

Effect of volatiles erupted from Mesozoic and Cenozoic volcanic activities on paleo-environmental changes in China

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Abstract Based on the determination of composition of volcanic volatiles and petrologic estimation of the total mass of volatiles erupted, we showed important advances in the study of the impact of Mesozoic and Cenozoic volcanic activities on paleo-environmental changes in China. The volcanic activities include western Liaoning and Zhangjiakou Mesozoic intermediate-acidic explosive eruptions, southern Tibet and Shanwang Cenozoic volcanism, and Mt. Changbai volcanic eruption around one thousand years ago. The paper predominantly discusses the earth's surface temperature changes, ozone depletion, acidic rain formation and mass mortalities of vertebrate induced by the Mesozoic and Cenozoic volcanism in China.

Keywords volcanic gases, paleo-environmental changes, mass mortality of vertebrate, Mesozoic and Cenozoic volcanic activities, Tibetan Plateau

1 Introduction

Three parameters are critical to estimate the effect of volcanic activities on environmental changes: (1) the proportion and total amount of the volatiles erupted (2) composition of the volcanic gases emitted and (3) the maximum height of volcanic eruption column (Sigurdsson, 2000). The composition of volatiles emitted may constrain the trend of environmental change. The amount of volcanic gases and aerosol would be responsible for the intensity of environmental change (Sigurdsson, 2000). Maximum height of volcanic eruption column could constrain temporal and spatial scope of volcanogenically environmental change (Horn and

Schmincke, 2000; Schmincke, 2004). They are tightly related with the composition of the magma and eruptive type. Combining physical volcanology with geochemical study is an effective approach to explore the volcanic effect on environmental changes. It is impossible to create a link between volcanism and environmental changes without geological records. Moreover, assessment of the volcanic volatile force is an important aspect of the volcanic degassing effect. Microprobe and spectroscopic analyses have been considered to be an important approach for determining volcanic gas composition (e.g. Zhang et al., 2000; Li et al., 2006).

The study on the effect of volcanism on paleo-environmental change began in 1989 in China (Yin et al., 1989). Then, on the basis of the analyses of the volatiles (S, Cl, F, H₂O and CO₂) released from Mesozoic and Cenozoic volcanic activities, the possible links between volcanic activities and paleo-environmental changes have been explored in the volcanic fields. This paper focuses on the main advances in research on the effect of volcanism on paleo-environmental changes in China.

2 Analytical methods

Microprobe analysis is the main analytical method for major elements and S, Cl, F and H₂O concentrations of the samples studied in China. Melt inclusion in late-phase phenocrysts (e.g. anorthoclase, sanidine and quartz) and co-existing melt glasses, based on petrographic observations under the microscope, would be prepared for the composition analysis by electron microprobe. Melt inclusion within the phenocrysts for the analysis should be primary and colorless; the melt glasses would be fresh and free of micro-crystals (Guo et al., 2002). More detailed features of melt inclusions and melt glasses are consistent with the criteria shown (Horn and Schmincke, 2000; Guo et al., 2003c; Guo et al., 2006). The operating conditions of the microprobe

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analyses (Guo et al., 2006) are as follows: 15–20 kV accelerating voltage, 5–20 nA current, 1–10 μm electron beam in diameter for melt inclusion and 10–20 μm for melt glasses. Relative analytical precision was $F < 2\%$, $\text{Cl} < 4\%$ and $\text{S} < 5\%$ on the basis of repeated analyses of international standards and samples. More detailed procedures follow those of the references (Guo et al., 2002, 2003c; Guo et al., 2006). Total H_2O concentration of melt inclusions and melt glasses were estimated by the difference between the total of an electron microprobe analysis and 100% (so called “difference method”) (Guo and Liu, 2002, Guo et al., 2003c). Relative proportion of $\text{S}^{6+}/\text{S}_{\text{total}}$ was analysed on the basis of determinations of shift of S $\text{K}\alpha$ wavelength peak position. Water and CO_2 concentrations were determined by spectroscopic analyses. More details on the analytical methods are indicated in the references (e.g. Li et al., 2006; Zhang et al., 2000).

