

Supplementary Material

Mechanism of surface reactions and dissolution of fluorite surface in an aqueous electrolyte solution

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1) Calibration of ion-selective electrodes

a) Calibration procedure

The ion-selective electrodes (ISE) were used for measuring the electromotivity (difference in electrode potential) between ISE and reference electrode as a function of F^- or Ca^{2+} concentration. The pH measurements were performed by a combined microelectrode (6.0234.100, Metrohm) with $Ag|AgCl|3 \text{ mol dm}^{-3} \text{ KCl}$ as a reference electrode. Prior to each measurement, the combined electrode was calibrated at 25 °C using five standard buffer solutions (Fluka) with pH values 3, 4, 5, 6 and 7. During calibration of the ISE system was thermostated at 25 °C and kept under argon atmosphere. Argon 5.0 (Messer) from a tank was used. All calibration experiments were done in a KCl (Sigma-Aldrich) supporting electrolyte solutions of relatively high concentration (1 or 5 mmol dm^{-3}) to have a constant ionic strength. Prior to every kinetic measurement, an ISE was calibrated in the same experimental condition as measurement done by titration with prepared standard solutions. During calibrations, a titrand solution was stirred with a magnetic stirrer (728, Metrohm) and pH of a titrand solution was regulated by 0.1 mol dm^{-3} HCl (Riedel-de Haën) and 0.1 mol dm^{-3} NaOH (Riedel-de Haën) solutions. The entire measuring system was placed in a Faraday cage so that external electrical interferences were avoided. ISE and combined pH electrode were connected to a separate pH meter (826 and 913, Metrohm) and measured electromotivities signals were collected as follows. After each addition of standard solution, the electromotivity signal was waited to get stabilized ($dE/dt < 0.05 \text{ mV/min}$). After the stabilization of the reading, the procedure was repeated. The equilibration time for each portion of the standard solution usually lasted up to 5 min.

b) Fluoride ion-selective electrode

Fluoride ion-selective electrode (F-ISE) of model Orion 9409BN was purchased from Thermo Scientific. According to the user guide (*Thermo Scientific Orion Fluoride Ion Selective Electrode* 2011) the membrane of the F-ISE was conditioned in a 0.01 mol dm^{-3} NaF solution at least two days before each calibration. A three stock F^- solutions of concentration 0.001, 0.01 and 0.1 mol dm^{-3} were prepared from reagent grade sodium fluoride (Sigma-Aldrich) which has been dried for 2 h at 130 °C. These stock solutions were used as a standard F^- solution for the calibration of F-ISE. The calibration of an F-

ISE was performed by titration with a standard F^- solutions as described earlier. An example of a F-ISE calibration curve is shown in Fig. S4. The performance of F-ISE was excellent as can be seen from almost ideal Nernst slope ($S = -59.2$ mV).

c) Calcium ion-selective electrode

The membrane of the calcium ion-selective electrode (Ca-ISE) was prepared according to recommended membrane composition (*Calcium* 2013) from calcium ionophore I (ETH 1001), bis(1-butylpentyl)decan-1,10-diyl diglutarate, potassium tetrakis(4-chlorophenyl)borate and poly(vinyl chloride) of high molecular weight. All mentioned chemicals were purchased from Sigma-Aldrich. After drying the prepared membrane was embedded in a homemade plastic body of Ca-ISE previously filled with the inner filling solution (0.001 mol dm^{-3} $CaCl_2$) as recommended (*Calcium* 2013). At least three days before the calibrations and kinetic measurements Ca-ISE was conditioned in a 0.001 mol dm^{-3} $CaCl_2$ solution. A two stock Ca^{2+} solutions of concentration 0.01 and 0.1 mol dm^{-3} were prepared from reagent grade calcium carbonate (Sigma-Aldrich) which has been dried for 2 h at 130 °C and dissolved by potentiometric titration with 0.1 mol dm^{-3} HCl (Riedel-de Haën). These stock solutions were degassed and used as a standard Ca^{2+} solution for the calibration of Ca-ISE. The calibration of Ca-ISE was performed by titration with a standard Ca^{2+} solutions as described in a calibration procedure section. An example of a Ca-ISE calibration curve is shown in Fig. S5. Although the slope of the calibration curve ($S = 25.7$ mV) is lower than the theoretically expected one ($S_t = 29.6$ mV), literature values ($S_i = 27.8$ mV) are comparable to those calculated here (Anker et al. 1981; Bedlechowicz-Śliwakowska et al. 2006). These result prompted the use of Ca-ISE for kinetic measurements.

