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Geochemical and Sedimentary Setting of the Ordovician in Central Hunan

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Due to the comprehensive tectonic transformation, the type of the basin of early Paleozoic in the central Hunan area has been a controversial issue. The Ordovician is an important transitional period for the basin type of the early Paleozoic in the south China. The widely distributed black siliceous rocks of the middle Ordorvician, with stable chemical properties, can well indicate the sedimentary and tectonic evolution of the basin. This paper synthesized the major and rare earth elements(REE) of cherts from Maduqiao (MDQ) section in Qidong county and Mianhuaping (MHP) section in Ningyuan county. Chert samples in MDQ section shows that the SiO_2 content ranges from 90.36 to 94.73%, with the average of 92.91%, Al_2O_3 content is in the range of 2.36~3.88%, the average is 2.73%, Fe_2O_3 content is from 0.61 to 1.21%, the average is 0.90%, Simples in MHP section showed SiO_2 values (89.40~91.90%, average 90.76%) , Al_2O_3 values (2.47*9~4.42%, averaged 3.43%) and Fe_2O_3 values (0.72~1.71%, average 1.12%) , which represent that the terrigenous clastic content in these chert samples is very low . The Al/(Al+Fe+Mn) ratios in MHP and MDQ is 0.54~0.83 and 0.65~0.79 respectively, which demonstrated that cherts in the two regions are biogenic and have little relation with hydrotherm. The Al/(Al+Fe) ratios in MHP and MDQ are 0.55~0.83 and 0.65~0.79, which means that the cherts have been mainly deposited in environment of the continental margin. Plotting diagrams of $100\times TFe_2O_3/SiO_2$-$Al_2O_3/(Al_2O_3+TFe_2O_3)$, $TFe_2O_3/(100-SiO_2)$- $Al_2O_3/(100-SiO_2)$ and La_N/Ce_N- $Al_2O_3/(Al_2O_3+TFe_2O_3)$, showes that most of the cherts have deposited in the continental margin and a small amount deposited in the transition regime from the margin to pelagic environment. The concentration of the ΣREE in MHP (36.07 ~ 98.84) and MDQ (27.87~60.02), were far below the ΣREE concentration of the North American average shale (NASC), which suggested that the speed of cherts deposition in the shelf environment is higher. And $(La/Yb)_N$ values were 0.72~1.30, and 1.05~1.30 and the enrichment of LREE was not obvious, mean that the sedimentation was not impacted by the terrestrial sources very much. And the negative to positive Ce anomalies (0.89~1.46) represented an anoxia and reducing environment. Combining with the previous research and chemical characteristics of the cherts in adjacent regions, this paper has concluded that: the south China ocean in the central Huanan was closed in the late Neoproterozoic and left a multi-island sea basin similar to the Mediterranean. Besides the early Cambrian, the basin was not very deep. Intracontinental down thrusting by the Cathysia at the beginning of the middle Ordovician, and the basin began to subsidy and transgress. Islands provided a small amount of clastics and obstructed circulation of water, making the sedimentary environment both with the characteristics of the continental margin and limited condition where the cherts deposited. After all, the whole area has been transformed to be fold belt in the late Silurian.

1. Introduction

The Caledonian of early Paleozoic is a significant episode in the geologic history of south China plate. At that time, a large scale of magmatic activity took place, intensive fold deformation zone and regional unconformity were formed during this period (Xiao et al., 2016; Rong et al., 2010). The central Hunan area located at the junction of the Yangtze and cathaysian plate. Many crucial geological problems were controversial, because of

