**Supplemental Material**

**Clay minerals modulate early carbonate diagenesis**

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**Materials**

Two bulk sediment powders are created using homogenized, natural sediments collected from Integrated Ocean Drilling Program (IODP) sediment cores. They include the Nankai and Gulf of Mexico sediment powders. The Nankai sediment originates from the Nankai Trough, offshore Japan, and was collected during IODP Expedition 322 at Site C0011 (main text Fig. 1A). This sample is from two lithologic units composed of hemipelagic muds at depths ranging between 580-865 m below sea floor (mbsf; Reece et al., 2013). The Gulf of Mexico sediment was collected from the Ursa region in the Gulf of Mexico during IODP Expedition 308 at Site U1324 (main text Fig. 1B). This sample comes from two distinct lithologic units with the first being composed of hemipelagic muds at depths ranging between 4-32 mbsf and the second being composed of silt and mud overbank deposits at depths ranging between 493-502 mbsf (Flemings et al., 2006). After collection, the samples were individually air-dried, disaggregated into clay- and silt-sized particles, and homogenized into two distinct bulk sediment powders.

**Material Characterization Methods**

*Particle size analysis*

Particle size analysis is carried out for the Nankai and Gulf of Mexico sediments using the hydrometer method as specified by ASTM D7928-17 (ASTM International, 2017). This method utilizes principles from Stoke’s law, namely that larger and denser particles fall out of a sediment suspension faster than smaller and less dense particles. A 1L sediment-water suspension was created in a graduated cylinder by mixing 50g of sediment and 5g of sodium hexametaphosphate (dispersant) with nanopure water. After thoroughly mixing the sediment-water suspension, timed sedimentation begins and the specific gravity of the suspension is measured with a hydrometer at discrete points in elapsed time. Thus, we calculate the sediment mass still in suspension and the particle diameter at that particular time and depth below the suspension surface. Ultimately, results of the hydrometer tests are reported as the percent of sediment in suspension finer than a given particle diameter.

*Mineralogy*

Mineralogy of the Nankai and Gulf of Mexico sediments was determined by X-ray powder diffraction (XRD). The whole rock and clay-size fraction (particles <2μm) XRD analyses were performed with a Bruker D8 Advance X-ray diffractometer using a CuKα source (λ=0.154 nm) operating at 40 kV and 40 mA. The whole rock XRD patterns were recorded from 2-70° 2θ with a dwell time of 3° 2θ per minute. To obtain the clay-size fraction the bulk sample was first pretreated with 1M sodium acetate at a *p*H of 5 in an 80°C water bath and 30% hydrogen peroxide to remove all carbonate minerals and organic matter, respectively. The clay-size fraction was then obtained via centrifugation after deflocculation and Na saturation. Ions in the resultant clay-size fraction suspension were removed by dialysis. Subsequently, the clay-size fraction was treated with Mg and K separately then transferred to their respective glass slides for analysis. Clay fraction XRD patterns were recorded from 2-32° 2θ with a dwell time of 3° 2θ per minute. These XRD patters were recorded in the air-dried state and after the Mg saturated sample was treated with glycerol and after the K saturated sample had been heated to 330°C and 550°C. Semi-quantitative analysis was performed using the reference intensity ratio method for the bulk mineralogy and the mineral intensity factor method for the <2μm fraction.

*Potentiometric titrations*

Potentiometric titrations were performed in order to obtain *p*Ka and total acidity values for the Nankai and Gulf of Mexico sediments. To obtain the clay fraction from each sediment sample, the bulk samples were first pretreated with 1M sodium acetate at a *p*H of 5 in an 80°C water bath and 30% hydrogen peroxide to remove all carbonate minerals and organic matter, respectively. The clay fraction was then obtained for each sample via centrifugation after deflocculation and Na saturation. Ions in the resultant clay fraction suspension were removed by dialysis.

