Effects of Volcanic Activity on Organic Matter Enrichment in the Sediments and its Implications for Oil and Gas Exploration and Development

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Abstract. Volcanic activity is an important geological phenomenon in the evolution and development of the earth and brings rich resources to benefit human society, such as geothermal resources, valuable minerals, petroleum, and natural gas, although volcanic eruptions cause serious threats to the ecological environment of our planet. The co-development of oil and gas and volcanic activity in the same basin is a common phenomenon globally. Volcanic activity can bring abundant nutrients into the basins, conducive to the development of algae and other microorganisms in the water body. After the death of organisms, their remaining settles down to the water bottom and accumulate in the sediments. Meanwhile, reducing gases, releasing along with the volcano eruption, including H2S, CO2, etc., result in anoxia in the water body, benefiting the preservation of organic matter at the bottom and brings a large amount of material basis for the generation of oil and gas. Additionally, volcanic activity and hydrothermal fluids are rich in acid substances, will dissolve part of the minerals in the formation, generates a large number of migration channels for oil and gas migration. Some volcanic rocks are rich in pores, making them natural tanks for oil and gas storage. However, volcanic activity also has destructive effects on oil and gas accumulation. High hydrothermal/volcanic input can dilute primary productivity or reduce the abundance of organic matter due to high deposition rates, while excessive volcanic activity or hydrothermal fluid input can introduce large amounts of sulfate into the water, causing strong bacterial sulfate reduction (BSR). The high consumption of organic matter can hamper the organic matter enrichment. Therefore, how to define appropriate volcanic activity conducive to organic carbon preservation, and to establish the relationship model between volcanic activity and organic matter enrichment, are key scientific issues.

Keywords: Volcanoes; Corresponding authors; Copyright; Publishing.

1. Modern volcanos distribution

There are four major volcanic zones in the world, including the Pacific Ring of Fire, the Mediterranean-Himalayan Ring of Fire, the East African Rift Valley Ring of Fire, and the Atlantic-Caribbean Ring of Fire, which contain about 1,500 active land volcanoes, 2,000 extinct land volcanoes, and thousands of underwater volcanoes (Figure 1). Today, nearly 70 percent of these volcanoes lie under the sea, including several well-known active volcanoes, such as the Hunga Tonga- Hunga Haapai volcano in Tonga, which erupted on 15 January 2022 with a magnitude VEI-6 eruption and brought fatal effects to the local environment.

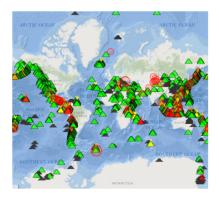


Fig. 1. Distribution of the world's volcanoes, including volcanoes in normal activity (green), that is unrest (yellow), and currently erupting (Source: Volcano Discovery).

The Pacific Ring of Fire contains several famous active volcanoes, accounting for about 80% of the world's volcanoes and about 90% of the world's earthquakes [1].

The "Ring of Fire" is 40,000 kilometers long and runs through New Zealand, Tonga, Indonesia, Japan, Russia's Kamchatka Peninsula and the west coast of the Americas (Figure 2). It is directly caused by the movement and collision of plates and made up of the Pacific Plate, Nazca plate, Cocos plate, Philippine Sea plate, and numerous smaller plates. Most of the tectonic plate movements in this region are subduction zones or convergent plate boundaries, in which a dense, less thick oceanic plate dives beneath a dense, larger continental plate and melts into the mantle, where flux melting begins [2]. During this process, because the minerals of the oceanic plate contain abundant water and volatile compounds such as carbon dioxide (CO₂) which are sucked into the seawater, when they penetrate into the hot solid rocks of the aesthenosphere, the melting temperature of the rocks will be reduced, thus causing the solid rocks to be transformed into magma and rise to the surface to form volcanic eruption. The "Ring of Fire" has been the site of dozens of large-scale volcanic eruptions over its long geological history, such as Mount Tambora in Indonesia in 1815, which led to Napoleonic Waterloo and crop failures and famine in the Northern Hemisphere [1]. The eruption is thought to have spewed out nearly 60 million tons of sulfur dioxide, causing the Earth's atmosphere to reflect a lot of sunlight and causing a global volcanic winter. About 92,000 people died in the disaster. The impact of the volcanoes on the "Ring of Fire" on humanity is still present today and cannot be ignored [2]. In January 2022, a Phreatoplinian eruption occurred on the island of Hunga Tonga - Hunga Haapai, 56 km west-north of the capital Nuku 'alofa, in the Kingdom of Tonga. The top of the ash column rose to a height of 58 km in the mesosphere, which is thus rates the eruption on a volcanic explosivity index (VEI) of 6. The sound waves reverberated around the globe, and several coastal countries around the Pacific detected atmospheric anomalies within hours of the eruption. For example, Guangzhou Meteorological Station detected a significant pressure change between 20:15 and 20:50 on the 15th, which peaked at about 1017.7 hectopascals at 20:30. The collapse of the island and pyroclastic flows caused by the eruption triggered large-scale tsunamis in the Pacific region, even reaching the west coast of South America, which is approximatly 10,000 kilometers to the east. The eruption caused an estimated \$125 million in damage to Tonga, according to the Australian Broadcasting Corporation.

