

Facilitation or Inhibition: the role of volcanic ash in lacustrine organic matter production

Liangrong QIAN

qianliangrong@foxmail.com

Exploration and Development Research Institute, Daqing Oilfield of CNPC

Xiujian DING

China University of Petroleum

Huajun GUO

PetroChina Hangzhou Research Institute of Geology

Hengyuan QIU

Exploration and Development Research Institute, Daqing Oilfield of CNPC

Wenjun HE

PetroChina Xinjiang Oilfield Company

Wenlong JIANG

PetroChina Xinjiang Oilfield Company

Xuemei YANG

China University of Petroleum

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Abstract

The role of volcanic ash in organic matter production is complex. It can both bring nutrient elements to facilitate organic matter production and introduce harmful substances to inhibit it. The organic matter abundance in the Lucaogou Formation of the Jimsar Sag in the Junggar Basin varies greatly, and the volcanic ash content changes significantly, making it a natural laboratory for studying the role of volcanic ash in organic matter production. Based on biomarker compounds, and optimized elemental indicators, the organic matter source and paleoproductivity of the Lucaogou Formation were analyzed. The role of volcanic ash in organic matter production was explored. Research suggests that the organic matter in the Lucaogou Formation primarily originates from a mixed sedimentation of algae, bacteria, and terrestrial higher plants, with a higher content of hydrobiont. The content of volcanic ash is calculated through a combination of microscopic identification and geochemical methods. When the volcanic ash content is low ($< 20\%$), there is no correlation between volcanic ash and paleoproductivity, and volcanic ash does not significantly facilitate or inhibit organic matter production. This may be due to the low nutrient content carried by volcanic ash, and did not cause biological growth. When the volcanic ash content is moderate ($20\%-40\%$), an increase in volcanic ash content facilitates organic matter production. This is related to the release of various nutrients and elements from volcanic ash, which leads to the flourishing of organisms. When the volcanic ash content is high ($> 40\%$), it brings a large amount of harmful substances and makes the lake water turbid, causing biological death and inhibiting organic matter production.

1. Introduction

As a critical conduit for material and energy exchange between Earth's deep interior and surficial spheres, volcanism represents a core geological process within the interplay system of various Earth's spheres. Occurring at the lithosphere—the transitional interface between deep and shallow Earth spheres, volcanism profoundly intervenes in the global carbon cycle via magma eruption, greenhouse gas degassing, and volcanic ash deposition. On one hand, volcanism directly regulates the carbon budgets of the atmosphere and hydrosphere, altering the rates of carbon migration and transformation across different spheres. On the other hand, it modulates organic matter production in the biosphere by releasing bioavailable nutrients and adjusting climatic conditions. Investigating the regulatory mechanisms of volcanism on organic matter production not only refines the theoretical framework of sphere interactions in Earth system science, but also provides scientific insights for deciphering geological carbon cycle and organic matter enrichment patterns. This has significant theoretical and practical implications.

Controversies remain regarding the role of volcanic ash in organic matter production. A number of researchers have proposed that volcanic ash releases key nutrient elements including Fe, N and P after entering the water column. These bioessential nutrients serve as critical drivers for the growth of plankton and algae, and facilitate organic matter production (Duggen et al., 2010; Olgun et al., 2013). In contrast, an alternative hypothesis asserts that volcanic activity inhibits organic matter production,

mainly through its adverse impacts on biological communities. Beyond the release of nutrients, volcanic ash also generates toxic substances such as Pb and Hg, which trigger declines in chlorophyll concentrations and extensive biological mortality (Mcknight et al., 1981). Concurrently, the insoluble volcanic particles block sunlight, jeopardizing the survival of organisms inhabiting the benthic zone (Genin et al., 1995). Moreover, previous studies focusing on the role of volcanic ash in organic matter production have been predominantly restricted to qualitative assessments, with a notable scarcity of quantitative research exploring the correlations between volcanic ash content and paleoproductivity levels. This research gap has constrained the advancement of theories pertaining to organic matter enrichment and hydrocarbon exploration.

Core samples from the Permian Lucaogou Formation in the Jimsar Sag, Junggar Basin, exhibit excellent continuity, abundant volcanic ash, and pronounced variations in ash content (Wang et al., 2022; Jiang et al., 2020; Liang et al., 2023), making it a natural laboratory for investigating the relationship between volcanic ash abundance and paleoproductivity. Based on organic biomarker compounds and a set of optimized elemental proxies, this study analyzes the organic matter sources and paleoproductivity of the Lucaogou Formation, evaluates the relative contributions of terrestrial and aquatic organisms to paleoproductivity, and explores the relationship between volcanic ash content and paleoproductivity. The findings are of great significance for refining organic matter enrichment theory, revealing the formation mechanisms of organic-rich shales in volcanic ash bearing settings, and guiding shale oil exploration.

2. Geological setting

The Junggar Basin is one of the four major petroliferous sedimentary basins in western China. To date, 25 oil and gas fields have been discovered within the basin, mainly distributed along the northwestern margin, the Luliang Depression, the eastern basin, and the southern margin. The Jimsar Sag is situated at the western edge of the eastern uplift of the basin (Fig. 1A). To the west, it is bounded by the Xidi and Laozhuangwan Faults and adjoins the Santai Uplift. To the east, it transitions into the eastern slope and uplift area (Fig. 1B). This setting determines that the sag both receives sediment supply from the surrounding uplifts and maintains a relatively independent depocenter and hydrocarbon accumulation center during tectonic subsidence (Cao et al., 2016; Kuang et al., 2012).

The principal source rocks in the Junggar Basin are of Carboniferous (C) and Permian (P) age, followed by the Jurassic (J). Exploration results indicate that the vast majority (about 94%) of the discovered oil and gas in the basin was derived from deep Permian source rocks (Kuang et al., 2012; Jiang et al., 2015; Ding et al., 2019). The Permian Lucaogou Formation represents the most important source rock in the Jimsar Sag. Frequent peripheral volcanism during Lucaogou deposition resulted in multiple interbedded tuff and volcanic ash fallout layers. The Lucaogou Formation is a dark-colored, fine-grained lithological strata and constitutes the principal target interval for shale oil exploration and development (Kuang et al., 2012). Its thickness is relatively large, generally ranging from 200 to 350 m in the area, with a maximum of over 500 m. Within the sag, the favorable area with a thickness > 200 m covers approximately 800 km², and the total distribution area of the Lucaogou Formation is about 1278 km².

The formation is commonly divided into the lower Lucaogou Formation (LLFM) and the upper Lucaogou Formation (ULFM) (Fig. 1C) (Jiang et al., 2015).

3. Samples and methods

The samples used in this study were collected from Well J174, which penetrated the Permian Lucaogou Formation in the Junggar Basin. Its location is shown in Fig. 1B. The samples span a depth interval of 3124.34–3354.46 m. The samples were analyzed by gas chromatography–mass spectrometry (GC-MS) and Rock-Eval analysis. All measurements were performed at the State Key Laboratory of Deep Oil and Gas, China University of Petroleum (East China). Sample pretreatment and the analytical procedures strictly followed the laboratory manual.

3.1. GC–MS analysis

Powdered samples (< 200 μm) were extracted with dichloromethane/methanol (93:7, v/v) via solvent extraction at 100°C and 1500 psi. The crude extract was fractionated on an activated silica gel column into aliphatic and aromatic fractions using stepwise elution with n-hexane and a DCM/hexane blend. Compounds were separated on an HP-5MS capillary column (30 m $\times$ 0.25 mm) under helium flow and identified by GC–MS (70 eV EI, m/z 50–550) using NIST matching and linear retention indices from an n-alkane suite. The results are summarized in Table 1.

3.2. Rock-Eval analysis

Approximately 100 mg of the samples (< 200 μm) was analyzed by pyrolysis using a Rock-Eval VI instrument. The sample was first heated at 300°C under helium to release free hydrocarbons (S_1), then ramped from 300 to 650°C at 25°C min⁻¹ to generate pyrolytic products (S_2) and record the maximum temperature (T_{max}). Residual carbon was combusted at 850°C to yield CO₂ (S_3) and total organic carbon (TOC). Hydrogen and oxygen indices were calculated from S_2 and S_3 normalized to TOC. Replicate runs showed Tmax and TOC reproducibilities within $\pm 2^\circ\text{C}$ and $\pm 5\%$, respectively. Data summaries are provided in Table 2.

Table 1
Results of part biomarker compounds of the Lucaogou Formation in the Jimsar Sag

Depth /m	Pr/ Ph	Pr/ nC ₁₇	Ph/ nC ₁₈	TAR	S/H	C ₂₇ /%	C ₂₈ /%	C ₂₉ /%	β/ C _{max}	C ₂₉ β/ (α + β)	C ₂₉ S/ (S + R)
3109.54	1.17	1	0.86	/	0.3	16.75	33.83	49.42	0.55	0.32	0.42
3113.44	1.19	0.94	0.87	/	0.33	14.62	34.39	50.99	/	0.35	0.46
3115.34	1.2	1.05	1.05	0.5	0.35	13.38	34.8	51.83	0.57	0.33	0.44
3117.75	1.23	0.84	0.85	/	0.17	20.59	32.54	46.88	0.22	0.24	0.41
3122.14	1.87	1.12	0.69	0.53	0.31	15.76	31.31	52.93	0.03	0.18	0.31
3137.01	1.52	1.41	1.03	0.98	0.53	22.35	35.68	41.98	0.42	0.17	0.30
3142.13	1.15	1.3	1.32	0.71	0.3	13.3	35.45	51.24	1.37	0.29	0.44
3142.95	1.18	1.29	1.3	0.36	0.31	13.22	35.61	51.17	2.69	0.29	0.43
3149.26	1.05	0.18	0.11	0.61	0.24	20.55	42.56	36.89	0.02	0.26	0.44
3152.31	1.19	0.87	0.7	1.11	0.32	14	56.2	29.79	0.05	0.26	0.39
3152.98	1.4	0.62	0.51	0.21	0.32	14.69	52.95	32.36	0.03	0.23	0.37
3156.94	1.77	0.62	0.3	0.4	0.48	13.42	37.19	49.39	0.03	0.18	0.30
3161.44	1	0.11	0.08	/	0.24	21.48	39.23	39.29	0	0.27	0.36
3165.32	1.33	0.22	0.13	0.36	0.31	20	44.98	35.02	0	0.18	0.34
3166.19	1.39	0.3	0.17	1.08	0.61	21.34	41.88	36.77	0	0.19	0.35
3170.39	1.07	0.54	0.47	0.97	0.57	15.15	35.55	49.3	0.02	0.20	0.34
3173.56	1.2	0.24	0.16	0.73	0.38	15.64	47.83	36.53	0	0.20	0.35
3175.09	0.88	0.16	0.13	0.33	0.44	15.51	43.06	41.44	0	0.20	0.35
3177.34	1.26	0.43	0.32	1.04	0.28	22.49	33.16	44.35	0.06	0.22	0.38
3188.62	1.46	0.52	0.58	0.97	0.28	23.91	35.46	40.62	0.06	0.21	0.36
3190.79	1.2	1.36	1.48	0.42	0.43	12.13	34.14	53.72	0.93	0.31	0.46
3198.81	1.44	1.3	1.13	/	0.21	20.89	35.5	43.61	0	0.21	0.36
3200.81	1.51	1.55	1.28	0.43	0.59	17.11	34.77	48.12	0.69	0.23	0.37
3204.57	1.44	1.53	1.17	0.66	0.32	21.11	35.4	43.49	0.33	0.21	0.36
3210.89	1.43	1.45	1.28	0.3	0.45	18.37	37.38	44.25	0.41	0.25	0.38

