SPECIAL REPORT

Paleoceangraphic significance of redox-sensitive metals of black shales in the basal Lower Cambrian Niutitang Formation in Guizhou Province, South China *

YANG Jinghong, JIANG Shaoyong **, LING Hongfei, FENG Hongzhen, CHEN Yongquan and CHEN Jianhua

(State Key Laboratory for Mineral Deposits Research, Department of Earth Sciences, Nanjing University, Nanjing 210093, China)

Received June 16, 2003; revised August 18, 2003

Abstract Black shales of the Lower Cambrian Niutitang Formation occur widely on the Yangtze Platform. In this study, we analyzed black shales from two sections (Zhongnan and Zhijin) in Guizhou Province. The redox-sensitive metal concentration and distribution of black shales from the two sections provide good evidence for the anoxic conditions of the basal Cambrian ocean on the Yangtze Platform. Our geochemical data suggest that the black shales from the Zhongnan section may have deposited in a more strongly anoxic environment than the black shales in the Zhijin section.

Keywords: **redox-sensitive metals, black shales, Early Cambrian, Yangtze Platform, South China.**

The Lower Cambrian black shale sequence occurs in South China along an arc-parallel linear belt extending more than 1600 km. These organic-rich black shales formed in various marine environments and typically contain higher amounts of molybdenum, nickel, vanadium, and a number of other economically important metals than do any other sedimentary rocks[1, 2]. Therefore, the study of these black shales has not only paleoceangraphic implication but also economic significance.

Marine sediments such as black shale are complex mixtures of detrital phases and seawater-derived materials, and only the latter record paleoceangraphic conditions and chemistry of the water mass. In particular, the redox-sensitive trace metals, such as Mo, V, U, Re and Mn, in marine sediments can yield powerful information linked to local or global paleoceanographic variability[3, 4]. In this paper, we employed a new acid-leaching approach for the black shales in the Lower Cambrian Niutitang Formation in Guizhou Province to study variation and distribution of the selected redox-sensitive trace metals. This new approach can avoid bulk analyses of primary seawater precipitates with detrital components, obtain the primary paleo-ocean seawater signatures, and conclude their depositional environments during the Early Cambrian time on the Yangtze Platform.

1 Geological setting

The Yangtze Platform exposes well preserved Sinian to Cambrian sedimentary successions. In Guizhou Province, the Lower Cambrian Niutitang Formation consists of a thick black shale sequence that hosts a conformable Ni-Mo polymetallic ore horizon and other non-metal mineralization such as barite, phosphorite and "stone coal" beds[1, 5, 6]. The Niutitang Formation rests unconformably on the Sinian Dengying Formation of dolomite. Absolute age determinations for the Early Cambrian strata in South China are very controversial. Recent work on Re-Os and Pb-Pb dating of the black shales and interbedded Ni-Mo sulfide ores indicates a depositional age for the black shales of the Niutitang Formation of around 535 Ma[6~8].

In this study, we collected black shale samples of the Niutitang Formation from two sections, i. e. Zhongnan section near Zunyi and Zhijin section in Guizhou Province (Fig. 1). The Zhongnan section is located in the Zhongnan village ~10 km west of Zun-

* Supported by the National Natural Science Foundation of China (Grant Nos. 40172041, 40232020 and 40221301)
** To whom correspondence should be addressed. E-mail: shyjiang@public1.ptt.js.cn

yi City, and the Zhijin section is located in the Gezhongwu village ~10 km east of Zhijin Town. A paleogeographic environment reconstruction reveals that the sedimentary facies at the Zhongnan section belong to near-shore shelf facies, whereas the sedimentary facies at the Zhijin section is the shallower water inshore shelf facies (Fig. 2). In the Zhijin section, phosphorites of the Early Cambrian Gezhongwu Formation are overlain by the investigated black shales, whereas in the Zhongnan section the black shales directly rest unconformably on the dolomite of Dengying Formation (Fig. 3).

