

## Study on the chemical weathering of black shale in northern Guangxi, China

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### Abstract

The black shale rocks are widely distributed in northern Guangxi, China. Some engineering problems are caused by the black shale chemical weathering, in which pyrite oxidation plays important role in the process. The identification of minerals and chemical constituents as well as the observation of submicroscopic morphology was conducted to provide insight into the nature of the black shale rock. Comparing to the materials produced by the black shale weathering in the field and laboratory, it is evidenced that the acid solution and Fe-sulfate minerals as the same weathering products have significant effects on the rock's properties and ecological environment.

**Keywords:** Black shale, Chemical weathering, oxidation

### 1. Introduction

Black shale weathering is typical geological processes dominant by chemical weathering. The sulfide minerals contained in the black shale can be oxidized to produce corrosive acidic water and some minerals, such as gypsum and jarosite with poor engineering property in the oxidation environment. Therefore, the black shale is one of the typical strata which can cause engineering problems (Chigira and Oyama, 1999; Zheng et al, 2007). The Cambrian black shale is widely distributed in Guizhou, Hunan and Guangxi regions, China. The Qingxi formation black shale as one type of Cambrian black shale is turbidity deposition mainly distributed in the northern Guangxi region. Some previous studies have been conducted to understand the causes of ore-forming, petrological and geochemical characteristics of the Cambrian black shale in northern Guizhou and western Hunan regions (Wei et al, 2006; Liao et al, 2013). In this paper, the mineralogy, chemical composition, sub-microstructure and water-rock interaction characteristics of the Qingxi

formation black shale are studied to reveal its chemical weathering features.

### 2. Geological setting

The study area is located in the Sanjiang county, Guangxi province (Fig. 1). It is the hilly area with some mountains and less flat ground, where the terrain tilts from north to south. The Qingxi formation strata are mainly carbonaceous shale, black shale and carbonaceous siliceous shale with gray-black laminate or lenticel limestone interlayer in the Rongshui and Quanzhou counties; In the Rong'an area, gray and black carbonaceous shale and sandy shale are in the lower part, gray-black fine-grained quartz sandstone, black shale and sandy shale with a small amount of lenticel limestone are in the middle and upper parts, while the black carbonaceous shale is in the top part. On the whole, the Qingxi formation strata show decrease in sandy and siliceous rocks and increase in shale and carbonaceous shale from southeast to

northwest on the cross section (Xiang, 1999).

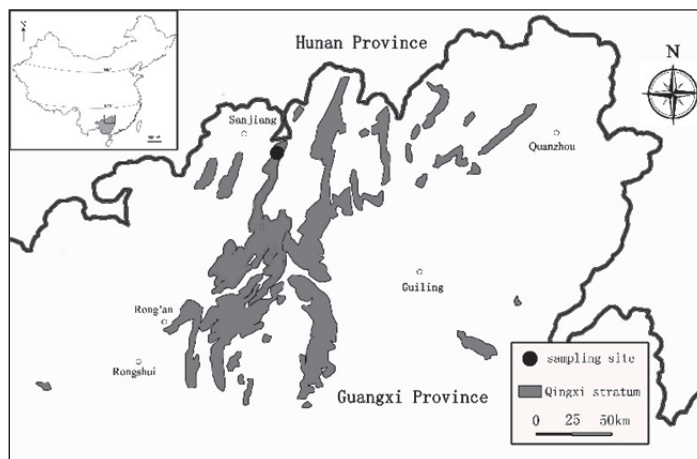


Fig. 1 Distribution map of cambrian Qingxi Formation in Guangxi

### 3. Sampling and methods

The Qingxi formation black shale samples were collected at the outcrop near a power station (Fig. 2). Some fine-grained quartz crystal particles are visible from the dark black and hard rocks. The pyrite particles were found rich along the bedding plane or accumulated to pyrite nodule locally. The sedimentary structure is parallel bedding showing laminated structure. Seven rock samples were collected from slightly weathering to fresh. Two precipitates occurred on the rock surface and two fissure water sample were collected as well.

