Cambrian and Ordovician Oceanic Oscillations: New geochemical evidence from the Tarim Basin

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The Tarim Basin is a large endorheic basin located in the northwest China with a northern boundary of the Tianshan Mountain and a southern boundary of the Kunlun Mountain. This premier petroleum basin contains huge succession of Paleozoic, Mesozoic and Cenozoic sedimentary rocks ranging up to a thickness of locally exceeding 15 km in some regions. Previous studies have concluded that the major oil source rocks are from Cambrian-Ordovician. This current project was designed to better understand the paleoenvironment development of Paleozoic marine sediments, the potential source rocks of the huge natural gas. This paper is particularly focused on Earlier Paleozoic, namely Sinian-Cambrian-Ordovician succession. A deep drilling core recovered from the east part of theTarim Basin, Well TD2 was finely sub-sampled for stable carbon and oxygen isotope analyses ($\delta^{13}C$ and $\delta^{18}O$ of carbonate phases and TOC) and trace elemental measurements (ICP-MS). Our data shows that very strong fluctuations of geochemical parameters occur in the lower part of the core, i.e., from the Precambrian-Cambrian transition to Middle Ordovician sediments. Isotopic compositions of the carbonate phases vary in a very dynamic range, i.e., $\delta^{13}C = -10.1$ to +3.2 ‰(STDEV = 3.19,VPDB) and $\delta^{18}O = -17.4$ to -5.1‰ (STDEV = 2.89,VPDB), respectively, showing at least seven depletion-enrichment ‘cycles’ during that ~100 Ma of time. Trace elemental compositions (Co, P, V, Zn etc.) and ratios (V/Ni) are significantly higher (~2-4 times) during those ^{13}C and ^{18}O depleted ‘breaks’. The ‘negative’ correlation of stable isotope values and certain trace elemental concentration/ ratios led us to suggest that the cause of the multiple ‘cycles’ of isotopic depletion/ enrichment, in a rough pattern of about 10 Ma each cycle, could be due to strong episodic upwelling of oceanic waters. Our high resolution data suggests that at least seven major oceanic upwelling events occurred, leading to complete replacement of water bodies, thus causing large scale shifts of stable isotopic ratios of the carbonate rocks, marking the major transitions of geological units (formations) independent of lithologies basinwide.

The molecular level dissolution mechanisms of quartz under different pH conditions

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It is generally believed that the hydrolysis of Si-O-Si bonds is the key step in the dissolution processes of quartz-water system. High level *ab initio* molecular orbital calculations have been carried out to investigate the molecular level dissolution processes of the Q1(Si) site and Q2(Si) site of quartz at difference pH conditions. Theoretical methods including potential energy surface calculation, transition states searching, reaction pathway optimization and *ab initio* molecular dynamics (ADMP) are used in this study. Our results show that under acidic condition, the protonation takes place at the terminal Si-OH unit but not at the bridging oxygen of Si-O-Si linkage. Such way of protonation results in stronger Si-O-Si bonding and makes the dissolution slightly slower than that at neutral condition. The rate-determining steps for both neutral and acidic conditions are the breaking process of Si-O-Si bonds. However, under base condition, rate-determining step for the dissolution of Q1(Si) site is the process of one water molecule approaching the Q1(Si) site. The activation energy results (at M05-2X/6-311+G(d,p) level) of transition states show that the dissolution rate will increase a lot at the base condition comparing with those at acidic or neutral conditions. Suggested by the activation energy results, the dissolution rate at acidic condition will be even slightly smaller than the dissolution rate at neutral condition. These findings are consistent with existing experimental evidences and correct a well-known previous theoretical model (Xiao and Lasaga, 1994) for the case of quartz dissolution.

[1] Xiao and Lasaga (1994) *GCA*, 5379-5400.