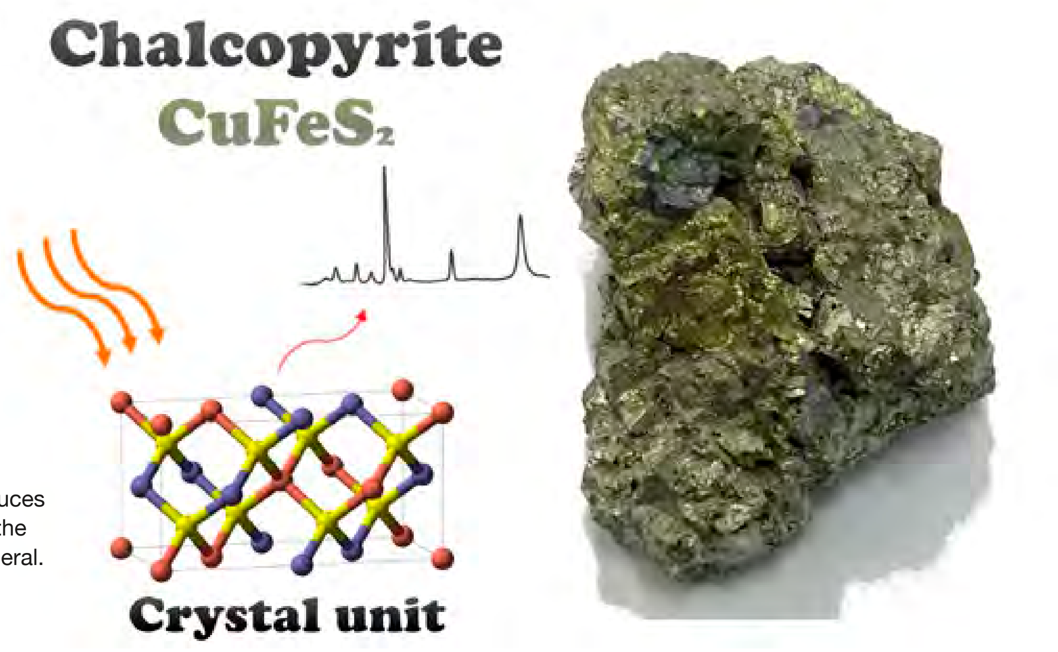

Figure 1. Laser excitation produces Raman photons, which reveal the fingerprint spectrum of the mineral.

Raman spectroscopy: **online mineralogy for process control**

TEXT: **KATARIINA RAHKAMAA-TOLONEN**, **SANNA UUSITALO**, **JANNE PAASO**, **MARKO PAAVOLA**

Mining and metal industries are essential for the wellbeing of people and societies in a modern world. All our appliances at home and day-to-day operations at work benefit from minerals, which have been excavated, enriched and processed into materials used to build the framework of our societies: tools, devices and infrastructure. Sustainable supply of raw materials is a major European challenge as EU countries contribute to more than 20% of the global consumption of metals and minerals, but only produce around 3% of the total supply. Mining has been ongoing for over thousand years in Europe and the long-standing activity has consumed many of the rich mineral deposits. As a result, we need more efficient mineral excavation and beneficiation process control in order to remain competitive and to utilize our resources efficiently and sustainably now and in the future. This sets requirements for better mineral characterisation tools in mineral drill core analysis, beneficiation and mineral processing.

Optical Measurements team located at VTT Oulu and Kuopio has competence in combining diverse spectroscopic and machine vision technologies to solve customers' needs in various applications fields - we bridge the gap between optical measurement technologies and industrial applications. The team leader Katariina Rahkamaa-Tolonen concludes that the team has two aims in developing measurements for mineral beneficiation and excavation: first to develop novel on-line measurement tools to make the mining of small and complex deposits economically feasible and second to increase the potential European mineral resources without generating adverse environmental impact. Accurate and reliable data supports both the mineral and metal process control and contributes significantly to the competitiveness of European industry by making processes faster, more efficient and better for the environment.

Raman spectroscopy has been applied for the characterisation of minerals in laboratory settings during the last decades. However, it is also a new tool for on-line mineral characterisation. The conventional tools used in the mining industry such as

Optical Measurements team

- Research team at VTT Oulu and Kuopio
- Team leader Katariina Rahkamaa-Tolonen
- Team consists of 27 researchers with different backgrounds ranging from mathematicians to engineers
- Expertise in machine vision, optical design, UV-VIS-IR and Raman spectroscopy, X-ray fluorescence and transmittance imaging
- 30-year experience in development of optical solutions for the process industry

Figure 2. a) Pyhäsalmi beneficiation facility's froth flotation tanks, b) Raman instrument connected to online XRF analyser at Pyhäsalmi.

