OH defects in quartz as monitor for igneous, metamorphic, and sedimentary processes

ROLAND STALDER1*, ALEXANDER POTRAFKE1, KJELL BILLSTRÖM2, HENRIK SKOGBY2, GUIDO MEINHOLD3, CHRISTIAN GÖGELE1, AND THOMAS BERBERICH1

1Institute for Mineralogy and Petrography, University Innsbruck, Innrain 52f, A-6020 Innsbruck, Austria
2Department of Geosciences, Swedish Museum of Natural History, S-11418 Stockholm, Sweden
3Geoscience Center, University of Göttingen, Goldschmidtstrasse 3, D-37077 Göttingen, Germany

ABSTRACT

Oriented sections of more than 500 quartz grains from sediments, igneous, and metamorphic rocks from different localities in Sweden, Austria, Germany, and South Africa were analyzed by FTIR spectroscopy, and their OH defect content was determined with respect to the speciation and total defect water content. Systematic variations of defect speciation and statistical evaluation of total defect contents were used to evaluate the potential of FTIR spectroscopy on quartz as a thermometer in quartzite, as a tool for differentiation trends in granitic systems, and for provenance analysis of sedimentary rocks. In addition to the analyses of natural crystals, high-pressure annealing experiments at lower crustal conditions (1–3 kbar and 650–750 °C) were performed to document the effect of high-grade metamorphism on the defect chemistry. Results indicate that (1) quartz grains from unmetamorphosed granite bodies reveal interesting differentiation trends; (2) sediments and sedimentary rocks are valuable archives to preserve the pre-sedimentary OH defect chemistry, where individual signatures are preserved and can be traced back to potential source rocks; (3) OH defects are retained up to 300 °C over geological time scales; (4) long-term low-grade metamorphic overprint leads to a continuous annealing to lower defect water contents, where Al-specific OH defects survive best; and (5) middle to high-grade annealing drives toward a homogeneous defect partitioning from grain to grain, where the degree of attainment of equilibrium depends on temperature and duration of the thermal event.

In summary, OH defects in quartz crystals monitor parts of their geological history, and the systematic investigation and statistical treatment of a large amount of grains can be applied as an analytical tool to study sedimentary, metamorphic, and igneous processes.

Keywords: Quartz, hydrous defects, provenance, quartzite, granite

INTRODUCTION

Quartz is an important rock-forming mineral that crystallizes or anneals in different chemical systems over a wide range of conditions within the Earth’s crust. Depending on the thermochemical factors pressure, temperature, and chemical composition, impurities of trace metals, and defects protons form different impurity-specific OH defects that can qualitatively and quantitatively be analyzed by Fourier transform infrared (FTIR) spectroscopy. In general, proton incorporation follows the charge-balance equation

\[ [\text{H}^+] = [\text{B}^+] + [\text{Al}^{13+}] - [\text{Li}^+] - [\text{K}^+] - [\text{P}^5+] \]

(Bambauer 1961; Kats 1962; Müller and Koch-Müller 2009; Baron et al. 2015). The role of Li in this equation is more complicated, because it can be on either side of the equation and act both as an OH defect-forming species (such as LiOH) and an OH defect-reducing species that charge balances Al13+ (Frigo et al. 2016). Four major defect-types have been described that can be distinguished by their absorption frequency in the IR range: protons that are charge balanced by Al13+ are responsible for an absorption band at 3595 cm−1 (Miyoshi et al. 2005; Müller and Koch-Müller 2009; Baron et al. 2015), and Li+ is responsible for an absorption band at 3470–3480 cm−1 (Bambauer 1963; Aines and Rossman 1984). Another absorption band has been observed at 3585 cm−1 (Chakraborty and Lehmann 1976; Paterson 1986; Rovetta 1989). It occurs independent of metal impurities and is strongly dependent on water pressure (Stalder and Konzett 2012), and therefore most probably represents a silicon vacancy charge balanced by protons, i.e., hydrogarnet substitution (Si4+ → 4H+).

The OH defects mentioned above have all been observed in natural samples, but averaged over the whole Earth’s crust, the Al-specific OH defect is by far most abundant, followed by the Li- and B-related defects (Stalder and Neuser 2013; Stalder 2014). The abundance of the hydrogarnet defect is present in small quantities in some quartz grains, but insignificant on a global scale.

Integral absorptions in the infrared range can be used to calculate absolute defect water concentrations using the calibrations of Aines et al. (1984), Libowitzky and Rossman (1997), or Thomas et al. (2009) that all result in very similar values for natural samples. A significant problem for the quantification of OH defects is fluid micro-inclusions of molecular water that overlap the absorption bands caused by OH defects and often are the most abundant hydrous species (Bambauer 1961; Müller and