Geochemical Characteristics of the Late Cretaceous Lower Zhoutian Formation in the Jitai Basin, Southeast China: Implications for palaeoenvironment and provenance

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Abstract

Major, trace and rare earth element geochemistry of the late Cretaceous lower Zhoutian Formation from the Jitai Basin of Southeast China were measured by inductively coupled plasma mass spectrometry (ICP-MS) analysis. The paleoclimate, paleo-environment and provenance of lower Zhoutian Formation in the Jitai Basin are analyzed in detail with these data. According to the research, the range of Sr/Cu values is wide, which indicates the changeable palaeoclimate, the curves of FeO/MnO and Al₂O₃/MgO are negatively correlated with the Sr/Cu curves. These changes indicate that the palaeoclimate of the late Cretaceous lower Zhoutian Formation in the Jitai Basin was divided into two parts. The lower part experienced two cooling events; the upper part was dominated by warm humid climate. The changes of B/Ga and Sr/Ba curves are similar to Sr/Cu curves. According to these values, the salinity of the late Cretaceous lower Zhoutian Formation in the Jitai Basin was consistent with palaeoclimate. The salinity of lower part changed from salt water to fresh/brackish water. The upper part was mainly fresh/brackish water, and there were many changes from fresh/brackish water to salt water. The values of Ni/Co, V/Cr, V/(V + Ni) and Ce/Ce* are relatively stable, indicating a long-term oxidation environment. The diagrams of La-Th-Sc, Th-Sc-Zr/10, La/Th-Hf and sandstone-siltstone background function show that the provenance in lower Zhoutian Formation mainly is a mixture of upper crust felsic sediments and old components.

Introduction

As an important carrier of geological information, the geochemical characteristics of clastic rocks record the significant information of provenance, structure, environment and ecological evolution in a real and detailed way. In the process of deposition, the distribution, circulation and differentiation (deficit and enrichment) of trace elements sensitive to redox in water and sediments are not only related to their own chemical properties, but also controlled by the physical and chemical conditions of the deposition medium and palaeoclimate conditions^{1–4}. Hence, some major and trace elements that dissolve in water and sensitive to climatic change, which can be used as a valuable proxy of palaeoclimate evolution⁵.

Mesozoic was a period of drastic tectonic changes in South China and even the whole East Asian continent, and it was also a turning point in the development of East Asian tectonics^{6–10}. During the late Cretaceous-Paleogene, a series of rift basins were formed in the central part of South China, such as Jiangnan Basin, Jitai Basin. At this time, most of the lakes in these Basins evolved into saline lakes and deposited huge amounts of halite and other saline minerals^{11–12}. Deep brine is found in the late Cretaceous strata of Zhoutian Formation in Jitai Basin, which is rich in potassium, lithium, boron, rubidium, cesium, bromine, iodine and other high-value and emerging strategic mineral resources^{13,14}.

The formation of deep brine deposits is controlled by material sources, paleoclimatic conditions during the sedimentary period, tectonic conditions of the basin where the water occurs^{15–17}. At present, the basic geological research in Jitai Basin is very rare, and the existing data are not enough to study the formation mechanism of deep brine. In order to understand more geological information and characteristics of the late Cretaceous in the Jitai Basin, here we report the geochemical data of major, trace and rare elements of silty mudstone and calcilutite in the late Cretaceous lower Zhoutian Formation. Based on our geochemical data and previous studies, we discuss the palaeoclimate and palaeoenvironment characteristics and provenance of the late Cretaceous lower Zhoutian Formation in the Jitai Basin.

Materials And Methods

Study area. The Jitai Basin is located in the transition zone between central uplift and southwest depression of Jiangxi province. The basin is about 120 km long and 10–30 km wide, with an area of about 1850 km²¹⁸. The basement of the basin varies from region to region. The northern part is dominated by late Paleozoic strata and the southern part by early Paleozoic epimetamorphic series. There is a set of Cretaceous continental red strata in the basin with a thickness of several thousand meters. The lower Cretaceous is exposed at the western edge of the basin. The lower strata are mainly composed of magenta coarse clastic formations, the middle strata are mainly composed of magenta medium fine clastic formations, and the upper strata are mainly composed of argillaceous formations, forming a sedimentary cycle from coarse to fine. The upper Cretaceous is composed of magenta coarse clastic formations and medium fine clastic formations¹⁹. The lithium-rich ore occurs in the Zhoutian Formation of the late Cretaceous²⁰. Since the late Cretaceous, the Jitai Basin began to form in the research area due to the intensification of the Yanshan movement and the strong influence of the fault of Suichuan-Wan'an (Fig. 1).

Sampling and methods. The samples were collected for this research from Well M2 in south Jitai Basin (Fig. 1). A total of 40 core samples from depths between 1100 to 1435 m were collected from the lower Zhoutian Formation (Table 1).

Table 1
All samples of the late Cretaceous lower Zhoutian Formation from Well M2, Jitai Basin.

No.	Depth	Lithology	No.	Depth	Lithology	No.	Depth	Lithology
M2-1	1101m	Silty mudstone	M2-15	1174m	Silty mudstone	M2-29	1315m	Silty mudstone
M2-2	1106m	Calcilutite	M2-16	1179m	Silty mudstone	M2-30	1320m	Silty mudstone
M2-3	1111m	Silty mudstone	M2-17	1197m	Silty mudstone	M2-31	1327m	Calcilutite
M2-4	1115m	Calcilutite	M2-18	1205m	Calcilutite	M2-32	1340m	Calcilutite
M2-5	1121m	Calcilutite	M2-19	1209m	Calcilutite	M2-33	1350m	Silty mudstone
M2-6	1127m	Silty mudstone	M2-20	1217m	Silty mudstone	M2-34	1360m	Silty mudstone
M2-7	1130m	Mudstone	M2-21	1221m	Silty mudstone	M2-35	1375m	Silty mudstone
M2-8	1134m	Mudstone	M2-22	1245m	Silty mudstone	M2-36	1386m	Calcilutite
M2-9	1145m	Silty mudstone	M2-23	1255m	Silty mudstone	M2-37	1397m	Silty mudstone
M2-10	1152m	Siltstone	M2-24	1270m	Silty mudstone	M2-38	1405m	Calcilutite
M2-11	1155m	Silty mudstone	M2-25	1275m	Calcilutite	M2-39	1415m	Calcilutite
M2-12	1159m	Silty mudstone	M2-26	1284m	Silty mudstone	M2-40	1436m	Calcilutite
M2-13	1164m	Silty mudstone	M2-27	1295m	Silty mudstone			
M2-14	1170m	Silty mudstone	M2-28	1306m	Silty mudstone			

X-ray fluorescence spectrometry was used to determine oxides of major elements, such as SiO_2 , TiO_2 , Al_2O_3 , Fe_2O_3 , FeO , MnO , MgO , CaO , Na_2O , K_2O , P_2O_5 . An inductively coupled plasma mass spectrometer (ICP-MS) was used to determine the contents of trace and rare earth element. The samples were fused into glass sheets by alkali fusion and tested on a sequential X-ray fluorescence spectrometer (AB104L, Axios-mAX). The dissolved trace and rare earth elements were measured using an ICP-MS instrument (ELEMENT XR).