Automated potentiometric titrations were carried out using a Metrohm Titrando 907. Each titration consisted of 0.25g or 0.5g of sample in 50mL of a 0.56M NaCl background solution, which is used to approximate the ionic strength of marine waters. Because our titrations were performed in this 0.56M NaCl solution, we also performed a blank titration and subtracted it from our clay mineral titrations. Prior to each titration the solution *p*H was adjusted to 3.5 with 2M HCl and during each titration the *p*H was adjusted up, down, and back up again in the range of 3.5-11 using 0.1 M NaOH (for the up titrations) and 0.1 M HCl (for the down titrations). In each titration, titrant was only added after the *p*H electrode reached a stability of 0.1mV/s. Each titration solution was bubbled with N2 for 30 minutes prior to, and throughout, each titration and the containers were sealed with parafilm to prevent CO2 contamination. We performed titrations of each sample at two sediment concentrations to investigate whether or not the *p*Ka and total acidity values change with sediment concentration. The titrations consisting of 0.25g of sediment were performed in duplicate, while the titrations consisting of 0.5g of sediment were performed once.

The *p*Ka values for the Nankai and Gulf of Mexico sediments were obtained from the experimental data and from a simple surface complexation model. We used Gran Plots to obtain *p*Ka and clay acidity values from the experimental data. We then calculated *p*Ka values using a surface complexation model (Stumm, 1992), which is detailed in Davranche et al. (2003). This method calculates the surface charge of a solid for each point in a titration as a function of *p*H. Then the surface charge and the total concentration of surface species (obtained from the equivalence points in the Gran Plots) can be used to calculate an acid dissociation constant (Ka).

**Material Characterization Results**

*Particle size analysis*

Hydrometer results for the Nankai and Gulf of Mexico sediments are reported in Table S1. The clay-size fractions (<2μm) for the Nankai and Gulf of Mexico sediments are 56% and 59%, respectively.

Table S1. Hydrometer results showing the particle size distribution for the Nankai and Gulf of Mexico sediments expressed as wt.%.

|  |  |  |  |
| --- | --- | --- | --- |
| Sample | % Sand (63-2000μm) | % Silt (2-63μm) | % Clay (<2μm) |
| Nankai | 0 | 44 | 56 |
| Gulf of Mexico | 0 | 41 | 59 |

*Mineralogy*

The mineralogies of the bulk and clay-size (<2μm fraction) fractions, determined by XRD analyses, are presented in Tables S2 and S3, respectively. Most notably, the Nankai sediment contains more smectite than illite in the <2μm fraction, while the Gulf of Mexico sediment contains more illite than smectite in the <2μm fraction (Table S3). However, both sediments contain a mixture of smectite, illite, and kaolinite (Table S3).

Table S2. Bulk mineralogy of the Nankai and Gulf of Mexico sediments expressed as wt.%.

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Sample | Quartz | Feldspar | Calcite | Dolomite | Pyrite | Smectite | Illite | Kaolinite | Chlorite |
| Nankai | 33 | 16 | 2 | - | 1 | 22 | 14 | 9 | 3 |
| Gulf of Mexico | 38 | 7 | 6 | 15 | - | 10 | 16 | 6 | 2 |

Table S3. Mineralogy of the clay-size (<2μm) fraction shown as relative wt.% (P = present but not quantified in the <2μm fraction).

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Sample | Smectite | Illite | Kaolinite | Chlorite |
| Nankai | 48 | 31 | 21 | P |
| Gulf of Mexico | 32 | 49 | 19 | P |