Four samples including two black shale rocks and two weathering precipitates were selected to grind less than 200 mesh. Mineral analyses were conducted with

X-ray diffraction (XRD; Rigaku Geigerflex RAD-IIB) using Cu Ka radiation at 20 kV and 50 mA from 3° to 40°. The scanning speed is 2°/min and the stepper angle is 0.1°. Chemical analyses were conducted with an X-ray fluorescence spectrometer (ARL Advant' XP). Seven rock samples including slightly weathered (SW) and relative fresh (RF) shale were chosen for analysis. The rock powder samples after grinding were pressed into piece. Polished thin sections of black shale were analyzed by scanning electron microscopy (SEM; HITACHI S3500). The hydrochemical analyses were conducted with the inductively coupled plasma mass spectrometry (ICP-MS) for the water samples under the conditions of 23°C and humidity 53%.



Fig 2. Outcrop in the study area

(Note: 1#、2#、3#—rock sampling location, 4#—white precipitate, 5#—yellow precipitate, A、B—water samples)

## 4 Results

### 4.1 Mineralogy

The mineral analysis results determined by XRD were shown in Table 1. Black shale samples were mainly consist of illite, muscovite, quartz and small

amount of pyrite. The white weathering product was mainly rozenite ( $\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$ ) and small amounts of illite, quartz, pyrite as well as trace amounts of jarosite and gypsum. The yellow weathering product was mainly copiapite ( $\text{Fe}^{2+}\text{Fe}^{3+}_4(\text{SO}_4)_6(\text{OH})_2 \cdot 20\text{H}_2\text{O}$ ) and small amount of quartz, ferricopiapite, jarosite and magnetite.

#### 4.2 Chemistry

The results of the chemical analyses are reported in Table 2. It is shown that the highest major element is  $\text{SiO}_2$  ranging from 67.0 to 74.5%. The following is  $\text{Al}_2\text{O}_3$  and  $\text{K}_2\text{O}$  ranging from 12.0 to 14.0% and 4.2 ~ 5.1%, respectively. The content of  $\text{Fe}_2\text{O}_3$  and  $\text{MgO}$  are close, ranging from 0.5 to 2.6% and 0.5 to 2.6%, respectively. The contents of other chemical components are relative lower.

#### 4.3 Sub-microscopic observations

The sampled two weathering products were observed using the SEM. The copiapite is triclinic and parallel double-side crystal. The structure of the single

crystal is tabular, flaky or granular, which cleavage surface can be clearly visible with the magnification of 2000. The diameter and thickness of the flaky crystal is 3-5 $\mu\text{m}$  and 0.3 $\mu\text{m}$ , respectively. Generally, the crystal is quite small and can aggregate into sulfur-yellow to lemon-yellow powdered or hemispheric particle (Fig 3.a). The rozenite is monoclinic and its crystal structure is tabular with the thickness of 2-3 $\mu\text{m}$ . The crystal can aggregate into white sheet and granular powders with quantities of interior pores (Fig 3.b). The white aggregates have glassy luster and white Stripes by naked eyes.

#### 4.4 Hydrochemistry

The hydrochemical analyses results are shown in Table 3. The pH value of the water samples were about 2.5 which indicated the solution was strongly acidic. The total salinity was between 3 ~ 10 g/L on behalf of moderate mineralized water. Thus, the type of the water samples were  $\text{SO}_4^{2-}-\text{Fe}^{2+/3+}$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ . Besides, the content of the sulfate and total iron ions were very high, which was inferred to be the result of the pyrite oxidation.

