Chin.J.Geochem.(2010)29:212–216
DOI: 10.1007/s11631-010-0212-9

Modeling experimental study on weathering-leaching of Emeishan basalt and its relation with metallogenesis

WANG Fudong[1,2], ZHU Xiaoqing[1*], HAN Tao[1,2], and LI Zengsheng[1,2]

[1] *State Key Laboratory of Ore Deposit Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550002, China*

[2] *Postgraduate School of the Chinese Academy of Sciences, Beijing 100049, China*

* *Corresponding author, E-mail: zhuxqcas@sohu.com*

Received March 1, 2009; accepted November 18, 2009

Abstract The Emeishan basalt has a high Cu background value (170×10^{-6} on average), and thus provides a ore-forming material source for copper ores. The collected samples were exposed in basalt lavas of the third segment of the Emeishan basalt eruptive cycle. By using a set of automatically cycling glass apparatuses, weathering-leaching experiments by three kinds of rainwater on the collected samples were carried out in the open system (at normal temperature and normal pressure). The analysis results showed that the most intensive export of Cu occurred under acidic rainwater-induced weathering-leaching conditions, almost 2–3 orders of magnitude the export of Cu by modern air rainwater, and 1–2 orders of magnitude higher than the export of Cu by CO_2 rainwater. In addition, the total amount of Zn, Cu, U, Ni and Sr exported by acidic rainwater are greater than 1%. All this indicates that copper in the Emeishan basalt provided the copper source for Cu mineralization at the contact between the basalt and the Maokou Formation limestone at the bottom.

Key words Emeishan basalt; copper ore; weathering-leaching experiment; ore deposit

1 Introduction

Emeishan plume-hot spot metallogenesis is one of the hot subjects with which many scientists engaged in ore deposits. However, much has been reported concerning copper ores in association with the Emeishan basalt even up to now, but only a few research papers have been published in the research from the viewpoint of weathering-leaching processes. In this paper modeling experiments on the Emeishan basalt were carried from the viewpoint of supergene weathering-leaching processes and a discussion was given to the relations between weathering-leaching and basalt mineralization.

2 Geological background and the basis for modeling experiments

2.1 The Cu abundance values of the Emeishan basalt and three types of copper deposits associated with the basalt

The large igneous province (LIP) caused by Emeishan plume activities is widespread within the rhombus region bordering Sichuan, Yunnan and Guizhou provinces and it is one of the most important large igneous provinces formed during the Paleozoic throughout the world (Mahoney and Coffin, 1997). Rapid large-scale basaltic magma eruption brought about a large amount of ore-forming elements from the deep mantle upwards, resulting in relatively high background values of Cu for the Emeishan basalt (170×10^{-6} on average) (Yunnan Provincial Bureau of Geology and Mineral Resources, 1990; Guizhou Provincial Bureau of Geology and Mineral Resources, 1990), thus providing ore-forming material source for copper metallogenesis. Additionally, there are three types of Cu deposits in association with the basalt, i.e., (1) Sedimentary-type copper deposits occurring in the Upper Permian sedimentary rocks overlying the basalt; (2) hydrothermal-type copper deposits occurring in the basalt; and (3) weathering-leaching-type copper deposits occurring at the interface between the basalt and the Maokou Formation (Zhang Zhengwei et al., 2004).

2.2 Geological characteristics of the weathering-leaching-type copper deposits occurring at the

interface between the basalt and the Maokou limestone

2.2.1 Ore-host strata

The bottom of the Emeishan basalt is in unconformable contact with the underlying Maokou limestone. The basalt is dominated by tuff and amygdaloidal basalt while the Maokou limestone is a suite of strata consisting of light-grey marine thick-layered to massive limestones and dolomites. The contact between basalt and limestone is always the favorable locus of copper mineralization, for example, the Bingba Cu deposit in Guanling County, Guizhou Province. The copper deposit was further controlled by the paleo-weathering surface and second-ordered faults in the basalt (Fig. 1).

