

## Chapter 10

### The geochemical behavior of selected elements

This chapter is intended to provide a geochemical overview of a number of important elements. The elements will be grouped according to mixed criteria, in particular their position in the periodic table and their geochemical properties. We will describe the major mineral phases that host these elements in the mantle and the crust, their properties in solution, and the processes by which they are transferred from any major reservoir (mantle, crust, ocean) to its neighbors. We will not reproduce here the terrestrial abundances, which can be found in Appendix A. We will nevertheless provide the reader with some important data. Condensation temperatures in the solar nebula (Wasson, 1985) define the volatile versus refractory character of the element. The solubility and complexation data in surface waters (Morel and Hering, 1993) and the residence times in seawater (Broecker and Peng, 1982) constrain the concentration level and speciation in natural waters at low temperature. Different parts of geochemical cycles may receive uneven attention. This inhomogeneous treatment reflects the power of geochemistry: different elements are used to trace different processes. The elements that essentially fractionate in atmospheric and oceanic processes (N, O, H) have not been dealt with, while only the long-term aspects of the carbon cycle have been considered.

#### 10.1 Silicon

Most common form:  $\text{Si}^{4+}$

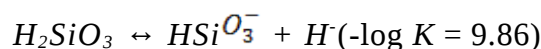
Ionic radius: 0.26 Å

Stable isotopes: 28 (92.23%), 29 (4.67%), 30 (3.10%)

Atomic weight: 28.086

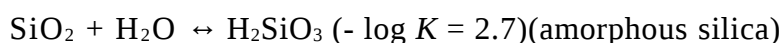
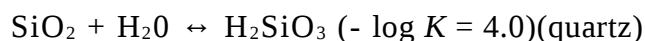
Condensation temperature: 1311 K

Dissociation of silicic acid in water:



No significant complex in waters

Reactions limiting solubility in water:



Residence time in seawater: 20 000 years

Silicon is, after oxygen and iron, the third most abundant element in the Earth. Although Si concentration in the core may reach several per cent, this ubiquitous element is essentially lithophile and refractory. It is the most abundant cation of the silicates that form the mantle at shallow depth (olivine, pyroxene, plagioclase, garnet), at intermediate depth (ringwoodite, majorite), and in the deep mantle (perovskite). It also forms the major igneous minerals in the crust of both mafic igneous rocks (olivine, pyroxene, amphibole, plagioclase) and felsic igneous rocks (quartz, feldspars). Silicon is a major constituent of elastic sediments (quartz and clay minerals) and makes up a substantial fraction of metamorphic minerals.

At pressures corresponding to the surface, the crust, and the upper mantle, Si is tetrahedrally coordinated and occupies the center of a four-oxygen tetrahedron. At very high pressure, Si can be accommodated in octahedral sites. Since melts from the mantle are systematically enriched in silicon with respect to the residue, this element may be classified as slightly incompatible. It forms stoichiometrically fixed minerals: the various forms of silica  $\text{SiO}_2$  are stable at different pressures: quartz and amorphous silica are stable in the crust and the upper mantle, while coesite and stishovite are stable at increasingly higher pressures. A basalt typically contains 45-50 wt %  $\text{SiO}_2$  and granitic melts 70 wt %  $\text{SiO}_2$ . Quartz is unstable in the presence of Mg-rich olivine. Silica solubility in hydrous fluids increases with temperature and with pH (see Chapter 7).

High-temperature fluids transport large quantities of  $\text{SiO}_2$  which, upon cooling, form the ubiquitous quartz veins seen in metamorphic basements. Warm diagenetic fluids carry silica, which precipitates in the upper sedimentary layers: this is the origin of the familiar flintstones that grow on any seed (fossil, pebble) occurring in limestones. When the replacement of the initial sediment is total, a siliceous rock known as chert is obtained.

As a result of the very low solubility of silica at ambient temperature, quartz is essentially left untouched by erosion and forms the familiar sands that, upon diagenetic cementation, become sandstones. For the same reason, silica concentration in seawater is very low and, as a result of biological activity, the ocean is actually under-saturated in silica.  $\text{SiO}_2$  is used by both phytoplankton (diatoms) and zooplankton (radiolaria). Silica is therefore depleted in the upper layer of the oceans, while the falling debris re-dissolves at depth. Deep old waters are the most enriched in silica. Oceanic upwellings, such as the Atlantic Ocean off the coast of Morocco or the equatorial belt, bring up abundant sources of silica. Sediments from those areas are rich in silica deposited by falling organisms. Other localities, with warm hydrothermal springs on the seafloor such as in the neighborhood of ridges and other volcanic areas, are also rich in siliceous sediments. The older waters from the Southern Oceans being rich in silica, it is not surprising to see a substantial fraction of the seafloor of the southern hemisphere covered with diatom-rich oozes.