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its old age, thick cap, little exposure and deep burial of the Lower Paleozoic, and the transformation and deformation caused by multiphase tectonic superposition and magma intrusion. There are no agreement on the geological problems related to the junction zone, such as the convergence site of the Yangtze and cathaysia plate, the basin prototype and the precise closing time, the dynamic mechanism and driving force of collision and the tectonic evolution process of etc. Therefore, whether the *paleo-south China ocean* still had been existing until the early Paleozoic the Lower Paleozoic of the research area (strata of the *Qianhuixiang* fold belt now) were developed in the residual ocean basin and finally closed during the caledonian movement, or the early ocean was closed along with the Grenville orogeny, then the south China entered into the stage of intra-continental evolution, and the south China rift basin formed along with the breaking up of the Rondinia, i.e., the residual ocean did not exist? This is still a big dispute. Chemical elements analysis is a common method in many fields (Nyakuma et al., 2017; Olofin and Liu, 2016; Simone et al., 2009). The Ordovician is an important transition period of the basin type in the early Paleozoic of the south China. Sediments are mainly composed by siliceous rocks, limestone, shale and a small amount of silty sandstone. Among which the sediments of the central Hunan area were consisted of the silty shale, the siliceous shale and carbonaceous shale with abundant graptolite and cherts. Siliceous rocks (cherts) which is special in the marine sediments has an important instruction effect. Its primary chemical composition is SiO_2, and its structure is compact. So it could survive in weathering and other epigenesis and could well preserve the diagenetic information of the sediments. This property of siliceous rocks can indicate the structure and paleogeographic evolution of the sedimentary basin (Murray, 1994). Many researchers have been done and relevant comparison standards have been established by precursors, and have been widely used now.

The sedimentary environment and genesis of the cherts deposition in the residual basin have been studied by many scholars and a lot of progress have been made (He et al., 2016; Du et al., 2007; Jian et al., 2015; Semache et al., 2015). The silica of the Qianguixiang sea area in the ordovician mainly originate from the siliceous organism, hydrotherm and upwelling. Because the complicated tectonic backgrounds of the research area, the previous cognition about the research area were diverse and complex. In order to comprehensively understand the sedimentary setting of the Paleozoic in the central Hunan area, by combining with the previous data, the authors analyzed and compared the genesis of cherts in this area. Furthermore, the source and sedimentary environment of cherts and the paleogeographic pattern and prototype of the basin of Ordovician in the central Hunan province were also studied and discussed in this paper.

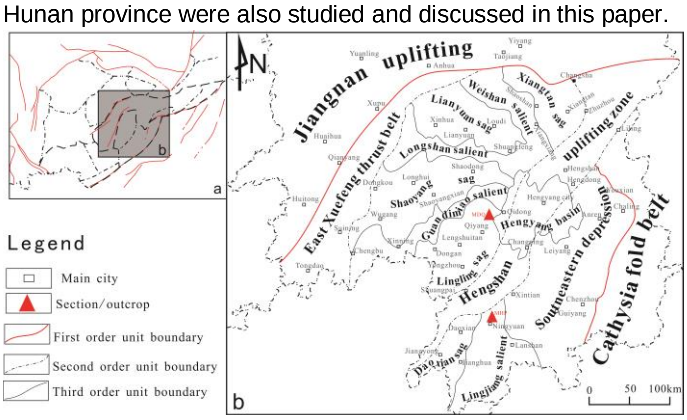

Figure 1: Simplified geological map showing Paleozoic strata and distribution of samples in the study area Distribution of the siliceous series

2. Geological setting

The central part of Hunan province, was part of the middle Yangtze platform of south China block before its isolation from the southeastern depression of Hunan by the Hengshan uplift. Structurally, it is located in north of Caledonian fold belt of south China and south to the southeast edge of Xuefeng mountain. Influenced by the caledonian, the Lower Paleozoic intensively deformed and uplifted after the late Ordovician. The caledonian structural layer was formed and contacted with the overlying strata in a high angle unconformity. And this relationship deformed by other tectonic superposition, the prototype and distribution of the basin remains controversial. After the early Cambrian, with the rapid development of carbonate construction of the Yangtze platform and the excavation of the Cathysia after the early Cambrian, the central Hunan area gradually became a relative limited sedimentary basin, the basin is composed mainly by fine silty shale sediments of the early Ordorvician. The basin was hit by a widely transgression during the middle Ordovician, the sediment in the study area was a set of 20 -135 m thick black shale and siliceous rocks (Figure 2), and the sediments of lower Ordorvician were flysch with the thickness more than 2000m, was composed by lithic sandstone, greywacke, arkose intersected with a small amount of shale. Among which the siliceous rock series of the middle Ordorvician is stably distributed and rich in fossils (mainly consist of graptolite and radiolarian), is the best layer for studying the biostratigraphy, sedimentary characteristics and tectonic background of the basin.