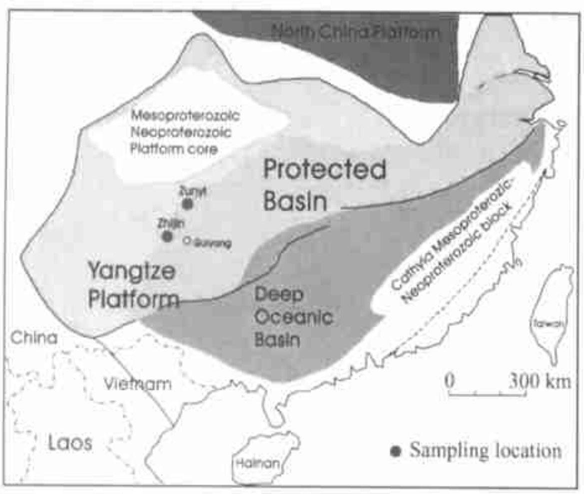

Fig. 1. Simplified geological map of Yangtze Platform showing the studied areas.

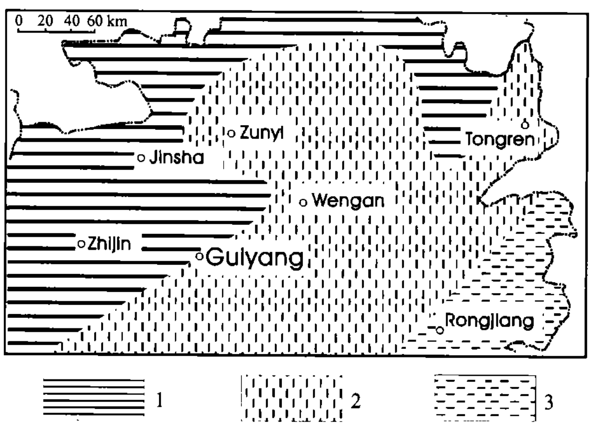

Fig. 2. Paleogeographic map of the studied sections in Guizhou Province during Early Cambrian (after Wu et al.[9]). 1, shallower water inshore shelf facies; 2, near-shore shelf facies; 3, deeper water near-shore shelf facies.

2 Analytical methods

Black shales contain both authigenic and detrital components. The detrital phases provide information on the geographical provenance of that material and its transport mechanism, whereas the authigenic phases record seawater chemistry. Previous studies on geochemistry of the black shales on the Yangtze Platform usually employed the whole-rock digestion technique using $HF + HClO_4 + HCl + HNO_3$, which dissolved everything in black shales and may have mixed signatures of provenance and water mass (e.g. Steiner et al.[10]). During this study, we used reverse *aqua regia* (2∶1 HNO_3/HCl) to dissolve the black shales in an Anton Paar High Pressure Asher HPA-S instrument at high temperature (320 ℃) and high pressure (130 bar). The combination of high pressure wet decomposition in the HPA-S and subsequent measurement with ICP-MS or ICP-OES represents a universal and advanced method for the fast and accurate dissolution and analysis of a variety of samples such as organic materials, alloy, and rocks with a proven analytical reliability[11]. By this technique, the authigenic component such as sulfide, carbonate, and clay minerals and organic carbon are dissolved which largely carries a seawater-like chemical signature, whereas the detrital minerals such as feldspar, quartz, and minor heavy minerals (e.g. zircon) remain unattacked. The dissolved solutions were centrifuged and separated from the detritus. Trace elements of the sample solutions were then measured using a Finnigan HR-ICP-MS at the State Key Laboratory for Mineral Deposits Research. The analytical precision of the samples is better than 10%.

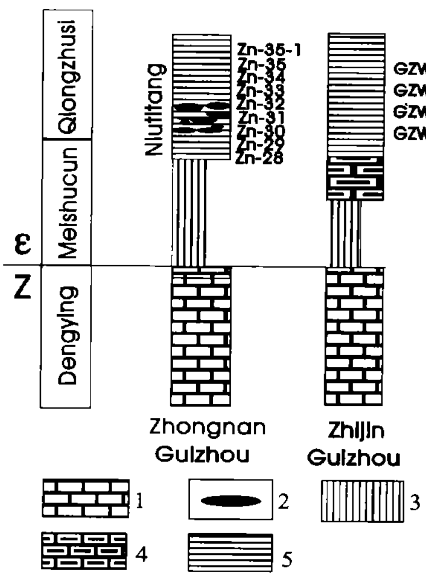

Fig. 3. The studied two sections of Neoproterozoic Denying Formation and Early Cambrian Niutitang Formation in Guizhou Province. 1, dolomite; 2, phosphorite nodule; 3, hiatus; 4, phosphorite; 5, black shale.