In addition, copper deposits of this type have also been discovered in Ganluo, Sichuan Province, for example, the Dawanhe copper deposit at Xinjian Town, and copper mineralization also occurs in the contact zone between the Lower Permian limestone and the Upper Permian basalt, and what is different is that the contact zone is more obviously controlled by faults (Fig. 2). Faulting led to fracturing and cracking of the limestone, and therefore, copper mineralization is distributed along the contact zone between basalt and limestone and the fissure planes of the limestone. Fault gouge is also relatively developed on the cracking zone, in which is observed pyrite which is perfect in crystal form. According to the regional geological survey report (1: 200000 scale), the ore grade is about 0.4%–1%. There is also found a minor amount of gold in blister copper.

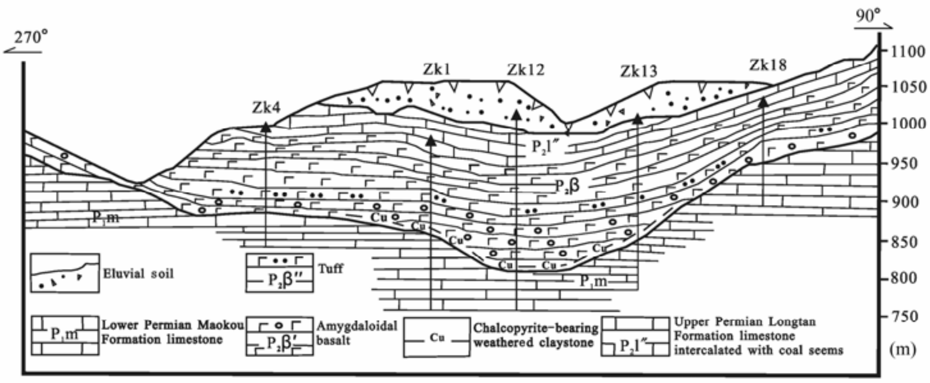


Fig. 1. Section of the Jiuwuji ore block of the Bingba copper deposit in Guanling County, Guizhou Province (after Chen Wenyi, 2003).

2.2.2 Characteristics of mineral assemblages

Cu-bearing sulfides in the copper ores of this type of copper deposits include chalcopyrite, bornite and tetrahedrite; secondary oxide minerals include azurite and malachite, also associated with pyrite. Following the oxidation of the ore, there would be more limonite. Gangue minerals are quartz, calcite, etc. The wall-rock alterations in close relation to copper ore enrichment are dominated by silicification, the degree of enrichment of copper is positively correlated with the intensity of silicification (e.g. the Bingba copper deposit in Guanling County), but has nothing to do with the type of basalt. That is to say, either in high-Ti or in low-Ti basalt regions there will be discovered the basalt-type copper deposits (Zhang Qian et al., 2006). Much better copper mineralization of the Dawan deposit at Xinjian Town, Sichuan Province is seen in the contact between basalt and limestone and in the limestone at the tope of the Lower Permian series, which occurs as vein-like, compact and asterism-shaped copper ores. In the overlying basalt is also noticed copper mineralization, which occurs as small lump- and nest-like ores. These copper ores are less better in quality than those occurring in carbonate rocks. Wall-rock alterations include silicification (the Bingba deposit), carbonation, calcitization and limontization (copper deposits at Xinjian Town).

2.2.3 Analysis of the metallogenic process

The formation of this copper deposit may be attributed to the weathering-transport of Cu-bearing basalt chippings, followed by resorting and accumulation as copper ore occurrences. Additionally, the wall-rock alterations of this deposit are dominated by silicifiction, and the enrichment extent of copper mineralization is positively correlated with silification. Then, deep-source Si- and alkali-rich ore-bearing hydrothermal solutions may impose late-stage reworking and superimposition toward copper ores. However, what the authors stressed here is the copper ore occurring in the contact between the limestone and the basalt, The ore-forming fluid was derived mainly from initial rainwater (Mao Jingwen et al., 2003). Acidic rainwater, in particular, infiltrated structurally weak zones (fault, cleavage fracture) or loose, well porous basalt, and leached out Cu ions. These Cu ions would be enriched as copper ores when they met with the minerals of strong absorbance (organic matter, clays). So, in this paper the following leaching modelling experiment will be made for further analysis.