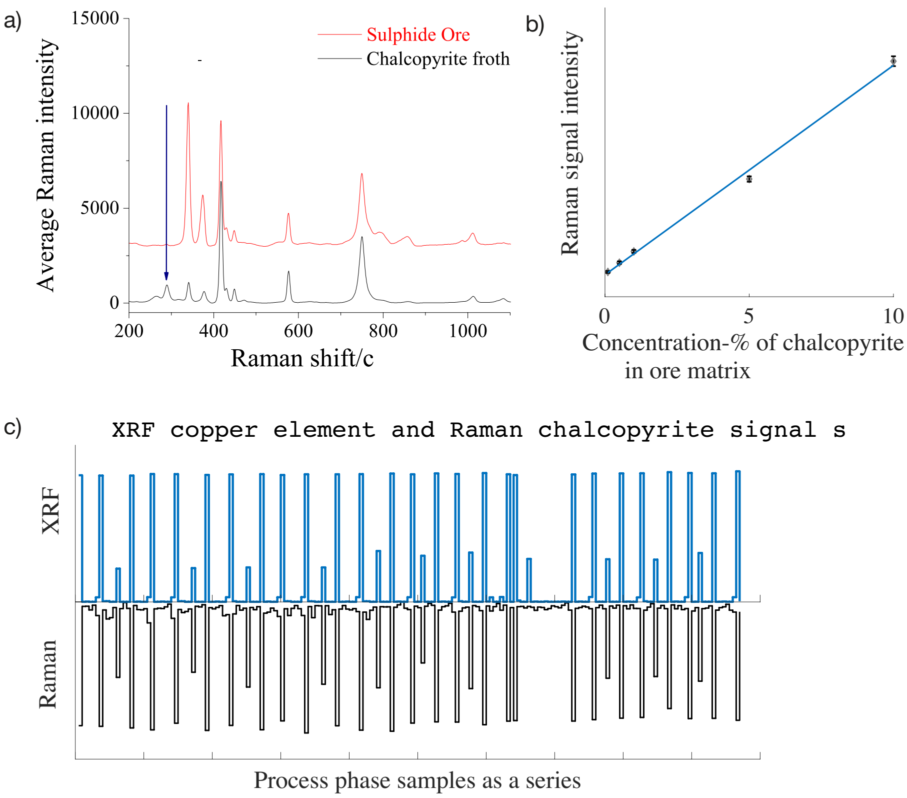

Figure 3. a) Chalcopyrite and ore Raman spectra, b) Relation of chalcopyrite concentration to Raman signal intensity, c) Recorded signals for XRF analyser copper amount and Raman chalcopyrite amount.

X-Ray Fluorescence (XRF) for online process control or Atomic Absorption Spectroscopy (AAS) for online system calibration in laboratory setting are based on the detection of material elements. Elemental information does not reveal the exact minerals present in the ore or in the manufacturing process. It gives indication and requires a priori information on the geology of the mine site or the materials used in the process.

The data provided by XRF and AAS for the process control relies on a priori information and successful calibration of the mineral estimation algorithms, because many minerals have similar elemental compositions. Without supporting information it is not possible to do successful mineralogical analysis from elemental data, and even when the supporting information is available, the mineral estimations can have challenges with accuracy. Raman spectroscopy is not looking at the elemental compositions; it provides information on the material bonds and creates a specific fingerprint for each mineral as depicted in Figure 1 for chalcopyrite. Laser excitation makes material bonds vibrate and, in some cases, the material releases a Raman scattered photon during the relaxation of the excited energy state. The detection of Raman photons creates a spectrum, where the characteristic peaks indicate the material composition provided that the material is Raman active.

The development of Raman spectroscopy as an online tool at mining facilities was initiated during a large EU funded Horizon project called Intensified-by-Design®. Janne Paaso, Senior Research Scientist from Optical Measurements team, organised collaboration between VTT, Outotec and Pyhäsalmi mine to study the benefits of Raman in the beneficiation process of sulphides. Project conducted the first online Raman spectroscopic measurements from an industrial froth flotation process at Pyhäsalmi mine during year 2018. The performance of Near Infrared Raman spectroscopy as an online tool was analysed for three different sulphide minerals chalcopyrite, sphalerite and pyrite[1]. Figure 2 shows pictures taken of the online measurement trial at Pyhäsalmi facilities.

