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Controls of Ca/Mg/Fe activity ratios in pore water chemistry models of the Callovian-Oxfordian clay formation

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Abstract

In the pore water chemistry model of the Callovian-Oxfordian clay formation, the divalent cations Ca, Mg, and Fe are controlled by equilibrium reactions with pure carbonates: calcite for Ca, dolomite for Mg, and siderite for Fe. Results of a petrological study and computing of the Ca/Mg and Ca/Fe activity ratios based on natural pore water chemistry provide evidence that equilibrium with pure calcite and pure dolomite is a reasonable assumption for undisturbed pore waters; on the other hand, siderite cannot be considered at equilibrium with pore waters at the formation scale.

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1. Introduction

The Callovian-Oxfordian clayrock formation (COx) in eastern France has been selected by the French National Radioactive Waste Management Agency (Andra) as the host rock for installation of a future deep underground facility for disposal of radioactive wastes. Much effort has been invested in evaluating the composition of the porewater present in this clay mineral-rich formation since it will influence both the evolution of the various materials present in the facility (steel, concrete, glass etc.) and the transfer characteristics of radionuclides through the host rock. Two complementary approaches have been used to do this: (i) by geochemical modeling based on knowledge of the minerals present in the clayrock and the cation exchange characteristics of the clay minerals [1] and (ii) by collection of representative pore water

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samples by means of dedicated experiments carried out in Andra’s underground research laboratory (URL) located at a depth of approximately 500 m in the COx near Bure, France [4].

The model of COx pore water chemistry considers that present-day pore waters are at equilibrium with the clay mineral-based (illite, I/S mixed layers) cation exchanger and a suite of diagenetic minerals in a nearly closed system [1]. This supposition is considered to be locally valid given the long residence time of pore water chemical constituents, i.e. very low advective and diffusive fluxes within the formation. This in turn means that the relative amounts of such divalent cations as Ca²⁺, Mg²⁺ and Fe²⁺ on the cation exchanger will reflect the state of equilibrium with respect to the corresponding activities of dissolved species. These activities are considered to be controlled by three pure carbonate minerals in the present form of the model: calcite (for Ca), dolomite (for Mg) and siderite (for Fe). However more detailed information [2] concerning the chemical composition of carbonate minerals at equilibrium with present-day pore waters, as well as their distribution within the geological formation indicates that the latter assumption is excessively simple.

2. Characterization of carbonates at equilibrium with present-day pore waters

The identification of carbonate phases, which are at equilibrium with present-day pore waters is based on the principle that diagenetic minerals have recorded the local pore water chemistry present at different geological times. Consequently, carbonates at equilibrium with present-day pore waters are probably late diagenetic carbonates and carbonate grain rims in contact with interstitial waters. The diagenetic mineral sequence established for the COx formation, combined with electron microprobe analyses of carbonates and stable isotopes on diagenetic minerals, was used to identify the different carbonate generations, determine their chemistry and identify the processes/mechanisms involved in their deposition (Fig. 1).

Fig. 1. (a) Diagenetic sequence of the Callovian-Oxfordian Clay; (b) Chemistry of diagenetic carbonates reported in a Ca-Fe-Mg ternary diagram with details of the different calcite generations (according to [2]).

Observations indicate that early micrite, with minor euhedral calcite and dolomite, were formed at the same time as pyrite was formed by bacterial reduction of dissolved marine sulphate (BSR) at the sediment/water interface. These minerals are characterized by low Fe/(Fe+Mg) ratios (noted XFe) (<0.4 for calcite and almost pure dolomite) due to iron consumption by pyrite formation. At the end of the BSR activity, pore water chemistry changes as a result of the vanishing iron consumption by pyrite formation.
Available iron in pore waters is incorporated into late carbonates and glauconite. Among late calcites, the rims of euhedral calcite grains, microsparite \((\text{Ca}_{0.94-0.99}\text{Fe}_{0.01-0.04}\text{Mg}_{0.02-0.03}\text{CO}_3)\) and most of the calcite filling the residual porosity have \(X_Fe\) of 0.6-0.7. Late dolomite, represented by rims of euhedral dolomite grains \((\text{Ca}_{1.08}\text{Fe}_{0.14}\text{Mg}_{0.76}\text{(CO}_3)_2)\), exhibits \(X_{Fe}\) up to 0.15 and the siderite contains significant contents of Ca and Mg \((\text{Ca}_{0.1-0.3}\text{Fe}_{0.5-0.7}\text{Mg}_{0.2-0.4}\text{CO}_3)\). Carbon and oxygen isotopic data indicate that dolomite and siderite were formed in a temperature range corresponding to the maximal burial attained by the sediments [2]. Most recent calcite that occurs as crack infillings indicates precipitation from meteoric water and has a \(X_{Fe}\) of 0.7-0.8.

Observations of late carbonates in samples taken throughout the formation show that rims of euhedral calcite and dolomite, as well as microsparite, are ubiquitous, but that siderite is only detected in a roughly thirty meter thick clay-rich sequence located approximately in the center of the ~130 m thick COx formation.

