

Chapter 3

Minerals in Sediments and Their Impact on the Changes of Organic Substances in Geosphere

Keywords Silicates · Carbonates · Sulphides · Sulfates · Halides · Certain classes of organic compounds · Free bitumens · Bound bitumens · Pyrolysis of kerogen · Added minerals · Native minerals

3.1 Mineral Composition of Sediments

Outline

Almost all of minerals in the geosphere can be identified in sedimentary rocks. However, at this point there will be more discussion only about silicate, carbonate and sulphide minerals, as they are the most common and most important in studies of the interactions of inorganic and organic matter in sedimentary rocks.

All sedimentary, igneous or metamorphic rocks of the Earth's crust, consist of one or more components which are called minerals. It is estimated that the Earth's crust contains about 2400 mineral species, with about 7000 subspecies. Out of this huge number, only around 150 mineral species and subspecies are of higher importance as they determine dominantly the structure and properties of rocks. In the geological literature these minerals are called *petrogenic minerals*. Mineral species found in ore deposits and which do not have a greater role in the structure of the rocks, are called *ore minerals*.

Box 3.1: *General Note*

In sedimentary rocks, two types of minerals can be distinguished. Allogenic (*allogenos*—strange) or terrigenous (*terra*—earth) compounds are fragments of other rocks, which were formed in an earlier igneous, sedimentary or metamorphic cycle, i.e. before the foundation of the investigated rock. Autogenic minerals (auto—self) are genetically related to the sedimentary rock itself and were formed at the same time.

From the organic-geochemical point of view, sedimentary rocks are the most significant ones, because almost the entire organic matter in the geosphere is found in them. It has been estimated, that the sedimentary rocks account for only 5% of the volume of the upper parts of the lithosphere. However, considering only the surface of the lithosphere the sedimentary rocks cover 75% of the Earth's surface.

Sedimentary rocks are formed from the products of chemical or mechanical transformations of the previously created igneous, sedimentary and metamorphic rocks. They are usually deposited in layers as strata in the area of sedimentation, which covers an area of lithosphere and hydrosphere.

Overview of the major silicate, carbonate, sulphide, oxide and hydroxide, sulphate, haloid and phosphate minerals is given in Table 3.1. This overview contains more details than necessary for the study of organic-inorganic interactions in sediments. But with this more extended form a better picture of the complexity of the mineral composition of sediments can be obtained.

3.1.1 Silicates

Minerals, in whose composition silicon and oxygen are predominant, are called silicate minerals, or simply silicates. They occur not only widespread and abundant in the lithosphere, but also numerous and diverse, despite the fact that their composition comprises a relatively small number of other elements. The existence of a large number of silicate mineral species is possible thanks to special features of silicon and oxygen bound to it.

The silicon ion (Si^{4+}) is surrounded by four oxygen ions (O^{2-}) which are always arranged in the same way. The oxygen ions are at the tips of an imaginary tetrahedron with a silicon ion in the centre (Fig. 3.1). SiO_4 -tetrahedron is the basic structural unit of all silicate minerals.

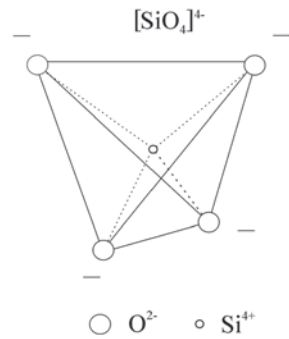
Since the SiO_4 -tetrahedron is a negatively charged ion (SiO_4^{4-}), it easily binds to positive ions such as Ca^{2+} , Mg^{2+} , Fe^{2+} , Fe^{3+} , Na^+ , K^+ , or Al^{3+} . SiO_4 -tetrahedra can be bound to each other through a shared oxygen ion. Also, a number of silicon ions in the lattice can be replaced by aluminum ions. Silicates in which at least 10% silicon ions are substituted with aluminium ions are called aluminosilicates. Thanks to the described features of SiO_4 -tetrahedrons, different combinations and forming of different types of silicate mineral species are possible.

According to the type and degree of polymerization of SiO_4 -tetrahedrons, the silicates are divided to tectosilicates, phyllosilicates, inosilicates, nesosilicates and soro- and cyclosilicates (Table 3.1). The basic silicon-oxygen groups and ways of bonding between silicon and oxygen in these mineral species are illustrated in Fig. 3.2. For studying the interactions with the organic matter of sediments, the most important are silicon dioxide minerals and feldspars belonging to tectosilicates, and clay minerals that belong to phyllosilicates.

Table 3.1 Important minerals in geosphere

<i>Silicates</i>							
<i>Tectosilicates</i>				<i>Phyllosilicates</i>			
Group of SiO ₂ minerals	Group of feldspars	Group of feld-spathoids	Group of zeolites	Group of mica	Group of chlorite	Group of serpentine	Clay minerals
Quartz Cristo-balite Tridimite Opal	K ⁻ , Na ⁻ , Ca— feldspars (Sanidine Orthoclase Albite- Microline Anorthite)	Leucite Nepheline	Natrolite- Heulandite Phillipsite Desmin Chabazite	Biotite Muscovite Paragonite		Antigorite Chrysotile Serpophite Talc	Kaolinite Montmo-rillonite Nontronite Saponite Illite Vermicu-lite Glauc-onite
<i>Inosilicates</i>		<i>Nesosilicates</i>			<i>Soro- and cyclosilicates</i>		
Group of amphi-boles	Group of pyroxenes	Group of olivine	Group of Al-silicates	Group of garnets	Group of epidote		
Antho-phyllite Tremolite Actinolite Horn-blende	Enstatite Bronzite Hypersthe-ne Alkalinepyroxenes	Forsterite Fayalite	Disthene Andalusite Sillimanite	Pyrope Almandine- Spessartine Uvarovite Grossu-lar Andra-dite	Epidote	Beryl Tourmaline	
<i>Carbonates</i>							
Group of rhombohedron carbonates			Group of rhombic minerals		Group of Na-carbonates		
Calcite Dolomite Ankerite	Magnesite Smithsonite Siderite	Rhodochrosite	Aragonite Witherite	Strontianite Cerussite		Soda Trona Thermonatrite	
<i>Sulfides</i>							
Pyrite chalcopyrite marcasite melnikovite pyrrotite							
<i>Oxides and hydroxides</i>							
Oxide of hydrogen	Fe-oxides and hydroxides	Al-oxides and hydroxides	Ti-oxides and hydroxides	Mg-oxides and hydroxides	Mn-oxides and hydroxides	Ba- and Al-oxides	Complex Fe-, Mg-, Al-, Cr-, Zn- and Mn-oxides
Ice	Magnetite Hematite Limonite	Corundum Diaspore Hydrargil-lite	Brookite Rutile Anatase Perovskite	Periclase Brucite	Psil-omelane Pyro-lusite	Chrysoberyl	
<i>Sulfates</i>							
Group of barites		Group of Ca-sulfates		Group of alunites		Group of sulfates of salt deposits	
Barite Anglesite	Celestine	Gypsum				Epsomite Polyhali-te Kainite Glauberite	
<i>Halides</i>							
Chloride of salt deposits			Group of Ag-, Cu- and Pb—chlorides			Fluorides	

Fig. 3.1 Position of silicon and oxygen ions in SiO_4^{4-} -tetrahedron



Group of Silicon-Dioxide Minerals

Silicon-dioxide is found naturally in six crystalline modifications (α - and β -quartz, α - and β -tridymite, α - and β -cristobalite), in one crypto-crystal to micro-crystal modification (chalcedony), and may appear also in the amorphous state (quartz glass—lechatelierite). When SiO_2 contains a certain amount of water, it appears in the form of amorphous opal.

