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Effect of Mesozoic volcanic eruptions in the western Liaoning Province, China on paleoclimate and paleoenvironment

GUO Zhengfu (郭正府)[1], LIU Jiaqi (刘嘉麒)[1] & WANG Xiaolin (汪筱林)[2]

1. Institute of Geology and Geophysics, Chinese Academy of Sciences, Beijing 100029, China;
2. Institute of Vertebrate Paleontology and Paleoanthropology, Chinese Academy of Sciences, Beijing 100044, China
Correspondence should be addressed to Guo Zhengfu (email: zhengfuguo@hotmail.com)

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Abstract Well-preserved Mesozoic vertebrate fossils were found from lacustrine deposits interbedded with tuff and tuffites in the lower part of the Yixian Formation, western Liaoning Province, China. The fossil-rich layers were preserved in the intermediate-acid volcanic deposits in Sihetun excavating profile. Based on the petrographic studies of samples of the tuff and tuffites collected from the profile, this paper determines major element concentrations and volatile compositions of the melt inclusions in phenocrysts and matrix glasses with electron microprobe analysis. Volatile (S, F, Cl and H_2O) contents emitted into the atmosphere were estimated by comparing pre- and post-eruptive volatile concentrations. Amount of volatiles (except for water) emitted in western Liaoning are much higher than those in the historic eruptions which had a substantial effect on climate and environment. Based on the nature and amount of the gases emitted in the eruptions of western Liaoning, we present a hypothesis that volatile-rich volcanism could result in mass mortality of vertebrates in the study area by injecting a large amount of volatiles (e.g., SO_2, H_2S, HCl, HF and H_2O) into the stratosphere that would have triggered abrupt environmental and climate changes and altered lake chemistry. In terms of contents of volatile emissions, the eruptions in western Liaoning can be subdivided into the following three categories. The first group is dominated by HF emission, which had a fatal but possibly short-lived effect on paleoclimate and paleoenvironment and finally caused the mass mortality of the primitive birds. The second group presents the highest halogen concentrations emitted. However, contents of chlorine erupted is higher than those of fluorine emitted. The reactive chlorine compounds probably led to the ozone layer depletion and, therefore, caused mass mortality of most of all vertebrates including fishes, turtles and dinosaurs. The third one consists mainly of sulfur gases (primarily SO_2 and H_2S) released. They declined the surface's temperatures and formed large-scale toxic acid rains. Eventually, such environmental trauma killed many land- and freshwater-based vertebrates and formed vertebrate (including feathered theropod dinosaurs) fossil-rich layers. The results show that the Mesozoic volcanic activities on either a large scale or frequent moderate scales in western Liaoning could lead to mass mortality of the vertebrates.

Keywords: volcanic eruption, paleoclimate, mass mortality, ozone layer, acid rain, western Liaoning Province.

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Volatiles emitted during volcanic eruptions have an significant effect on the climate and environmental changes[1]. Different compositions of volatiles released may result in different trends of climate and environmental changes. Amounts of the erupted gases and aerosols are responsible for the intensities of climate and environmental changes[1]. Maximum eruption column heights constrain the temporal and spatial scopes of the volcanogenic environmental changes[2,3]. Therefore, quantitative assessment of composition and amount of volatiles and aerosols is useful for study of the climate and environmental effects of volcanic eruptions based on the estimations of maximum eruption column heights using the isopleths of clast distribution.

Many layers of intermediate-acid Plinian fallout deposits are distributed and intercalated within the Early Cretaceous lake beds of the lower part of the Yixian Formation, western Liaoning Province, China, which have yielded more than ten well-preserved vertebrate fossil-rich layers. These fossiliferous horizons are located within the tuff and tuffites. The well-known Jehol Biota are distributed in the volcanic deposits[4—6]. The fossils are mainly composed of fishes, frogs, turtles, dinosaurs (including feathered dinosaurs), primitive birds, mammals and the earliest Angiosperm *Archaefructus*. Moreover, there is a wide range of superbly well-preserved other plant and invertebrate fossils (e.g. shrimps, insects, bivalves, conchostracans, ostracods, gastropods and salamanders)[4,6]. These unique fossil assemblages provide important evidence for the study of the origin and early diversification of birds and bird-dinosaur relationships[4]. Previous excavating studies have shown that almost all vertebrate fossils are exceptionally well-preserved within the ash tuff, tuffaceous sandstone, tuffaceous siltstone, tuffaceous mudstone and shale[4—7]. The fossil-rich layers are regarded as the records of mass mortality events of the vertebrates[5]. This feature of preservation and distribution of the fossil-bearing layers indicates that the mass mortality was possibly associated with the volcanic activities[5,7]. However, whether the eruptions represented by the volcanic products in the lower part of Yixian Formation could cause such catastrophic effect on plaeoclimate and paleoenvironment that would have led to mass mortality of the vertebrates has not been well understood. Given this assumption granted, what was the genetic mechanism? Why could the fossils be well preserved in western Liaoning Province, China? These aspects related to the cause of mass mortality of the different classes of vertebrates (e.g., fishes, amphibians, reptiles, birds) also remain unclear. In this study, we analyzed the volatile concentrations of melt inclusions trapped in phenocrysts and matrix glasses unambiguously correlated with the main vertebrate fossil assemblages in the lower part of the Yixian Formation in the Sihetun section (fig. 1). On the basis of the compositions, contents and stratospheric chemical processes of the erupted volatiles, we presented a hypothesis concerning the effect of the intermediate-acid volcanic activities on plaeoclimate and paleoenvironment and the main cause of the mass mortality events occurred in this area.

