	29	14	–	–	1	2
Kaolinite	–	29	14	–	–	2	–
Calcite	3	3	3	53	–	10–15	17.5
Dolomite	3	3	3	35	–	–	4
Sulfides	0.07	–	0.8	0.3	–	–	0.7

^aIndividual analyses by E. SCHLICHTING and H.P. BLUME (eolian sand, marly glacial till) and D. SCHROEDER (loess)

^bIncluding three-layered clay minerals

^cIncluding organic matter

^dValues for Central German loess

^eThe chemism is based on sandstone in the broad sense, the mineral constituents on sandstones in a more strict sense

^fNot determined

matrix indicate special deposition conditions. Bomb tuffs are formed when lava fragments fall into volcanic ash, or suevite when molten fragments fall into debris, or with mudflows into lakes or marginal seas like with greywackes.

2.3.2.3 Sands and Sandstones (Psamments)

Sands and sandstones are sediments or sedimentary rock with more than 50 % of the particle size fraction being sand (0.063–2 mm). The second most common components can be added to the name (e.g. silty sandstone with 25–50 % silt).

Sands are generally coastal or continental Cenozoic deposits by water, e.g. from the melt water of glaciers, as well as by wind (eolian sands, dune sands). Various proportions of fine, medium and coarse sand characterize the particle size distributions of the different sands.

Sandstones are found in all geological periods. In the strict sense, sandstones contain >75 % quartz. Red sandstones colored by hematite from the Paleozoic and Mesozoic (old red and young red sandstones) are widespread.

Greywackes are dark grey sandstones containing mica and chlorite and rich in rock

fragments, while arkoses contain kaolinite and are rich in feldspars.

2.3.2.4 Silts and Siltstones, Clays and Claystones (Pelites)

The texture of silt sediments is dominated by the 2–63 μm particle size fraction. The most well-known and significant silt sediment in soil science is **loess** (see Sect. 2.3.2.6). Silt-rich sediments are also formed in lakes with high sediment input.

Clays are sediments with high contents in the $<2\ \mu\text{m}$ particle fraction. They are dominated by the generally platy clay minerals, giving clays their plasticity. **Silt sediments**, in contrast, are non-plastic. In addition to clay minerals, quartz, feldspars and micas occur in both types, but also calcite, pyrite, Fe oxide and other minerals. Clays are generally formed under calm sedimentation conditions with low water transport forces.

With the diagenesis of clays and silts, water is pressed out and the platy clay particles are bedded densely parallel to each other, so that they turn into claystones and silt stones. In doing so, they progressively lose their plasticity. Claystones and siltstones are widespread in the Southern German cuesta landscapes, and claystones in the Rhenish Slate Mountains on either side of the Middle Rhine.

Poorly consolidated claystones are often easily eroded, and therefore form plains. Naturally, claystones give rise to clayey soils (Vertisols, *germ.* Pelosols).

2.3.2.5 Carbonate Rocks and Marls

Carbonate rocks are rocks with $>5\%$ Ca and Ca–Mg carbonates, predominantly as calcite and dolomite. They can be classified according to their carbonate content into **limestones** with $>75\%$ and **marl** with 25–75 % carbonate. There are transitions to claystones and sandstones. Carbonate rocks usually contain a few percent Mg, which is mainly attributed to additions of dolomite. If the dolomite content is $>50\%$ (Mg content $> 6.6\%$), they are called **dolomites**. Most carbonate rocks were formed biogenically in the ocean, so that they often have a high fossil content. They occur as unlayered compact

limestones (e.g. ‘reef limestone’) and as broad-bedded to thin-layered limestones.

During soil formation from carbonate rocks, the carbonates are dissolved and transported away. The non-carbonate dissolution residues (mainly layered silicates and quartz) form the mineral constituents of these soils (e.g. Rendzic Leptosol, Lixisol).

2.3.2.6 Quaternary Sediments

Unconsolidated sediments that were formed during and after the Quaternary glaciation are very significant for soils. They are discussed here separately according to their genesis, although they could also be classified into the scheme above.

(a) Loess, sands, floodplain sediments and mud

During the Quaternary glaciation, silt-rich material was blown out of the periglacial, vegetation-poor melt water and frost debris or rubble floodplains, tundra and arctic arid regions, which was then deposited with rainfall, decreasing winds or on the lee side of hills: loess. In recent times, wind-blown silts mainly come from hot deserts (e.g. Sahara). The Pleistocene loess belt stretches from France over the northern edge of the central European low mountain range in the Ukraine and towards Central Asia. There are other large loess areas in North America and in Argentina. In Germany, the loess thickness varies from a few decimeters up to 140 m, but it can also reach several 100 m, e.g. in China. However, a thin loess layer (4–6 dm) also covers large areas of higher terrain up to 600 m a.s.l.

Loess usually contains carbonates, is yellow in color and has a pronounced maximum grain size between 10 and 60 μm in diameter; its clay content in Central Europe is of 10–25 %, the silt content of 65–80 %, and the sand content of 10–15 % (mainly fine and medium sand). Illite dominates the clay mineral constituents in Central German loess (Table 2.9); in contrast, Southern German loess contains higher proportions of smectite. Because it was blown out of carbonate-rich deposits, the

carbonate content of Southern German loess can account for up to 35 %; in Central Germany, it is usually of 5–20 %. A coarse-grained variation of loess is **sand loess**, occurring in several patches in North and South Germany, but also at the border of loess belts like Western China, Southern Argentina or Southern Israel.

Pedogenesis began under the humid climate conditions of the post-glacial period. During this time, the carbonates in the loess of Central Europe were leached up to depths of about 0.8–1.5 m (decalcification), and the light-yellow loess was transformed into yellowish-brown loess loam through iron oxide and clay formation (brownification). Soils with higher natural fertility were formed, e.g. Chernozems and Luvisols.

In addition to loess, sands were also blown out of areas with little or no vegetation, so-called **eolian sands**, which are found all over the world as shifting sand covers or hill systems (dunes). They are found especially at coastal or valley margins, where they were populated by plants during the Holocene and thus included in pedogenesis. In deserts, eolian sands cover large areas (e.g. Sahara 28 %, Arabia 26 %, Australia 31 %). The maximum grain sizes of eolian sands are of 0.2–0.6 mm; they are generally rich in quartz, and can also be rich in calcite or gypsum in arid areas.

Loose sediments are deposited in river valleys, deltas and at the coasts around the world, their grain size ranging between gravel and clay depending on the transport conditions. The sediments in river valleys are called **fluvial sediments** (or floodplain loams), and those at the coasts are called tidal flat muds and **sands** (Chaps. 7 and 8). Young anthropogenic sediments with variable grain sizes are called **colluvium**, which are often formed at the hillside toe when soils on slopes are used for agriculture and are therefore more strongly eroded (see Chap. 7).

(b) **Glacial sediments**

When glaciers are melting, they leave moraines and lake basins behind in the areas

formerly covered by the glacier, and river terraces and sands in the areas in front of the glacier. **Moraine** material is usually poorly sorted and contains large rocks, the so-called boulders, and depending on the texture and carbonate content, is called **glacial till, boulder clay, boulder marl** or glacial sand. The former glacier boundaries were marked by wall-shaped, often sandy-gravelly terminal moraines, in which the crushed gravelly sediments are better sorted than in the ground moraines, because the fine material was washed out by melt water during the glacier's retreat. The fluvioglacial gravels of the river terraces formed at the foot of the glaciers, sands of the melt water areas, and lacustrine silts and clays in glacier tongue formed closed basins are also better sorted than moraine material.

