

## Otolith microchemistry: Monitoring trace elements in lacustrine environments

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Otoliths, the hard calcareous (typically aragonite) structures located in the inner ear of teleost fish, are used to determine age, life history events, and environmental conditions of fish and fish populations. Whereas strontium has seen extensive use, particularly to determine migratory behaviour of fish, zinc is also ubiquitous. The advantage conferred by otolith microchemistry stems from otoliths being metabolically inert, retaining a complete record of chemical exposure over several years, whereas contaminants in muscle or visceral tissue are only useful indicators of recent exposure. Metabolic transformation and tissue re-compartmentalization of trace elements makes their use as temporal markers tenuous. Coupling microchemistry and annular structure of otoliths adds a time scale to the chemistry, providing a unique opportunity to track changes in trace element concentrations over the duration of the fish's life. This may be used to reconstruct historical levels of trace elements and monitor, or even restore aqueous environments.

In this work, LA-ICP-MS has been used to examine trace element compositions in otoliths from several lakes in Manitoba that are impacted by different types of mining activity. Analyses of otoliths taken from fish in the vicinity of a rare element pegmatite mine have shown that the incorporation of lithium and cesium is dependant on proximity to the pegmatite. Otoliths from fish captured near, or downstream from the pegmatite contained these elements, whereas fish from lakes distant to or upstream from the pegmatite do not have these elements. This suggests that otoliths incorporate a chemical signature related to the ambient water, which in turn can be related to the geology of the surrounding watershed. Variations in abundance of the trace elements amongst species from within the same water body point to the incorporation of a chemical signature related to diet. Zinc may provide information on the nutritional status of fish but, when found with copper and lead, also indicates proximity to mining activity.

## Modelling nucleation and growth of nano- to micro-size secondary clay particles in weathering processes

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In order to simulate the formation of nano- to micro-size particles in water-rock interaction processes, we have developed a theoretical approach of nucleation, growth and ageing processes, relevant for precipitation of secondary mineral phases in aqueous solution [1, 2]. This has led to the elaboration of the numerical code Nanokin which makes possible the simulation of weathering processes, including thermodynamic as well as kinetic effects [3].

We will present results relevant to the weathering of a granitic rock, successively including the formation of competitive kaolinite and halloysite and then more complex clay phases (from montmorillonite to illite). The secondary clay phase populations are described versus time, and display progressive size growths and evolution of their crystal size distribution (CSD), showing very realistic sizes when compared to natural cases

An extension of this model is presently under progress to simulate complex clay phases as solid solutions combining chemical variations and particle size variations [4, 5].

The evolution of the chemical composition of the aqueous solution compares very well with a natural system in a watershed equipped for geochemical research, both when short term reactions (years) are involved or in the long term (tens of years).

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[1] C. Noguera, B. Fritz, A. Clément & A. Baronnet (2006) *J. Cryst. Growth* **297**, 180-186. [2] C. Noguera, B. Fritz, A. Clément & A. Baronnet (2006) *J. Cryst. Growth* **297**, 187-198. [3] B. Fritz, A. Clément, Y. Amal & C. Noguera - "NANOKIN, a geochemical computer model for dissolution, nucleation & growth in aqueous solutions" (in preparation). [4] C. Noguera, B. Fritz, Y. Amal & C. Clément (2008) *GCA*, this volume. [5] Y. Amal (2008) PhD, University Louis Pasteur, Strasbourg.