2) Figures

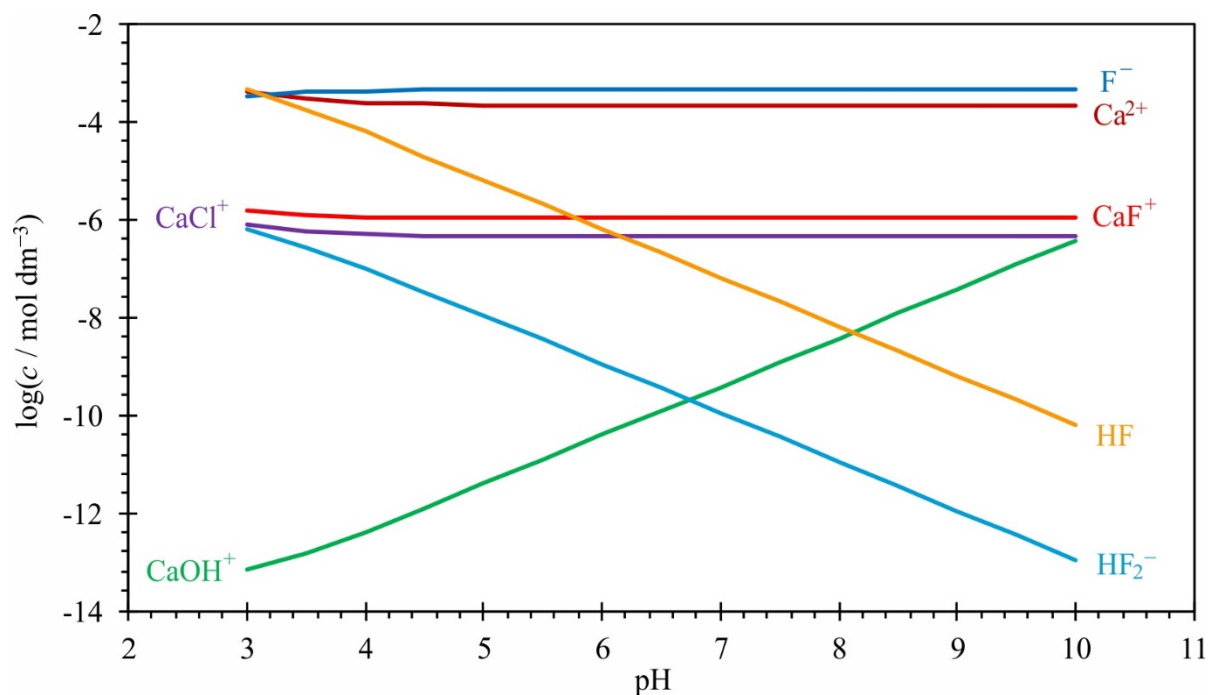


Fig. S1. The distribution of the aqueous species as a function of pH for the CaF_2/KCl aqueous solution (1 mmol dm^{-3}) system calculated by Visual MINTEQ (Gustafsson 2016) at 25°C .

