Weathering characteristics of the Lower Paleozoic black shale in northwestern Guizhou Province, south China

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The northwestern Guizhou in the Yangtze Craton of south China has a tremendous potential of shale gas resource. In this paper, we present results from major and trace elements, total organic carbon, mineralogical composition analysis and petrophysical parameters to characterise shale weathering features. Further, the differences of black shale between underground and outcrops have also been presented to examine the changes of black shale after weathering. Our results show that the trace elements of shale have varying degrees of loss in the weathering leaching process, both in Niutitang shale and Longmaxi shale, the loss of B, V, Ni, Cu, Zn and Ba is obvious, but the element migration quantity in the former is greater than in the latter. Decomposition of minerals such as pyrite, feldspar and calcite result in the leaching of Na, Ca, Mg and Fe. The loss rate of total organic carbon (TOC) in black shales ranges from 18% to 70% with an average of 43%; moreover, the loss of organic carbon in samples with high TOC content is larger than in those samples with low TOC content. Results following the testing of porosity and permeability show that porosity increases significantly after weathering but permeability changes little. Furthermore, the increment of porosity is greater in the Niutitang shale (with more sulphide minerals) than in the Longmaxi shale, suggesting that the oxidation of sulphide minerals may have led to the formation of an acidic environment, causing the other minerals in the black shale to weather more quickly, thus resulting in increased porosity. The content of clay minerals in the core samples is slightly lesser than the outcrop samples, but the TOC content in the core samples is greater and has a larger specific surface area. This suggest that the TOC content played a decisive role on the specific surface area of shale. In addition, changes in the black shale caused by the weathering process mainly depend on the mineral composition and the TOC content in shale. In this study, we try to establish relations between outcrop samples and core samples, in order to better understand the underground characteristics of shale reservoir.

1. Introduction

Shale gas refers to natural gas that typically accumulates in an adsorbed or unbound state, which is mainly found in black shale or carbonaceous shale

(Curtis 2002; Chen *et al.* 2003; Zhang *et al.* 2003, 2004, 2007; Li *et al.* 2007). The shale gas in North America is developing very rapidly with the breakthrough of horizontal wells and the staged fracturing technology (Huang *et al.* 2009), so the strategic

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position of shale gas resources is paid great attention gradually. Shale gas also has good development prospects in China and the resource is about twice as many the continental conventional natural gas resources (Yan *et al.* 2009; Zou *et al.* 2010). The marine facies, Paleozoic black shale, in Yangtze Craton has good hydrocarbon generation and shale gas reservoir conditions, which is the most famous shale gas production area in China, at present. The Niutitang shale in the Lower Cambrian and the Longmaxi shale in the Lower Silurian, on the other hand, have the most enriched shale gas formation (Jia *et al.* 2012). Geologic reserves of shale gas in the Guizhou province is $10.48 \times 10^{12} \text{ m}^3$ and account for 12.8% for the whole China, which has a tremendous potential as shale gas resource (Wu *et al.* 2012).

Black shales, with a wide global distribution, were often deposited in relatively deep, anoxic ocean basins (Horan *et al.* 1994; Tuttle and Breit 2009), where sediments accumulated, often times, very slowly. As such, black shales usually have a high content of organic carbon and sulphides and are important hosts for a remarkable array of ore metals such as Co, Ni, V, U, Mo, Mn, P, and the PGE (platinum group elements) (Horan *et al.* 1994; Mao *et al.* 2002; Jiang *et al.* 2006). Because of their high organic carbon and sulphide contents, black shales are susceptible to alteration when exposed, and thus mining in shales throughout the world has

accelerated the weathering of these sedimentary rocks. The weathering of black shale is an important environmental concern because of the dispersion of toxic metals hosted by the shales, the production of acid mine drainage – which can harm the ecosystem due to oxidation of sulphides (Peng *et al.* 2004, 2009a), and the release of CO_2 , which may contribute to the global carbon cycle (Petsch *et al.* 2000, 2001; Jaffe *et al.* 2002). Oxidative weathering of black shales produces CO_2 and releases many redox-sensitive trace elements (RST) U, Re and Mo into rivers. Therefore, this process contributes significantly to atmospheric CO_2 budgets in geological time scale as well as RST and their isotope budgets in the oceans, as some of them are used as paleo-oceanographic proxies (Dalai *et al.* 2002; Jaffe *et al.* 2002). The weathering of black shale has therefore received substantial research attention, especially the chemical changes during weathering (Littke *et al.* 1991; Jaffe *et al.* 2002; Tuttle and Breit 2009; Tuttle *et al.* 2009). Such chemical changes are generally explained by mineral dissolution, secondary mineral formation, cation exchange and loss and gain of amorphous oxide phases (Tuttle and Breit 2009).

Most of the weathering process includes physical and chemical weathering, but physical weathering often occurs only near the surface while chemical weathering can extend to the range of hundreds

Figure 1. (a) The location of the northwestern Guizhou area within the Yangtze Craton. (b) Geological sketch map of the northwestern Guizhou Province.

of meters below the surface (Chorley 1969). Black shales have become the focus of many weathering studies because they contain phases such as sulphides and organic matter that host elements of environmental concern (Petsch *et al.* 2000; Jaffe *et al.* 2002; Peng *et al.* 2004, 2009). During weathering, these phases are easily altered, releasing contaminants into the environment where they are transported from the site or fixed in secondary weathering products. Semi-arid and arid climates play a key role in the accumulation of soluble weathering phases, providing large reservoirs of easily mobilised contaminants to watersheds and their rivers when hydrologic or climatic conditions change. However, the weathering of black shale, as the shale gas reservoir, has not been reported as yet and a comparison of the black shale between outcrops and underground has also not been tried.

In this paper, we present the geochemistry, mineralogical composition and petrophysical parameters data of black shale to understand the significant change on its organic and inorganic features such as lithological and mineral composition after weathering. We also attempt to evaluate the distinction and establish the relationship between the black shale from underground and those from outcrops. This is conducive to restore the original features of the strata from outcrop data, thereby guiding the exploration of shale gas.

