Re–Os Dating of Bitumen from Paleo–Oil Reservoir in the Qinglong Antimony Deposit, Guizhou Province, China and Its Geological Significance

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Abstract: Abundant organic inclusions are present in the Qinglong antimony deposit. However, the source rocks of these organic matters have not been reliably identified. Recently, a paleo–oil reservoir was found in the Qinglong antimony deposit. In view of similar components of gaseous hydrocarbon, we propose that the organic matters observed in inclusions in Qinglong antimony deposit would come from this paleo–oil reservoir. We used the Re–Os dating method to determine the age of the bitumen from this paleo–oil reservoir, and obtained an isochron age of 254.3±2.8 Ma. The age indicates that the oil-generation from source rock occurred in the early Late Permian, earlier than the Sb mineralization age (~148±8.5 Ma) in the Qinglong antimony deposit area. After oil generation from Devonian source rock, first and secondary migration, the crude oil have probably entered into the fractures and pores of volcanic rocks and limestone and formed a paleo–oil reservoir in the western wing of Dachang anticline. As burial process deepened, the crude oil has turned into natural gas, migrates into the core of Dachang anticline and formed a paleo–gas reservoir. The hydrocarbons (including CH_4) in the reservoirs can serve as reducing agent to provide the sulfur required for Sb mineralization through thermal chemical reduction of sulfates. Therefore, the formation of oil–gas in the area is a prerequisite for the Sb mineralization in the Qinglong antimony deposit.

Key words: bitumen, Re–Os isotopic dating, paleo–oil reservoir, relationship between hydrocarbon accumulation and mineralization, the Qinglong antimony deposit

1 Introduction

Many ore deposits (Cu, Au, Pb, Zn, Ag, Hg, Sb, Ni, V, etc.) in the sedimentary basin have a close relation with oil and gas reservoir. For example, Kaili oil residual reservoir and Majiang paleo-oil reservoir are close to the Kaili-Duyun Pb-Zn ore belt in the southern Guizhou (Han et al., 1982; Hu et al., 2007; Gao et al., 2012a), Laizishan paleo-oil reservoir being close to the Lannigou gold mine in the southwest Guizhou (Gu et al., 2010), Yangye residual oil reservoir and Akemomu gas reservoir being close to the Wulagen Pb-Zn deposit in southwest of Tarim basin (Wang et al., 2003; Wang et al., 2005), MVT-type Pb-Zn deposit and oil field being symbiotic in the Cincinnati uplift in Tennessee and Kentucky (Kesler et al., 1994), the oil-gas reservoir and Carlin type gold deposit both being located in Nevada (Hulen et al., 1998). The spatial proximity of these ore deposits and oil-gas reservoirs implies possible genetic relationship between them (Gu et al., 2007a).

Qinglong antimony deposit in the Guizhou province is an important antimony deposit in China. Different ore genetic models have been proposed for the formation of the deposit, e.g., volcanic- gas-hydrate deposit (Liao, 1983), volcanic-exhalation deposit (Zhang et al., 1998) and stratabound ore deposit or volcanic sediment-reworking deposit (Tu, 1984; Chen et al., 1984; Liao, 1990; Chen, 1991). Hydrocarbon has been found in the

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fluid inclusions of Qinglong antimony deposit (Ye, 1996; Hu, 2011; Wang, 2011). This indicates that the organic matter originated from coal seam strata and crude oil may have played a role in the mineralization (Ye, 1996; Cai and Zhang, 1997; Zhuang et al., 1997; Liu et al., 1997; Wang et al., 2002). However, the understandings of the relationship between organic matter and antimony mineralization have been hindered by a lack of detailed study of the suitable organic matters, such as bitumen.

In 2012, we found a paleo-oil reservoir with a large area of thick bitumen layers through five exploration drilling holes in Qinglong antimony deposit area. The paleo-oil reservoir occurs at the top of Maokou Formation of Middle Permian, Dachang Layer and Emeishan basalt of Upper Permian. In this paper, we use Re-Os dating of bitumen from paleo-oil reservoir in the Qinglong antimony deposit to provide new evidence for the understanding of the genetic relationship between the organic matter and metal mineralization in the region.

2 Geological Setting

The Qinglong antimony deposit is located in Southwestern Guizhou (SWG) depression (west of SWG) of South China fold system and near the south-western margin of Yangtze platform. It is in a triangular area which is surrounded by Nanpanjiang fault, Mile–Shizong fault and Yadu–Ziyun fault. Outcropped strata of the mining area from early to young is limestone of Middle Permian Maokou Formation (P_2m), volcanic rock of Dachang stratum, Emeishan basalt($P_3\beta$) and clay rock, sandstone, limestone and coal seam of Upper Permian Longtan Formation (P_3l). Antimony ore body which appears in bedded, stratiform–like and lenticular shapes and antimony mineralization are strictly controlled by the core of Dachang anticline, contemporaneous fault and Dachang Layer (Fig. 1; Hu et al., 2014). The main ore types include quartz–stibnite, fluorite–stibnite and quartz–fluorite–stibnite. Metal minerals mainly include stibnite and pyrite, and gangue minerals include quartz, fluorite, calcite, gypsum and barite. Hydrothermal alteration mainly consists of silicification, clayization, fluoritization, pyritization, arbonatization and baritization (Wang, 2016).

