## A synthetic silica glass reference material for determination of Ti in zircon by LA-ICP-MS

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The proper use of Ti-in-zircon thermometer mostly depends on the accurate determination of Ti content in zircon. Because of lacking homogeneous matrix-matched mineral standards available, a silica glass (LCD-1) was fused at 1680°C. The major element contents of the glass, SiO<sub>2</sub> (73.89±0.29)%, Al<sub>2</sub>O<sub>3</sub> (8.22±0.14)%, ZrO<sub>2</sub> (5.96±0.09)%, K<sub>2</sub>O (5.53±0.04)% and Na<sub>2</sub>O (7.35±0.11)% (all in1 $\sigma$ ), were determined by electron microprobe. The Ti content in the glass is 998±23µg/g (1 $\sigma$ ) measured by using solution-ICP-MS method and 1009±22µg/g (1 $\sigma$ ) using LA-ICP-MS method calibrated by taking <sup>29</sup>Si as an internal standard and NIST SRM 610 as the reference material.

The fractionation index of Ti/Zr is less than Ti/Si in zircon. So, LCD-1 as reference material, Ti contents in zircon 91500, GJ-1 and M257 are determined by LA-ICP-MS. The result for one analysis calibrated using <sup>29</sup>Si as an internal standard is lower 16-20% than that using <sup>96</sup>Zr. The results calibrated using NIST 610 and LCD-1 as reference material and <sup>29</sup>Si as an internal standard are nearly same, their differences are less than 2.3%. All these facts suggested that LCD-1 glass is a better reference material than NIST 610 in determination of Ti in zircon.

## Scanning transmission X-ray and atomic force microscopy mapping of exopolymer fractionation in *Bacillus subtilis* biofilms on goethite

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The surface properties of goethite are vital for many environmental processes, such as adsorption and transport of contaminants and nutrients. This study aims at understanding of how biofilm formation changes the mineral surface. Adhesion and mechanical properties (e.g. elastic modulus) were investigated by atomic force microscopy (AFM), while the chemical composition of the biofilm was mapped by scanning transmission X-ray microscopy (STXM).

We investigated single-layered biofilms formed by *Bacillus subtilis* on Lysogeny broth-agar plates in the presence or absence of goethite. Synchrotron-based STXM C K-edge image sequences, recorded at a spatial resolution of  $\leq 25$  nm, were converted to component maps of proteins, polysaccharides, nucleic acids and lipids by linear combination fitting. STXM revealed that proteins, nucleic acids and lipids were mainly located inside the cells, while polysaccharides dominate in the extracellular polymeric substances (EPS). In the presence of goethite, we found a higher concentration of nucleic acids in the EPS and the goethite needles were covered by nucleic acids. This supports the view that nucleic acids mediate EPS binding to mineral surfaces and are required for establishing biofilms [1].

Quantitative nanomechanical properties measurement by AFM indicated that the DMT modulus (elastic modulus) of the goethite surface decreased from ~40 GPa to ~84 MPa after biofilm formation. The adhesion between the AFM tip and the goethite surface in air increased from ~2 nN to ~12 nN after biofilm formation.

We hypothesize that nucleic acids are intentionally excreted by B. *subtilis* when e.g. goethite surfaces are present. This preferentially adsorbed nucleic acid-rich material is responsible for the observed changes in the mechanical surface properties of goethite.

[1] Whitchurch (2002) Science 295, 1487.

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