2. Regional geological setting

The Guizhou province is located at the southwestern margin of the Yangtze Craton. This area is covered by the strata from Mesoproterozoic and Neoproterozoic to Quaternary, which is mainly marine sedimentary. Sedimentary strata of middle to Upper Proterozoic are dominated by marine terrigenous clastic rocks, pyroclastic rock and carbonatite, Paleozoic to Middle-Upper Triassic are mainly composed of marine carbonate and clastic rocks, Middle Triassic are mainly terrigenous clastic rocks (figure 1) (Fu *et al.* 2008; Liu *et al.* 2008; Zhang *et al.* 2009; Dong *et al.* 2009; Huang 2009; Nie *et al.* 2011).

Northwestern Guizhou is mostly located in Guizhou uplift zone which is one of the east-west uplift belts in Yangtze Craton is formed in the early Paleozoic. The exposed stratigraphic sequence in this area mainly consists of Cambrian, Ordovician, Silurian, Carboniferous, Permian, Triassic, Jurassic, and Quaternary units. During Cambrian to Middle Silurian time, the region experienced a large transgression-regression cycle influenced by the initial stage of Caledonian movement. This transgression-regression cycle resulted in the deposition of Cambrian to Silurian strata in this area

(Guizhou Provincial Geological Survey Bureau 1987). Because of NNE-directed compression in this region, NNE-trending anticlines, synclines and faults are ubiquitous. The black shales, usually cut by faults and fractures, are strictly controlled by anticlines and synclines (figure 2). The oldest rock in the area is the Upper Sinian of the Doushantuo Formation. The Ordovician consists of dolomite, limestone and argillite and is overlain by the lower-Middle Silurian, which is composed of black or greyish green shales with intercalated sandstones and siltstones. During Upper Silurian to Upper Carboniferous time, a drop in the sea level led to an epeirogenic phase that exposed the Silurian to intense weathering (Guizhou Provincial Geological Survey Bureau 1987). There are no outcrops of Upper Silurian, Devonian or Lower to

System	Series	Group	Lithology
Permian	Upper	(P ₂)	Limestone Shale
	Lower	(P ₁)	Limestone Coal
Silurian	Middle	(S ₂)	Shale Limestone
	Lower	Shiniulan(S _{1sn})	Limestone
		Longmaxi(S _{1lm})	Shale
	Upper	(O ₃)	Shale Limestone
Ordovician	Middle	(O ₂)	Limestone
	Lower	(O ₁)	Siltstone Limestone
Cambrian	Upper	(Є ₃)	Limestone
	Middle	Gaotai(Є _{2g})	Dolomite
	Lower	Qingxudong(Є _{1q})	Limestone
		Jindingshan(Є _{1j})	Siltstone
		Mingxinsi(Є _{1m})	Silty Shale
		Niutitang(Є _{1n})	Shale
Sinian	Upper	Dengying(Z _{6dn})	Dolomite
		Doushantuo(Z _{6d})	Shale

Figure 2. Lithological and stratigraphic system of north-western Guizhou area.

Table 1. Major and trace elements of the black shale in northwestern Guizhou area.