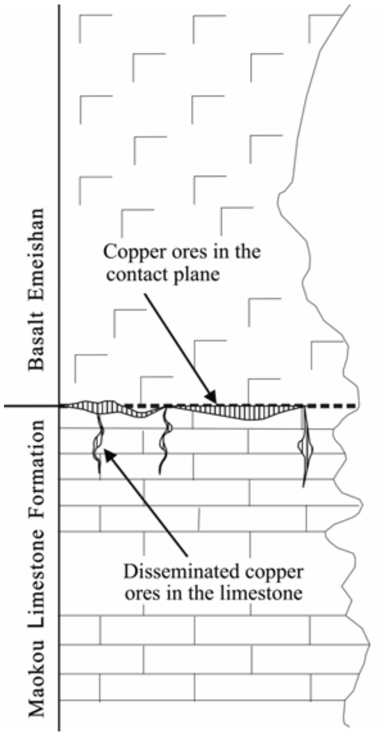


Fig. 2. Sketch showing the prismatic section of the Dawanhe copper deposit at Xinjian Town, Ganluo County, Sichuan Province.

3 Experimental method and procedure

The Emeishan basalt is characterized by such eruptive phases as marine, terrestrial and river/lake alternative phases, with multi-stage and multi-episodic cycle (Chen Wenyi et al., 2003). This indicates that the Emeishan basalt once experienced leaching and soaking by many kinds of rainwater. From the study of modern volcanic gases we can know the main components of volcanic gases formed in the process of degassing of the Emeishan basalt, including such intermediate-acid gases as Cl, HF, Cl_2, SO_2, etc. and such reductive gases as H_2, CO, CH_4, H_2S, etc. (Chen Fu and Zhu Xiaoqing, 1987), so as to consider that condensed water from early volcano-eruptive gases of the Emeishan basalt exhibited acidic and reductive properties. Secondly, during the intermittent period of eruption of the Emeishan basalt, due to the circulation of Earth's surface water, the acidic gases in atmosphere would be washed up and transported into seas by Earth's surface runoff, then the seawater would be evaporated into atmosphere. As a result, the pH of rainwater would be translated to CO_2-saturated and oxidizing rainwater conditions (Chen Fu and Zhu Xiaoqing, 1984), i.e., forming weakly acidic and slightly oxidative rainwater during the intermittent period of volcanic eruption. It can be known from this that From the eruption (269 Ma) and ending (251 Ma) of the Emeishan basalt eruption till today (Zhou Meifu et al., 2002; Lo Chinghua et al., 2002; Boven et al., 2002; Guo Feng et al., 2004; Xu Yigang et al., 2001), the basalt has experienced weathering-leaching by rainwater under three kinds of conditions: (1) the conditions of weathering-leaching by strongly acidic and reductive rainwater during Early volcanic degassing; (2) the conditions of weathering-leaching by weakly acidic and slightly oxidative CO_2-saturated rainwater during the intermittent period of volcanic eruption; and (3) the conditions of weathering-leaching by modern-air rainwater when the volcanic eruption came to the end.

3.1 Experimental equipment

A set of automatic cycling glass apparatuses were employed in the experiment (Cheng Fu and Zhu Xiaoqing, 1987, 1984). Three leaching columns (HCl, CO_2 and air) were prepared, with each of them consisting of three fractions: rainwater mixed, weathering-leaching and filtrate-evaporated fractions.

Rainwater mixed fraction: The instrument is a hollow counter-flow pipe through which water can pass (the rainwater synthesizer), with the aim to let vapor from the filtrate mix with the inlet gas (air/HCl/CO_2) to form rainwater which will circulate onto the sample so as to leach the sample.