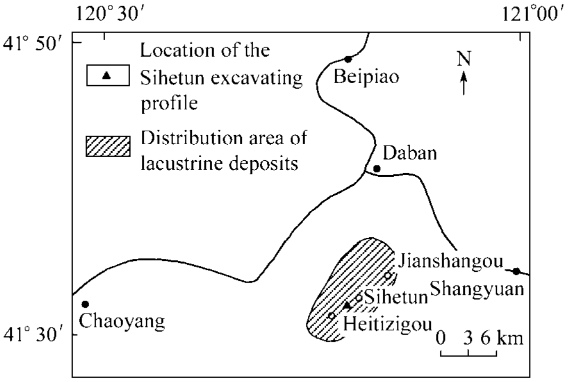

Fig. 1. Location of the Sihetun excavating profile, western Liaoning Province, China.

1 Geologic setting

The study region, western Liaoning Province, is complicated in Mesozoic structure where there are two groups of the tectonic lines. One strikes in E-W direction and the other trends in NNE-SSW direction[8]. In the Mesozoic times this region was characterized by frequent tectonic movements and intensive volcanic activities. Distribution area of the volcanic rocks covers the whole study area. Compositionally, the rocks consist mainly of basic-intermediate-acid associations.

This paper focuses on intermediate-acid tuff and tuffites, which are intercalated with lacustrine deposits in western Liaoning Province. These volcanic layers have yielded well-preserved vertebrate fossil assemblages[4—6]. Almost all of the vertebrate fossils in the lower part of the Yixian Formation came from the surrounding areas of the small village of Sihetun, western Liaoning Province, China (fig. 1). Outcrops of the lacustrine deposits strike in the NNE direction. The distribution area is restricted within 12—14 km in length and 4—5 km in width (fig. 1). ^{40}Ar/^{39}Ar dating of sanidine from the tuffs gave an age of 124.6 Ma[9]. Because there are no vertebrate fossils in the upper part of Sihetun excavating profile, all samples studied here came from the lower part of the profile, which correspond to layers 18—37[4,6]. The collected samples in this paper came from an interval of seven meters in the Sihetun profile.

2 Sample collection and analytical methods

We collected one sample once every 5 cm from the bottom to top of the Sihetun excavating profile. Therefore, all of tuff and tuffites recognized in the fieldwork were taken in the fossil-rich layers and fossil-poor layers in whole profile. Crystals separated from the volcanic rocks were prepared as polished thin sections for electron microprobe analyses of melt inclusions. Matrix glasses and melt inclusions in phenocrysts were analyzed for the major element oxides and sulfur, chlorine and fluorine on a wave-length-dispersive Cameca SX-50 electron microprobe. The analytical conditions for all melt inclusions and matrix glasses were 15 kV accelerating voltage, 6—15 nA beam current, 1—10 μm (melt inclusions) and 15—20 μm (matrix glasses) beam diameter. All thin sections and standards were carbon-coated to a thickness of 25 Å. For glass and inclusion analyses, a counting time of 30 s was used for the elements Si, Ti, Al, Fe, Mg, Ca and K, 20 s for Na, 80 s for Mn, and 100 s for P. In order to improve detection limits for Cl (300 ppm), S (120 ppm) and F (800 ppm), a counting time of 300 s was used for these three elements. The elements fluorine and sodium were determined first because of their strong volatile behavior during analysis. These operating conditions produced reproducible results and replicate analyses of the standards KN18 and CFA 47 for glass. The relative analytical precision is < 5% for S, < 3% for F, and < 4% for Cl, based on repeated analyses of glass standards. Total H_2O contents of melt inclusions and matrix glasses were estimated by the difference between the total of an electron microprobe analysis and 100% (the so-called “difference method”)[10]. In order to preserve melt inclusions as closed system and improve analytical precision of volatiles, only inclusions from phenocrysts were analyzed, that correspond to the criteria for primary inclusions defined by Horn and Schmincke[3] and Guo et al.[11].