Depth /m	Pr/ Ph	Pr/ nC ₁₇	Ph/ nC ₁₈	TAR	S/H	C ₂₇ /%	C ₂₈ /%	C ₂₉ /%	β/ C _{max}	C ₂₉ β/ (α + β)	C ₂₉ S/ (S + R)
3216.7	1.06	1.78	2.19	0.89	0.43	12.97	40.85	46.18	0.29	0.24	0.40
3217.75	1.05	1.78	2.39	0.38	0.51	12.24	36.03	51.73	1.21	0.25	0.40
3228.53	1.03	1.56	2.04	0.54	0.5	9.04	44.52	46.44	0.05	0.23	0.39
3255	1.11	1.79	2.45	0.39	0.37	12.04	34.02	53.94	2.54	0.25	0.40
3291.79	0.91	1.89	3.2	0.43	0.33	13.11	32.6	54.29	2.14	0.22	0.39
3295.85	1.02	1.88	2.82	0.38	0.19	13.23	34.57	52.21	1.8	0.24	0.42
3298.64	0.92	2.29	3.84	0.49	0.14	11.8	34.78	53.43	6.14	0.23	0.39
3301.93	0.98	1.6	2.62	0.37	0.34	12.99	36.04	50.97	1.26	0.23	0.42
3316.35	1.26	0.76	0.7	0.49	0.92	8.32	36.85	54.83	0.11	0.31	0.42
3320.91	0.93	1.38	1.95	0.49	0.21	18.22	32.08	49.7	2.49	0.28	0.43
3327.24	1.46	0.96	0.68	0.41	0.18	19.61	37.55	42.83	0.5	0.28	0.44
3332.81	0.73	0.34	0.41	1.54	1.04	17.12	44.42	38.46	0	0.32	0.43
3341.56	0.67	0.3	0.35	1.79	0.52	13.71	20.4	65.88	0.04	0.35	0.43
3355.65	1.63	0.29	0.19	0.7	0.26	29.26	25.29	45.45	0	0.34	0.42

TAR, Terrestrial/Aquatic Ratio, $TAR = (nC_{27} + nC_{29} + nC_{31}) / (nC_{15} + nC_{17} + nC_{19})$; S/H, Sterane/Hopane, $S/H = (C_{27} \text{ sterane} + C_{28} \text{ sterane} + C_{29} \text{ sterane}) / (C_{29} \text{ hopane} + C_{30} \text{ hopane})$; β/C_{max} , β -carotane / C_{max} ; $C_{29}\beta/(\alpha + \beta)$, $C_{29} \alpha\beta\beta/(\alpha\alpha\alpha + \alpha\beta\beta)$ steranes; $C_{29}S/(S + R)$, $C_{29} 20S/(20S + 20R)$ steranes.

Table 2
Results of total organic carbon and Rock-Eval pyrolysis of the Lucaogou Formation in the Jimsar Sag

Depth /m	TOC /%	S ₁ /(mg/g)	S ₂ / (mg/g)	S ₁ +S ₂ / (mg/g)	HI/ (mg/g·TOC)	T _{max} /°C
3204.01	1.92	0.59	4.03	4.62	209.90	448
3232.14	2.91	2.66	5.96	8.62	204.81	442
3245.89	0.8	0.41	0.49	0.9	61.25	443
3255.72	3.1	3.14	5.03	8.17	162.26	444
3269.74	3.79	5.05	8.74	13.79	230.61	444
3292.01	3.5	1.38	8.66	10.04	247.43	446
3303.48	2.84	0.26	9.4	9.66	330.99	454
3309.89	2.35	0.22	7.58	7.8	322.55	450
3318.01	1.77	4.06	4.81	8.87	271.75	436
3329.68	5.56	0.6	33.82	34.42	608.27	455
3332.81	1.17	0.49	1.86	2.35	158.97	451
3336.38	3.52	0.64	11.16	11.8	317.05	454
3341.56	0.36	0.16	0.17	0.33	47.22	448

4. Results

4.1. Organic geochemical characteristics

The Lucaogou Formation in the Jimsar Sag exhibits a notably high organic matter abundance. With the exception of a few samples, The TOC values exceed 2.0%, ranging from 0.35%–19.01% and averaging 3.55% (Table 3, Fig. 2). Correspondingly, the S₁+S₂ of the kerogen ranges from 0.48 to 49.99 mg/g, with a mean of 12.49 mg/g (Table 3, Fig. 2). Applying the classification scheme of Peters and Cassa (1994), the Lucaogou Formation develops good source rocks. The hydrogen index (HI = S₂/TOC) varies between 35.90 and 798.51 mg/g TOC (Table 3, Fig. 2), pointing to a predominance of type I₁ and I₂ kerogens. Maturity assessments show that the Lucaogou Formation has reached the oil window. Specifically, T_{max} falls in the range 436–458°C, the C₂₉ αββ/(ααα + αββ) sterane ratio lies between 0.16 and 0.35, and the C₂₉ 20S/(20S+20R) sterane ratio ranges from 0.30 to 0.46. These maturity parameters indices demonstrate that the Lucaogou source rocks are in a mature stage.

4.2. Biomarker characteristics

In the past years, biomarkers have attracted extensive attention as an important tool for organic geochemical research (Peters et al., 2005). The distribution characteristics of biomarkers of samples from the Lucaogou Formation are shown in Fig. 3. The distributions and parameters of n-alkanes and isoprenoid alkanes are generally obtained from TIC mass chromatograms, those of the tricyclic and pentacyclic terpanes from m/z 191 mass chromatograms, and those of the steranes from m/z 217 mass chromatograms.

The source rock extracts of the Lucaogou Formation contain a full range of C_{13} – C_{31} n-alkanes and isoprenoids, including pristane and phytane. N-alkanes include short-chain (nC_{12} – nC_{21}) and long-chain (nC_{22} – nC_{35}) n-alkanes, and the samples are mainly bimodal (Fig. 3). Pristane (Pr) and phytane (Ph) are usually the most important isoprenoids (Powell and mckirdy, 1973; Peters et al., 2005). The distribution range of Pr/Ph in the Lucaogou Formation is 0.67–1.87, with an average of 1.21. The values of Pr/ nC_{17} are between 0.11 and 2.29 while the values of Ph/ nC_{18} are between 0.08 and 3.84 (Table 1). The relative contents of C_{29} steranes, C_{28} steranes and C_{27} steranes in the Lucaogou Formation were 29.79%–65.88%, 20.4%–56.2% and 8.32%–29.26%, respectively. β -carotane is usually recognized in the m/z125 mass spectra, and the content in TIC is very low. However, β -carotane can be observed clearly in TIC of the Lucaogou formation (Fig. 3), indicating the high β -carotane content. The great changes in the relative abundances of pristane, phytane, hopane, sterane and β -carotane in the samples suggest the changes of the sources of organic matter in the Lucaogou Formation.

4.3. Element characteristics

Phosphorus (P), copper (Cu) and barium (Ba) are closely related to biological survival and are common indicators of biological productivity (Rimmer et al., 2004; Dymond et al., 1992; Brumsack et al., 1986). To minimize the influence of terrigenous detritus on elemental concentrations, the P/Ti and Cu/Ti ratios are conventionally employed as proxies for paleoproductivity. The distribution range of P/Ti in the samples of the Lucaogou Formation is 0.15–0.77, with an average of 0.27 (Table 2). The P/Ti value is low, which may reflect low paleoproductivity. The Cu/Ti ratios of the samples from the Lucaogou Formation range from 0.03 to 0.21, with an average of 0.07, which are much higher than those of the Post-Archaean Australian Shale (PAAS) and the source rocks of Chang 7 member in Ordos Basin, China (0.008 and 0.039). This reflects the high productivity of the Lucaogou Formation. Ba preserved in sediments is typically divided into biological Ba and terrigenous Ba, of which only the biogenic fraction records primary productivity. Biogenic Ba (Ba_{bio}) is most often quantified using the expression: $Ba_{bio} = Ba_{total} - (Al \times Ba / Al_{aluminum})$ (Dymond et al., 1992). This equation assumes that sedimentary Al is exclusively of aluminosilicate origin and therefore applies the $Ba / Al_{aluminum}$ ratio to approximate the lithogenic barium contribution (Taylor et al., 1964). The distribution range of Ba_{bio} is -217.50–218.86 in the Lucaogou Formation, with an average of -19.39. There are many negative values of Ba_{bio} index (Table 2). This result is obviously problematic, which may be caused by low Ba content or high Al content brought by terrigenous input. It requires further analysis about whether Ba_{bio} index can be used to characterize the paleoproductivity of the Lucaogou Formation.

5. Discussion

5.1. Volcanic ash and sources of organic matter

5.1.1. Biomarkers and sources of organic matter

The origin of organic matter in source rocks of major sedimentary basins has long been a subject of extensive debate. Available evidence indicates that paleoproductivity was predominantly sustained by a range of primary and secondary producers—such as plankton, bacteria, and higher plants (Murphy et al., 1985). These organisms are viewed as the principal contributors to primary productivity in ancient lacustrine systems, and they were central to both the establishment and the persistence of the ancient lake ecosystem.

