Sedimentary geochemical records and their depositional environmental significance during Cambrian-Ordovician transition in well YD 2, eastern Tarim Basin, NW China

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\textbf{Abstract.} In the eastern part of Tarim Basin, thick carbonate rocks were developed in the Upper Cambrian, while thick grey-black mudstone in the Lower Ordovician. Due to the complex tectonic and geological conditions in the basin, there are still many uncertainties in the study of the sedimentary environment, post-diagenesis and hydrocarbon accumulation conditions during the Cambrian-Ordovician transition. In this paper, 24 drilling core samples of the key strata of the Upper Cambrian-Lower Ordovician in the well YD2 were selected as the main research objects. Their mineral composition, major and trace elements (including REE) were analyzed. The results showed that the proportion of carbonate-siliciclastic sources in the rocks was controlled by the sedimentary environment, especially seawater depth. The oxic-suboxic sedimentary environment is indicated by the redox-sensitive elements and other trace elements (especially REE). This is consistent with the mineralogical features of the samples and the relatively low TOC. The elements Mn, Cr, V, Ni, on the whole, show a trend of first increasing, then decreasing, and repeated occurrence, indicating the sea level fluctuation cycle. In addition, according to the Ba/Sr and Mn/Sr ratios, the upper Cambrian carbonate rocks were normal marine sediments with weak post-diagenesis. Quartz, dolomite and calcite veins filling the fissures of the samples may have formed in the stage of intense uplift denudation, which was unfavourable to the formation of large oil and gas reservoirs.

1. \textbf{Introduction}
Tarim Basin, covering an area of about 560,000 square kilometers, is an inland superposed basin that has undergone multiple major structural alterations [1]. It is also a large petroliferous basin with the complex formation and distribution of oil and gas reservoirs in northwest China. In the eastern Tarim Basin, the Upper Cambrian karst cave-type dolostone reservoir and the Lower Ordovician thick layer of gray-black mudstone were explored, which constituted excellent reservoir-cap assemblage. Therefore, it has been one of the most important exploration targets.

However, because of the complex tectonic and geological conditions in the basin, there are still many controversies in the sedimentary environment, post-diagenesis, stratigraphic correlation and hydrocarbon accumulation within this region. By selecting the drilling core samples from the key
strata of the Upper Cambrian-Lower Ordovician in well Yingdong 2 (YD2) as the main research objects, herein, from the perspectives of sedimentology and sedimentary geochemistry, we discussed the changes of sedimentary environment, the process of post-diagenesis retransformation and its influence on the formation of oil and gas reservoir in this geological period. Meanwhile, this work could provide more evidence for the stratigraphic correlation in the Tarim Basin.

2. Geological background and analytical methods
The tectonic pattern that platform in the west and basin in the east was developed in the Tarim Basin during the late Cambrian (Figure 1). The eastern part of Tarim Basin, with an area of about 120,000 square kilometers, is an important block with good prospects for oil and gas exploration. This region contains multiple secondary construction units. The well YD2 is located in Yingdong tectonic belt of central uplift. According to the sedimentological studies, the well YD2 was deposited in the lower moderate slope. The well was drilled into lower Paleozoic. Among them, the upper Cambrian could be developed as the thick dolomite of the effective reservoir, and the lower Ordovician can be developed as the mudstone of the high-quality cap layer.

Figure 1. Schematic diagram of Late Cambrian-Early Ordovician paleo-sedimentary environment in the Tarim Basin (modified after ref. [2, 3], the yellow star indicates research well location)

A total of 24 core samples were collected from the Upper Cambrian-Lower Ordovician in the well YD2. The samples were divided into four groups according to their depths for discussion. These samples were cleaned, dried, and ground to smaller than 200 mesh before the analyses of their mineral composition, major and trace elements composition.

The mineralogical compositions (same as whole rock geochemistry) were determined semi-quantitatively by identifying XRD spectra of powdered samples with OLYMPUS Innova-X BTX X-ray diffractometer (XRD) instrument. Trace elements including rare earth elements analyses were carried out on an Agilent 7700x ICP-MS after the digestion with HNO₃-HClO₄-HF-HCl mixture, and the major elemental compositions were determined by an X-ray fluorescence (XRF) spectrometry.

3. Results and discussion

3.1. Mineral composition
The samples were divided into four groups according to depths. The mineral composition of each sample from the Cambrian-Ordovician transition is displayed in Figure 2. The well YD2 is comprised
of a continuous stratigraphic succession of mixed carbonate-siliciclastic sedimentary rocks. Some minerals are relatively low in content. The main differences between carbonate and siliciclastic rocks are, mineralogically, the abundance of calcite, dolomite versus quartz, phyllosilicates, and chemically, the content of CaO, MgO versus SiO₂, Al₂O₃, respectively. As a result, the raw data of the main mineral composition of the samples after normalization was used. The results showed that the first group mainly consists of dolomite, which constitutes principally dolostone, except for the one at the top of this part. Cyclicity was demonstrated by dolomite and calcite in the second group while the relative content of quartz increased significantly compared with the first group. The main minerals of the third group are quartz and calcite, because the third group is composed of limestone and argillaceous limestone. In the last group, the main mineral composition identified accurately is quartz, which constitutes mainly mudstone. In general, the relative contents of CaO, MgO versus SiO₂, Al₂O₃ are in accordance with the results of mineral composition.

