

Computer modelling of organic/biomineral interfaces

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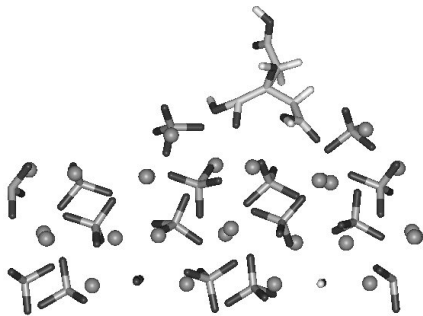
Geologically important minerals such as hydroxyapatite $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ and calcite CaCO_3 often have a biogenic origin, resulting from exo-skeletons, bones and shells. Unlike inorganic minerals, these biominerals have been grown under controlled conditions within organisms, where organic templates have usually played a crucial structure-directing role, often leading to unusual and thermo-dynamically unfavourable mineral morphologies.

The study of biomineralisation is a rapidly expanding field of research, where computer simulations can contribute significantly to our atomic-level understanding of the processes occurring at the interface between the growing mineral and the organic reagents.

We present a comprehensive computational study of the interaction of surfaces of calcium carbonate (calcite and aragonite) as well as the natural bone mineral apatite with a number of organic molecules that have important growth enhancing or inhibiting effects. We calculate both the energies of the adsorption of the organic molecule to each surface, hence providing a quantitative measure of the strength of interaction to particular surface features, and the surface energies of the adsorbate/substrate system, which allows us to calculate the effect of the adsorbate on the crystal morphology.

For the calcium carbonates, it is found that carboxylic acids often adsorb preferentially to particular surface features, such as growth steps on the calcites surface, leading to asymmetric surface morphologies in agreement with experiment. In addition, the presence of organic adsorbates is found to drastically alter the morphology of the aragonite crystal.

A number of citric acid derivatives are known to affect apatite growth, whereas the citric acid itself is instrumental in its dissolution. Simulation of its adsorption to hydroxyapatite shows a distinct preference of the citric acid to adsorb to the the $\{10\bar{1}0\}$ and $\{11\bar{2}1\}$, planes compared to the $\{0001\}$ surface, which affects both the morphology and the growth behaviour of the mineral.



Citric acid adsorbed to the hydroxyapatite $\{10\bar{1}0\}$ surface

Search for Cr isotopic anomalies in unequilibrated carbonaceous chondrites

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Previous leaching studies [e.g., 1-2] revealed the existence of both negative and positive ^{54}Cr anomalies in carbonaceous chondrites, with the highest excesses in the CI chondrites (up to 250 ϵ -units) [3]. In such studies, direct mineralogical and chemical information regarding the carrier phase of the isotopic anomalies is lost. The main focus of this work is to find the carrier phase of the ^{54}Cr anomalies by physically separating different phases from primitive carbonaceous chondrites (e.g., low-FeO and high-FeO chondrules, refractory inclusions, matrix enriched material etc.), to characterize the separated phases by electron probe, and to measure the Cr isotopic composition by TIMS.

To assure that the high excesses in ^{54}Cr found in the CI and CM chondrites also exist in the most unequilibrated chondrites such as the CO3.2 chondrite Kainsaz, we will first carry out leaching studies following the procedures of [1] and [2] before physically separating different chondritic components. Each leachate is measured by atomic absorption to determine the Cr content in the leaching fractions before carrying out the Cr chemistry and measuring the ^{54}Cr isotopic composition.

Most of the previous ^{54}Cr studies were concentrated on CI and CM chondrites. Our study will focus on chondrites from the petrographic subtypes 3.0 to 3.2 as these meteorites have largely avoided aqueous alteration and metamorphic events. It is possible that these secondary processes have dissolved some of the carrier phase(s) of the isotopic anomalies and that leaching studies of the most unequilibrated chondrites may display larger ^{54}Cr anomalies.

We chose the CO3.2 chondrite Kainsaz because it is a highly unequilibrated fall and because the least altered CO chondrites experienced much less aqueous alteration than the least altered CV chondrites.

References

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- [2] Rotaru *et al.* (1992), *Nature* **358**, 465-470.
- [3] Nichols *et al.* (1998), *LPS XXIX*, 1748.