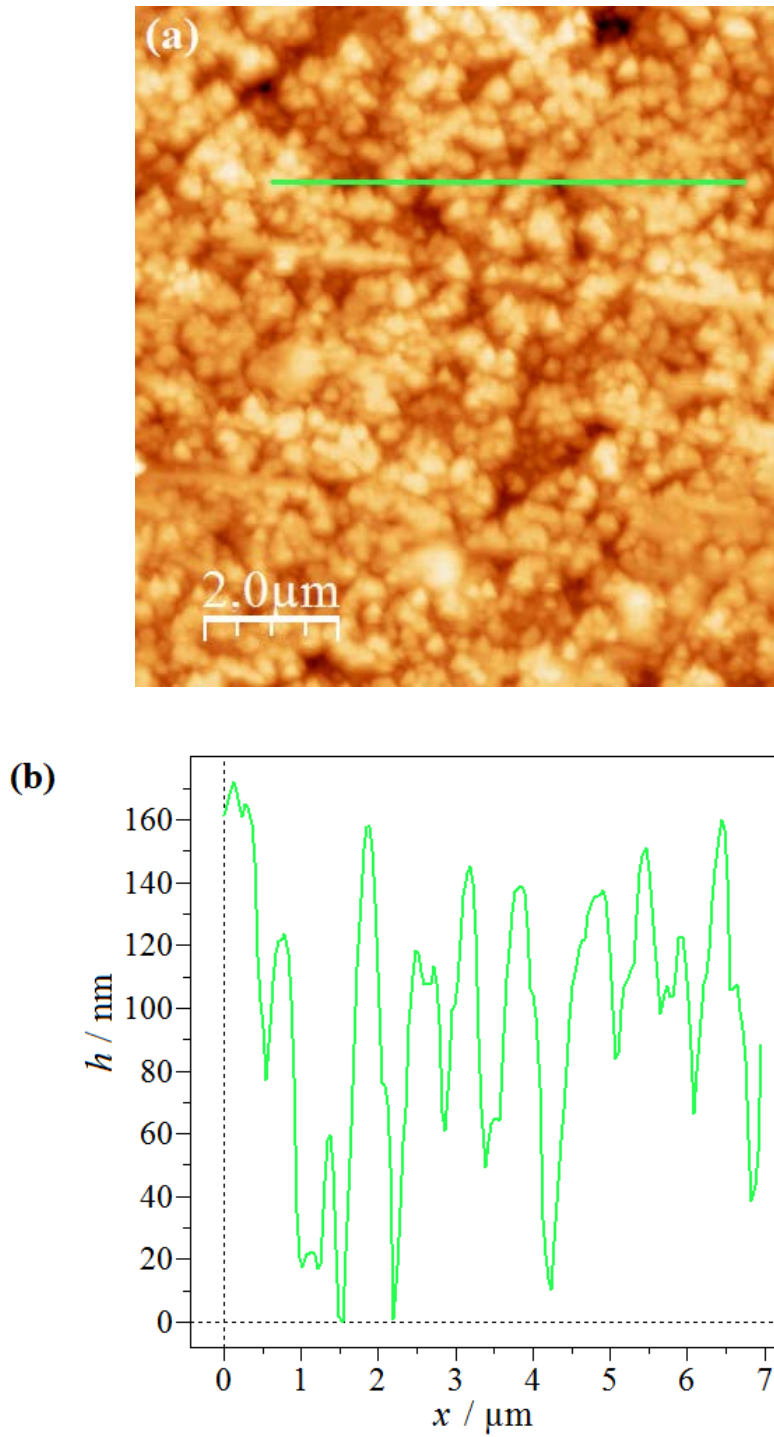


Fig. S2. (a) $10 \mu\text{m} \times 10 \mu\text{m}$ AFM image of a fluorite (111) crystal surface after exposure to aqueous electrolyte solution and dissolution process for about 96 h. (b) The height profile along the line indicated in (a). AFM images were processed by using the WSxM program (Horcas et al. 2007).

