

Sb(V) retention mechanisms in alkaline environments

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The increased application of antimony has allowed it to find its way to a number of environments such as soils and groundwaters but also to wastes and residues of industrial processes like smelting or waste incineration. The latter materials have a much higher pore water pH (>10) than average soils and sediments, often a high salinity and thus a quite distinct geochemistry which has been thoroughly studied because these residues contain relatively high amounts of toxic heavy metals. Sb has, however, received little attention due to its relatively low total content but its high mobility calls for a better understanding of the geochemistry in alkaline matrices. In most instances the most important oxidation state is Sb(V), occurring as the oxyanion antimonate ($\text{Sb}(\text{OH})_6^-$) in aqueous media. It has been established that in soils of intermediate porewater pH, $\text{Sb}(\text{OH})_6^-$ is closely associated with iron (hydr)oxides. At high pH, however, the retention mechanisms are at present unknown.

To develop efficient geochemical models to predict Sb(V) leaching in alkaline environments, the precipitation equilibria of $\text{Sb}(\text{OH})_6^-$ with the most abundant multivalent cation, Ca^{2+} , was studied as well as the interaction of $\text{Sb}(\text{OH})_6^-$ with commonly occurring minerals. Simultaneously, alkaline residues such as municipal solid waste incinerator bottom ash and a Sb^{V} -spiked cement sample were characterised with respect to leaching. It was found that regardless of pH, no other calcium antimonates other than $\text{Ca}(\text{Sb}(\text{OH})_6)_2$ precipitate but modelling with the geochemical speciation code PHREEQC showed that in alkaline environments, saturation of $\text{Ca}(\text{Sb}(\text{OH})_6)_2$ is seldom attained. However, $\text{Sb}(\text{OH})_6^-$ was found to associate with portlandite ($\text{Ca}(\text{OH})_2$), ettringite ($\text{Ca}_6\text{Al}_2(\text{OH})_{12}(\text{SO}_4)_3 \cdot 26\text{H}_2\text{O}$), mono-sulphate ($\text{Ca}_4\text{Al}_2(\text{OH})_{12}\text{SO}_4 \cdot 13\text{H}_2\text{O}$) and hydrogarnet ($\text{Ca}_3\text{Al}_2(\text{H}_4\text{O}_4)_3$). It was suspected that in alkaline environments, $\text{Sb}(\text{OH})_6^-$ forms solid solutions replacing sulphate in the structure of ettringite and monosulphate. To demonstrate this, Sb^{V} -analogues of ettringite and monosulphate were synthesized and characterised using XRD, SEM-EDX and TGA. Solubility experiments and calculations in PHREEQC allowed the determination of the solubility product (K_{sp}) of these analogues. It was shown that assuming ideal solid solution as an additional mechanism next to precipitation of $\text{Ca}(\text{Sb}(\text{OH})_6)_2$, greatly improved modelling of Sb leaching behaviour in alkaline environments. However, the leaching potential of $\text{Sb}(\text{OH})_6^-$ was now underestimated which calls for quantification of non-ideality to allow more precise modelling.

Geochronology, geochemistry and isotopes of orthogneisses from the Greek Rhodope

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The Hellenides formed from Cretaceous to Mid-Tertiary times as a result of plate convergence and collision of Africa and Europe. The easternmost part of the Hellenides is represented by the Rhodope Massif which occupies the major part of NE Greece and S Bulgaria. Two groups of orthogneiss protolith-ages have been established in the central Rhodope Massif: A Permo-Carboniferous group (275-290 Ma), corresponding to the structurally lower part of the massif, the Thracia Terrane and a Late Jurassic-Early Cretaceous group (134-164 Ma), corresponding to the structurally upper part, the Rhodope Terrane (Turpaud & Reischmann 2003, Turpaud 2006). In this study, felsic orthogneisses from the northeastern part of the Greek Rhodope were geochemically and geochronologically investigated, to find out, if the two terrane-model is applicable here. Zircons from 15 orthogneisses from the Eastern Rhodope were dated by LA-SF-ICPMS (U-Pb) and U-Th-Pb SHRIMP, respectively. Most of the analysed samples are around 300 Ma in age and contain many inherited cores whereas zircons from one bt-gneiss gave an age of 145 ± 5 Ma. The chemistry of all samples is very similar to orthogneisses from the Thracia Terrane in the central part of the Rhodope. The protolith of the orthogneisses can be chemically classified as subalkaline granite of a volcanic-arc tectonic setting. The isotopic ratios of $^{87}\text{Sr}/^{86}\text{Sr}$ range between 0.7031 and 0.7167; ϵ_{Nd} values are negative and vary mostly between -3.8 to -7.9. REE patterns show enrichment in LREE and negative Eu anomalies. We conclude that the Thracia Terrane can also be identified in the northeastern part of the Greek Rhodope whereas the identification of the Rhodope Terrane is still under question.