The role of volcanic ash in the formation of organic-rich source rock and its source identification

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Abstract Volcanic ash promotes the formation of organic-rich source rocks by increasing the productivity of sedimentary basins and the formation of conducive preservation environment. In terms of productivity, volcanic ash provides Fe, Mn, Zn and other trace metal elements to sedimentary basins, and promotes the prosperity of water organisms and the improvement of primary productivity. The thickness of volcanic ash deposition is proportional to the concentration of nutrients released. Generally, the thickness of volcanic ash deposits around the crater is much thicker than far away, and more like to obtain the high concentration of nutrients, and make it easier to bloom. In terms of preservation environment, by increasing the salinity of sedimentary basins and participating in the biological sulfate reduction reaction (BSR), volcanic ash promote the formation of a reducing environment conducive to the preservation of organic matter. In addition, in order to deepen the research on the relationship between volcanic ash and the distribution of high-quality source rocks, this article discusses the sources and identification methods of volcanic ash, and proposes that lithium, as an effective geological tracer may have the ability to identify volcanic ash sources.

Keywords: Volcanic ash; productivity; preservation environment; lithium isotope; tracer; "water-carrying type"; "airborne type"

1. Introduction
Pyroclastic rock is a type of transition rock between volcanic lava and clastic sedimentary rock. Tuff refers to the pyroclastic rock with a particle size of less than 2 mm formed by the consolidation and compaction of volcanic ash. Existing exploration evidences show that there are many oil and gas reservoirs with tuff as reservoirs at home and abroad. Foreign countries such as the Jatibarang oil and gas field in the Java Basin of Indonesia (Thomas et al., 1994), and the tuff oil reservoir in the Iiyoshi-Hashikashiki gas field in Japan (Tomaru et al., 2009). In China, there are also: Alxa sinking tuff reservoir in Erlian Basin (Gao et al., 2006), sinking tuff reservoir of Wuerhe Formation in Junggar Basin (Gong et al., 2010), Karamay Oilfield Lower Permian Jiamuhe Formation sinking tuff reservoir (Zhu Guohua et al., 2008), etc. In the early exploration, tuff was only used as a special type of reservoir, and there was a lack of research on the content and type of organic matter contained in it and its ability to become an effective source rock. In recent years, with the rapid development of isotope analysis technology and the research on the influence of exogenous materials on the formation and enrichment of organic matter in sedimentary basins, more and more scholars have begun to pay
attention to tuff as a product of magmatic activity, which has a significant impact on sedimentary basins as well as the influence on the formation of source rocks, the evolution of organic matter, and the generation of oil and gas.

In fact, as early as 1989, Zhou Zhongyi pointed out that tuff has the potential to become a source rock. He believes that the Permian tuff in the Junggar Basin has high hydrocarbon-generating potential and can become an effective source rock (Zhou et al., 1989). Wang et al. (2011) conducted a geochemical analysis on the sedimentary tuff in the eastern part of Gar, and believed that this set of tuff could be used as a new type of source rock in the eastern part of Junggar. Wang et al. (2013) conducted a detailed geochemical analysis of the Carboniferous tuff in the Santanghu Basin, fully explored the source and enrichment mode of its organic matter, and believed that this set of tuff can be used as a source rock. In addition, as the main reservoir for tight oil development in the Ordos Basin, the source rock of the Yanchang Formation also widely develops interbedded tuff (Zhang et al., 2007; Yang et al. 2013).

In recent years, with the development of the "organic-inorganic interaction" during oil and gas formation process, the influence of materials outside the basin exert on the formation and enrichment of organic matter in sedimentary basins as well as the formation and evolution of oil and gas has received an increasing attention. In terms of hydrocarbon generation, exogenous materials represented by hydrothermal fluids and volcanic ash mainly promote the formation of organic-rich source rocks by increasing the productivity of sedimentary basins and forming an environment that is conducive to the preservation of organic matter.

2. Volcanic ash promotes the enrichment of organic matter by increasing productivity

Increasing the productivity of sedimentary basins and forming an environment conducive to the preservation of organic matter are two basic conditions for the enrichment of organic matter and the formation of high-quality source rocks. Volcanic activity is a potential geological force leading to global climate change and the extinction of biomes (Wignall, 2001). "Productivity view" believes that extremely high productivity and the following lack of oxygen in the ocean are the main conditions for organic deposition. The addition of volcanic ash provides the sedimentary basin with Fe, Mn, Zn, Co and other trace metal elements, promotes the prosperity of water organisms and increases the primary productivity, in the meanwhile, it also creates a favorable material guarantee for the formation of source rocks. The tuff with high content of organic matter also has the potential to develop into source rocks.