Glacial sediments cover large areas of the Pleistocene Arctic glaciation in the northern part of the entire northern hemisphere, and of the alpine glaciers in high mountains and at their base (Alps, Himalayas, Cordilleras etc.).

(c) **Periglacial cover beds (scree) and cryogenic substrates**

Periglacial cover beds (scree) and cryogenic substrates are loose sediments that moved freely on slopes ($>2^\circ$) as a slurry over frozen underground. They occur at annual mean temperatures around -2°C in permafrost regions. In the today temperate zones, they were formed during the Pleistocene and are mainly found now in low mountain ranges as a 1–4 m-thick cover, consisting of several layers above various unconsolidated rocks or bedrock. **Solifluction material** can be recognized by the arrangement of stones parallel to the slope, flow patterns, and often platy structure.

They often display a regular sequence of basis (Basislage), main (Hauptlage), top (Oberlage) and cover layers (Decklage) (German soil description rules). The texture and mineral constituents of **solifluction material** are determined by the parent material and can therefore vary considerably. **Solifluction material** is often rich in silts,

because thin loess layers are transported and mixed with frost debris from the underlying rock. Stone-rich **solifluction material** is called solifluction debris. Cryogenic soils occur on level terrain due to **cryoturbation** triggered by freeze/thaw cycles.

2.3.3 Metamorphic Rocks

Igneous and sedimentary rocks can be so strongly altered by high pressure, high temperature and tectonic movement (metamorphism) that they sometimes turn into an entirely different rock, called metamorphic rock. Metamorphic rocks originating from igneous rocks have the prefix **ortho-** (e.g. **orthogneiss**), and accordingly, those originating from sediments have the prefix **para-**. Depending on the parent material and the degree of metamorphism, they can have very different chemical properties and especially mineralogical properties. Higher pressures and/or temperatures result either from the high load applied by overlying thick layers of rock, or from the formation of mountains (regional metamorphism). Furthermore, rocks can be transformed by contact with hot magma (contact metamorphism).

Metamorphism begins at about 200 °C and, except for contact metamorphism, 200 MPa (corresponding to a depth of 7 km), and reaches up to about 600–700 °C and 1–2 GPa (corresponding to a depth of 35–70 km). Typical for metamorphism is the transformation of a mineral inventory defined by the parent material into a new mineral association adapted to the pressure and temperature conditions. It changes the rocks much more drastically than diagenesis (Sect. 2.3.2.1), because the minerals are aligned, coarsened and transformed. The chemism of the rocks hardly changes, unless there is migration of pore solutions (metasomatism).

The alignment of the minerals, i.e. the parallel arrangement of sheet or platy minerals perpendicular to the main direction of pressure, results in schistosity, a characteristic feature of many metamorphic rocks. The position of the schistosity areas in the crystalline rock is usually not identical with the position of the layers in the

parent sediments. Coarser calcite crystals (sugar like grains) result e.g. from the metamorphism of carbonate rocks to **marble**. Typical new minerals include mica (sericite), epidote, chlorite, serpentine, talc, garnet, disthene, staurolite, andalusite and sillimanite.

Gneiss is a common metamorphic rock, originating from granite (orthogneiss) or various Si-rich sediments (paragneiss) and accounting for approx. 20 % of the lithosphere (Table 2.1). In terms of their mineralogy, they are often similar to granites or diorites (>20 % feldspars), but differ from these because especially the mica plates or platelets are arranged in parallel. **Phyllites** and **mica schist** (<20 % feldspars) are also widespread, usually originating from clays, claystones greywackes. While there are hardly any micas in claystones, they can already be clearly seen in phyllites as fine flakes, and in the form of larger crystals in mica schists. Si-poor igneous rocks (e.g. basalt) are transformed into **green schist**, **amphibolites** and **eclogites**. High-purity limestones are changed into marble, marls are transformed into mica schist with highly variable mineral constituents, depending on the degree of metamorphism. **Quartzites** are formed from the metamorphism of quartz-rich sands and sandstones. Contact metamorphism of siliceous rocks results in very fine, massive **hornfels**. Under very strong metamorphic conditions, there is initially partial melting (anatexis) and finally, total melting (diatexis) of the rocks.

Metamorphic rocks are most commonly found worldwide in the old continental shields (cratons), which were later exposed through erosion or covered with younger rocks (basal complex or basement). They form large areas in Scandinavia and Canada, where they are often covered with Quaternary sediments. There are continuous areas of metamorphic rocks in the tropics and subtropics (West and Central Africa, Brazil, West Australia, India). Younger metamorphic rocks are found in the alpinotype mountains (Alps, Himalayas, Andes etc.). In Central Europe, metamorphic rocks are found e.g. in the Black Forest, in the Vosges, the Bavarian-Bohemian Massif, the Rhenish Massif, the Harz and the Central Alps.

2.3.4 Anthropogenic Substrates

Especially in urban industrial areas, humans relocate naturally developed soil or rock material, and/or deposit technogenic substrates. Soils also develop from such anthropogenic substrates or mixed substrates.

Relocated natural substrates are usually from soil removal by leveling and excavation for construction projects (buildings, verges and road cuts, railroad cuts and canals), some of which are spread over an area, and some are piled up in banks, dams or hills. Large-scale mine piles, some of which were populated at a later time, were created due to the mineral extraction of e.g. coals and ores. A very special form of natural substrate is the broken igneous rock used as rail pavement in railway construction, where the interstices of the crushed rocks can contain transported dusts (soil material, emissions) and formerly also soot from steam engines; it serves as a harsh rooting medium and arid site for wild plants. The fill can be attributed to dumping or flushing. Both lead to stratification: In general, dumped rock is bedded more loosely than flushed material, but it can be compacted with leveling.

The relocated substrates are divided according to their textures, because these strongly influence the ecological properties of the soils that develop from them.

Most mine piles from coal mining (e.g. in the Ruhr, Saxon, British and American coal mining areas) contain pyrite. Within a few years, the pyrite is oxidized with the participation of bacteria (e.g. *Thiobacillus ferrooxidans*) to form Fe (III) oxides and sulfuric acid (Chaps. 5, 6, Sect. 8.2). Depending on the pH, jarosite, schwertmannite, ferrihydrite or goethite are formed.

Already during Roman and medieval times, dwelling mounds were often covered with topsoil material or sod. The current building regulations prescribe that the 'topsoil' be separately removed and spread back over the surface after termination of the construction measures.

Artificial **technogenic substrates** are defined as fill made of material that was created or

strongly altered by humans, such as brick, mortar, concrete, slag, waste, sewage sludge or ashes. It is not only characteristic for these substrates to contain highly variable solids, minerals are per definition of natural origin but also a pronounced heterogeneity in the composition and the contaminants. These substrates therefore differ greatly in their properties and lead to very different soils (Sect. 8.7.4).

Building rubble usually consists of a mixture of brick and mortar debris with 20–75 % porous rocks, 5–10 % limestone, and various proportions of gypsum. Brick debris from the Middle Ages can also be completely free of carbonates. Secondary components may include ashes, coal, concrete, gypsum, metals, glass and porcelain fragments, leather and bones.

Ashes may occur as fine-grained fly ash, or as more coarse-grained boiler ash from coal fired power station or waste incinerating plants. They generally react strongly alkaline (pH values 8–12). Ashes from coal combustion are low in carbonates (<0.5 %), and those from waste incineration are rich in carbonates (>10 %). They were spread over areas or dumped on mine piles, but fly ashes also hydraulically pumped and cover large areas.