Fifteen bitumen layers had been found by 5 drill holes during the prospecting process of Shaziling ore section in Qinglong antimony deposit (Fig. 2). The distribution area of the bitumen layers has reached about 1km^2, and the maximum thickness is 8.39 m with an average thickness of 2.82 m. The maximum content of effective surface porosity of bitumen varies from 0.5% to 15% with an average of 4.86%. The bitumen layers mainly occur in Emeishan basalt and only a small fraction in volcanic rock of Dachang Layer and limestone of Maokou Fm. The bitumen is mainly distributed in the fractures and pores of basalt, tuff and limestone (Fig. 3). The bitumen which is black and brown with oily luster cannot stain hands and cannot be burn, and it is hard and brittle with conchoidal fracture. Antimony mineral was not found in the bitumen layers by the naked eyes and microscopic observation. The analysis of trace element shows that the content of Sb is between 0.048–2.06 ppm with an average of 0.635 ppm (n=4; the data to be published), lower than the Sb abundance in the Earth crust.

3 Re–Os Isotopic System of Bitumen

Based on ^{187}Re becoming to ^{187}Os and Os isotope anomaly via $^{-}\beta$ decay, the geological age can be calculated by Re-Os isotopic dating. Re–Os isochron equation which is standardized by ^{188}Os is $(^{187}Os/^{188}Os)_t = (^{187}Os/^{188}Os)_i + (^{187}Re/^{188}Os)_t(e^{\lambda t}-1)$. Among them, λ is decay constant of ^{187}Re, t is formation age of sample, $(^{187}Os/^{188}Os)_t$ is current estimated value of sample, $(^{187}Re/^{188}Os)_t$ is current value of sample. If a group of samples are formed at same time and have same initial ratio, and the Re and Os isotopic systems are kept closed, the age could be calculated by the slope of isochron of samples and get the initial value ($(^{187}Os/^{188}Os)_i$) via the intercept of isochron.

Both Re and Os belong to the siderophile elements and have a certain affinity to copper, and more importantly, they have characteristics of affinity to organic matter (Yoshiro et al., 2007; Shen et al., 2011; Feng et al., 2017). The organic complex may make it possible that Re and Os can be preserved stably in the bitumen for a long time (Shen et al., 2011; Liang et al., 2016). Thus, Re–Os isotopic system can maintain a good closed system in bitumen and is not easy to be destroyed by later geological events (Creaser et al., 2002; Shen et al., 2011; Song and Song, 2015). Therefore, it is possible to use Re–Os isotopic method to date the forming of bitumen. Bitumen is derived from source rocks by the thermal degradation and thermal cracking. The formation of bitumen includes some processes such as hydrocarbon generation, migration, accumulation, thermal evolution and destruction which may be recorded in bitumen (Hwang et al., 1998; Gao et al., 2012b; Cai et al., 2014). The important information of hydrocarbon generation, migration, accumulation and Compared to the black rock series, the contents of Re and Os and radioactive isotopes are higher in bitumen. Re–Os isotopic age is frequently believed as the age of hydrocarbon generation (Selby et al., 2005; Finlay et al., 2011; Shen et al., 2011, 2015; Lillis and Selby, 2013) and initial ^{187}Os/^{188}Os is often used to determine the source rocks of hydrocarbon fluids (Selby

