Paleoclimate information from degassed groundwaters

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Degassing of groundwater is a complication for dating methods based on dissolved gases as well as for the noble gas thermometer. In order to account for the gas loss and derive age and temperature information, the mechanisms leading to degassing have to be adequately modelled and the time when degassing occurred in the past needs to be determined. The concept of closed-system equilibration between groundwater and trapped gas bubbles (CE model), which is often used to account for excess air, also provides a reasonable description of dissolved gases in degassed groundwaters.

A data set from the Ledo-Paniselian Aquifer in Belgium is used to demonstrate the feasibility of deriving reliable groundwater age and recharge temperature information from degassed samples. This data set encompasses groundwaters from the past 40 ka and includes 10 samples (from 8 wells) with reproducible degassing signatures along with 34 samples (from 31 wells) showing the usual excess air pattern [1]. The CE model provides good fits to all samples with excess air and half of the degassed samples. The recharge temperatures estimated for the two sample groups are consistent. The same is true for the calculated radiogenic He concentrations, if it is assumed that degassing took place at the time of recharge.

Hence, degassing may be related to the recharge conditions of the affected groundwaters. Interestingly, all degassed samples are younger than the last glacial maximum, when recharge in the area was inhibited by permafrost. We hypothesize that degassing in the period after the recharge gap was due to methane release during the thawing of the permafrost, as observed in modern analogs [2]. The results of this study demonstrate that degassing of groundwater is a systematic effect which can be described by appropriate models and which may contain relevant information on the climatic conditions during groundwater recharge. Moreover, they show that noble gases may be used to study both present and past events of gas production in the subsurface.

[1] Blaser et al. (2010) J. Quaternary Sci. in press. [2] Zimov et al. (2006) Science **312**, 1612–1613.

Environmental assessment using Pb and Cd isotopes at abandoned mining site, south of Portugal

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S. Domingos Mine (SDM) and refining complex (Iberian Pyrite Belt, Alentejo, southern Portugal) are abandoned since 1966. High quantities of metals and metalloids (Pb, Zn, Cd, Cu, Fe, Al, Mn, Cr, As, Sn) have been transferred to soils, water and crops. The SDM system of acid mine drainage waters (AMD) (pH = 0.5 – 3; 11 wt% Fe; 10 mg. kg^{-1} Pb; 55 mg. kg^{-1} As; 2480 mg. kg^{-1} Zn; 3980 mg. kg^{-1} Cu; 1 mg. kg^{-1} Cd) intensively affects the main stream valley. Human occupy soils containing up to 20wt% of Fe, 1.5wt% of Pb, 2500 mg. kg^{-1} of As, 800 mg. kg^{-1} of Zn, 400 mg. kg^{-1} of Cu, 10 mg. kg^{-1} of Cd. Lead and Cd isotopic ratios were measured on a Nu-Plasma MC-ICP-MS (ULB). Samples of tailings, unprocessed pyrite, cultivated soils, village soils and AMD minerals (e.g. jarosite (KFe_3^{+3} $(SO_4)_2$ $(OH)_6$) and melanterite ($FeSO_4.7H_2O$)) were analyzed. Lead isotope ratios are homogeneous and confirm the primary pyrite ore body ($^{208}Pb/^{204}Pb$=38.253; $^{207}Pb/^{204}Pb$=15.636; $^{206}Pb/^{204}Pb$=18.173) as the main Pb source. At 7 km south, Pb isotopic ratios of soils show a mixing trend between the isotopic fields of host rocks and SDM ore. Preliminary Cd isotopic results show δCd/amu range from -0.27±0.02 to -0.02±0.02 ‰ (2SD) for unprocessed pyrite ores and soils. However, one village soil showing the strongest enrichment in light Zn isotopes [1], also displays the largest Cd fractionation of ≥ -1 δCd/amu. This multitracer approach would provide sensitive tools to discriminate the relative contribution of slag residues, unprocessed ores and distal fallouts (from factory chimney) in metal contaminated soils.

[1] Mattielli et al. (2010) GCA, this volume.