Table 1 Mineral composition of the samples

Sample	Illite	Muscovite	Pyrite	Copiapite	Rozenite	Jarosite	Gypsum	Magnetite
RF	++	+	-	(*)	(*)	(*)	(*)	(*)
SW	++	+	-	(*)	(*)	(*)	(*)	(*)
WP	-	(*)	-	(*)	++	--	--	(*)
YP	(*)	(*)	(*)	++	(*)	-	(*)	-

SW: slightly weathered. RF: relative fresh. WP: white precipitate. YP: yellow precipitate

++: abundant, +: medium, -: small amount. --: trace amount. (\*): none. Quartz is contained in all samples.

Table 2 The major element contents of the Qingxi Formation black shale

Sample	$\text{SiO}_2$	$\text{Fe}_2\text{O}_3$	$\text{Al}_2\text{O}_3$	$\text{CaO}$	$\text{MgO}$	$\text{K}_2\text{O}$	$\text{Na}_2\text{O}$	$\text{P}_2\text{O}_5$	$\text{TiO}_2$	$\text{MnO}$	$\text{SO}_3+\text{S}$
RF1	74.53	0.57	12.11	0.30	1.31	4.26	0.05	0.00	0.70	0.10	0.09
RF2	68.56	0.61	12.03	2.88	1.28	4.36	0.05	0.00	0.79	0.25	0.09
SW1	66.98	1.80	13.97	0.07	1.33	5.04	0.05	0.06	0.77	0.10	0.19
SW2	67.29	2.00	13.52	0.78	1.38	5.07	0.07	0.04	0.71	0.16	0.61
SW3	67.45	2.29	13.50	0.09	1.34	4.97	0.04	0.09	0.69	0.14	0.17
SW4	67.02	2.56	13.64	0.10	1.32	4.99	0.05	0.10	0.76	0.09	0.19
SW5	67.35	2.60	13.26	0.24	1.33	4.78	0.09	0.05	0.68	2.19	0.49

SW: slightly weathered. RF: relative fresh.

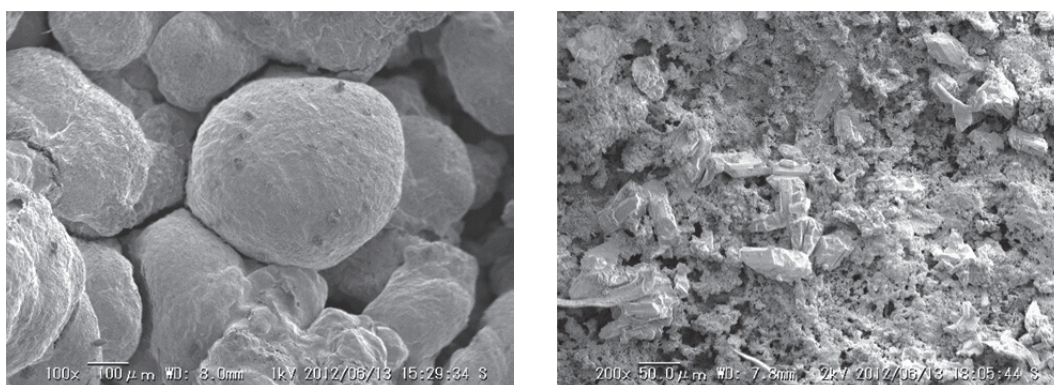


Fig 3. Representative SEM micrographs of weathering products. a) copiapite, b) rozenite.

Table 3. Chemical compositions of fracture water unit: (mg/L)

Sample	CO <sub>3</sub> <sup>2-</sup>	Cl <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	SiO <sub>2</sub>	HPO <sub>4</sub> <sup>2-</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	K <sup>+</sup>	Na <sup>+</sup>	Al <sup>3+</sup>	TFe	pH
A	0.00	<2	5977	99.5	0.40	114	265	1.11	0.61	377	1367	2.46
B	0.00	<2	2234	32.4	0.61	51.6	33.4	1.15	0.39	69.3	678	2.43

## 5. Half-immersion test in laboratory

### 5.1 weathering behaviors under laboratory observation

The indoor half-immersion experiment lasted about six months. Because the experimental time was between autumn and winter, the temperature and humidity ranged about 8 ~ 28 °C and 60 ~ 70% in the laboratory. The samples were placed in a transparent plastic vessel and immersed in deionized water. The immersion height was about one-third to one-half of the height of the samples. After the water level was below the tick line about 1/3 by evaporation, deionized water was supplied to return to the initial water level.