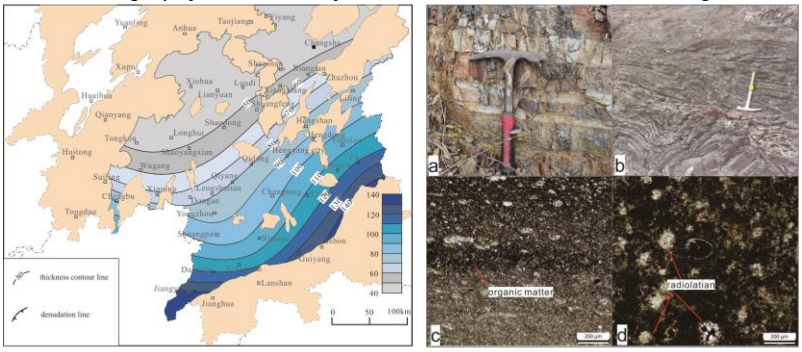

Figure 2: Isopach map, outcrop and microscope photograph of of the Middle Ordovician cherts series in central Hunan

3. Sampling and analysis

Samples of this paper were collected from Maduqiao(MDQ) section of Qidong county and Mianhuaping (MHP) section of Ningyuan county in the middle Ordovician siliceous rock series. The samples are collected in different sublayers from the bottom to top. The lithology of the samples is thin laminated chert with a small amount of organic matters. The major and rare earth elements have been tested in MLR Chongqing Mineral Resources Supervision and Test center, the instruments ICP-MS-X series II and XRF - PW4400 were used in the testing, and the deviation were less than 5%. the REE are standardized by NASC and the analysis results could be find in Table 1.

4. Geochemical characteristics

4.1 Major elements

As it shows in Table 1, the SiO_2 concentration of MDQ section is from 90.36 to 94.73 wt.% with an average value of 92.91 wt.%, the content of Al_2O_3 ranges from 2.36 to 3.88 wt.% with an average of 2.73 wt.%, and the Fe_2O_3 concentration is 0.61~1.21wt.% with the average value of 0.90 wt.%. The he SiO_2 concentration of MHP section is from 89.40 to 91.90 wt.% with an average value of 90.76wt.%, the content of Al_2O_3 ranges from 2.47 to 4.42 wt.% with an average of 3.48 wt.%, and the Fe_2O_3 concentration is 0.72~1.71 wt.% with the average value of 1.12 wt.%. The concentration of the rest of the oxides are very low. Compare with the two sections, the percentage of the major elements of MDQ and MHP are very similar which indicates that they come from same paleogeographic environment. The high concentration of the SiO_2 with the average value more than 90wt.% means that the terrigenous clastic components in the chert of the two sections are very low, and the MDQ section got a greater distance with the provenance.

In addition, the concentration of the major elements Fe, Mn and Al are excellent indicators for distinguishing the sedimentary environment of the chert. The enrichment of Fe and Mn are known to be affiliated with hydrothermal input while the Al is related to the terrigenous input. Previous studies have suggested that the value of Al/(Al+Fe+Mn) can reflect the genesis of the marine sediments. Take Al/(Al+Fe+Mn)0.4 as the boundry, the sediments might be related to hydrothemal genesis when the value less than 0.4, it might be related to terrigenous input when it is above 0.4 (Bostrom et at ,1973), and this ratio ranges from 00.1 (pure hydrothermal) to 0.60 (pure biogenetic) (Adachi et al., 1986). The hydrogenous element Mn was precipitated from the diagenesis of the chert, the ratio of Mn/Al can not reflect the sedimentary environment accurately, and the ratio of Al / (Al+Fe) was suggested to distinguish the tectonic setting of the chert, the graphic projection zone of the continental margin, pelagic basin and oceanic ridge were delineated by using the samples from the known environments (Murray et al.,1990; 1991; 1992; 1994). The ratio of Al/(Al+Fe+Mn) of the chert samples in MHP section ranges from 0.54 to 0.83 and the ratio of MDQ section is 0.65 ~ 0.79. These indicated that the chert of the two areas were biogenesis and had little relation to hydrotherme. The ratio of Al/(Al+Fe) in MDQ and MHP is 0.55~0.83and 0.65~0.79 respectively, it indicates that the chert mainly deposited in the continental margin.

