

# Competition between metal-carboxylate complexing, mineral precipitation, and carboxylate decomposition reactions.

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## Introduction

Dicarboxylates such as oxalate ( $\text{COO}^- \cdot \text{COO}^-$ ) and malonate ( $\text{COO}^- \cdot \text{CH}_2 \cdot \text{COO}^-$ ) form strong aqueous complexes with metals such as Al, Fe and Ca and thus have the potential to control mineral dissolution and precipitation during diagenesis. Dicarboxylates are less thermally stable than monofunctional species such as acetate, which is reflected in their lower concentration in oil field waters. The unstable nature of oxalate and malonate is however important, since at their peak concentration they will promote dissolution, but during decomposition metals will precipitate. To assess whether dicarboxylates are significant to secondary porosity and clay precipitation in sandstone reservoirs, and to sedimentary ore formation, it is necessary to estimate both the formation constants of the various metal dicarboxylate species, and the rates of decomposition of the dicarboxylate ligand. Here we present results of experiments studying the decomposition of oxalate and examine the effect that complexing with Al and Fe has on oxalate thermal stability. We find that metal complexes stabilise oxalate and malonate and that metal complexing and dicarboxylate decomposition are closely related.

## Methodology

Experiments were performed in Dickson fluid sampling autoclaves at 160°C and 50 MPa using 200ml flexible gold-titanium reaction cells (Seyfried *et al*, 1987). Starting solutions initially contained 10mM/l oxalic acid or malonic acid. Four oxalic acid experiments are discussed in detail here:

Expt. 1 contained pure oxalic acid.

Expt. 2 examined effects of Al complexing by reacting the oxalic acid with 1 g of sintered gel of composition  $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ , within the gold reaction cell; a core of Fontainebleau sandstone was included in the cell to act as a substrate for clay precipitation.

Expt. 3 examined Al complexing in the absence of solids. The gel was reacted with oxalic acid at 80°C then filtered ( $<0.2\text{mm}$ ) before loading into the cell.

Expt. 4 examined the additional effect of Fe and reacted Al/Si gel and amorphous  $\text{Fe}(\text{OH})_3$  with oxalic acid.

The experiments were heated from 25°C to 160°C in around 5 hours and fluid samples taken at intervals. Oxalate was analysed by ion chromatograph and metal concentrations measured by ICP-AES. Dissolved gases and other carboxylates resulting from oxalate decomposition were analysed to examine the attainment of metastable redox equilibrium between the organic species (Small and Manning, submitted).

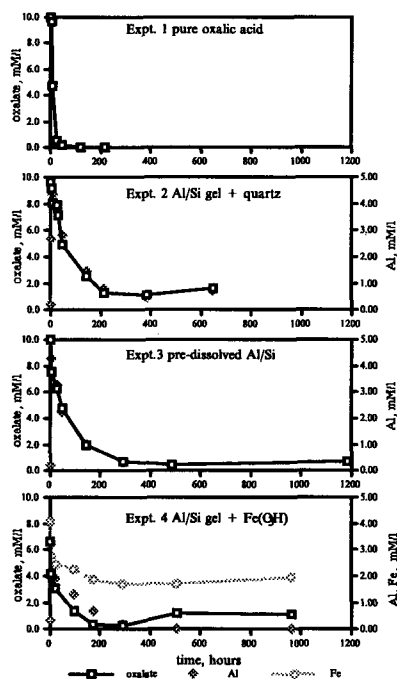


FIG. 1. Concentration versus time data.

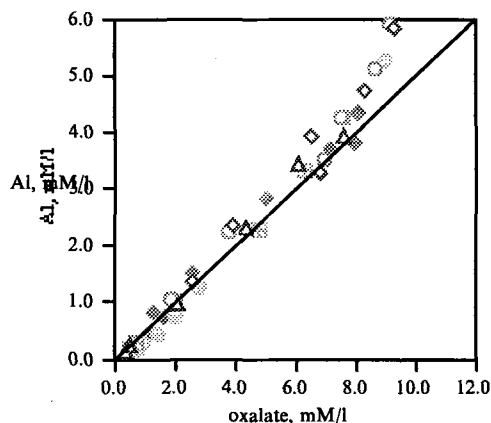


FIG. 2. Correlation of Al with oxalate.

