Supporting Information for:

Lipid Peroxidation Induced by Expandable Clay Minerals

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Additional Considerations on the Effect of the Clay Type and Surface Area on TBARS Production.

The effect of the type and surface area of the clay on TBARS production was further evaluated (Table 1S; See also Figures 1S and 2S). To study the effect of structural iron on lipid peroxidation, the production of TBARS by iron-bearing clays (NAu-1 and NAu-2) was normalized to the production of TBARS in the presence of hectorite (SHCa-1). The assumption made here is that TBARS amount produced by SHCa-1 suspensions, $\{TBARS\}_{SHCa-1}$ is significantly lower than TBARS amount produced in NAu-1 or NAu-2 suspensions, $\{TBARS\}_{NAu-1}$ or $\{TBARS\}_{NAu-2}$, where $\{TBARS\}_{SHCa-1} << \{TBARS\}_{NAu-1}$ or $\{TBARS\}_{NAu-2}$. The relative production of TBARS is referred as P_{rel} (Table S1):

$$P_{rel} = \left[\left(\left[TBARS\left(\frac{nmol}{mgprotein} \right) \right] \right)^{NAu-1, NAu-2} / \left[TBARS\left(\frac{nmol}{mgprotein} \right) \right] \right]^{SHCa-1}$$

eq. S1

Secondly, the effect of clay specific surface area (a_s) on the relative production of TBARS production was evaluated by normalizing P_{rel} to clay a_s values reported in the literature (Dogan et al., 2006; Dogan et al., 2007), namely reported a_s values for SHCa-1, NAu-1, and NAu-2 corresponded to 35.6, 52.8, and 10.6 $m^2\ g^{-1}$, respectively, and were estimated using the multi-point BET method. Resulting P_{rel} values are referred to as $P_{rel}{}^{as}$:

$$P_{rel}{}^{a_s} = \left[\left(\left[TBARS\left(\frac{nmol}{mgprotein} \right) \right] / a_s{}^{NAu-1, NAu-2} \right) / \left[TBARS\left(\frac{nmol}{mgprotein} \right) \right] / a_s{}^{SHCa-1} \right]$$

eq. S2

Variations of P_{rel} and $P_{rel}{}^{as}$ values as affected by incubation time(t_i) were evaluated according to

$$\left(P_{rel}\right)_t = \left[\left(\left[TBARS\left(\frac{nmol}{mgprotein}\right)\right]\right)^{NAu-1,NAu-2} \cdot \left[TBARS\left(\frac{nmol}{mgprotein}\right)\right]^{SHCa-1}\right]^{-1} \cdot t(t=t_i)$$

eq. S3

And

$$\left(P_{rel}^{\ a_s}\right)_t = \left[\left(\left[TBARS\left(\frac{nmol}{mgprotein}\right)\right]a_s^{\ NAu-1,NAu-2}\right) \cdot \left[TBARS\left(\frac{nmol}{mgprotein}\right)\right] \cdot a_s^{\ SHCa-1}\right]^{-1} \cdot t(t=t_i)$$

eq. S4

Finally, variations of P_{rel} and P_{rel}^{as} as affected by clay concentration in suspension ($\{cc\}$) were also considered.

$$\left(P_{rel}\right)_{cc} = \left[\left(\left[TBARS\left(\frac{nmol}{mgprotein}\right)\right]\right)^{NAu-1,NAu-2} \cdot \left[TBARS\left(\frac{nmol}{mgprotein}\right)\right]^{SHCa-1}\right]^{-1} \cdot \{cc\}$$

eq. S5

And

$$\left(P_{rel}^{\ a_s}\right)_{cc} = \left[\left(\left[TBARS\left(\frac{nmol}{mgprotein}\right)\right]a_s^{\ NAu-1,NAu-2}\right) \cdot \left[TBARS\left(\frac{nmol}{mgprotein}\right)\right] \cdot a_s^{\ SHCa-1}\right]^{-1} \cdot \{cc\}$$

