

Geochemical behavior of heavy metals in iron oxide minerals formed by weathering of black shale

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Background

Black shales are enriched with heavy metals and cause severe problems such as acid rock drainage (ARD) upon exposure to the atmosphere due to rapid oxidation of the contained sulfides [1]. During weathering, with leaching of heavy metals, new iron oxide minerals having high sorption capacity also precipitates [2]. However, the roles of these iron oxide minerals from black shale on those metals have not systematically studied.

Study Area and Methods

The black shales in Goesan and Dukpyong areas in Korea are known to contain high concentrations of heavy metals. Sampling was carried out at two sites of black shales where local fault zone was interbedded. The samples of black shales and weathering product with different colors were collected. XRD and ICP-MS, AES were mainly used to identify the mineral species and estimate metal contents.

Results and Discussion

Illite, kaolinite, quartz, feldspar were identified as main silicate minerals with small amount of iron oxide in black shales. The weathering products contain mainly iron oxide minerals such as jarosite and goethite with silicate minerals such as illite, chlorite, feldspar, quartz, and kaolinite. The main chemical components of weathering products were mainly SiO₂ and Fe₂O₃. The chemical analysis shows that the concentrations of Pb and Cr in weathering products were lower than those of black shales. However, Cu and Zn were relatively enriched in the weathering products. The concentrations of Co, Cd, and As were low in both black shales and weathering products. Further experiment will be conducted to characterize the mineral and the behaviors of heavy metals in iron oxide minerals in detail.

[1] Kwong *et al.* (2009) *Appl Geochem* 24, 221-231, [2] Gräfe *et al.* (2008) *J Coll Inter Sci* 322, 399-413

Sulfur isotope systematics of the Paleoproterozoic Bushy Park and Pering MVT deposits

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The Bushy Park and Pering Zn-Pb deposits, Earth's oldest Mississippi Valley-type (MVT) deposits [1], are hosted by Neoproterozoic platform carbonates of the Transvaal Supergroup on the Ghaap Plateau in South Africa. MVT ore and gangue minerals are precipitated from (sedimentary) basinal brines, and almost all known deposits are of Phanerozoic age. These Paleoproterozoic Zn-Pb MVT deposits are of special interest because they provide insights into the geochemistry of sulfur in the Paleoproterozoic-Neoproterozoic sedimentary basin that hosts them. We report here, the results of a multiple sulfur isotope ($\delta^{33}\text{S}$, $\delta^{34}\text{S}$, and $\delta^{36}\text{S}$) study of sulfide minerals of different paragenetic stages from the two MVT deposits. We undertook this study to examine the mechanisms of ore deposition and the sources of sulfur for these Paleoproterozoic MVT mineralization events.

Our isotope data indicate that the Bushy Park and Pering MVT deposits possess unusual sulfur isotope variations that reflect distinct sources of sulfur and mechanisms of ore genesis. Sulfide minerals from the Bushy Park deposit show strong mass-independent signals ($4\% < \Delta^{33}\text{S} < 6\%$) with relatively uniform $\delta^{34}\text{S}$ values, and sulfide minerals from the Pering deposit exhibit smaller mass-independent signals ($-0.7\% < \Delta^{33}\text{S} < 2\%$) that are strongly correlated with $\delta^{34}\text{S}$ variation. We will discuss the implications of these findings for conditions of Zn-Pb MVT mineralization, the chemistry of ore-forming brines in Paleoproterozoic-Neoproterozoic sedimentary basins, and the sources of sulfur for these deposits, in the context of other geochemical and geological information [e.g. 2, 3].

[1] Kesler & Reich (2006) *Geological Society of America Memoir* 198, 185-204. [2] Gutzmer (2006) *Mineralium Deposita* 40, 664-685. [3] Huizenga *et al.* (2006) *Mineralium Deposita* 40, 686-706.