As organisms are transformed into sediment, lipid compounds with stable chemical structure enter the sedimentary system, and saturated straight chain hydrocarbons with source information become the main component of organic matter in source rocks (Peters et al., 2005). Therefore, biomarkers are routinely employed to trace the origin of organic matter. The n-alkane distribution carries information on the source of organic matter. Specifically, long-chain n-alkanes (C_{22} – C_{35}) are characteristic of higher terrestrial plants, whereas short-chain n-alkanes (C_{12} – C_{21}) are usually derived from algae and plankton (Eglinton and Hamilton, 1967; Meyers, 1997). In general, a dominant n-alkane peak falling between nC_{15} and nC_{19} defines the front-peak pattern, which reflects the source of organic matter is terrestrial higher plants. A dominant peak within nC_{25} – nC_{33} corresponds to the back-peak pattern, reflecting a contribution of terrestrial higher plants. A bimodal distribution points to a mixed organic matter source (Moldowan et al., 1991). The main peak carbons of n-alkanes of the Lucaogou Formation are nC_{17} and nC_{23} (Fig. 3), and there are more samples with the main peak carbon of nC_{23} . It indicates that the organic matter of is a mixed source of terrestrial higher plants, algae and bacteria. Because there are many samples with nC_{17} as the main peak carbon, and there are not a large number of samples with the main peak carbon number greater than nC_{25} , it is speculated that hydrobiont account for a higher proportion of the source of organic matter in the Lucaogou Formation.

Pristane (Pr) and phytane (Ph) are usually the most important isoprenoid alkanes, which can be used to reflect the source of organic matter and sedimentary environment (Powell and Mckirdy, 1973; Peters et al., 2005). The distribution range of Pr/Ph in the Lucaogou Formation is 0.67–1.87, with an average of 1.21 (Fig. 4). Pr/ nC_{17} values are between 0.11 and 2.29, and Ph/ nC_{18} values are between 0.08 and 3.84 (Fig. 5, Table 1). The relationship between Ph/ nC_{18} and Pr/ nC_{17} can be used to evaluate the source of organic matter and redox conditions. In the diagram (Fig. 5), the samples of the Lucaogou Formation mainly fall in the area of mixed sources and lower hydrobiont, indicating the characteristics of mixed source input of organic matter.

Short-chain n-alkanes nC_{15} , nC_{17} , and nC_{19} are generally believed to have a marine or lacustrine algal origin, whereas the long-chain n-alkanes nC_{27} , nC_{29} , and nC_{31} are attributed to terrestrial higher plants. On this basis, the terrestrial/aquatic ratio (TAR) was used as a proxy for organic matter source. The calculation formula is $TAR = (nC_{27} + nC_{29} + nC_{31}) / (nC_{15} + nC_{17} + nC_{19})$ (Gelpi et al., 1970; Tissot and Welte, 1984). The distribution range of TAR of the Lucaogou Formation is 0.21–1.79 (Fig. 4, Table 1), with an average of 0.63. The TAR values of most samples in the Lucaogou Formation are less than 1.0, indicating that hydrobiont were mainly developed during the sedimentation period of the Lucaogou Formation. A small number of samples have TAR values close to or greater than 1.0, indicating the mixed sources of organic matter.

Hopanes are generally regarded as diagenetic products of bacterial membrane precursors, whereas steroidal hydrocarbons are principally sourced from eukaryotes such as algae. Accordingly, the sterane/hopane ratio (S/H) serves as a proxy for the relative abundance of algae (eukaryotes) versus bacteria (prokaryotes) (Peters et al., 2005). The S/H values of Lucaogou Formation range from 0.14 to 1.04 (Fig. 4, Table 1), with an average of 0.39, which is basically less than 1.0. Only a small number of samples have S/H values greater than 1.0 and they are concentrated at the bottom of the Lucaogou Formation. This reflect that the abundance of bacteria is higher than that of algae in organic matter derived from bacteria and algae.

The relative abundance of steranes is widely used as a diagnostic marker for assessing organic matter source (Seifert and Moldowan, 1978). Specifically, C_{27} steranes are typically linked to plankton or metazoans; C_{28} steranes are generally assigned to particular phytoplankton groups, such as diatoms, dinoflagellates, and chlorella, which bear chlorophyll a and c; and C_{29} steranes are predominantly sourced from terrestrial higher plants together with phytoplankton such as green algae and cyanobacteria (Ji et al., 1982; Volkman, 1986). The relative content diagram of C_{27} - C_{28} - C_{29} steranes (Fig. 6, Table 1) shows that the Lucaogou formation has the highest relative content of C_{29} steranes (29.79%–65.88%, average 46.21%), followed by C_{28} steranes (20.4%–56.2%, average 37.24%), and the lowest of C_{27} steranes (8.32%–29.26%, average 16.56%). Through organic petrological analysis and scanning electron microscope observation, Liu et al. (2022) conclude that C_{28} steranes of the Lucaogou Formation are mainly derived from cyanobacteria, and green algae are an important source of C_{29} steranes. Accordingly, the relative content diagram of C_{27} - C_{28} - C_{29} steranes indicates that the organic matter was mainly contributed by aquatic organisms, with green algae being more abundant than cyanobacteria (Fig. 6).

The characteristics and content of organic matter macerals can directly identify the source of organic matter. Ding et al. (2023) observed the samples of the Lucaogou Formation under the microscope and found that the contents of cutinite, sporinite and liptodetrinite are very low, while the contents of bituminite and alginite are very high. This indicates that the content of organic matter from hydrobiont is high, while that from terrestrial higher plants is low (Ding et al., 2023).

In summary, the organic matter in the Lucaogou Formation mainly comes from the mixture of aquatic algae, bacteria and terrestrial higher plants, with significant contributions of hydrobiont. When the organic matter is mainly from bacteria and algae, the bacterial abundance is relatively high. In addition, the algae in the Lucaogou Formation are mainly green algae and cyanobacteria and the content of green algae is higher. Green algae tend to be enriched in C_{29} steranes, whereas cyanobacteria are typically enriched in C_{28} steranes.

5.1.2. Impact of volcanic ash on organic matter sources

The role of volcanic ash in organic matter production is closely related to its content. The boxplot is adopted to discuss the role of volcanic ash in organic matter production. The boxplot takes the volcanic ash content as the horizontal axis and the related indicators about organic matter production as the vertical axis. In order to make the data display more intuitive, outliers are excluded when drawing boxplots. The data of volcanic ash content comes from Ding et al. (2023).

The ratio of 1/TAR (reflecting the content of hydrobiont to terrestrial higher plants) can indicate the content of hydrobiont in organic matter sources. According to the boxplot, as the volcanic ash content increases, the content of hydrobiont in the Lucaogou Formation shows a trend of small change at first, then increase, and finally decrease (Fig. 7A). When the volcanic ash content is lower than 20%, the 1/TAR changes slightly with the increase of the volcanic ash content (Fig. 7A), reflecting that volcanic ash has no obvious facilitating or inhibiting effect on hydrobiont. Research by Longman et al. (2019) shows that volcanic ash after diagenetic alteration will lose a lot of nutrients compared with fresh volcanic ash. Because the volcanic ash of the Lucaogou Formation is mainly carried by the wind or water around the depression, it has undergone alteration during deposition (Jiang et al., 2015), so its nutrient element content has decreased. This may be the reason that the content of hydrobiont did not increase immediately after the volcanic ash was input into the water column. When the volcanic ash content increases to 20%–40%, there is a good positive correlation between volcanic ash content and 1/TAR. As the volcanic ash content increases, the content of hydrobiont also increases steadily (Fig. 7A). The facilitating effect of volcanic ash on hydrobiont may be due to the release of various nutrients (such as nitrate, phosphate, etc.) and nutrients (Fe, N, P, etc.) after being input into water column, facilitating the proliferation of hydrobiont such as bacteria and algae (Xiao et al., 2023). When the volcanic ash content exceeds 40%, 1/TAR shows a significant decrease with the increase of volcanic ash content (Fig. 7A), indicating that the high content of volcanic ash inhibits the survival of hydrobiont. This phenomenon may be caused by two reasons. On the one hand, volcanic ash not only carries nutrients, but also releases harmful substances such as Pb and Hg (Mcknight et al., 1981), which may lead to the decrease of chlorophyll concentration and massive biological death. This situation is more obvious when the volcanic ash content is very high. On the other hand, a large amount of volcanic ash input will make the water turbid and reduce its transparency, and thus have a negative impact on plant photosynthesis, ultimately inhibiting the survival of underwater organisms.

In order to deeply analyze the specific impact of volcanic ash content on various hydrobiont, different biomarkers were selected to represent different types of hydrobiont. Specifically, the relative content of C_{28} sterane is used to represent the content of cyanobacteria, the relative content of C_{29} sterane is used to represent the content of green algae, and the H/S ratio is used to reflect the relative content of bacteria.

With the increase of volcanic ash content, the content of cyanobacteria showed a trend of first increasing and then decreasing (Fig. 7B). When the volcanic ash content is lower than 25%, the relative content of C_{28} sterane gradually increases with the increase of volcanic ash content. Especially when the volcanic ash content is 20%–25%, it reaches the peak (Fig. 7B), indicating that the increase of volcanic ash content facilitates the growth of cyanobacteria. When the volcanic ash content is greater than 25%, the relative content of C_{28} sterane decreases rapidly, which means that the high content of volcanic ash has an inhibitory effect on the growth of cyanobacteria.

The impact of volcanic ash content on green algae in the Lucaogou Formation is complex (Fig. 7C). Different from cyanobacteria, when the volcanic ash content is lower than 25%, the relative content of C_{29} steranes decreases rapidly with the increase of volcanic ash content, reaching its lowest point when the volcanic ash content is between 20% and 25%. The results indicate that the increase of volcanic ash content in this situation inhibit the growth of green algae. When the content of volcanic ash increases to 25%–40%, the relative content of C_{29} sterane begins to rise rapidly again, indicating that the increase of volcanic ash content facilitates the bloom of green algae in this situation. When the content of volcanic ash exceeds 40%, the relative content of C_{29} steranes decreases again, indicating that high levels of volcanic ash also have an inhibitory effect on the growth of green algae.

