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Geochemical characteristics of elements in sedimentary environment and its geological significance

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Abstract

Elements, especially inorganic elements, are geochemical tracers widely used to study the evolution of various geological processes, material sources and environmental changes, especially in the fields of ocean, environment, mineral deposits and so on. The geochemical characteristics of elements in the sedimentary environment are of great significance for tracing the provenance of sediments. The content of elements changes with the change of rock type, sedimentary process and sedimentary environment. Some elements with relatively stable chemical properties are basically not affected by the weathering, denudation, redeposition and diagenesis of rocks, and can well reflect the provenance characteristics of source rocks. Other elements have different characteristics in different sedimentary environments. Some elements are enriched in marine sediments, while others are enriched in terrigenous sediments, and are affected by sedimentary fluid environment in this process. For example, the enrichment degree of some metal elements will also change in different oxidation-reduction environments. With the process of sedimentary evolution, trace elements will also be dispersed and enriched during the formation, sedimentation and burial of sedimentary organic matter. Therefore, the analysis of the geochemical characteristics of elements in the sedimentary environment is of great significance for identifying the provenance and tectonic setting of sediments.

Keywords

Major elements; Trace elements; Rare earth elements; Geochemical characteristics; Sedimentary environment; Geological significance

1. Introduction

Element geochemistry is mainly divided into major element geochemistry, trace element geochemistry and rare earth element geochemistry. As early as the middle of the 20th century, scholars began to use the stable characteristics of some elements to conduct tracer principle experiments on elements, and use the characteristics of different elements to study the evolution laws of rocks, mainly including various geological processes such as magma and metamorphism[1]. In recent decades, scholars have found that elements will be dispersed and enriched in the process of rock weathering, denudation, transportation and deposition, which will change the distribution of elements. Combined with the principle of element tracing, it can well reflect the changes of sedimentary environment during rock deposition.

The use of element geochemistry to reflect the changes of sedimentary environment, such as the use of major, trace and rare earth elements to characterize geochemical characteristics, so as to restore the ancient water depth, ancient salinity, ancient climate, ancient productivity and redox environment[2], has been studied in major domestic basins, such as Liujiang Basin[3], Ordos Basin[4], Sichuan Basin[5], Dongpu depression, etc. Researchers have also conducted a large number of elemental geochemical analyses of sediments from many rivers around the world, such as the Amazon River[6], the Ganges River[7], the Yangtze River[8], and the Yellow River[9], and have achieved research results on sediment provenance tracing analysis, rock weathering in the source area, and related climate change analysis. Therefore, the analysis of geochemical characteristics of elements in the sedimentary environment has important theoretical significance and practical application value for identifying the material source of sediments, sedimentary tectonic background and paleoenvironmental evolution.

2. Geochemical characteristics of major elements

Major elements refer to elements with mass fraction greater than 1% in geological bodies. These elements can form independent mineral phases in rocks, soils and sediments, which are usually expressed in the form of oxides. The major elements are also the main components of the chemical composition of sediments, and the overall properties of the major elements are different under different environmental conditions.

The sediments produced by weathering of source rocks under different tectonic settings have different major element compositions and distribution characteristics. Therefore, the provenance characteristics and sedimentary environment of sediments can be inversely analyzed through the variation laws of major element content and characteristic element ratio in sediments. In the process of judging sediment provenance, the ratio of characteristic elements with relatively stable chemical properties and good correlation is mainly selected as the source tracer index to trace and analyze the sediment provenance. Because these characteristic principal elements of sediments are controlled by provenance, their relative contents remain basically unchanged in the process of weathering, erosion, transportation and deposition, which makes the sedimentary area and provenance area have a certain contrast, and can be used as good provenance indicator elements, which is of positive significance for studying the chemical composition of sediments to trace the nature of provenance and identify its tectonic background. Moreover, the ratio of major elements can eliminate the changes of chemical elements caused by the changes of particle size and mineral composition, highlight the provenance information as much as possible, and more accurately judge the provenance characteristics of sediments. In addition, the chemical composition of terrigenous sediments is closely related to the tectonic environment of sedimentary basins. Some major elements are widely used to identify the tectonic nature of ancient sedimentary basins. Therefore, the element composition and content of sediments have a certain relationship with the tectonic background of the source area. The geochemical elements of sediments record the changes of the tectonic background of the source area. The geochemical elements of sediments can be used to restore the tectonic background of the source area.

3. Geochemical characteristics of trace elements

Relative to the major elements, some people call the elements less than 0.1% in the geochemical system trace elements. In different systems of nature, whether an element is a major element or a trace element is relative. For example, Mg is a trace element in quartz, but it is a major element in olivine and pyroxene. Generally, Zr is a trace element, but it is a major element in zircon or clinopyrite. The concentration of trace elements in natural systems is very low, and they often cannot form independent minerals with themselves as the main component, but exist in mineral solid solutions, melts or other fluid phases as secondary components. Therefore, the distribution of trace elements is not limited by phase law and stoichiometry, but obeys the law of dilute solution.