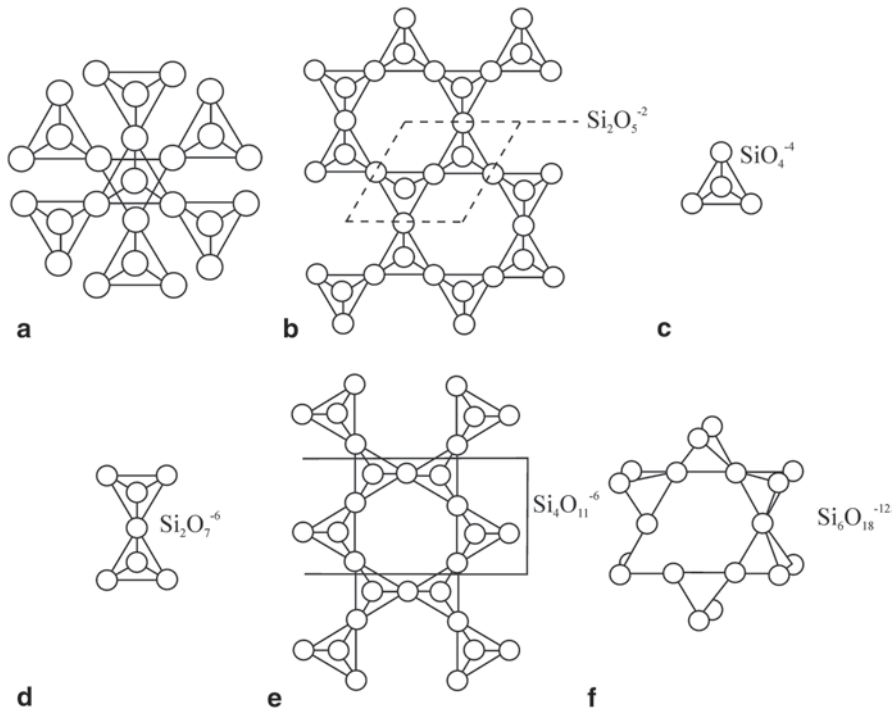
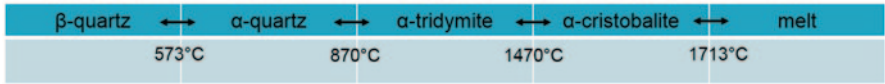


Fig. 3.2 Bonding of silicon and oxygen in tectosilicates (a), phyllosilicates (b), inosilicates (c), nesosilicates (d), sorosilicates (e) and cyclosilicates (f)

Stability of some crystalline modifications depends on heat and pressure. The influence of pressure is thereby less important than the effect of heat. Under the pressure of about one bar certain modifications are stable in the temperature ranges illustrated in the following:



(3.1)

Transformations of one form to another in most cases are very slow, even for the geological time conditions. This especially applies to the transformation of α-quartz to α-tridymite and α-tridymite to α-cristobalite. Generally, the rate of transformation largely depends on the crystal lattice of individual modifications (Fig. 3.3).

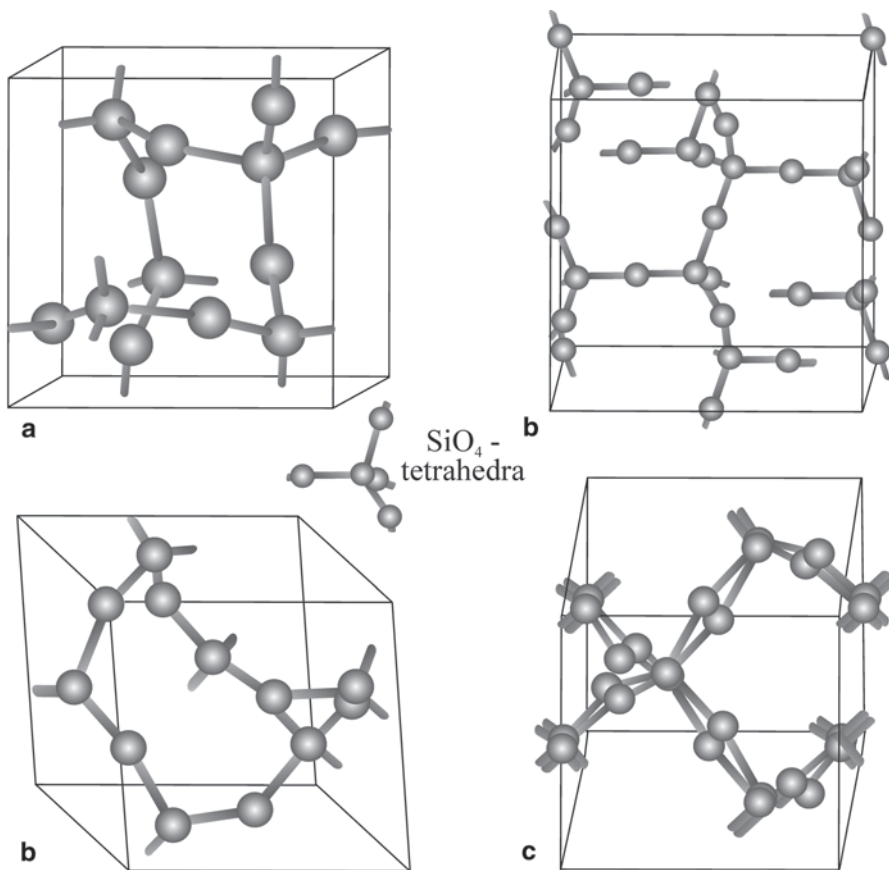


Fig. 3.3 Crystal structures of α-cristobalite (a), α-tridymite (b), α-quartz (c), and β-quartz (d), noticeable difference between the crystal structures of α-cristobalite and α-tridymite, and similarity between α-quartz and β-quartz

Table 3.2 Names and composition of isomorphous mixtures of albite and anorthite

Albite	0–10%	Anorthite
Oligoclase	10–30%	“
Andesine	30–50%	“
Labradorite	50–70%	“
Bytownite	70–90%	“
Anorthite	90–100%	“

Quartz is the most important petrogenic mineral from the group of silicon dioxide minerals. According to some estimates, quartz makes up about 12% of the lithosphere.

Feldspars

In terms of their chemical composition, feldspars are aluminosilicates of potassium ($K_2O \times Al_2O_3 \times 6SiO_2$), sodium ($Na_2O \times Al_2O_3 \times 6SiO_2$) and calcium ($CaO \times Al_2O_3 \times 2SiO_2$) (Table 3.1). Minerals from the group of feldspars usually contain at least two of these elements. Feldspars occur mainly as isomorphous mixture of sodium and potassium or sodium and calcium aluminosilicates.