Slags from blast furnaces (with lump slag, foamed slag and slag sand) or steelworks are coarse-grained, porous, calcareous and react strongly alkaline (pH values 9–12), in contrast, gasworks slags react very acidic. They are found in mine piles or as building material for structural, underground and traffic route engineering.

Waste is divided into household waste, over-size waste, trade waste, road litter and industrial hazardous waste. Household waste contains materials such as ashes, metals, glass and ceramic fragments, rubber, cardboard, leather, bones, plastics, wood and other substances. Since the introduction of waste separation, plant material should mainly be disposed of in the organic waste bin, making it rich in protein and thus readily decomposable by macro- and micro-organisms. Waste is fine to coarse grained and reacts alkaline. Its lime content fluctuates greatly (especially depending on the proportion of building rubble). Waste was formerly disposed of over large areas

or used to fill depressions (e.g. gravel quarries), and today, it is stored in the form of compact, supervised dumps or incinerated in waste combustion facilities (thermal power plants); the resulting slags and ashes are landfilled.

Sewage sludge is the residues from wastewater treatment. Fresh sludge from the mechanical treatment is inhomogeneous; in contrast, decayed or rotten sludge is fine-grained and homogeneous. Sewage sludge is rich in readily decomposable organic matter, however, depending on the type of conditioning, it may also contain higher amounts of carbonates and metal sulfides. It reacts strongly alkaline and is generally landfilled as rinsed material, unless it can be used as a soil conditioner on fields (see Sect. 7.4).

Industrial sludge comes from the treatment of commercial and industrial wastewater. There are more than 100 different kinds of sludge, depending on the sector, with highly variable properties: sludge from the metal-working industry is generally rich in metals and poor in carbonates; tar and oil sludge as well as lacquer and paint sludge contains a wide variety of organic compounds, lime sludge is rich in carbonates; paper pulps represent a mixture of cellulose, lime and kaolin clay, sludge from flue gas desulfurization is rich in gypsum; sludge from breweries, distilleries, dairies and the food industry is rich in readily decomposable organic matter, contains bentonite or diatomaceous/infusorial earth.

2.4 Weathering

Minerals in igneous and metamorphic rocks were formed under completely different physico-chemical conditions, as they occur in soils, the direct contact between the lithosphere, atmosphere, hydrosphere and biosphere. As a result, parent materials and their minerals weather in soils. In addition to humification, weathering is the most important matter-altering process of soil formation; it comprises a multitude of physical, chemical and biotic processes.

2.4.1 Physical Weathering

Physical weathering causes the decay of rocks and minerals into smaller particles, without altering the minerals chemically. It is mainly initiated by pressure release of overburden, by temperature, ice and salt bursts, through root pressure, as well as through mutual mechanical strain in the rocks.

When solid bedrock is gradually freed from overlying rock or ice masses by erosion, the load is reduced and they expand as a result of the **pressure release**. This leads to the formation of joints, and cracks, where the other forces of physical weathering can attack.

Among these forces, the effect of **temperature bursting** increases the greater the range of the temperature fluctuations and the greater the speed of temperature change. Extreme values are reached e.g. in high mountains and in subtropical and tropical deserts. Daily fluctuations of 30–50 °C were measured in deserts with annual mean temperatures of >17 °C. The temperatures of rock surfaces reached up to 84 °C, and then dropped to 20–30 °C within a short time due to rain. Because the thermal conductivity of rocks is low, their outside and inside are warmed or cooled at different rates through rapid changes in temperature. Therefore, they expand or contract differently, leading to pressure differences reaching up to 50 MPa. This results in fissures parallel to the surface, but also to cracks straight through larger boulders (core cracks). Rock flakes break off the surface and rock boulders fall apart into sharp-edged rubble. This process is accelerated by different color and expansion coefficients in adjoining mineral grains. Granite is more easily decayed than basalt, because it has a coarser structure and consists of light- and dark-colored minerals.

The effect of **ice bursting** (cryoclastic) can be even stronger than the bursting effect caused by temperature differences. This is based on the properties of water, which increases its volume by about 10 % when it freezes. For this reason, ice is able to develop a considerable bursting effect in rock fractures and cracks. Jointed rocks and minerals with good cleavability, such as

micas and feldspars, are particularly vulnerable. The bursting effect, which can reach a pressure of 210 MPa with temperatures dropping down to -22°C , only reaches its maximum potential if the ice cannot expand into voids that are filled with air, i.e., if the cracks or pores are closed by a firmly adhering ice plug during cooling. As a result, the effect of ice bursting increases with the size of the joint and pore volume, the degree of water saturation, and above all, the frequency of freeze-thaw cycles. Ice bursting transforms solid rock into angular rock fragments, grit, sand, silt and even coarse clay. Its effect is particularly strong in climate regions where there are frequent alternations between freeze and thaw periods (e.g. in periglacial regions; see Sect. 8.2.1.1).

Salt bursts work similarly to ice bursting. In arid regions (hot and cold deserts), dissolved substances are not eluviated, accumulating in the soil and on the outer surfaces of rocks with the evaporation of water. If salts crystallize out of oversaturated salt solutions, significant pressure can arise if the sum of the volumes of the saturated solution and the precipitated crystals is greater than the volume of the oversaturated initial solution. The volume can also increase through the formation of hydrates, e.g. when anhydrite, CaSO_4 , turns into gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. This may result in pressures of several tens of MPa. Analogous to with ice bursting, salt burst is promoted by frequently alternating drying and wetting cycles.

Mechanical weathering of rocks can also take place through swelling and shrinking processes in layered silicates. The hydration of cations in the interlayer space of such silicates takes place in stages, where, e.g. in smectites, up to four layers of water molecules are incorporated (**intracrystalline swelling**). The swelling pressure arising from the embedding of the first water layer is of ~ 400 MPa, and from the second and third layers of ~ 110 and ~ 27 MPa. If claystones with dehydrated layered silicates are exposed at the surface through erosion, the load becomes lower than the swelling pressure and the layered silicates can take up water layers and increase in volume.

Further expanding takes place through **osmotic swelling**, where the water between the clay particles diffuses, and dilutes the higher ion concentration in the diffuse double layer surrounding it relative to the outer solution. However, the pressures generated by osmotic swelling are much lower, only around 2 MPa.

Plant roots can also penetrate into fissures and cracks and press rocks (root burst) apart through their growth (thickening). This results in pressures of max. 1–1.5 MPa.

The rock fragments formed by physical weathering are rubbed and hit against each other during transport by ice, water or wind. This mechanical strain rounds the rock fragments and creates fine material, occurring faster and more strongly when the individual mineral grains are softer and easily divided. Feldspars, micas and amphiboles and pyroxenes are therefore more rapidly reduced to small fragments than quartz. For example, to be reduced to a size of 2 cm in a creek with 0.2 % slope, a 20 cm large granite boulder would have to be transported over a distance of approx. 11 km, a boulder of gneiss of the same size over 5–6 km, and a soft sandstone only 1.5 km.

In vegetation-poor regions, sand transported with the wind can contribute to the physical weathering of solid rocks (**abrasion**).

The significance of physical weathering for soil formation is presumably low in humid tropical and subtropical regions, where chemical weathering dominates. In former glacial regions of the northern hemisphere, in contrast, it generated large amounts of fine material from solid rocks (see Sect. 2.3.2.6), in which pedogenesis could take place faster than on solid bedrock.

2.4.2 Chemical Weathering

Chemical weathering includes all heterogeneous reactions, i.e. occurring between the solution and solids, causing the minerals, contrary to physical weathering, to change their chemism or be fully dissolved. Because it attacks the surface of the minerals, its effect increases with decreasing

grain size of the minerals. In this respect, physical weathering is a forerunner of chemical weathering.