3 Results

Observations under microscope show that phenocryst minerals in the latest crystallization stage are sanidine and quartz. The petrologic method to estimate minimum volcanic syn-eruptive degassing is based on the assumption that the volatile contents in melt inclusions trapped in phenocrysts crystallized in late stage of the magma evolution processes represent those of the pre-eruptive magma. The coexisting matrix glasses are representative of the partially degassed, post-eruptive magma. The difference between pre- and post-eruptive volatile concentrations is taken as concentrations of the volatiles erupting into the atmosphere[3,11]. The major element and volatile concentrations of matrix glasses and representative melt inclusions in sanidine and quartz phenocrysts of the samples are given in table 1. The contents of volatile emissions are listed in table 2. Contents of volatiles released by the eruptions, which are contemporaneous with fossil-rich layers, are higher than those emitted in these eruptions of some active volcanoes of the same (or similar) composition worldwide (table 2). Composition of melt inclusions in these minerals and matrix glasses (table 1) could represent that of the magma erupted. Fig. 2 is a plot of Na_2O+K_2O vs SiO_2 (TAS). Most of volcanic rocks in table 1 are trachyandesite, trachyte, trachydacite and rhyolite, consistent with their mineralogy. The rocks fall on the boundary of the alkaline and subalkaline series (fig.2).

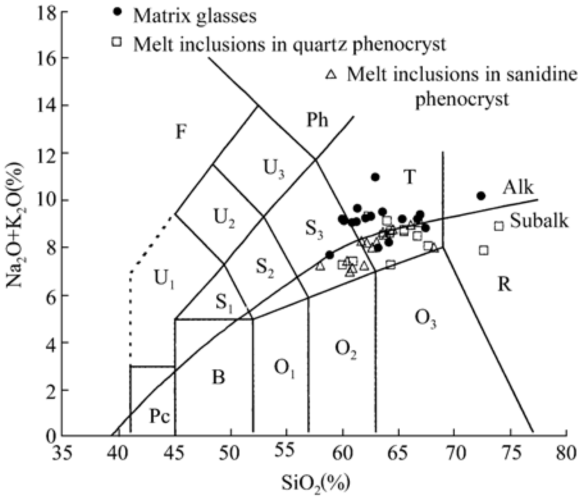

Fig. 2. Variations of total alkalis (Na_2O+K_2O) with SiO_2 in the matrix glasses and melt inclusions of phenocrysts. The subdivision of volcanic rocks into alkaline and subalkaline series refers to ref. [12]. The nomenclature of the volcanic rocks is as follows[13]: R, rhyolite; O_3, dacite; O_2, andesite; O_1, basaltic andesite; B, basalt; Pc, picrobasalt; T, trachyte (q < 20%) and trachydacite (q > 20%); S_3, trachyandesite; S_2, basaltic trachyandesite; S_1, trachybasalt; Ph, phonolite; U_3, tephriphonolite; U_2, phonotephrite; U_1, tephrite (ol < 10%) and basanite (ol > 10%); F, foidite.

4 Discussion

There are two cycles in the variations of the emitted volatile concentrations represented by volcanic products from the excavating profile (fig. 3). The rocks from layer 37 to layer 25 represent the first cycle, and the samples within layers 24—18 fall in the second cycle. Generally, contents of volatiles emitted in the eruptions increase from the lower part to the upper in each cycle. The first and second cycles are 456 cm and 244 cm in thickness, respectively. Previous studies

Table 1 Major element and volatile contents of representative melt inclusions and matrix glasses from intermediate-acid tuff and tuffites in western Liaoning Province (%)

