

## SEDIMENTARY GEOCHEMISTRY

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**Keywords:** weathering, diagenesis, carbonates, dolomites, shales, cherts, sandstones, evaporites, phosphorites, black shales, organic matter, kerogen, petroleum, coal, geochemistry

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### Summary

The chemical composition of sedimentary rocks is a result of a complex sequence of processes acting on starting geological materials. Such starting materials could originate in the disintegration and weathering of preexisting rock systems, or in precipitation of compounds from solutions with or without assistance of living organisms. Here we would like to underline that the evolution of mineral and organic constituents of sediments are not to be separated from each other. The composition, structure, and relationships between constituents of sediments are also precise fingerprints of processes of ulterior transformation during burial and basin subsidence. During the evolution of sedimentary systems, economic accumulations of gas, oil, and coal can be generated. The accumulation of metals leads to the origin of deposits of different types.

Here individual steps of the sediment genesis and evolution are presented, including data important for geochemical investigations of these rocks.

## 1. Introduction

The chemical composition of sediments and sedimentary rocks is extremely diverse, reflecting the variability of the mineralogical composition. Sediments may be classified according to the origin of the minerals composing the bulk sediment. End members are designated as terrigenous (siliciclastic), biogenic, and metalliferous. Terrigenous sediments are products of physical and chemical weathering and erosion of upper crustal rocks exposed at Earth's surface. During these processes, major changes in mineralogy and chemistry occur, because primary igneous and metamorphic rocks formed and equilibrated at elevated temperatures and pressures are thermodynamically unstable at surface conditions. Biogenic sediments result from the production, preservation, and diagenetic transformation of minerals initially produced by living organisms. Metalliferous sediments commonly result from exhalative processes along mid-ocean ridges and are enriched in Fe, Mn, Zn, Cu, and other metallic elements.

Three main groups of information can be obtained by investigating the composition of sedimentary rocks. The first group includes knowledge on source area of sedimentary constituents. In this context especially, chemical and mineralogical data are useful to obtain information on the primary character of original rocks. The description of the composition and structure of organic matter, and eventually the identification of fossilized biological material, are also useful to estimate the character of the state of the ancient biosphere. The second group of information concerns the sedimentary environment of formed rocks. This concerns hydrodynamic conditions of the sedimentary environment, the oxidation–reduction states of the sedimentary basin, and/or the state of the atmosphere during the time of sedimentation. Here, data about granulometry, relationships between minerals, and in some cases neo-formed cement are important, as well as information on the preservation of organic matter. The third big group of information reflects post-sedimentary transformation of the rock. Such a process, called diagenesis, is characterized by elevated temperature and pressures. In fact, when chemical, structural, and isotopic composition of minerals, organic matter, and/or whole rocks are determined, estimations of the conditions of transformation processes can be realized.

What does the term sedimentary geochemistry mean? What kinds of data are used in this field? First, general, silicate analysis including main elements (or presented as oxides of main elements) is useful. Mineralogical research permits us to identify individual phases and forms that are present in sedimentary rocks. Not only can individual crystalline phases be identified, but also the structural state of both inorganic and organic non-crystalline compounds and mixtures can be determined. This is allowed by the development of instrumentation (compositional and structural point analysis, including different types of electron microscopy and elemental microanalyzers, infrared and Raman spectroscopy and microscopy).

More trace elements are actually determined by modern methods of analysis Inductively Coupled Plasma Mass Spectrometry (ICP-MS), for example, and can complete the

elemental composition of the rock. Concentrations of complete series of rare earth elements (REE) are, for example, determined and are useful for provenance studies of the sedimentary material. In the past twenty years, isotopic analysis has been well developed and represents extremely powerful method of characterization of geomaterials. This concerns both stable (C, S, O, N, etc.) and radiogenic isotopes.

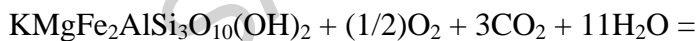
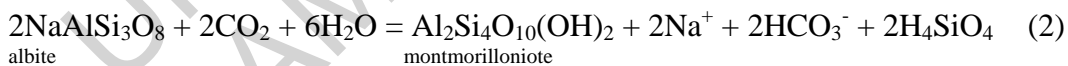
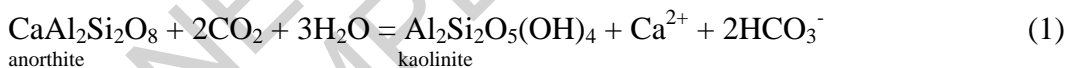
For the purposes of this review, let us describe the diverse steps of the genesis of sedimentary rocks. Different geochemical aspects will be considered from the perspective of the origin of the sedimentary material, sedimentary environments, and diagenetic transformations.

