

Study of iron-bearing dolomite dissolution at various temperatures: Evidence for the formation of secondary nanocrystalline iron-rich phases on the dolomite surface

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Mathieu Debure, Pascal Andrezza, Aurélien Canizarès, Sylvain Grangeon, Catherine Lerouge, et al.. Study of iron-bearing dolomite dissolution at various temperatures: Evidence for the formation of secondary nanocrystalline iron-rich phases on the dolomite surface. Goldschmidt2017, Aug 2017, Paris, France. hal-01499660

HAL Id: hal-01499660

<https://hal-brgm.archives-ouvertes.fr/hal-01499660>

Submitted on 31 Mar 2017

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**Study of iron-bearing dolomite
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Evidence for the formation of
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phases on the dolomite surface**

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We investigated the dissolution of a natural Fe-containing dolomite [$\text{Ca}_{1.003}\text{Mg}_{0.972}\text{Fe}_{0.024}\text{Mn}_{0.002}(\text{CO}_3)_2$] under acidic conditions (pH 3-5.5) with atomic force microscopy (AFM) at 20 °C, and with batch dissolution experiments at 80 °C. Dolomite dissolution proceeded by two identified mechanisms: removal of dolomite layers through spreading and coalescence of etch pits nucleated at defect points, and stepped retreat from surface edges. The dolomite dissolution rate increased when pH decreased (from 0.410 nm s⁻¹ at pH 3 to 0.035 nm s⁻¹ at pH 5). Rates calculated from edge retreat (v_{edges}) and from etch-pit spreading rates (v_{sum}) were consistent; the etch-pit digging rate was almost 10 times slower than its spreading rate. Nanocrystalline secondary phases precipitated in the course of dolomite dissolution at pH 3 and 80 °C were identified as (nano)hematite, ferrihydrite and an ankerite like mineral using X-ray diffraction, transmission electron microscopy, Raman and X-ray photoelectron spectrometry. In addition, Mg enrichment of the surface layer was observed at 80 °C, due to preferential release of Ca in solution. The characterizations performed at a nanocrystalline scale highlighted the role played by impurities in the dolomite dissolution/precipitation scheme and proved that two mechanisms explain the incongruent dolomite dissolution: secondary phase precipitation and preferential release of Ca over Mg.