The effect of volcanic ash content on the relative bacterial content of the Lucaogou Formation is similar to that on green algae (Fig. 7D). When the volcanic ash content is lower than 25%, the H/S value decreases rapidly with the increase of volcanic ash content, and reaches the minimum when the volcanic ash content is 20%–25%. This indicates that the increase of volcanic ash content inhibits the growth of bacteria. When the content of volcanic ash is between 25% and 40%, the H/S value gradually increases, indicating that an appropriate amount of volcanic ash facilitates the proliferation of bacteria. However, when the content of volcanic ash exceeds 40%, the H/S value decreases again with the increase of volcanic ash content, indicating that the high content of volcanic ash inhibits the development of bacteria. This inhibitory effect is closely related to the destructive effects of high content of volcanic ash on hydrobiont. A large number of hydrobiont such as cyanobacteria, green algae, and bacteria all die when the volcanic ash content is high.

5.2. Volcanic ash and paleoproductivity

As a basic parameter of lacustrine systems, paleoproductivity strongly influences ecological dynamics, redox conditions, and the biogeochemical cycling of nutrients such as carbon, nitrogen, and phosphorus (Levinton, 2021). Major and trace element geochemistry represents a routine approach for

reconstructing paleoproductivity. The principal elemental indicators include biological phosphorus (P_{bio}), Ba_{bio} , and Cu (Nelson et al., 1995; Rimmer et al., 2004; Dymond et al., 1992).

5.2.1. Indicator optimization and paleoproductivity

P element is an important constituent element of organisms. Upon death, P is transferred to sediments and preserved in the form of phosphorus minerals during subsequent mineralization processes. P is often used as a key indicator to assess water column productivity. The sources of P mainly include terrigenous phosphorus and biological phosphorus (P_{bio}). The weathering and erosion of rocks generate P containing detritus, which are transported to the sedimentary basin by rivers, winds and other external forces, and ultimately deposited as clastic grains, giving rise to terrestrial phosphorus. P_{bio} refers to the phosphorus absorbed, fixed, and accumulated in the body or remains of organisms through metabolic processes (Ruttenberg, 1992; Filippelli, 2008). Biological phosphorus (P_{bio}) is an effective indicator for evaluating paleoproductivity. To obtain a more accurate paleoproductivity estimate and reduce the interference of terrestrial P, the P/Ti ratio is widely applied (Rimmer et al., 2004). Empirical thresholds from Algeo et al. (2007) classify that a P/Ti ratio exceeding 0.79 as a sign of high paleoproductivity. The ratio between 0.34 and 0.79 as medium and the ratio below 0.34 as low (Algeo et al., 2007).

The vertical variation diagram of paleoproductivity indicators of the Lucaogou Formation in the Jimsar Sag (Fig. 8) shows that P/Ti is generally less than 0.34, indicating low paleoproductivity. A small number of samples have a P/Ti ratio greater than 0.34 but less than 0.79, indicating medium paleoproductivity. It should be noted that the paleoproductivity indicated by the P/Ti may be influenced by redox conditions. Under reducing conditions, P_{bio} is affected by microbial reduction to generate organic phosphorus compounds such as phosphate, which are recycled into the water (Cappellen et al., 1994). Under oxidation conditions, P_{bio} is oxidized to phosphate ions (PO_4^{3-}) under the influence of microbial oxidation and chemical precipitation. At this time, it is more likely to combine with metal ions (such as iron, aluminum, calcium, etc.) in sediments to form insoluble phosphate minerals, which are preserved in sediments. Therefore, P_{bio} is more accurate in evaluating paleoproductivity under oxidation conditions (Algeo et al., 2007). Qian et al. (2024) found that the Lucaogou Formation was mainly in a reducing environment, under which P_{bio} was not preserved in sediments. Therefore, the paleoproductivity of the study area evaluated by P_{bio} indicators may be lower than the actual situation.

The Ba element in sediments is mainly distributed in sediments and water column in the form of barium sulfate. The amount of barium sulfate precipitation is proportional to the input of organic matter. Therefore, the increase of Ba content in organic rich sediments usually reflects the enhancement of biological productivity (Dymond et al., 1992). Ba_{bio} can serve as an effective indicator for evaluating paleoproductivity. There are many negative values of Ba_{bio} in the Lucaogou Formation (Fig. 8), which is obviously problematic. The applicability of Ba_{bio} indicator in the Lucaogou Formation needs further analysis. According to calculation formula of Ba_{bio} ($Ba_{\text{bio}} = Ba_{\text{total}} - (\text{Al} \times Ba / \text{Al}_{\text{aluminum}})$), the negative values of Ba_{bio} may be caused by the low Ba content or the high Al content brought by terrigenous input.

Previous studies have shown that the anoxic sedimentary environment will lead to the reduction of Ba content. Under anoxic conditions, sulfate reduction reactions often occur on the surface of sediment and the bottom of water (Taylor et al., 1964; Schoepfer et al., 2015). As barium sulfate is a potential source of sulfate, partial barium sulfate may dissolve when the supply of sulfate is limited. This process will reduce the content of Ba, which will affect the accuracy of paleoproductivity estimation. Therefore, the effect of redox conditions should be considered when using Ba_{bio} to evaluate paleoproductivity. The study by Qian et al. (2024) showed that the Lucaogou Formation was mainly in a reducing environment during sedimentation and underwent bacterial sulfate reduction reactions. This may be the reason for the negative value of Ba_{bio} in the Lucaogou Formation. Therefore, the Ba index cannot be used to evaluate the paleoproductivity in the study area, and its estimated paleoproductivity is relatively low.

Cu, as a key nutrient element, often combines with organic matter or forms complexes to precipitate (Brumsack et al., 1986). High Cu content usually indicates high organic carbon input, which in turn reflects an increase in ancient paleoproductivity. Since Cu is fixed in mineral form in the reducing environment, it is mainly suitable for reducing conditions when used as an indicator of paleoproductivity (Tribovillard et al., 2006). The study shows that the Lucaogou Formation is mainly a reducing sedimentary environment (Qian et al., 2024), and it is speculated that Cu can be used to evaluate the paleoproductivity of the study area. To reduce the impact of terrestrial clasts, Cu/Ti is used to indicate paleoproductivity (Rimmer et al., 2004). The distribution range of Cu/Ti in the Lucaogou group samples is 0.033–0.21, with an average of 0.070 (Fig. 8). Research has found that the average Cu/Ti value of PAAS is 0.008, and the average Cu/Ti value of the source rocks of Chang 7 member in the Ordos Basin is 0.039 (Yuan et al., 2019). Compared with PASS and the source rocks of Chang 7 member, the Cu/Ti value of the Lucaogou Formation samples is significantly higher, indicating high productivity of the Lucaogou Formation. The paleoproductivity evaluated by Cu is significantly higher than that by P_{bio} , which is consistent with the previous conclusion that the paleoproductivity evaluated by P_{bio} may be than the actual situation.

In summary, Cu/Ti is a suitable indicator for evaluating the paleoproductivity of the Lucaogou Formation, while Ba_{bio} and P/Ti cannot be used. The paleoproductivity of the Lucaogou Formation is high and higher than that of the PASS and the source rocks of Chang 7 member in the Ordos Basin. A large number of hydrobiont provide guarantee for the high productivity of the Lucaogou Formation, indicating its good potential for oil and gas generation.

5.2.2. Impact of volcanic ash on paleoproductivity

With the increase of volcanic ash content, the paleoproductivity index Cu/Ti exhibits a good three-stage distribution characteristic. When the volcanic ash content is less than 20%, the Cu/Ti value changes little (Fig. 9). This reflects that the paleoproductivity is almost unchanged, which is the same as the change of the content of hydrobiont. When the volcanic ash content reaches the range of 20%–40%, as its content increases, the Cu/Ti value also shows an increasing trend (Fig. 9), reflecting the improvement of paleoproductivity. The increase of volcanic ash content has played a constructive role in

paleoproductivity, which is consistent with the conclusion that volcanic ash facilitates the prosperity of hydrobiont. In addition to improving paleoproductivity by facilitating biological prosperity, CH_4 and CO_2 in volcanic gases also participate in the global carbon cycle, improving the efficiency of plants in transforming light energy into chemical energy (Xiao et al., 2023), which is also beneficial for paleoproductivity improvement. However, when the volcanic ash content is greater than 40%, the Cu/Ti value shows a significant reduction (Fig. 9). The high content of volcanic ash leads to the reduction of paleoproductivity, which may be related to the massive death of hydrobiont.

5.3. The influence model of volcanic ash on organic matter production

In conclusion, the role of volcanic ash with different contents in biological growth and paleoproductivity are complex. The impact of volcanic ash on organic matter production in the study area can be divided into three models (Fig. 10).

When the content of volcanic ash is less than 20%, the content of hydrobiont changes slightly as the volcanic ash in the Lucaogou Formation has undergone alteration and the content of nutrient elements is low. During the sedimentation period, a large number of cyanobacteria grew in the lake, while the development of green algae and bacteria was inhibited (Fig. 10-A). As a response to the development of hydrobiont, the paleoproductivity is relatively low and changes little in this model. In this model, the impact of volcanic ash on paleoproductivity is minimal.

When the volcanic ash content is between 20% and 40%, the increase of nutrient elements in the lake facilitates the development of hydrobiont, thereby driving the improvement of paleoproductivity (Fig. 10-B). Specifically, when the volcanic ash content is between 35% and 40%, both the content of hydrobiont and paleoproductivity reach their peak. In this model, the content of algae and bacteria changes frequently. When the volcanic ash content is 20%–25%, the content of cyanobacteria reaches the highest and the content of green algae and bacteria reaches the lowest. Subsequently, the content of cyanobacteria began to decrease, while the content of green algae and bacteria began to increase. In this model, volcanic ash facilitates organic matter production.

When the content of volcanic ash exceeds 40%, a large amount of volcanic ash not only brings high concentrations of harmful substances such as Pb and Hg, but also makes the lake water turbid. Cyanobacteria, green algae, bacteria, and other hydrobiont gradually die in large numbers. Therefore, the content of hydrobiont began to decrease gradually, leading to a decrease in paleoproductivity (Fig. 10-C). In this model, volcanic ash inhibits organic matter production.

6. Conclusion

Taking the Permian Lucaogou Formation in Jimsar Sag, the Junggar Basin as the research object, the source of organic matter and paleoproductivity of the Lucaogou Formation are analyzed through the

indicators of biomarkers and elements. On this basis, whether volcanic ash with different contents facilitates or inhibits organic matter production was discussed, and the following conclusions can be drawn:

(1) The characteristics of biomarkers indicate that the organic matter in the Lucaogou Formation mainly comes from a mixture of algae, bacteria, and terrestrial higher plants, with the highest content of hydrobiont among them. In organic matter derived from bacteria and algae, the abundance of bacteria is higher than that of algae. The algae in the Lucaogou Formation are mainly green algae and cyanobacteria, with a higher content of green algae.

