OH incorporation in quartz as a tracer of formation conditions

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Quartz as a common nominally anhydrous mineral of the Earth's crust contains traces of hydrogen as a molecular water in fluid inclusions, or as structurally incorporated hydroxyl ions. The structurally bound hydrogen commonly acts as a charge compensator, associated with point defects, such as substitution of Si^{4+} by Al^{3+} and/or B^{3+} with charge balance maintained by monovalent cations substitutions (H^+, Li^+ and Na^+). The occurence of hydrogen affects thermodynamic properties of minerals and influences their kinetic behavior during diffusion and phase transformations. Even small amounts of OH defects can dramatically change physical properties of minerals that are a key to understand rock-formation mechanisms within the crustal conditions.

The geochemical behavior of OH incorporation in quartz in the systems granite-tourmaline-water and granite-spodumene-water was studied in order to explain the effect of pressure and temperature on structural defect generation. Piston-cylinder experiments were carried at pressures between 5 and 25 kbar and temperatures between 800 and 1050°C. Oriented and polished quartz crystals from each run were characterized with FT-IR spectroscopy and water contents were calculated using mineral-specific and general wavelength-specific calibrations.

The OH absorption features were assigned to Al^{3+}-substitution (Al-H defect, band-triplet at 3320, 3383 and 3434 cm^{-1}), B^{3+} -substitution (sharp absorption band at 3597 cm^{-1}), Li^+ -substitution (weak absorption band at 3475 cm^{-1}) and hydrogarnet $(4H)_{Si}$ defect (absorption at 3585 cm^{-1}).

In this study point defects cause various OH contents in quartz, depending on different pressures, temperatures and chemical environments. Synthesized crystals showed a negative correlation of calculated water content vs. pressure. Under lower pressures quartz incorporates more hydrogen (5 kbar: 450-750 ppm H_2O) than at higher pressures (25 kbar: 72-106 ppm H_2O). Therefore, our results imply that IR spectra of quartzes have a potential to be used as a geobaromether to indicate petrological formation conditions. Moreover, the B- and Li-specific OH absorption bands may be used to quantify the charge balancing B^{3+}- and Li^+- content that could be used as a novel and indirect analytical tool to detect traces of B and Li in quartz crystals.

Ion microprobe U-Pb dating of individual phosphate grains in Martian meteorite

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A Martian meteorite ALH 84001 shows extremely old age of over 4 Ga and is expected as a key to the ancient history of Mars. Its crystallization age is still controversial due to the complicated impact history. While volumetrically minor, phosphates are important carriers of trace elements. Previous SIMS U-Pb dating of several merrillite and apatite grains in ALH 84001 showed ~4 Ga [1]. However, intra-grain systematics was not observed because of limited spatial resolution. In-situ analysis of a single grain will provide further information regarding cooling and reheating process. Here we measured single grain U-Pb ages using a laterally high-resolution secondary ion mass spectrometer (NanoSIMS) at Atmosphere and Ocean Research Institute, University of Tokyo.

Two polished thick sections of ALH 84001 were firstly observed by SEM-EDS. Two merrilite grains with ~100 μm in diameter were found. The sections were polished again, gold-coated and baked overnight, and then analyzed by a NanoSIMS. A 2-10 nA O- primary beam was used with spot size of ~10-20 μm. An apatite from Prairie Lake circular complex, PRAP, with a known age of 1155 ± 20 Ma [2] was used as a standard of UO/UO_2-Pb/UO calibration.

For both analyzed grains, the obtained ^{238}U-^{206}Pb and ^{206}Pb-^{207}Pb ages show good agreement with ~4 Ga, suggesting the intra-grain U-Pb system is concordant. There is also chemical zoning of U abundance. Since diffusion rate of U in apatite is slower than Pb by ~4 orders of magnitude [3], the observed zoning was possibly made during crystal growth and preserved since then. Meanwhile, Pb may have been homogenized within a grain at crystallization (and/or later impacts), which makes single grain U-Pb dating possible. The interpretation of the ages (igneous or impact-reset) is related to the processes of crystallization and impacts. Further studies including micro scale analyses of other elements are required. This is the first report of single grain U-Pb dating of phosphates using a NanoSIMS.

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