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Geochemical Transformation of Organic Sulfur Compounds: Role of Birnessite Catalysis

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Introduction: Sulfur is intimately involved in the geochemical transformation of organic matter in soils and sediments. Major types of organic sulfur compounds in soils and sediments include thiols, organic sulfides, di- and poly-sulfides, thiophenes, sulfonates and ester-linked sulfate.
While there is significant contribution of organic sulfur compounds to soils and sediments from the original biological organic matter, an important fraction of sedimentary organic sulfur is generated through abiotic reactions of inorganic sulfur nucleophiles with functionalized organic matter. For example, abiotic reactions involving polysulfide ions represent a major pathway for forming organic polysulfides. Although it is believed that the thiophenic compounds are generated chemically, the exact mechanisms are not clear.

Methods and Materials: We used a simple model thiol, 3-mercaptopropionic acid (3-MPA), as to understand the transformations of thiols mediated by birnessite. Sulfur XANES spectroscopy and mass spectrometry gave information of reaction products.

Results: Our results suggest that geochemical catalysis involving transition metal oxides, particularly birnessite (MnO_2), could be important for forming this class of molecules. The disulfide was the main product when the thiol was reacted alone with birnessite. However, in the presence of catechol, an important lignin derivative, a thiophenic end product was formed. Evidence suggests that the mechanism involves ring cleavage of catechol forming unsaturated products followed by reaction with 3-MPA. Our results illustrate the importance of mineral catalysis in the transformation of organic sulfur compounds in the geosphere.

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