All geochemical analysis samples were crushed and ground to less than 200 mesh. The powered samples were first heated and then fused with the mixture of anhydrous lithium tetraborate, lithium fluoride and ammonium nitrate heating in a muffle furnace to determine LOI. The fused samples were heated to 800°C for XRF analysis. Calibrations of accuracy and reproducibility were conducted by GB/T 14506.14–2010 and GB/T 14506.28–2010. Powered samples were heated with HF and HNO_3 . After evaporated, HNO_3 was added to dissolve the samples. And HNO_3 was added to the beaker again heating to 130°C . Finally, the solution was diluted by distilled water for trace analyses, according to GB/T 14506.29–2010 and GB/T 14506.30–2010. And all the experiments were carried out in Analytical Laboratory Beijing Research Institute of Uranium Geology.

Result

Major elements. The contents of SiO_2 are the highest in most sample, but they vary greatly, ranging from 13.48–86.48%, Al_2O_3 contents are between 0.981% and 31.12%, Fe_2O_3 contents are between 0.685% and 26.81% (Table 2). The contents of CaO and MnO from silty mudstones in Well M2 have strong depletion relative to PAAS, but CaO contents of calcilutites in Well M2 show an obvious enriched. The contents of Al_2O_3 and TiO_2 from calcilutites are slight depletion. And the Na_2O contents of all samples are lower than of PAAS and show strong depletion by the plot that normalized to post Archean Australian average shale values (Fig. 2a and b). According to the Table 5, the Sr/Cu values range from 0.99 to 106.56, with an average of 12.89. The FeO/MnO values range from 4.15 to 412.22, with an average of 125.51. The $\text{Al}_2\text{O}_3/\text{MgO}$ values range from 0.21 to 63.48, with an average of 15.73. The Mg/Ca values range from 0.04 to 13.95, with an average of 3.89.

Table 2
The content of major elements from Well M2, Jitai Basin (unit in %).

No.	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	MnO	CaO	MgO	K ₂ O	Na ₂ O	P ₂ O ₅	FeO	LOI	Total
M2-1	66.74	18.34	1.56	0.786	0.008	0.577	0.834	4.36	0.327	0.036	0.65	6.34	100.6
M2-2	20.75	8.51	4.27	0.341	0.06	30.13	2.48	2.37	0.2	0.034	1.06	30.3	100.5
M2-3	76.03	11.95	4.34	0.672	0.016	0.208	0.541	1.51	0.165	0.027	2.6	4.54	102.6
M2-4	17	0.981	0.685	0.036	0.135	39.04	4.69	0.264	0.098	0.023	0.56	36.69	100.2
M2-5	39.39	3.7	3.56	0.101	0.138	27.28	1	0.783	0.103	0.04	1.99	23.41	101.5
M2-6	75.32	11.22	5.13	0.68	0.014	0.153	0.72	1.8	0.179	0.022	3.6	4.35	103.2
M2-7	43.87	28.36	9.66	1.04	0.023	0.219	1.41	4.28	0.39	0.119	6.35	10.53	106.3
M2-8	44	14.9	26.81	0.58	0.099	0.508	2.91	0.68	0.137	0.376	19.24	8.43	118.7
M2-9	62.57	22.31	3.68	1.07	0.013	0.094	0.806	3.04	0.267	0.043	2.72	6.06	102.7
M2-10	66.59	19.79	3.76	1	0.018	0.148	0.966	2.96	0.249	0.046	2.71	4.41	102.6
M2-11	60.71	22.1	5.45	1.04	0.02	0.138	1.36	2.79	0.229	0.036	3.87	6.07	103.8
M2-12	69.22	17.42	3.76	0.952	0.012	0.106	0.769	2.32	0.21	0.032	2.5	5.15	102.5
M2-13	59.93	21.17	5.93	1.05	0.024	0.134	1.1	2.79	0.229	0.041	3.67	7.41	103.5
M2-14	58.36	25.79	3.94	1.15	0.013	0.107	0.742	2.99	0.232	0.051	2.72	6.57	102.7
M2-15	50.89	28	3.95	1.1	0.008	0.116	0.699	3.57	0.292	0.044	1.37	11.3	101.3
M2-16	64.9	21.18	3.67	0.997	0.016	0.145	0.836	2.24	0.201	0.031	2.33	5.76	102.3
M2-17	58.55	24.53	4.95	1.09	0.014	0.1	1.01	2.6	0.252	0.047	3.31	6.86	103.3
M2-18	49.1	5.62	5.75	0.61	0.318	15.38	2.38	0.967	0.111	0.028	4.88	19.26	104.4
M2-19	24.59	8.85	13.21	0.419	0.535	17.37	5.9	1.37	0.16	0.063	11.31	27.04	110.8
M2-20	65.65	8.05	10.36	0.823	0.008	0.159	0.323	1.11	0.191	0.029	1.76	13.2	101.7
M2-21	65.17	19.01	4.77	0.934	0.025	0.12	0.914	2.18	0.211	0.035	3.46	6.56	103.4
M2-22	49.73	29.83	4.91	1.22	0.006	0.1	0.634	3.36	0.432	0.05	2.08	9.72	102.1
M2-23	57.59	19.52	8.2	0.954	0.099	1.24	1.71	2.18	0.206	0.152	5.14	8.12	105.1
M2-24	49.86	25.77	7.19	0.998	0.037	0.632	1.53	2.95	0.33	0.13	4.75	10.53	104.7
M2-25	13.48	4.41	6.78	0.121	0.264	38.24	2.11	0.473	0.095	0.35	5.04	33.19	104.6
M2-26	64.78	22.6	3.17	1.01	0.01	0.136	0.356	1.61	0.234	0.068	2.08	6	102.1
M2-27	50.2	31.12	2.41	1.25	0.009	0.418	0.837	5.64	0.483	0.053	1.34	7.49	101.3
M2-28	86.46	7.08	1	0.324	0.024	0.461	0.371	1.88	0.125	0.034	0.73	2.14	100.6
M2-29	73.71	12.58	4.33	0.568	0.069	0.933	1.34	3.39	0.147	0.084	2.46	2.37	102.0
M2-30	76.59	12.04	2.86	0.504	0.022	0.33	1.06	3.07	0.139	0.088	2.22	2.88	101.8
M2-31	18.1	7.06	5.18	0.307	0.253	21.5	11.45	2.11	0.125	0.052	4.18	33.33	103.6
M2-32	55.15	3.53	4.78	0.249	0.257	10.92	6.16	0.645	0.079	0.047	3.89	18.13	103.8
M2-33	80.5	7.75	2.32	0.199	0.016	1.79	1.24	1.77	0.085	0.144	1.87	3.76	101.4
M2-34	74.54	9.13	3.81	0.432	0.065	2.15	2	2.41	0.107	0.156	2.91	5.1	102.8
M2-35	61.24	19.26	5.4	0.818	0.009	0.172	2.16	5.88	0.154	0.059	3.71	4.78	103.6
M2-36	59.29	6.75	2.82	0.342	0.211	8.17	5.17	2.06	0.098	0.184	2.47	14.86	102.4
M2-37	72.6	12.19	3.69	0.592	0.016	1.1	1.77	3.31	0.114	0.052	2.83	4.1	102.4
M2-38	58.21	9.54	2.67	0.397	0.053	9.59	2.85	2.54	0.138	0.083	1.27	13.36	100.7
M2-39	14.57	4.7	4.77	0.131	0.141	22.26	11.52	1.65	0.078	0.056	3.63	40.03	103.5
M2-40	70.15	11.71	2.93	0.565	0.086	1.9	1.94	3.66	0.133	0.183	2.34	6.69	102.3

