

Secondary minerals in mine wastes at Sb deposits in Slovakia

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In this work, we have summarized results from a detailed mineralogical study of the weathering products formed in the environment of tailing ponds and soils from five Sb deposits in Slovakia, based on 250 samples of flotation tailing materials and soils, 2500 electron microprobe analyses and 500 micro-X-ray diffraction (μ -XRD) analyses. All studied bulk samples are rich in Fe (24.2–181 g/kg), As (0.1–13.5 g/kg), and Sb (1.2–15.7 g/kg). The most frequent sulphides in the flotation wastes are pyrite (FeS_2) and arsenopyrite ($FeAsS$); stibnite (Sb_2S_3) is rare owing to its rapid oxidation.

The most common Sb-bearing secondary oxide is triphyllite ($FeSbO_4$) with variable Sb (15.94–50.83 wt. %) and Fe content (4.13–41.52 wt. %). Unit cell volume is in the range from 64.70 Å³ to 75.83 Å³ and depends mostly on the Fe/(Fe+Sb) ratio of the triphyllite grains. In the tailings and soils rich in Ca, secondary minerals with the pyrochlore structure have been identified. These phases are rich in Sb (up to 52.90 wt. %), Fe (up to 21.22 wt. %) and Ca (up to 7.40 wt. %) and the μ -XRD patterns fit well with the structural models of stibiconite ($Sb^{3+}Sb^{5+}O_6(OH)$) and lewisite ($Ca, Fe^{2+}, Na_2(Sb, Ti)_2O_7$). The most frequent secondary mineral at all studied sites is goethite (α -FeOOH), with high content of Sb (up to 14.49 wt. %) and As (up to 6.49 wt. %). Cell parameters depend on incorporation of foreign elements, in agreement with earlier studies. Frequent are also X-ray amorphous Fe oxides with variable amounts of adsorbed elements (up to 6.66 wt. % of Mg, 13.91 wt. % of Sb and 10.64 wt. % of As). Simple secondary Sb oxides such as cervantite (α - Sb_2O_4) and senarmontite (Sb_2O_3) were observed each just in one soil sample. The most common product of arsenopyrite oxidation – scorodite ($FeAsO_4 \cdot 2H_2O$) occurs rarely. Beudantite ($PbFe_3(AsO_4)(SO_4)(OH)_6$) was identified in a few samples with increased content of Pb. In one sample, a porous secondary oxide rich in Pb and As was identified by μ -XRD as clinomimetite ($Pb_5(AsO_4)_3Cl$).

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Experimental constraints on the composition of slab liquids below arc volcanoes

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The flux of elements from the slab into the mantle wedge is governed by the composition of the different subducted lithologies, the partitioning behaviour of trace elements and the subduction geotherm. Recently it has been shown that the concentration of key elements such as K, Zr, Ti, Nb and REE depends primarily on T and is controlled by the solubility of accessory phases, such as phengite, zircon, rutile and allanite, in the melt [1, 2]. This T-concentration relationship can be used as a geothermometer to determine the top slab T in subduction zones and suggests values that vary from 750 to 950 °C for different subduction zones [3]. Crucial questions that remain open are the effect of pressure and the presence of additional volatiles such as S, Cl and F on the stability of accessory phases and the composition of slab liquids.

Here we report preliminary results on crystallisation experiments on a H₂O-saturated and trace element-doped MORB composition at 5 GPa and 750–1000 °C. Together with previous results at 2.5 GPa and 750–900°C [2] the experimental dataset now covers the full range of P-T conditions predicted for the slab below volcanic arcs. The dataset will be augmented with a few runs containing additional S and F.

First results show that at 5 GPa the wet solidus of basalt is <900 °C. Experimental melts at 5 GPa are granitic compared to trondhjemite melts at 2.5 GPa. With increasing P, D_{Na} in cpx increases and hence Na/K in the melt decreases. All runs contain gt, cpx and rutile. Allanite is present up to 950 °C. No effect of P on allanite composition has been recognised so far. Coesite is found to be stable at P > 5 GPa. The trace element contents of the glasses are currently investigated by LA-ICPMS. One run at 950 °C and 5 GPa, containing small quantities of F, crystallised REE-bearing CaF₂ and allanite. From these preliminary results we anticipate that a) increasing P (increasing depth of the slab) can explain the change from Na-rich to more K-rich signal in arc magmas and thus K is not only controlled by phengite stability and b) addition of F in the fluid stabilises REE-bearing CaF₂ in the solid residue.

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- [2] Klimm *et al.* (2008) *J Pet* **49**, 523–553. [3] Plank *et al.* (2009) *Nature Geoscience* **2**, 611–615.