Sample[a)]	Layer[b)]	Host/ matrix	SiO_2	TiO_2	Al_2O_3	FeO^*	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	S	F	Cl	H_2O	Total
18(L)	18(6)	Qz	61.88	0.68	14.85	4.32	0.11	2.14	3.64	4.41	3.83	0.38	0.052	0.224	0.387	3.097	96.903
18(L)	18(6)	Qz	62.57	0.63	14.66	3.68	0.12	1.97	3.08	4.31	4.02	0.37	0.051	0.236	0.403	3.900	96.100
18(L)	18(6)	Qz	62.72	0.65	14.73	3.79	0.11	1.93	3.06	4.22	4.05	0.37	0.051	0.245	0.416	3.658	96.342
18(L)	18(6)	San	61.83	0.71	15.08	4.41	0.09	2.17	3.69	4.39	3.85	0.41	0.055	0.227	0.365	2.723	97.277
18	18	MG	62.09	0.68	15.59	3.63	0.13	2.14	3.16	6.52	4.28	0.36	0.032	0.136	0.078	1.174	98.826
19	19	San	55.38	0.81	17.49	5.27	0.08	3.88	4.83	3.76	3.14	0.76	0.069	0.134	0.158	4.239	95.761
19	19	MG	56.94	0.78	16.96	5.16	0.07	3.81	4.75	3.88	3.54	0.82	0.044	0.124	0.125	2.997	97.003
20(U)	20(2)	San	60.11	0.81	15.32	4.82	0.18	1.91	4.57	4.15	3.54	0.54	0.071	0.172	0.156	3.651	96.349
20(M)	20(5)	Qz	61.09	0.91	15.07	4.75	0.14	1.84	3.51	4.28	3.87	0.38	0.064	0.156	0.145	3.795	96.205
20(L)	20(10)	San	59.61	0.82	15.68	4.59	0.14	2.07	4.51	4.06	3.79	0.58	0.053	0.166	0.138	3.793	96.207
20	20	MG	61.32	0.95	15.49	4.82	0.11	1.92	3.83	4.91	4.18	0.46	0.045	0.149	0.125	1.691	98.309
21(U)	21(1)	Qz	60.18	0.79	15.08	4.27	0.12	1.98	4.69	4.59	4.36	0.48	0.054	0.129	0.144	3.133	96.867
21(U)	21(1)	MG	60.59	0.85	15.71	4.59	0.07	2.16	4.81	4.85	4.64	0.37	0.034	0.124	0.112	1.090	98.910
22	22	San	58.69	0.89	15.29	4.98	0.21	1.96	4.67	4.59	3.28	0.59	0.074	0.165	0.161	4.450	95.550
22	22	MG	59.33	0.76	15.99	4.88	0.18	1.64	4.51	4.42	4.34	0.72	0.053	0.135	0.139	2.903	97.097
23(L)	23(8)	San	61.08	0.89	15.13	4.77	0.11	1.76	3.64	4.46	3.82	0.35	0.049	0.128	0.117	3.696	96.304
23(L)	23(8)	MG	62.17	0.91	15.08	4.58	0.08	1.67	3.59	4.77	4.47	0.37	0.039	0.113	0.111	2.047	97.953
24(U)	24(1)	Qz	64.08	0.53	14.02	3.49	0.09	1.84	2.91	4.46	4.17	0.28	0.083	0.172	0.186	3.689	96.311
24(L)	24(3)	Qz	63.84	0.58	14.26	3.51	0.12	1.89	2.94	4.26	3.84	0.38	0.051	0.124	0.131	4.074	95.926
24	24	MG	64.83	0.55	14.16	3.44	0.11	1.85	2.88	4.65	4.26	0.34	0.036	0.111	0.102	2.681	97.319
25(U)	25(1)	Qz	58.43	0.76	16.34	6.05	0.14	3.87	4.01	3.62	3.45	0.67	0.091	0.178	0.164	2.227	97.773
25(U)	25(1)	MG	59.31	0.65	16.46	5.11	0.13	3.67	3.97	4.58	4.47	0.51	0.024	0.132	0.086	0.898	99.102
25(L)	25(2)	San	58.97	0.82	16.29	4.98	0.16	3.57	4.89	3.32	3.46	0.74	0.088	0.246	0.177	2.289	97.711
25(L)	25(2)	MG	61.49	0.56	15.24	4.69	0.11	3.26	4.06	5.13	3.98	0.48	0.024	0.123	0.114	0.739	99.261
26	26	Qz	64.56	0.55	14.07	3.37	0.11	1.77	2.87	4.01	3.67	0.39	0.076	0.237	0.176	4.141	95.859
26	26	MG	65.28	0.51	13.59	3.61	0.09	1.85	2.88	4.71	4.42	0.43	0.024	0.111	0.114	2.381	97.619

(*To be continued on the next page*)

(*Continued*)