eq. S6

Magnitude values of $P_{rel\ NAu\text{-}1}$(t) and $P_{rel\ NAu\text{-}2}$(t) were found to be comparable, while $P_{rel}^{as}{}_{NAu\text{-}1}$(t) > $P_{rel}^{as}{}_{NAu\text{-}2}$(t), regardless of incubation time. The effect of incubation time on TBARS production strongly depended on the type of clay (either iron-bearing or not). These results agree with the idea that structural iron help stabilize reaction intermediates formed after H-abstraction of organic compounds by iron-rich smectites clay minerals (Cervini-Silva et al., 2000). Furthermore, a direct comparison between $P_{rel\ NAu\text{-}1}$(cc) and $P_{rel\ NAu\text{-}2}$(cc) show comparable magnitude values. Likewise, $P_{rel}{}^{as}{}_{NAu\text{-}1}$(cc) values were found to surpass $P_{rel}{}^{as}{}_{NAu\text{-}2}$(cc) values, regardless of ({*cc*}). This further substantiates that structural iron plays a major role in promoting lipid peroxidation by clays.

Susceptibility of TBARS production as affected by t and {cc}. A direct comparison between $P_{rel}{}^{as}{}_{NAu\text{-}1}$(t) and $P_{rel}{}^{as}{}_{NAu\text{-}2}$(t), and $P_{rel}{}^{as}{}_{NAu\text{-}1}$(cc) and $P_{rel}{}^{as}{}_{NAu\text{-}2}$(cc) values provide evidence to support that NAu-2 bearing suspensions are more susceptible to changes in *t* and {*cc*}. Differences in reactivity between NAu-1 and NAu-2 are found to be higher with {*cc*}. Noteworthy, $P_{rel}{}^{as}{}_{NAu\text{-}2}$(cc) can change five times as much as $P_{rel}{}^{as}{}_{NAu\text{-}1}$(cc) with {*cc*}. Table 1, bottom lists the structural formulae for SHCa-1, NAu-1, and NAu-2. In particular, the content of structural iron of NAu-2 accounts for *ca*. 4 times that NAu-1, which explains in part the differences in relative TBARS production values by NAu-1 or NAu-2 (Table 1S). At any rate, based on these results it follows that TBARS production ought to vary with clay structural composition, while it becomes evident that the production of TBARS is surface specific.

Finally, calculations listed in Table 1S show P_{rel} values ≤ 1, which serves as an indication that TBARS production resulted higher in SHCa-1 suspensions, in suspensions bearing low or intermediate {cc} values. These observations further substantiate the hypothesis that plausible competing mechanisms contribute to TBARS production by aforementioned soluble compounds. It follows that the solution composition contributes to the TBARS production and deserves further scrutiny.

Table 1S.TBARS Production (nmol/ mg protein) normalized to Clay Surface Area (m² g⁻¹) as function of Incubation Time [$(P_{rel})_t$, $(P_{rel}^{\ as})_t$] and Clay Concentration [$(P_{rel})_{cc}$, $(P_{rel}^{\ a_s})_{cc}$]

	NAu-1		NAu-2	
TBARS production as function of incubation time [$(P_{rel})_t$, $(P_{rel}^{\ as})_t$]				
Time (h)	$(P_{rel})_t$	$(P_{rel}^{\ as})_t$	$(P_{rel})_t$	$(P_{rel}^{\ as})_t$
1	1.2	1	1.4	4
2	2.2	1.4	3.1	9.4
3	3.4	2.6	3.8	13.4
4	4	2.8	3.7	12.5
TBARS production as function of clay concentration $(P_{rel})_{cc}$, $(P_{rel}^{\ a_s})_{cc}$				
Clay concentration {cc}, ppm	$(P_{rel})_{cc}$,	$(P_{rel}^{\ a_s})_{cc}$	$(P_{rel})_{cc}$,	$(P_{rel}^{\ a_s})_{cc}$
0	1	1	1	2.5
100	0.6	0.5	0.4	1.25
180	0.6	0.55	0.4	1.55
320	1.2	0.5	1.1	2.4
570	1.4	0.9	1.5	4.8
1000	2.3	1.6	2.4	8.7