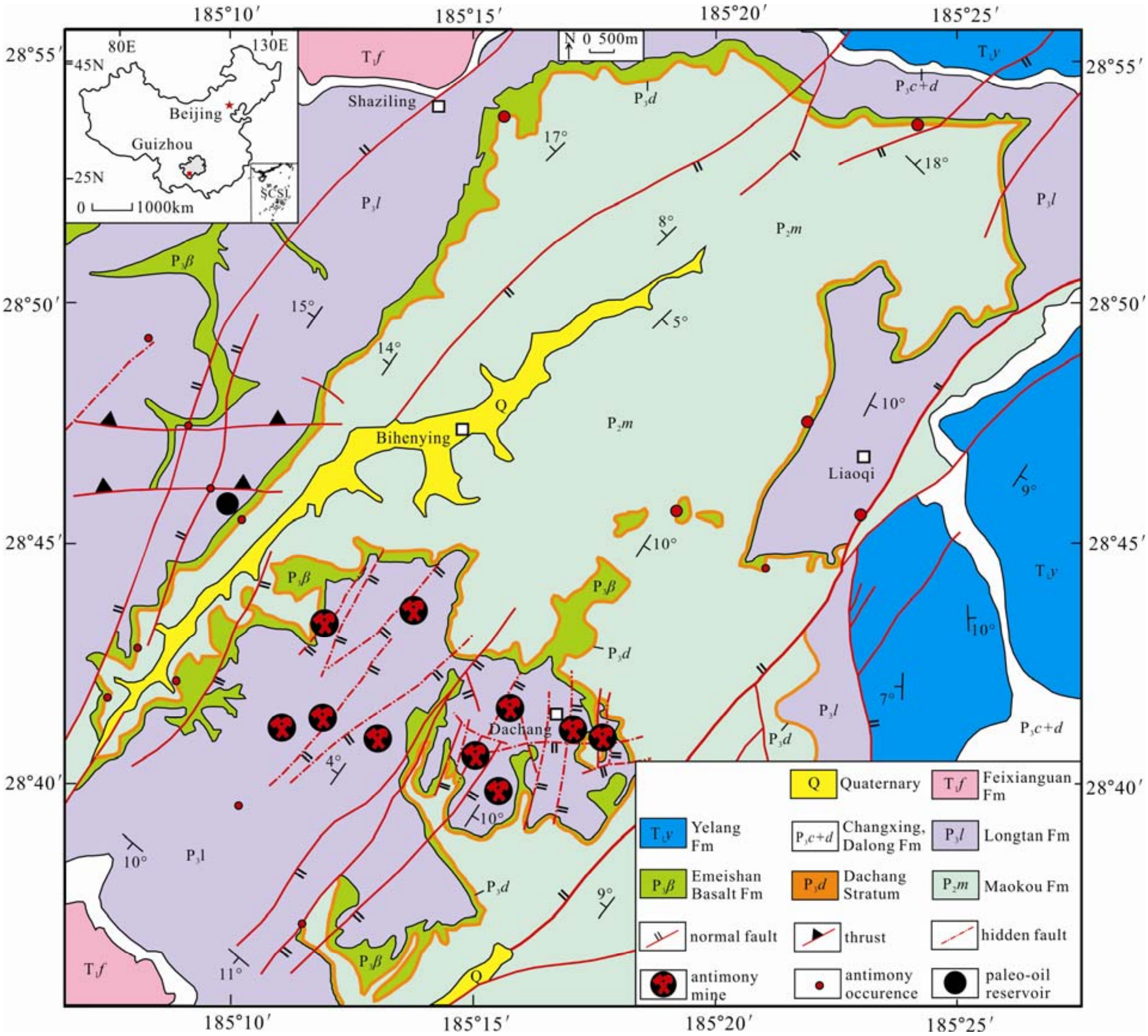

Fig. 1. Geological map of Qinglong antimony deposit, Guizhou, China.
Based on the 1/50000 geological map by Bureau of Geology and Mineral Resources of Guizhou Province and auctorial investigation of geology.

et al., 2005).

4 Sampling and Testing Methods of Re–Os Dating

4.1 Sample collection and processing

To determine reliable age of Re–Os isochron, the samples have to be homologous and contemporaneous, and later geological events do not disturb the isotopic system for construction of isochron (Selby et al., 2005; Wang et al., 2008; Chen et al., 2010; Shen et al., 2015; Chen et al., 2007). The samples of bitumen were collected from the drill holes in Shaziling section of the Qinglong antimony deposit, which were mainly distributed in the fractures and pores of basalt, tuff and limestone. During the field sampling, 3–5g of bitumen grains of every sample was collected from fresh cores by wooden tool and then was packed up within a sealable plastic bag. These samples were grinded to 0.5–1mm by the agate mortar and then were hand-picked to ensure the purity of bitumen beyond 99.5%. About 0.2g of every sample was used for isotopic determination.

4.2 Analytical method

These Re–Os isotopic analyses were performed in the Re-Os isotopic laboratory of National Research Center for Geoanalysis, China. The testing work includes dissolving samples, separating and purifying Re and Os elements, determining Re and Os isotope abundance by Mass Spectrometry and analyzing and processing data by using Isoplot software. The detailed procedures for isotopic measurement can be found in the literatures (Du et al., 1994, 2001, 2009; Shirey and walker, 1995; Qu and Du, 2003; Mao et al., 2003; Zeng et al., 2004; Chen et al.,