(2) Elemental geochemical analysis shows that Cu/Ti is a suitable indicator for evaluating the paleoproductivity of the Lucaogou Formation, while Ba_{bio} and P/Ti cannot be used. The Cu/Ti indicates that the paleoproductivity of the Lucaogou Formation is high.

(3) The role of volcanic ash in organic matter production can be divided into three models. When the volcanic ash content is less than 20%, the content of hydrobiont in the Lucaogou Formation changes little, resulting in relatively low paleoproductivity. Cyanobacteria thrive in large numbers, while the growth of green algae and bacteria is inhibited. When the volcanic ash content is between 20% and 40%, due to the increase in nutrient elements in the lake, the development of hydrobiont is facilitated, and the paleoproductivity increases accordingly. In this situation, the growth of cyanobacteria is inhibited, while the content of green algae and bacteria rapidly increases. When the volcanic ash content exceeds 40%, a large number of hydrobiont die and the paleoproductivity decreases. Organic matter production is inhibited. In summary, low content of volcanic ash facilitates organic matter production, while high content of volcanic ash inhibits it.

Declarations

Author Contribution

Liangrong QIAN: Conceptualization, Formal analysis, Writing – original draft, Writing – review & editing
Xiujian DING: Methodology, Writing – review & editing, Funding acquisition
Huajun GUO: Methodology, Supervision
Xiandong WANG: Methodology, Writing – review & editing, Funding acquisition
Wenjun HE, Wenlong JIANG, Xuemei YANG: Visualization, Resources

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Figures

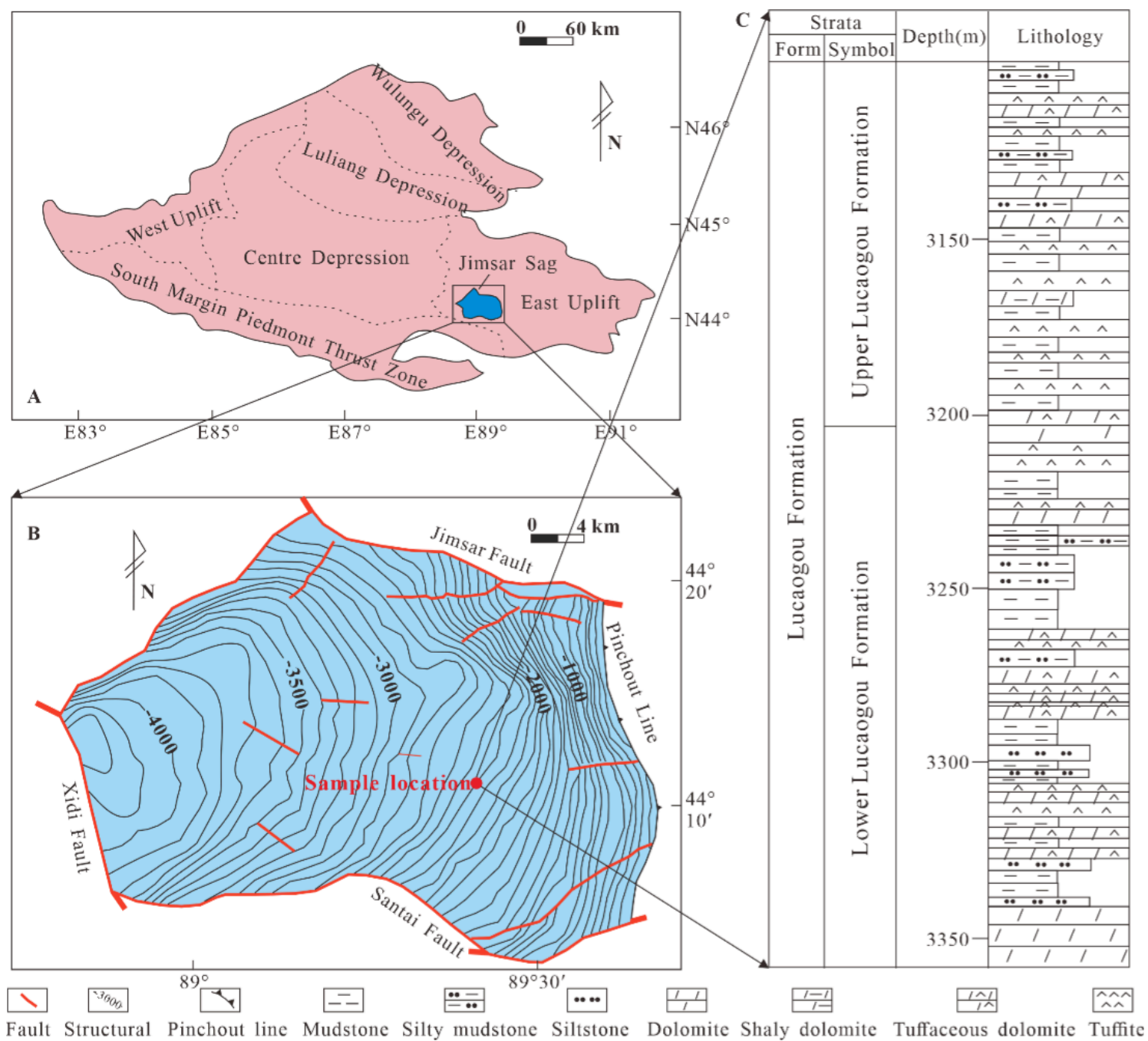


Figure 1

A: Tectonic location of the Junggar Basin; B: Tectonic location of the Jimsar Sag; and C: Stratigraphic column of the Lucaogou Formation (Modified after Ding et al., 2017).

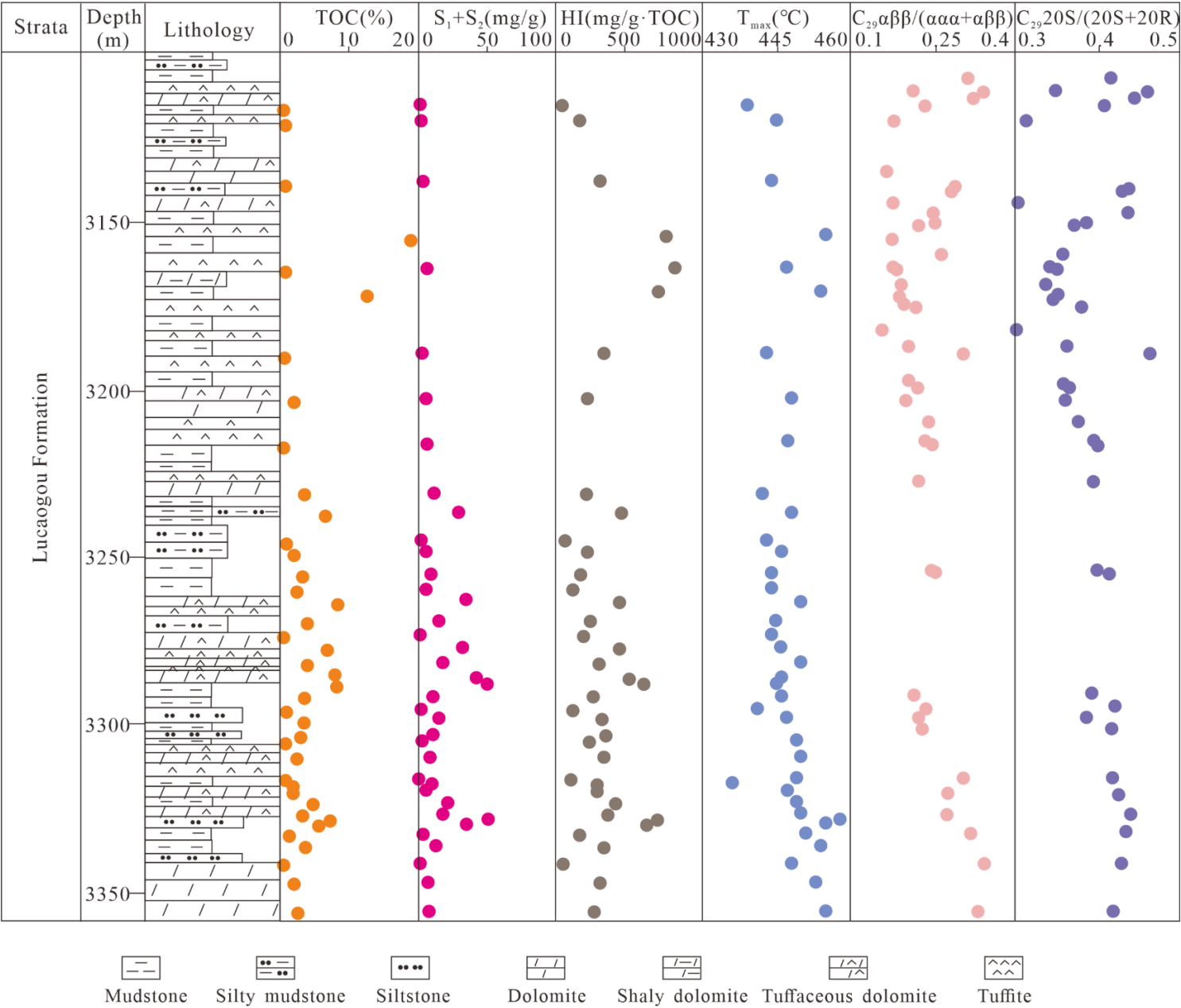


Figure 2

Vertical variations in TOC, S₁+S₂, HI, T_{max}, C₂₉ αββ/(ααα+αββ) steranes and C₂₉ 20S/(20S+20R) steranes data for samples of the Lucaogou Formation in the Jimsar Sag of the Junggar Basin. Part of the data comes from Ding et al., 2023 and Hu et al., 2016.