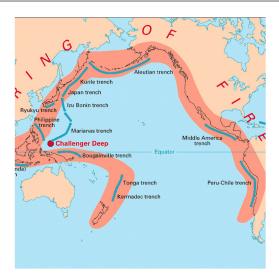


Fig. 2. The "Ring of Fire" rings the Pacific Ring of Fire (Source: Official US Geological Survey website (USGS).

Besides the Pacific Ring of Fire, the Mediterranean-Himalayan Ring of Fire also belongs to the convergent plate boundary ring of fire, which is the longest ring of fire in Eurasia. The volcanic belt runs through southern Europe, the Aegean Sea, West Asia, the Middle East, China's Qinghai-Tibet Plateau and Sichuan Basin, including China's Ashikule volcano in Xinjiang, which erupted in 1951 [2]. The above volcanoes are all stratiform volcanoes directly caused by the collision and subduction of the African and Indo -Australian plates with Eurasia. The process began around 200 million years ago with the breakup of Pangea, the breakup of India and Antarctica and the movement toward Eurasia, the shrinking of the Tethys Ocean, and the subduction of the oceanic plate also led to the formation of some volcanic arcs in southern Eurasia. Some of the remnants of these volcanoes are now in the form of granite in the basement of the Himalayas. What remains of the Tethys Ocean today is only the Mediterranean Sea.

2. The effects of volcanic activity on the formation of sedimentary basins

The volcanic activities forge the spatial distribution pattern of "basin-ridge interphase". Wilson regarded the Earth's history as "a complex series of alternating ocean opening and closing cycles"[3]. In fact, the continental crust also developed and evolved in tectonic cycles of opening and closing. When the continental crust opens up, magma flows to the crust surface along the deep and large faults, forming volcanic rock mass. At the junction of the deep faults, magma activity is frequent, forming larger magmatic rock mass and forming mountain peaks [3]. The volcanic activities cause the time configuration sequence of "fire followed by water". The largest feature of the filling sequence of petroleum basins is that volcanic rocks fill first, which is followed by the sedimentary rocks [3, 4]. The sedimentation of the lithosphere is caused by the outflow of a large number of deep asthenosphere materials caused by the volcanic eruption triggered by volcanic activities in the underlying asthenosphere. As a result, the sedimentation of the lithosphere is caused by the lack of the ability to support the lithosphere. And the materials leaking from the earth's deep asthenosphere form the filled materials in the sedimentary basin, and the sequence is mostly based on volcanic rock, followed by sedimentary rock accumulation [3].

3. The influence of volcanic activities on oil and gas generation

Oil and gas are closely related to every aspect of our life, whether it is clothing (polyester fiber), diet (plants and vegetables cultivated from natural gas and chemical fertilizers) or transportation (motor vehicles, planes, tanks, etc.). The material basis of oil and natural gas is life, mainly a large number of aquatic microorganisms such as phytoplankton and algae [4]. When the aquatic microorganisms die in water surface (including oceans, rivers and lakes), their remains will be deposited to the water bottom and gradually preserved under anaerobic conditions. Together with other fine-grained sediments, they form organic-rich sediments, including black shale and dark mudstone, which are called source rocks able to generate oil and gas [5].