## 10.2 Aluminum

Most common form:  $\text{Al}^{3-}$

Ionic radius: 0.39 Å (tetrahedral) and 0.54 Å (octahedral)

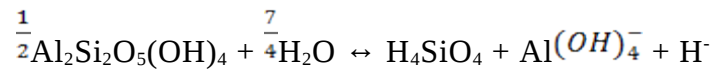
Stable isotope: 27 (100%)

Atomic weight: 26.982

Condensation temperature: 1650 K

Complexes in water: hydroxides

Reactions limiting solubility in water:



Aluminum is the sixth most abundant element in the Earth. Al is a highly refractory lithophile element. The radioactive isotope  $^{26}\text{Al}$  quickly decayed into  $^{26}\text{Mg}$  in the very first millions of years of the Solar System's evolution. It provided substantial heating to the early planets, and the isotopic composition of Mg is one of the most widely used chronometer based on extinct radioactivities. It is unlikely that Al enters in large proportions in the core, but Al is in many major minerals at any depth in the mantle and in the crust. In the mantle, it enters plagioclase up to pressure of about 1 GPa, spinel to 2 GPa, and garnet beyond. At these high pressure, Al also enters clinopyroxene in large proportions: garnet and clinopyroxene dissolve into each other to form majorite, an essential mineral phase of the mantle above the 660 km discontinuity. At higher pressure, Al is hosted in a perovskite structure, but its precise behavior is still largely unknown. The major plagioclase occurs in basalts, while plagioclase and alkali feldspar may occur together in felsic rocks. Biotite mica may occur in both types of rocks but normally accounts for a small part of the Al inventory. In sedimentary rocks, Al is hosted in clay minerals such as kaolinite and illite and, occasionally, in detrital feldspars. In metamorphic gneisses and schists, Al largely resides in feldspars and micas.

Aluminum can be tetrahedrally coordinated and in this coordination it replaces Si in the center of oxygen tetrahedra. It can also be octahedrally coordinated and form solid solutions with elements such as Ca, Mg, and Fe. During melting, the Al-rich minerals (feldspar, spinel, garnet) quickly dissolve into the melt and Al therefore behaves as a moderately incompatible element. During low-pressure fractionation of basalts, Al is removed by plagioclase precipitation. At higher pressure, plagioclase solubility in silicate melts increases, and this mineral does not precipitate until a late stage in the magmatic differentiation. Aluminum is therefore useful in assessing the depth of differentiation of basaltic series. In mid-ocean ridge and continental flood basalts, Al concentrations do not vary much with fractionation because they are buffered by plagioclase removal: these lavas are differentiated at low pressure in the plagioclase stability field. In contrast, Al concentrations increase steadily with fractionation of Hawaiian basalts: these rocks evolve at higher pressure in the absence of plagioclase. Typical concentrations of  $\text{Al}_2\text{O}_3$  in basaltic and granitic melts average 15 wt %.

Aluminum solubility in hydrous fluids is low, except at very high temperature and high pH. This solubility is controlled by the stability of different complexes with the hydroxyl ion  $\text{OH}^-$  and the solubility of clay minerals in equilibrium with the solution, e.g. kaolinite. The minimum in solubility at  $\text{pH} \approx 6$  reflects the amphoteric character of this element. During weathering, Al solubility is controlled by kaolinite reactions of alkalinity production (6.15). The destruction of feldspars by  $\text{CO}_2$ -rich fresh water leaves Al in clays: this element is most efficiently transported by rivers to the sea in the suspended load. In seawater, Al solubility is controlled by the input of airborne clay particles transported from deserts, which gives Al distribution in the water column an unusual profile with concentration decreasing down the thermocline (Fig. 6.12).

### 10.3 Potassium

Most common form:  $K^+$   
Ionic radius: 1.51 Å (octahedral) and 1.64 Å (dodecahedral)  
Stable isotopes: 39 (93.26%), 40 (0.011%), 41 (6.73%)  
Atomic weight: 39.098  
Long-lived isotope: 40 ( $T^{1/2} = 1.25 \times 10^9$  a)  
Condensation temperature: 1000 K  
No significant complex in waters  
Residence time in seawater:  $12 \times 10^6$  years

Potassium is an alkaline element i.e. both volatile and lithophile. Its concentration in the Earth is therefore poorly constrained. As for other volatile elements, K is depleted in the Earth with respect to carbonaceous chondrites and enriched with respect to Mars and the Moon. The dual decay of the radioactive isotope  $^{40}K$  into either  $^{40}Ca$  by  $\beta^-$  emission or  $^{40}Ar$  by electron capture makes this element, after U and Th, one of the three significant sources of heat in the Earth and accounts for about 20% of the radioactive heat production. As discussed in Chapter 8, it is not known whether K enters into the core composition.