From the morphological observations on the side and cross profiles after the experiment (as shown in Fig. 4), it is shown that yellow and white precipitates occurred in patches on the upper surface exposed to air and yellowish-brown precipitate formed on the lower surface immersed in water under the influence of water-rock interactions. Furthermore, the yellow and white precipitates were examined to be copiapite and rozenite by XRD. Both of them were soluble and

produced in strong acidic environment. The yellowish-brown precipitate was inferred to be iron oxides and hydroxide, which were produced by ferric ion hydrolysis and attached on the rock surface. The significant differences between the upper and lower rock surfaces were that there were many visible white quartz minerals but no copiapite or rozenite on the lower rock surface. Besides, it is also worth noting that the immersion solution gradually changed from near neutral to strongly acidic during the whole half-immersion period.

### 5.2 Electrical conductivity and pH

The pH and electrical conductivity (EC) of the immersion solution were measured at the interval of one day after 7 days. The results showed the immersion solution was acidic and the pH ranged from 2.4 to 4.0. The EC values ranged from 0.09 to 1.63 mS/cm. Based on the correlation analysis of these two parameters, it was indicated that they showed exponential relation in the half-immersion process (Fig. 5).

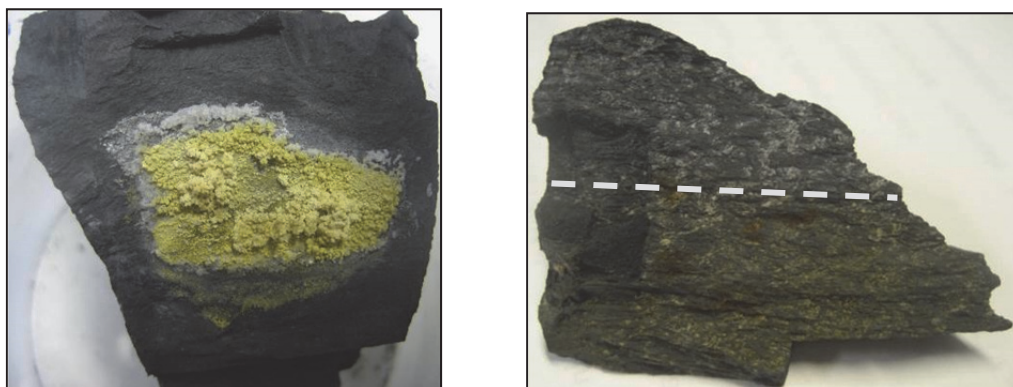


Fig 4. Weathering phenomenon after half-immersion. a) weathering products on the rock surface exposed in the air; b) the profile represented for the rock surface above and under the water level (the dashed line).

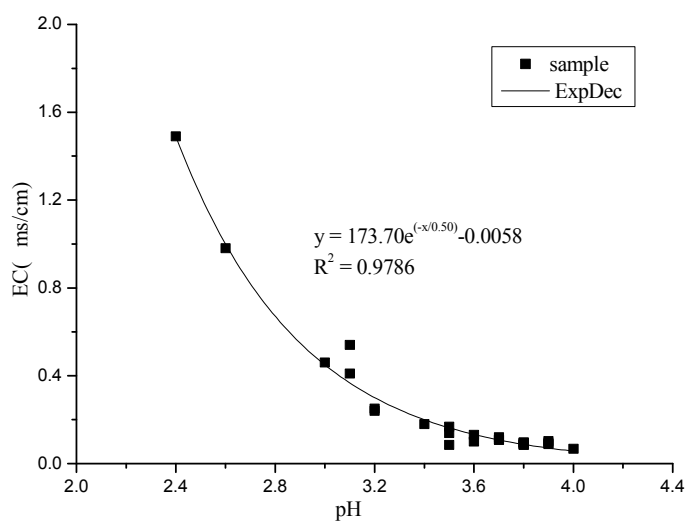
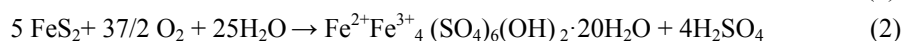
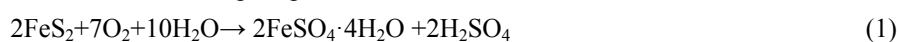