Table 3
The content of trace elements from Well M2, Jitai Basin (unit in ppm).

No.	Sc	V	Cr	Co	Ni	Cu	Zn	Ga	Rb	Sr	Y	Cs	Ba	Pb	Th	U	Nb	Ta	Zr
M2-1	12.9	85.8	143	5.95	32.7	68.3	126	24	140	67.4	7.39	11.3	540	34.4	15	47	17.6	1.39	313
M2-2	6.84	102	46.1	7.13	38.7	29.9	172	11.5	75	205	9.99	6.27	173	26.1	7.28	3.45	7.88	0.64	92.5
M2-3	9.23	48.6	168	9.08	23.2	13.3	42.9	14.6	48.4	45.3	13.9	3.56	450	9.4	10	2.31	13.6	1.06	199
M2-4	1.27	23.4	47.5	5.28	23.2	155	64.6	1.65	7.84	207	9.08	0.996	18.6	24.1	1.01	0.612	0.89	0.081	14.7
M2-5	4.29	40.1	29.2	6.89	39.7	12.7	126	5.51	19.7	117	14	1.31	78.6	9.08	2.94	0.95	2.27	0.184	19
M2-6	11.7	53.5	206	7.93	23.3	12.6	146	14.9	56.3	34.5	14.8	3.79	290	32	8.78	2.75	13.6	1.17	307
M2-7	15.9	149	133	29.9	53.5	24.6	113	35.5	129	72.4	30.5	12.9	563	34.4	19.7	4.03	22.3	1.67	233
M2-8	20.7	167	122	29	66	16.3	236	23.6	20.6	44.1	46.9	1.46	134	26.9	15.8	2.8	11	0.934	155
M2-9	17	86.2	188	15.1	36.3	15.7	56.5	26.2	96	56.6	28.4	7.55	570	9.77	17.7	3.73	21.7	1.66	343
M2-10	16.2	85	154	8.6	32.3	11.1	68.9	26.3	97.6	60.1	31.6	5.44	669	6.74	15.1	3.49	19.9	1.62	403
M2-11	17.5	103	163	14.6	39.3	15.6	90.8	31.6	95.2	49.3	18.3	8.16	638	8.56	13.2	2.83	21.6	1.69	273
M2-12	14.3	78.6	194	13.3	31.5	16	56.2	21.3	73.9	48.4	25.6	4.24	482	10.1	13.3	3.18	18.3	1.5	290
M2-13	16.3	96.8	113	22.3	38.2	28.2	71.4	27.9	88.1	57	17.4	6.2	610	19.8	16	3.63	20.8	1.61	381
M2-14	13.3	114	145	6.87	25.7	12.8	57.5	30.5	90.7	58.1	20.2	7.91	656	6.77	19	3.79	24.2	1.9	317
M2-15	12.5	158	138	29.5	47.4	23.7	49.8	34.7	78.1	40.7	19.2	8	691	39.5	12	3.75	24.4	1.84	275
M2-16	10.3	109	162	15	35.1	10.7	64.5	26.1	70.8	38	13.3	3.93	489	8.43	14.7	2.53	21.6	1.76	234
M2-17	16.8	110	156	16.5	62.3	20.5	88.6	34.8	94.2	64.4	34.2	5.92	707	9.04	29.8	4.36	26.4	2.06	421
M2-18	7.29	49.5	140	5.9	16.9	5.42	26.2	7.48	28.8	102	38.3	0.949	2562	4.75	17.9	3.72	11.4	0.856	529
M2-19	12.4	62.3	63.4	12.4	28.9	8.17	36.1	11.3	41.3	73.6	26.7	2.21	308	5.3	7.14	2.61	8.98	0.665	122
M2-20	8.41	55.8	217	19.5	75.3	31.2	47.6	14.2	35.7	32.2	17	1.84	227	99.8	15.1	3.62	15	1.39	492
M2-21	14	73	144	11.9	34.1	14.2	145	25.3	71.3	49.9	36.7	4.55	543	7.07	16.5	3.84	20.6	1.62	397
M2-22	8.77	106	129	26	79.4	19.1	56.9	34	85.8	70.4	22.1	7.79	568	32.5	18.2	5.8	28	2.06	286
M2-23	134	191	138	28.9	61.4	19.5	98.8	27.2	42.8	64.6	16.8	4.87	517	29.3	14.2	3.35	22	1.71	337