Feldspar of the first type is called alkali feldspar, and feldspar of the second type is plagioclase. Alkali feldspar occurs in three modifications (sanidine, orthoclase and microcline; Table 3.1). Plagioclases are isomorphous mixtures of sodium feldspar—albite and calcium feldspar—anorthite (see Table 3.2).

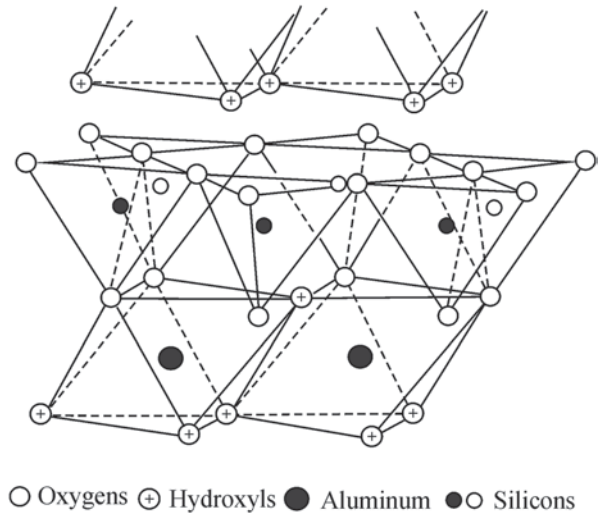
Structural feldspar lattice is built from SiO_4 -tetrahedra connected in all directions. Thereby in every second and fourth SiO_4 -tetrahedron, silicon ions can be replaced by aluminium ions, thus becoming a complex structure $/Al_2Si_2O_8/^{2-}$ and $/AlSi_3O_8/^-$ that easily bind ions of potassium, sodium and calcium.

Clays

Clay minerals are one of the most important groups of minerals that participate in the formation of sedimentary rocks. They are generally formed by aluminosilicate weathering in the surface layers, although some may be formed by hydrothermal alterations of rocks at relatively low temperatures. The most important clay minerals in this group are kaolinite, montmorillonite and illite.

Kaolinite can be represented by an aggregate formula: $Al_2Si_2O_5(OH)_4$. Silicon and aluminium ions cannot replace each other, but they build separate interchanging layers (Fig. 3.4). Kaolinite is formed by transformation of igneous and metamorphic rocks (mainly acidic) by aluminosilicate weathering (feldspar, feldspathoides or mica). It is formed in acidic environments under oxidation conditions and at low concentrations of Na^+ , Mg^{2+} and Fe^{2+} .

Fig. 3.4 Crystal structure of kaolinite



Montmorillonite is structurally different from other clay minerals. In the structural montmorillonite grid two layers are built up of SiO_4 -groups, and between them a layer made of Al^{3+} , Mg^{2+} and Fe^{2+} . Between these “packages” there are water molecules that are weakly bound (Fig. 3.5). Thanks to this structure, it is possible to

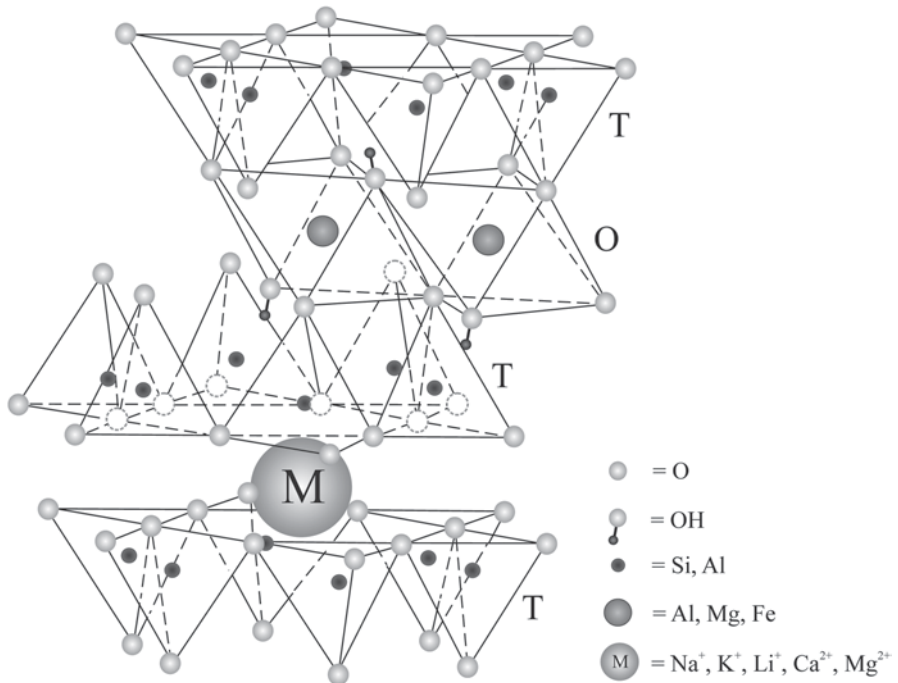


Fig. 3.5 Crystal structure of montmorillonite

easily narrow or expand the space in which water molecules are found. Montmorillonite can lose the interlayer water without disrupting the structure by heating at 100–200 °C, but can just as easily receive it back.

In terms of its chemical composition, montmorillonite is a hydrated aluminosilicate. It can be represented by an aggregate formula: $\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2 \times 2\text{H}_2\text{O}$. Part of Al^{3+} ions can be replaced with Mg^{2+} or Fe^{3+} . Montmorillonite is formed in alkaline environments from solutions which must be rich in Na^+ , Mg^{2+} and Fe^{2+} . The more alkaline the environment the easier is the formation of montmorillonite. Therefore, in contrast to kaolinite, montmorillonite is formed also in the marine environment.

Illite is a clay mineral which is formed by transformation of feldspar or muscovite degradation. Chemical composition of this mineral can be represented by the formula: $\text{K}_x(\text{AlFe}^{3+})_4\text{Si}_8 \times \text{Al}_x\text{O}_{20} \times n\text{H}_2\text{O}$ where x is less than 2. Instead of Al^{3+} , Mg^{2+} or Ca^{2+} ions may be included.

3.1.2 Carbonates

Carbonates are an important group of petrogenic minerals that are widespread in the lithosphere and comprise a large number of mineral species. They can be divided into two large groups: carbonate minerals without water and other anions and carbonate minerals with water and other anions.

The first group of minerals is subdivided into two further groups: carbonates that crystallize in rhombohedral system and carbonates that crystallize in rhombic forms (Table 3.1). Rhombohedral carbonates are those of calcium, magnesium, manganese, zinc and iron. Rhombic carbonates are built by calcium, strontium, barium and lead. Ions of rhombohedral minerals have smaller diameters than the orthorhombic mineral ions (0.078–0.106 nm compared to 0.127–0.143 nm). Ions of smaller ionic radius are surrounded by six oxygen ions each (coordination number to oxygen is 6), while the ions with larger ionic radius are surrounded by nine oxygen ions each (coordination number to oxygen is 9). Calcium ion is the only one that can be incorporated in both types of crystal lattice, and therefore calcium carbonate is dimorphic.