Sample[a)]	Layer[b)]	Host/ marix	SiO_2	TiO_2	Al_2O_3	FeO^*	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	S	F	Cl	H_2O	Total
27	27	San	63.02	0.56	14.38	3.56	0.13	1.87	2.87	4.59	3.92	0.41	0.052	0.131	0.127	4.380	95.620
27	27	MG	63.89	0.59	15.08	3.67	0.18	1.96	2.77	4.69	4.28	0.56	0.037	0.101	0.097	2.095	97.905
28(U)	28(1/2)	Qz	59.29	0.76	16.28	4.78	0.13	3.53	4.55	3.51	3.67	0.68	0.079	0.251	0.162	2.328	97.672
28(L)	28(3/4)	San	58.67	0.77	16.21	5.89	0.13	3.76	4.12	3.67	3.56	0.37	0.091	0.261	0.157	2.341	97.659
28	28	MG	60.18	0.56	16.17	5.06	0.11	3.66	3.78	4.51	4.39	0.35	0.031	0.132	0.085	0.982	99.018
29(M)	29(3)	San	58.32	0.66	15.64	5.91	0.17	3.72	3.92	3.48	3.34	0.57	0.084	0.173	0.159	3.854	96.146
29(M)	29(3)	MG	59.02	0.61	16.37	5.13	0.11	3.58	3.75	4.52	4.38	0.53	0.026	0.137	0.084	1.753	98.247
29(U)	29(2)	Qz	68.19	0.44	13.69	1.12	0.05	1.02	1.42	3.48	3.89	0.52	0.037	0.249	0.137	5.757	94.243
29(L)	29(4)	Qz	69.54	0.25	12.31	1.23	0.04	0.73	1.21	3.61	4.71	0.23	0.034	0.258	0.152	5.696	94.304
29(U/L)	29(2/4)	MG	70.44	0.16	14.42	0.78	0.08	0.08	1.02	4.12	5.76	0.33	0.030	0.112	0.040	2.628	97.372
30(U)	30(1)	San	64.89	0.57	14.06	3.05	0.13	1.69	2.62	3.58	4.05	0.54	0.068	0.206	0.138	4.408	95.592
30(U)	30(1)	MG	65.33	0.48	13.59	3.17	1.11	1.86	2.39	4.09	4.41	0.33	0.024	0.124	0.109	2.983	97.017
31(L)	31(3)	Qz	60.84	0.75	15.09	4.31	0.09	1.83	4.35	3.11	3.75	0.36	0.053	0.159	0.142	5.166	94.834
31(L)	31(3)	MG	61.37	0.77	15.23	4.21	0.06	1.62	4.17	3.15	4.68	0.33	0.029	0.125	0.111	4.145	95.855
32	32	San	61.02	0.77	15.01	4.38	0.08	1.58	3.02	4.27	4.02	0.44	0.051	0.119	0.122	5.118	94.882
33(U)	33(1)	San	59.59	0.83	15.43	4.76	0.13	1.97	3.51	4.19	3.57	0.52	0.046	0.145	0.159	5.150	94.850
34(U)	34(2)	Qz	60.89	0.78	15.06	4.42	0.09	1.59	3.09	4.23	3.99	0.48	0.065	0.132	0.137	5.046	94.954
35	35	San	59.47	0.82	15.08	4.81	0.14	1.96	3.77	4.12	3.65	0.49	0.044	0.148	0.146	5.352	94.648
36	36	Qz	61.07	0.78	14.96	4.29	0.12	1.62	3.15	4.38	4.29	0.67	0.041	0.127	0.137	4.365	95.635
37(L)	37(3)	San	58.87	0.72	15.28	5.11	0.12	3.61	3.81	3.43	3.47	0.64	0.062	0.138	0.146	4.594	95.406
32-37	32-37	MG	60.82	0.51	15.11	4.29	0.1	3.56	3.67	3.43	4.22	0.48	0.024	0.103	0.110	3.573	96.427

a) U, M, L represent the upper, middle and lower parts of the sample layer, respectively. b) Layers are the same as those of the Sihetun excavating profile from refs. [4,6]. Qz, quartz; San, Sanidine; MG, matrix glasses; FeO^*, total iron as FeO.

Table 2 Concentrations of volatiles emitted in the eruptions of western Liaoning Province and a comparison with those of some active volcano eruptions (%)

Sample a)	Host b)	S	F	Cl	H_2O
18(L)	Qz	0.020	0.088	0.309	1.923
18(L)	Qz	0.019	0.100	0.325	2.726
18(L)	Qz	0.019	0.109	0.338	2.484
18(L)	San	0.023	0.091	0.287	1.549
19	San	0.025	0.010	0.033	1.242
20(U)	San	0.026	0.023	0.031	1.960
20(M)	Qz	0.019	0.007	0.020	2.104
20(L)	San	0.008	0.017	0.013	2.102
21(U)	Qz	0.020	0.005	0.032	2.043
22	San	0.021	0.030	0.022	1.547
23(L)	San	0.010	0.015	0.006	1.649
24(U)	Qz	0.047	0.061	0.084	1.008
24(L)	Qz	0.015	0.013	0.029	1.393
25(U)	Qz	0.067	0.046	0.078	1.329
25(L)	San	0.064	0.123	0.063	1.550
26	Qz	0.052	0.126	0.062	1.760
27	San	0.015	0.030	0.030	2.285
28(U)	Qz	0.048	0.119	0.077	1.346
28(L)	San	0.060	0.129	0.072	1.359
29(M)	San	0.058	0.036	0.075	2.101
29(U)	Qz	0.007	0.137	0.097	3.129
29(L)	Qz	0.004	0.146	0.112	3.068
30(U)	San	0.044	0.082	0.029	1.425
31(L)	Qz	0.024	0.034	0.031	1.021
32	San	0.027	0.016	0.012	1.545
33(U)	San	0.022	0.042	0.049	1.577
34(U)	Qz	0.041	0.029	0.027	1.473
35	San	0.020	0.045	0.036	1.779
36	Qz	0.017	0.024	0.027	0.792
37(L)	San	0.038	0.035	0.036	1.021
Agung		0.038		0.061	1.16
Campanian		0.002		0.041	0.03
Krakatau		0.004		0.015	3.09
St. Helens		0.004		0.006	4.91
Tambora		0.007	0.063	0.089	3.07
Baitoushan		0.021	0.086	0.091	3.66
Pinatubo		0.003			4.06

a) Samples as in table 1. b) Abbreviations for host minerals as in table 1. Data of other active volcanoes are from refs. [1,3,14].