Sample sources	Sample ID	Trace elements content (μg/g)										Major elements content (%)							TOC	
		B	V	Cr	Ni	Cu	Zn	Ga	Sr	Ba	SiO ₂	Na ₂ O	MgO	K ₂ O	CaO	Fe ₂ O ₃	Al ₂ O ₃	(%)	CIA	
Outcrop of Longmaxi shale	LMX-1	104	98	66	99	71	136	23	42	778	51.9	0.2	0.6	2.5	0.2	2.1	9.2		73	
	LMX-2	95	296	58	74	49	108	21	39	721	56.4	0.2	0.6	2.0	0.1	2.2	8.0		75	
	LMX-3	91	248	68	59	44	76	19	48	767	54.3	0.3	0.5	1.9	0.2	2.2	7.8		74	
	LMX-4	42	194	59	33	21	56	20	36	742	55.8	0.1	0.5	2.1	0.1	1.0	8.2		76	
	LMX-5	138	187	63	59	50	92	25	193	437	61.8	0.3	2.2	2.0	6.1	3.0	10.1		76	
	LMX-6	98	182	71	71	48	98	23	161	456	58.2	0.4	1.2	2.2	3.8	2.1	8.4	2.3	70	
	LMX-7	98	179	82	57	48	86	27	136	518	59.8	0.3	1.0	2.5	2.5	2.1	9.3		71	
	LMX-8	92	205	74	65	42	95	26	140	179	52.9	0.4	1.4	2.4	3.9	2.5	9.1	2.03	70	
	LMX-9	96	189	70	69	43	100	28	150	388	56.8	0.3	1.2	2.4	3.4	2.4	9.3		71	
	LMX-10	85	115	58	34	39	51	24	95	215	57.3	0.3	1.0	2.4	2.4	2.5	9.2	2.05	73	
	LMX-11	175	161	90	48	39	91	32	138	328	56.0	0.6	1.7	3.1	2.7	4.0	10.9		66	
	LMX-12	117	152	91	43	40	78	29	99	149	51.9	0.7	1.6	3.2	2.0	3.3	11.2	0.92	67	
	LMX-13	133	121	77	33	26	64	29	189	300	40.8	0.7	2.1	2.7	3.8	3.1	10.0	0.35	65	
	LMX-14	112	115	88	29	23	57	28	90	384	45.7	0.8	1.6	3.1	1.3	2.9	12.1	0.18	67	
	LMX-15	126	114	83	30	24	68	28	106	255	66.1	0.7	1.7	3.2	1.9	3.3	12.3	0.17	68	
	LMX-16	143	125	92	30	26	68	28	102	482	54.0	0.7	1.8	3.2	1.8	3.5	12.2	0.2	68	
	LMX-17	141	132	98	31	31	95	32	106	429	58.3	0.6	2.0	3.4	1.8	3.6	12.5	0.18	69	
	LMX-18	169	145	102	29	27	76	34	90	629	55.5	0.4	2.1	3.7	1.3	4.1	14.7	0.06	73	
	LMX-19	170	138	79	28	31	92	33	106	521	64.7	0.3	2.5	3.7	2.2	4.3	14.8	0.05	75	
	LMX-20	173	144	116	34	32	79	39	69	911	57.8	0.3	2.0	4.1	0.7	4.2	16.3	0.04	75	
	LMX-21	157	141	103	28	31	83	37	100	632	54.8	0.4	2.1	3.8	2.0	4.0	15.2	0.05	73	
	LMX-22	181	146	84	40	40	101	38	133	545	51.8	0.4	2.2	3.7	2.4	4.0	14.8	0.06	73	
	LMX-23	149	131	71	25	28	84	33	171	373	56.7	0.5	2.0	3.8	2.9	3.6	15.4	0.03	73	
	LMX-24	162	147	105	29	34	73	35	173	465	56.4	0.4	2.1	3.6	3.6	3.7	14.4	0.07	74	
	LMX-25	156	147	104	30	31	84	32	182	399	58.6	0.3	2.1	3.6	4.6	3.9	14.6	0.06	74	
	LMX-26	159	148	92	32	45	78	36	174	228	41.4	0.4	1.9	3.6	4.6	3.5	14.4	0.07	74	
	LMX-27	148	131	102	26	36	77	34	262	487	54.2	0.4	1.9	3.5	6.2	3.5	14.0		74	
	LMX-28	160	158	114	31	29	84	36	137	735	54.5	0.3	1.9	4.0	3.6	3.8	15.8		75	
	LMX-29	154	138	93	25	21	65	35	130	572	64.3	0.3	2.2	4.1	3.0	3.8	16.1		75	
	Average	132	156	85	42	36	83	30	124	484	55.5	0.4	1.6	3.1	2.6	3.2	12.1		72	
Well Xiye 1	Xiye-1	164	123	86	47	51	115	22	160	1009	57.4	1.1	3.0	4.0	3.5	5.9	16.5	0.87	68	
	Xiye-2	162	130	89	49	34	340	22	150	1066	57.3	1.2	2.9	3.9	4.3	5.4	15.8	1.06	66	
	Xiye-3	313	213	67	80	56	249	22	171	1448	50.9	0.9	2.3	4.8	4.6	6.8	17.8	3.35	68	
	Xiye-4	163	129	92	53	35	116	23	147	1131	58.1	1.1	2.9	4.1	3.7	5.7	16.4	1.03	67	
	Xiye-5	123	69	65	40	24	78	18	194	1052	40.8	0.7	6.1	3.0	11.3	7.1	12.0	0.95	68	
	Xiye-6	161	90	100	55	30	128	25	135	1135	56.6	1.0	3.1	4.3	3.0	6.2	17.1	1.02	69	
	Xiye-7	120	141	63	88	57	103	16	162	951	62.1	0.8	2.0	2.9	5.7	4.4	10.9	3.84	66	
	Xiye-8	150	88	78	49	33	78	21	166	1032	56.3	1.3	2.9	3.6	5.6	5.3	14.8	1.22	64	
	Xiye-9	85	169	51	93	42	135	13	184	863	68.9	0.6	1.6	2.1	5.3	2.9	8.0	3.61	66	
	Xiye-10	96	623	80	123	124	152	14	152	828	58.7	0.6	3.1	2.4	7.0	3.3	8.4	6.46	65	
	Xiye-11	81	288	51	129	41	193	11	121	789	69.2	0.6	1.7	1.9	4.8	2.8	7.2	4.95	64	
	Average	147	187	75	73	48	153	19	158	1028	57.8	0.9	2.9	3.4	5.3	5.1	13.2		66	
Outcrop of Niutitang shale	NTT-1	396	120	62	2.8	28	14	28	37	46	52.4	0.8	0.5	2.6	0.0	11.0	9.9		70	
	NTT-2	162	201	81	42	59	69	31	35	291	52.7	0.0	2.1	3.8	1.2	4.2	15.3		78	
	NTT-3	48	124	48	18	25	16	27	70	98	56.7	1.6	0.5	3.2	0.1	1.2	12.4		67	
	NTT-4	57	122	91	58	20	28	23	54	269	56.1	1.3	0.5	2.9	0.1	1.5	10.7		66	
	NTT-5	38	387	101	41	13	19	25	58	118	53.7	1.8	0.4	2.9	0.3	1.0	10.7		62	
	NTT-6	135	135	84	120	35	162	23	95	628	49.1	1.8	1.1	2.7	1.4	3.2	10.1		55	
	NTT-7	85	614	101	321	54	568	22	18	538	58.1	0.0	0.7	3.2	0.0	2.4	12.1		77	
	NTT-8	154	87	55	81	28	276	35	169	365	54.3	1.0	3.7	2.4	7.0	4.3	15.5		72	
	NTT-9	126	664	95	139	38	46	25	88	689	54.7	1.5	1.0	3.1	0.9	3.1	12.1		62	
	NTT-10	83	687	49	117	29	234	19	226	238	53.2	0.1	2.2	1.0	1.7	1.5	11.2		88	
	NTT-11	33	333	233	22	47	63	14	29	504	57.8	0.0	0.5	1.9	0.4	0.8	7.2		78	
	NTT-12	136	892	104	82	27	63	23	94	387	55.2	1.4	0.6	2.7	0.5	3.7	10.2		62	

Table 1. (Continued.)

Sample sources	Sample ID	Trace elements content (μg/g)										Major elements content (%)							TOC	
		B	V	Cr	Ni	Cu	Zn	Ga	Sr	Ba	SiO ₂	Na ₂ O	MgO	K ₂ O	CaO	Fe ₂ O ₃	Al ₂ O ₃	(%)	CIA	
Well Renye 1	NTT-13	18	144	98	1	9	23	20	78	438	47.8	1.0	0.6	2.8	0.1	0.5	11.2		70	
	NTT-14	38	190	87	38	10	17	19	65	471	53.1	1.7	0.4	2.6	0.1	1.0	10.1		63	
	NTT-15	17	224	89	29	8	12	19	73	444	56.2	1.7	0.4	2.5	0.1	0.5	9.8		63	
	Average	102	328	92	74	29	107	24	79	368	54.1	1.0	1.0	2.7	0.9	2.7	11.2		69	
	Renye-1	131	219	115	60	46	152	23	205	1274	57.7	1.3	3.2	3.2	3.9	6.2	16.3		68	
	Renye-2	154	2152	1687	253	200	197	21	54	2317	54.7	0.1	2.0	4.7	0.7	5.9	15.4		74	
	Renye-3	127	176	97	54	63	256	22	196	2678	58.0	1.7	3.4	3.2	2.4	7.2	16.8		65	
	Renye-4	103	266	89	182	37	75	18	192	1018	54.4	2.1	3.3	2.4	5.0	5.3	12.1		56	
	Renye-5	102	235	94	79	48	184	22	314	984	53.4	1.7	3.2	2.7	6.6	6.1	14.4		63	
	Renye-6	91	244	94	95	63	173	19	170	1088	58.4	1.5	2.6	2.9	4.8	4.8	13.1		62	
Renye-7	117	313	104	97	66	197	22	167	1148	56.7	1.6	3.2	3.1	3.1	6.0	15.3		64		
Renye-8	69	393	82	394	44	402	13	411	939	56.4	1.0	2.1	2.1	9.1	4.7	8.5		60		
Average	112	500	295	152	71	204	20	214	1431	56.2	1.4	2.9	3.0	4.4	5.8	14.0		64		