## 2. Origin of Sedimentary Material

### 2.1 Distribution of Elements as a Provenance Indicator

During the process of weathering, minerals and rocks are physically disintegrated and dissolved. They are transformed to solutes and soils, and eventually to sediments and sedimentary rocks. The stability of minerals and their solubility in water differ, and are controlled by such factors as free energy of weathering reactions, pH, Eh, concentration of different ions in water, and of course by temperature. It is well known, that the stability decreases in the series of rock forming minerals feldspar–amphibole–pyroxene–olivine. In this series of reactions, the free energy of reaction (Gibbs free energy calculated for unit activities and standard pressure and temperature) decreases systematically. This means, for example, that the probability of finding olivine in shales or sandstones is near zero.

There are no unequivocal weathering reactions for the silicate minerals. Depending on the nature of parent rocks and hydraulic regimes, various secondary minerals are formed as reaction products. Some important dissolution processes of current silicates are given here:



The rate of chemical weathering is important in determining the rate of CO<sub>2</sub> consumption. Silicate weathering is more important than carbonate mineral weathering as a long-term control of atmospheric CO<sub>2</sub>. The HCO<sub>3</sub><sup>3-</sup> and Ca<sup>2+</sup> ions produced by weathering of CaCO<sub>3</sub> precipitate in the ocean as CaCO<sub>3</sub> (by incorporation by marine organisms).

In the course of weathering, because of their presence in numerous igneous rocks, feldspars are transformed in upper crust conditions and reaction products dominate the composition of many terrigenous sedimentary rocks. The degree of primary material transformation can be estimated in the system  $Al_2O_3 - (CaO^* + Na_2O) - K_2O$  (here  $CaO^*$  refers to silicate bound calcium) or for example by the so called Chemical Index of Alteration formulated by Nesbitt and Young:

$$CIA = 100 \times (Al_2O_3 / (Al_2O_3 + CaO^* + Na_2O + K_2O)) \quad (4)$$

which is calculated by using mole fractions (Figure 1).

Values of CIA vary from less than 50 for unweathered igneous and metamorphic rocks to 100 for pure kaolinitic residue. High values are characteristic for geochemically mature sedimentary rocks.

