U-Pb in situ dating and trace elements profiles in chrysocolla and pseudomalachite: Application to supergene copper mineralization.

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Over the past two decades, laser ablation coupled with the mass spectrometer has become a major analytical tool for the measurement of isotopic ratios and the determination of trace elements. The improvement of the sensitivity has provided new perspectives and permits to study new types of targets. For example, many questions remain open about the formation of supergene mineralization such as: what is exact timing for their deposition? What are the required associated physico-chemical conditions? To answer these questions, we focused on two copper deposits located in Chile (Mina Sur) and Burkina Faso (Gaoua) to develop U-Pb analysis and trace element profiles in pseudomalachite and chrysocolla. The analyses were carried out at the GET Laboratory (Toulouse). Different couplings between a femtosecond laser (fs-LA) or a nanosecond laser (ns-LA) and a HR-ICPMS or a MC-ICPMS were used. Trace elements determination and in situ U-Pb analysis present different challenges. For U-Pb analyses, matrix effects must be taken into account and the contribution of common lead ($^{204}$Pb) must be subtracted. As there is no chrysocolla or pseudomalachite reference materials, zircon and apatite were used as the primary external standards and fs-LA was used as a matrix independent sampling method. No significant U-Pb fractionation was observed, whatever the structure of the ablated matrix (silicate, phosphate). The bias linked to common lead was calculated from fs-LA-MC-ICPMS measurements. The $^{206}$Pb/$^{204}$Pb intensity ratio gives a first approximation on the possibility to determine the U-Pb age. Three cases have been distinguished: 1) If $^{204}$Pb is low ($^{206}$Pb/$^{204}$Pb ≥ 500) the U-Pb age obtained by this first analyze can be used. 2) If $^{204}$Pb is significant and the intensity ratio of $^{206}$Pb/$^{204}$Pb range between 500 and 5, a second step is necessary. In such a case, $^{204}$Pb must be determined more precisely using a MC-ICPMS to retrieve the common lead corrected U-Pb age. 3) If $^{204}$Pb is high ($^{206}$Pb/$^{204}$Pb <5), then it is not possible to determine the U-Pb age of the sample. Trace element profiles were also performed on the same chrysocolla and pseudomalachite samples. These analyses have been carried out using a ns-LA coupled to HR-ICPMS and NIST SRM 610 was used as primary standard. The reproducibility and accuracy of the analyses were verified by the ablation of secondary standards (91500 zircon and Durango apatite) and comparison with EMPA analyses. In this study we demonstrate that supergene mineralization can be directly dated and the trace elements in pseudomalachite and chrysocolla can be determined. The combination of these methods provides a new tool to understand the physico-chemical and geological conditions that are required for the formation of supergene mineralization.