*Potentiometric titrations*

The experimental *p*Ka and total acidity values for the Nankai and Gulf of Mexico sediments were obtained from the slopes and x-intercepts, respectively, of Gran Plots (Fig. S1). The *p*Ka values for both sediments from the 0.25g, 0.25g duplicate, and 0.5g titration runs and from the up, down, and second up titrations in each of those runs are presented in Table S4. The total clay acidity values (in mmol g-1) from the first up titrations in the 0.25g, 0.25g duplicate, and 0.5g titration runs are also presented in Table S4. The Gran Plots in Figure S1 show that the slopes between the 0.25g and 0.5g titrations are the same and that the equivalence points (x-intercept) for the 0.5g titrations are twice that of the 0.25g titrations meaning that the clay acidity values in mmol g-1 are the same. For a given *p*Ka value, we report the average *p*Ka from the up, down, and second up titrations for the titrations performed (0.25g, 0.25g duplicate, and 0.5g titrations) along with the range of *p*Ka values (expressed as ± from the average). The Nankai sediment yielded clay mineral *p*Ka values of *p*Ka1=4.28±0.06, *p*Ka2=6.64±0.13, *p*Ka3=8.71±0.05 with respective clay acidity values of 0.18 mmol g-1, 0.05 mmol g-1, and 0.07 mmol g-1. The Gulf of Mexico sediment yielded clay mineral *p*Ka values of *p*Ka1=4.79±0.06, *p*Ka2=6.92±0.08, *p*Ka3=8.96±0.06 with respective clay acidity values of 0.04 mmol g-1, 0.03 mmol g-1, and 0.05 mmol g-1. The Nankai sample had a *p*Ka value with a larger range (*p*Ka2 for Nankai). This is because two of the second up titrations yielded values that were outside of an otherwise smaller range (Table S4). We performed a regression analysis in an attempt to determine if our Gran Plot slopes (and consequently *p*Ka values) were statistically distinguishable between the 0.25g, 0.25g duplicate, and 0.5g titration runs and between the first and second up titrations in each of those runs (for example, for the first *p*Ka value from the Nankai sample 6 slopes were used). The regression analysis used dummy terms to test for differences in intercepts and interaction terms to test for differences in slopes. In each regression a few p-values were below 0.05, indicating that not all of the slopes were statistically the same. This is most likely because of slight variations between the 0.25g, 0.25g duplicate, and 0.5g titration runs and between the first and second up titrations in each of those runs. It could also indicate a small amount of clay alteration during the course of an up-down-up titration experiment. However, this alteration was minimal as the *p*Ka values calculated from Gran Plot slopes that had low p-values were still within ±0.08 log units of average values, with the exception of one *p*Ka value (*p*Ka2 from Nankai) that was farther from the averages (±0.13). While the regression analysis suggests that the slopes (*p*Ka values) are statistically different, a *p*Ka difference of 0.08 log units, or even 0.15 log units, does not produce significantly different model results, and it is unlikely to drive geologically significant differences in natural sediments.

The modeled *p*Ka values were obtained from the first up titrations in each of the 0.25g, 0.25g duplicate, and 0.5g titration runs and are reported as averages with their respective ranges (expressed as ± from the average). The surface complexation model yielded clay mineral *p*Ka values of *p*Ka1=4.26±0.05, *p*Ka2=6.65±0.04, *p*Ka3=8.75±0.05 for the Nankai sediment and *p*Ka values of *p*Ka1=4.86±0.02, *p*Ka2=6.93±0.03, *p*Ka3=8.92±0.03 for the Gulf of Mexico sediment (Table S4). These are the *p*Ka values reported in the main text. The *p*Ka values obtained from Gran Plots are all within ±0.07 log units of the *p*Ka values from the surface complexation model (Table S4).

As the total clay acidity values displayed in Table S4 represent a sediment with a porosity of ~99.8% (0.25g in 50mL solution), we obtain model input values for total clay acidity by upscaling the values in Table S4 to represent freshly deposited muddy sediments with a porosity of ~70% (e.g., Boggs, 2009; Tucker, 2001). This is done by using the following equation: upscaled clay acidity value (mM) = clay acidity (mmol g-1) \* ((1-porosity) / porosity) \* (1000 (cm3) / 1 (L)) \* clay density (g cm-3) \* the fraction of the sediment composed of clay minerals. We use the lowest reported clay density value from Osipov (2012) for a hydrated clay mineral (1.4 g cm-3), which places our upscaled clay acidity values at a minimum.

