Microstructures in lunar zircon: key to interpretation of U-Pb ages

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The interpretation of internal microstructures has become an integral part of geochronological studies using the U-Pb system in zircon from terrestrial samples. However, U-Pb analysis of lunar zircon was abandoned in late 80s and only recently resumed and combined with imaging utilising different methods available to reveal internal microstructures in these grains. Extensive study of lunar zircons during the last few years resulted in accumulation of data sufficient to build a preliminary classification of their internal structures. This classification is essential for the correct interpretation of U-Pb ages. It is particularly important because majority of lunar zircons occur as abraded, broken fragments in the matrix of the breccias, with no evidence of their origin or history. Also, increasingly, we are finding zircon grains with complex U-Pb age patterns, which makes interpretation difficult. The only way of addressing these issues is studying the textures and structures in lunar zircons and cross correlating this information with the observed pattern of U-Pb ages determined by ion microprobe analyses.

Lunar zircons are classified according to: (i) textural relationships between zircon and surrounding minerals in the breccias, (ii) the internal microstructures of the zircon grains and (iii) in-situ analyses of Th-U-Pb isotopic systems with ion microprobe. Both igneous (primary) and impact (secondary) features can be identified in lunar zircon.

Primary zircons occur as part of a cogenetic mineral assemblage (lithic clast) or as individual mineral clasts and are unzoned, or have sector zoning or rarely oscillatory zoning. U-Pb ages of zircons exhibiting these microstructures determine the timing of magmatic crystallisation.

Secondary microstructures include locally recrystallised domains, localised amorphization, crystal-plastic deformation, planar deformation features and fractures, and are associated with impact metamorphism. The first two types often yield internally consistent, concordant U-Pb ages that date impact events. The absolute ages of other secondary microstructures cannot be determined. Nevertheless, it is possible to define their relative timing from the relationships with other microstructures. In addition, regular occurence of these features (e.g. planar deformation features are found in lunar zircon along {001}, {110}, and {112}, typically with 0.1-25 µm spacing and {112} commonly contain micro-twin lamellae with 65° / <110> misorientation relationships, while dislocation creep commonly forms deformation bands parallel to {100} planes) can be explained in terms of elastic anisotropy of zircon and used to predict conditions experienced by different zircon grains during the impacts.

Planar deformation features, crystal-plastic deformation and micro-fractures can provide channels for Pb diffusion and their identification can explain some instances of partial resetting of the U-Pb isotopic system. Consequently their identification in a zircon grain should prompt a careful examination of the U-Pb ages obtained in this grain and their significance.

Metal speciation and dynamics of carrier phases in a boreal forested catchment under transient chemical conditions

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The formation and fate of natural aquatic colloids was investigated in a boreal catchment (68 km^2) with transient pH conditions (pH 3.8-6.4) and diverse landcover types (wetland, forest and sediment dominated). We examined the influence of colloids on metal speciation, i.e. iron, aluminum, arsenic, manganese, and rare earth elements (REE).

Flow-Field Flow Fractionation [1], membrane filtration (0.2 µm), cation exchange column separation [2], ultrafiltration (1 kDa) and scanning electron microscopy were used to characterize colloids and to quantify colloid-metal associations.

In the small headwater catchments, complexation with natural organic matter (NOM) was dominating the speciation of iron, aluminum, manganese and REEs. 50-70% of the total arsenic was associated with NOM, and substantial concentrations were present as dissolved species. Along the natural pH gradient we observed a gradual increase of iron in form of iron-oxy(hydr)oxide particles (50 nm up to several hundred nm). Despite this increase, REEs were still associated to colloidal NOM, while up to 30% of arsenic and manganese adsorbed or co-precipitated with the iron particles.

Chemical equilibrium modelling confirmed that complexation of REEs to NOM was stronger than the sorption of REEs to iron-oxy(hydr)oxides. The concentration of iron minerals can only be explained by a stronger than expected Fe-NOM complexation. The complexation constant would then be higher than in the data base of Minteq [3].

We quantified fluxes from all sub-catchments and used landscape type analysis for the estimation of metal export. Mass balances indicate that there is no loss of iron and trace elements during the transport through the catchment, despite the formation of relatively large iron-oxy(hydr)oxides particles. An additional source of iron, manganese, and sulphate through groundwater influx accounts for the observed total export from the catchment. Our study implies that the trace metals mobilized from the different upstream sites behave mainly conservative despite shifts in speciation. Mass balance calculation does allow for the quantification of the relative contribution of the different landscape elements for total metal flux.

[1] Neubauer et al. (2011) *J. Chromatogr., A.* **1218**, 6763-6773. [2] Hruska et al. (1996) *Water Resour. Res.* **32**, 2841-2851. [3] Sjöstedt et al. (2010) *Environ. Sci. Technol.* **44**, 8587-8593.