Middle Carboniferous sediments in the area. The Upper Carboniferous limestone is mostly eroded and crops out only at a few localities in the region. During the Lower to Middle Permian, *in situ* weathering zones developed on the Silurian and, after slight uplift, it was subjected to severe lateritic weathering, again, under warm humid climatic conditions.

In the early and late Paleozoic, the South China block experienced several large-scale transgressive events that caused the formation of the following four black shale formations, i.e., the Lower Cambrian, Upper Ordovician–Lower Silurian, Lower Permian, and Upper Permian (Wen *et al.* 2001). There are mainly three black shale formations developed in the northwestern Guizhou area, the Doushantuo shale formation in the Upper Sinian, the Niutitang shale formation in the Lower Cambrian and the Longmaxi shale formation in the Lower Silurian. However, the latter two shale formations are the main ones we examined in this study. The Niutitang shale mainly developed in the east and south parts of the study area, and the thickness of it varied between 200 and 300 m. The bottom of the Niutitang shale features siliceous rock formation with interbedded carbonaceous shale that generally contains phosphorite, the lower portion of the shale formation is primarily black carbonaceous shale, and the upper portion of this shale formation contains dark gray-green shale with siltstone interbed (Zeng *et al.* 2013). The Longmaxi shale mostly developed in the northeast part of the study area with the thickness ranging from 50 to 200 m. The black shale at the bottom of the lower section of the Longmaxi shale contains abundant graptolites and is an important hydrocarbon source in various regions of the Yangtze Craton (Wo *et al.* 2007; Zhang *et al.* 2009).

3. Samples and analytical methods

Samples for this study were collected mainly from outcrop and shale gas wells. The outcrop samples of the Niutitang shale were collected from a profile which is located in Zhunyi City, the core samples of the Niutitang shale were obtained from the well Renye-1 at a depth of 1272–1347 m. The outcrop samples of the Longmaxi shale were collected from a profile which is located in Xishui County, the core samples of the Longmaxi shale were obtained from the well Xiye-1 at a depth of 610–648 m (figure 1). In order to improve the accuracy, outcrop and core samples in the same formation were collected from the bottom to the top, and all samples were fresh.

Total organic carbon (TOC) was obtained by a Leco CS-230 carbon and sulphur analyser at the Geochemistry Laboratory of Yangtze University. The relative standard deviation was more than 5%.

Major elements were determined by XRF spectrometer on fused glass discs. The precision of the major element analysis is $\leq 3\%$. Trace elements in the black shale were determined by a Perkin–Elmer Sciex ELAN DRC-e ICP-MS at the Nuclear Industry Beijing Geological Research Analysis and Test Research Center. A 50-mg powder sample was dissolved in a high-pressure Teflon bomb with 1 ml HF and 2 ml HNO₃ at 190°C for 48 h. After removing HF by heating, the residue was dissolved in 2 ml H₂O and 2 ml HNO₃ with an appropriate amount of Rh at 145°C for 12 h (Qi *et al.* 2000). Rh was used as an internal standard to monitor instrumental drift during the analysis: analytical precision was better than 10% relative standard deviation.

Mineral compositions were derived from X-ray diffraction analysis. Shale samples were first ground into powder with average particle sizes of 100 mesh

(0.15 mm), then XRD analysis was performed on a Rigaku D/max-2500PC instrument at 40 kV and 100 mA. The samples were scanned from 5 to 80° 2 θ with 0.02° 2 θ step size and 2 s step time at room temperature (293.15 K) and relative humidity, 70%. These analyses were performed at the Nuclear Industry Beijing Geological Research Analysis and Test Research Center.

A combination focused ion beam milling scanning electron microscope (FIB–SEM) was used to investigate the microscopic pores and fractures with a temperature of 24°C and a humidity level of 35% (Zeng *et al.* 2013; Tang *et al.* 2014). The pore structure was measured by an ASAP 2020 BET surface area and pore size analyser following the method of Hou *et al.* (2014) and according to the BET equation calculating shale specific surface area (Brunauer *et al.* 1938). The porosity and permeability were performed with Ultrapore-200A helium porosimeter and ULTRA–PERMTM 200 permeameter following the method of Li *et al.* (2014). These tests were performed in the Research Institute of Petroleum Exploration and Development, North China Petroleum Administration.

4. Results

4.1 Major and trace elements

The results of major and trace elements from the Niutitang and Longmaxi shales are listed in table 1. Most of the trace element enrichment of different levels and the concentration degree of core samples are larger than the outcrop samples. The major elements content of core samples is also greater than the outcrop samples.

4.2 Mineral composition

The XRD analysis is presented in table 2. The content of clay minerals and quartz is the highest, followed by feldspar, calcite, dolomite and pyrite. The quartz content of the outcrop samples from the Longmaxi shale ranges from 17% to 64% with the mean value of 34.3%; core samples from the Longmaxi shale range from 33.2% to 69.9% with the mean value of 52.4%; outcrop samples from the Niutitang shale range from 14% to 57% with an average of 45.6%; core samples from the Niutitang shale range from 50.5% to 62.2% with an average of 54.8%. The total clay content in these shales are in the range of 31%–55% with an average of 53.4% in the outcrop of the Longmaxi shale; 17.9% to 40.1% with an average of 26.2% in the core of the Longmaxi shale; 26%–68% with an average of 43.3% in the outcrop of the Niutitang shale and 14.9%–40% with an average of 30.6% in the core of Niutitang shale.

Table 2. Correlation matrix for the correlation coefficient of the enriched elements in the black shale in northwestern Guizhou area.

