

**RAMAN MICRO-SPECTROSCOPY AS A TOOL TO CHARACTERISE COBALT - MANGANESE LAYERED OXIDES (HETEROGENITE - ASBOLANE – LITHIOPHORITE), STUDY ON CRYSTALLINE AND AMORPHOUS PHASES FROM THE DRC (DEMOCRATIC REPUBLIC OF THE CONGO).**

Burlet C.<sup>1</sup>, Vanbrabant Y.<sup>1</sup>, Decree S.<sup>1</sup>, <sup>1</sup>Royal Belgian Institute of Natural Sciences, Geological Survey of Belgium, 13 Jennerstreet, B-1000 Brussels

The largest cobalt ore reserves are located in DRC, the Democratic Republic of Congo. Most of cobalt is observed as black cobaltic oxide minerals: heterogenite [ $\text{HCoO}_2$ ] and asbolane [ $(\text{Ni},\text{Co})_{2-x}\text{Mn}(\text{O},\text{OH})_4 \cdot n\text{H}_2\text{O}$ ] which are hardly differentiable since they exhibit similar macroscopic habit and textures. These minerals are frequently observed in similar environment (oxidized horizon of ore deposits) and they are commonly poorly-crystallized, limiting their study with XRD [1]. The difference in mineralogy and chemical composition of the different cobalt minerals will have an impact on their metallurgical treatment. In this study, we define Raman reference spectra for these phases, and compare their natural chemical variability (EDS) using samples from DRC. Those observations are then completed with the Raman spectroscopic study of another layered manganese oxide, lithiophorite [ $(\text{Al},\text{Li})\text{MnO}_2(\text{OH})_2$ ].

Our observations on a set of heterogenite and asbolane samples from DRC combined with samples from other localities, including lithiophorite from Germany, Poland and USA, shows that each phase, even under an amorphous form, can be readily distinguished by Raman micro-spectroscopy. This technique is therefore attractive during ore deposit characterization campaigns or during the follow-up extraction operations where it is important to distinguish the main constituting Co-Mn-phase(s). The main advantage of this technique is its speed since no sample preparation is required during the collection Raman spectra that usually last few tens of seconds, using a careful selection of laser and acquisition settings to avoid sample degradation. The method provides information at a  $\mu\text{m}$ -scale and several points are thus required to fully characterize ore batches composed of different mineralogical phases.

Figure 1 shows reference spectra of crystallized heterogenite, asbolane and lithiophorite acquired during this study. All Raman responses are different, but they share nevertheless a similar pattern of peaks composed of two groups. The first one gathers 3 to 4 peaks located between 376 and 649  $\text{cm}^{-1}$ . The second group shows three small-amplitude peaks with Raman shifts between 938 and 1217  $\text{cm}^{-1}$  and with similar intensi-

ties. An additional very weak peak is observed at 3484  $\text{cm}^{-1}$  for asbolane and 3458  $\text{cm}^{-1}$  for lithiophorite.

Our petrographical observations show also that asbolane and heterogenite mineralogical phases can coexist at a  $\mu\text{m}$ -scale as two distinct phases into 'heterogenite' ore. The distinction between heterogenite and asbolane from our sample set can also be conducted on a chemical base showing that heterogenite represents the richer Co-phase with variable Cu concentrations. The chemical variability within the studied samples is assessed through the determination of geochemical composition of the two phases using about 800 EDS measurements. Those analyses showed that only Mn traces are usually observed in heterogenite minerals from DRC except in few samples, but always in lower concentration than in asbolane. The latter shows variable Mn/(Mn+Co) ratio between 0.85 and 0.3 and the decrease of this value is related to enrichment into Cu. Those observations, coupled with the classification of Raman responses with chemical variation in asbolane and heterogenite provide a new tool to assist the metallurgical treatment of these ores, manganese content being especially determinant for cobalt extraction yields in hydrometallurgy.

Finally, the asbolane and heterogenite samples from DRC have been compared to other world class cobalt ore deposits. DRC samples typically show only traces or small concentrations of Ni. This observation contrasts, for example, with Ni-richer asbolane samples from New Caledonia studied in this paper or those described by Llorca and Monchoux [2]. The composition of the primary rocks from which Ni and Co elements were mobilized and then concentrated into alteration horizons can explain this difference in Ni-content. In New Caledonia, primary ultramafic rocks represent the main Ni and Co source, whereas folded and thrust sedimentary formations form the bedrock of the mining district of the Katanga Province.

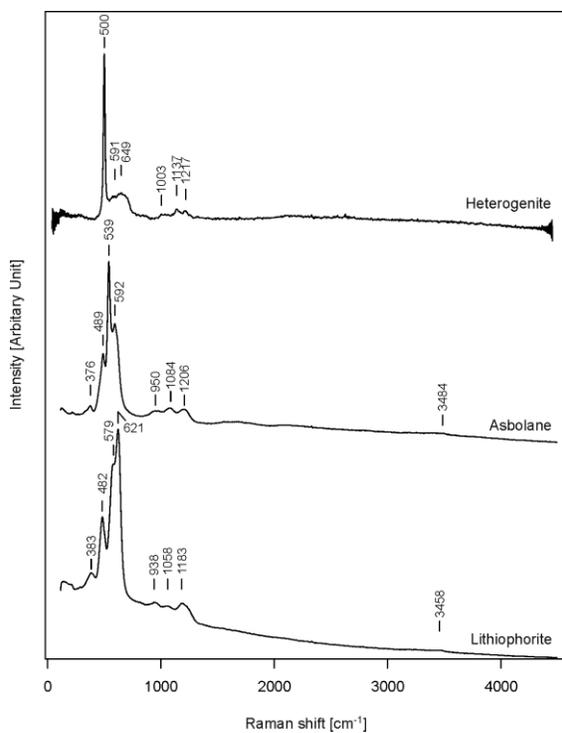


Figure 1. Reference Raman spectra of crystallized form of heterogenite, asbolane and lithiophorite[1].

#### References :

- [1] Vanbrabant, Y. et al. (2013), TMS Ni-Co 2013, 241–254  
 [2] Llorca S. and Monchoux P. (1991), Canadian Mineralogist, Vol.29, 1991), 149-161