The mineral phases that host K in the mantle are not well understood. Under upper mantle conditions, traces of high-K mineral phases, notably the Mg-rich mica phlogopite and occasionally alkali feldspar, may be present in those parts of the mantle that have been contaminated by subducted sediments or by fluids produced by the dehydration of the subducted oceanic crust. In the lower mantle, K may at least in part reside in the mineral hollandite, a high-pressure equivalent of alkali feldspar. The prime K repositories in igneous rocks are alkali feldspars, amphibole, and micas. In sedimentary rocks, most of the K inventory is sequestered in clay minerals, notably in smectites, illite, and in detrital feldspars.

The  $K^+$  ion is very large. Although it may enter octahedral sites, it often fits 12-coordinated sites as in feldspars and micas. During melting in the mantle and basalt differentiation, K is strongly incompatible and follows other incompatible elements such as Th and U to the extent that the K/U ratio remains essentially constant in the mantle and the crust. Mid-ocean ridge basalts are far less concentrated ( $\approx 0.1$  wt %) in K than ocean island basalts (1-2 wt %). Granitic melts typically contain 2-3 wt %  $K_2O$ . Felsic igneous melts are normally saturated in feldspar and biotite: K is therefore not incompatible in the genesis of granitic rocks.

At low temperature and therefore during weathering, feldspars react with water to produce clay minerals. The K-rich clay mineral illite is left as a residue and its ubiquitous presence keeps the concentration of K in low-temperature hydrous fluids (rivers, seawater) at very low levels. K is therefore transported to the sea with the suspended load. In high-temperature hydrothermal fluids, K reacts with country rocks to form the K-feldspar crystals commonly observed in the metamorphic aureoles of granitic intrusions. Upon cooling, K is leached preferentially to Na, while the converse becomes true when the temperature of interaction between fluids and their ambient rocks falls below about 300°C.

Solubility of KCl (sylvite, a major fertilizer) in water increases greatly with temperature. Through evaporation of brines in cool and cold ( $< 50^\circ$ ) landlocked or lagoonal environments, sylvite becomes saturated before NaCl (halite). In seawater, K is not biolimited and its concentration is essentially constant in the water column.

## 10.4 Sodium

Most common form: Na<sup>-</sup>

Ionic radius: 1.02 Å (octahedral)

Stable isotope: 23 (100%)

Atomic weight: 22.990

Condensation temperature: 970 K

No significant complex in waters Residence time in seawater: 83 x 10<sup>6</sup> years

Sodium is a volatile and lithophile alkaline element. As with K, Na terrestrial abundance is therefore not well known. Breaking down the inventory of Na among mantle minerals is very difficult. Most major mineral phases do not accept this element but, under upper mantle conditions, Na solubility in clinopyroxene increases substantially with pressure. In the crust, Na is essentially hosted in the albite component of plagioclase feldspar. In contrast with potassium, there is no major Na-rich clay mineral of major geological importance and most sedimentary Na resides in detrital feldspar. Evaporitic rock salt NaCl represents another significant surface repository of sodium.

In silicates, the Na<sup>-</sup> ion normally occupies octahedral sites. It is a moderately incompatible element during mantle melting and the early stages of basalt differentiation. Plagioclase saturation in basalts differentiated at low pressure such as mid-ocean ridge and continental flood basalts (see Section 10.2) and in more felsic melts turns Na into a moderately compatible element. Basalts typically contain 2-3 wt% Na<sub>2</sub>O and granitic melts 3-4 wt % Na<sub>2</sub>O. Although albite may be stable under near-surface conditions, it rarely reaches saturation in hydrous fluids at ambient temperature. Authigenic albite is known in sediments, but is not ubiquitous. Na is therefore preferentially leached by low-temperature hydrothermal fluids in contrast to K, which dominates in higher temperature fluids. Alteration of seafloor basalts by warm percolating fluids rich in sodium and silica leads to the replacement of calcic plagioclase (anorthite) by albite:



Basalts altered on the seafloor are therefore notably enriched in Si and Na with respect to their unaltered precursor. There is a stark contrast between K and Na behavior under surface conditions imposed by the lack of a major stable low-temperature Na-rich phase. Sodium ions set free by the weathering of feldspars are transported by rivers into the sea in the dissolved load. Sodium is the second most abundant element in seawater and the most abundant cation. Its concentration is limited mostly by interaction of seawater with the seafloor through diagenetic and hydrothermal fluids. Its concentration is constant throughout the water column. In warm landlocked or lagoon environments, NaCl saturation may be reached and evaporitic halite becomes a prominent sedimentary deposit.