	B	V	Cr	Ni	Cu	Zn	Ga	Sr	Ba	SiO ₂	Na ₂ O	MgO	K ₂ O	CaO	Fe ₂ O ₃	Al ₂ O ₃	TOC
B	1.000																
V	−0.192	1.000															
Cr	0.350	−0.169	1.000														
Ni	−0.259	0.702	−0.579	1.000													
Cu	−0.098	0.895	−0.225	0.698	1.000												
Zn	0.318	0.288	−0.202	0.501	0.294	1.000											
Ga	0.371	−0.376	0.724	−0.808	−0.447	−0.433	1.000										
Sr	0.084	0.053	−0.361	0.250	0.206	0.211	−0.365	1.000									
Ba	0.460	0.076	−0.096	0.419	0.219	0.591	−0.472	0.261	1.000								
SiO ₂	−0.222	0.217	−0.199	0.413	0.152	0.224	−0.319	−0.212	0.150	1.000							
Na ₂ O	0.193	−0.145	−0.089	0.183	0.017	0.442	−0.488	0.244	0.616	−0.035	1.000						
MgO	0.191	−0.038	0.019	0.002	0.042	0.162	−0.237	0.382	0.569	−0.310	0.391	1.000					
K ₂ O	0.871	−0.357	0.604	−0.477	−0.246	0.177	0.501	−0.063	0.411	−0.195	0.292	0.275	1.000				
CaO	−0.146	0.250	−0.492	0.467	0.357	0.237	−0.636	0.739	0.412	−0.176	0.245	0.688	−0.272	1.000			
Fe ₂ O ₃	0.643	−0.255	0.137	−0.063	−0.071	0.364	−0.128	0.280	0.797	−0.197	0.594	0.779	0.699	0.382	1.000		
Al ₂ O ₃	0.825	−0.408	0.601	−0.509	−0.298	0.152	0.508	−0.032	0.410	−0.175	0.285	0.303	0.987	−0.249	0.700	1.000	
TOC	−0.295	0.748	−0.634	0.960	0.776	0.437	−0.824	0.231	0.356	0.370	0.132	−0.011	−0.525	0.492	−0.102	−0.567	1.000

4.3 Total organic carbon

Total organic carbon (TOC) data from the shales are listed in table 3. The results show that TOC values are 3.30% to 0.18% from lower to upper of the outcrop of Longmaxi shale; 6.46% to 0.42% from lower to upper of the well Xiye 1 of Longmaxi shale; 8.13% to 0.18% from lower to upper of the outcrop of Niutitang shale and 10.8% to

0.32% from lower to upper of the well Renye 1 of Niutitang shale.

4.4 Porosity and permeability

Results from the porosity and permeability analysis from the shales are listed in table 4. The effective porosity values of outcrop samples from

Table 3. Mineralogical composition of the black shale in northwestern Guizhou area.

Sample sources	Sample ID	Quartz (%)	Feldspar (%)	Calcite (%)	Dolomite (%)	Pyrite (%)	Total clay (%)
Outcrop of Longmaxi shale	LMX-3	64.0	5.0				31.0
	LMX-8	43.0	4.0	15.0	6.0	1.0	31.0
	LMX-13	34.0	11.0	5.0	10.0	1.0	39.0
	LMX-15	35.0	14.0	3.0		1.0	47.0
	LMX-18	34.0	7.0	3.0		1.0	55.0
	LMX-19	33.0	5.0	3.0	7.0	1.0	51.0
	LMX-21	37.0	5.0	4.0		1.0	53.0
	LMX-23	32.0	6.0	5.0	5.0	1.0	51.0
	LMX-24	33.0	6.0	7.0		1.0	53.0
	LMX-26	30.0	7.0	11.0		1.0	51.0
	LMX-27	31.0	8.0	13.0			48.0
	LMX-29	28.0	5.0	11.0		1.0	55.0
	LMX-30	31.0	1.0	18.0	15.0	1.0	34.0
	LMX-31	17.0	6.0	19.0	18.0	2.0	38.0
	LMX-32	40.0	6.0		6.0	1.0	45.0
	LMX-33	23.0	22.0	18.0			32.0
	LMX-34	38.0	12.0	5.0			43.0
Well Xiye 1	Xiye-12	55.7	3.6	7.9	7.6	3.5	20.1
	Xiye-13	38.9	9.3	10.4	8.1	1.6	29.9
	Xiye-14	33.2	4.5	12.7	6.5	4.1	37.4
	Xiye-15	37.9	7.8	6.0	3.9	1.3	40.1
	Xiye-16	40.2	9.4	5.8	4.4	1.5	36.3
	Xiye-17	69.4	2.5	3.4	2.6	2.1	18.9
	Xiye-18	45.0	5.8	9.7	3.2	3.7	30.8
	Xiye-19	57.6	4.6	6.4	10.4	2.0	17.9
	Xiye-20	69.9	2.2	7.5	3.2	1.8	15.4
	Xiye-21	64.6	2.0	4.7	3.8	2.2	22.7
	Xiye-22	63.5	3.3	5.1	6.7	2.6	18.8
Outcrop of Niutitang shale	NTT-16	51.0	3.0				44.0
	NTT-17	57.0	3.0				35.0
	NTT-18	57.0	1.0			2.0	40.0
	NTT-19	37.0		13.0	5.0	2.0	43.0
	NTT-20	45.0	16.0		3.0	10.0	26.0
	NTT-21	56.0	1.0				43.0
	NTT-22	14.0	6.0			12.0	68.0
	NTT-23	48.0	5.0				47.0
Well Renye 1	Renye-9	50.5	3.9	3.5		2.1	40.0
	Renye-10	51.0	8.9	3.1		1.9	35.1
	Renye-11	51.3	6.8	4.4		3.8	33.7
	Renye-12	53.6	6.6	3.9	2.1	3.4	30.4
	Renye-13	62.2	7.1	4.8	6.3	4.7	14.9
	Renye-14	60.1	2.4	1.4	2.4	4.0	29.7