Weathering-leaching fraction: The instrument is a multi-connector leaching glass tube (leaching column). The sample was put into the tume, and the upper half of the sample which is not soaked in the filtrate is called the rainwater infiltrating zone; the lower half of the sample which is always soaked in the filtrate is called the underground water leaching zone. Its upper orificium is linked with the rainwater synthesizer and its lower orificium is connected with Bunsen beaker.

Filtrate-evaporated fraction: This fraction consists of a Bunsen beaker and an electric furnace, with which the filtrate can be continuously heated and evaporized to let vapor mix with the in-let gas (air/HCl/CO_2) in the rainwater synthesizer and then condense as rainwater. The rainwater is then dropped into the weathering-leaching fraction, constituting a leaching cycle.

3.2 Experimental procedure

The experimental samples were basalt samples collected from Tianba (07-TB), Weining County, Guizhou. Lithologically, the samples are grey-greyish-green amygdaloidal basalt, and the sampling location is the third section of the Emeishan basalt eruption cycle. The chemical compositions of the samples are listed in Tables 1 and 2. The samples were crushed as fine as 9–10 mesh, and 120 g of each sample were taken and put into the HCl, CO_2 and air leaching columns for leaching. The experimental procedure is described as follows. Firstly, HCl, CO_2 and air were linked with the leaching apparatuses, then cooling water was let to flow in and heated. Till the distilled water in the beaker was boiled, CO_2 and HCl were put through, so as to let water vapor pass through the rainwater synthesizer by the side pipe and in the rainwater synthesizer the water vapor mixed with a certain amount of gas and was condensed as rainwater. Then, the rainwater was dropped into the weathering-leaching columns for circular weathering of rock samples for about 100–120 hours.

Table 1. Results of XRF analysis of major elements for primary Emeishan basalt (w_B/%)

		Analytical results								
Sample No.	Lithology	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O
7-TB	Basalt	48.54	2.99	12.87	16.18	0.196	4.83	6.39	3.41	0.418

Analysis unit: The State Key Laboratory of Ore Deposit Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences. The total iron is expressed as Fe_2O_3.

Table 2. Analysis data of metallic elements of primary Emeishan basalt ($\times 10^{-6}$)

Metallic element	Cu	Ni	Zn	Pb	Mo	Co	Sr	U
07-TB	366	57.2	170	14.2	3.59	76.6	172	1.28

Analysis unit: The State Key Laboratory of Ore Deposit Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences.

3. 3 Experimental results

After the experiment lasted for 15 hours, the three filtrates showed significant differences in color. Under the conditions of acidic rainwater the filtrate tended to become colorless and transparent to greenish-yellow, and reddish-yellow when the experiment came to the end; under the condition of CO_2 rainwater the filtrate tended to become colorless and transparent to bluish-green, the color changing from darker and darker with the continuation of the experiment; under the condition of modern air rainwater the filtrate showed no change in color from the beginning to the end of the experiment. The analysis data of filtrates are listed in Table 3.

According to the carry-over intensity formula given by previous researchers (Chen Fu and Zhu Xiaoqing, 1984), the exporting intensities of metallic elements brought out of the samples leached by different supergene waters can be worked out. The exporting intensities of metallic elements leached out of the Emeishan basalt under the action of weathering-leaching by three kinds of rainwater are given in Table 4.

$$K_x = \frac{a_x \cdot V \cdot 10^6}{A_x \cdot t \cdot M}$$

where K_x is the exporting intensity of an element (x), a_x is the content of this element in the filtrate ($\times 10^{-6}$), A_x is the content of this element in rock sample (μg/g), V is the total volume of the filtrate (mL), M is the weight of rock sample in the leaching column, and t is the leaching time (h).