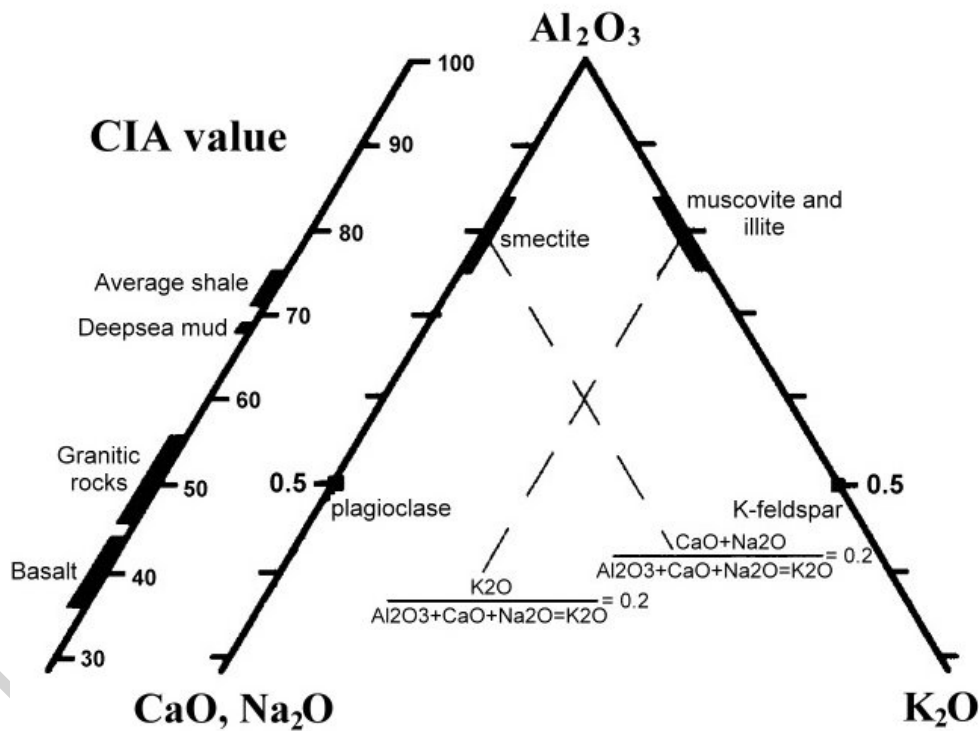


Figure 1. Representation of CIA values of different rocks

The composition of the primary sediment is, on the other hand, influenced by physical sorting of transported particles in water. This results in progressive enrichment of heavy minerals. Plots of  $Th/Sc$  against  $Zr/Sc$  ratios are useful to trace sedimentary recycling. Because of the quantitative importance of zircon in heavy minerals, during the recycling, the ratio  $Zr/Sc$  increases independently of changes in  $Th/Sc$ . Because of this transport-related fractionation, the  $TiO_2/Zr$  ratio is not recommended as a good indicator of the nature of the primary rocks.

The source of the sedimentary material could be determined by various parameters. They include those based on trace element ratios, especially on REE and, in the case of organic matter rich sediments, on chemical and structural characteristics of organic material.

The provenance of the sedimentary material of sandstones is traditionally determined by petrographic methods. Additional information could be obtained, however, from trace element ratios. It is known that La and Th are more concentrated in silicic than basic igneous rocks. On the contrary Co, Sc, and Cr are more enriched in basic rocks. Ratios of La or Th to Co, Sc, and Cr are good indicators of the source rock composition.

The behavior of Fe during weathering is the best record of the oxygen content of the contemporary atmosphere. The total Fe content remains near constant in most modern weathering profiles. Under an oxic atmosphere, Fe in weathering profiles is fixed as nearly insoluble  $\text{Fe}(\text{OH})_3$  and limonite/goethite. Iron from ferrous silicates may be removed from the weathering profile as  $\text{Fe}^{2+}$  in reducing solutions (in surface waters in peat bogs or swamps, for example). A high  $\text{Fe}_2\text{O}_3/\text{FeO}$  ratio of sedimentary rocks is evidence for an oxic atmosphere during weathering of source rocks.

Vanadium and molybdenum are removed easily from minerals in solutions sufficiently oxidizing. Aqueous species with higher valence states ( $\text{V}^{5+}$  rather than  $\text{V}^{3+}$ ) and  $\text{Mo}^{5+}$  and  $\text{Mo}^{6+}$  rather than  $\text{Mo}^{4+}$  are stable in these specific conditions. These elements are leached from source rocks during weathering in an oxygenated water environment and can precipitate from seawater under reducing conditions. Organic, carbon-rich black shales display, therefore, positive correlation between organic carbon ( $\text{C}_{\text{org}}$ ) and V and Mo.

The majority of sedimentary rocks display REE patterns similar to the post-Archean shales, and average shale REE concentrations are very similar to the average upper continental crust, which is on the other hand similar to the composition of granodiorites. These features include the enrichment of the light REE (La-Sm), characteristic for more differentiated igneous rocks, and the negative Eu (europium) anomalies relative to the neighboring Sm and Gd (samarium and gadolinium).

Silicic igneous rocks are characterized by negative Eu anomalies (from chondrite normalized plots of the REE); basic igneous rocks have little or no Eu anomalies. It has been observed that these relationships remain unchanged in fine-grained sediments.

Studies on shales, siltstones, and sandstones from central Colorado realized by Cullers are a good demonstration of the use of detailed geochemical investigation to access the source of clastic material of sediments. A more plagioclase-rich granitoid source and more intense weathering could be deduced for Belden formation relative to Maroon and Sangre de Cristo formations. This is based on the quartz/feldspar ratio in granitoids for the Maroon and Sangre de Cristo formations, and higher chemical index of weathering (CIW, here  $\text{Al}_2\text{O}_3/(\text{Al}_2\text{O}_3 + \text{Na}_2\text{O}) \times 100$ ) for the Belden formation. In general, elemental concentrations/ $\text{Al}_2\text{O}_3$  ratios and elemental ratios indicative of provenance of investigated shales-siltstones of the Maroon and Sangre de Cristo formations correspond to granitoids. Sediments of the Belden formation are however characterized by

statistically lower values of different elemental ratios (for example, Eu/Eu\*, La/Sc, and Th/Cr). From this it can be deduced that these rocks derive from a granitoid source formed by more fractional crystallization of feldspar or a lesser degree of melting from a feldspar-rich source than granitoids that served as a source for Maroon and Sangre de Cristo formation sediments.