In addition to oxygen, the most important agent of chemical weathering is water, which dissolves the minerals, cleaves them hydrolytically or disintegrates them. The effect of water is increased through inorganic (H_2CO_3) and organic acids as well as through rising temperatures (exception: poorly soluble carbonates). In addition to readily soluble minerals, chemical weathering also includes poorly soluble minerals, especially the silicates. It breaks them down into their components, from which new minerals are then formed, either at the weathering site, i.e. in the soil cover (pedogenic minerals), or after transport of the dissolved weathering products into depressions, lakes and oceans.

Many of these newly formed minerals differ from the parent minerals of igneous and metamorphic origin, in that they are more finely grained, more poorly crystallized, oxidized and/or richer in OH-groups and water. In this way, they reflect the specific conditions of mineral formation at the Earth's surface.

2.4.2.1 Dissolution Through Hydration

Dissolution is defined as the transition of a mineral in the aqueous weathering solution, without involving a chemical reaction in the strict sense. The driving force of dissolution is the striving of the ions at the mineral surface to surround themselves with H_2O molecules in the presence of water, i.e. to hydrate and thus to dissociate. The bonds of these H_2O molecules to the ions of the mineral are stronger than those of the ions within the crystals of such minerals. Accordingly, energy is released during hydration (hydration energy, see Table 5.8).

This is the process involved in the weathering (dissolution) of most alkaline and alkaline earth chlorides, sulfates and nitrates, whose solubility is quite high at several 100 g L^{-1} (Table 2.10). Readily soluble salts are those that are more soluble than gypsum. Dissolution weathering is significant in soil formation from salt and

Table 2.10 Solubility of salts that also occur as minerals in water at 20°C

Salt	Mineral name	Solubility/ g L^{-1}
$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	Gypsum	2.4
Na_2SO_4	Thenardite	48
NaHCO_3	Nahcolite	69
$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$	Mirabilite	110
$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$	Bischofite	167
$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$	Natrite (soda)	216
KNO_3	Nitrocalite (potash saltpeter)	315
KCl	Sylvine	344
$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	Epsomite	356
NaCl	Halite	359
CaCl_2	Hydrophilite	745
NaNO_3	Sodium nitrate Nitrohalite (chile saltpeter)	921
$\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	Nitrocalcite	1212

gypsum rocks, and in saline soils (Chap. 8). Salts such as NaCl and gypsum, which enter soils in humid regions through seawater, irrigation, fertilization and road salt, are rapidly leached out.

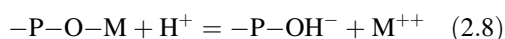
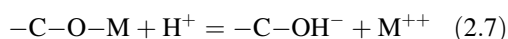
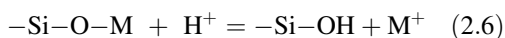
2.4.2.2 Hydrolysis and Protolysis

If the components of the minerals react chemically with the H^+ and OH^- ions of dissociated water, it is referred to as hydrolysis. Especially compounds that consist of a weak acid and/or weak base, e.g. carbonates and silicates, are subject to hydrolysis. Thus, the majority of rock-forming minerals are affected.

In soils of humid climate regions, the reaction with the H^+ ions of the solution is the actual driving force of this type of weathering. Here, oxygen bridge bonds between metals M (Fe , Al , Ca , Mg , K , Na etc.) and Si (silicates), C (carbonates) or P (phosphates) are broken, the Si-O-M , C-O-M and P-O-M groups are protonized to form $-\text{Si-OH}$ (silanol), $-\text{C-OH}$ (hydrogen carbonate) or $-\text{P-OH}$ (hydrogen phosphate), and the metals are liberated:

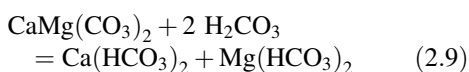
Table 2.11 Solubility of CaCO_3 in water depending on the CO_2 partial pressure at 25 °C

CO_2 partial pressure (kPa)	Solubility (mg $\text{CaCO}_3 \text{ L}^{-1}$)
0.031 ^a	49
0.33	117
1.6	201
4.3	287
10	390

^aCorresponds to the average partial pressure of air

Equations 2.6–2.8 show that the equilibrium shifts to the right side with increasing H^+ concentration (decreasing pH) of the solution; acidic solutions therefore weather more strongly than neutral solutions.

These weathering processes will first be described using the example of carbonates. Poorly soluble dolomite is decomposed by carbonic acid to form readily soluble Ca^{2+} and Mg^{2+} hydrogen carbonates:



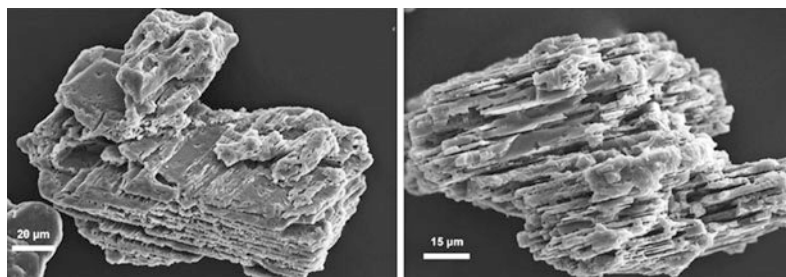
The concentration of carbonic acid in the weathering solution increases according to $\text{CO}_2(\text{g}) + \text{H}_2\text{O} = \text{H}_2\text{CO}_3$ (g = gaseous) with the CO_2 partial pressure of the air it is in equilibrium

with. For this reason, the solubility of the carbonates increases in the same direction (Table 2.11).

Contrary to many other weatherable minerals, the solubility of carbonates drops with increasing temperature, because the solubility of CO_2 in water decreases in the same direction. Thus, at a CO_2 partial pressure of 0.03 kPa, the solubility of calcite at 25 °C is of 49 mg, at 15 °C of 60 mg and at 0 °C of 84 mg $\text{CaCO}_3 \text{ L}^{-1}$. Still, carbonates in a warm soil are generally more readily dissolved than in cool soils, because the CO_2 partial pressure of the soil air is higher due to the more intensive biological activity. Carbonate weathering leads to the degradation of carbonate rocks, and to the decalcification of soils containing carbonates formed from loess, calcareous glacial till, and other rocks containing carbonates.

The hydrolysis of silicates is explained using the example of feldspar. Figure 2.23 shows feldspar crystals at different weathering intensities from a soil. The holes in the surface and its regular form indicate that during weathering, the feldspar dissolved without preference to individual components (e.g. Ca^{2+}), i.e. **congruent**, and the geometry of the leaching of the components depends on the crystal structure (here the framework structure). The same is true for the weathering of a hornblende, which then exhibits other weathering forms, corresponding to its band structure.

As solid products of hydrolytic cleavage of potash feldspars, clay minerals such as kaolinite are formed from the ionic and molecular decomposition products (Eq. 2.10)

**Fig. 2.23** Structure-oriented dissolution examples of mineral grains from a soil; potash feldspar (*left*) and plagioclase (*right*) with advanced weathering (*image* M. ZAREI)

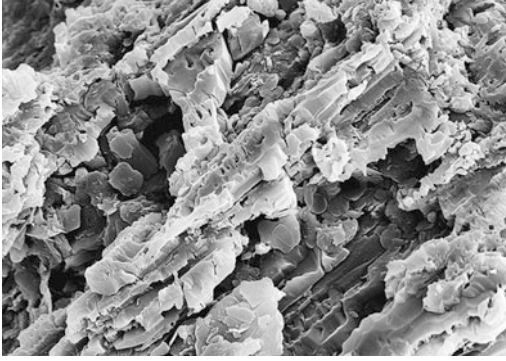
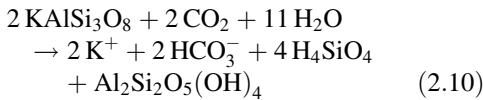
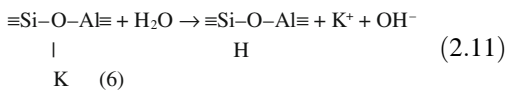


Fig. 2.24 Kaolinite newly formed by weathering in dissolution caverns of a potash feldspar (*image width 56 μm; SEM image by M. Zarei*)



In contrast, incorporation of liberated potassium leads to the formation of illite (Fig. 2.24).

