Geochemical and isotopes approach on the characterization of groundwater paths in Sintra Massive (Portugal)

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Groundwater from crystaline aquifers developed in the Sintra igneous massive is widely used for drinking water supply. The identification of recharge areas and flow paths are important for the correct definition of aquifer protection areas. Chemical and isotopic compositions of the groundwater samples were examined and water-rock interaction studies have been used in order to elucidate about the origin and the chemical evolution of the groundwater pathways.

Sub-alkaline to calc-alkaline granite dominates the high-level plutonic massif of Sintra, while two overlapping ring complexes recognised within it consist of four distinct alkaline to sub-alkaline quartz-bearing syenitic units, together with intrusions of a remarkable kaersutite- and (titan?) biotite-bearing theralite heteromorph (Mafraite) [1].

The water composition varies from sodium-chloride to calcium-bicarbonate, with a wide range of mineralization; the pH ranges from neutral to slightly acid (7.06-5.79). The Ca and Mg enrichement is observed in waters circulating in syenite and gabro aquifers. The dissolved silica concentration is higher in waters of syenite rocks (up to 45 mg/L), as a result of increased dissolution of plagioclase relative to quartz and feldspars.

Environmental isotope data (δ^2H and δ^{18}O) show an ^{18}O enrichment in waters from the N slope, with average values of -4.09 ‰ and -25.6 ‰ for δ^{18}O and δ^2H respectively; while in the S part –4.54 ‰ and -25.0‰ were obtained. This isotope enrichement could be related with the first condensation effect of the water vapour masses entering the continent and allowed to separate two main recharge areas.

The water-rock interaction studies have shown that the sea side location, aluminosilicates dissolution (sodium or calcium) and the water residence time in aquifers are the main responsible processes for the groundwaters chemical evolution.

[1] Ramalho *et al.* (1993) Notícia Explicativa *Carta Geológica Portugal*, Folha-**34**, SGPortugal, Lisboa.

Geochemistry of soils close to abandoned Sb-Au and As-Au mines from Valongo, northern Portugal

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The Valongo area lies c.18 km at east of Porto, in the Dúrico - Beirão district, northern Portugal. In this region Variscan folding gave rise to the large Valongo anticline and a syncline to the west. The Valongo anticline is limited at southwest by the Douro Shear Zone and at northeast by the granite. It comprises Cambrian to Carboniferous metasediments. The Cambrian schist-metagraywacke complex predominates in the region. The Sb-Au quartz veins outcrop on the western limb of the anticline, filling faults and shear zones and are hosted by Cambrian phyllites and metagraywackes. There are several abandoned mines, such as Montalto and Tapada. The As-Au quartz veins outcrop on the eastern limb and are hosted by Ordovician quartzites and schists and were exploited at Banjas mine. The Sb-Au quartz veins contain mainly quartz, arsenopyrite, pyrrhotite, pyrite, marcasite, sphalerite, chalcophyrite, galena, gold, tetrahedrite, jamesonite, plagionite, berthierite, stibnite, antimony and carbonates. The As-Au quartz veins consist of quartz, arsenopyrite, pyrite, pyrrhotite, cobaltite, sphalerite, boulangerite, tetrahedrite and siderite. Soils close to the Tapada Sb-Au mine have the highest Sb and As contents, 21776 ppm and 1116 ppm, respectively, whereas those close to the Montalto Sb-Au mine show up to 767 ppm Sb and 338 ppm As. Soils close to the Banjas As-Au mine contain up to 904 ppm As. Soils have acid to neutral pH (3.8-7.6), low conductivity (0-69 µS/cm), but few samples have 209 µS/cm and 732 µS/cm close to Montalto and 818 µS/cm close to Banjas, low to high organic matter content (17-134 g/kg) and low cation exchange capacity (1.6-9.7 cmol kg^{-1}). The particle size distribution shows a low clay content (2.2-5.3 %). Kaolinite is the most abundant clay mineral in soils. However, soils also contain muscovite, chlorite, smectite, vermiculite and mica-smectite, goethite, ferrihydrite, hematite and lepidocrosite. The BCR shows that Sb and As are not bioavailable in soils, because these metalloids are mostly retained in the residual fraction (71-100%) and only up to 101 ppm Sb and 54 ppm As are in oxyhydroxides. Sb and As are mostly adsorbed by clay minerals. Al, Cr, Cu, Fe, Mn, Ni, Pb and Zn are the most adsorbed in the highest available fractions and are bioavailable.