In recent years, with the development of satellite analysis technology, the phenomenon that volcanic ash promotes the growth of planktonic algae has been observed and confirmed. For example, in 2003, the Anatahan volcano erupted in the northeastern Mariana Islands, which caused a range of 4.8x10^3 km^2 algae blooms in the west Pacific Ocean (Lin et al., 2011). The Kasato-chi volcano eruption in Alaska, USA in 2008 prompted a large bloom of algae in the northeastern Pacific Ocean within an area of (1.5-2.0)x10^6 km^2. (Langmann, 2013)

Volcanic ash deposition is an important source of iron in marine ecosystems. Fe is an important life element in the growth and reproduction process of phytoplankton. It plays an irreplaceable role in many life processes, such as plant photosynthesis, respiration, oxygen metabolism, carbon fixation, nitrogen absorption and utilization, and synthesis of protein and chlorophyll. Remote sensing observations of modern ocean water bodies have found that once the volcanic ash produced by modern active volcanic eruptions encounters ocean surface water, does the acidic aerosols adsorbed on the surface of volcanic ash particles begin to dissolve and release a large amount of Fe into ocean waters. In the water body where volcanic ash is dissolved, the content of nutrients such as N and P decreases, the level of chlorophyll increases, phytoplankton grow rapidly, the biomass and primary productivity greatly increase (Price et al., 1991; 1994).

Duggen et al. (2007) carried out simulation experiments on the dissolution of volcanic ash and release of nutrient elements under environments with different ash thicknesses. The results showed that a layer of volcanic ash (about 20g) with a thickness of 1mm and an area of 1dm^2 deposit will
cause the Fe concentration in the water body increases by 0.4~2.4 nmol/L, and the Zn concentration increases by 0.1~1.1 nmol/L compared with the water body without volcanic ash deposition. When the thickness of volcanic ash increases to 1 cm, the concentration of elements such as Fe and Zn, in the water body will increase nearly 10 times. Therefore, the thickness of volcanic ash deposits is proportional to the concentration of nutrients released. Generally, the thickness of volcanic ash deposits around the crater is much thicker than far away, and more like to obtain the high concentration of nutrients, and make it easier to bloom.

3. Volcanic ash promotes the enrichment of organic matter by assisting the preservation of organic matter

The "preservation view" holds that organic-rich deposition is the result of ocean hypoxia, and emphasizes the significant impact of anoxic deposition environment exert on organic matter accumulation. Hydrothermal and volcanic activity erupted on land and oceans promoted the formation of anoxic sedimentary environments in sedimentary basins. Among them, volcanic ash and volcanic breccia erupted by volcanic activity bury the remains of animals and plants, isolate oxygen, and promote the preservation and enrichment of organic matter in an oxygen-deficient environment. On the other hand, the addition of volcanic ash increased the salinity of water in sedimentary basins, promoted the stratification and circulation of water, and created favorable water dynamics and redox environment for the enrichment of organic matter in sedimentary basins (Liu et al. 2018). Demaison and Moore (1979) pointed out that unlike oxygen-enriched water bodies, the oxygen-deficient bottom water survives the loss of organic matter caused by oxidation and decomposition during the deposition process, and provides an excellent environment for the preservation and enrichment of organic matter. In addition, the hypoxic water environment promotes the activation of some elements which are critical to life, which indirectly affects the development of biological productivity in the water body. For example, Van and Ingall (1994) proposed that the hypoxic submarine environment can promote the regeneration and recycling of active phosphorus. Phosphorus is an important component of cell membrane and genetic material, participates in the life metabolism of aquatic plants, provides energy for plant cells, has an important impact on the growth of phytoplankton and the development of community structure, and is a major limiting factor for the primary productivity of the ecosystem.

Recent studies have shown that Bacterial Sulfate Reduction (BSR) is also one of the important mechanisms that lead to the formation of a reducing environment in water bodies. Sulfate biological reduction process refers to the metabolic process in which Sulfate-Reducing Bacteria (SRB) absorbs sulfate under anaerobic reduction conditions, oxidizes organic compounds to obtain energy and reduces sulfate to H₂S (Bacterial Sulfate Reduction), BSR (Berner et al., 1984; Cai et al., 2003).