No.	Sc	V	Cr	Co	Ni	Cu	Zn	Ga	Rb	Sr	Y	Cs	Ba	Pb	Th	U	Nb	Ta	Zr
M2-1	12.9	85.8	143	5.95	32.7	68.3	126	24	140	67.4	7.39	11.3	540	34.4	15	47	17.6	1.39	313
M2-2	6.84	102	46.1	7.13	38.7	29.9	172	11.5	75	205	9.99	6.27	173	26.1	7.28	3.45	7.88	0.64	92.5
M2-3	9.23	48.6	168	9.08	23.2	13.3	42.9	14.6	48.4	45.3	13.9	3.56	450	9.4	10	2.31	13.6	1.06	199
M2-4	1.27	23.4	47.5	5.28	23.2	155	64.6	1.65	7.84	207	9.08	0.996	18.6	24.1	1.01	0.612	0.89	0.081	14.7
M2-5	4.29	40.1	29.2	6.89	39.7	12.7	126	5.51	19.7	117	14	1.31	78.6	9.08	2.94	0.95	2.27	0.184	19
M2-6	11.7	53.5	206	7.93	23.3	12.6	146	14.9	56.3	34.5	14.8	3.79	290	32	8.78	2.75	13.6	1.17	307
M2-7	15.9	149	133	29.9	53.5	24.6	113	35.5	129	72.4	30.5	12.9	563	34.4	19.7	4.03	22.3	1.67	233
M2-8	20.7	167	122	29	66	16.3	236	23.6	20.6	44.1	46.9	1.46	134	26.9	15.8	2.8	11	0.934	155
M2-9	17	86.2	188	15.1	36.3	15.7	56.5	26.2	96	56.6	28.4	7.55	570	9.77	17.7	3.73	21.7	1.66	343
M2-10	16.2	85	154	8.6	32.3	11.1	68.9	26.3	97.6	60.1	31.6	5.44	669	6.74	15.1	3.49	19.9	1.62	403
M2-11	17.5	103	163	14.6	39.3	15.6	90.8	31.6	95.2	49.3	18.3	8.16	638	8.56	13.2	2.83	21.6	1.69	273
M2-12	14.3	78.6	194	13.3	31.5	16	56.2	21.3	73.9	48.4	25.6	4.24	482	10.1	13.3	3.18	18.3	1.5	290
M2-13	16.3	96.8	113	22.3	38.2	28.2	71.4	27.9	88.1	57	17.4	6.2	610	19.8	16	3.63	20.8	1.61	381
M2-14	13.3	114	145	6.87	25.7	12.8	57.5	30.5	90.7	58.1	20.2	7.91	656	6.77	19	3.79	24.2	1.9	317
M2-15	12.5	158	138	29.5	47.4	23.7	49.8	34.7	78.1	40.7	19.2	8	691	39.5	12	3.75	24.4	1.84	275
M2-16	10.3	109	162	15	35.1	10.7	64.5	26.1	70.8	38	13.3	3.93	489	8.43	14.7	2.53	21.6	1.76	234
M2-17	16.8	110	156	16.5	62.3	20.5	88.6	34.8	94.2	64.4	34.2	5.92	707	9.04	29.8	4.36	26.4	2.06	421
M2-18	7.29	49.5	140	5.9	16.9	5.42	26.2	7.48	28.8	102	38.3	0.949	2562	4.75	17.9	3.72	11.4	0.856	529
M2-19	12.4	62.3	63.4	12.4	28.9	8.17	36.1	11.3	41.3	73.6	26.7	2.21	308	5.3	7.14	2.61	8.98	0.665	122
M2-20	8.41	55.8	217	19.5	75.3	31.2	47.6	14.2	35.7	32.2	17	1.84	227	99.8	15.1	3.62	15	1.39	492
M2-21	14	73	144	11.9	34.1	14.2	145	25.3	71.3	49.9	36.7	4.55	543	7.07	16.5	3.84	20.6	1.62	397
M2-22	8.77	106	129	26	79.4	19.1	56.9	34	85.8	70.4	22.1	7.79	568	32.5	18.2	5.8	28	2.06	286
M2-23	134	191	138	28.9	61.4	19.5	98.8	27.2	42.8	64.6	16.8	4.87	517	29.3	14.2	3.35	22	1.71	337

Table 4
The content of rare elements from Well M2, Jitai Basin (unit in ppm).