The ratio MnO/TiO_2 can be used to analyze the sedimentary environment and origin of the chert too, the ratio will be<0.5 when it deposited near the continent and the ratio will be between0.5~3.5 when it formed in the pelagic area. This ratio ranges from 0.04 to 0.26 which indicates that a continental margin environment in the research area.

Table 1: Major element (%) and rare earth element data (10^{-6}) of Middle Ordovician cherts in MDQ and MHP

Item	MHP					MDQ					
	4	11	16	24	34	1	5	10	14	28	34
SiO_2	89.95	91.90	90.39	89.40	91.67	93.48	94.07	92.53	90.36	92.27	94.73
Al_2O_3	4.42	2.81	2.74	4.42	2.47	2.44	2.53	2.75	3.88	2.36	2.39
Fe_2O_3	0.72	1.05	1.52	0.96	1.71	0.89	1.21	1.05	0.92	0.61	0.69
FeO	0.15	0.10	0.15	0.05	0.31	0.08	0.13	0.08	0.08	0.10	0.08
CaO	0.05	0.04	0.80	0.14	0.37	0.04	0.05	0.11	0.04	0.03	0.04
MgO	0.19	0.19	0.41	0.26	0.32	0.09	0.11	0.17	0.13	0.05	0.17
K_2O	0.96	0.82	0.61	1.20	0.64	0.55	0.55	0.73	0.95	0.54	0.74
Na_2O	0.12	0.08	0.10	0.09	0.08	0.34	0.29	0.29	0.39	0.05	0.09
TiO_2	0.18	0.11	0.11	0.18	0.11	0.11	0.12	0.12	0.16	0.11	0.14
P_2O_5	0.03	0.02	0.04	0.05	0.03	0.03	0.04	0.03	0.04	0.03	0.02
MnO	0.01	0.02	0.03	0.01	0.03	0.01	0.01	0.01	0.01	0.01	0.01
LOI	0.50	0.41	0.34	0.51	0.40	0.28	0.46	0.30	0.49	0.40	0.28
Total	97.28	97.55	97.24	97.26	98.13	98.33	99.56	98.17	97.45	97.69	99.38
Al*	0.83	0.70	0.62	0.81	0.54	0.71	0.65	0.71	0.79	0.76	0.75
Al_2O_3/TiO_2	24.56	25.55	24.91	24.56	22.45	22.18	21.08	22.92	24.25	21.45	17.07
Al/(Al+Fe)	0.83	0.71	0.62	0.81	0.55	0.71	0.65	0.71	0.79	0.77	0.76
La	15.30	11.80	7.61	8.21	12.50	6.74	8.66	8.15	8.69	12.50	5.88
Ce	32.90	23.30	15.60	16.00	23.40	13.90	16.20	16.00	25.60	25.60	11.60
Pr	4.76	2.71	1.72	1.98	2.90	1.59	2.15	2.09	1.99	2.93	1.34
Nd	22.70	10.40	6.51	8.02	11.30	6.33	8.50	8.44	7.55	11.30	5.20
Sm	5.74	1.72	1.06	1.42	1.90	1.08	1.38	1.39	1.19	1.76	0.86
Eu	1.33	0.25	0.14	0.22	0.27	0.14	0.18	0.19	0.15	0.26	0.11
Gd	4.90	1.63	1.01	1.35	1.63	1.04	1.18	1.26	1.20	1.69	0.77
Tb	0.82	0.25	0.15	0.21	0.24	0.16	0.17	0.19	0.17	0.24	0.12
Dy	4.58	1.39	0.89	1.11	1.44	0.91	0.92	1.08	0.99	1.37	0.71
Ho	0.88	0.28	0.17	0.21	0.29	0.18	0.19	0.22	0.21	0.28	0.15
Er	2.34	0.84	0.51	0.59	0.88	0.55	0.57	0.61	0.61	0.87	0.45
Tm	0.33	0.13	0.08	0.10	0.14	0.08	0.09	0.10	0.10	0.14	0.07
Yb	2.00	0.86	0.55	0.63	0.92	0.52	0.63	0.66	0.72	0.94	0.53
Lu	0.26	0.13	0.08	0.09	0.13	0.07	0.09	0.10	0.11	0.14	0.08
ΣREE	98.84	55.69	36.07	40.14	57.94	33.29	40.91	40.48	49.28	60.02	27.87
$(La/Yb)_N$	0.72	1.29	1.30	1.23	1.28	1.22	1.30	1.16	1.14	1.25	1.05
$(La/Ce)_N$	0.98	1.07	1.03	1.08	1.13	1.02	1.13	1.08	0.72	1.03	1.03
δEu	1.18	0.70	0.63	0.75	0.72	0.62	0.66	0.67	0.59	0.71	0.63
δCe	0.91	0.98	1.02	0.94	0.92	1.01	0.89	0.92	1.46	1.00	0.98

