

Authigenic carbonate precipitation at the end-Guadalupian (Middle Permian) in China:  
Implications for the carbon cycle in ancient anoxic oceans

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Carbonate precipitation is a major process in the global carbon cycle. It was recently proposed that authigenic carbonate (carbonate precipitated in situ at the sediment-water interface and/or within the sediment) played a major role in the carbon cycle throughout Earth's history. The carbon isotopic composition of authigenic carbonates in ancient oceans have been assumed to be significantly lower than that of dissolved inorganic carbon (DIC) in seawater, as is observed in the modern oceans. However, the  $\delta^{13}\text{C}$  values of authigenic carbonates in the past has not been analyzed in detail. Here, we report authigenic carbonates in the uppermost Guadalupian (Middle Permian) rocks at Chaotian, Sichuan, South China. Monocrystalline calcite crystals <20 mm long are common in the black mudstone/chert sequence that was deposited on a relatively deep anoxic slope/basin along the continental margin. Textures of the crystals indicate in situ precipitation on the seafloor and/or within the sediments. The calcite precipitation corresponds stratigraphically with denitrification and sulfate reduction in the anoxic deep-water mass, as indicated by previously reported nitrogen and sulfur isotope records, respectively. Relatively high  $\delta^{13}\text{C}$  values of the authigenic carbonates (largely -1‰) compared with those of organic matter in the rocks (ca. -26‰) suggest that the main carbon source of the carbonates was DIC in the water column. The calcite crystals precipitated in an open system with respect to carbonate, possibly near the sediment-water interface rather than deep within the sediments. The  $\delta^{13}\text{C}$  values of the carbonates were close to the  $\delta^{13}\text{C}$  value of seawater due to mixing of  $^{13}\text{C}$ -depleted remineralized organic carbon (that was released into the water column by the water-mass anaerobic respiration) with the large DIC pool in the oceans. Our results imply that  $\delta^{13}\text{C}$  values of authigenic carbonates in the anoxic oceans might have been systematically different from the values in the oxic oceans in Earth's history, controlled by the depth of the redoxcline in the water column and sediments. If our model is correct, authigenic carbonates with relatively high  $\delta^{13}\text{C}$  values in the ancient anoxic oceans may have had a less substantial influence on the bulk  $\delta^{13}\text{C}$  values in geologic records than has been previously suggested.

[ref.] Saitoh et al. (2015) Progress in Earth and Science 2:41