### 2.1.1 Isotopes

(See *Stable Isotope Geochemistry*) Important information concerning the origin of different mineral phases or organic matter in sedimentary rocks is obtained through isotopic investigations. The basis of isotope partitioning is the difference in the rate at which two isotopes of the same molecular species will react in a thermodynamic reaction. The result of this partitioning is a different concentration or fractionation of one isotope over the other in the reactant and product reservoirs. During different subsequent processes, isotopic composition is modified. The resulting observed composition in nature can be used to decipher individual fractionating processes during the geological history of a system. In particular, isotopes of light elements are used, which participate in fundamental hydrologic, biological, and geological processes. Important stable isotope ratios include  $^2\text{H}/^1\text{H}$ ,  $^{13}\text{C}/^{12}\text{C}$ ,  $^{15}\text{N}/^{14}\text{N}$ ,  $^{18}\text{O}/^{16}\text{O}$ , and  $^{34}\text{S}/^{32}\text{S}$ .

The fractionation factor  $\alpha$  is the thermodynamic expression of isotope partitioning. Measurements of isotope ratio are usually reported as  $\delta$  values—the normalized difference from the isotope ratio of known standard.

For carbon isotopes:

$$(^{13}\text{C}/^{12}\text{C})_{\text{sample}} - (^{13}\text{C}/^{12}\text{C})_{\text{standard}} = \delta^{13}\text{C} \text{ (in ‰)} = x \ 1000 \ (^{13}\text{C}/^{12}\text{C})_{\text{sample}} \quad (5)$$

In nature, isotope separation between compounds can record temperatures of reactions. Temperature is an important factor, with increased fractionation occurring at lower temperatures. Thermodynamic equilibrium is a condition for isotopic equilibrium in physicochemical reactions. Displacement from this state favors unidirectional reaction, and the ratio of rate constants for the two isotopic species defines a kinetic factor. Kinetic fractionation is characteristic of enzymatic reactions in biological systems. Important reactions with strong fractionation of C in this way include photosynthesis and methanogenesis.

## 2.2 Organic Matter as Provenance Indicator

Interesting information about the source of different organic compounds can be obtained by studying the composition of organic matter of sedimentary rocks. As an example, there is a clear contrast between the composition of higher plants, in which cellulose and lignin represent up to 75 % of the organic material, and phytoplankton, which do not contain these oxygen-rich compounds. There are, of course, variations throughout geological time. Lignins, as parts of higher plant inputs, do not appear before the Silurian. Thus, the fingerprint of preserved organic compounds reflects the stage of evolution of the biosphere. It is also possible to assess different sedimentary contributions using optical microscopy, identifying remnants of organisms. However, in

general these parts may not survive in older sediments. The molecular signature remains in the form of biomarkers.

Biomarkers are defined by Peters and Moldowan as complex molecular fossils derived from once living organisms that are found in ancient and modern sediments and petroleum. Which groups of compounds can be used as biomarkers of original organic matter and eventually of the environment from which these organisms originated? For the application of biomarkers studying recent sediments, it is of course necessary to understand the changes occurring in such molecules during the course of time. Here, biomarkers characteristic of different organisms from recent and ancient sediments will be presented; in Section 4, other characteristic molecules will be reviewed that are rather markers of diagenetic processes.

Source indicators in recent sediments include fatty acids, sterols, carbohydrates, and lignins. Another important fingerprint can be used: the isotopic composition of carbon. In ancient rocks, the information from isotopic data is more complex and includes transformation processes. Source indicators in ancient rocks are different and include especially hydrocarbons.