Table 4. *The TOC content of the black shale in northwestern Guizhou area.*

Sample sources	Sample ID	Depth (m)	TOC (%)
Outcrop of Longmaxi shale	LMX-44		3.30
	LMX-45		2.33
	LMX-46		2.30
	LMX-47		2.03
	LMX-48		0.95
	LMX-49		0.51
	LMX-50		0.92
	LMX-51		0.35
	LMX-52		0.18
	LMX-53		0.17
	LMX-54		0.20
	LMX-55		0.18
Well Xiye 1	Xiye-40	648	6.46
	Xiye-41	644	4.20
	Xiye-42	638	3.82
	Xiye-43	633	3.35
	Xiye-44	628	1.21
	Xiye-45	625	0.95
	Xiye-46	618	1.18
	Xiye-47	600	0.74
	Xiye-48	570	0.48
	Xiye-49	556	0.45
	Xiye-50	544	0.48
	Xiye-51	534	0.42
Outcrop of Niutitang shale	NTT-37		8.13
	NTT-38		6.83
	NTT-39		7.15
	NTT-40		0.59
	NTT-41		0.18
Well Renye 1	Renye-28	1347	10.80
	Renye-29	1342	8.30
	Renye-30	1336	8.60
	Renye-31	1292	2.00
	Renye-32	1272	0.32

the Longmaxi shale range from 2.9% to 6% with an average of 4.7%, the effective permeability values range from 0.0058×10^{-3} to $0.0185 \times 10^{-3} \mu\text{m}^2$ with an average of $0.0096 \times 10^{-3} \mu\text{m}^2$; the effective porosity values of core samples from the Longmaxi shale range from 0.6% to 4.4% with an average of 1.8%, the effective permeability values range from 0.0066×10^{-3} to $0.1098 \times 10^{-3} \mu\text{m}^2$ with an average of $0.0387 \times 10^{-3} \mu\text{m}^2$; the effective porosity values of outcrop samples in the Niutitang shale range from 0.5% to 12.9% with an average of 7.8%, the effective permeability values range from 0.0021×10^{-3} to $0.1138 \times 10^{-3} \mu\text{m}^2$ with an average of $0.0212 \times 10^{-3} \mu\text{m}^2$; the effective porosity values of core samples in the Niutitang shale range

from 0.2% to 0.8% with an average of 0.4%, the effective permeability values range from 0.0038×10^{-3} to $0.0059 \times 10^{-3} \mu\text{m}^2$ with an average of $0.0047 \times 10^{-3} \mu\text{m}^2$.

4.5 BET specific surface

BET specific surface data from the shales are listed in table 5. The BET specific surface values of outcrop samples from the Longmaxi shale range from 1.768 to 7.067 m^2/g with an average of 3.277 m^2/g , the values of core samples from the Longmaxi shale range from 10.735 to 24.646 m^2/g with an average of 19.745 m^2/g ; the values of outcrop samples from

Table 5. Porosity and permeability of the black shale in northwestern Guizhou area.

Sample sources	Sample ID	Length (cm)	Diameter (cm)	Density (g/cm ³)	Effective porosity (%)	Effective permeability ($\times 10^{-3}$ μm^2)
Outcrop of Longmaxi shale	LMX-40	2.50	2.50	2.60	4.10	0.0058
	LMX-41	2.50	2.50	2.54	6.00	0.0067
	LMX-42	2.50	2.50	2.62	2.90	0.0073
	LMX-43	2.50	2.50	2.56	5.60	0.0185
Well Xiye 1	Xiye-30	2.50	2.50	2.68	1.60	0.0136
	Xiye-31	2.50	2.50	2.41	2.10	0.0617
	Xiye-32	2.50	2.50	2.68	0.60	0.0367
	Xiye-33	2.50	2.50	2.66	2.10	0.0111
	Xiye-34	2.50	2.50	2.39	4.40	0.0253
	Xiye-35	2.50	2.50	2.66	1.60	0.1098
	Xiye-36	2.50	2.50	2.65	1.80	0.0994
	Xiye-37	2.50	2.50	2.67	1.50	0.0066
	Xiye-38	2.50	2.50	2.68	0.90	0.0069
	Xiye-39	2.50	2.50	2.67	1.20	0.0071
Outcrop of Niutitang shale	NTT-28	2.50	2.50	2.65	0.50	0.0047
	NTT-29	2.50	2.50	2.00	8.90	0.1138
	NTT-30	2.50	2.50	2.31	12.90	0.0336
	NTT-31	2.50	2.50	3.00	9.60	0.0176
	NTT-32	2.50	2.50	2.04	6.60	0.0067
	NTT-33	2.50	2.50	1.70	12.80	0.0021
	NTT-34	2.50	2.50	1.64	11.30	0.0023
	NTT-35	2.50	2.50	2.37	6.50	0.0070
	NTT-36	2.50	2.50	2.66	0.70	0.0031
Well Renye 1	Renye-20	2.50	2.50	2.65	0.60	0.0039
	Renye-21	2.50	2.50	2.71	0.40	0.0059
	Renye-22	2.50	2.50	2.74	0.40	0.0049
	Renye-23	2.50	2.50	2.67	0.20	0.0038
	Renye-24	2.50	2.50	2.72	0.80	0.0053
	Renye-25	2.50	2.50	2.67	0.40	0.0046
	Renye-26	2.50	2.50	2.74	0.20	0.0052
	Renye-27	2.50	2.50	2.66	0.30	0.0043

Niutitang shale range from 0.600 to 8.138 m²/g with an average of 4.090 m²/g, the values of core samples from Niutitang shale range from 3.338 to 20.013 m²/g with an average of 10.589 m²/g.

5. Discussion

5.1 Inorganic and organic geochemistry of shale weathering

The participation of organic matter is a necessary factor for the formation of exogenous deposits (Ye 1996); organic matter or its breakdown products has the close relation with the accumulation of some metal and nonmetal elements (Yin 1999). From table 1, many trace elements in core samples

such as B, V, Ni, Cu and Zn are higher than the content of outcrop samples (figure 4a). In the TOC and Cu, V, Cr, Ni, Zn, Sr diagram (figure 3), the TOC content of the black shale presents a positive correlation with some trace elements (Cu, V, Ni, Zn). Cu, V, Ni especially (table 2), showed the adsorption and complexation of organic matter to some elements that led to the enrichment of related elements. Moreover, when the core samples are compared with the outcrop samples, the loss of these trace elements are not obvious with the low TOC content, but the loss degree goes up with increased TOC content. These suggest that the progressive weathering of the black shale releases elements during sulphide and organic matter oxidation. Moreover, loss of trace elements in shale with high TOC content is greater than in shale with low TOC content in the weathering process (figure 3).