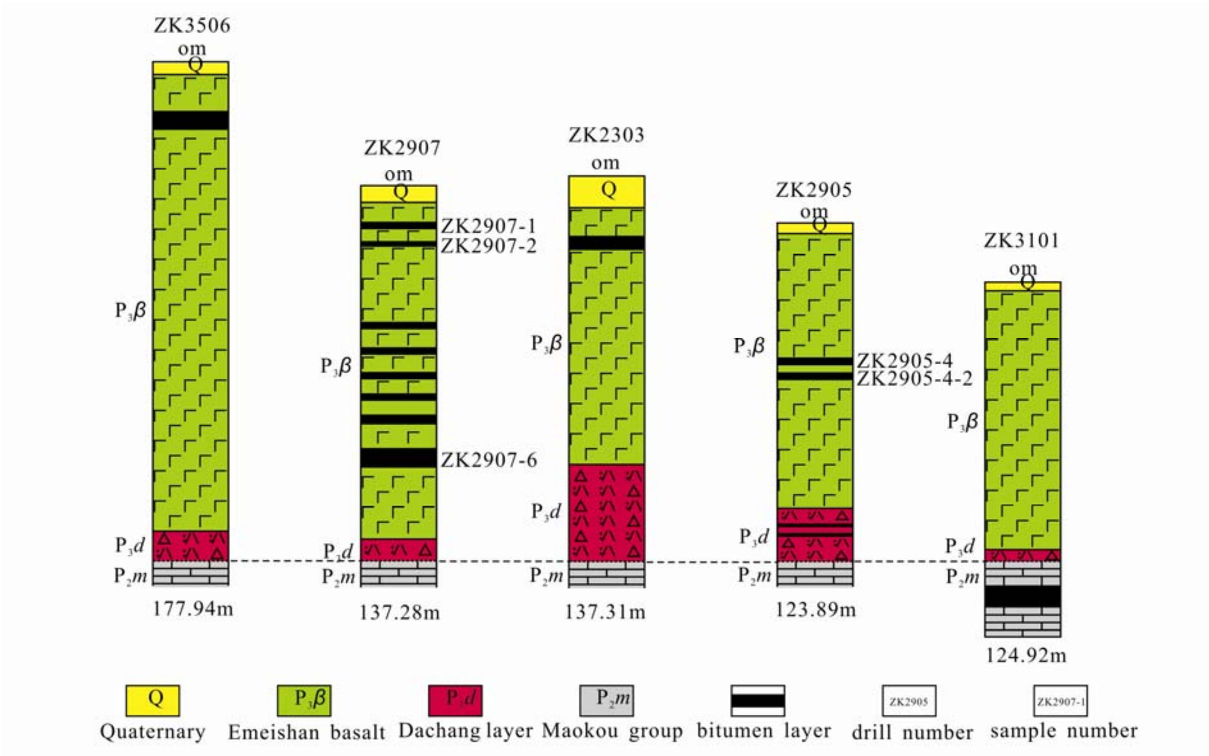

Fig. 2. The sketch map of bitumen layers in five drill holes in the Qinglong antimony deposit.

2007; Li et al., 2010).

5 Results and Discussions

The Re–Os isotopic results of five bitumen samples from the Qinglong antimony deposit are presented in the Table 1 below. Test results show that Re contents vary from 0.617 to 52.88 ppb with common Os contents of being from 0.0629 to 1.486ng/g, and ^{187}Os volumes vary from 0.0046 to 0.1471 ppb. The ^{187}Re/^{188}Os rations vary from 47.13 to 2544, and ^{187}Os/^{188}Os rations is from 0.5646 to 11.26. Fig. 4 shows that the five samples exhibit a good linear relation in Re–Os isochron. The five bitumen samples yield an isochron with an age of 254.3±2.8 Ma, and the ^{187}Os/^{188}Os initial ratio is 0.531±0.02, MSWD is 0.56.

5.1 Source Rock

The Devonian carbonaceous mudstones have high abundance of organic matter and high hydrocarbon generating ability (Zhao et al., 2006). Rare earth element (REE) analysis of the bitumen samples show close relationship between the bitumen and the Devonian carbonaceous mudstone of Luofu Formation (Wang et al., 2017). In addition, the value of carbon isotope of bitumen in the paleo-oil reservoir varies from −27.7‰ to −28.8‰ with an average of −28.1‰. Comparing with the value of carbon isotope of Devonian source rock (range −24.6 ‰–−27.6‰ with an average of −26.6‰; (Zhao et al., 2007).) and Permian source rock (range −22.4‰–−24.7‰ with an average is −23.6‰; Zhao et al., 2007), the carbon isotope of bitumen of paleo–oil reservoir in the Qinglong antimony is closer to Devonian source rock. Comprehensively, we suggest that the source rock of this paleo-oil reservoir in Qinglong antimony is probably Devonian carbonaceous mudstone (Wang et al., 2016). This understanding is similar to previous study in other paleo–oil reservoirs in Nanpanjiang and Youjiang basin (Zhao et al., 2007).

5.2 Ages of oil generation, oil accumulation and mineralization of antimony deposit

The Re–Os isochron age of 254.3±2.8 Ma of bitumen in the paleo–oil reservoir indicates the age of oil generation. This age is consistent with previous study who conjectured the age peak of oil generation of Devonian source rock would be from ~254 Ma to ~241 Ma in Nanpanjiang and Youjiang basin by analysis of thermal evolution (Zhou, 1999; Zhao et al., 2007). After generation, oil has to slowly migrate (first and second migration) through pathway, and then enters into the trap to form oil reservoir. The accumulation is closely associated with tectonic movement. The extrusion of the Indosinian movement (235 Ma between Middle and Late Triassic) may be the cause of huge oil migration and accumulation in Nanpanjiang and Youjiang basin (Zhou,

