

## 4.64.P09

### The effect of a Mg-oxychloride-brucite backfill material on the Pu behavior in MgCl<sub>2</sub>-NaCl-brines

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Retention of actinides and especially Pu in the near field is critical for the long-term disposal and storage of radioactive waste in geological salt deposits, e.g. for the WIPP (USA) and the Asse mine (Germany). There is currently a strong interest in developing backfill materials which provide favorable chemical conditions with respect to low Pu solubility [1-3]. For the Asse mine, where cemented low level and intermediate level radioactive waste is emplaced, a combination of Mg-oxychloride and brucite has been proposed as backfill material. According to modelling predictions, the Mg-oxychloride-brucite backfill buffers the pH at 8 – 9, and scavenges CO<sub>2</sub> produced by microbial degradation of organic waste constituents. For the presence of the backfill material and dissolved inorganic carbon (DIC) concentration < 10<sup>-3</sup> M, Pu solubility is calculated to be 10<sup>-7</sup> M for the equilibrium of a Pu(IV) solid with colloidal Pu(IV) and aqueous Pu(V) species. Radiolytic oxidation of the Pu(IV) solid is not considered, because it is excluded by the Pu distribution in the cemented waste forms.

Laboratory experiments were undertaken to study the interactions of Pu, a Mg-oxychloride-brucite based backfill material and Portland cement in concentrated NaCl- and MgCl<sub>2</sub>-NaCl-brines. An excellent agreement is found for experimental and calculated results regarding the interaction of the backfill material and cement in the studied brines. Only at pCO<sub>2</sub>(g) > 3 bar the predicted reduction of the DIC concentration by precipitation of magnesite is qualitatively confirmed in the Mg-Na-H-OH-Cl-CO<sub>2</sub>-H<sub>2</sub>O system. Unlike to that, experiments at atmospheric conditions show, the Mg-oxychloride-brucite backfill causes fast precipitation of metastable Mg-OH-carbonates, resulting in DIC < 10<sup>-3</sup> M. When Pu solubility is determined by dissolution of <sup>239</sup>PuO<sub>2</sub>(s) in CO<sub>2</sub>-free brines, radiolytic oxidants are formed (Eh > 750 mV), <sup>239</sup>Pu(IV) is oxidized to <sup>239</sup>Pu(V) and <sup>239</sup>Pu(VI), resulting in an concentration of 10<sup>-5</sup> M at pH 8. Measuring <sup>238</sup>Pu solubility from oversaturation, <sup>238</sup>Pu concentration is ≤ 10<sup>-7</sup> M at pH 8. When considerable amounts of DIC (HCO<sub>3</sub><sup>-</sup>/CO<sub>3</sub><sup>2-</sup>) are added to the studied brines in presence of the backfill material, the observed <sup>238</sup>Pu concentration is < 10<sup>-10</sup> M, indicating sorption of <sup>238</sup>Pu onto solids such as precipitating Mg-OH-carbonates.

#### References

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## 4.64.P10

### U-Pb zircon geochronology of the Franceville series at Bidoudouma, Gabon

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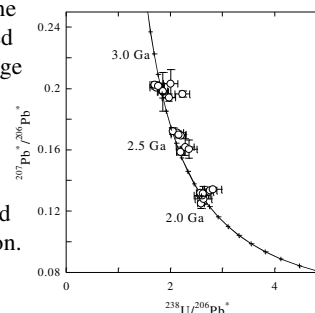
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The Franceville basin in the Republic of Gabon includes unique uranium deposits such as Oklo, Okelobondo and Bangombé where natural fission reactions occurred at 1.97 Ga. Previous works reported the formation age of Archean basement and the deposition age of the basal unit (FA formation) which is the host rock of uranium deposits. FA formation is overlain by black shales with interlayered volcanic rocks (N'Goutou) dated at 2143 ± 143 Ma (Bonhomme et al. 1982). In this study, we report new data for the deposition age of Franceville series.

Samples were taken from Bidoudouma which is located 63km north from Oklo. All samples are welded tuff in FD formation and were taken from a cinerite and an ignimbrite mainly made of quartz and albite. *In-situ* U-Pb isotopic analyses and rare earth element measurements of zircon were performed using a SHRIMP at Hiroshima University.

U-Pb data of the Franceville zircons show three populations with concordant ages (2.8, 2.5 and 2.1 Ga). The age of 2.8 Ga is consistent with the formation age of the Mitzic gneiss and the Ebel orthogneiss (Caen-Vachette et al., 1988), and their zircons were from the Archean metamorphic rocks when the lava came up to the surface. Sediments of the Ogooué system was deposited at 2.5 Ga (Feybesse et al., 1998). It indicates that the sediments were poured into the tuff layer. The age of 2.1 Ga is consistent with granite of Lecoue (Feybesse et al., 1998) and indicates the volcanic activity recorded in the FD formation.



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