Table 3. Analysis data of metallic elements in different filtrates obtained from weathering-leaching experiment

Characteristics of supergene water	Content of metals in filtrate ($\times 10^{-9}$)															
	Cu		Ni		Zn		Pb		Mo		Co		Sr		U	
Acidic rainwater pH<1	601.7	1230	86.9	187	342.4	486	4.98	4.99	2.78	4.98	125	132.1	2680	2750	0.535	11.8
CO_2 rainwater pH≈4.5	19.3	26.9	0.978	2.67	5.01	20.6	0.224	0.244	2.51	2.52	0.030	3.18	439	602	0.030	0.105
Modern rainwater pH≈6.5	0.337	3.2	0.141	0.869	4.89	5.11	0.050	0.224	1.99	2.21	0.076	0.350	34	147	0.006	0.019

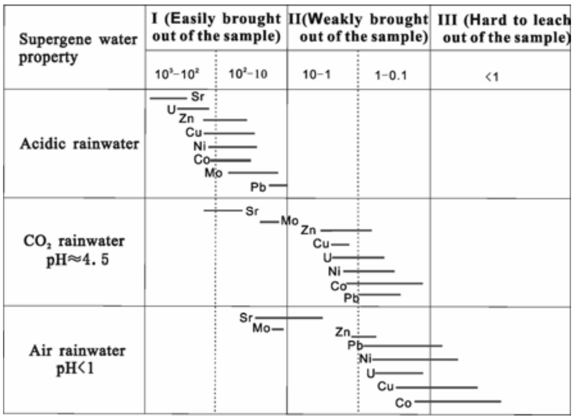
Analysis unit: The State Key Laboratory of Ore Deposit Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences.

4 Experimental results and discussion

During early basalt eruption, the conditions of weathering-leaching by acidic rainwater resultant from contamination of acidic volcanic gases are most favorable to the transport and enrichment of metallic elements. From Tables 2 and 3 metallic elements in the basalt copper ores are mostly leached out of the rock samples by acidic rainwater, whose total amount being greater than 1% (Zn 1%, Cu 1.1%, U 3%, Ni 1%, Sr 5%), but the amounts of Mo, Pb and Co leached out of the rock samples are one order of magnitude lower, more than 1‰. As can be seen from Table 4, the conditions of weathering-leaching by acidic rainwater resultant from contamination of volcanic gases are most favorable to strongest weathering-leaching of the Emeishan basalt, hence it is easiest to form ore-bearing solutions. The ore-forming elements brought out of the basalt by such solutions are as high as 2–3 orders of magnitude those by modern air rainwater and 1–2 orders of magnitude those by

CO_2 rainwater. The lower the pH of rainwater is, the higher the export intensity of elements will be. Obviously, the conditions of weathering-leaching by acidic rainwater play an important role in the mobilization and migration of these elements and the formation of ore deposits, and these conditions are corresponding to both volcanic degassing stage and later initial volcanic intermittent period. What was earliest leached out by modern air rainwater are not metallic elements, but halogen elements (Zhu Xiaoqing et al., 2005). The above phenomena indicate that in the long geological metallogenesis acid-alkaline environments play a role which can not be ignored in metallogenesis. In addition, as viewed from the colors of the three kinds of leaching filtrates, under acidic rainwater conditions the filtrate will change from colorless to yellow, with the color progressively darkening, indicating that the contents of Fe ions tend to increase continuously.

Table 4. Comparison of exporting intensities of elements under weathering-leaching of the Emeishan basalt by different rainwaters



Although modeling weathering-leaching experiments were accomplished in an open system, as viewed from the modeling results, the process of weathering-leaching-type copper metallogenesis on the interface between the basalt and the Maokou limestone can be well explained, i.e., the various kinds of rainwater resultant from Emeishan basalt eruption infiltrated structurally weak zones (faults, cleavage fractures) or loose and well porous basalts, and leached out Cu ions. Those Cu ions, in the case of encountering with minerals (clay, organic substances) of strong adsorbability, would be enriched to form copper ores in the favorable geological loci (faults, contact zones).

