

## Behaviors of sulfur and arsenic-related elements in the marine clay layers of subareal Osaka Group sediments

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Higher arsenic is included in the marine clay layers than in the intercalated fresh water sediments of Quaternary Osaka Group formations. The marine clay layers should be the sources of arsenic contaminated groundwaters in the Osaka Group sediments, although dissolution mechanism(s) has still unknown. Since Sato et al. (2002) reported that high arsenic concentration was found in the marine clay layers Ma 13 and Ma12, major mineral and major and minor chemical compositions were studied for the same sediment column. According to the results, the dissolution behaviors of sulfur and arsenic are discussed in this report.

The drilled core sediments were taken from 0.5m interval between 9 and 47m depths from the surface. The marine clay layer Ma13 is in between 15.4 and 27.3m and Ma 12 in deeper than 44.4m. In the previous report by Sato et al. (2002), the marine clay layers contained 8~15ppm arsenic, while the intercalated fresh water sediments less than 7ppm. SiO<sub>2</sub> more than 60% is the most dominant major chemical composition of the all sediments, and it well positively correlated to the quartz intensities, which is the most dominant minerals. Chlorite and smectite are the characteristic minerals in the marine clay layers. Loss of ignition, contents of Al, Mg and Fe are large in the marine clay layers, corresponding to the higher amounts of clay minerals. In the marine clay layers, heavy metals such as Pb, Cu and Zn and P are concentrated more than in the fresh water sediments. The heavy metals would be concentrated in the sediments by the adsorption and precipitation with clay minerals and/or hydrogeneous metal hydroxides during sedimentation. Phosphorous should be originated from the biogenic skeleton. The concentration of P and arsenic have a well positive correlation, suggesting that the arsenic would originally be concentrated by the biological activities at the same timing of P concentration. In the less permeable clay layers, heavy metals and P have not been moved and kept the original concentrations after the emergence.

Sulfur content is obviously high in the marine clay layers, containing more than 1%, however, it is less than a few hundreds ppm in the fresh water sediments. Such a sulfur was originated from the sulfate ion in the seawater, which was reduced to sulfide to precipitate pyrite under anoxic condition in the ocean bottom sediments. Both sulfur and arsenic are concentrated in the marine clay layers, however, distribution of these elements are slightly different in the Ma13. Sulfur content decreases towards upward and downward from the middle part of the Ma 13 to the boundaries to the adjacent fresh water sediment layers. Arsenic also decreases in the uppermost and lowermost part of the Ma13. However, it highly concentrates at the boundaries to the middle part of the layer, in which arsenic contents does not vary. Those concentrations are not observed in sulfur distribution. The arsenic in the marine clay layer is mostly fixed in pyrite, although the behaviors of these elements are different after the decomposition of the mineral. Sulfur is removed with flowing groundwater as sulfate ion, while arsenic stays in the sediments that adsorb arsenic on the clay mineral and/or iron oxide surfaces. Thus, it will be concluded that arsenic does not move from the sediments into the groundwater when the groundwater is flowing and preserving the oxic condition at the iron can be stable as oxyhydroxide.