Al*= Al/(Al+Fe+Mn), $\delta Ce = 2 Ce_N /(La_N + Pr_N)$

4.2 Rare earth elements

The total REE concentration (ΣREE) is much higher in the marginal basins and residual sea basins where the chert contaminated by the terrigenous sedments and decrease dramatically when away from land like in the pelagic basin. And the concentration of Ce anomalies (δ Ce) and the NASC-normalized La_n /Yb_n and La/Ce ratio are reliable criteria for delineating the sedimentary environment. The La_n /Yb_n ratio of terrigenous sediments deposited in continental margin is always higher (1.49~1.74) than in pelagic sediments (0.5~0.8) which shows depletion in LREE, and the minimum value of the ratio were detected at the axial zone of the oceanic ridge (around 0.3). The δ Ce of the coastal water with the value of 0.8~1.2 is not obvious, but it become very low (0.2~0.3) in the open sea water. The δ Ce can change with the depth of the water and much higher in the anoxic conditon than oxidizing environments. Statistically, the δ Ce within the range of 0.67 to 1.35 were deposited in a continental margin environment. The negative Ce anomalies are also not obvious in the restricted sea basin and oceanic basin where contaminated by the terrigenous inputs. The great negative Ce anomalies exhibited in a typical open oceanic basin. The surface of the abysmal sea sediments shows a pronounced Ce depletion with the δ Ce≈0.25, for example the δ Ce is only 0.04 at the depth of 2000 to 3000 m of the east Pacific oceanic rise. That is to say, the pronounced Ce depletion can indicate the pelagic environments (Murray, 1994). As the influence of the hydrotherm in the research area is not obvious, the REE can reflect the geological setting of the cherts series with a high accuracy. The ΣREE concentration of MHP and MDQ section ranged of 36.02 to 98.84($\times10^{-6}$) and 27.87 to 60.02($\times10^{-6}$) respectively, i.e., much lower than that in the NASC standard, whose ΣREE concentration is 172.61$\times10^{-6}$. It indicated that the Middle Ordovician cherts of the research area deposited in the shelf environment where the deposition rate is high. The $(La/Yb)_N$ ratio calculated from data of the cherts of MHP and MDQ section (range from 0.72 to1.30) do not show obvious positive anomalies , it also demonstrated the research area was not seriously affected by the terrigenous inputs .