3 Calculations of total mass of volatiles released and maximum height of volcanic eruption column

Previous studies (e.g. Guo et al., 2002, 2003c, 2006) have indicated that volatile content in melt inclusions of host mineral crystals may represent those trapped in the pre-eruption magmas, while concentrations of volatiles in melt glasses may represent contents of volatiles in post-eruption magmas. Differences between content in the melt inclusions and co-existing melt glasses may be considered concentrations of volatiles erupted during the volcanic activities. To calculate the total mass of volatiles erupted during the volcanic activities, we applied the “Petrologic method” (Guo and Liu, 1998; Zhang et al., 2000; Guo et al., 2002, 2003a; Li and Wu, 2004) based on estimations of the difference of volatile content of pre- and post-eruption, melt density, melt proportion and volume of dense rock equivalent (DRE). Detailed calculation methods of the above-mentioned parameters are given in the references (Guo et al., 2002, 2003a, 2006). Maximum height of volcanic eruption column may be calculated by either isopleths of clast distribution (Guo et al., 2003c) or physical volcanologic modelling (Guo et al., 1998).

4 Effect of volatiles from Mesozoic volcanic activities on paleo-environmental changes in China

Main studies on the effect of volatiles from Mesozoic volcanic activities on paleo-environmental changes include the western Liaoning Province and Zhangjiakou volcanic field in China.

4.1 Effect of volatiles from Mesozoic volcanic activities in western Liaoning Province on paleo-environmental changes and mass mortalities of vertebrate

Field geological observations (e.g. Guo and Wang, 2002; Guo et al., 2003b, c; Jia et al., 2004) have indicated that fossil-rich layers, which were well-preserved in Mesozoic volcanic rocks, are records of mass mortality events of vertebrates in western Liaoning Province. Analytical results of volcanic volatile compositions indicated that the contents of volatiles released from the eruptions represented by volcanic deposits yielding the fossil-rich layers are much higher than those indicated by tuffs and tuffites of fossil-poor layers. Based on detailed studies on the compositions and concentrations, the volatiles emitted from volcanic activities have been subdivided into three types: (1) dominated by HF gas, (2) mainly composed of HCl gas, and (3) consisting mainly of sulfur-rich gases. Results show that volatiles with different compositions yielded the different paleo-environmental effects shown below. HF gas from volcanic activities resulted in the most lethal gas-related volcanic event in the volcano-induced fluorosis of livestock (Sigurdsson, 2000). More than one thousand primitive bird fossil specimens (e.g., *Confuciusornis*) have been found in the western Liaoning Province (NE China), almost all of which were preserved within two layers of the intermediate-acidic volcanic tuff that have the highest content of HF erupted as shown by microprobe analyses. Previous studies (e.g. Guo and Wang, 2002; Guo et al., 2003b) have indicated that the *Confuciusornis* fossils represent an important mass mortality event of primitive birds caused by high-HF-release volcanic activities. Volcanogenic HCl gas erupted into the stratosphere may lead to ozone depletion (Horn and Schmincke, 2004). Moreover, the HCl gas emitted into the atmosphere would result in acid rain, pollute plants and even collapse food chains (Wingnall, 2001). The biggest Mesozoic mass mortality event occurred in western Liaoning Province, indicated by the thickest tuff preserving almost all kinds of vertebrates (e.g., dinosaurs, turtles and fishes) and many invertebrates. This has been considered to result from unique volcanic activity which shows the highest content of HCl gas emissions (Guo et al., 2003c). Immediately after that, the heavy volcanic ash could fall down, rapidly burying the dead animals and plants, and preserve fossils in the tuff. Volcano-induced sulfur-rich gases would give rise to the decline in the Earth’s surface temperature and even generate a “volcanic winters” effect (Rampino et al., 1988) because the resultant sulfuric acid aerosols may affect radiation budget in the atmosphere (Li, 2000). Moreover, volcanogenic H_2SO_4 aerosols might destruct the ozone layer in the stratosphere (Brasseur and Granier, 1992; Wingnall, 2001). A large number of theropod dinosaur (including feathered dinosaur) fossils were preserved within the volcanic tuff, which erupted the highest contents of S-rich gases emitted

into the atmosphere (Guo et al., 2003c; Jia et al., 2004). Previous studies (Guo et al., 2003b, c) show that the mass mortality of cold-blooded dinosaurs resulted from the S-rich eruptions.