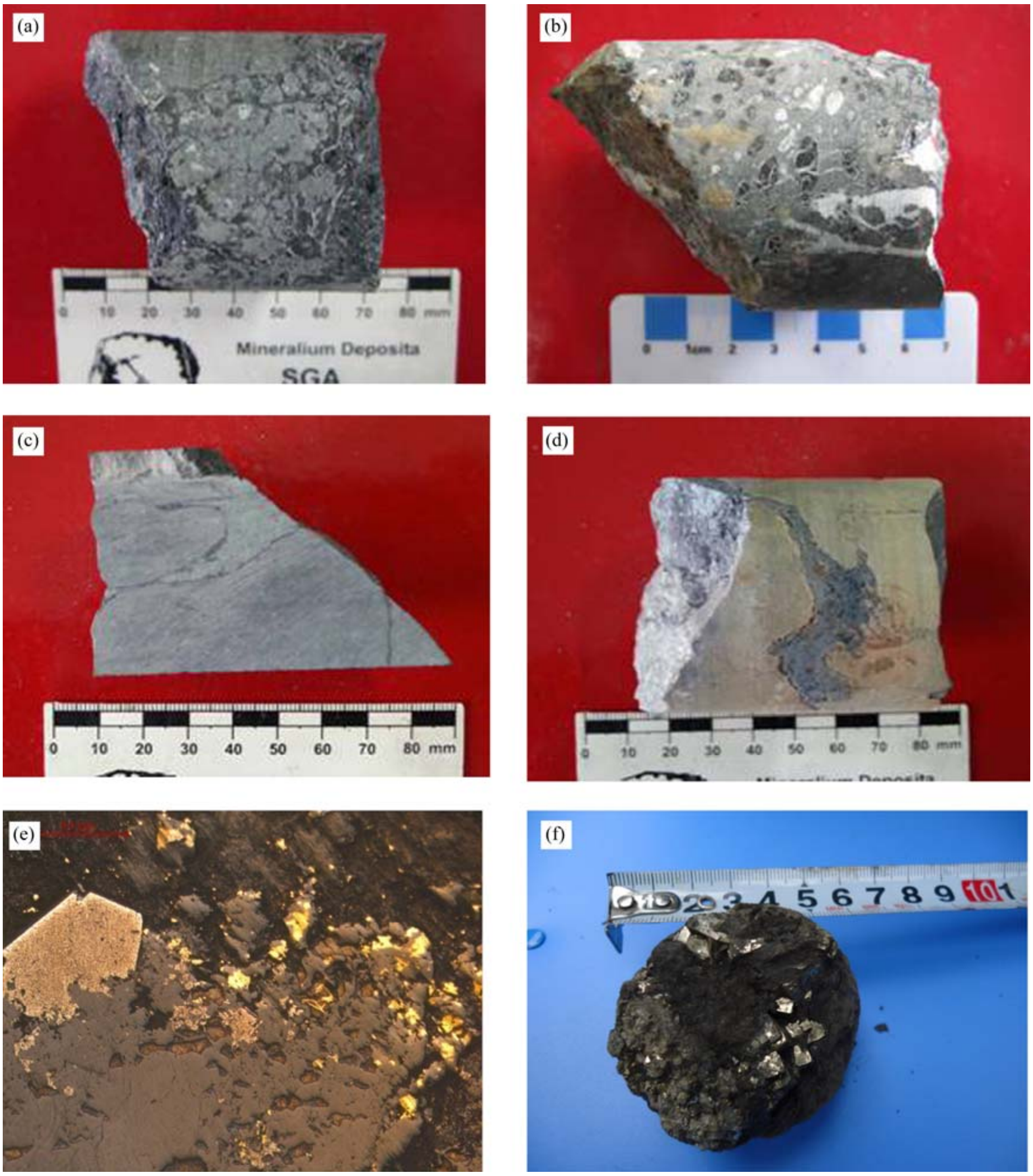

Fig. 3. The distribution of bitumen in the paleo-oil reservoir in Qinglong antimony deposit.
(a) Bitumen in the fracture of basalt, ZK2303; (b) Bitumen in the pores of basalt, ZK3505; (c) Bitumen in the fracture of tuff, ZK2905; (d) Bitumen in the fracture of limestone, ZK3101; (e) Symbiosis of bitumen, chalcopyrite and pyrite, the reflected light, 5×, ZK2907; (f) Bitumen and pyrite, ZK2303.

Table 1 The analysis results of Re–Os isotopic compositions of the bitumen in the Qinglong antimony deposit

Sample no.	Sample weight (g)	Re (ppb)		Common Os (ppb)		^{187}Os (ppb)		^{187}Re/^{188}Os		^{187}Os/^{188}Os	
		Measured	2σ	Measured	2σ	Measured	2σ	Measured	2σ	Measured	2σ
ZK2907-1	0.096	12.24	0.04	0.1224	0.0007	0.0412	0.0003	481.4	3.2	2.578	0.023
ZK2907-2	0.071	14.55	0.04	1.486	0.031	0.1416	0.0026	47.13	1.00	0.7298	0.0204
ZK2907-6	0.079	0.617	0.004	0.0629	0.0016	0.0046	0.0003	47.21	1.25	0.5646	0.0417
ZK2905-4	0.197	52.88	0.16	0.1001	0.0009	0.1471	0.0015	2544	24	11.26	0.16
ZK2905-4-2	0.144	49.09	0.15	0.0998	0.0010	0.1388	0.0017	2367	25	10.65	0.17

The quoted uncertainties include the calibration error of sample and diluent, the calibration error of diluent, the calibration error of mass spectrometry, and the error of the sample isotope ratio.

1999; Zhao et al., 2006, 2007).