3 Results

Four samples of black shales from the Zhijing section and 9 samples of black shales from the Zhongnan section were analyzed for selected redox-sensitive trace metals, and the results are listed in Table 1. Overall, concentrations of Mo, V, Ni, Th and U of black shales from the Zhijin section are lower, but Mn contents are higher than that in the Zhongnan section. Compared to the average upper continental crust value (data from GERM Reservior Database http://www.earthref.org), Mo and V show 10 ~ 300 times enrichments, Ni and U show ~10 times enrichment, and Th is only 1 ~2 times enriched, but Sr is depleted. Mn in the Zhongnan section is depleted, whereas in the Zhijin section, it is 1 ~ 2 times enriched relative to the average upper crust.

Table 1. Results of ICP-MS analyses of selected trace elements in black shales of the Niutitang Formation in Guizhou Province (in μg/g)

Sample No.	Mo	V	Ni	Mn	Sr	Th	U	U/Th	V/(V+Ni)
Zhijing Section									
GZW-27	79.7	684	278	325	101	23.7	25.5	1.08	0.71
GZW-28	26.2	405	191	1146	104	22.2	13.0	0.59	0.68
GZW-29	25.6	372	176	977	88.9	22.5	13.0	0.58	0.68
GZW-30	23.3	417	143	1142	108	22.9	11.6	0.51	0.74
Zhongnan Section									
ZN-28	173	254	167	184	50.8	7.33	21.5	2.93	0.60
ZN-29	42.0	537	26.1	23.4	57.2	11.1	41.2	3.70	0.95
ZN-30	70.2	1234	186	80.9	168	18.3	31.6	1.73	0.87
ZN-31	53.9	8232	42.6	19.0	56.7	69.2	80.9	1.17	0.99
ZN-32	74.4	3168	124	170	229	19.5	57.1	2.92	0.96
ZN-33	80.5	8603	254	126	64.3	22.8	81.0	3.55	0.97
ZN-34	132	11339	308	70.5	75.0	22.6	71.5	3.16	0.97
ZN-35	315	15652	399	61.7	74.4	28.4	66.7	2.35	0.98
ZN-35-1	261	16515	337	89.2	70.4	26.9	80.9	3.01	0.98
Upper Crust	1.5	60	20	600	350	10.7	2.8	0.26	0.75

4 Discussion

4.1 Redox-sensitive metals and their implication for depositional redox environment

Previous studies have demonstrated that concentrations of redox-sensitive metals such as Mo, V, U, Mn in marine sediments are sensitive indicators for paleoceangraphic conditions[3, 12, 13]. The enrichments of these elements are influenced by the following factors: (1) variations in oxygenation of the water column; (2) oxygenation of the bottom water-surface sediments; (3) concentration of the given metals in the biogenic sources; (4) portions of the detrital inventory; and (5) secondary enrichment/depletion processes in geological samples in some cases.

The redox-sensitive metals are usually highly enriched in anoxic sediments, sensitive to changes in the area of seafloor overlian by oxygen-depleted seawater. As shown in Fig. 4, the enrichment factors for redox-sensitive metals in marine sediments vary according to the redox conditions[3, 4]. Toward more reducing environment (and elevated primary production), the concentrations of redox-sensitive metals are increasing.

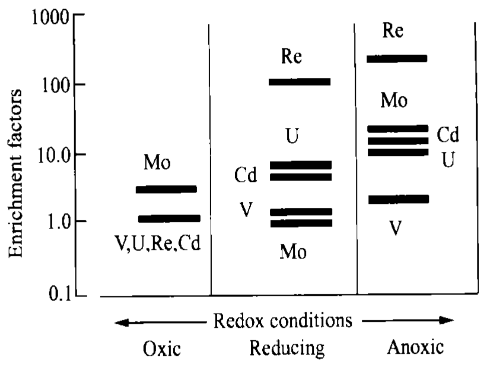

Fig. 4. A general model for enrichment factors of redox-sensitive metals in marine sediment of oxic, reducing and anoxic environments (modified from Ref. [4]).

