Resolving sub-micrometer-scale zonation of trace elements in quartz using TOF-SIMS

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ABSTRACT

Quartz is abundant in the Earth’s continental crust and persistent throughout the geological record. Trace element signatures in silica minerals can be used to infer processes operating in magmatic and hydrothermal systems. Conventional analyses of trace elements in silica minerals are limited by either spatial or mass resolution [e.g., wavelength-dispersive X-ray spectroscopy, micro-X-ray fluorescence, laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS), and secondary ion mass spectrometry (SIMS)]. Time-of-flight SIMS (TOF-SIMS) is a relatively new technique for geological applications and provides both high spatial and mass resolution. This minimally destructive, in situ technique rapidly acquires a full suite of elements down to tens of nanometers depth. No previous study has utilized TOF-SIMS to analyze quartz or silica. Four samples of silica minerals representing distinct environments in a magmatic-hydrothermal system were characterized with optical microscopy and qualitative cathodoluminescence (CL), quantitatively analyzed for trace elements with a 157 nm LA-ICP-MS, and qualitatively mapped for trace elements using TOF-SIMS. The novel technique produced maps of trace element distribution in silica minerals to a maximum resolution of 65 nm and consistently resolved light elements (including Li) to 195 nm. That makes this study the highest resolution geochemical characterization of silica minerals and places it among the highest resolution analyses by TOF-SIMS, or any technique, for that matter. TOF-SIMS isotope maps differentiate trace elements hosted in nano- and micro-inclusions from lattice incorporation in quartz and cryptocrystalline silica—an impossibility for lower resolution techniques, allowing insights into cations substituting for Si4+ in the crystal lattice and their role in activating CL in low-temperature epithermal quartz. Further development of this technique could see TOF-SIMS become a routine tool for measuring diffusion profiles in a range of other geological materials. Quantification of TOF-SIMS would revolutionize mineral characterization, especially given its temporal efficiency and low-sampling volume.

Keywords: TOF-SIMS, quartz, trace element, in situ, silica

INTRODUCTION

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Quartz is ubiquitous throughout the Earth’s continental crust, deposited in a diverse array of igneous, metamorphic, sedimentary, and hydrothermal settings. Its abundance and persistence in the geological record (Taylor and McLennan 1985) make it an ideal candidate to preserve chemical archives in magmatic and hydrothermal systems. Changes in the microstructure and trace element composition of quartz are used to infer the environment of crystallization (Götze 2009).

Relative to other silicate minerals, quartz hosts a limited range of trace elements in solid solution. Trace elements that substitute into the tetrahedral silicon site in quartz include Ti4+ or Ge4+, or trivalent ions such as Al3+ or Fe3+ coupled with a charge-compensating ion such as K+, Na+, Li+, Cu2+, Ag+, or H+ (Müller et al. 2003; Götze 2009). The combination of trace element incorporation and microstructural defects in quartz give rise to the wide range of intra-crystalline textures visible in cathodoluminescence (CL) imagery. Unlike routine imaging techniques [e.g., transmitted light, reflected light, and backscattered electron (BSE) imaging], CL imaging reveals that quartz grains are rarely homogeneous. Quartz grains typically exhibit micrometer to sub-micrometer-scale textures ranging from oscillatory zonation, healed fractures, planar features, streaks, or mottled patches depending on their provenance (cf. Seyedolali et al. 1997; Bernet and Bassett 2005). However, CL is a qualitative imaging technique that cannot reliably decouple the contribution from multiple trace elements and crystal defects (Müller et al. 2003, 2010; Rusk et al. 2006, 2011; Vasyukova et al. 2013). Therefore, in situ techniques with high spatial resolution are required to analyze the trace element signature of most quartz grains.

While quartz hosts a limited range of trace elements in solid solution, changes in quartz chemistry help petrologists track magmatic and hydrothermal processes (e.g., Breiter et al. 2017; Monnier et al. 2018; Müller et al. 2018; Peterková and Dolejš 2019) and determine the provenance of sediments (e.g., Dennen 1967; Götze and Zimmerle 2000; Götze 2009; Müller and Knies 2013; Ackerson et al. 2015). In magmatic systems, quartz chemistry elucidates crystallization temperatures, pressures, and fluid compositions (Müller et al. 2018) as well as recording