The relative production of TBARS is referred as P_{rel} (eq. S1). P_{rel} magnitude surface area (a_s) values reported in the literature (Dogan et al., 2006; Dogan et al., 2007), namely reported a_s values for SHCa-1, NAu-1, and NAu-2 corresponded to 35.6, 52.8, and 10.6 m^2 g^{-1} respectively ($P_{rel}{}^{as}$)(eq. S2). Variations of P_{rel} values as affected by incubation time(t) and clay concentration in suspension ($\{cc\}$) are referred to as $(P_{rel})_t$ and $(P_{rel})_{cc}$, respectively and variations of $P_{rel}{}^{as}$ values as affected by incubation time(t) and clay concentration in suspension ($\{cc\}$) are referred to as $(P_{rel}^{as})_t$ and $(P_{rel}^{as})_{cc}$, respectively (eqs. S3-S6).

References:

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Figure 1S. The effect of incubation time on TBARS formation (Figure 1) normalized to clay specific surface area.

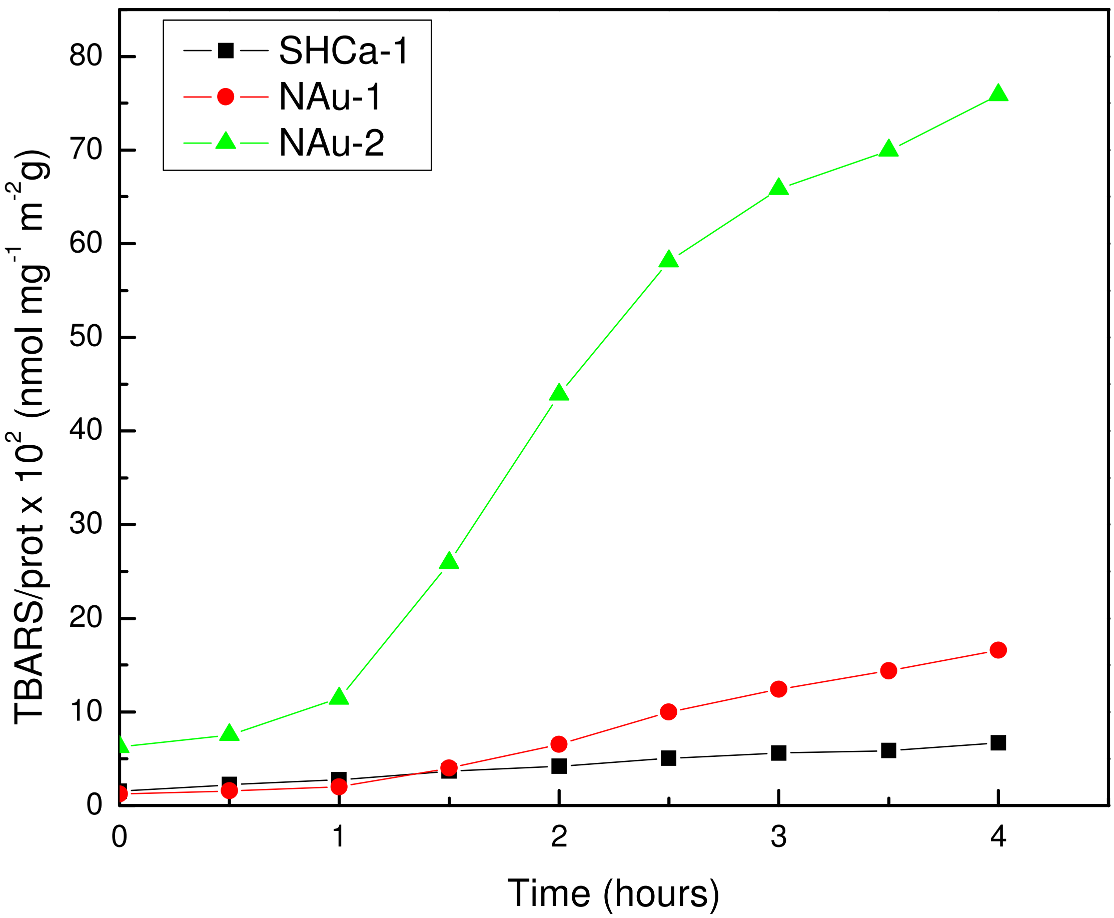

Figure 2S. The effect of clay concentrations on TBARS formation (Figure 2) normalized to clay specific surface area.