In-situ analyses of phosphorus contents of carbonate minerals with primary textures by LA-ICP-MS

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Phosphorus (P) is one of the bio-essential elements to form DNA, RNA and bone, whereas P is a major biolimiting nutrient as well as nitrogen. Therefore, it plays a key role on sustaining the biological productivity of the world's oceans because there is a few in surface oceans. The major animal phyla began to acquire the carbonate- or phosphate-biomineralization in a relatively short interval slightly before and/or during the Cambrian explosion. As a result, the organisms with shell/hard skeleton appeared in those days. In addition, Calcium isotopic compositions of animal embryos, phosphorite and dolomite indicate that Ca-biomineralization started in the Neoproterozoic. Therefore, it is very important to estimate P concentration of seawater.

This work presents the analytical procedures of phosphorus content in natural carbonate minerals and a preliminary report of phosphorus content in carbonate minerals with primary textures from the Late Proterozoic to early Cambrian in Three Gorge area, south China. In the Three Gorge area, very stable sequence from the 630 Ma Marinoan Glaciation to the early Cambrian is well preserved. In addition, carbon, oxygen and strontium isotopic compositions of drill core samples are already available, indicating presence of very large biological perturbation.

Phosphate, especially carbonate fluorapatite, can contain very small amounts of carbonate ion, substituting with phosphate ion. However, contamination of even the small grains of phosphate results in the large error of the phosphorus content because of the small amounts. Therefore, we should establish a method to avoid the contamination of phosphate minerals. We performed sequential procedures to avoid them: microscopic observation, microprobe analyses including compositional mapping, in-situ microanalyses with LA-ICP-MS. In addition, we analyzed a carbonate mineral based on sequential analytical method, and avoided an anomalously positive excursion in phosphorus signals. In addition, phosphorus content was estimated based on mixing trends of some trace and major elements between phosphate and carbonate.

Carbonate rocks at the uppermost part of the Doushantuo Formation in the Ediacaran contains about 250 ppm or less in phosphorus content, whereas a limestone of the Shipai Formation has about 50 ppm. The preliminary data suggests that depletion in phosphorus content in the early Cambrian, possibly depends on the onset of biomineralization.