Equation 2.10 is an example for an **incongruent** dissolution reaction, because the activities of the dissolved species are controlled and altered by the newly formed solid phase (in this case kaolinite), and no longer corresponds to the chemism of the parent mineral. However, the formulation of the equation does not say anything about the mechanisms of dissolution on an atomic level. In the first step, the K^+ ions at the surface of the fresh feldspar are replaced by H^+ ions and enter the solution. If this reaction takes place in pure water, KOH is formed, which can be seen in the alkaline reaction of a suspension of feldspar powder in water:



The protonation destroys the Si–O–Al bond and leads to the complete dissolution of the feldspar with the liberation of dissolved ions, from which secondary (clay) minerals are formed if their solubility products are exceeded. Si–O–Si bonds must also be broken. The stability of the Si–O–Si bond depends on the type of structurally

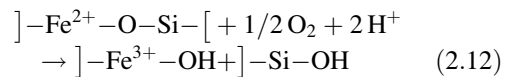
neighboring metal ions. It is higher the stronger its tendency towards covalent bonding; the bond therefore becomes stronger in the sequence $\text{K} < \text{Na} < \text{Ca} < \text{Mg} < \text{Al}$. For this reason, pure Al silicates such as andalusite are found detrital and unaltered in some sandstones.

The newly formed minerals can be deposited at the surface of feldspars, or when the feldspar is dissolved, they can fill its volume and take on its former shape (**pseudomorphosis**), as is often observed with kaolinite and gibbsite.

The transformation explained for potash feldspars can be also applied, in a more or less modified form, to other silicates such as plagioclase, pyroxene and amphibole and olivine. A special characteristic of platy phyllosilicates (mica, chlorite) is that in the first weathering stage, they only loose the embedded components between the elementary layers (e.g. K^+ in micas), so that although the layer bonding is weakened, the sheet-like structure as a whole is initially maintained (cf. Sect. 2.2.5).

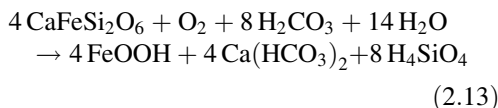
2.4.2.3 Oxidation and Complex Formation

Many minerals such as biotite, pyroxene, amphibole and olivine contain Fe and Mn in the reduced, divalent form. They are therefore oxidized in weathering environments containing O_2 , i.e. in contact with the atmosphere. This breaks the bonds in the mineral and liberates the oxidized Fe and Mn, which are hydrolytically transformed to oxides and hydroxides. For silicates, this results in the following basic reaction (with] as solid phase):



The oxidation of iron can also take place inside the mineral structure, so that the positive charge increases. To equalize the charge, other cations, e.g. K^+ in biotite, can exit the structure or OH groups can be transformed into O groups. With the weathering of biotite, Fe^{2+} is liberated in addition to K^+ and precipitated as Fe(III) oxide. Biotite thus loses its black color and becomes

bleached. Protolysis is also involved in the oxidative weathering of Fe(II) silicates, as shown by the following weathering reaction for pyroxene:

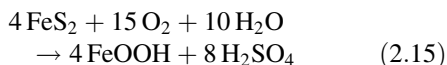


The oxidation of magnetite, Fe_3O_4 , results in maghemite or hematite (Eq. 2.14), and the oxidation of titano-magnetite correspondingly in titano-maghemite or titano-hematite:

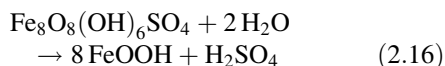


Oxidation processes in minerals therefore promote their further degradation. In addition to Fe(II) silicates, siderite (FeCO_3) and other Fe(II) minerals are also subject to oxidative-hydrolytic weathering. Because the formed Fe(III) oxides have a pronounced brown, yellow or red color, the weathering of most rocks is accompanied by the corresponding coloration (e.g. brunification, browning).

With iron sulfides such as FeS and FeS_2 (pyrite), the sulfide ions are also oxidized in addition to Fe^{2+} . This oxidation results in goethite (FeOOH) and sulfuric acid (H_2SO_4):



If the pH falls below 3, Fe^{2+} can only be oxidized bacterially by *Thiobacillus ferrooxidans*. Furthermore, at these low pH values, the Fe^{3+} ion is no longer fully hydrolyzed ($\text{OH}/\text{Fe}^{3+} < 3$), and instead of Fe(III) oxides, Fe(III) hydroxysulfates such as schwertmannite or jarosite are formed, where the potassium comes from the weathering of minerals containing K. If the sulfate concentration drops or the pH changes, schwertmannite is hydrolyzed to goethite:



Depending on the proton buffering capacity of the accompanying minerals, the pH may drop to such low levels in oxidizing mining dumps containing

pyrite or in marshes that they significantly impede plant growth. The toxic effect of low pH values is even amplified by the liberation of Al^{3+} from silicates. Mine pile contamination can be counteracted either by liming or preferably by covering (air exclusion) to prevent oxidation.

2.4.3 Role of the Biota

Weathering is generally more intensive in a living, rooted soil than in a lifeless environment. This is particularly due to the contribution of plant roots and the lower representatives of the soil flora (bacteria, algae, fungi).

In principle, the mechanisms taking place with biotic weathering are the same as for chemical weathering. The main effect is from the biotically produced acids, e.g. during the decomposition of litter. In addition to carbonic acid, these are especially low-molecular organic acids such as oxalic acid, tartaric acid, malic acid and citric acid, but also aromatic acids such as benzoic acid. The liberation of metals, which form stable complexes with organic ligands (e.g. citrate), is promoted by organic complexing agents. Mainly Al, Fe and Mn, as well as heavy metals like Cu and Pb, are bound by organic complexing agents. Humic substances, especially fulvic acids, also participate in the complex formation with metals (see Chap. 3).

Furthermore, the microbial oxidation of organic sulfur and nitrogen favors the formation of H_2SO_4 and HNO_3 . Finally, this also includes proton release from plant roots in exchange for absorbed metal cations (see Chap. 4).

In soils, the surfaces of the crystals of primary silicates are often densely covered with fungal hyphae, bacteria or algae, so that there is close contact between the organisms and the mineral surface. This contact can lead to more intensive weathering due to the excretion of organic acids and complexing agents. Lichens produce e.g. oxalic acid, which reacts with Ca^{2+} and Mg^{2+} from the rocks to form Ca- and Mg-oxalate. The low solubility of these oxalates promotes weathering because the liberated metals are

excluded from the weathering solution. Thus, biotites lost potassium after spending a longer period in the A horizon of acidic forest soils. Here, the hyphae penetrated between the exfoliated biotite crystals. From 1 kg of granite fragments within a period of 30 days, 160 mg Fe, 100 mg Al and 220 mg Mn were dissolved in the presence of a complex soil microflora; in contrast, only 0.2 mg Fe, 0.5 mg Al and 10 mg Mn were dissolved in a sterile environment.