Figure 3. The cross plots of TOC content *vs.* the Cu (a), V (b), Cr (c), Ni (d), Zn (e) and Sr (f).

Chemical weathering process can be divided into three periods according to the elements activity order in the rock: early stage of the relative release of Ca, Na, middle stage of the relative release of K and late stage of the relative release of Si (Nesbitt and Young 1984). The major elements of shale also present different degrees of leaching, Na, Ca, Mg and Fe in the core samples are significantly higher than in the outcrop samples and there is also a slight loss of K (figure 4b). Ca and Na suffered strong leaching with the dissolution of calcite and plagioclase minerals, followed by K which suffered major leaching with the weathering of K-feldspar and mica.

The chemical index of alteration (CIA) is well established as a method of quantifying the degree of source weathering (Nesbitt and Young 1982, 1984). The paleoweathering index of the Lower Cambrian and Lower Silurian shales (core samples) indicates a sediment supply from weakly weathered sources with CIA values of 56–74 with an average of 64 and 64–69 with an average of 66, respectively. However, the Niutitang and Longmaxi shales from outcrop samples show strongly weathered sources with the CIA values of 55–88 with an average of 69 and 65–76 with an average of 72, respectively. On an A-CN-K ternary plot (figure 5), most data cluster near the A-K edge, near illite composition, and

Figure 4. The trace element content (a) and major element content (b) of the Lower Paleozoic black shale in northwestern Guizhou Province.

Figure 5. A–CN–K plots (Nesbitt and Young 1984) for black shale samples in northwestern Guizhou area. A: Al₂O₃, CN: CaO* + Na₂O, K: K₂O. Mineral compositions – PI: plagioclase; Ksp: K-feldspar; Ka: kaolinite; Gb: gibbsite; Chl: chlorite; UCC: upper continental crust; PAAS: post-Archean Australian shale (Taylor and McLennan 1985).

spread towards the A apex, significantly greater than the post-Archean Australian shale (PAAS) for average shales (Taylor and McLennan 1985). The data of the Niutitang and Longmaxi shales all plot along the same weathering trend line, which implies that they are derived from a common lithology.

Organic carbon as one of the basic index of the abundance of organic matter can indirectly reflect the number of original organic matter and represent the abundance of organic matter in rocks (Shang *et al.* 1990). The samples used in the study of organic matter leaching are collected from lower to upper of the Longmaxi and Niutitang shales, there is a one-to-one correspondence between outcrop samples and core samples of the same shale

Figure 6. The diagram showing the TOC content varieties with the black shale from lower to upper in the same formation.

formation. The TOC content of these two shales diminishes gradually from lower to upper, the greater TOC content in the core samples, the more loss of organic matter in the outcrop samples (figure 6). In the TOC content of outcrop samples and core samples diagram (figure 7), we found that the data of the two types of samples show a good linear relationship, the $TOC_{(core)} = 1.173 \times TOC_{(outcrop)} + 0.6342$. Tang *et al.* (unpublished) studied the weathering process of the Lower Triassic shale in the Ordos Basin wherein they indicated that the average value of TOC from core samples is 2.22% and the average value of TOC from outcrop samples is 1.32%. These data are in good agreement with the linear relationship observed in this study. It suggested that the weathering

process has a significant impact on organic matter abundance, moreover, the relationship between TOC content of core samples and outcrop samples can be used to predict the TOC content of black shale underground, by the data of outcrop samples. In plots of TOC and TOC loss rate ($\text{TOC}_{(\text{core})} - \text{TOC}_{(\text{outcrop})} / \text{TOC}_{(\text{core})}$) vs. depth, the

TOC of black shale was observed to significantly increase with increasing depth, but those of TOC loss rate is not monotone increasing. The loss rate of TOC in black shales range from 18% to 70% with an average of 43% and the Longmaxi and Niutitang shales all show that the TOC loss rate of black shale with low TOC content is more than those with high TOC content during weathering process (figure 8).

Figure 7. The cross plots of TOC content for outcrop samples vs. the TOC content for core samples.

5.2 Mineralogical composition characteristics of shale weathering

Brittle mineral content is an important factor which influences the matrix pore, the degree of micro fracture development, the hydrocarbon content and the way of fracturing of shale. In addition to quartz, feldspar and dolomite are also brittle mineral components of black shales (Nelson 1985). The higher the content of brittle minerals such as quartz, feldspar and calcite in shale, the more conducive they are to form natural and induced cracks under the action of external force (Zou *et al.* 2010). The mineral composition of shale samples is illustrated in figure 9. It is clear that the brittle mineral content in the core samples is significantly higher than outcrop samples but clay mineral is lower than the outcrop samples. Major elements (Si, Al, and Mg) change little across the weathering profile. In contrast, Na and K are depleted relative to the concentrations predicted by the abundance of the mineral phases. Feldspars, illite and

Figure 8. Plots showing the depth variation for TOC and TOC loss rate.

illite-smectite host these elements whose low ratios may represent incongruent dissolution and change in the interlayer cation abundances in response to the acidic weathering conditions.

Because the black shale contains significant amounts of pyrite, the result is acidic weathering that prevails across the outcrop and controls much of the mineral alteration and secondary mineral formation. In certain intervals, a subtle increase in pH can result in profound mineral alteration. Along with acidity, SO_4 and Fe (II) are generated during pyrite oxidation. Sulphate forms secondary minerals, but many of these are relatively soluble in water and eventually are eluted from the weathering profile (Tuttle and Breit 2009; Tuttle *et al.* 2009). This may be the main factor leading to the loss of Fe, in the outcrop shale samples.

Figure 9. Mineralogical composition of the black shale in northwestern Guizhou area.

