Modelling of rare earth element sorption to *Bacillus subtilis* bacteria

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In this study, rare earth element (REE) binding constants and site concentration on the Gram+ bacteria surfaces were quantified using a multi-site Langmuir isotherm model, along with a linear programming regression method (LPM). This approach found one discrete REE binding site on the Gram+ *Bacillus subtilis* surface for the pH range of 2.5 to 4.5. Average log REE binding constants from 1.08 ± 0.04 to 1.40 ± 0.04 for the light REE (LREE: La to Eu), and from 1.36 ± 0.03 to 2.18 ± 0.14 for the heavy REE (HREE: Gd to Lu) at 1.3 g/L of Bacillus subtilis bacteria. Similar values were obtained for bacteria concentrations of 0.39 and 0.67 g/L Within the experimental pH range in this study, *Bacillus subtilis* was shown to have a lower affinity for LREE (e.g. La, Ce, Pr, Nd) and a higher affinity for HREE (e.g. Tm, Yb, Lu) suggesting an enrichment of HREE on the surface of Gram+ bacteria. Total surface binding site concentrations of 6.73 ± 0.06 to 5.67 ± 0.06 and 5.53 ± 0.07 to 4.54 ± 0.03 moles/g of bacteria were observed for LREE and HREE respectively, and a log $K_{REE,j}$ of 1.46 ± 0.02 for a biomass content of 1.3 g/L. The difference in these values (e.g. a lower affinity and increased binding site concentration for LREE, and the contrary for the HREE) suggests a distinction between the LREE and HREE binding modes to the Gram+ bacteria reactive surface at low pH. A multisite Langmiur isotherm approach along with the LPM regression method, not requiring prior knowledge of the number or concentration of cell surface REE complexation sites, were able to distinguish between the sorption constant and binding site concentration patterns of LREE and HREE on the Gram+ *Bacillus subtilis* surface. This approach quantified the enrichment of Tm, Yb and Lu on the bacteria surface and it has proven to be a useful tool for the study of natural reactive sorbent materials controlling REE partitioning in the natural environment.

The conditions of formation of the Castro de Rei reduced W-skarn

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The reduced W-skarn of Castro the Rei (Villalba Gold District, NW Spain) is hosted by marbles and calc-silicate hornfels of the contact aureole of a blind poskinematic Variscan granitoid [1, 2]. A hornblende-hornfels facies metamorphism is related to these granitoids, at pressures up to 2 kb [3]. Prograde skarn developed in marble is characterized by garnet (Gr_{41-77}), pyroxene (Hd_{33-100}), quartz and calcite with minor scheelite, K-feldespar and apatite. Locally, it can be formed by wollastonite, garnet (Gr_{62-82}) and piroxene (Hd_{43-70}). Prograde skarn and calc-silicate hornfels were overprinted by two stages of retroskarn. The first stage consists of ferrotremolite, epidote (Ps_{19-31}), zoisite (Ps_{0-19}), quartz, calcite, K-feldspar and sulfides and the second stage is characterized by prehnite or chlorite, quartz, calcite and sulfides. Based on mineral associations, fluid inclusion and stable isotope studies, a T-X(CO_2) isobaric (2kb) diagram with selected phase equilibria [4] was used for establishing the conditions of the skarn formation.

Fluid inclusions in garnet and quartz indicate that the prograde skarn was formed from a low-CO_2 (<0,06 mole fraction) aquocarbonic fluid. At this X(CO_2) the minimum formation temperature of the wollastonite-bearing skarn is 555ºC. For the garnet (Gr_{41-77}) and pyroxene (Hd_{33-100}) skarn, the formation temperature is above 520ºC, in agreement with the ^{18}O fractionation between quartz and garnet that yields a temperature of 534ºC. Ferrotremolite, epidote (Ps_{19-31}) and zoisite (Ps_{0-19}) from the first stage of retroskarn are formed at lower X(CO_2) (<0.04 mole fraction) and a temperature below 450ºC. For the second stage of retroskarn, fluid inclusions and occurrence of prehnite indicate near 0 X(CO_2) and temperatures below 385ºC. This is consistent with the maximum formation temperature calculated for the chlorite [5], up to 325ºC.

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