3. Chemistry of natural pore waters and carbonate equilibrium

The \(\text{Ca/Mg}\) and \(\text{Ca/Fe}\) activity ratios were computed (using Phreeqc v2.18 with the THERMOCHIMIE database, see [1]) based on solute concentration measured on four well-preserved pore waters obtained from the in-situ experiment in the Bure URL [4]. These values were compared with \(\text{Ca/Mg}\) and \(\text{Ca/Fe}\) activity ratios calculated for the calcite/dolomite and the calcite/siderite equilibrium from dissolution reactions and the corresponding log \(K\) values for the three carbonates [(1), (2) and (3)].

\[
\begin{align*}
\text{CaCO}_3 &= \text{Ca}^{2+} + \text{CO}_3^{2-} , \text{K}_{\text{calcite}} \quad (1) \\
\text{CaMg (CO}_3)_2 &= \text{Ca}^{2+} + \text{Mg}^{2+} + 2 \text{CO}_3^{2-} , \text{K}_{\text{dolomite}} \quad (2) \\
\text{FeCO}_3 &= \text{Fe}^{2+} + \text{CO}_3^{2-} , \text{K}_{\text{siderite}} \quad (3)
\end{align*}
\]

At calcite/dolomite equilibrium, the \(\text{Ca/Mg}\) activity ratio is given by the log \(K\) of the reaction (4), which can be deduced from the log \(K\)'s of the dissolution reactions of pure calcite and dolomite, \(K_{\text{calcite}}\) and \(K_{\text{dolomite}}\), (5). Its value is estimated at 0.070.

\[
\begin{align*}
2 \text{CaCO}_3 + \text{Mg}^{2+} &= \text{CaMg (CO}_3)_2 + \text{Ca}^{2+} \quad (4) \\
\log \left( \frac{a_{\text{Ca}^{2+}}}{a_{\text{Mg}^{2+}}} \right) &= 2 \log K_{\text{calcite}} - \log K_{\text{dolomite}} \quad (5) \\
\log \left( \frac{a_{\text{Ca}^{2+}}}{a_{\text{Fe}^{2+}}} \right) &= \log K_{\text{calcite}} - \log K_{\text{siderite}} \quad (6)
\end{align*}
\]

As shown in Fig. 2, most of \(\text{Ca/Mg}\) activity ratio values calculated are close to the calcite/dolomite equilibrium (dotted line).

Similarly, at calcite/siderite equilibrium, the \(\text{Ca/Fe}\) activity ratio can be deduced from the log \(K\)'s of calcite and siderite dissolution reactions (6). Its value is estimated at 0.92, using the values for pure calcite and siderite, \(\log K_{\text{calcite}}\) and \(\log K_{\text{siderite}}\), given in the database.

Log \(\text{Ca/Fe}\) activity ratios calculated for two Fe concentrations measured on samples taken from in-situ experiments give values of 3.3 and 4.3. These values are significantly different from the 0.92 value.
expected from calcite/siderite equilibrium. However, the Fe(II) concentration values measured in borehole water samples are highly uncertain (> factor of 10) due to analytical difficulties.

4. Discussion

The model of COx pore water chemistry as proposed by [1] considers that present-day pore waters are at equilibrium with several pure carbonates: calcite (for Ca), dolomite (for Mg) and siderite (for Fe) in a nearly closed system. According to the petrological study, carbonates in contact (and probably at equilibrium) with present-day pore waters at the scale of the COx Clay Formation are essentially represented by the surfaces of micrite grains, the rims of euhedral calcite and dolomite grains, and by microsparite. The Ca/Mg activity ratios calculated in pore waters are almost identical to the activity ratio calculated for pure calcite/pure dolomite equilibrium. The combined data confirm that calcite and dolomite are at equilibrium with present-day pore waters, and that considering pure calcite and pure dolomite in the model is a reasonable assumption. Several points indicate, however, that siderite may not be the controlling mineral phase for Fe(II) at all locations in the formation. These are (i) its presence seems to be limited to the maximum clay zone in the center of the formation and (ii) the Ca/Fe activity ratios calculated based on pore water compositions are inconsistent with that calculated for calcite/siderite equilibrium. A recent study of the magnetic properties of mineral crystals in COx rock samples has shown for the first time the presence of nano-goethite [5]. This is consistent with the model proposed by [1], in which a super-saturation of oxy-hydroxides is calculated. Nano-goethite, if present at formation scale, could be an iron-phase at equilibrium with pore waters which can be proposed to control iron in the model instead of siderite. In that case, the Fe system is fully constrained by the equilibrium with pyrite and nano-goethite, giving access to the total Fe concentration as well as the Fe(II)/Fe(III) ratio. However measurements of magnetic properties were performed on samples, which had undergone oxidation. Further investigations of magnetic measurements are being carried out on well-preserved COx samples (N2-drilling, conservation under liquid N2 and sample preparation in N2 glove-box) in order to validate preliminary data and determine the distribution of nano-goethite in COx formation.

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