Previous studies show that mineralization of Qinglong antimony deposit occurred in ~142±16 Ma and ~148±8.5 Ma by using Sm-Nd isotopic date of fluorite (Peng et al., 2003) and ~142.3±7.9 Ma and ~148±13 Ma by using Sm-Nd isotopic date of calcite (Wang et al., 2012). Therefore, the oil generation and accumulation age of paleo-oil reservoir is earlier than mineralization age of Qinglong

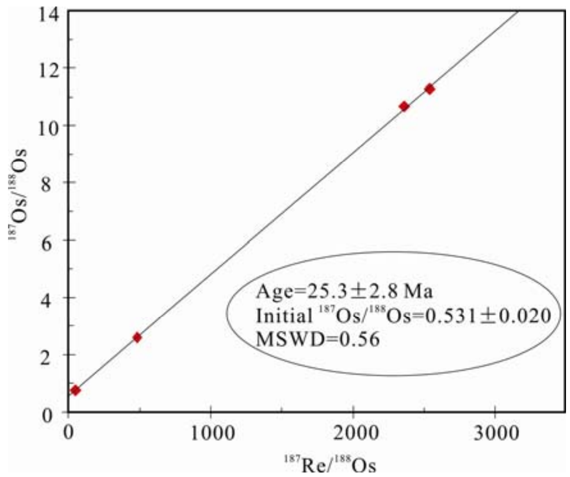

Fig. 4. The Re–Os isochron diagram of the bitumen in the Qinglong antimony deposit.

antimony deposit (Fig. 5).

5.3 Relationship between oil accumulation and mineralization

The Qinglong antimony deposit and the paleo–oil reservoir have a close spatial relationship which the former is located in the core of Dachang anticline and the latter is located in western wing of the anticline. Stratigraphically, the paleo–oil reservoir is mainly distributed in Emeishan basalt, small part in volcanic breccias of Dachang Layer and limestone of Maokou Fm, but the antimony ore bodies are distributed in volcanic breccias of Dachang Layer. The coexistence of the antimony deposit and paleo–oil reservoir has not been found. No antimony minerals are observed in the bitumen and Sb content is also not high, indicating that they did not form in the same process. Instead, the isotopic ages indicate that the mineralization occurred later than oil accumulations, as mentioned above.

Fluid inclusions provide further clues about the relationship between oil accumulation and mineralization at microscopic scale. A small amount of organic inclusions have been found in the fluorite and quartz inclusions of the Qinglong antimony deposit (Wang, 2011). Black and brown organic-bearing gases are also found in two–phase vapor–liquid inclusions in the paleo–oil reservoir (Liu et al., 2016). The measured gas compositions of the inclusions are mainly CO_2, N_2, CH_4, and C_2H_6 etc (Zhuang et al., 1997; Cai, 1997; Wang, 2011; Hu, 2011). Methane and ethane are also found in inclusions in the paleo–oil reservoir by Raman Spectra

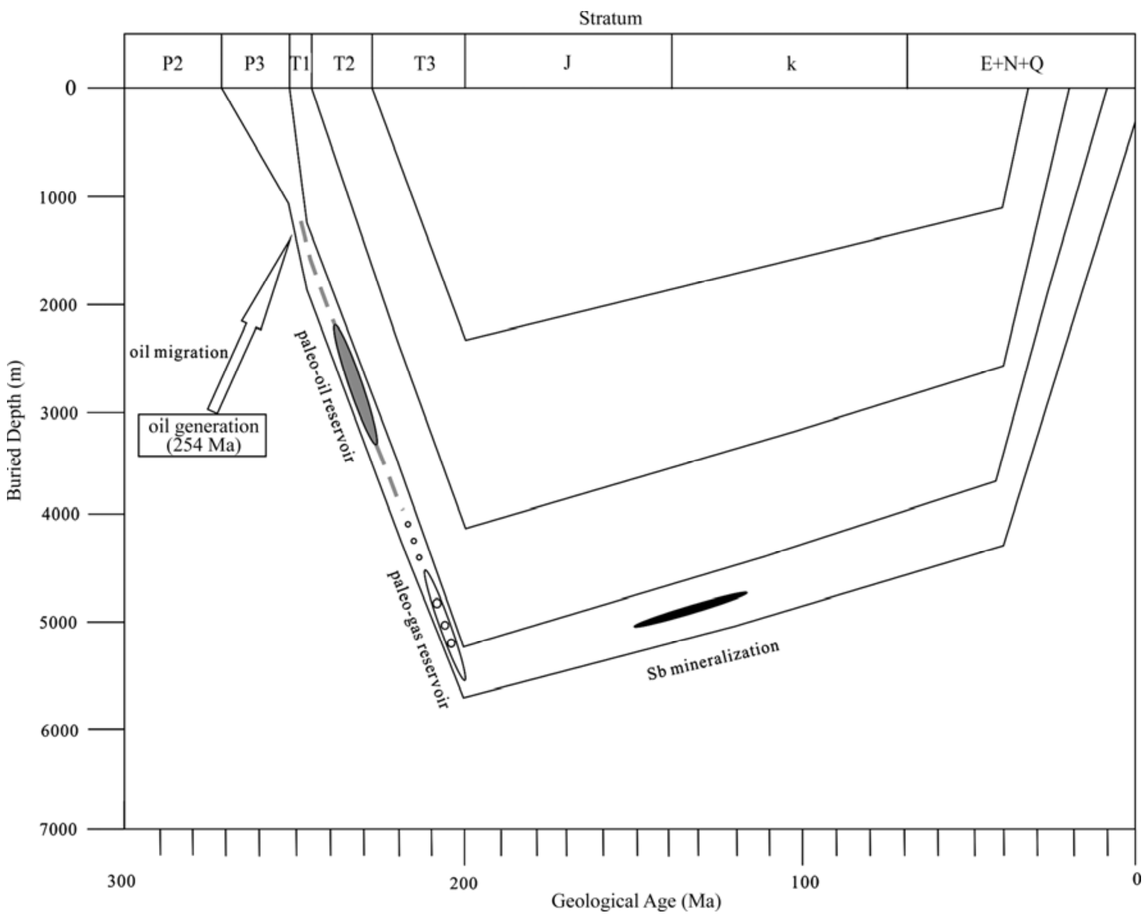

Fig. 5. The burial history curve of accumulation and mineralization in the Qinglong antimony deposit (modified from Hu, 2011).