In all kinds of differentiation and evolution of the crust, trace elements are more sensitive to the changes of environmental physical and chemical conditions than major elements. The lithophile elements with large ions and some elements with high field strength are stable in the process of weathering, denudation, transportation and even sedimentation and diagenesis of sedimentary parent rock, showing a considerable degree of inertia, and are not easy to be transformed, migrated and fractionated. However, in the process of element deposition, the content of elements and their sedimentary characteristics are different due to the different components of sediments, which makes the trace elements with different or similar chemical properties enriched or dispersed, showing different fractionation laws, and truly recording the geochemical characteristics of sedimentary source rocks. Based on this, the relative content of trace elements or their correlation can be used as a tracer or indicator to identify the sedimentary environment.

As a variable valence element, Mn is usually enriched in carbonate rocks (mainly enriched) and mudstones. The process of its transfer and enrichment is greatly affected by the pH and redox value in the sedimentary environment. For example, in alkaline environment, manganese containing compounds are relatively easy to precipitate and form sedimentation. Generally, the content of Ti varies greatly in sedimentary rocks, mainly because its main material comes from terrigenous clastic materials, and the participation of volcanic materials may lead to a sharp increase in the content of Ti. The content of Ti in limestone is also affected by terrigenous clasts. Sr is mainly enriched in carbonate rocks and shales, because the ion radius of Ca and Sr in carbonate rocks is similar, and the adsorption capacity of clay minerals such as shale is relatively strong, so Sr is easy to be adsorbed in them. In addition, the content of Sr in organisms is relatively high, which will make Sr relatively locally enriched after the death of organisms. The content of Ga in carbonate rocks is much lower than that in shale and mudstone. The content of Ga in marine sediments is lower than that in freshwater sediments. In addition, Al and Si elements are mainly from terrigenous materials, which are greatly affected by terrigenous invasion. Na, K, Ca, Mg and Fe are essential elements in the process of biological growth, among which Ca, Mg and Fe are the main rock forming mineral elements, and the content of Na and K in marine fluid is relatively high.

4. Geochemical characteristics of rare earth elements

Rare earth elements are a special group of trace elements, which play an important role in the study of trace element geochemistry. Because all rare earth elements form stable trivalent cations with similar ion radius, they have very similar physical and chemical properties and tend to appear in groups in any geological body. In nature, when silicate phase and metal sulfide phase coexist, rare earth elements are preferentially concentrated in silicate, and they are lithophile.

Rare earth elements are often used as a good parameter index to indicate the sedimentary environment, which is mainly because their chemical properties are relatively stable and the deposition rate is relatively fast in the process of deposition, resulting in the basic preservation of the original geochemical characteristics of rocks, and at the same time, dispersion and accumulation under the influence of the external environment[10].Generally, the analysis of the characteristics of rare earth elements is mainly realized through the standardized distribution pattern diagram of rare earth elements, which can directly reflect the basic characteristics of rare earth elements. When the distribution patterns of rare earth elements in the standardized distribution patterns of the samples are similar, it shows that the formation mechanism of the samples is relatively consistent with the material source. When the standardization curve is inclined to the right, it shows that light rare earth elements are enriched relative to heavy rare earth elements[11].

5. Geological significance

5.1. Provenance

The content and correlation ratio of major and trace elements can be used as an important index to identify the source of sediments and the tectonic background of provenance area. For example, carbonate rocks are the product of endogenous sedimentation, and the elements are mainly inherited from the marine water, but the terrestrial mineral composition and diagenesis have an impact on their abundance. Si and Al elements are mainly from the terrestrial source, and the marine self differentiation is less. Therefore, the source of elements in carbonate rocks can be preliminarily judged by the relatively large content. If the average content of SiO2 and Al2O3 in the sample is low, it indicates that the impact of terrigenous mixing is small, and it is mainly marine sedimentation; If the content of SiO2 and Al2O3 in the sample is generally high, it indicates that the element source is mainly from land. The ratio of K2O/Al2O3 in clastic rocks can reflect the status of minerals mainly controlled by major elements, and the ratio of K2O/Al2O3 in clay minerals is generally less than 0.3. In addition, the Al2O3/(CaO+K2O) value in sedimentary rocks can well characterize the proportion of stable and unstable components. Generally, kaolinite and illite constitute unstable components. If the Al2O3/(CaO+K2O) value is greater than 0.85, it indicates that the relative content of stable components in clastic rocks is large.