Carbonates crystallizing in rhombohedral system are more important since they act as petrogenic minerals.

Rhombohedral Carbonates

The general chemical formula of rhombohedral carbonates is MCO_3 , where M are the bivalent cations of calcium, magnesium, manganese, iron or zinc. Although all these minerals are morphologically similar, even identical, and structurally completely analogous, there is no possibility of complete isomorphic mixing between all these minerals due to the differences in the ionic diameters (Mg—0.078 nm, Fe—0.082 nm, Zn—0.083 nm, Mn—0.091 nm, Ca—0.106 nm). Only ions that are similar in size can be replaced, so that those that can be mixed are siderite and rhodochrosite, siderite and magnesite, and finally calcite and rhodochrosite. Such a

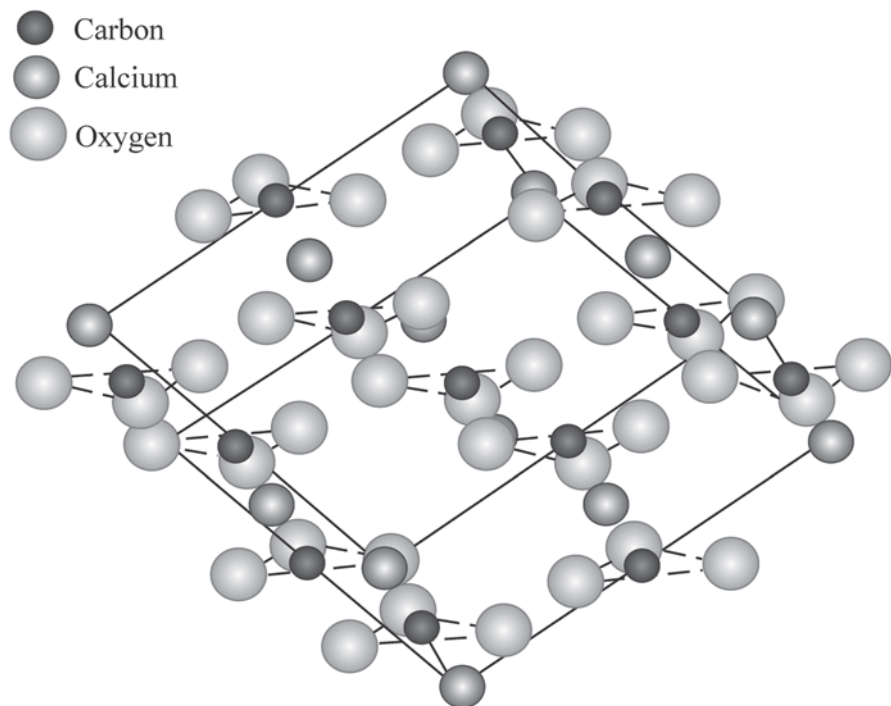


Fig. 3.6 Crystal structure of calcite

dual mineral is dolomite ($\text{CaCO}_3 \times \text{MgCO}_3$; Table 3.1), in which all magnesium, or portion thereof, may be substituted with Fe or Mn (ankerite; Table 3.1). Due to the large differences in ionic diameters of calcium and magnesium, isomorphous mixing of calcite and magnesite is almost impossible.

Among rhombohedral minerals the most important are calcite, magnesite, siderite and dolomite as petrogenic minerals. Calcite (CaCO_3) is the most widespread mineral from the group of rhombohedral carbonate minerals. It occurs in platy crystals (Fig. 3.6), but builds also aggregates with irregular grain shapes. It is formed in many ways, mostly in the water, at lower temperatures, in the presence of easily soluble $\text{Ca}(\text{HCO}_3)_2$. In the surface layers of sediments it is dissolved and converted into calcium bicarbonate.

Magnesite (MgCO_3) is magnesium carbonate. It occurs in small-grained aggregates of irregular shape. It is formed by hydrothermal alteration of Mg-silicates.

Siderite (FeCO_3) is a mineral composed of iron carbonate. It is formed as a product of activity of hydrothermal solutions or cold waters rich in carbon dioxide in minerals with higher iron content. During the surface decomposition it is converted into limonite.

Dolomite ($\text{CaCO}_3 \times \text{MgCO}_3$) is a double salt known as calcium and magnesium carbonate. It is formed in many ways, often in diagenetic processes, by the influ-

ence of magnesium containing solutions on the calciumcarbonate rocks. It can be formed also hydrothermally.

3.1.3 Sulphide Minerals

Sulphide minerals are mostly components of ores, although they are also found in a considerable amount in sedimentary rocks. This is especially true of iron sulfide (FeS_2). Group of petrogenic minerals includes also pyrrhotine (FeS) and chalcopyrite (CuFeS_2) (Table 3.1).

Iron sulfide occurs in nature in three modifications: in the tesseral one as pyrite, in the rhombic one as marcasite and the amorphous one as the melnikovite pyrite. The most prevalent among them, and among all the sulphide minerals in general, is pyrite. Under normal conditions, among sulphide minerals only pyrite is stable. Melnikovite is unstable in the amorphous state, which can be quickly and easily converted to pyrite. Marcasite also tends to convert into tesseral—pyrite modification, but that process is slower.

Pyrite crystallizes in a tesseral form of pentagon. As this form is characteristic of pyrite, it is often called also pyritoedron. Pyrite occurs as granular masses and fine-grained aggregates. It is formed in many ways and is found in all kinds of rocks. It is usually generated by hydrothermal processes. During the surface decomposition it is converted into limonite.

3.2 Influence of Minerals on the Alterations of Organic Matter in Sediments

Outline

Microorganisms have a dominant influence on the alterations of organic matter in the geosphere during diagenesis, but temperature and pressure in the phase of catagenesis. Studies of interaction of minerals and organic part of sedimentary rocks have shown in the last 30 years that the influence of minerals on diagenetic and especially catagenetic changes in organic matter is not negligible. It is realised as a catalytic effect, but also by adsorption.

The influence of minerals on organic matter alterations in the geosphere can be considered in two ways, by monitoring the effects of minerals on certain classes of organic compounds that can be found in the geological environment (for example, fatty acids, *n*-alkanes, alcohols, or steroids), or by monitoring the effects of minerals on complex sedimentary organic materials, mostly on bitumen and kerogen. These approaches will be explained in more detail in this chapter.

3.2.1 *Interactions of Minerals with Certain Classes of Organic Compounds*

One of the oldest known examples regarding the influence of minerals on certain organic compounds in geological samples is the influence of bentonite on the changes in behenic acid. If behenic acid ($C_{21}H_{43}COOH$) is heated in the presence of bentonite at $200^{\circ}C$ without access of air, n - C_{21} hydrocarbon is obtained. Concentration of all other n -alkanes in the range C_{12} – C_{36} in this case is only about 0.3%. In this way it is proved that bentonite catalyzes the process of decarboxylation of behenic acid. A similar result is obtained when behenic acid is heated with montmorillonite at 200 and $250^{\circ}C$. Product of transformation of behenic acid in this case is as well n - C_{21} . Concentration of all other n -alkanes in the range C_{16} – C_{28} is only about 1%. CPI calculated from the abundance and distribution of these n -alkanes is about 1.5. Thus, in the presence of mineral catalysts generation of n -alkanes are related to dominantly two reactions—decarboxylation of fatty and cracking. Activation energy of decarboxylation in this case is much lower than the activation energy of cracking the hydrocarbon chain (150.7 compared to 194.6 kJ/mol). On the other hand, activation energy of thermal cracking of hydrocarbon chain of behenic chain is 230 kJ/mol. Since this value exceeds the value of activation energy of cracking of behenic acid in the presence of montmorillonite (194.6 kJ/mol), montmorillonite catalyzes this type of reaction, but to a lesser extent than decarboxylation.