(Liu et al., 2016), indicating organic matter both in Qinglong antimony deposit and in the paleo–oil reservoir have same evolution degree and same source.

Other researchers have discussed the relationship between the antimony mineralization and the organic matter in southwestern Guizhou (Shi et al., 1995; Ye et al., 1997; Wang et al., 2002; Yang et al., 2010; Hu, 2011). The hydrocarbon gases in the fluid inclusions of the hydrothermal minerals clearly indicate that the organic matter in the ore-forming fluid is the product of the petroleum cracking in Carlin type gold deposits in the east of southwestern Guizhou (Gu et al., 2007b). The role of organic matter in the antimony mineralization includes three aspects, such as leaching of organic acid, extraction and migration of liquid hydrocarbon, and reductive precipitation of gaseous hydrocarbons (Ye et al., 1997).

Thus, we propose that the crude oil entered within the fractures and pores of Emeishan basalts, volcanic breccias of Dachang Layer and limestone of Maokou Fm after it generated. As burial process deepened, the crude oil become natural gas and migrated into the core of Dachang anticline. The hydrocarbons in the reservoirs helped generation of the reduced sulfur required for Sb mineralization through thermochemical sulfate reduction (TSR). The net mass reaction of the TSR can be expressed as (e.g., Machel, 2001): Hydrocarbons + SO_4^{2-}⟶altered hydrocarbons + solid bitumen + H_2S (HS^-) + HCO_3^- (CO_2) + H_2O + heat. This reaction would occurred in the paleo–oil reservoir in the western wing of the Dachang anticline and altered hydrocarbons (include CH_4 and C_2H_6), H_2S (HS^-), HCO_3^- (CO_2) and H_2O would migrated into the core of the anticline. The TSR of gaseous hydrocarbon also occurred in the core of this anticline. Note that this region generates reduced sulfur (H_2S/ HS^-) that is needed to form main sulfide minerals stibnite (Sb_2S_3) and pyrite observed in the ores. The sulfur isotope of pyrite in paleo–oil reservoir varies from -1.9‰ to 2.9‰ with an average of 1.0‰ (n=6; the data to be published).Above results are close to sulfur isotope of stibnite (−2.6‰–−0.6‰; n=7) and of pyrite (−5.3‰–3.6‰; n=5) in Qinglong antimony deposit (Chen et al., 1984), indicating that these sulfurs are homologous. Therefore, organic matter in the oil and gas reservoir is prerequisite for the formation of the antimony mineralization.

5.4 The role of the eruption of Emeishan basalt in oil-generation

The Emeishan basalts are the major strata outcropped in the Qinglong antimony deposit area. The earliest eruption time of the Emeishan basalt is 260 Ma and final eruption is mainly concentrated in 253–251 Ma (Fan et al., 2004), which is close to the time of oil generation. The volcanic activities related to the Emeishan basalt probably have increased the geothermal gradient in the region and promoted the generation of oil. Therefore, the Emeishan basalt in the region may have provided a heat source for oil generation.

5.5 Dynamic background of oil/gas accumulation and Sb mineralization

In the Late Paleozoic to Middle Triassic, the SWG depression evolved from passive continental margin rifting basin ($D–P_1$) to back-arc rift basin ($P_2–T_2$) (Liu et al., 2001；Gu et al., 2007a；Hu, 2011). The tectonic units in the region generally include the basins and platforms. The black fine clastic rocks and carbonate rocks which generally bear rich organic matter had been deposited in the basins (Zhao et al., 2006, 2007). As burial process deepened, the Devonian source rock had begun to generate oil which got the peak in the Late Permian. The volcanic rock and tuff of Dachang Layer contain rich metal elements such as Sb and Au in the SWG depression (Chen et al., 1984; Hu, 2011). The Dongwu tectonic movement happened in late of Middle Permian and formed large area of paleo–Karst in South China which would act as a good lateral pathway for basin fluid. The syndepositional faults which are usually developed in this area would provide a good vertical channel for the migration of ore–forming fluid and hydrocarbon fluid.

Many fault–related folds were formed by the Indosinian tectonic movement in the end of the Middle Triassic. Some researchers believed that the Indosinian tectonic movement would extend to early Yanshanian period (Chen, 1994; Mao et al., 1999). Tectonic movement in this period drove the large scale migration of hydrocarbon fluid and ore fluid along the permeable formation units, faults and unconformity. Many oil reservoirs and some ore deposits (such as Carlin–type gold deposits) were formed in the appropriate geological body (Zhou, 1999; Zhao et al., 2007; Chen et al., 2007, 2015). The oil migration, oil accumulation and formation of the paleo–oil reservoir in Qinglong antimony deposit area would occur in this stage.

