

Petrogenesis of CAMP dolerites from Suriname and West Africa

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We performed a petrological and geochemical investigation on dolerites from Suriname and West Africa to explore the extent to which CAMP products from areas on opposite sides of the present-day Atlantic have a common petrogenetic heritage. Dykes in Suriname and the Ivory Coast (IC) are mainly tholeiitic basalts, while sills in Burkina Faso (BF) are mostly basaltic-andesites with tholeiitic as well as calc-alkaline affinities. The Surinamese rocks are slightly more evolved (Mg#=34-46) than the IC dolerites (Mg#=43-51), whereas the BF dolerites include the least evolved compositions (Mg#=45-66).

A geographic subdivision into high-Ti (1.9-3.7 wt.% TiO₂) and low-Ti (0.9-1.2 wt.%) dolerites is consistent with findings in other CAMP regions. Nevertheless, overall geochemical characteristics of the studied rocks tend to be distinct. The Surinamese and IC dolerites fall in a narrow zone of high-Ti magmatism along the margins of the present-day Atlantic Ocean, where preferential upwelling shortly before initial rifting has been proposed. Trace-element signatures and inferences from partial melting models suggest that mantle sources of the Surinamese and IC dolerites were different from those of the BF rocks. Modestly contrasting geochemical signatures point to source inhomogeneity and variations in melting conditions on regional as well as local scales. Relatively deep melting of a garnet-rich source with primitive-mantle like composition may have produced the Suriname and IC magmas, whereas the BF magmas possibly originated by shallower melting of a more spinel-rich source that might have been affected by subduction-type enrichment. Our findings indicate that chemostratigraphic criteria, used in correlations of northern CAMP basalts, are not directly applicable to southern counterparts on both sides of the Atlantic.

Plutonium redox chemistry under anoxic conditions in the presence of iron(II) bearing minerals

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The environmental fate of plutonium, the major transuranium actinide in nuclear waste, is largely impacted by its sorption onto and redox reactions with iron oxide, carbonate or sulfide minerals that form as corrosion products of steel in the "near field" and occur widely in sediments. To obtain information on oxidation state and local structure of Pu in the presence of Fe(II) bearing minerals, electrolytically prepared Pu(V) or Pu(III) (²⁴²Pu, 1-3·10⁻⁵ M) were, under anoxic conditions, reacted with magnetite (Fe^{II}Fe^{III}₂O₄) (pH 6-8.5), chukanovite (Fe₂(CO₃)(OH)₂) (pH 8.5) and mackinawite (FeS) (pH 6-8.5). Pu-L_{III}-edge X-ray absorption spectra (XAS) were collected after 40 d and 8 months of reaction.

In all 14 samples, more than 98 % of Pu was associated with the solid phase and its redox speciation thus accessible by XAS. With magnetite, only the sample prepared at the highest pH and highest Pu loading contained Pu(IV)O₂ while in all others Pu was solely present as a tridentate Pu(III) surface complex [1]. The three chukanovite samples all contained both Pu(III) (15 to 40 %) and PuO₂. With mackinawite at pH 6 only Pu(III) was present, while all samples prepared at pH 7 and higher contained mostly PuO₂ and up to approx. 10 % Pu(III).

Through comparison of the different types of minerals (oxide, carbonate, sulfide), reaction pH and Pu/mineral ratios, it becomes apparent that the type of surface complexation (e.g. inner-sphere on magnetite vs. outer-sphere on mackinawite) and total mineral surface area are key parameters in controlling concentrations of dissolved Pu and in determining whether a PuO₂ solid phase precipitates. While PuO₂ provides an upper limit for concentrations of dissolved Pu, the available mineral surface area and sorption complex stability control what percentage of Pu is present in surface complexes. Under reducing conditions as established through the Fe(II) bearing minerals used here, this mineral surface associated Pu was found to be trivalent. Surface complexed Pu(III) and PuO₂ can be thought of being in equilibrium with each other via two processes: a sorption reaction between dissolved and surface complexed Pu(III) and a heterogeneous redox reaction between dissolved Pu(III) and solid phase Pu(IV)O₂. It remains to be investigated if and through what mechanisms the Pu solid phase speciation (sorbed Pu(III) vs. solid phase PuO₂) might impact the migration behavior of Pu and how, for risk assessment purposes, Pu(III) surface complexes with iron minerals can be implemented into geochemical models.

[1] Kirsch et al. (2011) *Environ. Sci. Technol.* **45**, 7267-7274.