

## Dissolution/precipitation phenomena on Ca carbonate crystals interacted with Pb<sup>2+</sup> ions in aqueous solutions

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### Introduction

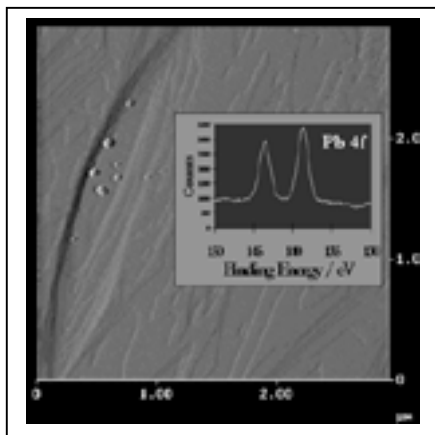
The study of the interaction of Ca carbonates with Pb<sup>2+</sup> ions in aqueous solutions, as related to dissolution and sorption phenomena, plays a key role to the understanding of geochemical, environmental and technological problems in respect of natural and industrial processes.

### Materials and Methods

Pure Ca carbonate (calcite and aragonite) crystals in the form of µm-sized (100-200 µm) fragments and mm-sized slices, were reacted with Pb solutions of varying concentrations. The investigation of the µm-sized samples was based on a batch-type procedure (10-1000 mg/L) using ICP, SEM-EDS, XRD and FT-IR. The mm-sized samples, interacted with slightly acidic aqueous solutions of 1000 mg/L Pb, were principally studied using a combination of surface techniques (*in-situ* / *ex-situ* AFM and XPS). Supersaturation calculations were used to evaluate the experimental results.

### Results and Discussion

**Fig. 1.** *In-situ* AFM image of ellipsoid (10-40 Å in height) Pb carbonate nuclei developed into an oval etch-pit of the dissolved calcite surface. The relevant XPS spectrum (Pb 4f region) is also shown.



The experimental results concerning the µm-sized samples showed that Pb is intensively sorbed by the Ca carbonates while dissolution of the solids takes simultaneously place. The main sorption mechanism is the surface precipitation of Pb carbonates (hydrocerussite and cerussite).

The above chemical processes are more evident in the case of the mm-sized samples according to the AFM and XPS surface studies (see Fig.1).

## Isotope constraints on brine formation in closed basin salars, NW Argentina

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The compositions of <sup>87</sup>Sr/<sup>86</sup>Sr, δD and δ<sup>18</sup>O were determined in streams and brines located within the Hombre Muerto drainage basin in NW Argentina. Lithium isotopic compositions were also determined to trace the source of Li in the basinal brines

Hombre Muerto is a largely dry saline lake (salar) within a closed basin located at 4000 m in the Andes of NW Argentina. Most years a terminal lagoon forms at the end of the principal stream, the Rio de los Patos. Much of the drainage basin is covered by the extensive 2.03 Ma Co. Galan ignimbrite which lies on the southern edge of the basin. The eastern edge of the basin has Paleozoic basement rocks at the surface. Palaeozoic and Cenozoic sediments outcrop in the western part of the basin. The basin is heavily faulted, and basalts and dacites occur close to faults. The climate is dry and rainfall averages 100-200 mm/yr.

The range in <sup>87</sup>Sr/<sup>86</sup>Sr is 0.7132 – 0.7206 with the most radiogenic compositions occurring in streams such as the los Patos that have contacted the basement rocks, even though the surface geology of their catchment is dominated by ignimbrites. The <sup>87</sup>Sr/<sup>86</sup>Sr of the salar subsurface brine is similar to these streams indicating a solute source from the los Patos. In contrast the brine δ<sup>18</sup>O and δD shows no evidence of evaporation and indicates hydrologic separation between the salar brine and the terminal lagoon brine. The brine is formed by dissolution of existing evaporite minerals that precipitated in the past during wetter climate conditions when the whole salar was covered by a perennial saline lake.

Geothermally-formed travertines occur in parts of the salar, generally close to best estimates of fault traces. The <sup>87</sup>Sr/<sup>86</sup>Sr of these travertines indicates a Sr source distinct from the immediate surface geology, indicating faults as a probable pathway for fluid flow.