Fig 5. The pH - EC relations of the immersion solution

## 6 Discussion and conclusions

### 6.1 Black shale weathering process and products

Based on the mineralogical and chemical analysis, it indicates that the sulfide mineral is mainly pyrite. The iron and sulfur element content increases with the development of weathering. It is inferred that the iron and sulfate ions produced by the water-rock interaction of the fresh shale migrate upwards under the capillary effects of the pore water. Therefore, the two elements content in the weathered rock samples were relative higher than that in the fresh rock samples. From the chemical formula of the yellow copiapite and white rozenite, it shows the two precipitates are both ferrous



sulfate minerals. Generally, they are prone to precipitate on the rock surface at outcrop, where the rocks are rich in the pyrite or marcasite particles (Jambor et al, 2000). It is speculated that they may originate directly from pyrite in study area. The overall reaction can be represented as equation (1) and (2).

In addition, with the development of the external condition and reaction process, the sulfate ions produced by pyrite oxidation could react with the other element in rocks or other ions contained in the underground water to form different kinds of sulfate minerals, such as the jarosite and gypsum.

## 6.2 The acidic environment and its engineering impact caused by the black shale weathering

Sulfide minerals as one of the important components of the black shale, could produce strong corrosive acid water through hydrolysis, oxidation and free organic acids during the oxygen-rich surface water leaching process. This acidification could bring argillization and failure to the rock masses. Based on the hydrochemical analysis of the water samples collected in the field, the pH - EC relationship of the immersion solution and the reaction formulas (1) and (2), the chemical weathering of black shale is an acid producing process which has been proved by previous studies (Lowson, 1982; Nesbitt et al, 1998; Yue et al, 2004; Liao et al, 2014). It is noteworthy that the electrical conductivity and pH values have no obvious mathematical relation. Because the EC value is relevant to the property of the ions and pH value only reflects the concentration of the hydrogen ion. However, the pH and EC values have exponential relationship for our immersion solution. It is inferred on one hand, the evaporation caused the hydrogen ion concentration increasing and pH value decreasing so that the EC value increases correspondingly. On the other hand, the hydrogen ion produced by pyrite oxidation reacts with the clay minerals to release more soluble ions, which makes EC value increase. Besides, the exponential relationship between the pH and EC value might be associated with the ionization equilibrium constant of the reaction products as well (Shi et al, 2013). The detailed mechanism should be further studied.

On account of the fast neutralization and decomposition of the acidic water, the quick changes in rock's composition and structure cause by acidic corrosion not only occur in the rock itself, but also prompt the corrosions to the adjacent rocks and relevant construction material. These effects could bring a series of engineering problems (Pye and Miller, 1990). What's more, the various products formed by black shale weathering have adverse effect on the rock mass integrity and engineering mechanical property as well. First, the sulfate minerals such as jarosite, copiapite and gypsum produced by the chemical weathering of the black shale have

remarkable swell-shrink characteristics as the crystal water gained and lost in the wet-dry cycling environment. These minerals generally occur on the fissure surface, which can cause constant expansion of the micro-cracks. Second, the acidic water can react with the feldspar minerals to produce clay mineral so that it could reduce the mechanical strength of the rocks.

Therefore, the study of the chemical weathering of the black shale makes an important theoretical and practical significance to the reaction mechanism itself and the evaluation of influence on the engineering constructions.

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