## 10.5 Magnesium

Most common form:  $Mg^{2-}$

Ionic radius: 0.72 Å (octahedral)

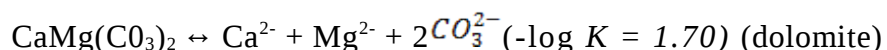
Stable isotopes: 24 (78.99%), 25 (10.00%), 26 (11.01%)

Atomic weight: 24.305

Condensation temperature: 1340 K

Complexes in water: hydroxides, carbonates, sulfates

Reactions limiting solubility in water:



Residence time in seawater:  $13 \times 10^6$  years

Magnesium is a refractory and lithophile alkaline-earth element. It does not enter core composition in substantial concentration. After oxygen, magnesium is the second most abundant element in the mantle where it is hosted in most major minerals (olivine, pyroxenes, garnet, spinel, ringwoodite, etc.). Its concentration in the average crust is relatively low: as a consequence, amphiboles, micas, Mg-rich clays (smectite), and carbonates (dolomite) normally remain minor mineral phases. Mg-rich calcite is a major form of carbonate precipitated by marine organisms. After Na, Mg is the second most abundant cation of seawater in which it is partly complexed by carbonate and sulfate ions.

In silicates, Mg ions occupy octahedral sites. Many of its properties are better understood by observing that Fe and Mg have identical ionic charges and similar ionic radii. In sedimentary and igneous carbonates, Mg substitutes for Ca. During mantle melting and magma differentiation, Mg is strongly compatible. Primary basalts are rich in Mg and rapidly lose most of it by gravitational removal of olivine and clinopyroxene. The most common indices of magmatic differentiation involve Mg, either as the MgO content, the FeO/MgO ratio or the fraction known as the mg# and which is the atom ratio  $Mg/(Fe + Mg) \approx 100/(1 + 0.56 \text{ FeO/MgO})$ . Relatively undifferentiated basalts may contain 8-16 wt % MgO with FeO/MgO ratios close to unity and mg# in excess of 65. Typical granitic melts only contain 2-4wt % MgO. Probably the most striking property of Mg in hydrous fluids is its strong shift in solubility between ambient temperature and about 70°C: seawater, cold ground water, and runoff contain substantial amounts of Mg, while all hydrothermal and warm diagenetic fluids are Mg-free. A number of processes help explain such a shift: precipitation of acid Mg-sulfate in the black smoker feeding zones (see Chapter 7), precipitation of Mg-Ca carbonate in coastal environments (dolomitization), etc. The removal of seawater Mg in the ridge-crest hydrothermal systems approximately balances out rhyolite input of Mg to the ocean.

Magnesium is liberated from silicates by weathering (6.23) and transported to the sea in the dissolved load. Its abundance is not limited by a low-solubility mineral phase and is essentially constant down the water column. Partitioning of Mg into calcium carbonate seems to be dependent on the temperature conditions of precipitation: the Mg content of carbonates can therefore be used as a thermometer of ancient marine environments.

## 10.6 Calcium

Most common form:  $\text{Ca}^{2+}$

Ionic radius: 1.00 Å (octahedral)

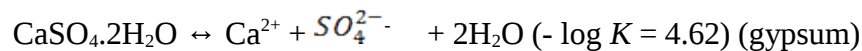
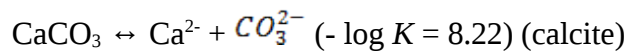
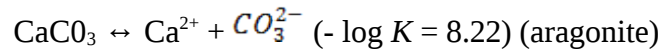
Stable isotopes: 40 (96.94%), 42 (0.65%), 43 (0.14%), 44 (2.09%), 46 (0.004%), 48 (0.19%)

Atomic weight: 40.078

Condensation temperature: 1518 K

Complexes in water: hydroxides, carbonates, sulfates

Reactions limiting solubility in water:



Residence time in seawater:  $1.1 \times 10^6$  years

Calcium is a refractory and lithophile alkaline-earth element. The abundance of the isotope 40 produced by radioactive decay of  $^{40}\text{Ar}$  is occasionally used as a chronometer. The relative abundances of non-radiogenic isotopes have also been used as a tracer of certain biological processes. Just like Mg, Ca does not enter core composition in substantial quantities. In the mantle, Ca is stored in clinopyroxene and in its high-pressure equivalent Ca-perovskite. In igneous rocks, as in the crust in general, calcic plagioclase (anorthite) and amphibole are major hosts for calcium. There is no major Ca-rich clay mineral. The major low-temperature Ca-rich phase is Ca carbonate in its two forms calcite and aragonite. Calcium phosphates are a ubiquitous form of Ca storage in igneous (fluorapatite) and sedimentary rocks (carbonate-apatite). Apatite is the essential ingredient of vertebrate hard parts (bones and teeth). Calcium sulfates (gypsum and anhydrite) are an essential component of evaporitic sequences.