Montmorillonite as the most effective catalyst among all silicate minerals, and among all minerals in sediments in general, has a catalytic effect on the transformations of alcohols. During these catalyzed reactions n -alkanes are also formed. However, the amount of n -alkanes formed in this manner is negligible compared to their total amount in bitumens or in oils.

Catalytic effect of some minerals, especially clay minerals in alkaline aqueous solutions originates primarily from adsorbed Al^{3+} - and Fe^{3+} -ions which act as Lewis acids. Activity of Al^{3+} -ions adsorbed on bentonite is by three orders of magnitude higher than the catalytic activity of Na^{+} -ions adsorbed on the same mineral. Although the activity of catalysts decreases with the increase in water

Box 3.2: *General Notes*

Minerals have an impact on the transformation of n -alkanes. For example, montmorillonite can be an effective catalyst in hydrocarbon cracking reactions thanks to dissociation of interlayer water and presence of ions Al^{3+} and Fe^{3+} that act as Lewis acids on the free mineral surfaces. In this way it is explained why oils originating from silicate dominated source rocks have higher contents of light hydrocarbons compared to oils from carbonate source rocks. However, montmorillonite is more effective as catalyst for cracking of hydrocarbon part of carbonic acids than higher n -alkanes.

Fig. 3.7 Structural formula of kumol

Kumol

content, Al^{3+} -bentonite is catalytically active also with 40% water content. Further on, Al^{3+} -bentonite can survive including its catalytic properties under alkaline conditions in which an insoluble hydroxide salt is generated, because Al^{3+} is in equilibrium with the dissolved form. The same interpretation can be applied also to Fe^{3+} -ion.

Water is an important factor determining thermocatalytic properties of clay minerals. It has been shown that it influences *iso*-butane/*n*-butane ratio in products during pyrolysis of behenic acid in the presence of bentonite as mineral catalyst. If the pyrolysis is performed without water, the ratio is higher, and, vice versa, in the presence of water this ratio is around 0.1. So, it could be said that under the conditions of dry pyrolysis, cracking of hydrocarbon part of behenic acid occurs by carboncation mechanism and under the conditions of hydrolysis by free-radical mechanism.

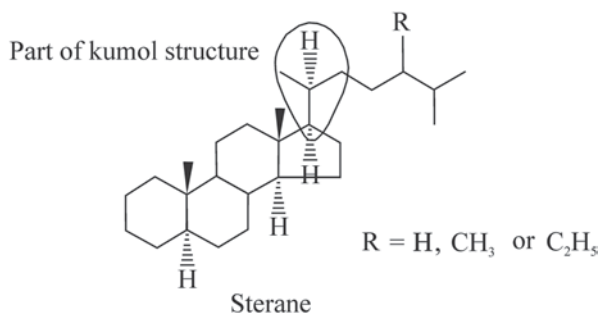
Clay minerals have a catalytic effect also on the structural and stereochemical changes of steroids. If cholesterol is heated to 140 °C for 16 h in the presence of these minerals, structural and stereochemical isomers of the corresponding sterane are obtained among which the vast majority (six out of seven) of those that can be identified in bitumens of ancient sediments and petroleum. The highest yield of these isomers is obtained with kaolinite and montmorillonite as catalysts.

An insight into the catalytic mechanism of montmorillonite on the stereochemical changes of sterane can be obtained by studying a simplified molecular analogon. For this purpose cumol can be used due to its structural similarities to steranes (Figs. 3.7 and 3.8).

Stereochemical changes in the cumol molecule adsorbed on a mineral catalyst are explained by hydrogen exchange mechanism. Active acidic centres on the surface of minerals polarize the bond between α -C-atoms and hydrogen atoms in cumol molecule, which leads to further polarization of the link between β -C-atom and connected hydrogen atoms. Thus, hydrogen atom on β -C-atom becomes more acidic. During the hydrogen exchange mechanism the adsorbed cumol molecule passes through a planar "alkene" form, which results in the preservation of configuration at the α -C-atom, and the change in the stereochemical arrangement on the β -C-atom.

When this model is applied to the sterane molecule, stereochemical changes at the individual chiral centres can be explained as follows: sterane molecule reacts

Fig. 3.8 Structural formulas of kumol and sterane



strongest with the mineral catalyst at C_{25} , followed by C_{17} , C_8 and C_{20} . Their adjacent C-atoms are C_{24} , C_{20} , C_{14} and C_{17} (Fig. 3.8). This means that during the interaction of minerals and sterane molecules the fastest stereochemical changes will take place at C_{24} , then C_{20} , C_{14} and C_{17} . Investigation of steranes of a large number of samples of bitumen of sedimentary rocks with different maturity level, led to the same conclusions when it comes to kinetics of stereochemical changes at chiral centres.

The structural and stereochemical changes in fatty acids, *n*-alkanes, alcohols, and steroids are most influenced by silicate minerals or clay minerals from which montmorillonite has the highest impact. However, it is known that calcite ($CaCO_3$) also has certain catalytic effect on transformations of fatty acids and that sulphur has catalytic effect to some extent on structural changes in cholesterol leading to aromatic and naphthenic moieties.

3.2.2 Interactions of Minerals with Geological Organic Materials

Interactions Between Minerals and Bitumens

Box 3.3: General Note

Knowledge of methods and intensity of the interaction between mineral components and bitumen of sedimentary rocks, and even the mineral components of reservoir rocks and oil, is of great importance for understanding the changes in organic matter in the geosphere and to determine factors that influence these changes. These findings are almost necessary precondition for a successful correlation of oil-oil and oil-source rock.

The interactions of minerals with bitumen are related to catalytic effects but also to adsorption phenomena. Interestingly, organic-geochemical studies have shown that the composition of bitumen and oil is influenced more by the adsorption effect

of minerals. For example, bitumen extraction yields from sedimentary rocks vary depending on the particle size. Highest amounts of bitumen are extracted from fractions of smaller grain size pointing to surface related accumulation.

Additionally, in sediment material of higher grain size bitumen is in the “trap” from which it can be hardly released. Extraction will release bitumen from the larger grain size rocks only from the so-called “open” pores, and a very small amount of bitumen from the “closed” pores. Grinding rocks creates conditions for better access of solvents to bitumen contained in the “closed” pores, which significantly contributes to increasing the yield of extraction.

Under laboratory conditions, bitumen is the most effectively released from the “closed” pores if mineral part of sediment is removed by chemical means creating kerogen concentrates. As already described, carbonates are usually removed with diluted hydrochloric acid, and silicates are removed using a mixture of concentrated hydrochloric and hydrofluoric acids. In this way the bound bitumen is mobilised which can then be extracted with a suitable solvent.