In terms of the oil and gas generation, volcanic activity is crucial and play controversial roles in different stages. The main source of organisms required for the formation of oil and gas is microorganisms, which inhabit every corner of the earth and require nutrients such as sulfur (S), phosphorus (P), iron (Fe), calcium (Ca), potassium (K), magnesium (Mg), etc. A volcanic ash cloud can carry billions of tons of minerals deep inside the Earth, rich in these nutrients, creating fertile water body that allow microbial life to flourish. The proliferation of microorganisms can add a large number of organic carbon (TOC) to the source rocks, thus promoting the formation of oil and natural gas [5, 6].

Currently, the reasons for the high original TOC caused by volcanic activity are still debated. Some scholars believe that volcanic ash deposition has a "fertilization" effect on water surface [7-9] that volcanic activities carry nutrients to promote the prosperity of organisms, which could also consume a large amount of oxygen in the water and cause the death of organisms. Figure 3 shows tow microphotographs for the interbedding of organic matter rich layer and tuff layer including Figure 3a the organic matter rich layer containing phosphate minerals formed after the tuff layer and Figure 3b the organic matter rich layer formed both before and after the tuff layer. This is direct evidence that volcanic activity could promote the development of organic matter rich shales. While promoting the eruption of some species, volcanic activities also release harmful substances such as copper and zinc and hydrogen chloride, chlorine gas, causing the largescale death of organisms, even leading to the extinction of biota, which can improve the ancient productivity of the water body [8-12]. In addition to providing sufficient organic matter for the formation of source rocks, soluble gases released by volcanic activity, such as H₂S, SO₂, CO₂ etc., can react with oxygen in water, resulting in seawater anoxia causing

stratification and anoxic seawater in the lower part. Some scholars have also pointed out that volcanic eruption (deep fluid intrusion) input a large amount of sulfate, promoting the occurrence of bacterial sulfate reduction reaction (BSR), so that the water becomes a strong reducing environment, conducive to the preservation of organic matter [13].





Fig. 3. Microphotographs for the interbedding of organic matter rich layer and tuff layer. a. the organic matter rich layer containing phosphate minerals formed after the tuff layer; b. the organic matter rich layer formed both before and after the tuff layer.

However, some scholars hold different views. Zhang Rui et al. (2019) believes that high deposition rate caused by high intensity hydrothermal/volcanic material input can dilute primary productivity or reduce the abundance of organic matter [14]. Others believe that excessive volcanic activity or hydrothermal fluid input will cause strong BSR effect and large amount of organic matter consumption, which is harmful to organic matter enrichment. Some also proposed that appropriate volcanic activity is beneficial to organic matter enrichment, while excessive volcanic ash, frequent volcanic eruption releasing large amounts of gas, intermittent hydrothermal fluids at high temperature and high pressure would not be conducive to organic matter enrichment [15]. How to define the beneficial effect of volcanic activity and what are the parameters used to define appropriate amount are critical research areas in the future. Fine experimental analysis is needed to analyze the variation patterns of organic matter type, content and hydrocarbon generation potential of fine-grained sedimentary rocks in different layers above and below the volcanic ash layer, determine relationship between volcanic activity paleoproductivity and the paleoenvironment that are conducive to the preservation of organic carbon, and establish the relationship model between volcanic activity and organic matter enrichment.

When the source rock enters the sedimentary layer, the organic carbon therein is ready to crack to generate the oil and gas. With the increasing burial depth, the temperature and pressure of the source rock under the action of geothermal gradient continue to rise. This rising heat energy could break the organic molecules of the organic carbon to generate oil and gas [12]. The magma generated by volcanic activity brings heat of 1 020 \sim 1 200 °C, and the hydrothermal fluid generated by volcanic activity also brings heat of 300 \sim 400 °C. These two kinds of heat provide the sedimentary basin with a critical heat source of volcanic activity in addition to the heat source supplied by earth heat flow from mantle radiation, promoting the breakage of the organic matter.