### Results and discussion

Figure 1 presents oxalate, Al and Fe concentration versus time plots for the four experiments. For pure oxalic acid (Fig. 1a) oxalate rapidly decomposed to below detection within 200 hours. Oxalic acid decomposition produces mainly  $\text{CO}_2$ ,  $\text{H}_2$  and formic acid ( $\text{HCOOH}$ ) together with trace amounts of acetic acid and hydrocarbons.

Addition of Al and Si (Figs. 1 b,c) produces a dramatic decrease in the rate of decomposition of oxalate, and oxalate attains a steady state concentration above detection limit. The rates of Al precipitation in Expts 2 and 3 are similar suggesting that nucleation on minerals present in Expt 2 does not influence precipitation. Al molal concentration in Expts. 2 and 3 decreases at precisely half the rate of oxalate (The Al scale in Fig 1 is set at half that of oxalate). The relationship between oxalate and Al concentration is further illustrated in Figure 2 with data from additional experiments. The data are consistent with the presence of an Al-oxalate complex with 2 oxalate ligands per Al, ( $\text{Al}(\text{OX})_2^-$ ).

Al precipitation produces 1mm sized kaolinite crystals together with larger Al-rich rhombs. TEM investigation suggests that the kaolinite forms secondary to the Al-rich phase; kaolinite is the stable phase under the final fluid conditions. XRD shows diffraction maxima partially consistent with pseudoboehmite, a poorly crystalline Al-oxyhydroxide ( $\text{AlOOH}$ ). It is possible that solid Al-oxalate is also present; such phases have been synthesised at  $25^\circ\text{C}$  (Bilinski *et al*, 1986). Dissolution of solid Al-oxalate could account for the small increase in oxalate concentration which is seen Expt. 2 and in other experiments.

The pH dependence of dicarboxylic acid

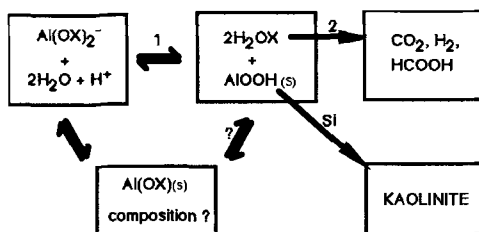


FIG. 3. Al-oxalate reaction summary.

decomposition is well documented (see Crossey, 1991), where the rate of decomposition of the undissociated species (e.g.  $\text{COOH.COOH}$ ) is much faster than that of the partially dissociated species ( $\text{COH.COO}^-$  and  $\text{COO}^-.\text{COO}^-$ ). The effect of Al-oxalate complexing is considered to be analogous to the pH effect where the activity of the thermally unstable undissociated acid is lowered by the formation of Al-oxalate. Figure 3 summarises the reactions involved in the decomposition of Al-oxalate. Either reaction 1, the precipitation of  $\text{AlOOH}$ , or reaction 2 the irreversible decomposition of oxalic acid could be the rate determining step in the overall process.

Preliminary study of the additional effect of Fe (Expt. 4, Fig 1d) reveal that these complexing, precipitation and decomposition reactions are even more complicated. Here Fe competes with Al for available oxalate, and initially the quenched solution contains the yellow Fe(III)-oxalate complex (Tait *et al*, 1992). Once Al/Si dissolution has progressed this colouration is lost, although both Al and Fe concentrations remain high. Crystals of humboldtine ( $\text{FeCOO.COO}$ ) were formed during this experiment indicating reduction of Fe by  $\text{H}_2$  released during oxalic acid decomposition. The increase in aqueous oxalate after 400 hours in Expt. 4 is most likely a result of dissolution of humboldtine.

These relatively simple experiments indicate that the factors controlling dicarboxylate stability and metal speciation during diagenesis are complex and closely interrelated. Further experimental study of the competing reactions between different metal complexes is required before these processes can be adequately modelled.

### References

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