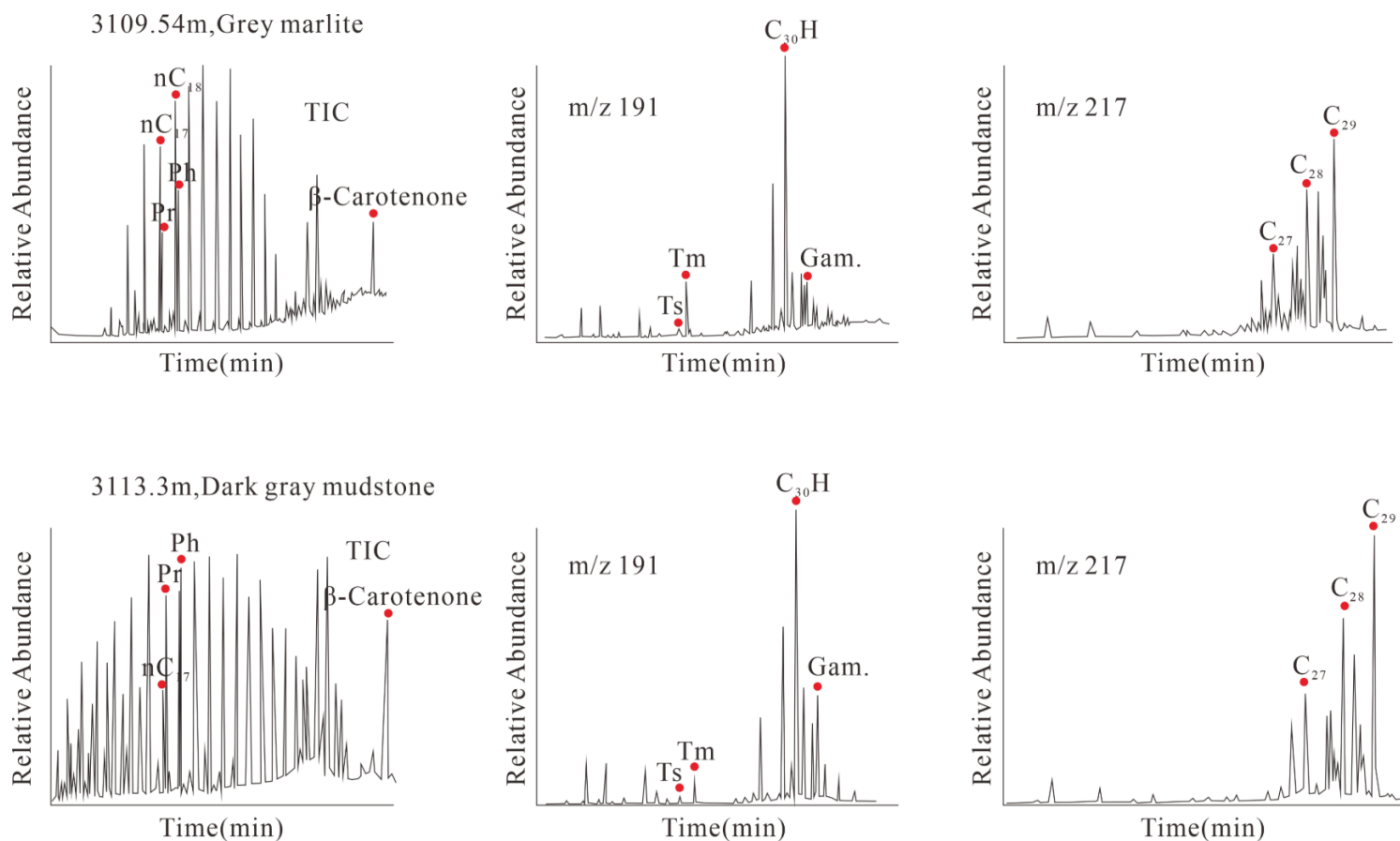


Figure 3

Typical biomarker compounds of source rocks of the Lucaogou Formation in the Jimsar Sag.

Pr =Pristane; Ph =Phytane; Ts =18a(H)-22, 29, 30-trisnorneohopane; Tm =17a(H)-22, 29, 30-trisnorhopane; $C_{30}H$ = C_{30} hopane; $Gam.$ =Gammacerane; C_{27} = C_{27} sterane 20R; C_{28} = C_{28} sterane 20R; C_{29} = C_{29} sterane 20R.

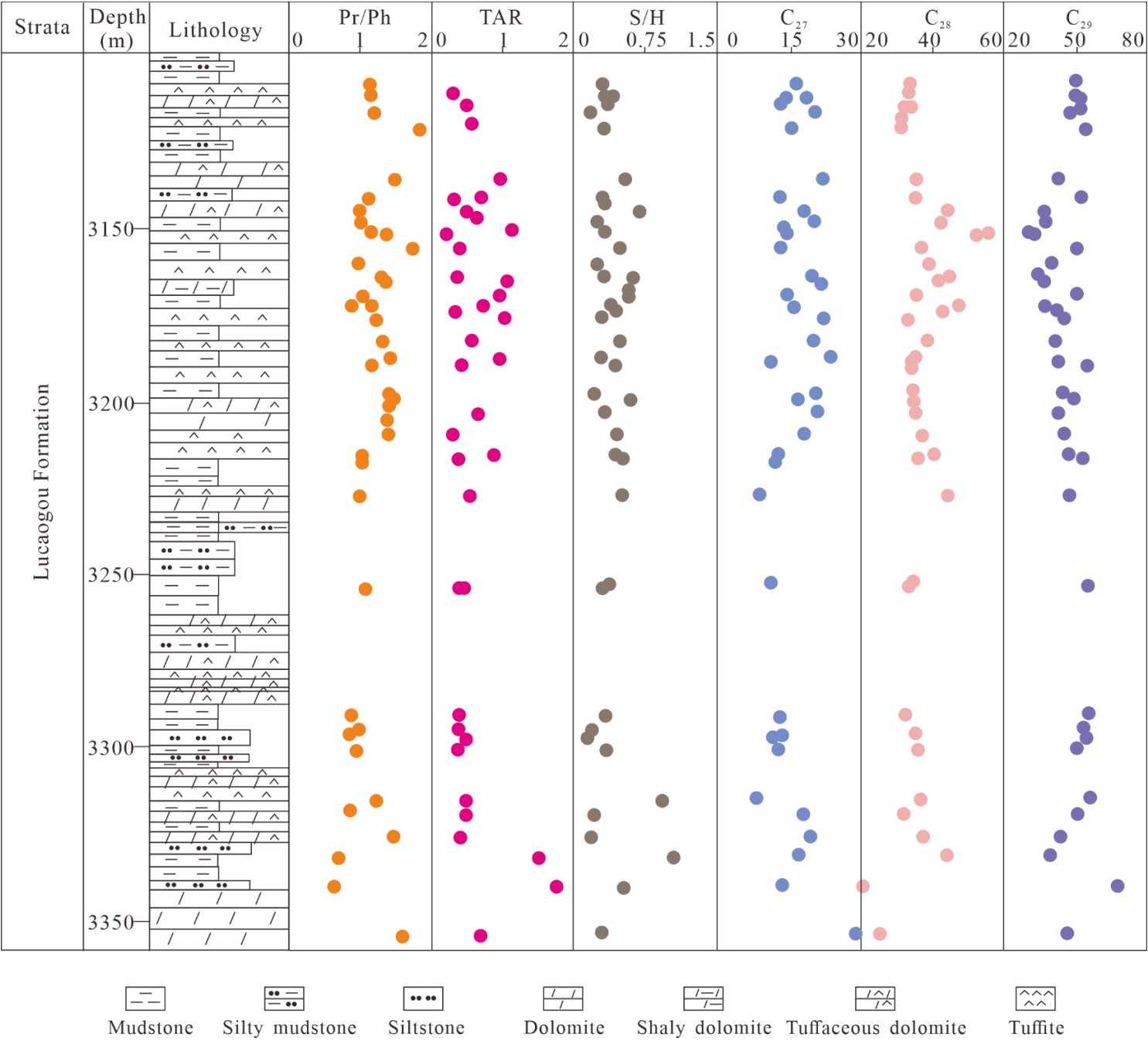


Figure 4

Vertical variations in Pr/Ph, TAR, S/H, C₂₇, C₂₈ and C₂₉ data for samples of the Lucaogou Formation in the Jimsar Sag of the Junggar Basin. Pr/Ph=Pristane/ phytane; TAR= (nC₂₇+nC₂₉+nC₃₁)/(nC₁₅+nC₁₇+nC₁₉); S/H= Sterane/ Hopane; C₂₇=C₂₇ sterane; C₂₈=C₂₈ sterane; C₂₉=C₂₉ sterane.