Such dissolution processes are important for plants because of the mobilization of phosphate from poorly soluble Ca-phosphates, e.g. apatite. Similar dissolution phenomena were also observed in the rhizosphere (=immediate root periphery). Iron-complexing root exudates, so-called **siderophores**, dissolve the Fe(III) oxides and thus ensure the Fe supply for some plants.

2.4.4 Weathering Stability

Minerals are thermodynamically stable, if they are in equilibrium with their chemical surroundings under the given pressure and temperature conditions. This definition only has limited applicability for soils, since equilibrium is seldom reached between the minerals and weathering solution in nature, because the weathering products are constantly being extracted by: (a) removal in dissolved form, (b) formation of poorly soluble new minerals (clay minerals, carbonates, oxides and hydroxides), and (c) the formation of organic complex compounds with Al and Fe, especially in soil horizons that are rich in humus. Soils are not closed, but rather open systems, with substances added to and/or removed from the system. For this reason, dynamic equilibria are established with time, where the mineralogical composition continuously adapts to the substance changes. This is why weathering always is a never-ending process. Chemical weathering and formation processes in soils should therefore always be considered both thermodynamically and kinetically.

2.4.4.1 Thermodynamic Stability Conditions

The stability of minerals against chemical weathering correlates with the water solubility. Readily soluble minerals such as salts (e.g. rock salt) therefore weather most rapidly. The sequence continues with the slightly less soluble gypsum, the carbonates (calcite > dolomite) and finally the even less soluble primary silicates.

The stability of primary silicates depends on several factors, which often interact. These include the structure type, the Si–Al substitution, the type of metal cations, which connect the SiO_4 tetrahedra, and the content of oxidizable cations like Fe^{2+} and Mn^{2+} . In general, the stability of the various structure types increases in the sequence orthosilicates- < chain silicates- < phyllosilicates- < tectosilicates, since the linking of the SiO_4 tetrahedra and therefore the proportion of Si–O–Si(Al) bonds increases in the same sequence. In the same structure type, the stability decreases with increasing substitution of Si by Al, i.e. in the sequence quartz > orthoclase > nepheline, and for the plagioclases from albite to anorthite. This is because the four oxygen atoms of the tetrahedra are pressed apart by the about 50 % larger Al ion.

The type of cations that link the SiO_4 tetrahedra influences the stability through their size and charge. The stability increases with the charge and decreases with the size of the linking cation. For this reason, structures where the larger cations Mg^{2+} , Ca^{2+} and Fe^{2+} (Table 2.2) link the tetrahedra are less stable than those linked by Al, e.g. biotite compared to muscovite. Because this influence can superimpose any other influence related to the structure, the orthosilicates exhibit the stability sequence zircon > andalusite, staurolite > olivine. The SiO_4 tetrahedra in zircon (ZrSiO_4) are linked by Zr^{4+} , in andalusite (Al_2OSiO_4) and staurolite by Al^{3+} , and in olivine by Mg^{2+} and Fe^{2+} .

The content of oxidizable metal ions such as Fe^{2+} and Mn^{2+} reduces the stability, because their oxidation disturbs the charge and structural ratios (in sixfold coordination, Fe^{3+} is 13 % smaller than Fe^{2+} , cf. Table 2.2) in the mineral.

Table 2.12 Average lifetime of a 1 mm crystal of various silicates in years in soils (acc. to Lasaga 2014)

Anorthite	Diopside	Albite	K feldspar	Muscovite	Quartz
1.1×10^2	6.8×10^3	8.0×10^4	5.2×10^5	2.7×10^6	3.4×10^7

The fact that biotite weathers more readily than muscovite is therefore closely related to its generally high Fe^{2+} contents. Pyrite is also particularly readily weatherable, because it can be oxidized although it is poorly soluble.

Altogether, these observations result in the following approximate sequence of increasing weathering stability for the rock-forming silicates: olivine < anorthite < pyroxene < amphibole < biotite < albite < muscovite ~ orthoclase < quartz. Values for the lifetime of 1 mm crystals of various silicates are listed in Table 2.12; they correspond to the previously mentioned sequence. Under aerobic, surface-near conditions, clay minerals as end products of weathering are about equally as stable as the structurally related muscovite.

The weathering stability can be qualitatively assessed using **stability diagrams**, where the stability fields for the individual minerals are represented as a function of the composition of the weathering solution at a state of equilibrium. They are calculated from the thermodynamic parameters (enthalpy of formation) of all of the participating phases. Stability diagrams such as Fig. 2.25 can be used to assess whether a mineral is stable with a given weathering solution or if it dissolves. Orthoclase and muscovite weather more readily the lower the K and Si activity and the higher the H activity (pH) in the weathering solution (Fig. 2.26). For the kinetics (see Sect. 2.4.4.2), a large deviation of the solution concentration from the equilibrium concentration (see Eq. 2.17) results in a rapid dissolution rate.

However, the precise location of the stability boundaries is uncertain and can thus only be used for a qualitative prediction, because (1) the free energies of the individual minerals differ only slightly from one another, and therefore the energies of the transformation reaction cannot be determined with sufficient precision; (2) equilibrium is seldom reached in the weathering environment, i.e. at low temperature and low

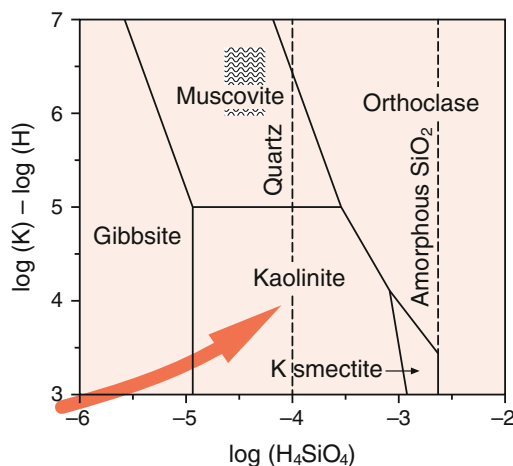


Fig. 2.25 Stability range of orthoclase, muscovite, kaolinite, smectite and gibbsite at 25 °C as a function of the activity (mol L^{-1}) of K^+ , H^+ and H_4SiO_4 . The two dotted lines mark the H_4SiO_4 saturation activities of quartz and amorphous SiO_2 , the wavy lines show the average composition of seawater. The arrow symbolizes the changing composition of strongly undersaturated rainwater, which becomes increasingly enriched with K^+ and H_4SiO_4 in contact with minerals

pressure; (3) metastable phases are preferentially formed, which only transform very slowly (if at all) into stable phases. Thus, for example, although the Si concentration in many weathering solutions is significantly above that of equilibrium with quartz, the latter is only formed very slowly, if at all.