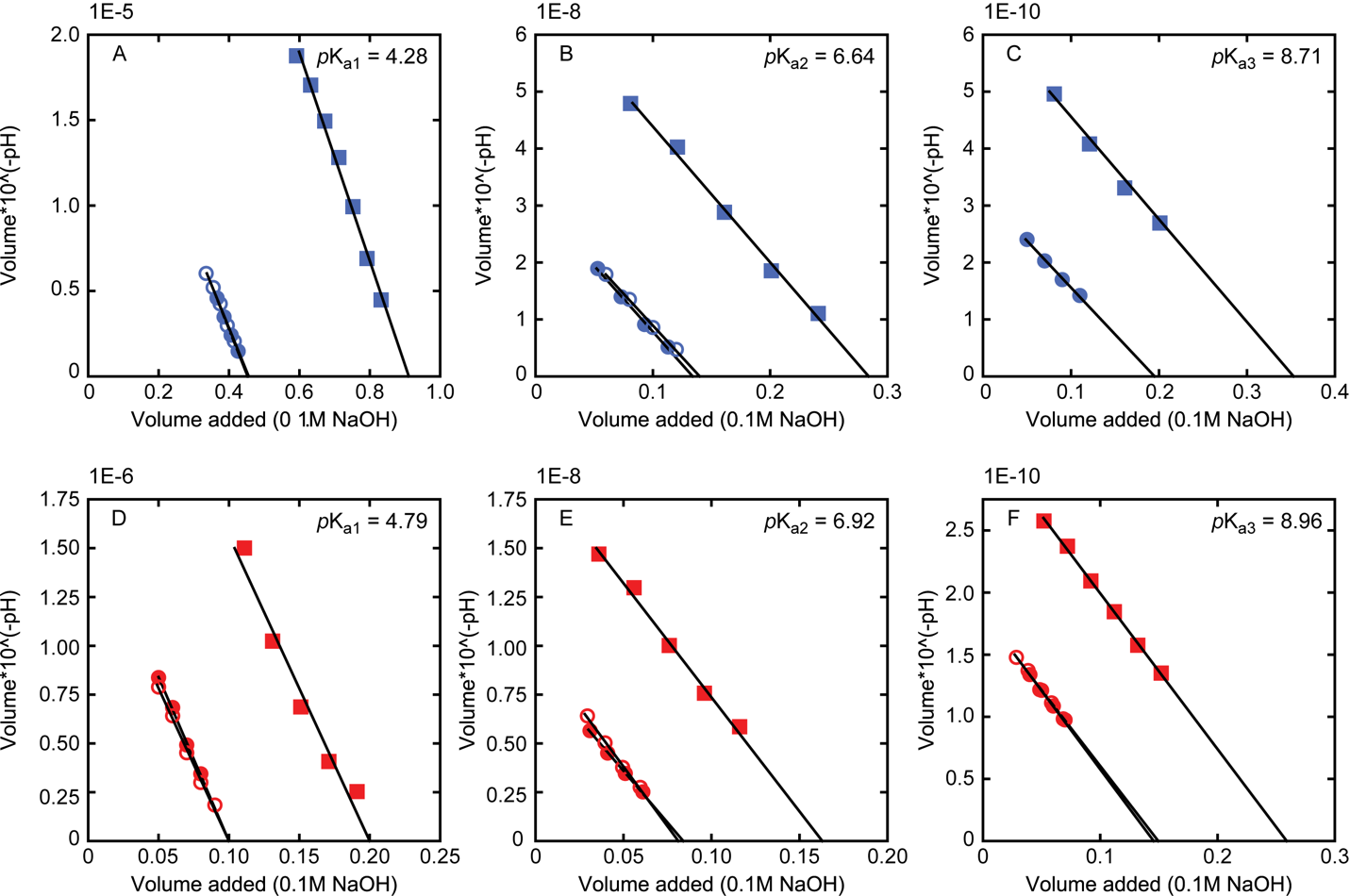


Figure S1. Gran plots showing titration data for the Nankai (A-C) and Gulf of Mexico (D-F) sediments. Clay mineral *p*Ka values are listed in the top right corner of each plot and were obtained from the slopes of the data, while the total clay acidity values were obtained from the x-intercept. Solid circles = 0.25g titrations, hollow circles = 0.25g duplicate titrations, solid squares = 0.5g titrations.

Table S4. Experimental and modeled titration results for the Nankai and Gulf of Mexico sediments. The experimental *p*Ka values for the 1st alkalimetric, acidimetric, and 2nd alkalimetric titrations and total clay acidity values for the 1st alkalimetric titrations (obtained from the Gran Plots in Fig. S2) are shown. The modeled *p*Ka values for the 1st alkalimetric titrations are also shown (obtained from a simple surface complexation model). TCA= total clay acidity, Up = alkalimetric titration, Down = acidimetric titration, dup = duplicate, GP = Gran Plot, SCM = surface complexation model, X = poor trend on Gran Plot near end of titration (i.e., high *p*H values on alkalimetric titration and low *p*H values on acidimetric titration).