3.2. Trace elements

![Figure 2. The vertical variation of mineral composition and trace element ratios of the four groups of samples in the well YD2](image)

It is obvious that the rock types and mineral compositions of the four groups are different. This seems to be related to the changes in water depth and environmental settings. From the upper-Cambrian to lower-Ordovician, the sediments transformed generally from carbonate (dolostone-dominated first and then limestone-dominated) to siliciclastic (calci-illite and mudstone) succession. It indicates the rise of sea level during the Cambrian-Ordovician transition in the eastern Tarim Basin. It also suggests that the area was deposited from the platform edge to the slope. The sedimentary characteristics were controlled by the sedimentary environment, especially seawater depth, which determined the source of the sediment.
The solubility of redox-sensitive elements in seawater is mainly controlled by the redox conditions of the sedimentary environment. Therefore, the content of redox-sensitive elements in sediments could provide information about the redox conditions of the bottom water [4, 5]. Redox-sensitive trace element ratios are valid proxies for assessing the paleo-redox conditions. For instance, U/Th>1.25, V/(V+Ni)>0.54, Ni/Co>7, and V/Cr>4.25 could serve as indicators of the anoxic condition, whereas these ratios decrease with the enhanced oxidation of the depositional environment [6]. In addition, euxinic situation (presence of H₂S) sometimes can be distinguished especially from anoxic condition (absence of H₂S) when V/(V+Ni)>0.84.

The four proxies display evident variations vertically (Figure 2). Nevertheless, the redox conditions indicated by the different proxies are not entirely consistent. For example, in the first group, the U/Th ratio indicates an anoxic state, while the V/(V+Ni) ratio indicates a euxinic state. On the contrary, Ni/Co and V/Cr reflect oxic and suboxic condition, respectively. This phenomenon is also observed in other groups. Frequent fluctuation of Molybdenum (Mo) concentration demonstrates the redox conditions of the ocean during that period was not stable. Therefore, there is a possibility that the contradictory redox interpretations, in part, are the consequence of different sensitivities of these proxies to high-frequency redox changes in oceans [7]. Moreover, these proxies are influenced by a number of factors, including sedimentation rate, organic matter accumulation, and diageneric process besides benthic redox condition [8, 9]. Even so, according to the mineralogical features and relatively low total organic carbon (TOC) contents, we suggested the redox conditions during the Cambrian-Ordovician transition was oxic-suboxic.

Variations on the contents of Mn, Cr, V and Ni in the well YD2 reflect the changes of sea level rise-and-fall in this region at that time. This is coincident with the results of mineral composition analysis. The Ba/Sr ratio of the samples is generally less than 1 except for the last three samples. Ba/Sr<1 indicate a normal marine sedimentation, while Ba/Sr>1 could result from submarine hot water. The Mn/Sr ratio of the samples ranges from 0.40 to 9.09, and there is no relative deficit of Sr, indicating weak post-diagenesis. Quartz, dolomite and calcite veins filling the fissures may have formed in the stage of intense uplift denudation. These veins would lower the porosity and permeability of the reservoir, and thus not be conducive to the formation of large oil and gas reservoirs.

3.3. Rare earth elements

The solubility of rare earth elements (REE) in seawater is very low, and they are highly stable in the process of weathering, handling, deposition and diagenesis [10, 11]. The REE distribution patterns of marine sediments are independent of time [12]. Therefore, it is an important indicator of the depositional environment. 

