

## Evolution of continental boundaries through time: predictions from numerical modeling

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Possible evolution of passive and active continental margins through time is analyzed by using a 2D coupled petrological-thermomechanical numerical model. This model includes spontaneous initiation of a retreating subduction, visco(elasto)plastic slab bending, dehydration of the subducted crust, aqueous fluid transport, partial melting of both crustal and mantle rocks and melt extraction processes resulting in new continental and oceanic crust growth and accretion. Numerical models predict that two major factors controlling transition from passive to active margin are (1) lithospheric thinning/heating processes (e.g. rifting) and (2) chemical density contrast between oceanic and continental mantle lithosphere.

In our numerical experiments, many realistic features characteristic for natural arc settings can be observed. One is the construction of an accretionary wedge, including frontal and basal accretion, as well as subduction erosion. The generation of a magmatic arc results in the growth of new volcanic sequences atop the continental crust and batholithic bodies in its interior. The lateral width of the magmatic arc is constricted to 30-70 km due to the limited extent of the melt extraction area in the hydrated mantle wedge atop the slab. In part of the experiments an intra-arc extension is documented. This process is followed by rapid slab retreat triggering the formation of a backarc basin with the new spreading center resulting in dry decompression melting of the mantle and building of new oceanic floor.

Numerical models also predict that plate tectonic style and, in particular, active margin processes notably change with hotter mantle temperature which are representative for the early Earth history. Transitions to pre-subduction (shallow undethrusting), two-sided subduction and plate fragmentation regimes are identified. According to numerical predictions major factor controlling changes in tectonic styles back in time is plastic strength of the lithosphere. This strength was much lower in the early Earth due to the wide spread/ global presence of partially molten sublithospheric mantle layer providing continuous source of melts weakening the overlying plates.

## Detection of uranylarsenates in acidic and alkaline solutions with time resolved laser-induced fluorescence spectroscopy(TRLFS)

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While complexation of uranium and phosphate is relatively well investigated, little information exists about interactions of uranium and arsenate. Based on the assumption that P(V) and As(V) form similar species with uranium, uranium arsenate complexation was investigated under both acidic and alkaline conditions with TRLFS. Three uranium arsenate species ( $\text{UO}_2\text{HAsO}_4$ ,  $\text{UO}_2\text{H}_2\text{AsO}_4^+$ ,  $\text{UO}_2(\text{H}_2\text{AsO}_4)_2$ ) have been identified previously by Rutsch *et al.* [1] in a pH range between 1.5 and 3 with TRLFS. In our investigation the pH range was extended up to pH 9.5. Fluorescence lifetime and main emission bands were used to characterize the above mentioned species and an additional species was determined to predominate within a pH range between 7 and 8.5. This species was, in analogy to  $\text{UO}_2\text{PO}_4^-$ , presumed to be  $\text{UO}_2\text{AsO}_4^-$ .

| Species                                   | Fluorescence life time [ $\mu\text{s}$ ] | Fluorescence emission bands (nm) |
|---|--|----------------------------------|
| $\text{UO}_2^+$                           | $1.54 \pm 0.05$                          | 471, 488, 510, 534, 560          |
| $\text{UO}_2\text{H}_2\text{AsO}_4^+$     | $10.6 \pm 6.0$                           | 478, 493, 515, 538, 565          |
| $\text{UO}_2(\text{H}_2\text{AsO}_4)_2^0$ | $26.8 \pm 9.1$                           | 485, 497, 518, 543, 567          |
| $\text{UO}_2\text{HAsO}_4^0$              | $1.74 \pm 0.69$                          | 500, 525, 549, 575               |
| $\text{UO}_2\text{AsO}_4^-$               | 14.7                                     | 506, 527, 551, 576               |

As uranium and arsenic often co-occur, uranylarsenates will have major implications on uranium mobility in the environment. Especially noteworthy is the wide range of predominance for the  $\text{UO}_2(\text{H}_2\text{AsO}_4)_2^0$  (pH 3-4) and  $\text{UO}_2\text{HAsO}_4^0$  complexes (pH 4.5 to 6.5). While  $\text{UO}_2^{2+}$ ,  $\text{UO}_2\text{OH}^+$ , and  $(\text{UO}_2)_3(\text{OH})_5^+$  form in the absence of arsenic and are retained effectively by cation exchange on clay minerals, non-charged uranyl-arsenates significantly alter sorption behavior in the presence of arsenic as preliminary studies with bentonite indicate.

[1] Rutsch M., Geipel G., Brendler V., Bernhard G. & Nitsche H. (1999) *Radiochimica Acta* **86**, 135-141.