Assessment of the heavy metal contamination in surficial sediments from Kalimanci Lake (Macedonia)

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Major disaster happened on the 30.08.2003 in the eastern Macedonia (Europe), when one part of the Sasa Mine tailings dam collapsed and caused intensive flow of the tailings material. 70 000-100 000 m^3 of the tailings material was discharged and dispersed through the Kamenica River valley, to the city of Kamenica and into the Kalimanci Lake. The damaging tailings flow comprised an elevated amounts of the heavy metals (Ag, As, Cd, Cu, Mo, Pb, Sb and Zn) that seriously affected the surrounding environments, especially Kalimanci Lake. This artificial lake is supplied by two rivers: the main, Bregalnica River and Kamenica River, flowing directly from the Sasa ore district. The Sasa mine is situated 10 km N from the Kalimanci Lake and has been in production for over 45 years yielding 90 000 t of the high quality Pb-Zn concentrate annually.

The sampling of the surficial sediment from the Kalimanci Lake occurred before the accident in August 2001 and was revised in September 2007, three years after the accident. The geochemical analysis of the heavy metals (Ag, As, Cd, Cu, Mo, Pb, Sb and Zn) were performed in Acme Analytical Laboratories, Ltd. by ICP-MS.

The results showed that the concentrations of the heavy metals in the study area are extremely high compared with the background concentrations and world average values. The calculated enrichment factor (EF) for the samples collected in the year 2001 was much higher than 1 for all heavy metals: Ag, 38; As, 36; Cd, 279; Cu, 6; Mo, 1.5; Pb, 140; Sb, 1.3 and Zn, 50. The EF values suggest anthropogenic impact on heavy metals input in sediments due to the acid mine drainage, waste and tailings effluents from the Sasa mine area which are including high concentrations of heavy metals and are flowing out into the Kamenica River and then to the Kalimanci Lake. The EF values for the investigated heavy metals in the sediment samples from the year 2007 are following: Ag, 146; As, 48; Cd, 735; Cu, 21; Mo, 2; Pb, 387; Sb, 10 and Zn, 151. They are strongly indicating the effects of the tailings dam accident.

For a further discussion more detailed studies on the heavy metal concentration in the sediments from the Kalimanci Lake and the remediation process of the sediment are essential.

Fe/Mn and $^{187}Os/^{188}Os$ ratios in mafic lavas from the Ethiopian flood basalts

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The Fe/Mn ratio in mafic lavas has become the subject of interest following its association with radiogenic Os isotope ratios in Hawaiian picrites[1]. Such characteristics have been attributed to the entrainment of core material in mantle plumes. Ti-rich mafic lavas from the 30ma Ethiopian flood basalts were derived from a primary magma with 16 wt% MgO and 8 wt% Al_2O_3, consistent with an origin at 5 GPa and a potential temperature of ~1600°C. Precise ICPMS analysis of the Fe/Mn ratio reveals a range of values between 65.4 to 78.5 in MgO rich samples, comparable with and greater than those observed for Hawaiian lavas. Os contents in the same samples vary from 46 to 3916 ppt although the majority have Os>1000 ppt. Age-corrected $^{187}Os/^{188}Os$ ratios are generally sub-chondritic, although samples with <1000 ppt Os have more radiogenic $^{187}Os/^{188}Os$ ratios. The latter are broadly correlated with the Re/Os ratio and lie close to a 1Ga reference line, implying contamination by the underlying late proterozoic crust. The more Os- and MgO-rich samples, however, also show possible evidence of contamination, indicating that the uncontaminated $^{187}Os/^{188}Os$ ratio of the primary magma may have been as low as 0.12608 to 0.12477 (γ_{Os} = -0.73 to - 1.76). These low values imply a depleted source with a sub-chondritic Re/Os ratio, consistent with the positive ε_{Nd} values of +6 [2]. The results demonstrate that radiogenic Os isotope ratios and high Fe/Mn ratios are not correlated and their status as indicators of core entrainment is challenged. Comparison with experimental results indicates that high Fe/Mn ratios are not generated during melt extraction but are a feature of some plume source regions. Moreover, in the case of the Afar plume, which bears many of the characteristics of a deep mantle origin, these results indicate a plume composition that is depleted in Mn rather than one enriched in iron and the siderophile elements.

[1] Humayun *et al*. (2004) *Science* **306**, 91–94. DOI: 10.1126/science.1101050 [2] Pik *et al*. (1999) *Geochim. Cosmochim. Acta* **63**, 2263-2279.