4.2 Concentration of Mo and its relation to other redox-sensitive metals in black shales

Black shales usually contain elevated Mo[14]. In the Black Sea, sapropelic muds have Mo concentrations up to 188 ppm[15]. Black shales of the Niutitang

Formation also show high Mo contents of 40 ~ 300 ppm[10], not to mention the intercalated Ni-Mo ore bed within the Niutitang black shale that may contain up to 5.5 wt% Mo[1]. Our new data also show high Mo contents in the black shales from the Zhongnan (Mo=42 ~315 ppm) and Zhijin (Mo=23 ~80 ppm) sections of the Niutitang Formation from Guizhou Province. The Mo contents are broadly correlated with the V and U contents (Fig. 5), which are well in accordance with a bottom water anoxic condition. Although Mo and V both behave conservatively in seawater, Mo is particularly useful for studies of bottom water oxygenation because its seawater concentration (10 ppb) is higher than that of other trace metals[16]. It can be seen in Table 1 and Fig. 5 that black shales from the Zhijin section display lower Mo, V, and U contents than the black shales from the Zhongnan section, which may indicate that the depositional redox conditions at Zhongnan are more anoxic than that of Zhijin.

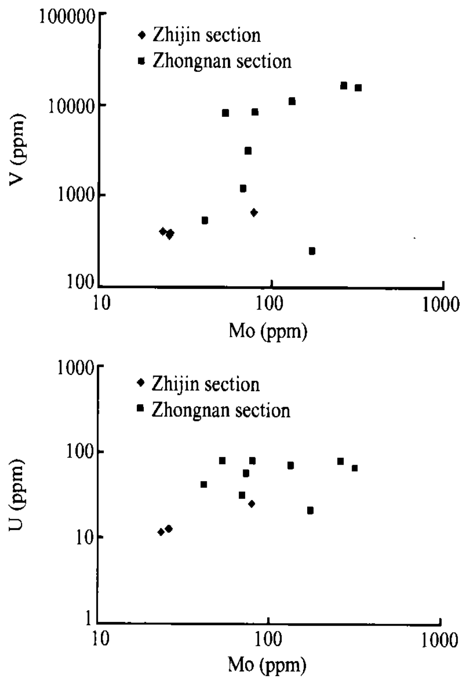

Fig. 5. Correlations of Mo and V, U in the Niutitang black shales.

4.3 U/Th and V/(V+Ni) ratios in black shales

Arthur & Sageman[13] suggested that U/Th ratio in black shales is sensitive to the relative inputs of Th-bearing clay minerals and U is fixed in sediments during early diagenesis in anoxic environments. Soluble uranium in its oxidized state must be reduced and fixed as tetravalent U in the sediments of anoxic basins as opposed to its unreactive behaviour in oxic marine basins[12]. The precipitation of U in the sediments drives diffusion of U into pore waters, and U is enriched in organic-rich sediments. It is suggested that high U/Th ratio reflects low redox conditions[13]. In Fig. 6, the black shales from the Zhongnan section display higher U/Th ratios (1.2 ~ 3.7) than the Zhijin black shales (0.5 ~ 1.1), which again may indicate a more anoxic environment at Zhongnan than at Zhijin.

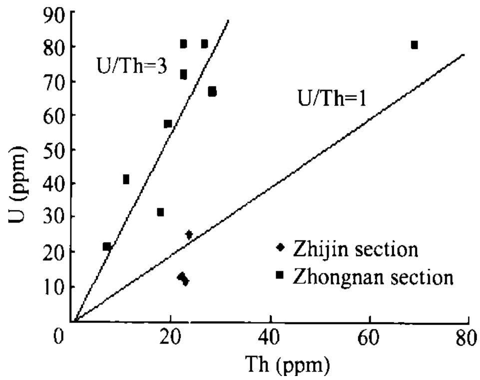

Fig. 6. Correlation between U and Th for the Niutitang black shales.

Compared to Ni, vanadium is apparently more effectively fixed in sediments in association with organic compounds in anoxic environments[17]. Hence, variations in the V/(V+Ni) ratio would indicate relative changes in oxygenation in the water column, and higher V/(V+Ni) ratios signal more strongly anoxic conditions of deposition[13]. In a plot of U/Th vs V/(V+Ni) for the Niutitang black shales (Fig. 7), the Zhijin samples show lower U/Th and V/(V+Ni) ratios than the Zhongnan samples. This is also consistent with a more anoxic depositional condition for the Zhongnan black shales.