No.	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	∑REE
M2-1	49.9	89.8	10.3	38.2	6.77	1.31	4.5	0.538	2.3	0.295	1.33	0.184	1.42	0.247	207.09
M2-2	20.7	38.4	4.57	17	3.22	0.588	2.61	0.334	1.96	0.375	1.14	0.17	1.33	0.198	92.60
M2-3	30.9	59.9	6.81	25.1	3.84	0.648	3.53	0.514	2.93	0.522	1.66	0.259	1.72	0.283	138.62
M2-4	3.2	4.88	0.787	3.4	0.85	0.242	0.894	0.209	1.21	0.281	0.76	0.139	0.836	0.113	17.80
M2-5	7.33	13.9	1.71	7.16	1.98	0.632	2.08	0.381	2.2	0.419	1.22	0.175	1.33	0.187	40.70
M2-6	23.9	44.9	5.43	18.8	3.54	0.693	2.76	0.418	2.56	0.531	1.78	0.352	2.11	0.374	108.15
M2-7	58.6	108	13.6	49.1	9.3	1.98	7.36	1.12	5.89	1.21	3.59	0.575	4.04	0.581	264.95
M2-8	46.3	96.6	11.5	43.6	9.4	2.15	7.73	1.42	7.85	1.64	4.59	0.747	4.6	0.635	238.76
M2-9	53.4	96.6	11.3	39.4	6.46	1.12	5.77	0.949	5.68	1.16	3.35	0.524	3.52	0.557	229.79
M2-10	47.1	92.4	10.6	40.1	7.03	1.58	6.21	0.957	5.2	1.05	3.24	0.532	3.28	0.504	219.78
M2-11	50.4	106	11.7	44.2	7.47	1.26	5.73	0.785	4.24	0.669	2.38	0.324	2.09	0.353	237.60
M2-12	40.8	78.2	8.4	33.9	5.86	1.26	5.16	0.875	4.76	0.933	2.44	0.399	2.75	0.423	186.16
M2-13	49.8	92.7	11.3	39.7	6.86	1.52	5.51	0.694	3.78	0.654	2.25	0.348	2.47	0.418	218.00
M2-14	54.5	106	13.3	47.1	8.36	1.3	5.82	0.891	4.69	0.828	2.68	0.389	2.69	0.401	248.95
M2-15	41.2	81.6	9.49	37.3	8.27	1.76	6.02	0.979	4.75	0.806	2.43	0.364	2.39	0.372	197.73
M2-16	42.6	77.4	9.45	34	6.29	0.731	4.73	0.649	3.49	0.495	1.8	0.237	1.74	0.252	183.86
M2-17	73.9	131	16.2	62.7	11.3	2.02	8.23	1.33	6.95	1.2	3.55	0.614	3.72	0.599	323.31
M2-18	47.1	96.7	12.7	55.7	14	2.34	10.1	1.6	8.08	1.35	3.98	0.584	4.16	0.605	259.00
M2-19	32.6	62.2	6.95	26.8	5.22	1.69	4.82	0.867	4.7	0.974	2.86	0.442	2.93	0.419	153.47
M2-20	41.3	77.9	8.18	28.2	4.13	0.476	4.07	0.579	3.44	0.705	2.18	0.374	2.79	0.456	174.78
M2-21	52.3	92	11.7	41.2	7.43	1.2	6.79	1.21	6.84	1.28	3.62	0.521	3.43	0.506	230.03
M2-22	52.7	105	12.5	44.5	8.29	2.03	6.28	0.946	4.86	0.927	2.8	0.406	2.79	0.381	244.41
M2-23	44	88.8	10.9	41.2	7.12	1.28	5.74	0.857	4.1	0.667	2.15	0.367	2.39	0.368	209.94
M2-24	66	123	14.4	54.3	9.82	1.82	7.49	1.06	6.03	1.06	3.2	0.5	3.61	0.503	292.79
M2-25	17.2	33.6	3.63	15.5	2.87	1.04	2.83	0.474	2.72	0.543	1.45	0.2	1.37	0.214	83.64
M2-26	35.1	73.4	7.01	25.7	4.36	0.836	3.84	0.523	2.79	0.471	1.44	0.204	1.33	0.196	157.20
M2-27	57.4	98.2	11.8	39.3	5.96	0.773	4.84	0.553	2.66	0.407	1.59	0.246	1.93	0.334	225.99
M2-28	18	30.9	3.3	11.8	1.95	0.343	1.67	0.24	1.15	0.216	0.741	0.13	0.942	0.134	71.52
M2-29	43.1	78.8	9.12	33.2	5.94	1.07	4.79	0.798	4.16	0.78	2.45	0.325	2.37	0.379	187.28
M2-30	44.6	89.9	9.46	32.9	5.98	1	4.7	0.682	3.46	0.586	1.94	0.272	1.9	0.289	197.67
M2-31	19.3	33	4.35	16.8	3.96	1.17	3.48	0.668	3.69	0.784	2.05	0.31	2.23	0.301	92.09
M2-32	31	55.7	6.29	23.5	5.54	0.985	4.07	0.827	4.83	0.955	2.3	0.442	2.83	0.385	139.65
M2-33	46.6	79.8	8.97	33	6.32	1.28	5.49	0.819	4.03	0.664	1.85	0.255	1.76	0.263	191.10
M2-34	43.4	87.4	10.1	36.2	7.1	1.24	5.76	0.952	4.91	0.853	2.51	0.41	2.71	0.405	203.95
M2-35	53.2	95.1	11.1	40.5	7.16	1.42	5.23	0.9	4.68	0.853	2.73	0.422	3.14	0.481	226.92
M2-36	34.4	65.9	7.99	29.5	6.03	1.04	5.03	0.887	4.65	0.892	2.73	0.353	2.77	0.396	162.57
M2-37	39.3	69.4	8.1	29.5	5.58	0.905	4.62	0.72	4.25	0.74	2.22	0.299	2.28	0.361	168.28
M2-38	22.1	37.9	4.68	17.1	3.25	0.691	2.94	0.507	2.75	0.651	1.7	0.264	2.08	0.29	96.90
M2-39	17.4	33.8	4.23	16.5	4.09	0.96	3.2	0.634	3.52	0.747	1.92	0.317	1.96	0.253	89.53
M2-40	48	92.4	12	45.2	9.05	1.71	7.53	1.27	6.4	1.24	3.32	0.534	3.64	0.538	232.83

Table 5
Values of selected elements from Well M2, Jitai Basin.