|  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Sample | Test | *p*Ka1  GP | *p*Ka1  SCM | TCA (mmol g-1) | *p*Ka2  GP | *p*Ka2  SCM | TCA (mmol g-1) | *p*Ka3  GP | *p*Ka3  SCM | TCA (mmol g-1) |  |  |  |  |  |  |  |  |  |
| Nankai |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
|  | 1st Up 0.25g | 4.28 | 4.29 | 0.18 | 6.63 | 6.68 | 0.054 | 8.66 | 8.79 | 0.078 |  |  |  |  |  |  |  |  |  |
|  | 1st Up 0.25g dup | 4.29 | 4.21 | 0.18 | 6.65 | 6.65 | 0.056 | X | 8.70 | X |  |  |  |  |  |  |  |  |  |
|  | 1st Up  0.5g | 4.22 | 4.29 | 0.18 | 6.62 | 6.61 | 0.054 | 8.68 | 8.76 | 0.071 |  |  |  |  |  |  |  |  |  |
|  | Down 0.25g | 4.29 |  |  | 6.68 |  |  | 8.72 |  |  |  |  |  |  |  |  |  |  |  |
|  | Down 0.25g dup | 4.33 |  |  | 6.70 |  |  | 8.66 |  |  |  |  |  |  |  |  |  |  |  |
|  | Down  0.5g | 4.34 |  |  | 6.61 |  |  | 8.70 |  |  |  |  |  |  |  |  |  |  |  |
|  | 2nd Up 0.25g | 4.23 |  |  | 6.61 |  |  | 8.70 |  |  |  |  |  |  |  |  |  |  |  |
|  | 2nd Up 0.25g dup | 4.27 |  |  | 6.53 |  |  | 8.76 |  |  |  |  |  |  |  |  |  |  |  |
|  | 2nd Up  0.5g | 4.26 |  |  | 6.51 |  |  | X |  |  |  |  |  |  |  |  |  |  |  |
| Gulf of Mexico |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
|  | 1st Up 0.25g | 4.77 | 4.87 | 0.04 | 6.98 | 6.90 | 0.032 | 8.91 | 8.94 | 0.061 |  |  |  |  |  |  |  |  |  |
|  | 1st Up 0.25g dup | 4.81 | 4.84 | 0.04 | 6.91 | 6.96 | 0.032 | 8.90 | 8.92 | 0.061 |  |  |  |  |  |  |  |  |  |
|  | 1st Up  0.5g | 4.81 | 4.87 | 0.04 | 6.94 | 6.93 | 0.033 | 8.90 | 8.89 | 0.051 |  |  |  |  |  |  |  |  |  |
|  | Down 0.25g | 4.76 |  |  | 6.95 |  |  | 8.99 |  |  |  |  |  |  |  |  |  |  |  |
|  | Down 0.25g dup | 4.77 |  |  | 6.94 |  |  | 8.95 |  |  |  |  |  |  |  |  |  |  |  |
|  | Down  0.5g | X |  |  | 6.99 |  |  | 9.01 |  |  |  |  |  |  |  |  |  |  |  |
|  | 2nd Up 0.25g | 4.80 |  |  | 6.85 |  |  | X |  |  |  |  |  |  |  |  |  |  |  |
|  | 2nd Up 0.25g dup | 4.75 |  |  | 6.86 |  |  | 9.00 |  |  |  |  |  |  |  |  |  |  |  |
|  | 2nd Up  0.5g | 4.85 |  |  | 6.84 |  |  | 9.01 |  |  |  |  |  |  |  |  |  |  |  |

**Biogeochemical Model**

The model assumes a pore fluid composition that is similar to modern seawater and the model uses effective speciation terms appropriate for seawater composition and ionic strength. We checked for the influence of ion pairs and when ion pairs were found to have an insignificant effect on pore fluid *p*H and *SI* they were dropped from our calculations. We also assumed that all clay mineral effective charge sites are available for H+ exchange. Initial conditions are the initial *p*H (*p*H0) and saturation index (*SI0*); model parameters are the acid dissociation constants (*p*Ka) and the total acidity values of the clay minerals (concentration of sites that can be protonated or deprotonated).

*Aerobic respiration*

Aerobic respiration is driven by microorganisms as they utilize oxygen (O2) as an electron acceptor and oxidize organic carbon (Equation S1; e.g., Froelich et al., 1979). We model this reaction by defining the reaction progress (*x*) as the total amount of O2 reduced. Using the stoichiometry from Equation S1, the total carbon (*CT*) in the system is equal to the initial dissolved inorganic carbon (*DIC0*) plus the reaction progress (*x*) (Equation S2).