In silicates, Ca ions occupy octahedral sites. During mantle melting, Ca is slightly incompatible. Its behavior during magmatic differentiation is controlled by the stability of plagioclase and clinopyroxene (see Section 10.2). High-pressure magmatic differentiation takes place in the presence of clinopyroxene but in the absence of plagioclase and therefore decreases the Ca/Al ratio in the residual melt. Low-pressure fractionation of basalts in the stability field of clinopyroxene and plagioclase leaves the Ca/Al ratio essentially constant. Although the Ca content of olivine is low (a fraction of a percent), it increases with decreasing temperature. Olivine phenocrysts in basalts may contain up to 0.5 wt % CaO, while mantle peridotites are normally far more depleted. Basaltic melts typically contain 10-12 wt % CaO and a granitic melt 2-4 wt % CaO.

Calcium is a mobile element during water rock interaction at any temperature. Plagioclase, clinopyroxene, and amphibole are easily weathered by water equilibrated with atmospheric  $\text{CO}_2$  and by seawater alteration of submarine basalts.  $\text{Ca}^{2+}$  goes into solution and is transported to the sea by runoff, while Ca-free mineral phases, silica and clay minerals, are left behind. Carbonate, sulfate, and phosphate complexes of Ca are strong. Calcium is the third most concentrated cation of seawater. The Ca concentration level in fresh water and seawater is controlled by the solubility of calcite and aragonite. Calcite is less soluble than aragonite. Surface oceanic water is saturated in calcite, while deep water is undersaturated. This results from the combined effect of temperature and pressure on the

solubility product of calcium carbonate and the dissociation constants of carbonic acid but also of the  $\Sigma\text{CO}_2$  content of local seawater. Removal of calcium carbonate from the ocean by biogenic carbonate precipitation is the most important control of seawater alkalinity and therefore is the crux of the response of the ocean-atmosphere system to  $\text{CO}_2$  fluctuations due to changes in volcanic activity, biological productivity, and erosion patterns.

In brines from landlocked and lagoonal environments, precipitation of calcium sulfate may occur as either hydrated gypsum at temperatures below about  $35^\circ\text{C}$  or anhydrous anhydrite at higher temperatures. Gypsum normally converts to anhydrite during burial.

## 10.7 Iron

Most common forms:  $\text{Fe}^0$ ,  $\text{Fe}^{2+}$ , and  $\text{Fe}^{3+}$

Ionic radius: 0.61 Å for  $\text{Fe}^{2+}$  and 0.55 Å for  $\text{Fe}^{3+}$  (octahedral)

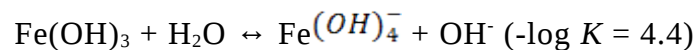
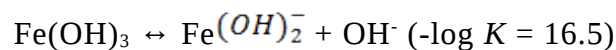
Stable isotopes: 54 (5.90%), 56 (91.72%), 57 (2.10%), 58 (0.28%)

Atomic weight: 55.847

Condensation temperature: 1336 K

Complexes in water: hydroxides, chlorides

Reactions limiting solubility in water:



Residence time in seawater: 55 years

Iron is the most abundant element in the Earth. It is refractory and, by definition, siderophile. It is the most abundant element of the core, both in the solid inner core and the liquid outer core in which convection generates the terrestrial magnetic field. In contrast with the core where Fe occurs in its metallic and most reduced form  $\text{Fe}^0$ , iron in the mantle is essentially in its  $\text{Fe}^{2+}$  form. Ferrous iron ( $\text{Fe}^{2+}$ ) substitutes for  $\text{Mg}^{2+}$  in most silicate mineral phases. Fe is, after Si and Mg, the third most abundant cation in the mantle. In the upper mantle, ferrous iron is found in olivine, pyroxene, garnet, and amphibole. In the deep mantle, it enters with Mg into the perovskite structure of ringwoodite but also into the oxide structure of magnesio-wüstite ( $\text{Fe}$ ,  $\text{Mg}$ )O. In igneous rocks, as in the crust in general, it is hosted in amphibole and biotite but also, together with  $\text{Fe}^{3+}$ ,  $\text{Al}^{3+}$ ,  $\text{Cr}^{3+}$ , and  $\text{Ti}^{4+}$ , in oxide minerals (magnetite, ilmenite). Ferric iron easily substitutes into the tetrahedral site of alkali feldspars, which is why so many granites turn reddish upon incipient weathering. When exposed to the atmosphere or seawater at low temperature, Fe is normally oxidized to  $\text{Fe}^{3+}$ . It is found in different forms of iron hydroxide (such as goethite, hematite, and limonite) that dominate soils, sediments, as well as ferromanganese nodules and encrustations from the deep sea. Iron-rich clay minerals and carbonates are uncommon. Organic compounds contain important Fe-rich proteins that have different functions, notably oxygen transport in the cell (porphyrins). Iron concentration in seawater is very low, again because of the very low solubility of hydroxides.