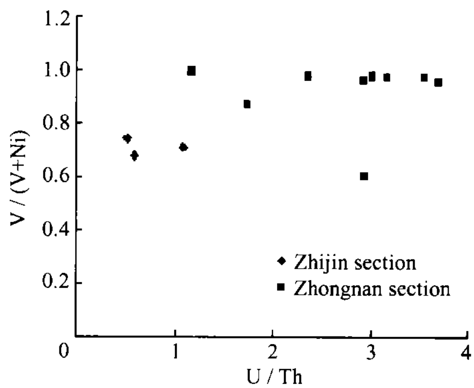

Fig. 7. U/Th vs V/(V+Ni) ratios for the Niutitang black shales.

4.4 Mn as an effective indicator for bottom water environment

Mn is an effective indicator of bottom water conditions due to the sensitivity of its solubility to redox changes. Marine sediments deposited under the oxygenated condition show relatively high Mn contents because Mn^{4+} precipitates readily as an oxyhydroxide. During reducing and anoxic conditions, Mn can be dissolved from the bottom sediment and diffused into the overlying anoxic water column, leading to concentrations that are depleted with respect to average shale[4]. For example, sediments from the Black Sea and Selwyn Basin that formed under anoxic conditions are commonly depleted in Mn[18~20]. Quinby-Hunt & Wilde[20] classified four types of redox conditions based on the Mn contents in Paleozoic black shales. Type 1 shales formed under oxic bottom water conditions and are characterized by relatively high Mn contents (average 1000 ppm). Type 2 and 3 shales deposited under anoxic condition. Mn is reduced to Mn^{2+}, and varies between 150 and 310 ppm, but Fe remains partly bound in oxides in type 2 shales in contrast to type 3 shales that all the Fe is reduced. In type 4 shales, the conditions are highly reducing and characterized by very low Mn (average 75 ppm) and high V (average 1500 ppm) contents. Accordingly, the black shales from the Zhijin section may have deposited in relatively oxic conditions due to their high Mn (325 ~ 1145 ppm) and low V (372 ~ 684 ppm) contents (Fig. 8). In contrast, the Zhongnan black shales formed under the highly anoxic condition because they show low Mn contents (19 ~ 184 ppm, average 92 ppm) and high V contents (254 ~ 16515 ppm, average 7282 ppm) (Fig. 8).

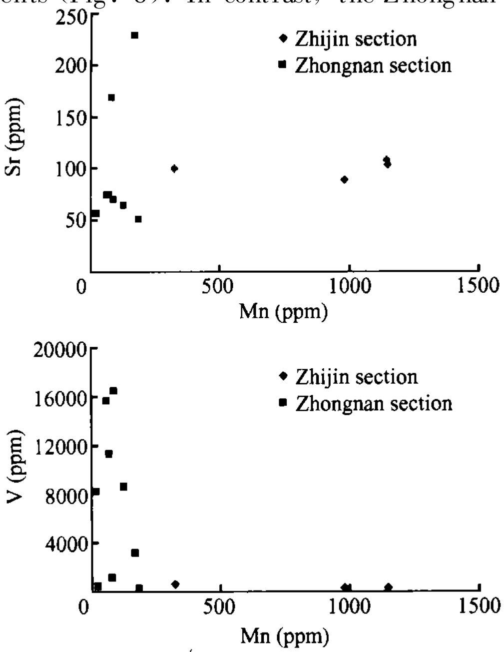

Fig. 8. Concentrations of Mn and V, Sr in the Niutitang black shales.

In the Black Sea, the carbonate-bearing sediments display relatively high Mn due to the substitution of Mn^{2+} for Ca^{2+} in calcite[21]. In the Zhongnan and Zhijin sections, the black shales contain negligible carbonate, and there is no correlation between Mn and Sr contents in the black shales (Fig. 8), which implies that carbonate-hosted Mn has no significance for the high Mn contents for the Zhijin samples.

5 Conclusions

(1) The acid-leaching portions of black shales can better represent the primary chemical signature of paleo-oceans.

(2) The redox-sensitive metal concentration and distribution of black shales from the Niutitang Formation can provide good evidence for the anoxic conditions of the basal Cambrian ocean in the Yangtze Platform.

(3) Black shales from the Zhongnan section show higher concentrations of Mo, Ni, V, and U, and higher U/Th and V/(V+Ni) ratios than that of the Zhijin section, suggesting a more strongly anoxic environment for the Zhongnan black shales.

(4) Black shales from the Zhijin section display higher Mn contents than that of the Zhongnan section, reflecting a relatively oxygen-rich depositional condition during Early Cambrian at Zhijin.