have demonstrated that lacustrine sediments interbedded with tuff in the profile developed in the Mesozoic maar lake environment, which have relatively constant sedimentary rate from early to late[15]. Thus, duration of the first cycle is longer than that of the second cycle. The number of vertebrate fossil-bearing layers is more in the first cycle than in the second cycle (fig. 3). Correspondingly, the number of the eruptions having relatively high contents of volatile emissions is larger in the first cycle than in the second cycle (fig. 3). Moreover, the concentrations of the volatiles released in the eruptions represented by the volcanic deposits containing the fossil-rich layers

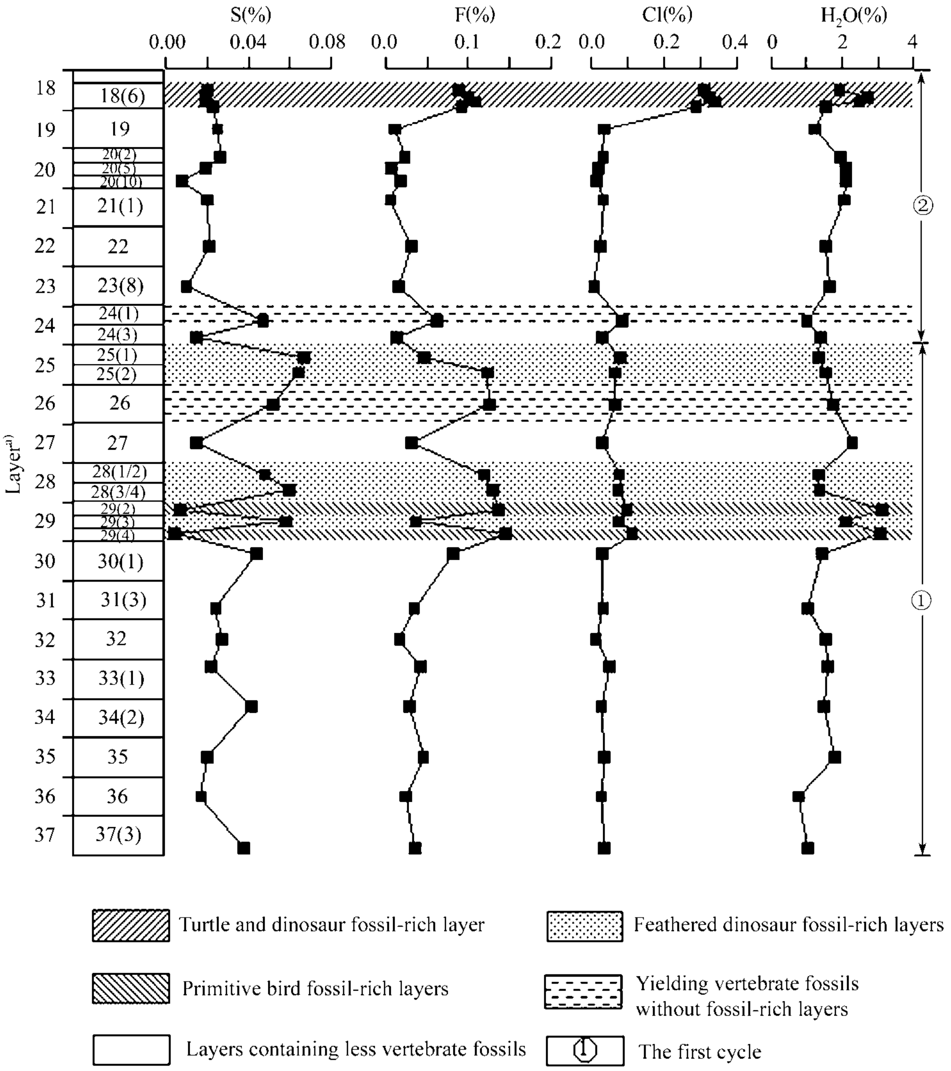

Fig. 3. Correlation between concentrations of volatiles emitted and vertebrate fossil assemblages in Sihetun excavating profile, western Liaoning Province. a) Layers as listed in table 1.

are much higher than those indicated by the tuffs of the fossil-poor layers in the profile. These features possibly imply a close relation between explosive volcanic activities and mass mortalities indicated by the fossil-rich layers. It should be pointed out that the estimates of volumes and maximum eruption column heights in western Liaoning are 200—320 km^3 and 18—38 km based on isopach and isopleth maps of volcanic deposits, respectively. Contents of volatile (except for H_2O) emissions in the study area are higher than those released from some active volcanoes with substantial effect on climate and creatures (table 2). When combined with estimates of melt abundance, density[7] and erupted volume, the amounts of volatiles (except for water) released into the atmosphere in western Liaoning are much larger than those in the historic eruptions, based on the petrological method[3]. Thus, we proposed that the abrupt climate and environmental changes induced by violent eruptions in the Mesozoic in western Liaoning Province could cause the events of mass mortalities as mentioned above.