The sites occupied by  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  are normally octahedral, but  $\text{Fe}^{3+}$  can be found in tetrahedral sites, especially in feldspars. During mantle melting,  $\text{Fe}^{2+}$  has a neutral



behavior (neither compatible nor incompatible) owing to its lack of octahedral site preference energy (see Chapter 1). In contrast,  $\text{Fe}^{3+}$  is highly incompatible. Silicates are very poor electrical conductors so magmas cannot exchange significant amounts of electrons with country rocks. Upon removal of ferrous iron into cumulate minerals, the  $\text{Fe}^{3+}/\text{Fe}^{2+}$  ratio therefore increases in residual melts. The apparently more oxidizing conditions of differentiated rocks are therefore not the result of an externally imposed higher "fugacity" of oxygen, but simply reflect the increasing electron deficit in smaller and smaller quantities of melt. Most basalts would contain 10-12 wt% total iron as FeO and granites 3-4 wt%. Typically, about 15 wt % of the iron present in a primary basalt is in the form of  $\text{Fe}^{3+}$ . Even when small quantities of ilmenite and magnetite are present at the liquidus, iron concentration in melts does not change when the fractionating assemblage is dominated by olivine and pyroxene: this is the case for the high-pressure differentiation of ocean island basalts and for the wet differentiation of orogenic (calc-alkaline) magmas. When plagioclase is present, as in mid-ocean ridge and continental flood basalts (see Section 10.2), iron is significantly more incompatible. These contrasting trends are known in the petrological literature as the Fenner trend (constant Fe) and the Bowen trend (increasing Fe), respectively.

The behavior of iron during water rock interaction must be understood with respect to the different properties of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  in solution. Although  $\text{Fe}^{3+}$  is strongly complexed by Cl ions, its concentration is greatly limited by the solubility of ferric iron hydroxides. In contrast,  $\text{Fe}^{2+}$  is highly soluble. Reducing solutions can transport huge amounts of ferrous Fe and reprecipitate it when the conditions become more oxidizing. This is the case of the hydrothermal solutions of the submarine black smokers that precipitate enormous amounts of hydroxides and form the metalliferous sediments observed in the vicinity of the mid-ocean ridges. This is also the case of the Archean oceans that precipitated the banded iron formations (BIF) that form our current prime iron ore: the low pressure of oxygen in the ancient atmosphere permitted the long-distance transport of ferrous iron until subtle changes in the marine oxidizing conditions triggered the massive precipitation of iron hydroxide. The modern atmosphere being oxygen-rich, iron is kept in its ferric form. Weathering of the continental crust leaves residues of hydroxide minerals that are transported to the sea with the riverine suspended load. Some of these hydroxides are in the form of colloids of very small dimension (smaller than the 0.45 micrometer pore dimension of common filtering devices). The very large surface area and the charged surface of these colloids allows their mutual repulsion and therefore maintains the colloids in suspension. Adsorption of many highly charged elements on these colloids is very efficient. This is the case of many transition elements such as  $\text{Cr}^{3+}$ , but also of all the rare-earth elements (3+), uranium, thorium, etc., that get their ride to the sea on these colloids. When rivers meet seawater in estuaries, the dielectric properties of the mixture change allowing the particles to flocculate and precipitate with clay minerals as estuarine sediments, entraining in this process a very large fraction of the highly charged elements before they reach the open ocean.

Iron is mostly introduced into the ocean as airborne particles of goethite and limonite transported by winds from arid areas (Sahara, Gobi). Its concentration profile in the water column is unusual (and is only matched by that of cobalt). It displays concentrations decreasing from the surface to the bottom, which is a result of the progressive dissolution of the falling airborne particles. Iron may play an important role in the control of biological productivity in the ocean, and, via  $\text{CO}_2$  consumption by phytoplankton, in the control of the greenhouse effect and climates. Some scientists believe that Fe, which is a trace nutrient (micronutrient) indispensable to biological

activity, is normally in short supply in surface waters. In this scenario, the introduction of Fe-rich airborne particles would fertilize the sea more efficiently during dry periods and quickly draw down part of the atmospheric CO<sub>2</sub>.

The behavior of iron at the interface between seawater and the oceanic crust also represents a set of major geochemical processes. Upon circulation of seawater through the fractured oceanic crust, basaltic Fe<sup>2+</sup> is oxidized into Fe<sup>3+</sup> at the expense of dissolved O<sub>2</sub>, then through the reduction of seawater SO<sub>4</sub><sup>2-</sup> into sulfide S<sup>2-</sup> (see Chapter 7). During diagenesis, a different process takes place in the oxygen-starved layers below the bioturbation layer: biological reduction of SO<sub>4</sub><sup>2-</sup> into sulfide S<sup>2-</sup> changes the redox conditions. Ferric iron hydroxides (such as those composing ferromanganese nodules) are reduced to soluble Fe<sup>2+</sup>, which then precipitates with S<sup>2-</sup> to form the pyrite Fe<sub>2</sub>S commonly found in reduced sediments.

