

## Tracers of pollutant sources and transport pathways using stable Cd and Pb isotopes in Ulsan Bay sediments

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### Abstract

Metal sources have been traced by exclusively Pb isotopes in the previous studies. Although Pb isotopes were successfully used for the identification of Pb sources and mixing processes, the explanation for other metals with different geochemical behaviour was restricted. Cd isotopes become a candidate to trace Cd sources and transport pathways because Cd isotopic ratios could be fractionated by high-T processes such as smelting and refinery processes. Evaporated Cd showed depleted isotopic composition while Cd in slags from refinery has heavy isotope enriched composition [1]. This study aimed to apply stable Cd and Pb isotope ratios in Ulsan bay sediments to identify their sources and transport pathways. To do this, firstly we setup the analytical procedures for precise and accurate Cd isotope ratios including chemical separation and instrument measurement steps [2]. And we presented stable Cd and Pb isotope ratios in real sediment samples.

Surface and core sediments were collected at the Ulsan Bay, Korea. After the chemical separation of matrix and interferent metals using AGMP-1 and TRU-spec, Cd and Pb isotope ratios were measured by MC ICP/MS equipped with APEX desolvation system

Cd concentrations in surface sediments ranged from 0.15 ppm to 1.6 ppm, and were the maximum at station close to Onsan industrial complexes and at station close to Jangsaengpo harbor. Offshore stations showed the lowest concentration of Cd.  $\epsilon^{114/112}_{NIST Cd}$  in surface sediments showed a little variation and ranged from -4.5 to 0.6. Sediments with the highest concentrations of Cd showed the most depleted (St. 30), non-fractionated (St. 4) and slightly enriched (St. 17). Sediments with the lowest concentration of Cd showed slightly depleted  $\epsilon^{114/112}_{NIST Cd}$  values (St. 36 and 7). Although isotopic composition of Cd did not show systematic aerial distribution, it might be suggested that most Cd in Ulsan bay sediments were negatively fractionated except for harbor and ship building plant, which indicates that atmospheric transport are important pathway for Cd in sediments.

Pb concentration in surface sediments ranged from 10 ppm to 215 ppm and was the maximum at station close to Onsan industrial complexes and was the minimum at offshore station. Pb contamination was focused at stations in the southern part of the Ulsan Bay but sediments in the northern parts showed also slightly enriched Pb concentration. 207Pb/206Pb showed the wide range of variation from 0.844 to 0.90. Combining isotope ratio and the inverse of Pb concentration (Fe/Pb), three end-members of Pb sources were identified; that is, the first one is high concentration and highly un-radiogenic Pb which has similar to those in Broken Hill ores, the second is high concentration and radiogenic Pb isotope similar to background value, and the last is background concentration and Pb isotope. In other words, imported ores and local ores were two major pollutant sources.

### References

- [1] Wombacher et al., (2004). GCA, 68(10): 2349-2357  
[2] Gao et al. (2008). ACA, 612: 114-120.

## Characteristic and Leaching behavior of Cd-, Pb-substituted goethite under CO<sub>2</sub>

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### Introduction and Methods

Transport of CO<sub>2</sub> from deep geological formations to shallow ground-water aquifers may threaten the long-term quality of drinking water resources in locations adjacent to sites of carbon sequestration. Metal transport resulting from potential CO<sub>2</sub> leakage into freshwater aquifers is a major concern accompanying carbon sequestration operations. Acidity resulting from dissolution of leaked CO<sub>2</sub> into aquifer waters may result in release of metals from aquifer minerals. Goethite ( $\alpha$ -FeOOH) is one of the most abundant and reactive iron oxides in soils and sediments. Goethite plays an important role in nature controlling the mobility of heavy metals cations as well as certain anions as it possesses a strong affinity to a variety of contaminants in subsurface environments. Natural goethite is usually associated with a number of metals. Heavy metals such as Pb(II) and Cd(II) are common in surface water and groundwater and their transport, toxicity, and bioavailability are mostly impacted by interactions with water and oxide and (oxy)hydroxide surfaces. In this study, we synthesized and characterized metal-substituted (Cd, Pb) goethite[1]. Dissolution experiments were performed with or in the absence of CO<sub>2</sub> and CaCO<sub>3</sub> at two different temperatures (room and 60°C). This study provides data from small-scale, short-term tests involving direct release of CO<sub>2</sub> in a system in order to provide constraints on potential migration of metals under CO<sub>2</sub> leaking carbon storage areas.

- [1] Kaur et al. (2009) *Clays and Clay Minerals* **57**, 234-250.