On the basis of the constituents of volatiles released into the atmosphere, the volcanic eruptions could be subdivided into three groups. The first group is dominated by HF gas, which has higher fluorine concentrations than chlorine released. The second one is mainly composed of HCl. In this group, chlorine concentrations are higher than fluorine. The third one consists mainly of sulfur gases (primarily SO_2 and H_2S). They correspond to three kinds of climatic and environmental effects.

4.1 Effect of HF emission on climate and environmental changes

The explosive eruptions represented by fossiliferous tuff of layers 29 (2) and 29 (4) in the Sihetun excavating profile (fig. 3) released sufficient volatiles containing the highest concentrations of HF in eruptive plumes in this area (table 2). Study results of active volcano eruptions have demonstrated that hydrogen fluoride is responsible for the most lethal gas-related volcanic events. For example, sufficient HF gas released from the Plinian eruption of Hekla volcano in Iceland in 1766—1768 AD was adsorbed on tephra (especially dust) and transported hundreds of kilometers from the active vent. Populated areas around the volcano have been heavily impacted due to significant tephra (ash, dust) fall, and by the lethal fluorosis of livestock[1,16].

Totally, there have been more than one thousand primitive bird fossil specimens (e.g. *Confuciusornis*) found in the studied region, and more than 95% of which came from layers 29 (2) and 29 (4). In average, the *Confuciusornis* fossils in 29 (2) and 29 (4) were preserved at a density of about 1 individual in every 5—6 m^2, and even 1 individual in every 1—2 m^2 in some local dense sites[5], indicating an great mass mortality event of the primitive birds. All the *Confuciusornis* skeletons were oriented in the same direction, and necks extended forward and wings stretched outward[5,6], showing that the mass mortality abruptly occurred in the process of flying of a large number and high density of the primitive birds. The bird fossils were located within tuffaceous mudstone and fine ash tuff and were preserved in articulation with both skeleton and soft tissue, keeping the rectric, flight and down feathers intact[4,5], suggesting a rapid deposition and burial process associated with volcanic activities. These characteristics, together with volcanogenic HF hazards mentioned above, imply that a large number of primitive bird fossils in layers 29 (2) and 29 (4) (fig. 3) resulted from high-HF-release eruptions. The nature of high contents of volcanic ash and dust in the volcanically erupted products in layers 29 (2) and 29 (4) also supports this hypothesis.

4.2 Effect of HCl on climate and environmental changes

The injection of HCl into the stratosphere is of special interest, because of the potential ozone-destroying effects of chlorine[1,3]. Furthermore, HCl is highly soluble in water and is therefore easily removed by rain from a volcanic plume, resulting in low-pH acid rains (e.g. Kilauea, Masaya volcano), which have severe effects on environment (e.g. polluting plants, altering lake water chemistry and pH value and causing collapse of food chains, etc.)[1,17]. Significant amount of HCl may also have been injected into the stratosphere during the cataclysmic eruption of El Chichon in 1982 with potentially serious environmental implications[1].

A notable feature of the eruption represented by the tuff of layer 18 (6) is the exceptionally high contents of HCl gas emission (table 2 and fig.3). The amount of HCl injected into the atmosphere (even the stratosphere) could be the largest among the eruptions in the studied area because the tuff of layer 18 (6) was the thickest in this region[4]. The injection of such large quantities of HCl gas, together with other toxic volatiles emitted, is of special interest due to the potential environment effects mentioned above. These facts, plus the fact that no vertebrate fossils outcropped above 18 (6) in the Sihetun profile (fig. 3) indicate that the eruption represented by the fossil-rich Plinian volcanic deposit of layer18 (6) had fatal effect on the vertebrates. Thus, we can draw a conclusion that this eruption may have severely destroyed the ecosystem, finally leading to the largest scaled mass mortality of almost all of vertebrates (e.g. dinosaurs, turtles and fishes, etc) and invertebrates in the basin of Sihetun. The fossil preservation features, together with the fact that fossil-bearing layer is distributed within and overlain by the tuffaceous rocks and tuff, show that a large amount of ash and fallout deposits would immediately fall on the surface and rapidly bury the dead animal bodies, forming the well-preserved fossil layer 18 (6).

