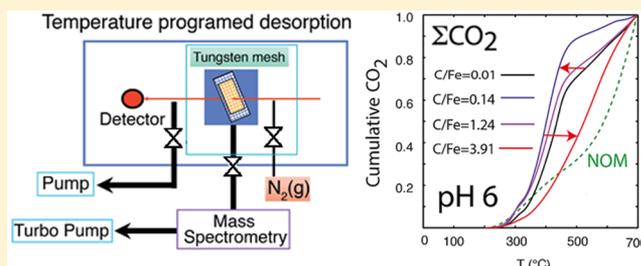


Thermal Stability of Goethite-Bound Natural Organic Matter Is Impacted by Carbon Loading

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Supporting Information

ABSTRACT: Dissolved natural organic matter (NOM) sorption at mineral surfaces can significantly affect the persistence of organic carbon in soils and sediments. Consequently, determining the mechanisms that stabilize sorbed NOM is crucial for predicting the persistence of carbon in nature. This study determined the effects of loadings and pH on the thermal stability of NOM associated with synthetic goethite (α -FeOOH) particle surfaces, as a proxy for NOM–mineral interactions taking place in nature. NOM thermal stability was investigated using temperature-programmed desorption (TPD) in the 30–700 °C range to collect vibration spectra of thermally decomposing goethite–NOM assemblages, and to concomitantly analyze evolved gases using mass spectrometry. Results showed that NOM thermal stability, indicated by the range of temperatures in which CO₂ evolved during thermal decomposition, was greatest in unbound NOM and lowest when NOM was bound to goethite. NOM thermal stability was also loading dependent. It decreased when loadings were increased in the 0.01 to 0.42 mg C m⁻² range, where the upper value corresponds to a Langmuirian adsorption maximum. Concomitant Fourier transform infrared (FTIR) spectroscopy measurement showed that these lowered stabilities could be ascribed to direct NOM–goethite interactions that dominated the NOM binding environment. Mineral surface interactions at larger loadings involved, on the contrary, a smaller fraction of the sorbed NOM, thus increasing thermal stability toward that of its unbound counterpart. This study thus identifies a sorption threshold below which NOM sorption to goethite decreases NOM thermal stability, and above which no strong effects are manifested. This should likely influence the fate of organic carbon exposed to thermal gradients in natural environments.



INTRODUCTION

Mineral particle surfaces are believed to play key roles in the long term resilience to abiotic and biotic stability of natural organic matter (NOM) in soils and sediments.^{1–3} NOM–mineral interactions are consequently considered for slowing CO₂ release to the atmosphere from soils and sediments.^{4–6} As such, these efforts are calling for a detailed understanding of the mechanisms through which minerals alter NOM stability.

The nature of NOM binding to minerals is predominantly controlled by the physicochemical and structural/steric properties of minerals and NOM,^{2,7,8} as well as the environmental conditions in which these reactions occur. Binding types and strength can, for instance, be considerably affected by pH, ionic strength, foreign dissolved ions, reaction temperature as well as NOM loading.^{9–13} The issue of NOM loading can be of particular importance especially in the light of the multilayer adsorption model,¹⁴ suggesting that increased sorption loadings shift mineral–NOM binding from direct (*e.g.*, coordinative surface metal–carboxylate or hydrogen bonding to surface hydroxo groups) to indirect (*e.g.*, outer-sphere, electrostatic, and van der Waals) interactions. Such shifts in binding modes may consequently impact the lability of NOM toward both abiotic (*i.e.*, (thermo)chemical) and biotic (*i.e.*, enzymatically catalyzed microbial decomposition) breakdown processes.

Though both processes proceed through mechanistically distinct pathways, a number of recent studies underscored potential links.^{15–18} These links stem from the facilitated pathway offered by the decomposition of the most labile fractions (*e.g.*, low weight molecular organic compounds) prior hitting an energetic barrier, which is then either overcome by (i) enzymatically mediated biotic decomposition at low-temperatures or (ii) externally applied heat in thermochemical abiotic processes. Although comparisons of this type are not likely to go beyond this point, knowledge of the intrinsic abiotic (thermo)-chemical stability of NOM remains of fundamental value in our quest to study the fate of organic carbon in the environment. For example, we recently showed how microbial decomposition altered the intrinsic thermochemical properties of organic matter of a recent podzols (up to 2150–2340 years before present) yet had little effect in the underlying paleosols (2750–7000 years before present).³

The potential links^{15–18} between biotic and abiotic degradation of NOM enable the application of thermal analysis to study biogeochemical stability of NOM. Recent studies show that the

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