![Image of volcanic activity impact on the sedimentary environment](image-url)

**Fig. 1** The model map of the impact of volcanic activity on the sedimentary environment

Volcanic activity will emit a large amount of sulfur-containing gases such as SO₂ and H₂S. SO₂ reacts photochemically with the water vapor in the atmosphere or from volcano gases to form H₂SO₄ aerosol. H₂SO₄ aerosol enters the lake basin in the form of acid rain. The concentration of SO₄²⁻...
increase, and provides a sufficient source of sulfur for the BSR reaction. In an anaerobic reduction environment, sulfate-reducing bacteria (SRB) use organic matter as a carbon source and promote it to react with sulfate ions ($SO_4^{2-}$) dissolved in water, this reaction will generate a large amount of H$_2$S. The reducing gas H$_2$S dissolves in water and combines with free oxygen in the water body, this process accelerate the consumption of oxygen in the water body and enhance the reducibility of the water body. After the formation of a reducing environment, additional H$_2$S can react with iron oxides to form pyrite. The consumption of H$_2$S reduces its toxic effect on sulfate-reducing bacteria, which make it possible for a continuous BSR reaction. Besides, the reducibility of the water body continues to increase, which provides a favorable environment for the preservation of deposited organic matter.

4. The identification of "water carry" tuff and "airborne" tuff

Volcanic ash creates conditions for the enrichment of organic matter in sedimentary basins and the formation of high-quality source rocks by increasing productivity and forming an environment conducive to the preservation of organic matter. Then, as a volcanic clastic rock with a particle size less than 2 mm formed by the consolidation and compaction of volcanic ash, can the spatial development of tuff be used to indicate the appearance of high-quality source rocks? To answer this question, we need to classify the interaction modes between volcanic ash and organic matter in sedimentary basins.

Generally, volcanic ash materials enter sedimentary basins mainly through "airborne" and "water-carrying", and participate in the sedimentary diagenesis and organic matter evolution process of the materials in the basin. Generally, the "airborne" tuff is transported by volcanic ash with the help of wind. When the wind slow down, the sediments carried by wind fall down and formed by compression and consolidation. This kind of tuff has a tuff structure and a positive-grained bedding and no obvious redeposition hint, it is easy to compare with other regions. "Water-carrying" tuff refers to the rock formed by the volcanic ash being weathered and denuded after being deposited, and then transported by rivers or other hydraulic power, and then redeposited together with the sand and mudstone in the basin. Generally, this kind of rock often develop crumpled, collapsed, wrapped bedding, it is hard to compare with other regions. "Airborne" volcanic ash directly enters the sedimentary basin, participating in and affecting the formation and enrichment process of organic matter in the basin. The tuff formed by "airborne" volcanic ash retains the geochemical characteristics of the original volcanic activity product, such as element and isotopic composition. The "water-carrying" tuff is formed by weathering, denudation, and re-sedimentation after the original volcanic ash subsidence. Its element and isotopic geochemical characteristics are affected by the water-rock interaction during the weathering process. At present, there is no effective geochemical identification method to distinguish the two types of tuff existing in sedimentary basins.

![Pattern of tuff formation](image)

**Fig. 2** Pattern of tuff formation
At present, the identification of "water-carrying type" tuff and "airborne type" tuff mainly relies on field observation and microscopic experiments. Conventional C, H isotope and trace elements as well as other geochemical methods cannot provide effective identification index. Qiu et al. (2011) conducted detailed petrographic observations and geochemical studies on the volcanic ash sediments of the Yanchang Formation in the Ordos Basin. According to the core sample microscope and field observation, two types of volcanic tuff were identified. The first has a typical tuff structure, a positive grain sequence, weak alteration, and spread in layers in the field, showing the characteristics of gradual weakening of wind and continuous precipitation of volcanic ash. Qiu et al. (2011) considered it to be "airborne" tuff. Another type of tuff is severely altered, with obscure mineral edges and high clay mineral content. The tuff develops crumpling or slumping together with sandstone and mudstone in the field. Enveloping and cross-bedding can be observed in some tuffs. It is believed that such volcanic deposits are affected by hydrodynamic forces when they are formed, and represent a "water-carrying" tuff. However, the main and trace element geochemical analysis results show that there is no obvious difference in element composition between the two types of tuffs. However, there are some uncertainty in distinguishing "water-carrying" and "airborne" tuffs only by observation under the microscope and in the field. The volcanic ash material that falls into the sedimentary basin when the wind slow down can also develop envelopment and cross-bedding under the influence of the dynamic environmental disturbance of the water body in the basin. An effective geochemical identification method is the key to further study the influence of different types of tuff on the formation and enrichment of organic matter in sedimentary basins.