The IbD®-project showed the feasibility of Raman spectroscopy as an online tool for the detection of sulphide minerals in froth flotation. Figure 3 shows the Raman response to chalcopyrite flotation samples. The characteristic Raman peak for chalcopyrite 291 cm-1 had a linear dependency on changes in chalcopyrite concentration in gangue mineral froth. These results show the potential of Raman spectroscopy for quantitative online mineral measurements in industrial froth flotation processes.

Although in many cases the conventional continuous wave Raman spectroscopy is able to produce a fingerprint spectrum for mineral identification, in some cases the minerals can have such a strong auto-fluorescence that the detection of Raman scattering is not possible. The challenges of Raman with auto-fluorescence of min- >

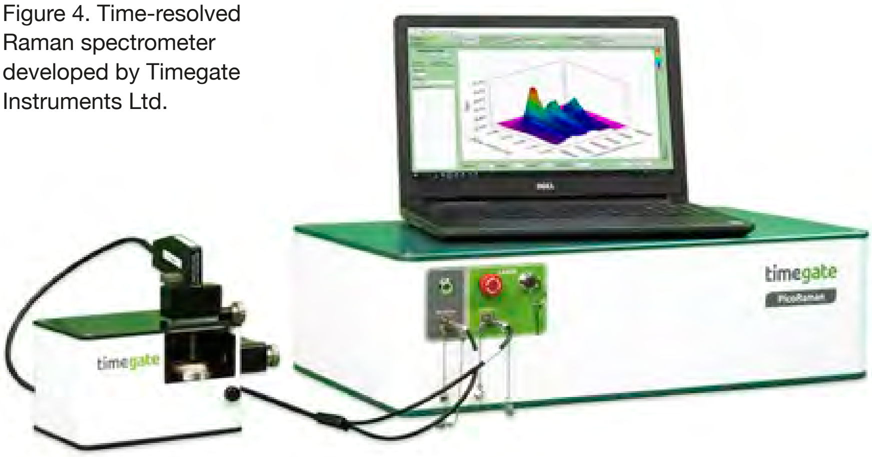

Figure 4. Time-resolved Raman spectrometer developed by Timegate Instruments Ltd.

Keliber Resources Ltd.

- Finnish mining and chemical company for battery grade lithium hydroxide production
- Planned annual production of 12,400 tons of lithium hydroxide using novel pressure leaching process
- Annual calcination operations for about 115000 tons of spodumene concentrate prior lithium leaching

Timegate Instruments Ltd.

- Company with expertise on time-resolved Raman spectroscopy
- Founded by co-inventors in 2014
- Team has experience in spectroscopy, research, mining, pharmaceuticals, PAT and data applications

erals can be minimised using a novel time resolved Raman spectroscopy, which can reduce the effect of fluorescence or high background emission.

The concept of time resolved Raman spectroscopy has been originally developed together by the Optical Measurement team from VTT, Optical Research Centre from Tampere University and Oulu University Electrical Engineering laboratory. The technology was commercialised in 2014 by a new company Timegate Instruments Ltd, which is continuing to drive the technological development further. Figure 4 shows a time-resolved Raman instrument PicoRaman. The optical measurement team has since then continued to study the applicability of the technology to different industrial processes including mineral characterisation for mining industry and metal processing with high thermal emissions. Compared to the conventional Raman technology, the time-resolved Raman is significantly less sensitive to ambient light and thermal emissions. Consequently it is more suitable for studying high temperature samples and their polymorphic and phase transitions. Time-resolved Raman can even provide data from samples reaching 1600°C as demonstrated by Timegate Instruments. This makes it possible to produce data from processes, which have previously lacked direct information on the progress of the production. One example of such a production process is the Calcination for Spodumene -conversion. Spodumene is the main mineral containing lithium and thus a critical mineral for the battery industry.