Because of incessant relaxation and collapses of the orogenic belt, the SWG depression entered into extensional stage in Yanshanian period, especially in late Yanshanian (Qin et al., 1996). Some reverse faults inverted into normal faults which formed some small faulted basin in the Late Cretaceous and Paleogene. A few of ultrabasic rocks had intruded into different strata. The formation of the Carlin–type Au and vein–type Hg, Sb, As, Tl, and Cd deposits at 135–80 Ma was contemporaneous with the emplacement of mantle–derived mafic dikes (Su et al., 2009; Hu et al., 1995, 2002, 2012). But new gathing data indicate that some Carlin–

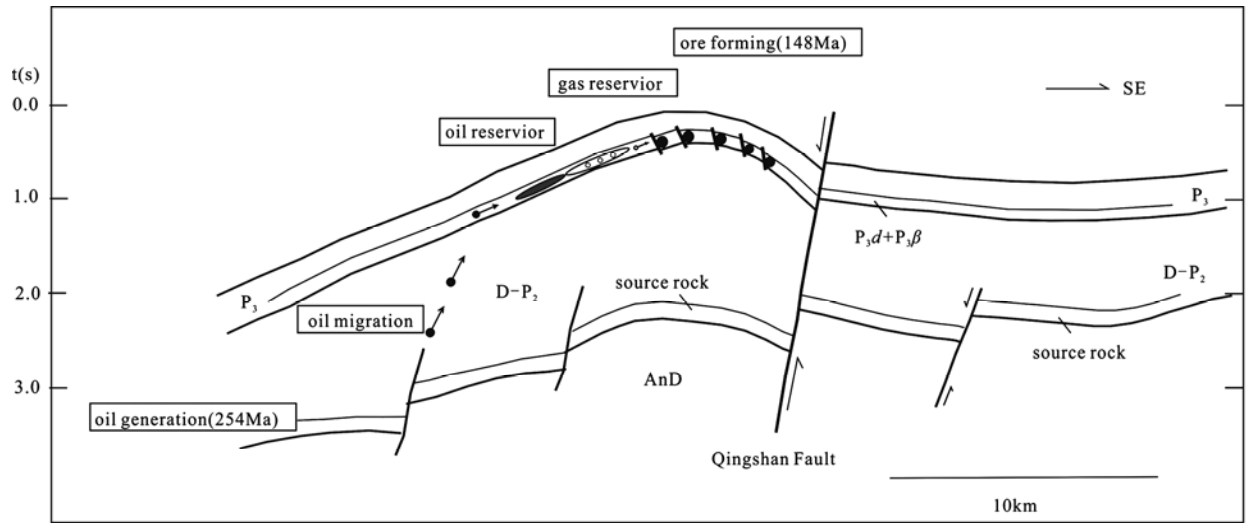

Fig. 6. Pattern of accumulation and mineralization in the Qinglong antimony deposit.
This figure is based on the interpretation of a seismic profile carried out by Sinopec in 2007 which cut across the north of the Qinglong antimony ore field.

type deposits in Southwestern Guizhou were formed in Indosinian period (Chen et al., 2007; Chen et al., 2015).

Some researchers believe that the Qinglong antimony deposit was formed in early Yanshanian period (Peng et al., 2003; Wang et al., 2012). Thus, we can sum up the oil/gas accumulation and Sb mineralization processes of the Qinglong antimony deposit: the source rock massively generated oil in the early Late Permian (~254 Ma), slowly migrated to the favorable reservoir layer (volcanic rocks) along syndepositional faults and the Dongwu unconformity and then formed oil reservoir (~235 Ma). The buried paleo–oil reservoir evolved into gas reservoir and migrated into the core of the Dachang anticline. The TSR reaction occurred in oil and gas reservoirs provided sulfide ion to the ore–forming fluid, and helped the Sb mineralization (~148 Ma) in the Qinglong antimony deposit (Fig. 6).

With rapidly uplifting of the SWG depression in the late Himalayan period, the oil and gas reservoir have been gradually destroyed and left only bitumen and a small amount of oil and gas near surface. The Qinglong antimony deposit also was uplifted near the surface.

6 Conclusions

(1) The Re–Os isochron age of bitumen from the paleo–oil reservoir in the Qinglong antimony deposit is 254.3±2.8 Ma. It indicates that the oil generation occurred in the early stage of late Permian.

(2) The paleo–oil reservoir provides liquid and gaseous hydrocarbon as a reducing agent to facilitate the thermochemical sulfate reduction to form sulfide for the antimony mineralization.

(3) The formation of oil–gas reservoir in the region is a prerequisite for the antimony mineralization in the Qinglong antimony deposit.

Acknowledgments

This study was financially supported by Natural Science Foundation of China (No. 41362007) , The Research of Scientific Base of Typical Metal Mineral from the Ministry of Land and Resources (No. 20091107) and the Research Project on the Metallogenic Regularity of the Typical Strata Controlled Deposits of National Crisis Mines in Southwest China (No. 20089943) .The authors acknowledge the support from the staff of Qinglong antimony deposit and help from the staff of Re–Os Isotopic Laboratory of National Research Center. We also thank Professor Wang Xuekun from Kunming University of Science and Technology for his comments on the manuscript. Dr Liu Weihua from CSIRO Mineral Resources in Australia helped improve the English manuscript.

Manuscript received June. 3, 2016
accepted May. 24, 2017
edited by Liu Lian

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