2.4.4.2 Kinetics of Chemical Weathering

Stability diagrams (Fig. 2.25) have already been used here to show that although undersaturation forecasts that a mineral is not stable and will dissolve, the stability diagrams do not say anything about the rate at which dissolution takes place. A quantitative description of the rate R at which a mineral is chemically weathered can be formulated as follows (White and Brantley 1995):

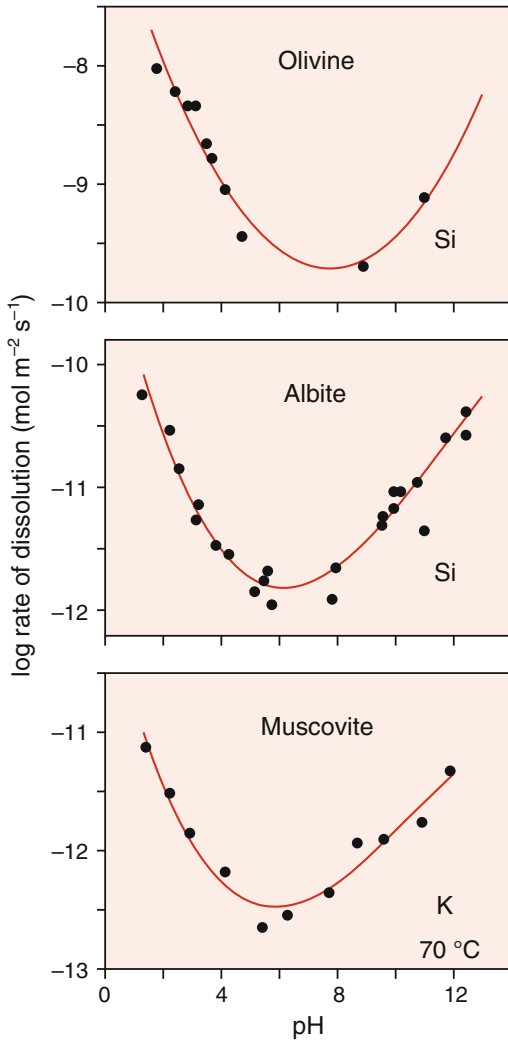


Fig. 2.26 Liberation rates of Si from olivine and albite, and of K from muscovite at 70 °C depending on the pH (after Knaus and Wolery 1986)

$$\text{Rate } R = k_0 A_{\min} \exp \frac{E_a}{RT} (a_{\text{H}^+}^n) g(I) (\prod a_i^n) f(\Delta G_r) \quad (2.17)$$

The individual terms in Eq. 2.17 can at least be qualitatively linked to important soil properties: The mineral type determines the mineral-specific rate constant k_0 , which is of $\sim 10^{-10}$ – 10^{-14} mol m⁻² s⁻¹ for silicates. The reactive surface A_{\min} increases with decreasing grain size, which in turn is a function of the parent material.

Thus, the coarse-grained minerals of acidic plutonite (e.g. granite) have less reactive surface than the fine-grained minerals of basic vulcanites such as basalt. The temperature-dependency of the reaction is accounted for by the exponential term, which comprises the activation energy E_a , the temperature T and the BOLTZMANN constant R . The chemical composition of the soil solution is accounted for by the next three terms: The first term is the proton activity (pH value), which is raised to the power of the number n of protons involved in the solution reaction. The liberation rates of Si from olivine and albite (Fig. 2.26) drop with rising pH in accordance with Eq. 2.10. The rise of the rates above pH 7 is due to an increase in the silicic acid solubility in the alkaline range. Such changes in the solubility behavior (e.g. also through complexing reactions) are accounted for by the rate equation in the product term $\prod a_i^n$. The term $g(I)$ takes account of the fact that dissolution rates also depend on the ionic strength.

Finally, the term $f(\Delta G_r)$ takes in account that the rate depends on the degree of undersaturation and varies between 1 (i.e. maximum rate k_0 at maximum undersaturation) and zero (equilibrium). For this reason, the water regime is of great importance, as it determines how long water is in contact with a mineral surface that is dissolving. With a very short residence time in very well-drained soils with high amounts of precipitation, the weathering solution remains highly undersaturated, so that even very poorly soluble minerals are also dissolved on the long term (e.g. quartz in tropical soils). The longer the soil solution is in contact with the solid phase, the more its composition will approach that that is in equilibrium with the dissolving mineral (e.g. orthoclase). However, the solubility product of a less soluble mineral is usually exceeded (e.g. of kaolinite) before this equilibrium is reached. The growth of this new mineral depletes the corresponding elements in the weathering solution, and therefore the solution composition of the seepage water percolating below no longer corresponds to the composition of the weathering primary minerals (see Eq. 2.10 for incongruent dissolution).

2.4.4.3 Weathering Intensity

The weathering intensity can be characterized mineralogically, e.g. using so-called **index minerals**. In humid climates, low weathering is indicated by the dominance of gypsum, calcite and olivine, moderate by biotite, illite and smectite, strong by secondary chlorite and kaolinite, and very strong weathering by gibbsite and anatase. However, deviations are possible depending on local weathering conditions. In addition to changes in the mineral constituents, increasing contents of mineral inclusions, e.g. of goethite and hematite, also indicate increasing weathering intensity.

Chemical indicators are also suitable for the characterization of the weathering intensity. Soils are initially mainly depleted of Na, Ca and Mg, while the K content decreases more slowly. Among the anions, especially chloride and sulfate are rapidly depleted, while even though phosphate is liberated from the apatite, it is then usually relatively strongly bound in another form. Although silicate is also already depleted in the initial phases of weathering, it is only recognizable at an advanced weathering stage. This desilification takes place in stages, because initially Si-rich secondary minerals (illite, smectite) are formed again, and then more Si-poor minerals (kaolinite) are formed, until finally in extreme cases, almost all of the Si is depleted. In this rare state, the elements Al, Fe, Ti etc. relatively accumulate strongly in form of oxides, and associated with them, also several microelements such as Ni and Cr, e.g. in bauxite.

The explained mobility sequence can be derived from the comparison between the mean element contents of the rocks (see Table 2.1) and those of the river water residues (Fig. 2.27). The sequence of decreasing mobility in an oxidative environment is:

Cl > S > Na > Ca > Mg > K > Si > Fe > Al

The rate at which silicates are weathered in soils can be calculated from the losses of Na, K, Ca and Mg in the soil profile, and from the loads of these elements and of Si in the watercourses. For soils in temperate-humid regions, values

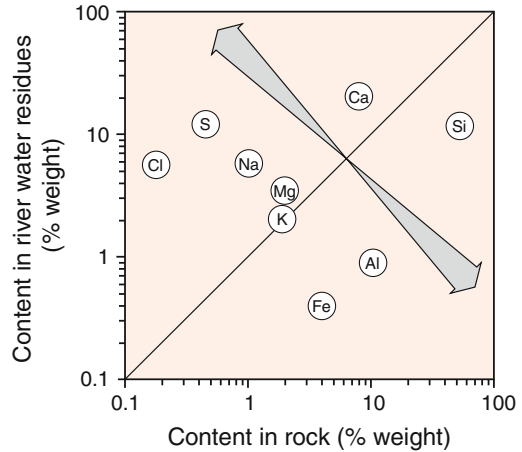


Fig. 2.27 Relationship between the element contents in rocks and in river water residues as a measurement for their mobility (after Hudson 1995). The arrow indicates accumulation in the river water or accumulation in the rock

between 0.02 and $0.08 \text{ mol m}^{-2} \text{ a}^{-1}$ were obtained.

The stability of rocks against physical and chemical weathering also depends on other rock properties in addition to the structural stability of their minerals. As mentioned above, e.g. granite physically weathers more readily and therefore more deeply than fine-grained basalt. It is the opposite for chemical weathering: Here, basic igneous rocks, especially fine-crystalline vulcanites due to their high content of readily weatherable minerals (olivine, pyroxenes, Ca-rich plagioclase), weather more rapidly and more deeply than acidic igneous rocks. As a result, granites in temperate-humid climates form deep soils whose mineral constituents (with the exception of biotite) have changed little compared to the parent rock, while basalts form shallow soils with strongly altered mineral constituents.