Lithium is extracted from spodumene by leaching. However, initially spodumene is in the α-form, which cannot be leached efficiently. In order to extract lithium, the crystal structure of spodumene must be converted from the α-form to the tetragonal β-form using a heat treatment. Currently the control of the conversion degree of this process relies on indirect data on the temperature of the vessel and a priori information on the best process parameters. Optical measurements team studied the

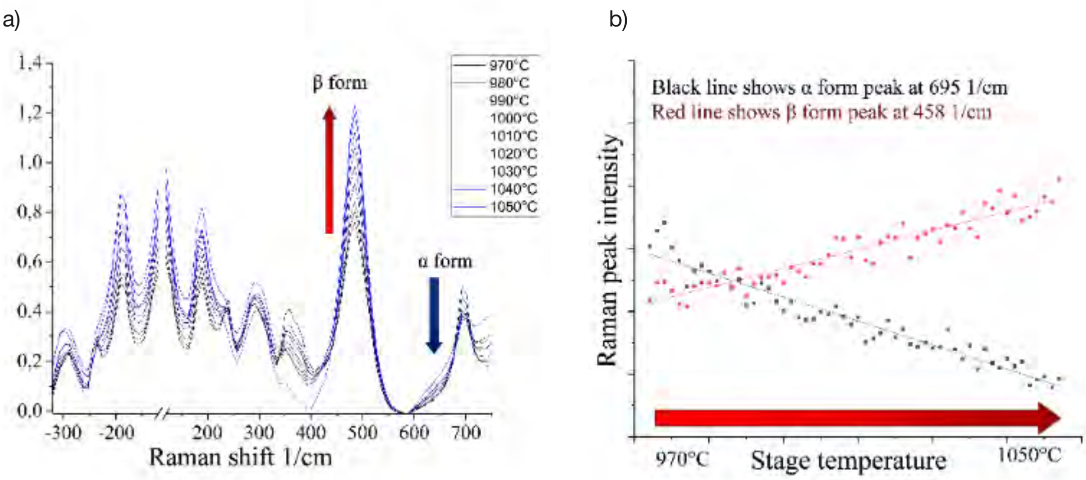

Figure 5. a) Spodumene phase transformation from the α-form to the β-form during heat treatment can be observed from time-resolved Raman spectra, b) Raman peak intensity shows the rate of the transformation.

ability of time-resolved Raman to monitor the calcination process in a collaboration project with Keliber Oy and University of Oulu. The results showed that the time resolved Raman spectroscopy is able to record direct data from this process, because it minimises the effect of the thermal emission with a time window between excitation and detection of the Raman photons. Figure 5 shows the transformation of spodumene during the calcination process in a small custom-built oven.

Currently the optical measurements team is continuing the development of Raman spectroscopy as an industrial mineral analysis tool in three collaboration projects. APASSI is a Business Finland -funded Co-Innovation project in which VTT is developing measurement intelligence for autonomous processes, instruments and sensors for Finnish industry. In this project, the development of Raman spectroscopy is taken forward as an online analysis tool in froth flotation processes together with Outotec. Project is especially focusing on understanding the effect of particle size and liquid – dry matter relation to the Raman signal intensity. The study of the Time resolved Raman spectroscopy continues in an EIT Raw Materials project called T-REX together with Timegate Instruments and DMT-group. DMT is a German based company providing comprehensive consulting for the mining industry in the fields of prospection, extraction and processing of natural resources. The project focuses on the automated mineralogy analysis of drill cores using sensor fusion of XRF and time-resolved Raman. Third project is also a Business Finland -funded Co-Innovation project 3DLIDAR, where the Raman research is focusing on the analysis of slag samples from Outokumpu steel factory. This project studies the use of time-resolved Raman in slag analysis. The ultimate aim for the team is to increase the use of high technology in European mines, to improve the process efficiency and thus decrease the environmental footprint of the industry as well as to support the European raw material sector. ▲

Katariina Rahkamaa-Tolonen, D.Sc. (Tech)
Team leader
Optical Measurements team VTT
Specialist in spectroscopy, project coordinator

Janne Paaso, D.Sc. (Tech)
Senior Research Scientist
Optical Measurements team VTT
Specialist in spectroscopy, project coordinator

Sanna Uusitalo, D.Sc. (Tech)
Senior Research Scientist
Optical Measurements team VTT
Expert in Raman and VIS-NIR spectroscopy

Marko Paavola, D.Sc. (Tech), Adj. Prof.
Senior Research Scientist
Optical Measurements team VTT
Specialist in industrial process control

[1] S. Uusitalo et. al., Online Analysis of Minerals from Sulphide Ore using Near–Infrared Raman Spectroscopy, Journal of Raman Spectroscopy, 2020, https://doi.org/10.1002/jrs.5859