

## The enrichment of Platinum Group Elements (PGE) in Co-rich crusts from the central and western Pacific

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Co-rich Mn crusts from central and western Pacific Ocean seamounts are markedly enriched in the Platinum Group Elements (PGE), with average contents of Ru, Rh, Pd, Os, Ir and Pt in 69 samples of 24.9 ng/g, 17.6 ng/g, 4.9 ng/g, 3.7 ng/g, 5.9 ng/g and 283 ng/g, respectively.

The Pt/Pd ratios of the samples vary considerably, in the range of 14.2~227, with an average of 65.1. Based on the ratios of Pt/Pd=100, the samples can be classified into two types: a Pt/Pd<100 type and a Pt/Pd>100 type. The Pt/Pd<100 type samples (59 samples) have high Pd contents (5.0 ng/g on average) and low Os, Ir, Ru, Rh and Pt contents (3.1 ng/g, 5.3 ng/g, 24.4 ng/g, 14.6 ng/g and 221 ng/g on average, respectively) with Pt/Pd ratios of 46.5 on average. These ratios are positively correlated with the Ce/La ratios of the crusts ( $r=0.43$ ) indicating that the enrichment of Pt relative to Pd is related to the oxidation of Pt in agreement with the previous hypothesis of oxidation of Pt from Pt<sup>2+</sup> to Pt<sup>4+</sup> in seawater and precipitated on the surface of Co-rich crusts. However, the Pt/Pd>100 samples (10 samples) have high Os, Ir, Ru, Rh and Pt contents (7.3 ng/g, 9.5 ng/g, 27.7 ng/g, 35.4 ng/g and 649 ng/g on average, respectively) and low Pd contents (3.8 ng/g on average) with Pt/Pd ratios of 175 on average which are negatively correlated with the Ce/La ratios ( $r=-0.46$ ). These results suggest that oxidation can not explain the abnormal enrichment of Pt relative to Pd of the Pt/Pd>100 type crusts.

The Pt/Pd>100 type crust samples have high contents of Mn, Co, Ni, Ce, CaO and P<sub>2</sub>O<sub>5</sub> (23.7 %, 0.70 %, 0.54 %, 1318 µg/g, 5.9 % and 1.96 % on average, respectively) suggesting that the enrichment of Os, Ir, Rh and Pt in the crust samples may be dominantly caused by hydrogenetic enrichment under oxidizing conditions, whereas the Pt/Pd<100 type crust samples with high Pd contents have high contents of SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Fe (10.5 %, 2.05 % and 17.5 % on average, respectively) indicating that the enrichment of Pd in the crusts may be related mainly to the incorporation of detritus.

## Coupled precipitation and dissolution kinetics of hydrocerussite in presence of aragonitic shells

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Elevated lead concentrations in surface and groundwater may cause serious health problems for aquatic biota and humans. Several processes are known for the removal of lead (Pb) from the aqueous solutions. In a previous study carried out by Cubillas *et al.* [1] cadmium uptake using aragonite surfaces has been studied. Further studies demonstrated a similar efficiency of aragonite surfaces in presence of other selected metals as lead (Pb), zinc (Zn) and cobalt (Co) [2]. Before optimizing such a process more a detailed study of the kinetic effects is necessary. In the present study we focused on the kinetics of the coupled precipitation/dissolution process for lead removal from polluted soils and waters by biogenic aragonitic carbonate (CaCO<sub>3</sub>) shell surfaces according to  $\text{CaCO}_3 + \text{Pb}^{2+} = \text{PbCO}_3 + \text{Ca}^{2+}$ .

This reaction has been investigated at various experimental conditions using synthetic model systems in batch and single pass flow through and fluidized bed reactors and a AFM fluid cell that allowed quantifying the kinetics of the process of metal carbonate formation. The reaction kinetics was successfully modelled using the geochemical code PHREEQC [3] using the Plummer-Wigley-Parkhurst equation for both the dissolution and precipitation process. The precipitated lead bearing solid phases were characterized mineralogically. Potential applications of this study will be discussed.

[1] Cubillas *et al.* (2005) *GCA* **69** (23), 5459-5476. [2] Köhler *et al.* (2007) *ES&T* **41** (1), 112-118. [3] Parkhurst (1998) PHREEQC (Version 2) U.S. Geol. Survey Wat.-Res. Invest. Report, pp 99-4259.