4. Effects of volcanic activity on petroleum migration and accumulation

After oil and gas are discharged from the source rock formations and enter the seepage channel, they move through the sedimentary layers depending on the potential energy given by burial depth and the thermal kinetic energy and finally accumulate in highly porous formations with appropriate geological structures to form oil and gas reservoirs [16]. The heat source brought by volcanic activity can generate the thermal energy to promote this migration. In addition, the volcanic ash in the sediments undergoes complex transformations during the diagenetic process, which will produce a large number of inorganic pores, increasing the porosity and permeability of the mud shale and the oil and gas content. Zhu Shifa et al. (2011) believed that a large number of volcanic glass materials in the Permian Fengcheng Formation in the northwestern margin of Junggar Basin would form zeolite, albita and other minerals after undergoing alteration and multistage transformation, and zeolite minerals generally dissolve in the acidic environment of diagenetic period, greatly improving the quality of the reservoir [17]. The Cretaceous subsalt Barra Velha Formation in the offshore area of Brazil is a typical alkali lake deposit. Influenced by volcanic effluvium, it initially contained a large number of magnesium-rich clay minerals. Tosca and Wright (2015) believed that a large number of secondary pores developed in the Barra Velha Formation reservoir were formed by the late dissolution of magnesia-rich clay minerals [18].

Moreover, the hydrothermal fluids brought by volcanic activity to sedimentary basins carry weak acid function with pH value less than or equal to 4, which could dissolve the carbonate minerals in the formations and enlarge the channels through which the petroleum fluids pass [19]. The higher permeable formation is conducive to oil and gas migration and storage. The magma sent to the sedimentary basin by volcanic activity condenses into volcanic or crystalline rock. These rocks are usually porous that can become excellent petroleum reservoirs. For example, the reservoirs of Qingshen Gas field in Songliao Basin and Arshan Oilfield, which has the largest reserves in Erlian Basin, are both volcanic rocks.

5. The influence of volcanic activity on oil and gas exploitation

The higher the content of brittle minerals, the stronger the brittleness of shale, the easier it is to produce natural fractures and induced fractures under the action of external forces, which is more conducive to the exploitation of shale oil and gas [13]. Jarvie et al. (2007) believed that mineralogical analysis is indispensable for the study of shale oil and gas reservoirs, and that the content of brittle minerals is an important factor determining the natural gas production of the Mississippi Subsystem Barnett shale and other mud shale formations in north central Texas [20]. Li Xiaomeng et al. (2016) compared the Lower Paleozoic shale gas reservoirs of

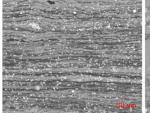
Qiongzhusi Formation and Longmaxi Formation in southern Sichuan, and concluded that the content of brittle minerals in Qiongzhusi Formation was higher than that in Longmaxi Formation, and thus had greater natural gas production potential [21]. The enrichment of dolomite and stable minerals such as quartz and alkaline feldspar formed by the conversion of tuffaceous materials derived from the volcanic activity in the later period in the alkali Lake source rocks resulted in a high content of brittle minerals. Therefore, natural fractures and artificial fractures generated after fracturing are highly developed and the initial oil and gas productivity tends to be high [13].

6. An example of volcanic activity affecting oil and gas exploration: Ordos Basin

Ordos Basin has a total area of about 370,000 square kilometers making it one of the largest sedimentary basins in China. Ordos Basin is an important oil-gas basin as well, rich in coal, ore and other mineral resources. The basin was formed 240 million years ago, mainly due to the Mesozoic Indosinian Movement and Yanshan Movement. In the early and middle Yanshanian movement, i.e., the Jurassic -- early Cretaceous period, the strong horizontal movement in the previously formed depression promoted the fault-fold belt on the western margin of the basin and the Weibei geological structural belt on the southern margin. In the middle and late Yanshanian Movement, crustal uplift occurred on the eastern side of the depression, and large-scale volcanic eruptions formed the Luliangshan Mountain and the western Jinxi flexural fold belt. The southern margin of the basin was the Qinling orogenic belt with a large number of volcanic eruptions. It is found that the shale of Chang 7 member of the Triassic Yanchang Formation in this basin contains a large number of tuffs, and the core is mainly composed of black shales and grayish yellow and grayish brown siltstones [13, 22].