## 10.8 Sulfur

Most common forms: S<sup>0</sup>, S<sup>2-</sup>, and SO<sub>4</sub><sup>2-</sup>

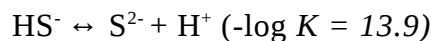
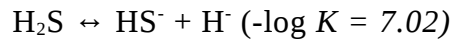
Ionic radius: 0.31 Å (tetrahedral), 0.29 Å (octahedral), and 1.84 Å (S<sup>2-</sup>)

Stable isotopes: 32 (95.02%), 33 (0.75%), 34 (4.21%), 36 (0.02%)

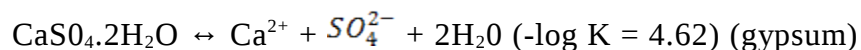
Atomic weight: 32.07

Condensation temperature: 648 K

Dissociation of H<sub>2</sub>S in water:



Reactions limiting solubility in water:



Residence time in seawater: not known but oceans are well mixed for sulfate

Sulfur is strongly chalcophile and volatile. It has been repeatedly suggested that very large quantities of this element are dissolved in the core and contribute to the relatively low seismic velocities of the core with respect to those of pure iron. Sulfur does not readily dissolve in silicates. Terrestrial sulfur is therefore stored in sulfides. At high temperatures, solid solutions of Ni and Fe dominate (monosulfide solid solution, MSS). At ambient temperature, sulfur enters a variety of sulfides. The major repository of sulfur in sediments is sulfides, notably pyrite. Because sulfates, the oxidized form of sulfur, are relatively soluble, these minerals play a minor role in the

making of continental crust, with the exception of gypsum and anhydrite in evaporites, and barite in hydrothermal veins. In seawater, river, and rain-water, in which substantial amounts of dissolved oxygen are present, the stable form of sulfur is the oxidized form, sulphate  $SO_4^{2-}$ , which is the third most abundant ion of seawater.

In magmas, sulfur is present as sulfide and also as sulfate in more oxidized granites. During mantle melting and magma differentiation, sulfur has a compatible behavior controlled by the exsolution and gravitational segregation of sulfide blebs (the melting point of Sulfides is lower than average magma temperature) that are occasionally observed as mineral inclusions. Sulfides are the most abundant minerals of inclusions in diamond. The high-temperature form of sulfides precipitated out of mafic magmas are characteristically rich in nickel (pentlandite). The high-temperature forms of igneous sulfides are very unstable with respect to low-temperature alteration.

Weathering oxidizes sulfides into soluble sulfate and all the sulfur from the crust is transported to the sea dissolved in the runoff. In landlocked and coastal environments, evaporation concentrates natural waters eventually to the point of gypsum and anhydrite saturation: these minerals are the most abundant form of evaporites. In seawater,  $BaSO_4$  saturation is often reached, but most of it is redissolved shortly after deposition. Microbial activity during early diagenesis turns marine  $SO_4^{2-}$  from interstitial fluids into sedimentary pyrite. Marine  $SO_4^{2-}$  introduced into submarine hydrothermal systems (black smokers) is first precipitated as anhydrite whose solubility decreases significantly with temperature, reduced by ferrous iron from ambient basalt, and mixed with sulfide leached from the basalts. The reduced forms  $H_2S$  and  $HS^-$  are present in hydrothermal fluids, largely leached from the basalts, in proportions that vary largely with the pH. Upon cooling, hydrothermal sulfur commonly precipitates as sulfides of Cu and Fe (chalcopyrite, pyrrhotite) at temperatures in excess of  $300^\circ C$ , and of Zn (sphalerite) at lower temperatures. Sulfur is abundant in volcanic fumaroles and is released as  $SO_2$  in large quantities into the atmosphere by volcanic eruptions. An important aspect of sulfur atmospheric chemistry is the production of gaseous dimethyl-sulfide (DMS) generated in vast quantities by phytoplankton.