Lithium, as the lightest metal element in nature, has two stable isotopes ($^7$Li and $^6$Li). The large atom mass difference between these two isotopes leads to significant differences in content and isotope composition in various systems in nature. The fractionation of lithium isotopes is not affected by processes such as redox reactions, biology activities, and volcano events (Faure and Mensing, 2005; Clergue et al., 2015), these properties make Li an effective tracer in tracing continental weathering (Huh et al., 2001), oceanic crust alteration (Seyfried et al., 1998), crust slow material cycle (Zack et al., 2003; Elliott et al., 2004) and other important geological processes. The research of lithium (Li) isotopes started from Mc Lennan and Ainslie (1922). Due to the undeveloped technique, the progress of Li isotopes research is limited. Recently, thanks to the technique advancement, such as the development of thermal ionization mass spectrometry (TIMS), secondary ion mass spectrometry (SIMS), and multi-receiver inductively coupled plasma mass spectrometry (MC-ICP-MS), accurate measurement of Li isotopes has been achieved. The advantages of Li isotopes in tracing geological processes have gradually emerged.

As mentioned before, the two stable isotopes of lithium ($^6$Li and $^7$Li) have large mass differences, and significant fractionation occurs during continental weathering. Therefore, the "water-carrying" tuff formed after being re-deposited by the weathering and denudation of rivers and other water bodies should have different lithium isotopic composition characteristics from the "airborne" tuff representing the original composition of volcanic activity. Theoretically, because the $^7$Li isotope is easier to migrate with water, the "water-carrying" tuff should have a heavier lithium isotope composition than the "airborne" tuff. Affected by different degrees of weathering of flowing water, the lithium isotope composition of "water-carrying" tuffs should have a greater range of variation. Currently, reports on the lithium isotope composition of pyroclastic rocks are only found in the 102 pyroclastic rocks in the ODP Site 801 sediment reported by Bouman et al. (2004). The lithium content and isotope composition are $14.1 \times 10^6$ and $+6.4\%$, respectively, which is considered to be the product of Magellan Seamounts pyroclastic alteration.

In addition, Henchiri et al. (2014) analyzed the river lithium geochemistry in volcanic rock development areas such as Guadeloupe, Iceland, and Java, and restored the lithium isotope composition of the river water terminal members based on the distribution characteristics of $\delta^{7}$Li/Li/Na. Studies have shown that the lithium isotope composition of river water in volcanic rock development areas is jointly controlled by soil weathering under low temperature conditions and
altered volcanic rocks under high temperature conditions, which proves that the lithium isotope composition of river water flowing through volcanic material development areas is, to a certain extent, carried traces of the products of volcanic activity.

The obvious fractionation of lithium isotopes in the process of continental chemical weathering provides new research ideas for the identification of "water-carrying" and "airborne" tuffs. However, whether lithium isotopes can be an effective means of identification, is still waiting to be tested by further analysis and research.

5. Conclusions
(1) Volcanic ash provides Fe, Mn, Zn, and other trace metal elements for sedimentary basins to promote the prosperity of water organisms and the increase of primary productivity. The thickness of volcanic ash deposition is directly proportional to the concentration of nutrients released. Generally, the thickness of volcanic ash deposits around the crater is much thicker than far away, and more like to obtain the high concentration of nutrients, and make it easier to bloom.

(2) Volcanic ash buries animals, isolate atmospheric oxygen, releases ions, increases the salinity of water, and promotes the stagnation and circulation of water, as well as participates in biological reduction reactions to generate reducing H$_2$S gas. As a result, it creates a favorable environment for organic matter storage and enrichment.

(3) At present, the identification of "water-carrying" and "airborne" tuffs mainly relies on field observation and microscopic experiments. Conventional geochemical methods like C, H isotope and trace elements cannot effectively identify them. Lithium, as an effective geological tracer element, undergoes significant isotopic fractionation during continental weathering, and has the potential to identify different sources of volcanic ash.

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