2.5 Mineral Constituents of Soils

Just like rocks, soils also consist of a mixture of minerals. During the course of weathering, a portion of the minerals was inherited unchanged

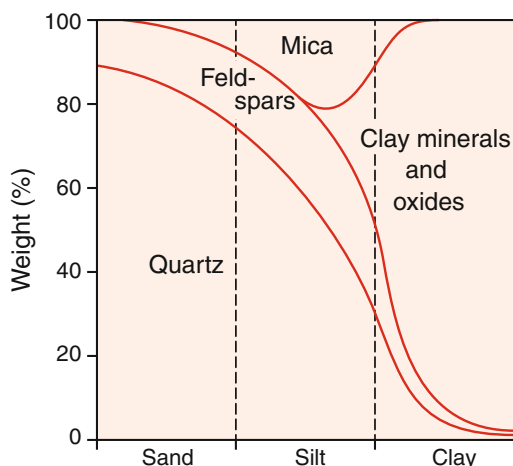


Fig. 2.28 Mineral constituents in the particle fractions sand, silt and clay (example from the glacial landscape of Northern Germany)

from the parent rock, and another portion is pedogenic. Thus, the less weathering and pedogenesis have taken place and the more poorly weatherable the parent materials, the more the mineral constituents of many soils reflect those of their parent materials. In contrast, pedogenic minerals are increasingly dominant in more mature soils. This also influences the distribution of the various minerals in the grain size fractions of the soils. The sand and silt fractions consist mainly of stable igneous and metamorphic minerals such as quartz, potash feldspars, micas (mainly muscovite) and numerous heavy minerals (zircon, rutile, ilmenite, magnetite, tourmaline) that remain after weathering, while in the clay fraction, the clay minerals and oxides from sediments and pedogenesis dominate (Fig. 2.28).

Soils originating from acidic igneous and metamorphic rocks (e.g. granite, gneiss) usually consist of >60 % quartz, those from sandstone, fluvial and eolian sands up to 95 %. In contrast, soils from loess, limestone and claystones are lower in quartz (<50 %), while those from basic igneous rocks hardly contain any quartz, unless it is from eolian input. The quartz content is highest in the sand fraction and decreases towards the finer fractions (see Fig. 2.28). However, quartz

can still be found in coarse clay after cryoclastic weathering. Soil development can lead to relative quartz accumulations, if less stable minerals, e.g. silicates, are degraded.

The feldspar content in soils in temperate-humid climate regions often ranges from 5 to 30 %; from which 80 to 90 % can be attributed to alkali feldspars, since Ca-rich feldspars weather more readily. The influence of weathering intensity is demonstrated by the fact that e.g. soils from lower Pleistocene sands usually contain <10 % feldspars, and those from the upper Pleistocene sands on average 15–20 %. Soils from loess, clay and clay schist have feldspar contents of 10–15 %. The feldspar content decreases towards the finer fractions (Fig. 2.28). In soils from parent rocks with a high alkali feldspar content, however, they can also still occur in the clay fraction. In many soils in the humid tropics, in contrast, feldspars are largely transformed into clay minerals.

Plagioclases, pyroxenes, amphiboles and olivines are only present in small amounts in the coarser fractions, since they weather more readily than alkali feldspars. Their proportion generally decreases within the profile from bottom to top, because weathering in the upper horizons is most intensive. They are completely absent in strongly weathered soils of the humid tropics (Ferralsols).

The mica content, consisting mainly of muscovite and bleached (=weathered) biotite, is highest in the silt fraction of soils, since micas are easily mechanically degraded due to their pronounced cleavability (Fig. 2.28).

In many young soils of temperate climate regions, clay minerals and oxides are inherited from sediments, however, they also originate from pedogenesis. Thus, mainly illite and smectite dominate in post-Pleistocene soils originating from loess, calcareous glacial till, fluvial sediments and marshes, but also from claystones and limestones. In contrast, the clay minerals in soils are always pedogenic on parent materials that do not contain any clay minerals, such as igneous rocks. They are determined by the mineral

Table 2.13 Dominating pedogenic clay minerals in orders of the soil taxonomy orders and WRB reference group (Chaps. 7 and 8)

Soil order/Reference group	Clay minerals
Alfisols	Illite, smectite, Al chlorite
Luvissols, Alisols	
Andisols	Allophane, imogolite, halloysite
Andosols	
Aridisols	Palygorskite, sepiolite, smectite
Calcisols, Solonchaks, Solonez	
Entisols	
Regosols, Leptosols, Anthrosols, Technosols	None
Inceptisols	
Cambisols, Umbrisols, Gleysols, Stagnosols	Illite, smectite, Al chlorite
Mollisols	
Chernozems, Kastanosems, Phaeosem	Illite, smectite, vermiculite
Oxisols	
Ferralsols, Plinthosols	Kaolinite, goethite, hematite, gibbsite
Spodosols	
Podzols	Illite, Al chlorite, (smectite), allophane
Ultisols	
Acrisols, Lixisols	Kaolinite, muscovite, hematite, goethite
Vertisols	
Vertisols	Smectite
Gelisols	
Cryosols	Illite

composition of the igneous or metamorphic rocks and the pedoclimate, and change with the degree of soil development.

At low weathering intensity, smectite is often found on basic igneous rocks (basalt etc.), in contrast, illite and vermiculite are found on acidic igneous rocks (granite u. a.), and primary chlorites are often found on metamorphic rocks. With stronger acidification, smectites and vermiculites are transformed into soil chlorites, and primary chlorites are partially dissolved. Local

accumulations of goethite, lepidocrocite and ferrihydrite occur in redoximorphic soils. On volcanic ashes, soils with higher Si concentrations contain allophane, and with lower concentrations, imogolite; at later stages of development, in contrast, halloysite and kaolinite dominate. However, allophane and imogolite are also found in the B horizon of Podzols.

Numerous soils in temperate-humid climate regions, e.g. Rendzic Leptosol, calcareous Regosols, young floodplain and tidal Fluvisols, still contain calcite and dolomite in the A horizon, usually in the silt fraction (e.g. in loess). Pedogenic calcite is also found with increasing aridity.

The mineral constituents in strongly developed soils of the perhumid tropics and subtropics are dominated by kaolinite, goethite, hematite, gibbsite and anatase. On acidic igneous and metamorphic rocks, weathering-resistant minerals such as quartz, orthoclase or muscovite are also found, which are largely lacking on basic igneous rocks. Smectite is widespread in neutral to slightly alkaline soils of seasonal wet and dry climatic regions, while under dryer, semiarid conditions and higher Mg concentrations, palygorskite and sepiolite and various salts (sulfates, chlorides, nitrates, borates) are found. In many regions (India, Central Africa) with kaolinitic soils on plateaus and slopes, smectite-rich soils (Vertisols) in plains with high groundwater tables and in hollows are connected by the landscape's water balance. Typical pedogenic minerals in the anaerobic soil zone are iron sulfides, siderite and vivianite.

Almost all soils contain small amounts (<2 %) of heavy minerals, e.g. apatite, magnetite, ilmenite, garnet, rutile, zircon, tourmaline etc. The poorly weatherable heavy minerals accumulate all the more with increasing intensity of soil weathering. In contrast, the apatite content decreases with increasing acidification.

Because the mineral soil orders of *Soil Taxonomy* and the soil reference groups of WRB are broadly defined following a sequence of development, they can be associated with dominant pedogenic minerals (Table 2.13).

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Scheffer/Schachtschabel Soil Science

Blume, H.-P.; Brümmer, G.W.; Fleige, H.; Horn, R.;

Kandeler, E.; Kögel-Knabner, I.; Kretzschmar, R.; Stahr,

K.; Wilke, B.-M.

2016, XVIII, 618 p. 255 illus., 218 illus. in color.,

Hardcover

ISBN: 978-3-642-30941-0