∑REE in different types of rocks varies. For sedimentary rocks, ∑REE in clastic rocks is obviously higher than that in carbonate rocks. The ∑REE of the four groups of samples ranges between 5~220ppm, and is lower than 50ppm in pure dolostone and limestone. With more argillaceous content, carbonate’s ∑REE content increases to 50~160ppm. ∑REE of the top group of mudstone samples reaches up to about 200ppm. The overall trend of ∑REE content from bottom to top is to increase, then decrease, and then increase. This may reflect the change of seawater depth in the area, which corresponds to the change of relative proportion of the input of terrigenous debris. The ratio between LREE (ΣLa–Eu) and HREE (ΣGd–Lu +Y) can comprehensively reflect the fractional distillation degree of REE [13]. The ΣLREE/ΣHREE for the four groups of samples ranges from 1.91~5.78. Ce is sensitive to the changes of redox environment in seawater. Thus it can be used as an indicator of the ancient marine environment [14]. Except for the sample YD2-16 (δCe=0.86, Ce deficit, indicating suboxic-anoxic environment), and the sample YD2-24 (δCe=1.27, Ce enrichment, indicating oxidizing environment), the δCe of the other samples is around 1. The REE distribution patterns of the four groups of samples at different depths in the well YD2, as a whole, display no obvious Ce anomaly, slightly negative Eu anomaly, and LREE enrichment (Figure 3). No positive Eu anomaly was observed, indicating that the well YD2 was not deposited in anoxic environment, and no hydrothermal activity was involved [15].
4. Conclusions
The rock types of the four groups of samples at different depths in the well YD2 were determined by the composition of main minerals and the oxides of the major elements through normalization. The proportion of carbonate-siliceous debris in the rocks was controlled by the sedimentary environment, especially the seawater depth. The oxic-suboxic sedimentary environment is marked by the redox-sensitive elements and REE. This is in concert with the mineralogical features of the samples and the relatively low TOC. The elements Mn, Cr, V, Ni, on the whole, show a trend of first increasing, then decreasing, and again, indicating the sea level fluctuations. Moreover, in light of the Ba/Sr and Mn/Sr ratios, the upper Cambrian carbonate rocks were normal marine sediments with weak post-diagenesis. Quartz, dolomite and calcite veins filling the fissures of the samples may have formed in the stage of intense uplift denudation, which was not conducive to the formation of large oil and gas reservoirs.

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References
[1] Li D S, Liang D G, Jia C Z, Wang G, Wu Q and He D F 1996 Hydrocarbon accumulations in the Tarim Basin, China AAPG Bulletin 80 1587-1603
[2] Zhang G Y, Liu W, Zhang L, Ding B S, Li H H, Zhang B M and Wang L D 2015 Cambrian-Ordovician prototypic basin, paleo-geography and petroleum of Tarim Craton Earth Science Frontiers 22 269-276 (in Chinese with English abstract)
[3] Zhao Z J, Luo J H, Zhang Y B, Wu X N and Pan W Q 2011 Lithofacies paleogeography of Cambrian sequences in the Tarim Basin Acta Petrolei Sinica 32 937-948 (in Chinese with English abstract)
[4] Challands T J, Armstrong H A, Maloney D P, Davies J R, Wilson D and Owen A W 2009 Organic-carbon deposition and coastal upwelling at mid-latitude during the Upper Ordovician (Late Katian): A case study from the Welsh Basin, UK Palaeogeogr. Palaeoclimatol. Palaeoecol.
273 395-410

[5] Pattan J N and Pearce N J G 2009 Bottom water oxygenation history in southeastern Arabian Sea during the past 140ka: Results from redox-sensitive elements Palaeogeogr. Palaeoclimatol. Palaeoecol. 280 396-405

[6] Rimmer S M 2004 Geochemical paleoredox indicators in Devonian–Mississippian black shales, Central Appalachian Basin (USA) Chem. Geol. 206 373-391

[7] Jin C, Li C, Algeo T J, O'Connell B, Cheng M, Shi W, Shen J and Planavsky N J 2018 Highly heterogeneous “poikiloredox” conditions in the early Ediacaran Yangtze Sea Precambrian Res. 311 157-166

[8] Algeo T J and Rowe H 2012 Paleceanographic applications of trace-metal concentration data Chem. Geol. 324-325 6-18

[9] Tribovillard N, Algeo T J, Lyons T and Riboulleau A 2006 Trace metals as paleoredox and paleoproductivity proxies: An update Chem. Geol. 232 12-32

[10] Murray R, Brink M, Jones L, Gerlach D and Iii G 1990 Rare earth elements as indicators of different marine depositional environments in chert and shale Geol. 18 268-271

[11] Murray R W, Buchholtz ten Brink M R, Gerlach D C, Russ G P and Jones D L 1992 Interocianic variation in the rare earth, major, and trace element depositional chemistry of chert: Perspectives gained from the DSDP and ODP record Geochimica et Cosmochimica Acta. 56 1897-1913

[12] Shields G A and Webb G E 2004 Has the REE composition of seawater changed over geological time? Chem. Geol. 204 103-107

[13] Deng Y, Ren J, Guo Q, Cao J, Wang H and Liu C 2017 Rare earth element geochemistry characteristics of seawater and porewater from deep sea in western Pacific Sci. Rep. 7 16539

[14] Holser W T 1997 Evaluation of the application of rare-earth elements to paleoceanography Palaeogeogr. Palaeoclimatol. Palaeoecol. 132 309-323

[15] Olivarez A M and Owen R M 1991 The europium anomaly of seawater: implications for fluvial versus hydrothermal REE inputs to the oceans Chem. Geol. 92 317-328