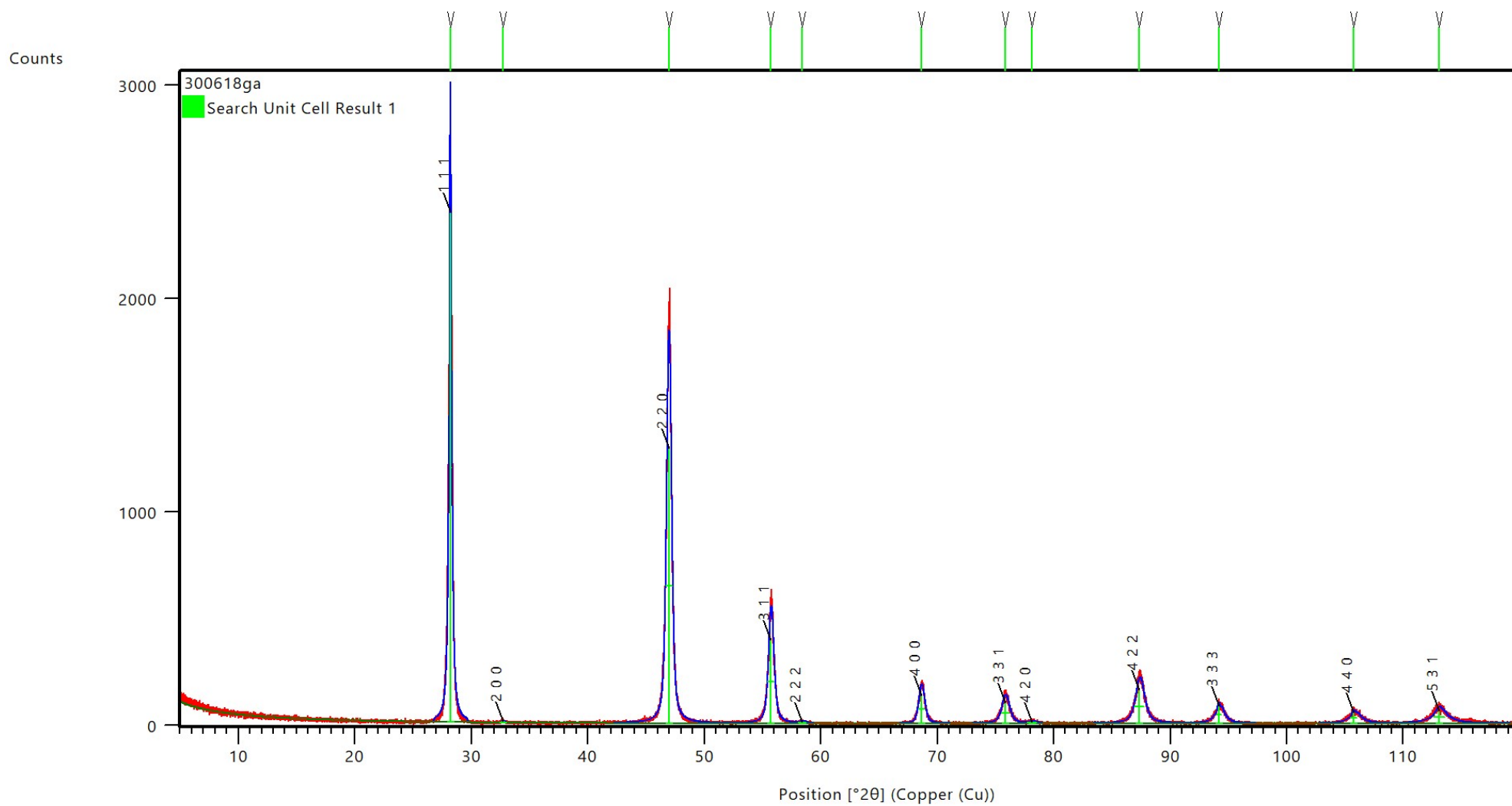


Fig. S3. X-ray powder diffraction pattern of the prepared fluorite particles.

