

## SIMS U-Pb ages for heterogenite from Katanga (DRC): Implications for the genesis of Co-U deposits in Shinkolobwe

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Heterogenite (CoOOH) deposits are the most abundant Co ore in the Katanga Copperbelt (DRCongo), which hosts world-class Co deposits accounting for ~50% of the world's reserves [1]. Most of the heterogenite deposits occur in the upper oxidized zone of the primary deposits, and were formed during a Mio-Pliocene major uplift and weathering episode [2]. However, U-rich heterogenite, present in deeper zones of several deposits, may have a different origin and age.

Assuming that U in this heterogenite is in the UO<sub>2</sub> form, we attempted to obtain *in situ* U-Pb ages for heterogenite samples from Shinkolobwe, using a Cameca IMS 1270 ion microprobe, with settings comparable to those used for standard U-Pb age measurements on uraninite. These analyses yield two distinct Neoproterozoic ages, recorded by the upper intercept of the concordia lines: 680.9 ± 7.4 Ma and 823.2 ± 2.2 Ma. In both cases, the lower intercepts provide imprecise near-zero ages indicating recent (or continuous) Pb loss from the heterogenite.

At the present stage of knowledge, the 823 Ma date cannot easily be related to a known oxidizing event in the area. It is, however, reasonably close to the 816 ± 62 Ma Re-Os age obtained for Zambian primary sulfides [3]. The 681 Ma date could correspond to the Nguba karstification/weathering event described for the area [4]. If our age is meaningful, heterogenite could have formed in a period of superficial weathering, during the formation of the Katanga basin. This supergene event would, however, be contemporaneous with significant precipitation/reconcentration of uraninite, since the oldest uraninite age obtained for the Shinkolobwe deposits (at 652.3 ± 7.3 Ma) overlaps with ages for heterogenite in <sup>207</sup>Pb/<sup>206</sup>Pb age density diagrams.

At this stage, the present study does not allow a full understanding of the timing and conditions of Co and U mineralization in Katanga. The results, however, indicate the importance of acquiring additional ages for heterogenite-uraninite deposits in order to understand the genesis of these giant Co-Cu-U ore deposits.

[1] USGS (2009) *Mineral Commodity Summaries 2009*, p. 195. [2] Decrée *et al.* (2010) *Min. Dep.* **45**, 621-629. [3] Selley *et al.* (2005) *Econ. Geol.* **100<sup>th</sup> anniversary volume**, 965-1000. [4] Buffard (1993) *Karstologia* **21**, 51-55.

## Chemical limits of trace elements in pyrite

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Pyrite in magmatic-hydrothermal settings contains significant concentrations of trace elements of economic and environmental importance, including Ag, As, Au, Bi, Cd, Co, Cu, Hg, Ni, Pb, Sb, Se, Te, Tl and Zn, which reflect the availability (solubility) of these elements in their parent hydrothermal solution. A review of our own and published analyses (including EMPA, SIMS, LA-ICP-MS, PIXE and HRTEM) of pyrite from Carlin-type, epithermal, and orogenic gold deposits reveals positive correlations for Sb-Pb-Bi, Au-Ag-Te, and Cu-Ag-Sb in all samples. Element-element ratios for most analyzed pyrites are: Au/Ag – 0.8-1.1, Au/Te – 0.8 to 1.0, Au/Sb – 0.7 to 1.1, Te/Pb – <1.1, Sb/Pb – 0.9-1.1, Sb/Cu – <1.0, Ag/Pb – 0.8-1.1, Bi/Pb – 1.0-0.7, and Bi/Sb – 0.7-1.1 in all types of deposits. Silver is enriched with respect to Te in low-T deposits, which have relatively high Ag/Te ratios of 1.0-1.2. Previous work has shown that As facilitates the incorporation of Au into pyrite via structural distortion and charge imbalance and that the Au content of pyrite is related to its As content such that the maximum Au content is  $C_{Au} = 0.02C_{As} + 4 \cdot 10^{-5}$ . Pyrite with Au-As contents above this maximum contain nano-inclusions of Au. These relations apply to epithermal and Carlin-type deposits, which form at relatively low temperatures. Au-As relations in pyrites from orogenic gold and skarn deposits, which form at higher temperatures, show similar relations but with smaller amounts of Au for any specific As content, suggesting that the solubility of Au in pyrite (as a function of As) decreases with increasing temperature. Arsenic also appears to facilitate incorporation of Ag, Te, Sb, Bi and Hg into the pyrite structure in the same mode as for gold, although analyses are not sufficient to establish specific solubility limits. Samples with contents of these elements that exceed the apparent solubility limits contain nanoparticulate sulfides and sulfosalts in distorted, polycrystalline areas of pyrite.