CH2O + O2 🡪 CO2 + H2O (S1)

*CT* = *DIC0* + *x* = [H2CO3\*] + [HCO3-] + [CO32-] (S2)

To incorporate clay minerals in our model, we account for the deprotonation (forward reaction in Equation S3) and protonation (reverse reaction in Equation S3) reactions of clay minerals (e.g., Avena et al., 2003; Mitchell and Soga, 2005).

(S3)

Charge balance dictates that the net charge of the system does not change as the reaction progresses. The charged species that undergo a change in concentration as the reaction proceeds are summed on the left side of Equation S4, while the charged species that remain constant throughout the reaction are not included.

(S4)

By adding the term [clay:O-] to the charge balance equation we can account for the acid-base properties of clay minerals, and alternatively, by removing this term we are able to model the aerobic respiration reaction alone. We rearrange the charge balance equation and write it in terms of [H+] and constants using equations for speciation (Equations S5-S8) and mass balance (Equations S9 and S10). Subsequently, collecting the term *d*[H+]/*dx* to the left side of the equation yields Equation S11.

(S5)

(S6)

(S7)

(S8)

(S9)

(S10)

(S11)

The change in *p*H with respect to the reaction progress, *x*, can be described by rewriting the relationship *p*H = -log10[H+] as:

. (S12)

Combining Equations S11 and S12 yields:

. (S13)

This equation then describes the evolution of the system and makes it possible to model system *p*H as a function of the amount of oxygen reduced for circumstances with and without clay minerals.

In like manner, we calculate the evolution of carbonate saturation during aerobic respiration. Critical saturation, *Ωc*, is expressed in Equation S14 and the change in *Ωc* with respect to the reaction progress, *x*, assuming that [Ca2+] remains constant (i.e., *d*[Ca2+]/*dx* = 0), is expressed in Equation S15.

(S14)

(S15)

The carbonate saturation index, *SI*, is simply expressed as *SI* = log10Ωc, and the change in *SI* with respect to the reaction progress, *x*, can be written as:

. (S16)

Combining Equations S15 and S16 yields:

, (S17)

where values for [CO32-] and *d*[CO32-]/*dx* are obtained from the *p*H model above (Equations S1-S13). For the case of aerobic respiration, the change in *SI* with respect to the change in the reaction progress can be written as:

. (S18)

These *SI* values can be obtained under circumstances with and without clay minerals present in the system. Thus, for both circumstances we are able to predict *SI* as a function of the amount of oxygen reduced. Equations S19-S22 are used to simplify Equations S11 and S13.

(S19)

(S20)

(S21)

(S22)

*Iron Reduction*

Iron reduction is driven by microorganisms as they utilize Fe3+ as an electron acceptor and oxidize organic carbon (Equation S23; Lovley, 1991). This model is adapted from Zeng and Tice (2014). We model this reaction by defining the reaction progress (*y*) as the total amount of iron reduced or the sum of Fe2+ species produced (Equation S24). Using the stoichiometry from Equation S23, the total carbon (*CT*) in the system is equal to the initial dissolved inorganic carbon (*DIC0*) plus the reaction progress (*y*) divided by 4 (Equation S25).

(S23)

(S24)

(S25)

To incorporate clay minerals in our model, we account for the deprotonation (forward reaction in Equation S3) and protonation (reverse reaction in Equation S3) reactions (e.g., Avena et al., 2003; Mitchell and Soga, 2005). Charge balance dictates that the net charge of the system does not change as the reaction progresses. The charged species that undergo a change in concentration as the reaction proceeds are summed on the left side of Equation S26, while the charged species that remain constant throughout the reaction are not included.

(S26)

By adding the term [clay:O-] to the charge balance equation we can account for the acid-base properties of clay minerals, and alternatively, by removing this term we are able to model the aerobic respiration reaction alone. We rearrange the charge balance equation and write it in terms of [H+] and constants using equations for speciation (Equations S5-S8 and S27) and mass balance (Equations S9 and S10). Subsequently, collecting the term *d*[H+]/*dy* to the left side of the equation yields Equation S28.