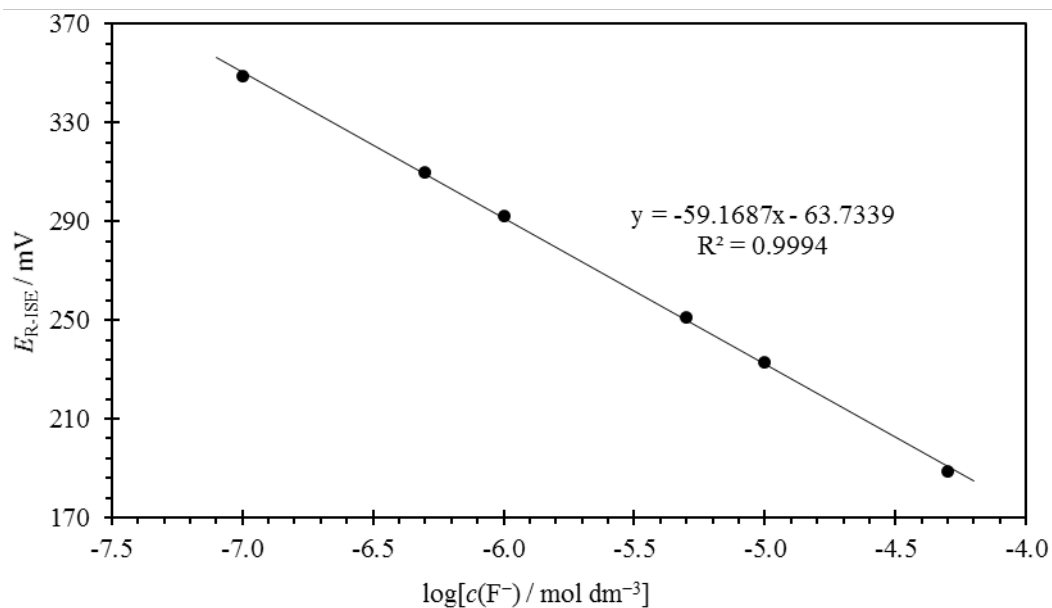


Fig. S4. Calibration curve of F-ISE. The calibration was carried out in a KCl solution (1 mmol dm^{-3}) under an argon atmosphere at $\text{pH} = 4.0 \pm 0.1$ and 25°C . During calibration reaction mixture was stirred with a magnetic stirrer at about 600 rpm.

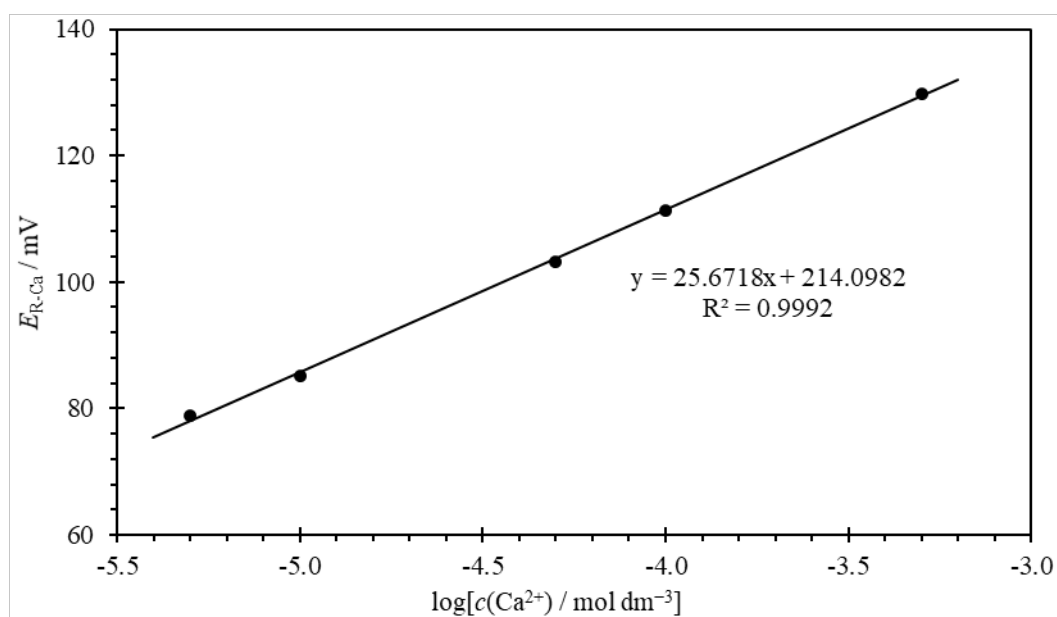


Fig. S5. Calibration curve of Ca-ISE. The calibration was carried out in a KCl solution (5 mmol dm^{-3}) under an argon atmosphere at $\text{pH} = 5.0 \pm 0.1$ and 25°C . During calibration reaction mixture was stirred with a magnetic stirrer at about 600 rpm.

3) References

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