Acknowledgements Financially supported jointly by "National Basic Research Program of China (973) Program) (2007CB411401) and the National Natural Science Foundation of China (Grant No. 40773035).

References

Boven A., Pasteels P., Punzalan L.E. et al. (2002) $^{40}Ar/^{39}Ar$ Geochronological constrains on the age and evolution of the Permo-Triassic Emeishan volcanic province, Southwest China [J]. *J Asian Earth Sciences*. **20**, 157–175.

Chen Fu and Zhu Xiaoqing (1987) Study on the evolution of supergene weathering-leaching and the capability to provide ore-forming materials to sedimentary ore deposits [J]. *Geochimica*. (4), 341–350 (in Chinese with English abstract).

Chen Wenyi, Wang Zhonggang, and Liu Jiaren (2003) Permian lithofacies paleogeography of Guizhou and its relations to sedimentary ore resources [J]. *Acta Paleogeographica Sinica*. **5**, 17–27 (in Chinese with English abstract).

Cheng Fu and Zhu Zioaqing (1984) Modeling experiment on banded Fe-Si formation resultant from paleo-weathering-leaching of basalts [J]. *Geochimica*. (4), 342–349 (in Chinese with English abstract).

Guizhou Provincial Bureau of Geology and Mineral Resources (1990) *Guizhou Regional Geology* [M]. pp.531. Geological Publishing House, Beijing (in Chinese).

Guo Feng, Fan Weiming, Wang Yuejun et al. (2004) When did the Emeishan Mantle Plume activity start? Geochronological and geochemical evidence from ultramafic-mafic dikes in southwestern China [J]. *International Geology Review*. **46**, 226–234.

Lo Chinghua, Chung Sunlin, Lee Tungyi, and Wu Genyao (2002) Age of the Emeishan flood magmatism and relations to Permian-Triassic boundary events [J]. *Earth Planet. Sci. Lett*. **198**, 449–458.

Mao Jingwen, Wang Zhiliang, Li Houmin et al. (2003) Carbon isotopes of copper deposits in the Permian basalts of the Ludian area, Yunnan Province and their significance in indicating metallogenesis [J]. *Geological Review*. **49**, 610–615 (in Chinese with English abstract).

Mahoney J.J. and Coffin M.L. (1997) *Igneous Province: Continental, Oceanic, and Planetary Flood Volcanism* [M]. AGU Geophysical Monography. **100**, 438.

Xu Yigang, Chung Sunlin, Jahn Bor-ming, and Wu Genyao et al. (2001) Petrologic and geochemical constraints on the petrogenesis of Permian-Triassic Emeishan flood basalts in southwestern China [J]. *Lithos*. **58**, 145–168.

Yunnan Provincial Bureau of Geology and Mineral Resources (1990) *Yunnan Province Regional Geology* [M]. Geological Publishing House, Beijing (in Chinese).

Zhang Qian, Zhu Xiaoqing, and Zhang Zhengwei (2006) Lead isotopic composition and lead source of the Tongchanghe basalt-type native copper-chalcocite deposit in Ninglang, western Yunnan, China [J]. *Chinese Journal of Geochemistry*. **25**, 112–121.

Zhang Zhengwei, Cheng Zhandong, Zhu Bingquan et al. (2004) The studies on the specific strata of Emeishan basalts formation are relationship with the copper-mineralization [J]. *Acta Geoscientica Sinica*. **25**, 503–508 (in Chinese).

Zhou Meifu, Malpas J., Song Xieyan et al. (2002) A temporal link between the Emeishan large igneous province (SW China) and the end-Guadalupian mass extinction [J]. *Earth Planet. Sci. Lett*. **196**, 113–122.

Zhu Xiaoqing, Huang Yan, Zhang Qian, He Yuliang, and Zhu Chaohui (2005) A simulating experiment on the geochemical variation trend at the initial period of meteoric waters converting to underground waters and ore fluids [J]. *Chinese Journal of Geochemistry*. **24**, 306–315.