No.	Sr/Cu	FeO/MnO	Al ₂ O ₃ /MgO	Mg/Ca	B/Ga	Sr/Ba	Ni/Co	V/Cr	V/(V + Ni)	Ce/Ce*	La/Sc	Th/Sc
M2-1	0.99	81.25	21.99	1.61	3.31	0.12	5.50	0.6	0.72	0.90	3.87	1.16
M2-2	6.86	17.67	3.43	0.09	3.03	1.18	5.43	2.21	0.72	0.90	3.03	1.06
M2-3	3.41	162.5	22.09	2.89	3.56	0.10	2.56	0.29	0.68	0.94	3.35	1.08
M2-4	1.34	4.15	0.21	0.13	1.90	11.13	4.39	0.49	0.50	0.70	2.52	0.79
M2-5	9.21	14.42	3.7	0.04	1.83	1.49	5.76	1.37	0.50	0.90	1.71	0.69
M2-6	2.74	257.14	15.58	5.23	6.03	0.12	2.94	0.26	0.70	0.90	2.04	0.75
M2-7	2.94	276.09	20.11	7.15	1.71	0.13	1.79	1.12	0.74	0.87	3.69	1.24
M2-8	2.71	194.34	5.12	6.36	1.03	0.33	2.28	1.37	0.72	0.96	2.24	0.76
M2-9	3.61	209.23	27.68	9.53	3.00	0.10	2.40	0.46	0.70	0.90	3.14	1.04
M2-10	5.41	150.56	20.49	7.25	3.80	0.10	3.76	0.55	0.72	0.95	2.91	0.93
M2-11	3.16	193.50	16.25	10.95	2.34	0.08	2.69	0.63	0.72	1.00	2.88	0.75
M2-12	3.03	208.33	22.65	8.06	3.54	0.10	2.37	0.41	0.71	0.96	2.85	0.93
M2-13	2.02	152.92	19.25	9.12	3.51	0.09	1.71	0.86	0.72	0.89	3.06	0.98
M2-14	4.54	209.23	34.76	7.71	2.96	0.09	3.74	0.79	0.82	0.90	4.10	1.43
M2-15	1.72	171.25	40.06	6.70	2.31	0.06	1.61	1.14	0.76	0.94	3.30	0.96
M2-16	3.55	145.63	25.33	6.41	3.54	0.08	2.34	0.67	0.75	0.88	4.14	1.43
M2-17	3.14	236.43	24.29	11.22	3.33	0.09	3.78	0.71	0.64	0.87	4.40	1.77
M2-18	18.82	15.35	2.36	0.17	12.5	0.04	2.86	0.35	0.75	0.90	6.46	2.46
M2-19	9.01	21.14	1.5	0.38	2.85	0.24	2.33	0.98	0.68	0.94	2.63	0.58
M2-20	1.03	220	24.92	2.26	12.54	0.14	3.86	0.26	0.43	0.97	4.91	1.79
M2-21	3.51	138.4	20.80	8.46	3.99	0.09	2.87	0.51	0.68	0.85	3.74	1.18
M2-22	3.69	346.67	47.05	7.04	2.63	0.12	3.05	0.82	0.43	0.94	6.01	2.08
M2-23	3.31	51.92	11.42	1.53	3.16	0.12	2.12	1.38	0.68	0.93	0.33	0.11
M2-24	5.80	128.38	16.84	2.69	2.40	0.16	3.88	1.22	0.57	0.91	3.55	1.20
M2-25	56.22	19.09	2.09	0.06	2.64	4.81	6.97	1.74	0.76	0.97	3.47	0.62
M2-26	8.83	208	63.48	2.91	4	0.44	4.59	0.55	0.76	1.07	5.96	2.39
M2-27	16.86	148.89	37.18	2.22	3.20	0.42	6.03	0.86	0.52	0.86	5.57	2.18
M2-28	4.49	30.42	19.08	0.89	14.63	0.08	2.19	0.29	0.74	0.91	7.59	2.60
M2-29	1.92	35.65	9.39	1.60	8.83	0.10	1.23	0.62	0.83	0.91	4.72	1.32
M2-30	3.24	100.91	11.36	3.57	7.45	0.18	2.83	0.68	0.88	1.00	2.92	0.58
M2-31	39.94	16.52	0.62	0.59	6.97	2.32	3.38	1.87	0.75	0.82	2.42	0.74
M2-32	106.56	15.14	0.57	0.63	12.58	2.99	2.64	0.35	0.76	0.91	10.99	3.23
M2-33	5.94	116.88	6.25	0.77	7.70	0.36	3.33	0.36	0.83	0.89	11.51	1.93
M2-34	3.06	44.77	4.57	1.03	12.80	0.40	5.17	0.24	0.63	0.95	7.59	2.19
M2-35	15.85	412.22	8.92	13.95	7.58	0.12	6.81	0.61	0.55	0.89	3.06	1.03
M2-36	75.68	11.71	1.31	0.70	14.00	1.93	4.96	0.33	0.74	0.91	6.53	1.86
M2-37	5.16	176.88	6.89	1.79	7.93	0.21	2.80	0.38	0.59	0.89	3.64	1.15
M2-38	18.67	23.96	3.35	0.33	42.78	6.70	2.53	0.42	0.68	0.85	2.58	1.11
M2-39	22.30	25.74	0.41	0.58	14.51	1.81	5.07	1.06	0.55	0.90	3.29	0.89
M2-40	25.27	27.21	6.04	1.13	13.6	0.29	2.85	0.36	0.76	0.88	5.19	1.54

Trace elements. The three elements with the most average content of trace elements are Ba, Zr and Sr, and their average contents are 451.20 ppm, 255.93 ppm and 148.85 ppm respectively (Table 3). According to the plot of trace element compositions normalized against UC (Fig. 2c and d), the contents of various elements varied greatly. In the plot of silty mudstones normalized to UC, Cr contents are enriched relative to UC in most samples, but Sr contents show strong depletion (Fig. 2c). In Fig. 2d, Cr contents of some calcilutites are enriched. According to the Table 5, the B/Ga values range from 1.03 to 42.78, with an average of 6.80. The Sr/Ba values range from 0.04 to 11.13, with an average from 0.99. The Ni/Co values range from 1.23 to 6.97, with an average of 3.48. The V/Cr values range from 0.24 to 2.21, with an average of 0.75. The V/(V + Ni) values range from 0.43 to 0.88, with an average of 0.70.

Rare elements. In Table 4, Ce, La and Nd are the three most abundant elements, with Ce content ranging from 4.88 ppm to 131 ppm, La content ranging from 3.2 ppm to 73.9 ppm, and Nd content ranging from 3.4 ppm to 62.7 ppm. On the chondrite normalized map (Fig. 2e and f), all samples of Zhoutian Formation show a set of steeply dips LREE curves, while the curves of HREE are flat. For the silty mudstone samples, Eu contents are negative anomalies, and curves of Eu are V-shaped in the standardized diagram. For the samples of calcilutite, Eu contents are light negative anomalies. According to the Table 4, the Σ REE values range from 17.80 to 323.31, with an average of 181.14. According to the Table 5, the Ce/Ce* values range from 0.70 to 1.07, with an average of 0.91. The Th/Sc values range from 0.58 to 3.23, with an average of 1.31. The La/Sc values range from 0.33 to 11.51, with an average of 4.20.

Discussion

Palaeoclimate. As one of the methods to distinguish palaeoclimate, element geochemistry, such as Sr/Cu, FeO/MnO, $\text{Al}_2\text{O}_3/\text{MgO}$ and Mg/Ca, has a good indication to distinguish palaeoclimate. The value of Sr/Cu is a sensitive indicator of climate, and the high Sr/Cu value reflects a hot arid climate, while the low value reflects a warm humid climate. According to the research of Lermann²¹, Sr/Cu value between 1.3 and 5.0 suggest a warm humid climate, while the value greater than 5.0 indicates a hot arid climate. Mn content is relatively high in the dry environment, but low in the relatively humid conditions, and Fe is easy to be quickly precipitated by Fe (OH) colloid in the humid environment. So, the high value of FeO/MnO in the sediment corresponds to the warm humid climate, and the low value is the response to the hot arid climate. The $\text{Al}_2\text{O}_3/\text{MgO}$ value in clay minerals and its variation can also reflect the palaeoclimate during deposition, with high values reflecting the warm humid climate and low values indicating the dry climate²². The Mg/Ca value is also very sensitive to climate change. In general, high values of Mg/Ca indicate arid climate, while low values reflect humid climate²³.

