

## **Repeat, fast, and high-resolution mapping of fine-scale trace element distribution in pyrite and marcasite by LA-Q-ICP-MS with the Aerosol Rapid Introduction System (ARIS)**

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### **ABSTRACT**

The minor and trace element composition of minerals provides critical insights into a variety of geological processes. Multi-element mapping by laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) is an important technique applied for this purpose and although the method is rapidly advancing, there remains a fundamental compromise between spatial resolution, detection limit, and experiment duration when using sequential mass analyzers. To address the limitation of limited analyte selection for high spatial resolution maps imposed by the sequential nature of typical quadrupole (Q)-ICP-MS, we tested the Aerosol Rapid Introduction System (ARIS) for repeat mapping of the same area. The ARIS is a high-speed transfer tubing system that reduces aerosol washout times, permitting resolution of individual pulses at 40–60 Hz. Here, the ARIS was tested not for pulse resolution but with novel operating conditions optimized to perform fast, high spatial resolution mapping of minor and trace element distribution in pyrite and marcasite. For this purpose, ablation was conducted with a 5  $\mu\text{m}$  beam aperture, a repetition rate of 50 Hz, and a continuous stage scan speed of 40  $\mu\text{m s}^{-1}$ . For each LA-Q-ICP-MS map, data were acquired for six elements with an acquisition time of 20 ms per element. This deliberately reduced the individual pulse resolution of the ARIS but instead exploited the spatial resolution and sensitivity gains afforded by the high-laser repetition rate combined with efficient aerosol transfer. The new method successfully mapped trace elements at single to double-digit parts per million levels, and the maps reveal fine-scale zoning of trace elements with an effective x and y resolution of 5  $\mu\text{m}$ , while white light interferometry showed that for each experiment, only ca. 1  $\mu\text{m}$  of the sample was removed. Repeated mapping of the same area showed excellent correspondence not only between element concentrations in successive experiments but also in the shape, dimension, and location of regions of interest defined by concentration criteria. The very good repeatability of the elemental maps indicates that for studies requiring more analytes, successive mapping of additional elements is possible. By contrast with conventional very small spot (i.e., 5  $\mu\text{m}$ ) analysis, fast repetition rate and stage scan speed mapping avoids down-hole fractionation effects and minimizes accidental analysis of buried invisible inclusions. Compared to conventional LA-ICP-MS mapping, the method reduces the experiment time by 4–8 times.

**Keywords:** Pyrite, marcasite, LA-ICP-MS, compositional heterogeneity, element mapping; Understanding paleo-ocean proxies: Insights from in situ analyses