Let us first focus on sterols and lignins. Sterols are found in organisms in both bound and free form. The carbon number of sterols permits us to differentiate between some groups of organisms. In higher plants, major sterols contain 29 atoms of carbon (β-sitosterol, stigmasterol); in phytoplankton, sterols with 28 atoms of carbon are dominant. Both of these molecules are called phytosterols. In zooplankton, however, C<sub>27</sub> sterols are present, especially cholesterol. Lignin represents an extremely important part of vascular plant bodies. Compositional variation between degradative products exists, and distinct molecules are characteristic of different types of plants. Laboratory alkaline oxidation products with copper (II) oxide of lignins from higher plants are collected, and compounds such as vanillin, syringaldehyde, syringic acids, and p-coumaric acids are found. Vanillyl is representative especially of woody gymnosperms and angiosperms, syringyl is more characteristic of woody angiosperms, and cinnamyl of non-woody angiosperms.

Other biomarkers are actually used to determine the provenance of the organic matter in ancient sedimentary rocks. In such rocks, the organic matter has been deeply transformed, and many biomarkers are different types of hydrocarbons. Biomarkers of epicuticular waxes of higher plants are represented by n-alkanes with odd carbon number (C<sub>27</sub>, C<sub>29</sub>, C<sub>31</sub>, C<sub>33</sub>), n-alkanols, and n-alkanoic acids (C<sub>24</sub>, C<sub>26</sub>, C<sub>28</sub>, C<sub>30</sub>). Bacterial markers include, for example, acyclic isoprenoids as C<sub>38</sub> head-to-head isoprenoidal alkane, C<sub>40</sub> alkane lycopane, or C<sub>30</sub> alkane squalane (which can be derived, however also from squalene occurring in other groups of organisms).

The source of carbon of sedimentary organic matter can be identified by isotope investigations. The isotopic composition of sedimentary carbon is controlled mainly by autotrophic organisms. Frequently, the C<sub>3</sub> path of photosynthesis results in light isotope carbon enrichment in the organic matter relative to the CO<sub>2</sub> source. Another pathway exists, involving carboxylation of phosphoenolpyruvic acid (PEP) instead of ribulose diphosphate (RDP), which subsequently forms a C<sub>4</sub> compound, oxaloacetic acid instead

of phosphoglyceric acid (PGA). This latter mechanism is developed under hot and dry climates, and such plants are called C4-plants. Bulk carbon isotopic data are useful to access the provenance of organic matter; data obtained on individual molecules are a promising way in isotopic geochemistry.

### 3. Sedimentation

#### 3.1 Siliciclastic Sediments

Siliciclastic sediments represent a major group of sedimentary rocks. They are composed of particles, including minerals of preexisting rocks, that have been weathered and transported. Siliciclastic (or terrigenous) sediments are those where the clasts are predominantly made of silicate minerals. Their classification is based on the clast size. The main groups are rudites, sandstones, and mudrocks in decreasing order of particle dimension. Sandstones are composed of at least 25 % of sand clasts (dimension 0.0625–2 mm). Another division of these rocks is based on the composition of clasts (quartz, feldspar, and rock fragments being extreme representatives). Mudrocks are composed primarily of clay minerals (about 60 %) with a lower amount of quartz (about 30 %) and low content of feldspars, rock fragments, carbonates, iron minerals, and organic matter. About 65 % of all sedimentary rocks fall in this group. Rudites contain more than 30 % of clasts of gravel grade (coarser than 2 mm) in a sand or mud matrix.

Studies of mineralogical and chemical composition of individual clasts of these rocks permit the identification of primary mineral or rock source and the area of origin. Examples of provenance studies are given in Section 2.1. Roundness and fabric, including preferential orientation of clasts, are good indicators of the degree of transport, environment of transport, and sedimentation, especially for coarser sediments.

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### **Biographical Sketch**

**Dr Jan Jehlicka**, is an associate professor of the Institute of Geochemistry, Mineralogy, and Natural Resources. From 1985 to 1991 he was assistant at the Department of Geochemistry of the Geological Survey Prague. In 1993, he obtained his PhD at the University of Orléans, France (Structural Studies of the Transformation of Organic Matter during Metamorphic Processes). He joined Charles University (Faculty of Science, Institute of Geochemistry, Mineralogy, and Natural Resources) in 1994. Here he prepared master courses of organic geochemistry, including sedimentary area, and metamorphic as well as environmental field. His research interests cover structural transformations of carbonaceous compounds from rocks, application of transmission electron microscopy and Raman microspectrometry to study carbonaceous phases, weathering of organic matter, relationship between organic adsorbents and toxic metals, and impact of PAH on soil and surface waters.