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Water-soluble organic acids at deep-ultradeep subsurface water in sedimentary basins: Experimental results and geological significances

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Water-soluble organic acids (WSOA) in subsurface water have been paid intensive attentions over the past couple of decades. They are shown many great significances, including natural gas precursor, tracer for the movement of underground fluid, indicator for porosity improvement, and detecter of deep subsurface life on the Earth. However, little is known on the distributions and origins of organic acids at deep-ultradeep depth underground. Herein, we reported the concentrations of WSOA in both rock and subsurface water from many sedimentary basins, as well as influencing factors. Beside before mature stage, there are considerable amounts of WSOA detected in both high-over mature source rocks and deep-ultradeep subsurface water. Slightly different from previous studies, WSOA mainly consist of monocarboxylates, predominately formate and acetate, especially in high-over mature stage. Although high-TOC oil-generating source rocks have large amounts of WSOA, but low production rate of WSOA relative to low-TOC ones due to lack of hydrogen (Fig. 1). Moreover, the types of source rock play an important role in the distributions of WSOA. Different source rocks have distinct ratios of formate to acetate concentration, expressed as c(formate)/c(acetate), due to significant differences in both initial molecular structure and metabolites. Type-III organic matters (OMs) have c(formate)/c(acetate) more than 1, while Type-II OMs do less than 1. Moreover, c(formate)/c(acetate) is shown quite another trend with ongoing maturity for diverse types of OMs (Fig. 2). This indicates that c(formate)/c(acetate) can be used to distinguish types of OMs. Concentrations of WSOA show a "sharp decrease-slight increase-slow decrease" evolution trend with progressive maturity, which are consistent with the higher production rates of organic acids under hydrous relative to anhydrous pyrolysis at ≥400 ℃. All geochemical signatures indicate that at both deep-ultradeep depth and high-over mature stages, the formation of organic acids is attributed to the thermochemical oxidation of organic components by mainly hydroxyl radicals, challenging the traditional model of organic acid evolution.

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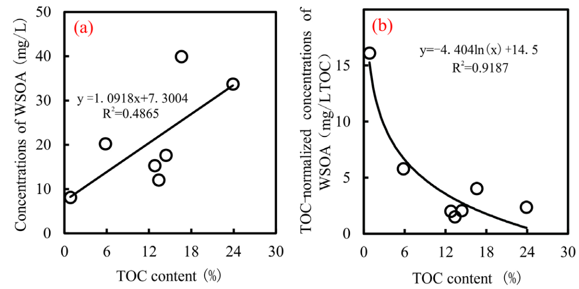

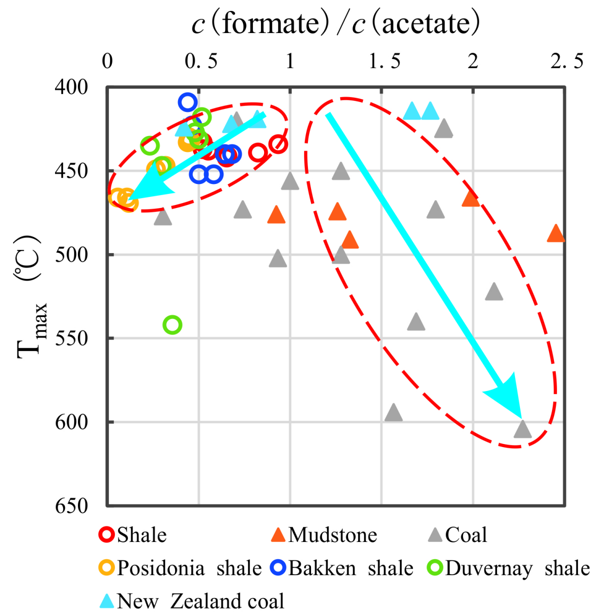

Note: Samples illustrated in the last four legends from Zhu Yaling et al. (2015)