The values of Sr/Cu vary widely, ranging from 0.99 to 106.56 (Table 5 and Fig. 3). This indicates that the Jitai Basin experienced relatively large climatic change during the late Cretaceous period. According to these values and curves, the Cretaceous palaeoclimate in the lower Zhoutian Formation is roughly divided into two parts, 1435-1270m and 1270-1100m respectively. The values of Sr/Cu in most sections between 1435 and 1270m is greater than 5.0. The values are less than 5.0 at 1321 to 1306m and 1360m. So, the palaeoclimate type in the 1435-1270m segment was a hot arid climate, and there was an obvious cooling event between 1321 and 1306m. The Sr/Cu values of the 1100-1270m segment are between 1.3 and 5.0 on the whole, and are greater than 5.0 at 1106m, 1121m, 1152m, 1205m and 1209m. Hence, the palaeoclimate type in the 1270-1100m segment was mainly warm humid climate, and there was a short period of climate fluctuation in some segments. In Fig. 3, FeO/MnO and $\text{Al}_2\text{O}_3/\text{MgO}$ curves show similar trend of change, but they are opposite to Sr/Cu curves. Since FeO/MnO and $\text{Al}_2\text{O}_3/\text{MgO}$ are negatively correlated with Sr/Cu, they all express the same geological meaning. And the change trend of Mg/Ca curve is also opposite to that of Sr/Cu curve. However, there is usually a positive correlation between Mg/Ca and Sr/Cu, so they are in conflict. Based on the comprehensive analysis of the above data, FeO/MnO, $\text{Al}_2\text{O}_3/\text{MgO}$ and Sr/Cu are more accurate indicators of geological significance than Mg/Ca. According to Table 5 and Fig. 3, the palaeoclimate of the late Cretaceous lower Zhoutian Formation in the Jitai Basin was mainly divided into upper and lower parts. The lower part (1435-1270m) experienced two cooling events and had the palaeoclimate characteristic of wet-dry cycling; the upper part (1270-1100m) was dominated by warm humid climate, which experienced many climatic fluctuations.

Salinity. Boron is one of the most concentrated trace elements in sea water and is mainly attached by illite in coastal to marine environments^{24,25}. By comparison, Gallium is principally come from terrestrial environments and is chiefly deposited in the form of smectite. According to studies of Wang et al.²⁶ and Lan et al.²⁷, the value of B/Ga is a reliable indicator of salinity. The value less than 3.0 indicates fresh water, the value ranging between 3.0 and 5.0 indicates brackish water, and the value great than 5.0 indicates salt water^{28,29}.

The combination of SO_4^{2-} in the sea/saline water and Ba^{2+} in the fresh water produces the precipitation of BaSO_4 . In contrast, the Sr is assumed to migrate and precipitate in the center of the open marine basin or saline lake as a result of the high solubility of SrSO_4 ³⁰. Therefore, the value of Sr/Ba can be used to distinguish marine and terrestrial environments. Overall, the value great than 1.0 usually indicates sea/saline water, and this value less than 1.0 means fresh water³¹⁻³³.

The values of B/Ga range from 1.03 to 42.78 by Table 5. The variation trend of B/Ga curves is similar to that of Sr/Cu curves, which can be divided into two parts (Fig. 3). One part is 1435-1270m, and all B/Ga values are greater than 5.0. This indicates a saltwater environment. The other part is 1270-1100m, and B/Ga values are mostly between 3.0 and 5.0, with some less than 3.0 and some great than 5.0. The salinity of this part is mainly brackish or fresh water, but it has undergone several changes in fresh/brackish and salt water. And the values of Sr/Ba range from 0.04 to 11.13 by Table 5. The values of Sr/Ba are similar to that of B/Ga and Sr/Cu, which are divided into two parts: 1435-1270m and 1270-1100m. Compared with B/Ga curve, Sr/Ba curve is more closely related to Sr/Cu curve (Fig. 3). Through the comparison of Sr/Cu and Sr/Ba curves, salinity is positively correlated with the change of palaeoclimate in the vertical direction. When the palaeoclimate as a whole was warm humid, the sedimentary water was fresh/brackish, and vice versa. To sum up, the salinity of the late Cretaceous lower Zhoutian Formation in Jitai Basin was mainly divided into upper and lower parts. The salinity of lower part (1435-1270m) changed from salt water to fresh/brackish water with the changes of palaeoclimate. The upper part (1270-1100m) was mainly fresh/brackish water, and there were many changes from fresh/brackish water to salt water.

Redox condition. Several trace elements, such as U, Ni, V, Mo, Cr, Co, are commonly enriched in anoxic sediments because of their solubility is controlled by the redox^{34–37}. In the study of late Jurassic redox environment in northwest Europe, Jones et al.³⁸ concluded that the values of Ni/Co, V/Cr and V/(V + Ni) were very reliable by comparing many parameters, and thus summarized a set of trace indexes for judging the redox environment (Table. 6). So, the trace element ratios of Ni/Co, V/Cr and V/(V + Ni) have been broadly used to identify redox conditions^{3,38–41}.

Likewise, Cerium anomalies in REE (rare earth element) distribution patterns are generally used to study redox conditions, too^{30,42–45}. Ce is present as of Ce³⁺ under reducing conditions and separates from other REE³⁺ in the form of Ce⁴⁺ under oxidized condition. The Ce/Ce* value is defined as $2(Ce)_{PAAS}/((La)_{PAAS} + (Pr)_{PAAS})$, and $PAAS$ refers to normalization of element concentrations against the Post-Archean Average Australian Shale (PAAS)⁴⁶. The value of Ce/Ce* can sensitively reflect the redox condition in the sedimentary environment. The Ce/Ce* value greater than 1 is a positive anomaly, indicating a reduction environment; while the value less than 0.95 is a negative anomaly, indicating an oxidation environment.

