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Probabilistic modeling of field-scale CO_2 generation by carbonate–clay reactions in sedimentary basins

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This Supplementary Material lists in Table 1 the mean values (μ_A and μ_D for $\widetilde{A}$ and $\widetilde{D}$, respectively) and the entries of the covariance matrix Ψ characterizing the bivariate Gaussian distribution of $\widetilde{A}$ and $\widetilde{D}$; in Table 2 the deterministic values of B, C and E parameters taken from Blanc et al. (2012) and appearing in Eq. (1) of the manuscript.

The probability distribution functions associated with the bivariate Gaussian distribution of $\widetilde{A}$ and $\widetilde{D}$ are estimated from raw data presented by Blanc et al. (2013) relying the procedure detailed in Ceriotti et al. (2017) and here briefly recalled using kaolinite as showcase mineral phase:

1. Laboratory scale mineral solubility data of kaolinite are taken from literature (Blanc et al., 2013) where kaolinite solubility is observed and quantified at various temperatures between 25 and 300 ° C.

2. Eq. (1) is fitted against solubility data upon estimating the parameters A and D through a standard least square criterion while B, C, E are set to the corresponding values reported in Thermoddem (Blanc et al., 2012, ; see Table 2). This procedure yields best estimates of μ_A and μ_D for $\widetilde{A}$ and $\widetilde{D}$ and their related uncertainty used to define the entries of the covariance matrix Ψ.

The same procedure is employed for characterizing calcite solubility as a function of temperature, by relying on experimental data reported in Plummer and Busenberg (1982). Experimental studies reporting values of solubility of mineral and gas phases as a function of temperature are scarce. In particular for clay minerals (Blanc et al., 2015) direct references to data are not included in the available databases, which prevents direct characterization of uncertainty. Therefore, we assume that the values of μ_A and μ_D coincide with the values of parameters A and D reported in the Thermoddem database (Blanc et al., 2012). As for what concerns the covariance matrices, we assume that affine minerals are associated with similar uncertainty levels. Based on this assumption we define the entries of covariance matix of dolomite equal to those of calcite, being dolomite and calcite both carbonates minerals. Similarly, covariance matrices of all clay minerals (i.e., clinichlore,microcline, beidellite, illite, albite and analcime) are considered identical and fixed according to kaolinite solubility data of Blanc et al. (2013). Additionally, we assume that solubility of quartz and the water transition phase equilibrium are characterized by negligible uncertainty while the uncertainty associated with solubility of $CO_{2,(g)}$ is assumed to be highest available among those estimated from experimental data (i.e., the related covariance matrix is assumed equal to the one obtained from kaolinite solubility data).

Phase	μ_A	μ_D	$\psi(1,1)$	$\psi(2,2)$	$\psi(1,2) = \psi(2,1)$
Dolomite	-1781.4510	647.1432	0.0104	0.0017	-0.0042
Kaolinite	-982.6440	353.0673	13.1892	1.9185	-5.0267
Quartz	-19.9877	6.8807	0	0	0
CO_2	-593.1318	212.7890	13.1892	1.9185	-5.0267
H_2O	-23.2140	5.9253	0	0	0
Clinochlore	-2858.9199	1029.1247	13.1892	1.9185	-5.0267
Calcite	-851.1478	310.0792	0.0104	0.0017	-0.0042
Microcline	-639.6228	231.0754	13.1892	1.9185	-5.0267
Beidellite	-1235.8761	441.9503	13.1892	1.9185	-5.0267
Illite	-1339.8366	480.0898	13.1892	1.9185	-5.0267
Albite	-689.9685	249.3863	13.1892	1.9185	-5.0267
Analcime	-701.7714	252.2284	13.1892	1.9185	-5.0267

Table S 1: Characterization of means (μ_A and μ_D) and the entries of the covariance matrix (ψ) of the bivariate Gaussian random variables $\widetilde{A}$ and $\widetilde{D}$ for all phases included in CCR1, CCR2 and CCR3: calcite, kaolinite, dolomite, CO_2, H_2O, clinochlore, microcline, beidellite, illite, albite, analcime.

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Phase	B	C	E
Dolomite	-2.8852827$\times 10^{-1}$	9.9264201$\times 10^{4}$	-5.5534198$\times 10^{6}$
Kaolinite	-1.6227654$\times 10^{-1}$	5.7278099$\times 10^{4}$	-2.5386392$\times 10^{6}$
Quartz	-2.1688586$\times 10^{-3}$	5.5357231$\times 10^{2}$	-8.4503401$\times 10^{4}$
CO_2	-9.6074033E$\times 10^{-2}$	3.2546625$\times 10^{4}$	-1.9324505$\times 10^{6}$
H_2O	-4.7007808$\times 10^{-4}$	3.0569427$\times 10^{3}$	-4.880326$\times 10^{3}$
Clinochlore	-4.4322807$\times 10^{-1}$	1.7663305$\times 10^{5}$	-7.6602963$\times 10^{6}$
Calcite	-1.3947146$\times 10^{-1}$	4.6881027$\times 10^{4}$	-2.6591521$\times 10^{6}$
Microcline	-1.0356825$\times 10^{-1}$	3.522897$\times 10^{4}$	-1.723989$\times 10^{6}$
Beidellite	-1.9667428$\times 10^{-1}$	7.2285809$\times 10^{4}$	-3.392105$\times 10^{6}$
Illite	-2.127979$\times 10^{-1}$	7.9520722$\times 10^{4}$	-3.7078528$\times 10^{6}$
Albite	-1.1425341$\times 10^{-1}$	3.8942781$\times 10^{4}$	-1.8606376$\times 10^{6}$
Analcime	-1.0854141$\times 10^{-1}$	4.1184756$\times 10^{4}$	-1.909524$\times 10^{6}$

Table S 2: Deterministic values of B, C and E parameters for all phases included in CCR1, CCR2 and CCR3: calcite, kaolinite, dolomite, CO_2, H_2O, clinochlore, microcline, beidellite, illite, albite, analcime. Data are reported from Blanc et al. (2012).

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