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Preservation and Chemical Alteration of Biogenic Francolite and Calcite from Marine Organism

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Introduction

The francolite from fossil bones and calcite from shells of marine organism is applied as important tracer minerals in reconstructing the isotope composition of paleo seawater (e.g. Quing and Veizer 1994). As the initial isotope composition of these material is unknown, it is necessary to find independent indicators for determining the possible isotopic overprint by structural and chemical alteration. In the last decades numerous chemical analyses of phosphorite deposits (summary in Javris et al. 1994) verify, that the REEs respect parts of the geo-chemical evolution of natural phosporites. Generally, in natural apatite Ca^{2+} is often substituted by REE^{3+} and charge compensation is done by (a) intrinsic electron defects, (b) depletion of the constituent ions, and (c) a coupled substitution of the constituent ions by REE^{3+} and, e.g. OH^-, CO_3, OH^{3-} and SiO_4^{4-} . Consequently, the complex analyses of REE incorporation in apatite could give information about the chemical and structural alteration of biogenic francolite. Luminescence techniques are often used to determine diagenetic alteration of fossil "biogenic" calcite. The relation of intrinsic luminescence and Mn^{2+} -activated luminescence is often applied to determine unaltered biogenic and secondary calcite phases, but unfortunately these identification is not unequivocal (Barbin 2000). Thus, distinction between pristine mineralogy and diagenetic alteration remains difficult (Barbin 2000).

Experiments

The francolite samples are Eocene and Miocene shark teeth and Triassic conodonts (locations: Germany, Greece) prepared as powder sample and polished thin sections, respectively. The calcite samples are sea- and fresh-water pearls (from: China, Arabian, Japan and North America), corals, brachiopod shells, sepia shell and belemnite rostra. Samples of biogenic francolite (shark teeth and conodonts) were reacted in aqueous solutions containing a variety of REE at pH 4-6 and 25ºC, 50ºC and 100ºC. Parts of a sepia shell were used as nucleus in a crystal grow experiment using a aqueous solutions containing samarium. All unchanged and modified samples were analysed by the combination of: a) micro-PIXE - quantitative trace element analyses, b) CL-spectroscopy - analyzing the REE and Mn incorporation in Ca(I) and/or Ca(II) position of francolite and the Mn-distribution in recent and fossil biogenic calcite c) ESR-spectroscopy -determining structural defects by, e.g. REE incorporation to examine the chemical alteration of calcite and the REE exchange of Ca in biogenic francolite.

Results and discussion

The micro-PIXE analyses of fossil francolite samples from conodonts of Triassic age and shark teeth of Tertiary age indicate that most of the REEs are significantly enriched in Triassic conodonts comparative to the average shale standard (NASC). The PIXE analyses of fossil conodonts revealing the REE-distribution not to be in balance with the REE-distribution of seawater and recent fish bone debris. Strong inhomogeneous lateral REE-distribution in fossil conodont material is shown by CL-mapping and most probably not being a vital effect. It is not clear on which scale the documented enrichment occurs, but high REE-concentrations and enrichment of Ce and some REEs (Sm, Eu) are most probably affected by the chemical composition of surface water and/or burial ground water. This interpretation is supported by significant REE incorporation in surface reacting experiments. Hence, the resulting REE signal from fossil francolite used in this study is the sum of vital and post-mortem incorporation. The latter is basically controlled by local chemical and physical properties of the fluids. Consequently, if fossil francolite from marine organism does not show the REE pattern of seawater, these samples are most probably chemically affected by diagenetic processes and certainly not useful for reconstructing the isotope composition of paleo seawater. Spectroscopic data of the intrinsic phenomena of carbonates document that the CL emission is are marked by five bands between 400 and 660nm and caused by e.g. Ca^{+0}-CO_3^- -centre, broken bonds between Ca ion and oxygen ligands and oxygen vacancies. As these defects are not merely confined to biogenic calcite, defining unaltered biogenic calcite by their intrinsic CL is no unequivocal criterion. Our investigations on biogenic calcite are consistent with data from Barbin (2000) describing intrinsic and also intensive Mn^{2+}-activated CL also being common in biogenic carbonates reflecting environmental and lifetime characteristics. Results from present crystal grow-experiments with sepia shell will be presented.

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