

# Raman spectrometry as a tool to characterise cobalt secondary ore: the TRACE project

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The Lufilian fold-and-thrust belt (Katanga Province, Democratic Republic of Congo- DRC) is estimated to hold between a third and half of the world's known cobalt reserves. This non-renewable resource is mainly extracted as a secondary ore deposits, the heterogenite (CoO.OH) resulting from the oxidation of Cobalt sulphide primary bodies. This mineral bears frequently various amounts of Cu, Ni, Fe and Al.

Several years of civil wars and political instabilities in DRC have led to the development of an intensive informal small-scale mining sector associated with social-environmental issues and losses of incomes for the authorities. The TRACE project ("TRACeability of hETerogenite"), sponsored by the Belgian Science Policy follows an integrate scheme covering scientific studies and political and social aspects of this industry. The scientific approach is addressing the natural variability of ore bodies and the techniques that can be applied to conduct the analytical traceability of the ore.

In this presentation, we bring out the main results of the scientific measurements conducted on heterogenite samples from 16 mining sites throughout the Katanga Province. We put forward the relationship between the geochemical composition (microprobe and EDS analysis) of the samples and its Raman spectroscopic response.

One of the most common Raman spectra acquired on raw sample and polished section during the TRACE project were called type 1 - heterogenite. We regard these spectra as the real Raman response of heterogenite under the laser beam without structural transformation due to the heat produced by the laser. These spectra shows four Raman peaks at 494 cm<sup>-1</sup> (major peak), 565 cm<sup>-1</sup> and 627 cm<sup>-1</sup> (minor peaks), and a very minor peak, sometime absent, at 668 cm<sup>-1</sup> (fig.1a).

The second type, Spinel type, is the spectral response of heterogenite locally adopting a cubic spinel cristallographic structure (<sup>1</sup>Deliens, 1974) due to material heating induced by the laser. For the analysed samples, four Raman peaks were determined at 662 cm<sup>-1</sup> (major peak), 462 cm<sup>-1</sup> and 499 cm<sup>-1</sup> (minor peaks), and a very minor peak, sometime absent, at 602 cm<sup>-1</sup> (fig.1b).

An analytical procedure was defined to adapt Raman Spectrometry for systematic analysis of heterogenite samples (raw and polished sections). Comparison with

chemical analysis permits to enlighten the tendency of Cu-rich (> 12 wt.% Cu) heterogenite to be transformed at the  $\mu\text{m}$ -scale into a Co-spinel by the Raman laser heat flux. Besides the Cu-Co relationship, Ni-bearing heterogenite also presents specific Raman signature.

Series of iterative least-squares curve fittings were also made on selected Raman spectra in order to compare peaks position and relative intensity with spot chemical analysis. In heterogenite-type spectra this permitted to establish a close relationship between the Raman peaks relative intensity and heterogenite cation content (Cu, Mn, & Ni).

Raman spectrometer proved to be an excellent tool to process ore samples just minutes after collection. This allowed analyzing a large amount of raw samples in order to give a clear view of the Raman spectral response variability within a mine. After a systematic identification of the Raman spectra peaks and other distinctive features on these raw samples, comparative diagrams were made for the studied sites. These show a great variability of the spectral response as well as specific distribution patterns of these responses for each mine.

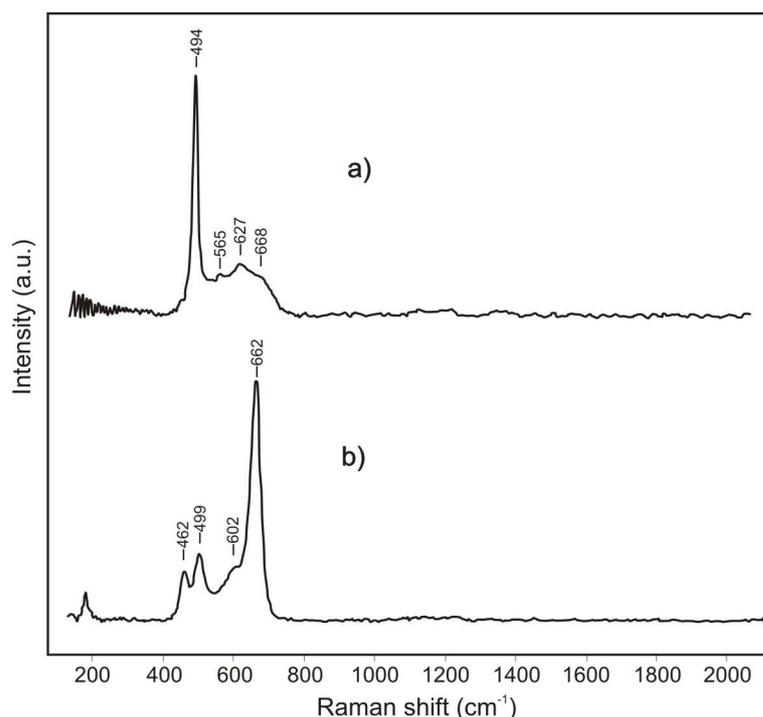


Fig.1: Raman spectra acquired on heterogenite samples from mines in DRC a) Mindigi, heterogenite type spectrum b) Kabolela, spinel type spectrum. Both spectra were acquired using 2mW 532nm laser, during 3 x 10s and with a 50x1000 $\mu\text{m}$  spectrometer slit.

<sup>1</sup> Deliens, M., *Les oxydes hydratés de cobalt du Shaba méridional (République du Zaïre)*, 1974 Annales du Musée Royal de l'Afrique centrale, **76**.