(S27)

(S28)

The change in *p*H with respect to the reaction progress, *y*, can be described by rewriting the relationship *p*H = -log10[H+] as:

. (S29)

Combining Equations S28 and S29 yields:

. (S30)

This equation then describes the evolution of the system and makes it possible to model the system *p*H as a function of the amount of iron reduced for circumstances with and without clay minerals.

In like manner, we calculate the evolution of carbonate saturation during iron reduction. Critical saturation, *Ωc*, is expressed in Equation S14 and the change in *Ωc* with respect to the reaction progress, *y*, assuming that [Ca2+] remains constant (i.e., *d*[Ca2+]/*dy* = 0), is expressed in Equation S31.

(S31)

The carbonate saturation index, *SI*, is simply expressed as *SI* = log10Ωc, and the change in *SI* with respect to the reaction progress, *y*, can be written as:

. (S32)

Combining Equations S31 and S32 yields:

, (S33)

where values for [CO32-] and *d*[CO32-]/*dy* are obtained from the *p*H model above (Equations S23-S30). These values can be obtained under circumstances with and without clay minerals present in the system. Thus, for both circumstances we are able to predict *SI* as a function of the amount of iron reduced. Equations S22 and S34-S40 are used to simplify Equations S28 and S30.

(S34)

(S35)

(S36)

(S37)

(S38)

(S39)

(S40)

*Sulfate reduction*

Sulfate reduction is driven by microorganisms as they utilize sulfate as an electron acceptor and oxidize organic carbon (Equation S41; e.g., Canfield et al., 1993; Froelich et al., 1979). We model this reaction by defining the reaction progress (*z*) as the total amount of sulfate reduced or the sum of H2S, HS-, or S2- species produced (Equation S42). Using the stoichiometry from Equation S41, the total carbon (*CT*) in the system is equal to the initial dissolved inorganic carbon (*DIC0*) plus the reaction progress (*z*) multiplied by 2 (Equation S43).

2CH2O + SO42- 🡪 2HCO3- + HS- + H+ (S41)

*z* = [SO42-]0 + [SO42-] = [H2S] + [HS-] + [S2-] (S42)

*CT* = *DIC0* + 2*z* = [H2CO3\*] + [HCO3-] + [CO32-] (S43)

To incorporate clay minerals in our model, we account for the deprotonation (forward reaction in Equation S3) and protonation (reverse reaction in Equation S3) reactions (e.g., Avena et al., 2003; Mitchell and Soga, 2005). Charge balance dictates the net charge of the system does not change as the reaction progresses. The charged species that undergo a change in concentration as the reaction proceeds are summed on the left side of Equation S44, while the charged species that remain constant throughout the reaction are not included.

(S44)

By adding the term [clay:O-] to the charge balance equation we can account for the acid-base properties of clay minerals, and alternatively, by removing this term we are able to model the aerobic respiration reaction alone. We rearrange the charge balance equation and write it in terms of [H+] and constants using equations for speciation (Equations S5-S8 and S45-S46) and mass balance (Equations S9 and S10). Subsequently, collecting the term *d*[H+]/*dz* to the left side of the equation yields Equation S47.

(S45)

(S46)

(S47)

The change in *p*H with respect to the reaction progress, *z*, can be described by rewriting the relationship *p*H = -log10[H+] as:

. (S48)

Combining Equations S47 and S48 yields:

. (S49)

This equation then describes the evolution of the system and makes it possible to model system *p*H as a function of the amount of sulfate reduced for circumstances with and without clay minerals.

In like manner, we calculate the evolution of carbonate saturation during sulfate reduction. Critical saturation, *Ωc*, is expressed in Equation S14 and the change in *Ωc* with respect to the reaction progress, *z*, assuming that [Ca2+] remains constant (i.e., *d*[Ca2+]/*dz* = 0), is expressed in Equation S50.

(S50)

The carbonate saturation index, *SI*, is simply expressed as *SI* = log10Ωc, and the change in *SI* with respect to the reaction progress, *z*, can be written as:

. (S51)

Combining Equations S50 and S51 yields:

, (S52)

where values for [CO32-] and *d*[CO32-]/*dz* are obtained from the *p*H model above (Equations S41-S49). For the case of sulfate reduction, the change in *SI* with respect to the change in the reaction progress, *z*, can be written as:

. (S53)

These values of *SI* can be obtained under circumstances with and without clay minerals present in the system. Thus, for both circumstances we are able to predict *SI* as a function of the amount of sulfate reduced. Equations S19-S22 and S54-S56 are used to simplify Equations S47 and S49.

