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Iron & manganese catalysis of reactive organic carbon molecules into stable forms within marine sediments.

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The balance between the preservation and degradation of organic carbon (OC) within marine sediments is of primary importance to the Earth's carbon and oxygen cycles over geologic timescales[1]. Despite this, the controls on OC preservation remain unclear[2]. The exposure time of OC to oxygen is thought to be the primary control on preservation[3], but in continental margins where >90% of OC preservation occurs[4], this relationship is weak[2]. Therefore in these environments, other mechanisms of OC preservation must play a role[4,5]. One mechanism that has received little attention is the geopolymerisation of small, relatively reactive OC molecules, into complex and stable forms via condensation reactions[6]. These reactions may generate OC molecules that are resistant to microbial degradation, but their contribution to OC preservation was previously thought to be minor due to slow reaction kinetics[7]. Here we show that dissolved iron and manganese ions, and solid iron and manganese minerals, abiotically catalyse the Maillard reaction by up to two orders of magnitude at temperatures, OC concentrations, and iron and manganese concentrations similar to those in continental margin sediments[8]. Furthermore, using STXM-NEXAFS we show that the chemical structures of these geopolymerised substances are consistent with OC in continental margin sediments from around the globe[8]. Our results indicate that the catalysed geopolymerisation of simple OC molecules into complex macromolecules accounts for 4-10% of global OC preservation in marine sediments and therefore the variation in iron and manganese fluxes to the ocean may have had a substantial impact on global OC preservation, atmospheric oxygen and carbon dioxide inventories over geological time[8].

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