However, under natural geological conditions there are no conditions for the release of the bound bitumen from the “closed” pores of sedimentary rocks, so that only bitumen from “open” pores can migrate. Since it is easiest for minerals of sedimentary rocks to adsorb heavier and more polar compounds, bitumen which migrates (from “open” pores), compared with bitumen which remains in the source rock, is enriched with lighter hydrocarbons. For this reason, the oil in reservoir rock contains higher proportion of the lighter hydrocarbons than the bitumen in the source rock.

The adsorption effect of minerals on bitumen can be estimated by the Rock-Eval method. As already explained, during pyrolysis of sedimentary rocks containing organic matter, according to the Rock-Eval method, three signals, which are marked with S_1 , S_2 and S_3 are obtained. Signal S_1 , or maximum S_1 , originates from the free bitumen, S_2 from kerogen pyrolysis products, and the maximum S_3 from CO_2 , so that its intensity is proportional to the amount of oxygen in the rock. However, a part of the S_2 peak derived from associated bitumen. Hydrogen index of the sample (HI—mgHC/g TOC) can be increased up to 40% as a result of the “release” of associated bitumen.

Adsorption depends to a certain extent on the origin of organic matter. The organic matter derived from terrestrial higher plants is concentrated in larger, “open” pores of the sediment, and the remains of algae and bacteria are adsorbed more in fine, “closed” pores. It could be concluded that in the source rocks, bitumen of algal origin will be retained to a higher extent than bitumen of terrestrial origin.

The best adsorbents are clay minerals, montmorillonite and illite. Carbonate and sulphide minerals have lower adsorption capacities. This means that sedimentary rocks dominated by silicate minerals will adsorb components of bitumen to a higher extent, primarily its heavier and more polar components. As a result of better adsorption on silicate minerals, the primary migration of bitumen through the siliceous sedimentary rocks is significantly more difficult than through carbonate sedimentary rocks. Therefore, oils derived from silicate-type source rocks are enriched with lighter hydrocarbons and have higher values of API-gravity than the carbonate-type oils.

There is another known reason why the oils from siliceous source rocks are enriched with easier and more thermodynamically stable components compared to oils that come from carbonate source rocks. Silicate minerals have also enhanced thermocatalytic properties and higher influence on the maturation changes of bitumen. Although the catalytic effect of minerals on the changes of bitumen is weaker than adsorption, bitumen in the silica type source rock still undergoes significant changes that result from thermocatalytic effects of these minerals.

Clay minerals have more or less catalytic effect on the structural and stereochemical changes of all classes of organic compounds belonging to the group of biological markers. Their effect on *n*-alkanes and steroids has already been discussed. The way and intensity of the catalytic effect of silicate minerals on other biological markers, such as isoprenoid aliphatic alkanes, polycyclic alkanes of triterpane type and aromatic steroids, will be discussed in more detail in the following chapters.

The composition of oil may be also influenced thermocatalytically by minerals in reservoir rocks. For example, silicate can catalyse the reactions of macromolecular asphaltene pyrolysis and thus contribute to increasing the contents of hydrocarbon compounds in petroleum. Theoretically, the silicate minerals in reservoir rocks can act catalytically to almost all the transformations of biological markers that lead to thermodynamically more stable isomers. However, in the reservoir rocks, the contact between oil and a possible catalyst is much weaker than the contact between the catalyst and bitumen in the source rock. Therefore, the catalytic activity in the reservoir rocks is mostly of lower intensity.

Differences in the Composition of Free and Bound Bitumens

Remembering the analytical treatment of sediment material, free bitumen (bitumen 1) can be distinguished from the bound bitumens (bitumens 2 and 3). The first can be extracted directly from a crude sedimentary rock, whereas the other two only after removal of carbonates (bitumen 2) and silicates (bitumen 3). Between these bitumens there are significant differences in the composition as a result of adsorption and thermocatalytic mineral effects. Bitumen 1, as bitumen, which is in the weakest interaction with minerals, has the least amount of polar NSO-compounds, and the highest amount of saturated hydrocarbons. Since the NSO-compounds easily adsorb on minerals, their amount is greater in the bound bitumens. An example of group composition of free and bound bitumens of an Aleksinac oil shale sample is given in Fig. 3.9.

Between these bitumens there are considerable differences in composition of biological markers. As for the *n*-alkanes, bitumen 3 has the lowest CPI-value. It is in the strongest interaction with the silicate catalysts, and therefore in this bitumen maturation changes of *n*-alkanes are most advanced (CPI is tending towards one). Bitumen 1 derived *n*-alkanes have the least uniform distribution (maximum value of CPI). For the same reason this bitumen is dominated by *n*-C₂₇. Example of gas chromatograms of the saturated hydrocarbon fractions of free and bound bitumens of one Aleksinac oil shale sample is given in Fig. 3.10.

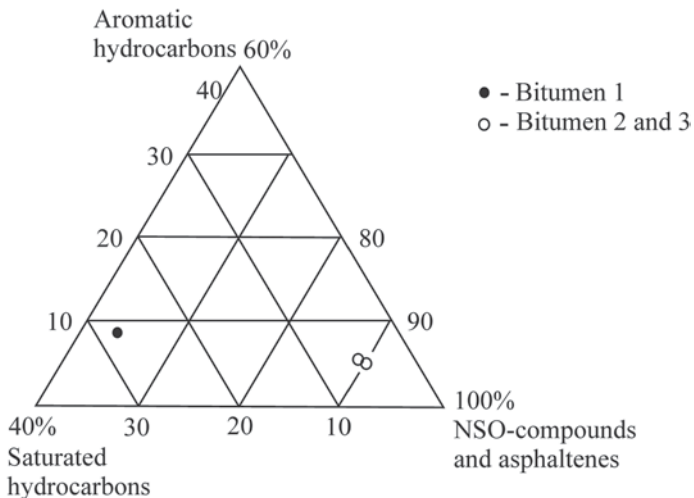


Fig. 3.9 Example of group composition of an oil shale with respect to free and bound bitumens, illustrated by the triangular diagram.

