Supplement of

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 (\( \mu_A \) and \( \mu_D \) for \( \tilde{A} \) and \( \tilde{D} \), respectively) and the entries of the covariance matrix \( \Psi \) characterizing the bivariate Gaussian distribution of \( \tilde{A} \) and \( \tilde{D} \); 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 \( \tilde{A} \) and \( \tilde{D} \) 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 \( \mu_A \) and \( \mu_D \) for \( \tilde{A} \) and \( \tilde{D} \) and their related uncertainty used to define the entries of the covariance matrix \( \Psi \).

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 \( \mu_A \) and \( \mu_D \) 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 matrix 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      | $\mu_A$  | $\mu_D$  | $\psi(1,1)$ | $\psi(2,2)$ | $\psi(1,2) = \psi(2,1)$ |
|------------|----------|----------|-------------|-------------|------------------------|
| 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$_2$O     | -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 ($\mu_A$ and $\mu_D$) and the entries of the covariance matrix ($\psi$) of the bivariate Gaussian random variables $\tilde{A}$ and $\tilde{D}$ for all phases included in CCR1, CCR2 and CCR3: calcite, kaolinite, dolomite, CO$_2$, H$_2$O, clinochlore, microcline, beidellite, illite, albite, analcime.

References

Blanc, P., Lassin, A., Piantone, P., Azaroual, M., Jacquemet, N., Fabbri, A., and Gaucher, E. C. (2012). Thermoddem: A geochemical database focused on low temperature water/rock interactions and waste materials. *Applied Geochemistry*, 27(10):2107–2116.

Blanc, P., Vieillard, P., Gailhanou, H., and Gaboreau, S. (2013). Thermodynamics of clay minerals. In *Developments in clay science*, volume 5, pages 173–210. Elsevier.

Blanc, P., Vieillard, P., Gailhanou, H., Gaboreau, S., Gaucher, E., Fialips, C. I., Made, B., and Giffaut, E. (2015). A generalized model for predicting the thermodynamic properties of clay minerals. *American journal of science*, 315(8):734–780.

Ceriotti, G., Porta, G., Geloni, C., Dalla Rosa, M., and Guadagnini, A. (2017). Quantification
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$_2$O, clinochlore, microcline, beidellite, illite, albite, analcime. Data are reported from Blanc et al. (2012).

| Phase      | $B$            | $C$            | $E$            |
|------------|----------------|----------------|----------------|
| Dolomite   | -2.8852827 × 10$^{-1}$ | 9.9264201 × 10$^4$ | -5.5534198 × 10$^6$ |
| Kaolinite  | -1.6227654 × 10$^{-1}$ | 5.7278099 × 10$^4$ | -2.5386392 × 10$^6$ |
| Quartz     | -2.1688586 × 10$^{-3}$ | 5.5357231 × 10$^2$ | -8.4503401 × 10$^4$ |
| CO$_2$     | -9.6074033E × 10$^{-2}$ | 3.2546625 × 10$^4$ | -1.9324505 × 10$^6$ |
| H$_2$O     | -4.7007808 × 10$^{-4}$ | 3.0569427 × 10$^3$ | -4.880326 × 10$^3$ |
| Clinochlore | -4.4322807 × 10$^{-1}$ | 1.7663305 × 10$^5$ | -7.6602963 × 10$^6$ |
| Calcite    | -1.3947146 × 10$^{-1}$ | 4.6881027 × 10$^4$ | -2.6591521 × 10$^6$ |
| Microcline | -1.0356825 × 10$^{-1}$ | 3.522897 × 10$^4$ | -1.723989 × 10$^6$ |
| Beidellite | -1.9667428 × 10$^{-1}$ | 7.2285809 × 10$^4$ | -3.392105 × 10$^6$ |
| Illite     | -2.127979 × 10$^{-1}$ | 7.9520722 × 10$^4$ | -3.7078528 × 10$^6$ |
| Albite     | -1.1425341 × 10$^{-1}$ | 3.8942781 × 10$^4$ | -1.8606376 × 10$^6$ |
| Analcime   | -1.0854141 × 10$^{-1}$ | 4.1184756 × 10$^4$ | -1.909524 × 10$^6$ |

of CO$_2$ generation in sedimentary basins through carbonate/clays reactions with uncertain thermodynamic parameters. *Geochimica et Cosmochimica Acta*, 213:198–215.

Plummer, L. N. and Busenberg, E. (1982). The solubilities of calcite, aragonite and vaterite in CO$_2$-H$_2$O solutions between 0 and 90°C, and an evaluation of the aqueous model for the system CaCO$_3$-CO$_2$-H$_2$O. *Geochimica et Cosmochimica Acta*, 46(6):1011–1040.