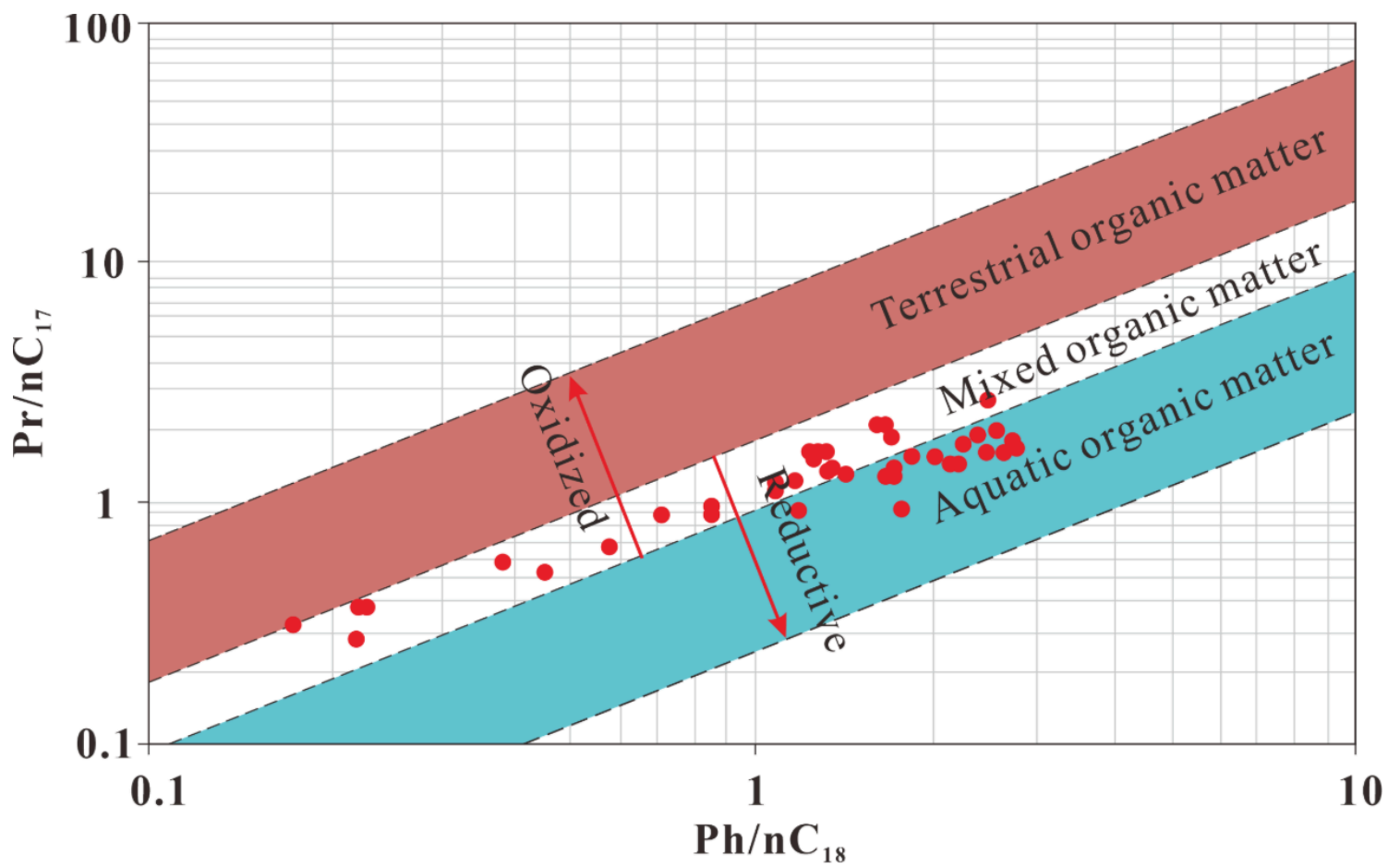


Figure 5

Ph/nC_{18} - Pr/nC_{17} indicates the the source of organic matter of the Lucaogou Formation in the Jimsar Sag (Modified after Peters et al., 1999). Pr/nC_{18} , Phytane/ C_{18} n-alkanes; Ph/nC_{17} , Pristane/ C_{17} n-alkanes.

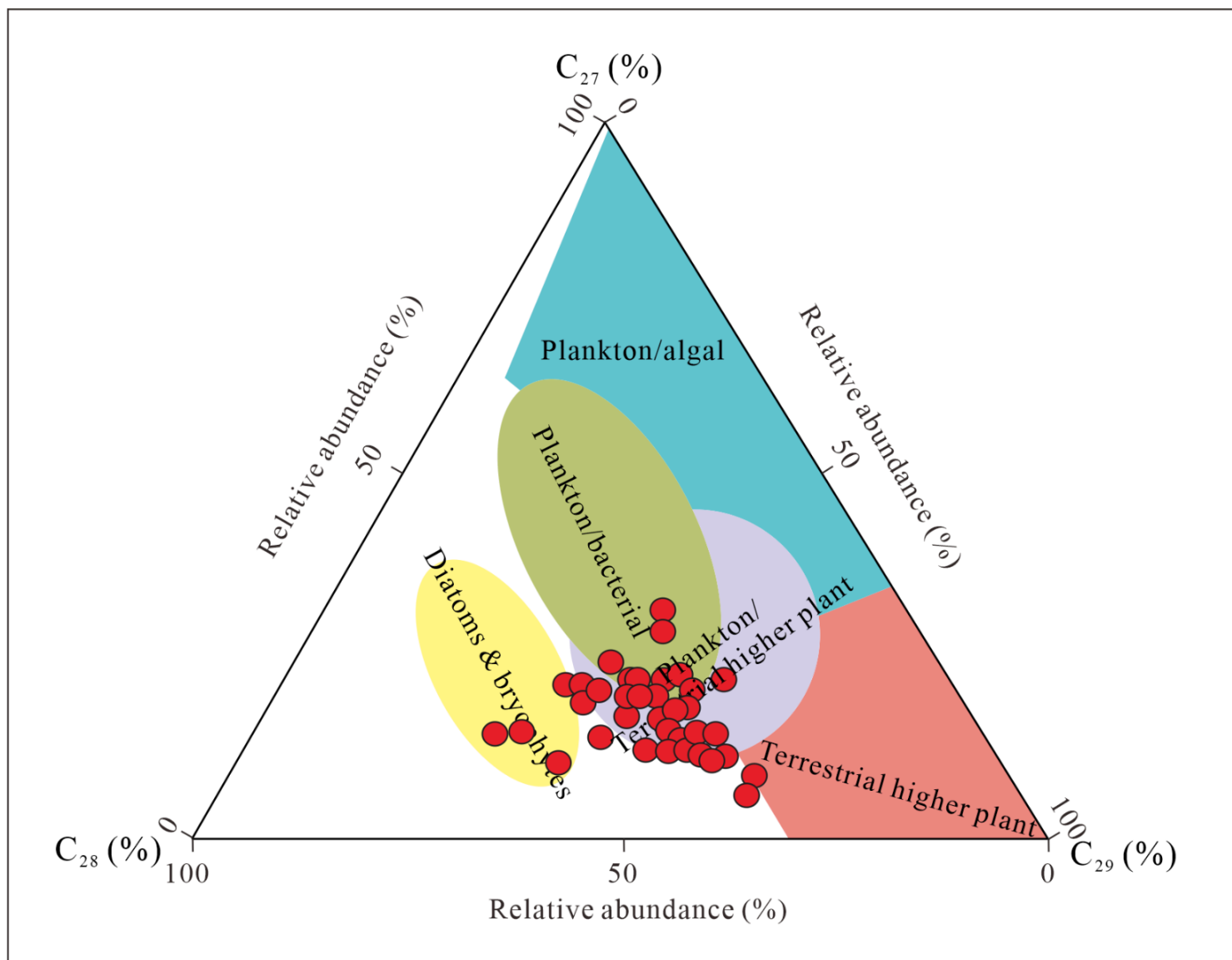


Figure 6

Relationship of relative content of C_{27} - C_{28} - C_{29} sterane of the Lucaogou Formation in the Jimsar Sag (Modified after Adegoke et al., 2014).

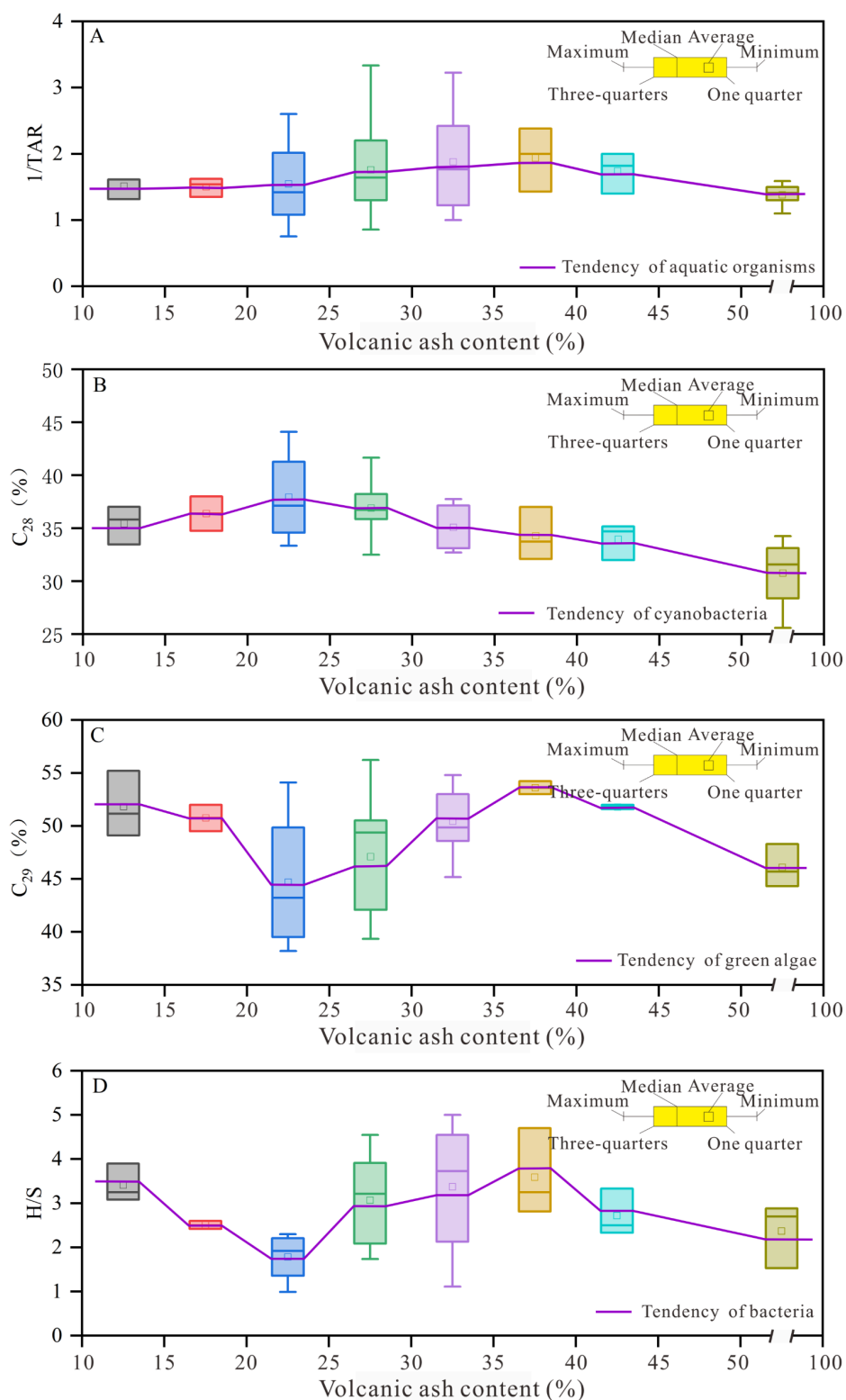


Figure 7

The relationship between volcanic ash content and organic matter sources of the Lucaogou Formation in the Jimsar Sag.