(5) The difference in redox conditions reflected by the Zhongnan and Zhijin sections may imply that the black shales deposited in different small basins or in different palaeoceanic environments in the same stagnated basin.

References

1 Fan, D. et al. Petrological and geochemical characteristics of a nickel-molybdenum-multe-element-bearing Lower Cambrian black shale from a certain district in south China. Geochimica, 1973, 3: 143.

2 Conveney, R. M. Jr. et al. Ore mineralogy of nickel-molybdenum sulfide beds hosted by black shales of South China. In: The Paul Queneau Symposium-Extractive Metallurgy of Copper, Nickel and Cobalt. Minerals, Metals and Materials Society, 1993, 1: 369.

3 Morford J. L. et al. The geochemistry of redox sensitive trace metals in sediments. Geochim. Cosmochim. Acta, 1999, 63: 1735.

4 Yarincik, K. M. et al. Oxygenation history of bottom waters in the Cariaco Basin, Venezuela, over the past 578000 years: Results from redox-sensitive metals (Mo, V, Mn, and Fe). Paleoceanography, 2000, 15(6): 593.

5 Gao, H. The biochemical sedimentary metallogenic model of barite and witherite deposits in Lower Cambrian in China. Mineralogy and Petrology, 1998, 18(2): 70.

6 Mao, J. et al. Re-Os dating of polymetallic Ni-Mo-PGE-Au mineralization in Lower Cambrain black shales of South China and its geologic significance, Economic Geology, 2002, 97: 1051.

7 Jiang, S. Y. et al. Re-Os Isotopes and PGE geochemistry of black shales and intercalated Ni-Mo polymetallic sulfide bed from the Lower Cambrian Niutitang Formation, South China. Progress in Natural Sciences, 2003, 13(10): 788.

8 Chen, Y. Q. et al. Pb-Pb isotope dating of black shales from the Lower Cambrian Niutitang Formation, Guizhou Province, South China. Progress in Natural Sciences, 2003, 13(10): 771.

9 Wu, X. et al. Phosphorites in Guizhou. Beijing: Geological Publishing House, 1999, 124.

10 Steiner, M. et al. Submarine-hydrothermal exhalative ore layers in black shales from South China and associated fossils- insights into a Lower Cambrian facies and bio-evolution. Palaeogeography, Palaeoclimatology, Palaeoecology, 2001, 169: 165.

11 Borszeki, J. et al. Application of pressurized sample preparation methods for the analysis of steel and copper alloys. Talanta, 1994, 41: 7.

12 Anderson, R. F. et al. Concentration, oxidation state, and particulate flux of uranium in the Black Sea. Geochim. Cosmochim. Acta, 1989, 53: 2215.

13 Arthur, M. A. et al. Marine black shales: depositional mechanisms and environments of ancient deposits. Annual Review of Earth and Planetary Science, 1994, 22: 499.

14 Wignall, P. B. Black Shales. Oxford: Claredon Press, 1994, 127.

15 Hirst, D. M. Geochemistry of sediments from eleven Black Sea cores. In: The Black Sea—Geology, Chemistry, and Biology. American Association of Petroleum Geologists, Tulsa, Oklahoma, 1974, 430.

16 Piper, D. Z. Seawater as the source of minor elements in black shales, phosphorites and other sedimentary rocks. Chemical Geology, 1994, 114: 95.

17 Lewan, M. D. et al. Factors controlling enrichment of vanadium and nickle in the Bitumen of organic sedimentary rocks. Geochim. Cosmochim. Acta, 1982, 46: 2547.

18 Cooper, J. R. et al. Isotope and elemental geochemistry of Black Sea sediments. In: The Black Sea. American Association of Petroleum Geologists, Memoir, 1974, 20: 554.

19 Goodfellow, W. D. et al. Environment of formation of the Howards Pass (XY) Zn-Pb deposit, Selwyn Basin, Yukon. In: Mineral Deposits of the Northern Cordillera. Canadian Institute of Mining and Metallurgy, Special Volume, 1986, 37: 19.

20 Qiunby-Hunt, M. S. et al. Thermodynamic zonation in the black shale facies based on iron-manganese-vanadium content. Chemical Geology, 1994, 113: 297.

21 Brewer, P. G. et al. Distribution of some trace metals in the Black Sea and their fluxes between dissolved and particulate sources. American Association of Petroleum Geologists, Memoir, 1974, 20: 137.