(S54)

(S55)

(S56)

*Hydrogenotrophic methanogenesis*

Hydrogenotrophic methanogenesis is driven by microorganisms as they utilize bicarbonate (HCO3-) as an electron acceptor and oxidize molecular hydrogen (H2) (Equation S57; e.g., Froelich et al., 1979). We model this reaction by defining the reaction progress (*m*) as the total amount of methane (CH4) produced (Equation S58). Using the stoichiometry from Equation S57, the total carbon (*CT*) in the system is equal to the initial dissolved inorganic carbon (*DIC0*) minus the reaction progress (*m*) (Equation S59).

(S57)

(S58)

*CT* = *DIC0* - *m* = [H2CO3\*] + [HCO3-] + [CO32-] (S59)

To incorporate clay minerals in our model, we account for the deprotonation (forward reaction in Equation S3) and protonation (reverse reaction in Equation S3) reactions of clay minerals (e.g., Avena et al., 2003; Mitchell and Soga, 2005). Charge balance dictates that the net charge of the system does not change as the reaction progresses. The charged species that undergo a change in concentration as the reaction proceeds are summed on the left side of Equation S60, while the charged species that remain constant throughout the reaction are not included.

(S60)

By adding the term [clay:O-] to the charge balance equation we can account for the acid-base properties of clay minerals, and alternatively, by removing this term we are able to model the aerobic respiration reaction alone. We rearrange the charge balance equation and write it in terms of [H+] and constants using equations for speciation (Equations S5-S8) and mass balance (Equations S9 and S10). Subsequently, collecting the term *d*[H+]/*dx* to the left side of the equation yields Equation S61.

(S61)

The change in *p*H with respect to the reaction progress, *x*, can be described by rewriting the relationship *p*H = -log10[H+] as:

. (S62)

Combining Equations S61 and S62 yields:

. (S63)

This equation then describes the evolution of the system and makes it possible to model system *p*H as a function of the amount of CH4 produced for circumstances with and without clay minerals.

In like manner, we calculate the evolution of carbonate saturation during hydrogenotrophic methanogenesis. Critical saturation, *Ωc*, is expressed in Equation S14 and the change in *Ωc* with respect to the reaction progress, *m*, assuming that [Ca2+] remains constant (i.e., *d*[Ca2+]/*dm* = 0), is expressed in Equation S64.

(S64)

The carbonate saturation index, *SI*, is simply expressed as *SI* = log10Ωc, and the change in *SI* with respect to the reaction progress, *m*, can be written as:

. (S65)

Combining Equations S64 and S65 yields:

, (S66)

where values for [CO32-] and *d*[CO32-]/*dm* are obtained from the *p*H model above (Equations S57-S63). For the case of hydrogenotrophic methanogenesis, the change in *SI* with respect to the change in the reaction progress, *m*, can be written as:

. (S67)

These values of *SI* can be obtained under circumstances with and without clay minerals present in the system. Thus, for both circumstances we are able to predict *SI* as a function of the amount of CH4 produced. Equations S19-S22 are used to simplify Equations S61 and S63.

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Figure S2. Effects of initial *p*H and clay *p*Ka on pore fluid evolution. Siltstone (A-D; ~10 wt.% clay minerals) and claystone (E-H; ~70% clay minerals) sediments could buffer pore fluid *p*H at a wide range of initial *p*H (*p*H0) and clay mineral *p*Ka values under aerobic, ferruginous, sulfidic, and methanic conditions. The contour lines represent the greatest Δ *p*H values for a set of particular *p*Ka and *p*H0 values used as initial conditions. The shaded areas represent the typical pore fluid *p*H values found in marine sediments (6.5-9; Ben-Yaakov, 1973) and clay mineral *p*Ka values found in nature (4-10; Duc et al., 2005). Δ *p*H is the difference between the *p*H curves with and without a clay buffer, where positive values (red) indicate increased *p*H and negative values (blue) indicate decreased *p*H.

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