5.3 Petrophysical changes of shale weathering

The opinion that ‘the higher the porosity, better the permeability’ has always been serving as a major guideline in the production operation of medium-high porosity and permeability reservoirs. In low porosity and low permeability reservoirs, however, there is often a conflict with this point of view (Pittman 1992). Figure 10 reveals that with the increase of porosity, the changes of permeability are not very noticeable both in core and outcrop samples. There are a few abnormal permeability values, this may be the existence of natural fracture which resulted in increased permeability value. Wildman *et al.* (2004) attribute porosity and permeability in shale to organic matter oxidation. By comparing the core and outcrop samples, not only was the porosity of outcrop samples found to increase after weathering leaching (figure 11), the data also showed that the porosity of core samples are more concentrated and mostly distributed in a relatively narrow range of 0.2% to 2%, whereas the porosity values of outcrop samples are scattered from 3% to 14%, which may be related to the pore structure of shales. Additionally, the Niutitang shale in the lower Cambrian is older and has a more compact structure than that of the Longmaxi shale in the Lower Silurian where the increment of porosity is larger after weathering. The cause of this result could be that the Niutitang shale has a higher content of organic matter and sulphide minerals, and the buffering of organic matter oxidation by pyrite that occurs in the shale reacts as an electron donor much faster than organic matter (Petsch *et al.* 2000). In addition, secondary pores created by the dissolution of unstable minerals such as feldspar and calcite constitute a part of the reservoir space of the shale reservoir and increase the porosity of shale. Therefore, we infer that weathering effect on the porosity and permeability of black shale has certain regularity: black shale weathering has strong heterogeneity, and the

Figure 10. Porosity and permeability diagram for the black shale in northwestern Guizhou area.

Figure 11. SEM photographs of the black shale in northwestern Guizhou area. (a, b) Core sample of Niutitang shale, well Renye 1, 1325 m, facial porosity=0.67%. (c, d) Outcrop sample of Niutitang shale, facial porosity=1.3%. (e, f) Core sample of Longmaxi shale, well Xiye 1, 643.5 m, facial porosity=3.67%. (g, h) Outcrop sample of Longmaxi shale, facial porosity=7.46%.

higher the organic matter and sulphide mineral content in shale, the more obvious is the increase of the porosity after weathering modification, but the change of permeability is very limited.

Previous research on black shale shows that 85% of organic carbon is closely related to the specific surface area of the rock (Weiler and Mills 1965; Suess 1973; Tanoue and Handa 1979; Mayer 1994). As illustrated in figure 12(a), BET surface area (the total surface area of a solid calculated by the BET (Brunauer, Emmett, and Teller) equation)

of black shale and TOC content present obvious positive correlation, it illustrates that TOC is the main controlling factor of the specific surface area. Because the internal porosity of organic matter is very developed and provides a large specific surface area, this is consistent with the opinion of Ross *et al.* (Ross and Bustin 2008). Through the comparisons of the core sample and outcrop samples (table 6), it is not hard to find that the core sample has a high TOC content, which has bigger BET surface area, but the specific surface area is

Figure 12. The cross plots of BET surface area *vs.* the TOC content (a) and clay mineral content (b).

Table 6. BET surface area of the black shale in northwestern Guizhou area.

Sample sources	Sample ID	Quartz	Total clay (%)	TOC (%)	BET surface area (m ² /g)
Outcrop of Longmaxi shale	LMX-35	31.00	34.00	1.72	2.111
	LMX-36	17.00	38.00	1.46	3.282
	LMX-37	40.00	45.00	1.99	7.067
	LMX-38	23.00	32.00	0.13	2.158
	LMX-39	38.00	43.00	0.47	1.768
Well Xiye 1	Xiye-23	37.90	40.10	0.95	10.735
	Xiye-24	55.70	20.10	3.84	22.818
	Xiye-25	38.90	29.90	1.22	11.272
	Xiye-26	33.20	37.40	3.35	22.906
	Xiye-27	57.60	17.90	4.20	24.646
	Xiye-28	69.90	15.40	3.61	22.275
	Xiye-29	63.50	18.80	4.95	23.566
Outcrop of Niutitang shale	NTT-24	45.00	26.00	4.34	0.600
	NTT-25	56.00	43.00	1.03	8.138
	NTT-26	14.00	68.00	6.53	1.237
	NTT-27	48.00	47.00	1.10	6.386
Well Renye 1	Renye-15	50.50	40.00	0.30	3.338
	Renye-16	51.00	35.10	0.50	5.994
	Renye-17	51.30	33.70	3.20	12.378
	Renye-18	53.60	30.40	4.50	20.013
	Renye-19	62.20	14.90	6.20	11.221

Figure 13. Three-dimensional plots relating BET surface area, TOC content and clay mineral content.

reduced due to the loss of organic matter in outcrop samples. Previous studies have shown the control action of TOC to BET surface area is stronger than the effect of clay minerals content to BET surface area, usually, the content of clay minerals in shale is low, the TOC content is relatively high (Cao *et al.* 2014). The increase of BET surface area caused by the increase of TOC is obscured by the decrease of BET surface area caused by the decrease of the content of clay minerals (figure 12b). However, under the condition of the same TOC content, with the increase of the content of clay minerals, BET surface area also has a tendency to increase. Therefore, because of the higher TOC content and relatively lower content of clay minerals in core samples compared with the outcrop samples, the increase of BET surface area brought by the high TOC content of the core samples makes up for the reduce of BET surface area caused by the decrease of the content of clay minerals (figure 13), thus makes the BET surface area of core samples greater than the outcrop samples.

In summary, the TOC content played a decisive role in the BET surface area of black shales, it also suggests that the loss of organic matter through weathering process is the key factor which leads to the differences between the core and the outcrop samples.

6. Conclusions

- (1) The major and trace element results show that the trace elements of shale have varying degrees of loss in the process of weathering and the migration quantity of Niutitang shale is higher than that of Longmaxi shale, the major elements such as Na, Ca, Mg, Fe reduced as the dissolution of minerals such as pyrite, feldspar and calcite.
- (2) The loss of organic carbon in samples with high TOC content is larger than those samples with low TOC content. The loss rate of TOC in black shales range from 18% to 70% with an average of 43%, and the linear relationship between TOC content of core samples and outcrop samples indicated that $TOC_{(core)} = 1.173 \times 1 TOC_{(outcrop)} + 0.6342$.
- (3) The increment of porosity of the Niutitang shale with more sulphide and organic matter is larger than the Longmaxi shale, but the permeability changes little with the increase of porosity, suggesting the organic matter and sulphide oxidation are the main factors of the change of porosity and permeability during black shale weathering process.
- (4) Combined with the results of the mineral composition, TOC content and BET surface area in

black shale, the data shows that the TOC content played a decisive role in the BET surface area of black shale.

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