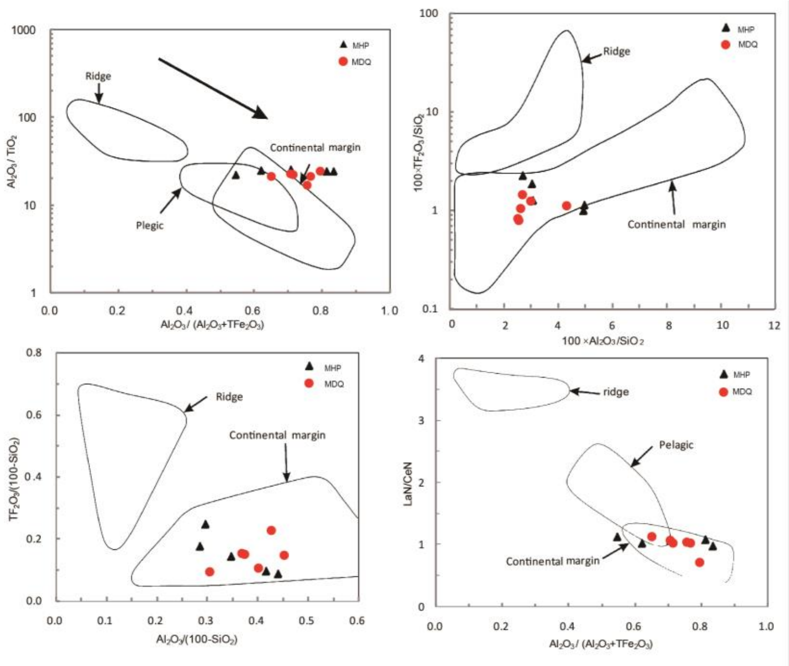

Figure 2: Discrimination diagrams for geological settings of middler Ordovician chert series in central Hunan, base map after reference (Murray,1994)

5. Sedimentary environment and tectonic background

According to the section correlation and microscope examination, abundant radiolarians and organic matter belts were found in the cherts of central Hunan, i.e., the cherts is originate from sedimentation. The Al/(Al+Fe+Mn) ratio displayed the cherts composed by pure biogenic SiO_2 . In the plot of $Al_2O_3/(Al_2O_3+T\ Fe_2O_3)$ －$Al_2O_3/\ TiO_2$, 100×T $Fe_2O_3/\ SiO_2$- $Al_2O_3/(Al_2O_3+TFe_2O_3)$,$TFe_2O_3$ /(100-SiO_2) - Al_2O_3/(100-SiO_2) and La_N/Ce_N - Al_2O_3 / (Al_2O_3+T Fe_2O_3) (Figure 3) , most of the rocks were accumulated in the continental margin and a few in the pelagic zone . Therefore, the cherts series of the central Hunan deposited in the zone proximal to continental margin with relative deep water where affected by the terrigenous inputs but very subtle. Comprehensively speculated by conclusions above, the central Huan existed a multi-island sea basin (so called Qianguixiang sea) whose water was relatively deep in the Middle Ordovician, however, the islands could supply small amount of inputs and hinder the water circulation. These provided the research area both the marginal characteristics and reducing environment. And combined with the conclusions of precursors', the writer considered the south China ocean in the central Hunan was closed in the late Neoproterozoic and left a multi-island sea basin similar to the Mediterranean, but a remnant ocean basin still exist along Nanning and Qinzhou of Guangxi. The sea water bacame very shallow after the Early Cambrian transgression. At the beginning of Middle Ordovician, the basin sank and water deepen when the compression from the Cathysia became fierce. The whole area transform to fold belt in the late Silurian.

6. Conclusion

Based on the genesis and analysis on sedimentary environment of cherts and combination of the cognition of precursors', it has been found that:

(1) The Middle Ordorvicain chert series in central Hunan were normal biogenic sediments, which slightly affected by the terrigenous inputs and deposited in multi-island sea basin in deep water. And the MHP area is closer to the depocenter than MDQ area.

(2) The Middle Ordovician is the transition period of the prototype basin in the central Hunan region, when the basin transformed from the shallow remnant basin to the foreland basin, and the environment in which the siliceous rocks formed was provided when the water rapidly deepened.

(3) The south boundary of the basin in Middle Ordovician is remain unclear, the impetus of the collision between the Yangtze and Cathysia blocks in the late Caledonian should come from the subduction of the residual oceanic crust of the Nandan-Qinzhou area.

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