Iron and trace elements cycling in mineralized paleolaterites from NW Tunisia

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The Tamra (NW Tunisia) iron mine is composed of a 50m-thick series of stacked shallowing-upward sedimentary sequences. Iron is concentrated within these sequences by combined pedogenetic and hydrothermal processes. We used Fe isotopes (by MC-ICP-MS) and trace elements analyses (by ICP-MS) to constrain Fe and trace elements distributions in the typical sedimentary sequence (from top to bottom): massive hematite + quartz bar; goethite + hematite mixed horizon; kaolinite + hematite clayey level.

Our results indicate that: (1) There is an overall depletion of MREE, U and light iron (^{54}Fe) into the clayey term: Th/U ratios ranges from 3.5 to 5.2 and δ^{56}Fe from +0.79‰ to +1.07‰. (2) Within the intermediate hematite- and goethite-rich term, selected REE (La, Eu, Yb, Lu) are depleted, producing a typical tetrad effect in the REE patterns. By contrast, U and light iron are concentrated, most probably through adsorption onto pre-existing iron oxides. Th/U ranges from 0.4 to 1 and δ^{56}Fe from -1.03‰ to +0.34‰. (3) The lowermost massive bar acts as drain and partially concentrates the REEs percolating downward from underlying terms. A moderate U depletion and light iron accumulation are noted: Th/U ranges from 3.5 to 6.9 and δ^{56}Fe from -0.44‰ to +0.58‰.

These data suggest that pedogenesis results in a downward redistribution of REE, U and ^{54}Fe (or Fe^{2+}_{aq}) onto the lower terms where they are efficiently trapped by adsorption. Complexing agents are present in the system to mobilize the elements: hydrothermal sulphates and pedogenetic humic/fulvic acids. Although a non-null elemental budget in the type sequence suggests that it does not act as a closed system, there is actually internal (re-) cycling of the studied elements within “semi-closed” cells.

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Decoupling of Cu and As in Magmatic-hydrothermal systems: Evidence from the Pueblo Viejo Au-Ag deposit, Dominican Republic

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Pyrite from the Pueblo Viejo high-sulfidation deposit provides evidence for decoupling of Cu and As in hydrothermal solutions. The pyrite that shows this decoupling is in the late-stage veins that also contain sphalerite and minor enargite. Pyrite in the veins shows growth zoning that varies in composition with depth into the deposit. Deepest veins (>150m below the present surface) contain fine-grained (<2□m) pyrite with 0.4% As, 0.5% Pb, 0.2% Cu, 0.1% Ag, 0.09% Te and 0.06% Sb (wt% by EMPA). At depths of 120-103m below the present surface, pyrite contains alternating growth zones with either Cu (<0.78%) or As (<0.69%), but never both. Farther upward in the deposit concentrations of Cu and As in the two types of pyrite increase and Pb (<1.8%), Sb (<0.33%), Ag (<0.1%) and Te (<0.08%) are also in As-rich zones. At a depth of ~20m, Cu and As reach concentrations of up to 3 wt% in separate, alternating growth zones. EMPA elemental maps of the shallowest pyrites reveal that increased concentrations of As and Cu coincide spatially with decreasing concentrations of Fe and show no relation to S, suggesting that both elements substitute for Fe. Chemical compositions of Cu-pyrite and As-pyrite are: $(Fe_{0.95}Cu_{0.06})_{1.01}S_2$ and $(Fe_{0.96}As_{0.05})_{1.01}S_2$, respectively. HRTEM observations on pyrite with highest Cu and As concentrations reveal that the pyrite consists of single crystals that are continuous from Cu-rich to As-rich growth zones. There is no visible (by TEM) grain boundary between Cu-rich and As-rich zones. Cu-rich growth zones contain no Cu-bearing inclusions, whereas As-rich growth zones contain numerous ordered nano-domains rich in As.

The alternating sequence of Cu-rich and As-rich zones appears to reflect separation of Cu from As during evolution of the hydrothermal fluids. Similar decoupling of As and Cu is seen in analyses of fumaroles and fluid inclusions (both vapor and liquid), which are enriched in As and Cu, respectively. This suggests that the decoupling is related to magmatic processeses, probably involving vapor-liquid transitions.