4.3 Effects of SO_2 and H_2S on climate and environmental changes

Studies of historic and recent volcanic activities (e.g. Tambora, 1815; Agung, 1963; El Chichon, 1982; Mt. Pinatubo, 1991) have demonstrated that the environmental and climate changes induced by high-S-release eruptions are as follows: (ⅰ) The sulfur gases (primarily H_2S and SO_2) are injected into the upper atmosphere (even stratosphere) by explosive eruptions and cause the photochemical reactions (e.g. $2SO_2+O_2\rightarrow 2SO_3$; $SO_3+H_2O\rightarrow H_2SO_4$) and finally form sulfuric acid aerosols in the lower stratosphere. The stratospheric aerosols could affect the global radiation budget by absorbing and backscattering incoming solar radiation, which causes cooling of the lower atmosphere and the surface, and even “volcanic winters”[18]. For instance, the eruption of Tambora in 1815 released a large amount of sulfur gases that led to decline of the temperature in the Northern Hemisphere and resulted in the “year without summer” in 1816. More than 88000 people perished from the direct and indirect effects on Sumbawa and neighboring Lombok[18]. (ⅱ) The H_2SO_4 aerosols, together with the ice crystals formed from volcanogenic water vapor in the stratosphere, provide large surfaces for the heterogeneous photochemical reactions in the stratosphere. These increase efficiency and rate of the reactions that might cause ozone destruction in the stratosphere. The importance of sulfur-rich eruptions was highlighted by Mt. Pinatubo eruption in 1991. Sulfur-rich gases released by this eruption were condensed into sulfuric acid aerosols that had an impact on stratospheric ozone[19,20]. (ⅲ) The sulfur gases might form acid rains in the eruption plume, which could also destroy the environment. Life would have been confronted with large-scale toxic acid rain[17].

The layers 25 (1), 25 (2), 28 (1/2), 28 (3/4) and 29 (3) are characterized by a large number of theropod dinosaur (including feathered dinosaur) fossils. The eruptions indicated by tuff and tuffites within these fossil-rich layers are characterized by high concentrations of sulfur gas emissions (table 2 and fig.3). They could form volcanogenic aerosols, lower surface temperature and even cause acid rains as mentioned above. Finally, these deleteriously environmental changes might lead to mass mortality of the cold-blooded dinosaurs in layers 25 (1), 25 (2), 28 (1/2), 28 (3/4) and 29 (3). The feature of well-preserved fossils[4—6] in these layers suggests the rapidly buried processes of the dead dinosaur bodies with volcanic ash.

Vertebrate fossil-bearing layers 24 (1) and 26 in the profile (fig. 3) correspond to transitional eruptions among the three types of volcanic activities mentioned above. Thus, they contain several classes of vertebrate fossils. However, amount of these vertebrates is relatively small compared with that of other fossiliferous horizons mentioned above, and none of them are dominant. Besides these, the following characteristics are shown in fig. 3. (ⅰ) Both a large-scale eruption (e.g. the eruption shown by tuff in layer 18 (6)) and several medium-scale eruptions (e.g. the eruptions occurred between layers 29—25) could cause mass mortalities of a large amount of vertebrates; (ⅱ) The variations of compositions and contents of volatile emissions in the profile (fig. 3) correspond to those of vertebrate fossil assemblages in terms of the predominant class; (ⅲ) The same class of vertebrate fossils to be located in different layers might be generated by different manners. For example, there are well-preserved fossils of reptiles[4,6] in layers 25 (1), 25 (2), 28 (1/2), 28 (3/4), 29 (3) and 18 (6). However, factors regarding the formations of these fossil-rich layers are different (e.g. contents of volatile emissions and their environmental effects) as mentioned above; (ⅳ) H_2O emitted in the eruptions could not directly lead to abrupt changes of climate and environment, rather, it might form compounds by reacting with other volatiles and finally cause mass mortality. For example, although concentration of water emission corresponding to layer 27 (fig. 3) is relatively high, this volcanic activity has less effect on the paleoclimate due to lower contents of other volatiles emitted (table 2). On the contrary, high contents of H_2O release in volcanic activities indicated by volcanic rocks within layers 29 (2), 29 (4) and 18 (6) would form volcanogenic compound (e.g. acid rains) and finally lead to the deleterious environmental change and mass mortalities as described above.

5 Conclusions

(1) There is a close correlation between the intermediate-acid eruptions of high contents of volatile release and vertebrate fossil-rich layers formed by mass mortality in western Liaoning Province, China.

(2) Concentrations of volatiles (except for H_2O) emitted in the eruptions represented by volcanic rocks interbedded within vertebrate fossil-rich layers are higher than those released from some active volcanoes of the same (or similiar) composition. Thus, the mass mortality events in

western Liaoning are mainly caused by explosive high-volatile-release eruptions.

(3) Based on the nature and contents of the volatile emissions, eruptions indicated by volcanic products in the Sihetun profile could be subdivided into three types. The first had a fatal effect on the paleoclimate and paleoenvironment because of high HF concentrations of the emissions. The second caused mass mortality of a large amount of vertebrates including fishes, turtles and dinosaurs, which is predominated by high-HCl release. The third is characterized by high contents of sulfur gases, which led to mass mortality of feathered theropod dinosaurs.

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