Differences are also visible in the sterane distributions (ion chromatograms of m/z 217, Figs. 3.11 and 3.12). In the chromatogram of bitumen 1 there is almost no peak originating from diasteranes, typical geoisomers. They were most intensive in the ion chromatogram of bitumen 3. The same accounts for the peaks originating

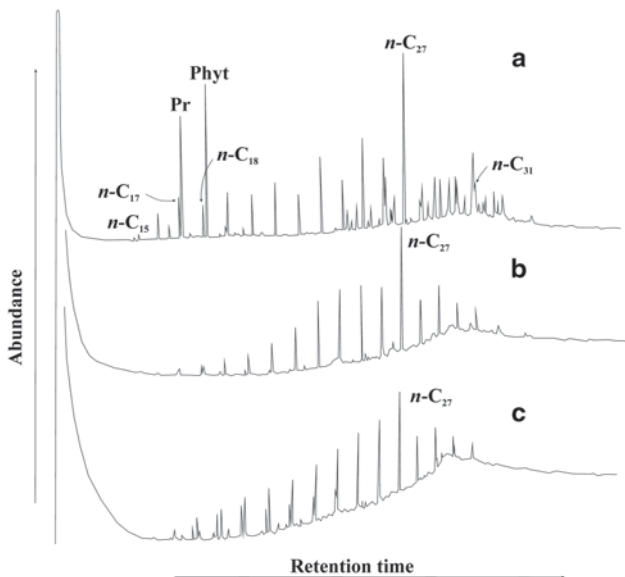
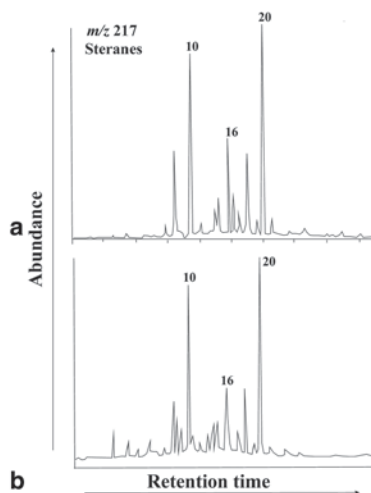


Fig. 3.10 Gas chromatograms of saturated hydrocarbon fractions of bitumen 1 (a), bitumen 2 (b), and bitumen 3 (c), of an oil shale sample

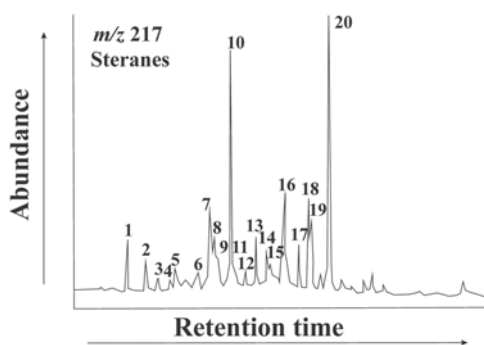
Fig. 3.11 Ion chromatograms m/z 217 (steranes) of free bitumen (a) and bound bitumens 2 (b), of an Aleksinac oil shale sample. (Peak identification is given in Table. 2.5)



from other thermodynamically stable isomers. A stronger interaction of bitumen 3 with silicate catalysts contributes to the increase in the amount of bitumen 3 geoisomers in relation to bitumen 2, especially in comparison with bitumen 1. Furthermore, bitumen 3 contains the largest amount of lower monoaromatic steroids C_{20} and C_{21} , compared to the higher ones C_{26} – C_{30} , and a maximum amount of lower triaromatic steroids, C_{20} and C_{21} , as compared to the higher ones C_{26} – C_{28} .

All differences between the free bitumen and the bound bitumens, as seen for to the group composition and the distribution of biological markers, clearly demonstrate that siliceous minerals have a significant adsorption and catalytic effect on the transformation of bitumen.

Fig. 3.12 Ion chromatograms m/z 217 (steranes) of bound bitumens 3. (Peak identification is given in Table. 2.5)



Interactions Between Minerals and Kerogen

Box 3.4: *General Note*

Minerals also exert adsorption and catalytic influence on kerogen in sedimentary rocks. However, while the composition of bitumen depends to a great extent on the adsorption properties of minerals, changes of kerogen are largely a consequence of their thermocatalytical activities.

Assessment of the influence of minerals on catagenetic changes in kerogen, or its degradation to gaseous and liquid products, can be made by comparing the experiment with pyrolysis of “pure” kerogen and pyrolysis of kerogen which is “enriched” with various minerals. His approach allows to track differences in the yield of gaseous and liquid products, but also differences in the composition of biological markers. Another approach might be to investigate the effects of native mineral materials to thermal changes in kerogen. To understand the influence of minerals on the thermal changes of kerogen it is useful to consider both approaches.

Pyrolysis of Kerogen in the Presence of Added Minerals

Tannenbaun et al. (1986) presented an example of the pyrolysis results of “pure” kerogen and the kerogen “enriched” with calcite, montmorillonite or illite.

Pyrolysis of “pure” type II kerogen gives a substantial amount of bitumen 1, a much smaller amount of bitumen 2 and C_1-C_9 hydrocarbons. The yield of free bitumen was highest after 100 h. After 1000 h the yield was slightly lower. With added calcite, changes in the yield of products are minimal, and the yield of bitumen 1 is the highest after 1000 h. However, with added montmorillonite, there can be seen significant differences in the yields of pyrolytic products. The amount of bitumen is considerably smaller, while the amounts of C_1-C_9 hydrocarbons and, in particular, bitumen 2, are noticeably higher compared to the amounts that are obtained by pyrolysis of “pure” kerogen. Lower yields of bitumen 1, with concurrent increase in the yield of bitumen 2, are observed when illite is added to the kerogen.

Relative reduction in the yields of free bitumen in the pyrolysis of kerogen with montmorillonite is not due to inhibitory effect of this mineral to the pyrolysis, but, on the one hand, to very pronounced catalytic effect of this mineral on cracking of compounds in free bitumen and on the creation of small molecules that enter into the composition of gaseous products and condensates. On the other hand, this effect can be attributed to adsorption of bitumen on montmorillonite.

Type I kerogen gives a similar result as type II kerogen. However, there are some differences observed. Namely, the yield of bitumen 2 and of C_1-C_9 hydrocarbons is noticeably increased when kerogen is enriched by illite and particularly by montmorillonite. However, pyrolysis of type I “pure” kerogen produces bitumen 1 in a

significantly higher yield, the yield of bitumen 1 and 2 together during the pyrolysis of kerogen with montmorillonite is not higher than the yield of these bitumens in pyrolysis of “pure” kerogen. Higher yield of bitumen at pyrolysis of type I kerogen can be explained by the higher potential to create hydrocarbons of type I kerogen compared to type II kerogen.

Montmorillonite and illite have a stronger effect on type II kerogen. This type of kerogen is in a stronger interaction with minerals because of a higher content of heteroatoms (oxygen and sulphur), and thus higher polarity.

The above considerations show how it is possible to assess on a laboratory scale the influence of minerals on the changes of kerogen. The question is whether it is the same under geological conditions, since under natural conditions the temperatures are much lower (temperatures in source rocks range from 50 to 150°C). On the other hand, the processes occur in a long geologic time period, measured in millions of years. Also the moisture and water content under natural conditions have to be considered. Water reduces the catalytic effect of minerals, which means that in the experiments of “dry” pyrolysis, the catalytic as well as the adsorption effect of minerals is probably stronger than in nature. Therefore, for a more faithful picture, an approach which involves the addition of water is considerably better. The experiments of the so-called “hydrolysis” carried out so far, showed, that minerals had somewhat weaker effects on changes in kerogen. However, it does not change the overall conclusion about the catalytic and adsorption effects of silicate minerals, on the changes of kerogen, which lead to the creation of bitumen and gaseous hydrocarbons.