4.2 Effect of volatiles emitted from Mesozoic volcanic activities in the Zhangjiakou volcanic field, Hebei Province, Northeast China, on paleo-environmental changes

Based on the principle of igneous petrology and atmospheric environmental chemistry, we set up a new model that may estimate total mass of the volatiles and resultant aerosols caused by volcanic activities (Guo and Liu, 1998). The estimated results indicate that the Zhangjiakou Mesozoic volcanic activities could have erupted 85 Mt CO₂, 6.5 Mt H₂S, 36 Mt SO₂ into the atmosphere and possibly resulted in a 1%–4% decline of total solar radiation. The volcanic eruption would lead to a decrease in average surface temperature.

5 Effect of volatiles released from Cenozoic volcanic activities on paleo-environmental changes in China

5.1 Effect of volatiles from Cenozoic volcanic activities in south Tibet on paleo-environmental changes

On the basis of analyses of the volatile composition of melt inclusions trapped in phenocryst minerals in Cenozoic intermediate-acidic volcanic rocks in the southern part of the Tibetan Plateau, the effect of volcanic gases emitted from south Tibet on the surface temperature has been discussed (Guo, 1997). This is the first attempt to explore the effect of Cenozoic volcanic activities in the Tibetan Plateau on paleo-environmental changes in China.

5.2 Effect of volatiles from Cenozoic volcanic activities in the Shanwang volcanic field, Shandong Province, North China, on paleo-environmental changes

There are many well-preserved fossils (including animals and plants) located within the tuff-rich lake sediments in the Shanwang volcanic field, Shandong province, North China. The ages of the contemporaneous volcanic rocks range from 10 to 16 Ma (Chen and Peng, 1985; Jin, 1985; Chen et al., 1988). Previous studies (Wang and Si, 2002) have shown that the well-preserved fossils in Shanwang resulted from events of mass mortalities. Using electron microprobe analysis, Guo et al. (2007) determined that the concentrations of S, Cl, F and H₂O emitted into the stratosphere were 0.18–0.24 wt %, 0.03–0.05 wt %, 0.03–0.05 wt % and 0.4–0.6 wt %, respectively, which were S-rich volcanic activities. Previous works (Guo et al.,

2007) have supported a genetic link between the events of mass mortalities and the volatile-rich Miocene basaltic volcanism in the Shanwang volcanic field because a great amount of volcanic volatiles (e.g., SO₂, H₂S, HCl, HF and H₂O) injected into the stratosphere would have triggered abrupt paleo-environmental changes (including formation of acid rain, temperature decline and ozone depletion), ultimately forming well-preserved fossils in Shanwang.

6 Effect of volatiles from Mt. Changbai active volcano during a historical period on paleo-environmental changes in China

Mt. Changbai active volcano, located in the Jilin province of NE China, is the biggest active volcano in China. One of its biggest eruptions during the historical period has been considered to occur around 1000 years ago (Li et al., 2000; Wei et al., 2003). Comenditic volcanic ash erupted from this activity has been recognized in Japan (Machida and Arai, 1983). Earlier studies (Horn and Schmincke, 2000; Li and Liu, 2000; Guo et al., 2002) have analysed the contents of volatiles released, suggesting that the activity of Mt. Changbai active volcano 1000 years ago yielded a significant amount of volatiles (including Cl, F, S and water). Comparison of the concentration and total mass of the volatiles between the Mt. Changbai active volcano and most catastrophic active eruptions worldwide indicates that the Mt. Changbai volcanic eruption may have resulted in obviously paleo-environmental changes by ozone depletion, pollution of water and plants and a temperature decline because the volcano emitted much higher contents and total mass of volatiles than others in the world (Guo et al., 2002). Numerical simulation studies (Li et al., 1996; Wei et al., 1997) suggest that stratospheric aerosols formed by the Mt. Changbai volcanic eruption 1000 years ago may have significant effect on solar radiation. Recent studies (e.g., Guo et al., 2006) have indicated that the abundance of volatiles from the Mt. Changbai active volcano formed cycled variations, which showed decreasing contents of F, Cl and H₂O emitted and increasing contents of S erupted from early to late. This shows that the paleo-environmental effect of the Mt. Changbai active volcano was different from early to late during the eruption.

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