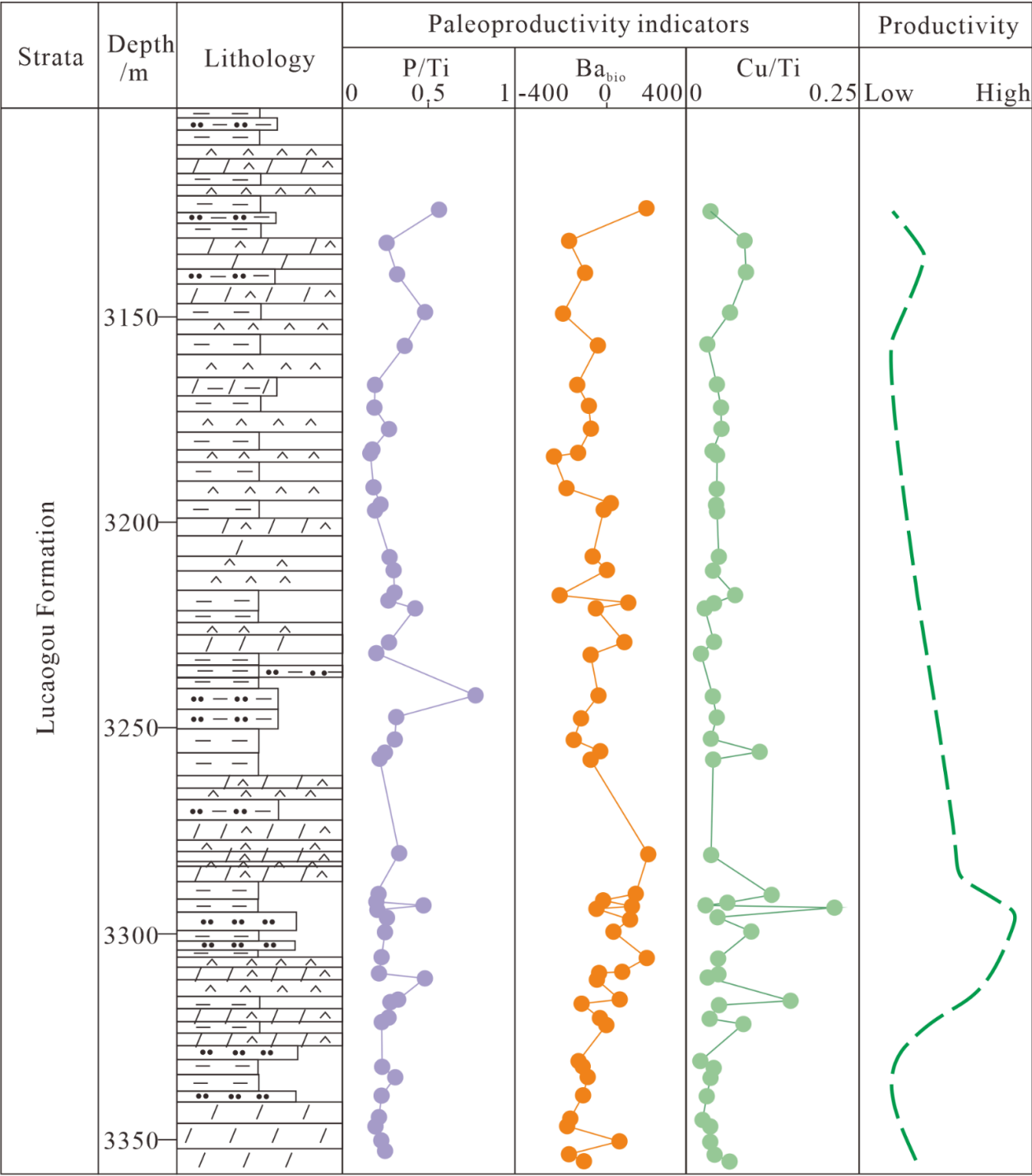


Figure 8

Vertical variations in paleoproductivity indicators for samples in the Lucaogou Formation of Well J174 in the Jimsar Sag. The data of major and trace elements comes from Ding et al., 2023.

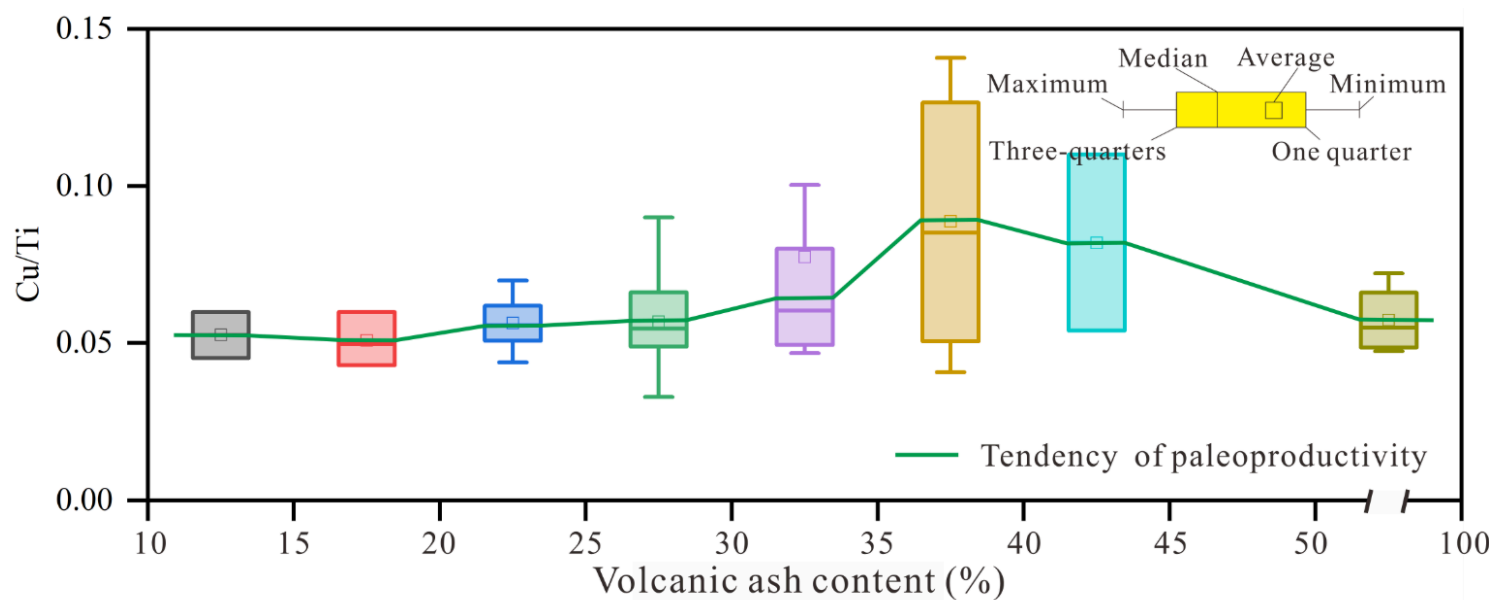


Figure 9

The relationship between volcanic ash content and paleoproductivity of the Lucaogou Formation in the Jimsar Sag

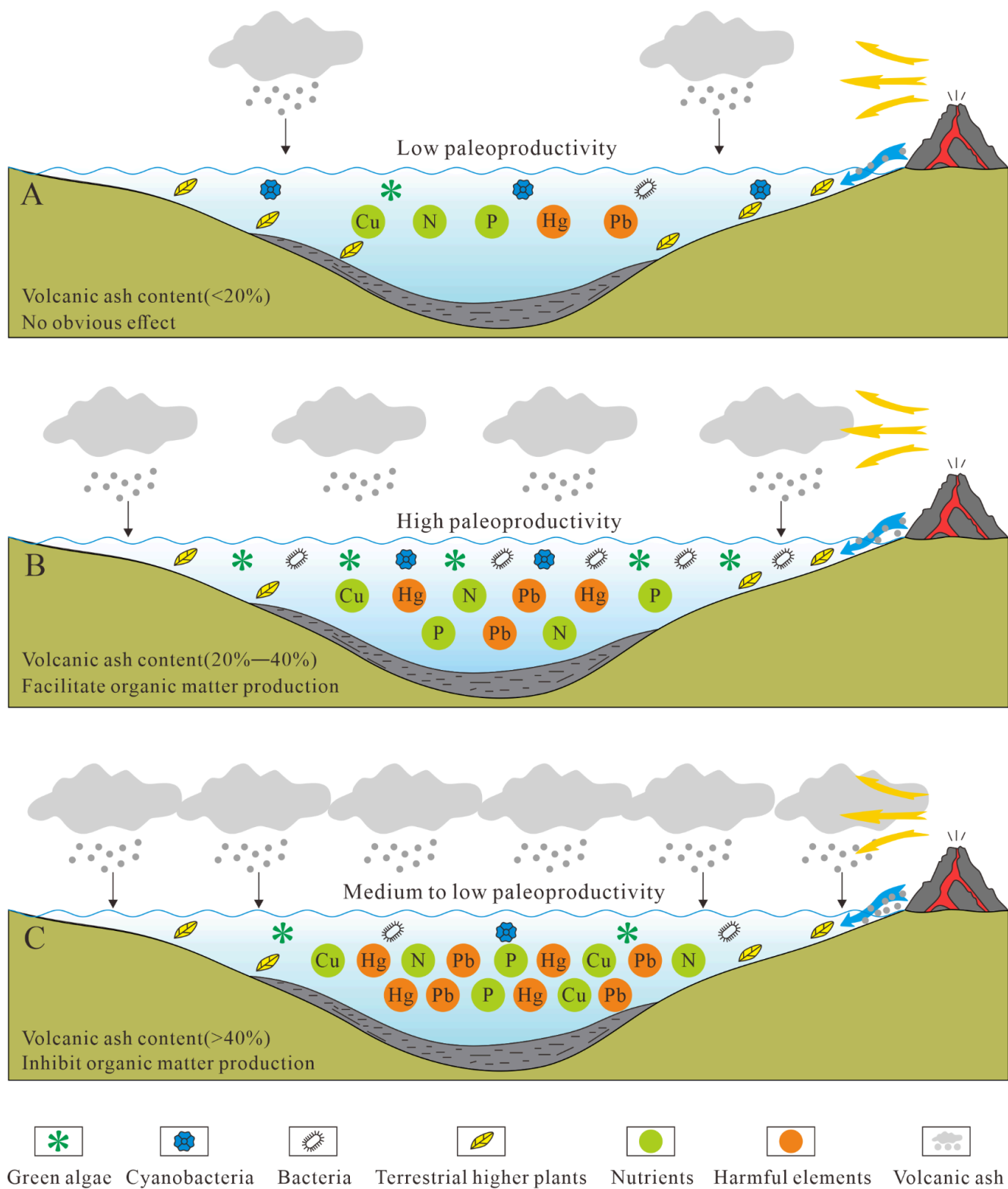


Figure 10

Model diagram of the impact of volcanic ash on paleoproductivity of the Lucaogou Formation in the Jimsar Sag.