## 10.9 Phosphorus

Most common form:  $PO_4^{3-}$

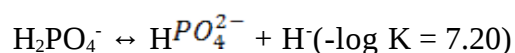
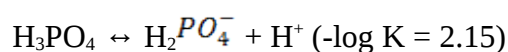
Ionic radius: 0.17 Å (tetrahedral)

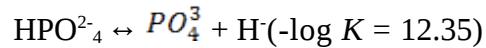
Stable isotopes: 31 (100%)

Atomic weight: 30.974

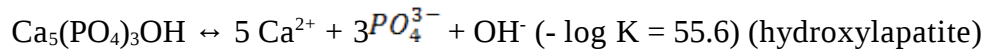
Condensation temperature: 1 151 K

Dissociation of  $H_3PO_4$  in water:





Reaction limiting solubility in water:



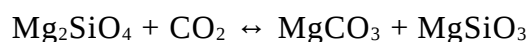
Residence time in seawater: 70 000 years

Phosphorus is a lithophile and moderately siderophile element. Substantial amounts of this element are probably dissolved in the liquid core. It is almost exclusively hosted in Ca phosphate (apatite) (see Section 10.6). Apatite may be of igneous origin. Although apatite is certainly present in the upper mantle. P repository in the deep mantle is not well understood. Biogenic (fish teeth and bones) and diagenetic apatites are the essential repositories of sedimentary phosphorus. They occasionally form huge deposits, as in West Africa, that are actively mined to provide agricultural fertilizer. Some of these deposits, found in particular in the Late Precambrian of China, are chemical precipitates and seem to be associated with episodes of global glaciation. In low-temperature waters, phosphates form numerous complexes and, as indicated by the dissociation reactions above, speciation is pH-dependent. Phosphorus concentration in seawater and river water is limited by the very low solubility of apatite. Phosphate radicals often attach themselves to the surface of iron oxi-hydroxide colloids when they precipitate in estuaries.

Phosphorus occurs principally in the center of oxygen tetrahedra. In seawater, P is one of the essential nutrients: in the Krebs cycle, adenosine triphosphate (ATP) is the major energy repository for cells, while ribose phosphates form the building blocks of nucleic acids DNA and RNA. Phosphate is brought to seawater by rivers and is removed, though only after many cycles across the thermocline, with the hard parts of biogenic debris. It is severely depleted in surface water but is regenerated during the dissolution of falling debris in deep water. It is depleted in young North Atlantic Deep Water with respect to the older Antarctic Bottom Water. Diagenetic dissolution, transport, and re-precipitation of apatite is common in sediments.

## 10.10 Carbon

Carbon is not an extremely abundant component of the Earth. It is both siderophile (in its reduced form) and atmophile (in its oxidized form). Substantial amounts of this element may be dissolved in the core. In the mantle, carbon occurs as graphite and, at depth in excess of about 120 km, as diamond when the conditions are reducing. In oxidizing conditions, carbon occurs as carbon dioxide, which, at depths of about 70-100 km, reacts with mantle silicates to form carbonates, e.g:



(olivine)

(magnesite) (pyroxene)

Carbon dioxide solubility in magmas rapidly changes with pressure and therefore depth. CO<sub>2</sub> outgassing from mantle-derived magmas starts at a depth of approximately 60 km and quickly strips the magma of many volatile species, such as rare gases, well before eruption. CO<sub>2</sub> is found as fluid inclusions in olivine phenocrysts (the prime target for He isotope measurements) and makes up a very important component of the gas phases in MORB and OIB.

Oxidized carbon in the crust occurs as sedimentary carbonates, mostly calcite which is two-three times more abundant than dolomite. The reduced forms are countless, from crystalline graphite to amorphous organic varieties (coal, oil, kerogene, methane). CO<sub>2</sub> is an important component of metamorphic gases and, in particular, is the dominant species in fluids from the granulite facies. In ground-, river-, and seawater, carbon occurs as carbonate oxi-anions  $CO_3^{2-}$  and HCO<sub>3</sub>, but traces of soluble organic components (humic and fulvic acids) are ubiquitous. Carbon dioxide makes up about 350 ppm per volume of the atmospheric gases.

The geochemical cycle of carbon is of particular significance because it is the most essential component of life. The extremely diverse polymerization modes of carbon compounds and their easy binding to a number of other elements and molecules (nitrogen, phosphate, iron, magnesium, and scores of other metals) are unique in nature. A major source of carbon dioxide is volcanic outgassing from the mantle. Carbonate groups are essentially indestructible except by biological activity or in extremely reducing environments. The prime sites for production of reduced carbon from atmospheric CO<sub>2</sub> and oceanic carbonates are the ocean surface, continental shelves, and continental biosphere. This production, fuelled by photosynthetic processes, is called primary productivity. Igneous and biogenic reduced carbon is easily oxidized by atmospheric oxygen during weathering. The resulting carbon dioxide is distributed almost equally between atmospheric CO<sub>2</sub> and oceanic carbonates. Burial and subduction of sediments rich in organic carbon (reverse weathering) leaves unbalanced oxygen that accounts for the high proportion of this gas in the atmosphere.

The short-term components (ten-100 000 years) of the carbon cycle are largely driven by fluctuations in biological activity and are affected by human activities such as coal and oil burning, land use, and deforestation. This aspect will be left to more specialized monographs and textbooks.

## Reference

Wasson, J. T. (1985) *Meteorites. Their Record of Early Solar System History*, Berlin, Springer.