Pyrolysis of Kerogen in the Presence of Native Minerals

The described approaches to study the catalytic effects of minerals on the thermal changes of organic matter in sediments were based on experiments of pyrolysis of some compounds identified in the sediments, or native geologic organic materials, with the addition of certain minerals. This roughly defined the thermocatalytic properties of minerals, but it was not accurately indicated to what extent minerals influence the maturation processes under natural geological conditions. Therefore, it is useful and necessary to define more reliably the influence of native mineral materials on the thermal changes of kerogen. Significant conclusions can be made if one compares the yields and composition of gaseous and liquid products that are obtained by pyrolysis of substrates of different mineralogical composition, obtained by gradual removal of carbonates, silicates and pyrite from a sample of a sedimentary rock. Figure 3.13 presents a diagram of the procedure for obtaining these substrates. The degree of success of demineralization is checked by X-ray analysis of minerals in the initial sample and the obtained substrates (Fig. 3.14).

Pyrolysis in this study is performed usually by heating at 550–600°C, during 50–60 min in a stream of an inert gas. The yield of gaseous and liquid products is determined separately. Additionally, the stable carbon isotope composition ($\delta^{13}\text{C}_{\text{PDB}}$) and

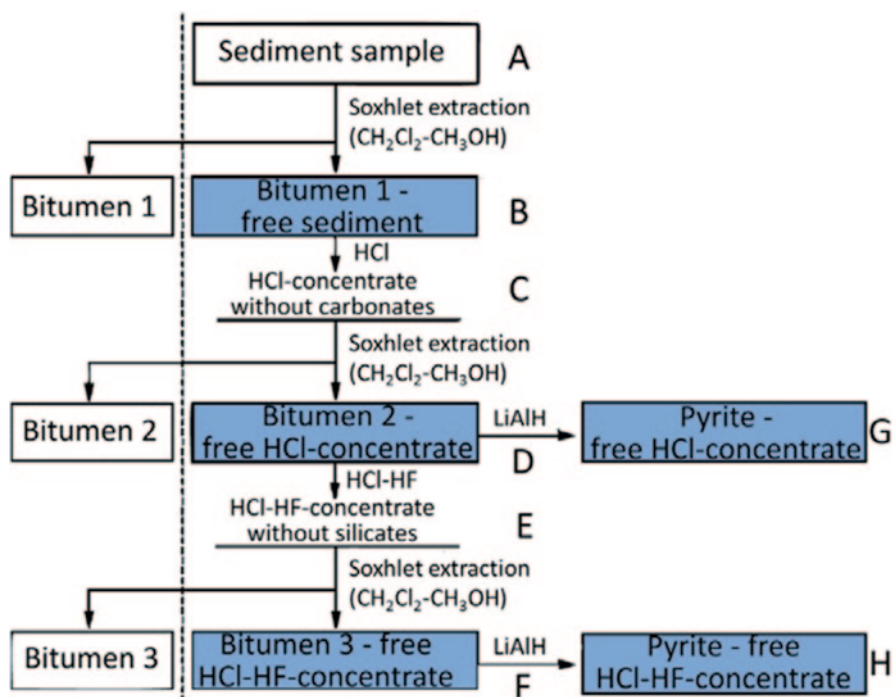


Fig. 3.13 Preparation scheme for obtaining substrates with different mineralogical composition from one sample of sedimentary rock

biological markers (*n*-alkanes, steranes, terpanes and aromatic steroids) are analysed. Comparison of the obtained results may be useful to reach conclusions about the intensity of interactions, as in all the substrates the same kerogen is found, but containing different mineral environment. It is of particular interest to compare the results of pyrolysis of the initial sample and substrates containing only silicate minerals (usually quartz, cristobalite, plagioclase, kaolinite, illite and montmorillonite), with the results of pyrolysis of the substrate that is free of minerals and containing only a certain amount of residual quartz (Figs. 3.13 and 3.14).

It was found that minerals in sediments have very little catalytic effect on the pyrolysis of kerogen. Certain catalytic effect is exerted only by silicate minerals when they are concentrated in a specific substrate. In the previous chapter it was pointed out that these are illite and montmorillonite. They influence to some extent the increase in the yield of gaseous and liquid products, the homolytic bonds cleavage involving the heavier carbon isotope, ¹³C, the reduction of *n*-alkanes in relation to *n*-alkenes, the formation of thermodynamically stable sterane and triterpane isomers, C₂₉ 14α(H), 17α(H), 20S sterane and C₃₁ and C₃₂ 17α(H), 21β(H), 22S triterpanes of hopane type, and the reactions of cracking of side chains of higher

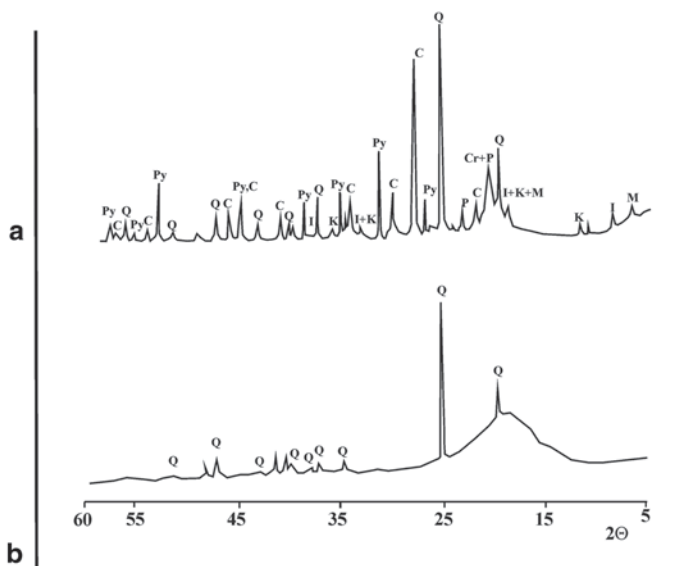


Fig. 3.14 X-ray diffractograms of initial oil shale sample and final substrate obtained according to the scheme given in Fig. 3.13. (C calcite, Q quartz, Cr crystalbaltite, P plagioclase, K kaolinite, I illite, M monmorillonite, Py pyrite)

members of triaromatic steroids, C_{26} – C_{28} , and thereby the forming of C_{20} and C_{21} isomers.

Catalytic effect of native calcite and pyrite is negligible. Pyrite may possibly be a source of sulphur for the formation of organo-sulphur compounds of thiophene type.

Box 3.5: *General Note*

In the chapter on the differences in composition of free and bound bitumens it was said that native silicate minerals have a significant adsorption and catalytic effect on the transformations of bitumen. On the other hand, the catalytic effect of silicates on the pyrolysis of kerogen is very low. Much more intensive catalytic effect of native silicate minerals on thermal changes of bitumen can be explained by a higher mineral/bitumen mass ratio than the mineral/kerogen ratio in a sedimentary rock and a stronger interaction between the silicate minerals and soluble bitumen than the insoluble kerogen of macromolecular nature.

As a consequence of the described interactions of minerals and fossil organic matter, the most commonly applied organic-geochemical parameters (such as CPI, n -alkane distribution, $Pr/n-C_{17}$ and $Phyt/n-C_{18}$ ratios, sterane and triterpane ratios,

mono- and triaromatic steroid parameter), may be applied as reliable maturation correlation parameters only if the investigated samples come from the sedimentary rocks of the same or similar mineralogical composition.

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