Concentration profiles of trace elements in fossil dinosaur bone

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Fresh bone is composed of nm-sized hydroxyapatite crystals which are embedded in a protein matrix of collagen. During early diagenesis, collagen decomposes rapidly and bone porosity is usually filled by recrystallizing apatite and additional secondary mineral phases (e.g. calcite, pyrite, Fe-Mn oxides). Trace metals such as REE are incorporated at high concentrations into bone apatite during early diagenetic recrystallisation, which occurs rapidly within 10^1 to 10^4 years post mortem. Especially REE and U are used to constrain the taphonomy, reworking, and age of fossil of bone. The Lu-Hf system can potentially be used for direct radiometric dating of fossil bones and teeth, however, only if after the initial early diagenetic REE uptake the fossil bone behaved as a closed system over geologic timescales.

To monitor the diagenetic history and element mobility, REE and trace element LA-ICP-MS profiles of 1 to 8 cm length were measured across the cortex of fossil bones, mostly dinosaurs from well-characteriszed diagenetic settings. General features of the element distribution profiles are: (1) high trace metal concentrations at the outer bone rim, gradually decreasing by a factor of 10^1-10^3 toward the inner bone. In contrast, other profiles display flat and homogeneous element distributions across the bone cortex, probably due to an intense diagenetic alteration or late diagenetic REE diffusion/recrystallisation, (2) intra-bone REE patterns display an increasing depletion of MREE towards the central bone cortex due to higher partitioning coefficients in apatite, thus scavenging MREE during intra-bone transport, (3) Y/Ho and Zr/Hf ratios are markedly higher than chondritic ratios. Ratios of Zr/Hf (up to 600) are relatively similar across the bone cortex. In contrast, Y/Ho usually increase from chondritic ratios (28) along the rim to ratios of up to 200 in the center, decreasing again towards the marrow cavity.

Non charge radius controlled behaviour of trace elements, resulting in differing chemical bonding properties, might be responsible for the observed REE and trace element distribution patterns in fossil bones. Fossilizing bone offers a huge variety of potential complexation ligands (e.g. PO_4^{3-}, F^-, Cl^-, OH^-, CO_3^{2-}, organics). Implications for interpreting depositional environment, taphonomy and for Lu-Hf chronometry of fossil bones will be discussed.

Structure refinement and spectroscopic analysis of di-octahedral Ba-micas

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Large ion lithophile, larger alkali-, and alkaline elements (i.e. Ba, Rb and Sr) may be referred to as "incompatible", reflecting their partitioning into the fluid/melt phase rather than silicate minerals. To satisfy the observation that the concentration of these elements in mantle-derived rocks has not decreased over geological time requires the identifcation of mineral(s) that survive subduction and can accommodate these elements. There are several localities of high-pressure rocks that contain Ba-enriched di-octahedral white mica. This suggests that the muscovite structure may be stabilised at high pressures by incorporation of Ba via a coupled substitution on the I- and T-sites ($[\mathrm{Ba}]^{\mathrm{IV}}[\mathrm{Al}][\mathrm{K}]_{-1}[\mathrm{Si}]_{-1}$), as well as by Tschermak (phengite) substitution, on the M- and T-sites ($^{\mathrm{IV}}[\mathrm{Si}]^{\mathrm{VI}}[\mathrm{Mg/Fe}]^{\mathrm{IV}}[\mathrm{Al}]_{-1}{}^{\mathrm{VI}}[\mathrm{Al}]_{-1}$).

Three natural samples of Ba-rich di-octahedral mica ranging between 13 and 47 mol % ganterite [1] were studied with powder XRD, FT-IR, and MAS NMR. Structure refinements show that there is no change in mica space group with increasing Ba content. However, variation in crystallographic properties, including contraction on the c-axis and expansion of the a-b plane, are observed. This agrees with single-crystal studies on similar material [2]. FT-IR data shows a frequency shift consistent with changes in cation ordering on non-equivalent sites. Peaks in the IR-spectra split into doublets in lower-Ba samples Similarly, in lower-Ba samples, the peak at 3600 cm^{-1} characteristic of structural hydroxyl, broadens and a second peak develops. ^{29}Si MAS NMR data confirm the presence of four environments under a single broad peak, consistent with Q^3 Si having 0, 1, 2, and 3 Al in nearest-neighbour tetrahedra. Peak-broadening is observed in lower-Ba samples. Observed trends in spectra indicate decreasing structural order with decreasing Ba.

Increased structural order brought about by increased Ba content in mica are predicted to decrease mineral entropy; a thermodynamically favorable process at higher pressures. Therefore, the white-mica structure may be a viable way of returning Ba to the mantle during subduction.

[1] Graeser *et al.* (2003) *Can. Mineral.* **41**, 1271-1280.
[2] Armbruster *et al.* (2002) *SMPM*. **82**, 537-548.