The Qinling volcano erupted a large amount of volcanic ash, and the volcanic ash gas carried a large amount of sulfate and hydrogen sulfide, causing acid rain into the water. Although it affects the survival of organisms to a certain extent, strong reducing gases such as H₂S can cause anoxia in the water and prevent the oxidation of organic matter, thus contributing to the preservation of organic matter. The elements such as aluminum (Al), iron (Fe), calcium (Ca) and magnesium (Mg) brought by volcanic ash and terrigenous detritus provide abundant nutrients for the reproduction of aquatic organisms. When the aquatic organisms die, their remains are deposited at the bottom of the lake bed. In the anaerobic environment, the biological remains gradually transform into organic carbon rich shales. Multilayer tuff is generally held in the shale of Chang 7 Member in Ordos Basin, indicating that the shale deposition period was accompanied by intense volcanic activity [23, 24]. The thickness of organic-rich shale increases with the number of tuff layers. In the deep lake area away from the provenance, the cumulative thickness of tuff at the bottom of Chang 7 Member is

positively correlated with the thickness of organic-rich shale [22]. The shale with tuff also contains abundant fossils of cyanobacteria, green algae and chrysophyte [22, 25]. The tuff reservoir of Chang 7 Member is compact, and a large number of micro-pores can be found under scanning electron microscopy, which are distributed in strips. The single pore volume is small, and the pore size is mainly micron-nano level (Figure 4).



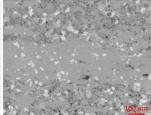


Fig. 4. The SEM images of organic-rich samples and tuff samples (modified from [13])

Further, under the high temperature and pressure provided by volcanoes, the temperature of the geothermal gradient rises, transforming solid organic matter (kerogen) into macromolecular organic matter (oil). Afterwards, with the increasing of the thermal effect, macromolecular organic matter can also be converted into small molecular organic matter (natural gas). After the formation of hydrocarbons, the Triassic volcanic rocks near the surface of the Ordos Basin became the storage place of oil and gas, and the ancient explosive eruption made the porosity structure of the rocks more developed. Therefore, if the formation conditions are suitable, oil and natural gas will move to the surface under the action of pressure, probably increased by the volcanic activity, and when they encounter volcanic rocks, they will be filled in them, and stored for hundreds of millions of years, forming rich oil and natural gas resources. The extensive development of organic-rich mud shale in the Chang 7 member of Yanchang Formation has made it rich in shale oil resources, and its resources are conservatively estimated to exceed 10 billion tons [26, 27]. Therefore, the study on organic-rich shale formation and hydrocarbon enrichment in Chang 7 Member of Ordos Basin has important indicative significance and reference value for effective exploration and development of shale oil in tuff shale layers.

7. Conclusions

Volcanic activities are critical geological phenomenon since the formation of the Earth and play important roles with the evolution of the earth and life systems. The distribution of modern volcanos is precisely monitored by different organisms globally as they can bring fatal effects to the ecological and economic societies. However, volcanic activities provide valuable natural resources that human life widely depends on, including but not limiting petroleum i.e., oil and natural gas. This study reviewed the important role of the volcanic activity on the petroleum system including the enrichment of organic carbon rich source rocks, the formation of hydrocarbons, the

migration and accumulation of the oil and natural gas and finally the exploitation of the petroleum system. Based on the theoretical review, a case study of the Chang 7 member in the Yanchang formation of Ordos Basin in China was analyzed. It is one of the most important oil and gas basins in China and currently contributes the largest volume of petroleum production. Through analyzing the organic-rich formation mechanism and oil content of the Chang 7 shale, the following understandings are obtained. Volcanic activity facilitates the flourish of the algae, bacteria and other hydrocarbonforming organisms to improve the ancient productivity. The sulphate introduced into the lacustrine basin by volcanic activity increased the concentration of sulfate in fresh water and provided sulfur source for BSR, which enhanced the reducibility of water and was conducive to the preservation of organic matter. Organic geochemical analysis of mud shale, tuff and silty mudstone of Chang 7 Member shows that mud shale has high TOC content and high hydrocarbon generation potential. This study sheds light to the relationship between volcanic activities and the development of the petroleum resources and proposes that this is an important scientific area needing more detailed research in the future.

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