According to the Table 5, the values of Ni/Co range from 1.23 to 6.97, the values of V/Cr range from 0.24 to 2.21, the values of V/(V + Ni) range from 0.43 to 0.88, the value of Ce/Ce* range from 0.70 to 1.07. All Ni/Co values are less than 7.0, indicating an oxidation/weak oxidation environment. The Ni/Co value of lower part (1435–1270m) varies greatly, with the maximum value of 6.97, but it is still in a weak oxidation environment. The Ni/Co value of upper part (1270–1100m) is relatively stable, which is greater than 5.0 at 1121m, 1106m and 1101m only. All V/Cr values were less than 2.0 except at 1106m, which were in an oxidation environment. Most of the V/(V + Ni) values are between 0.6 and 0.77, and only four are great than 0.77, of which three are in the lower part (1350m, 1320m and 1315m). Most of the Ce/Ce* values are around 0.95, 1.07 at 1284m and 0.70 at 1115m. Compared with Table 5, Table 6 and Fig. 3, all values indicate that the late Cretaceous lower Zhoutian Formation was in oxidized environment, in which there were some small fluctuation in lower part (1435–1270m).

Table 6
Geochemical indicates of redox environment.

Palec-oxygenation Facies	Oxygen Content (mL/L)	V/Cr	Ni/Co	V/(V + Ni)
Anaerobic, extremely dysaerobic	< 0.2	> 4.25	> 7.0	> 0.77
Dysaerobic, secondary aerobic	0.2–2.0	2.0–4.25	5.0–7.0	0.60–0.77
Aerobic	> 2.0	< 2.0	< 5.0	< 0.6

Provenance. The chemical composition of terrigenous clastic rocks is a comprehensive reflection of the nature, denudation and transport of the source area. During these processes, elements of Cs, Zr, Th, Hf, Ti, La and Yb have good stability, even during weathering, transportation and diagenesis. Because of their non-migration, they are often used to evaluate the tectonic setting and the type of source rock in source area^{46–50}. Rare earth elements change slightly during deposition. The REE abundance in source rocks and the weathering conditions in source area are the major factors controlling the REE in sediments. Hence, REE in clastic sedimentary rocks are widely used as the main indicator to identify the provenance^{46,51}. In general, La-Th-Sc, Th-Sc-Zr/10 and La/Th-Hf can be used to identify the tectonic environment of the source area^{48,52–54}.

The La-Th-Sc discriminant diagram can better distinguish the continental island arc, while the Th-Sc-Zr/10 discriminant diagram can distinguish the active continental margin from the passive continental margin. In Th-Sc-Zr/10 discriminant diagram, the samples are mainly located in the continental island arc, some in the passive margin, and a few points not in any region (Fig. 4a). In La-Th-Sc discriminant diagram, most of the samples are located in the continental island arc, some in the region of active/passive continental margin, and only one sample in the oceanic island arc (Fig. 4b). In La/Th-Hf discriminant diagram, most of the samples are located in the areas of increasing old sediment component, some in the regions of felsic source and felsic/basic source, and only one sample in the andesitic arc source (Fig. 5). And the values of Th/Sc range from 0.58 to 3.23, with an average of 1.31 (Table 5). Most of Th/Sc values are located in the range of felsic rocks (0.84–20.5) and are much larger than mafic rocks (0.05–0.22). The values of La/Sc range from 0.33 to 11.51, with an average of 4.20 (Table 5). Like the La/Sc values, Th/Sc values mostly lie within the felsic rock range (2.5–16.3)^{55–57}. Hence, most of the samples are plotted in the continental island arc, some in the passive margin. The sediments mainly come from the provenance of the mixing of felsic material in the continental upper crust with old sediments.

Conclusions

This study represents a first relatively systematic study on major, trace and rare elements of the late Cretaceous lower Zhoutian Formation in the Jitai Basin. The main conclusions are as follows:

The changes of palaeoclimate were mainly divided into upper and lower parts. The lower part (1435–1270m) was dominated by hot arid climate, and a cooling event occurred. And the upper part (1270–1100m) was dominated by warm humid climate, which experienced many climatic fluctuations.

The salinity of lower part (1435–1270m) changed from salt water to fresh/brackish water with the changes of palaeoclimate. The upper part (1270–1100m) was mainly fresh/brackish water, and there were many changes from fresh/brackish water to salt water. And the late Cretaceous lower Zhoutian Formation was in oxidized environment, in which the lower part (1435–1270m) had some small fluctuation.

The lower Zhoutian Formation in the Jitai Basin shows a major tectonic setting of continental island arc, follows by continental margin. And its provenance is a mixture of upper crust felsic sediments and old sediment components.

Declarations

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Author contributions

K.Y. and C.L.W. designed the research in the manuscript. S.M., J.Y.W. and L.J.S. revised the manuscript. X.C.Y. and L.Y.M. participated in sample collection and processing.

Competing interests

The authors declare no competing interests.

Additional information

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Figures

Figure 1

Regional tectonic map of Jitai Basin, Southeast China. Note: The designations employed and the presentation of the material on this map do not imply the expression of any opinion whatsoever on the part of Research Square concerning the legal status of any country, territory, city or area or of its authorities, or concerning the delimitation of its frontiers or boundaries. This map has been provided by the authors.

Figure 2

(a) PAAS-normalized major-element diagram of silty mudstones in Well M2. (b) PAAS-normalized major-element diagram of calcilutites in Well M2. (c) UC-normalized trace-element diagram of silty mudstones in Well M2. (d) UC-normalized trace-element diagram of calcilutites in Well M2. (e) Chondrite-normalized rare-element diagram of silty mudstones in Well M2. (f) Chondrite-normalized rare-element diagram of calcilutites in Well M2. Data from Table 2, Table 3 and Table 4.

Figure 3

Geochemical indicates of elements value from lower Zhoutian Formation in the Jitai Basin, Southeast China.

Figure 4

(a) Th-Sc-Zr/10 discriminatory plot (modified after Bhatia & Crook48) of late Cretaceous samples from the lower Zhoutian Formation, Jitai Basin. (b) La-Th-Sc discriminatory plot (modified after Bhatia & Crook48) of late Cretaceous samples from the lower Zhoutian Formation, Jitai Basin.

Figure 5

La/Th-Hf discriminatory plot (modified after Floyd et al.53) of late Cretaceous samples from the lower Zhoutian Formation, Jitai Basin.