The weathering, diagenesis and alteration in the late stage of deposition have little effect on the REE composition of sedimentary rocks, and the REE composition is mainly controlled by the composition of source rocks. Therefore, the characteristics of rare earth elements in sedimentary rocks can also effectively characterize the provenance of the study area. δEu is another important parameter for judging sediment source[12]. For example, when granite is the parent rock, the δEu value of sedimentary rocks usually shows negative anomaly; When basalt is the parent rock, the δEu value of sedimentary rocks usually shows no abnormality; When anorthosite is the parent rock, the δEu value of sedimentary rocks usually shows positive anomaly[13].

5.2. Hydrothermal action

The range of Y/Ho value in normal marine sedimentary environment is 44~74, and the Y/Ho value in magmatic rocks is similar to PAAS value (Y/Ho value is about 28). Therefore, the y/ho value can be used to distinguish the original sedimentary environment type from the normal seawater deposition or the sedimentary environment affected by the action of thermal fluid. In addition, europium anomaly can also be used as an important indicator to reflect the intensity of ocean floor hydrothermal activity[14]. Europium anomaly in sedimentary basins is often greatly affected by the temperature of sedimentary environment. When the environmental temperature is greater than 250 °C, the sediments often show positive europium anomaly, below which the absence of europium anomaly is the main factor, and the normal marine sedimentary environment shows negative europium anomaly.

5.3. Paleowater depth and paleosalinity

Sr/Ba is one of the important indicators indicating the depth of water body and the change of redox conditions[15]. In normal seawater, the solubility and migration ability of Sr element is significantly higher than that of Ba element. Ba^{2+}preferentially combines with SO_4^{2-} ions to form precipitation, while Sr^{2+}left in the water body tends to be enriched. With the shallower water body and the increasing hydrodynamic conditions, Sr forms precipitation in the form of $SrSO_4$, resulting in a significant negative correlation between Sr concentration, Sr/Ba ratio and paleo water depth.

Paleosalinity is an important criterion for restoring the Paleoenvironment of rock sedimentary period. At present, Couch's calculation formula based on the relationship between boron and paleosalinity is the most commonly used. In addition, the ratios of Sr/Ba, Y/Ho, Sr/Ca and V/Ni can also characterize the paleosalinity (Table 1)

Table 1: Criteria for determination of trace elements in paleosalinity.

Judgment index		Paleosalinity
ω(Sr) /($\mu g \cdot g^{-1}$)	ω(Sr):ω(Ba)	
<300	<0.6	freshwater
300~500	0.6~1.0	brackish water
>500	>1.0	salt water

5.4. Redox characteristics

The correlation between Ce and adjacent La and Nd is called Ce anomaly, and the abnormal value of Ce in sedimentary system can be used as an indicator of redox conditions of sedimentary water. Generally, when the water body is in an oxygen rich state, Ce is relatively depleted, δCe<1, on the contrary, when the water is in anoxic state, Ce is relatively enriched, and δCe>1. In general, V, Cr, Ni, Co, U, Th and other trace elements will differentiate during the deposition process under different oxidation-reduction conditions. The evolution of sedimentary environment in the study area can be effectively identified by using the ratio of trace element mass fraction (Table 2).

Table 2: Identification basis of oxidation-reduction environment.

<table>
<tr><th>Depositional environment</th><th>ω(V):ω(Cr)</th><th>ω(Ni):ω(Co)</th><th>ω(U): ω(Th)</th><th>δU</th></tr>
<tr><td>Oxidizing environment</td><td><2.00</td><td><5.00</td><td><0.75</td><td><1.0</td></tr>
<tr><td>Anaerobic environment</td><td>2.00~4.25</td><td>5.00~7.00</td><td>0.75~1.25</td><td rowspan="2">>1.0</td></tr>
<tr><td>Reducing environment</td><td>>4.25</td><td>>7.00</td><td>>1.25</td></tr>
</table>

6. Conclusions

Through the analysis of major elements, trace elements, and rare earth elements, the reflection of element geochemical characteristics on sedimentary environments has been revealed. The different types and properties of elements lead to different dispersion and aggregation patterns. From this process, information related to sedimentary environments can be found, which has important geological significance for restoring sedimentary environments. The content and related ratios of major and trace elements can identify the source of sediments, and the differential characteristics of rare earth element content in different tectonic backgrounds can be used to determine the tectonic environment of sedimentary periods. The Y/Ho value and europium anomaly can reflect the intensity of hydrothermal activity on the ocean floor. Sr/Ba can be used as an important indicator of changes in water depth and redox conditions, and ratios such as Sr/Ba, Y/Ho, Sr/Ca, V/Ni can characterize paleosalinity. The Ce anomaly can be used as an indicator of the redox conditions in sedimentary water bodies.

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