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Development of an extended matrix-matched calibration protocol for fast, high-resolution, quantitative chemical mapping of major and trace elements of polymineralic samples by laser-ablation coupled to time-of-flight-mass-spectrometry (LA-ICP-TOF-MS).

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In situ analysis conducted by LA-ICP-MS for the determination of trace elements in ore deposit studies provides precious information of chemical composition in a variety of minerals at the micrometer-scale. To date, most laser studies use quadrupole mass spectrometers (ICP-Q-MS) for the analysis of monomineral phases, using static spot (or line ablation), while chemical mapping can reveal important spatial (2D) information, such as growth zoning, exsolutions, micro-veins, micro-inclusions (Fig.1). However, peak jumping mode operation of ICP-Q-MS limits the acquisition speed and spatial resolution. Time-of-flight mass spectrometers (ICP-TOF-MS) can extract full mass range simultaneously at high rate (33,000 Hz), rendering the instrument attractive for routine analysis and allowing to take steps towards new research areas **[1]**. A new protocol was developed using a 193nm LA-system (RESOnetics, Applied Spectra) attached to an ICP-TOF-MS (TOFWERK) **[2]** to allow high-resolution quantitative mapping of polymineralic surfaces (Fig.1B-C). Simultaneous quantification of trace and major elements of different minerals (silicates, sulfides, oxides, zircon, apatite, calcite) within a single data processing, and without saturation of the ICP-TOF-MS detector, can be achieved by combining 7 reference materials of varied matrices (glasses, sulfide, apatite, zircon). Based on normalization of major elements without the use of an internal standard, a new data reduction scheme (DRS) was developed for IOLITE v4 software **[3]**. The DRS can recognize sulfide and calcite to apply appropriate Fe conversion factors or correct for “blind” element (CO_2), respectively. Using a 7µm beam in raster mode, a 1mm^2 area is covered in about 30 minutes.

Figure.1) Fe-Ti-oxide-apatite mineralisation (Sept-Iles Intrusion, Canada). [A] Reflected light microphotography. [B] LA-ICP-TOF-MS RGB composite image of Cu(red), Pb(blue) and Ni(green) revealing zonation in a pyrite grain in a late calcite-serpentine vein. Maximum intensity scales are Cu(500ppm), Pb(20ppm), Ni(150ppm). [C] Normalized Fe(%) distribution (LA-ICP-TOF-MS). Total map size is 2mm x 0.7mm, resolution is 7µm (28,600 pixels total), acquisition time ~50 minutes.

[1] Sylvester, P.J. and Jackson, S.E. (2016), Elements **12**, 307-310. [2] Bussweiler, Y. et al. (2017), Spectroscopy **32**, 14-20. [3] Paton et al. (2012), JAAS **26**, 2508-2518.