

From subducted organic matter to COH fluids: an experimental investigation on the redox dissolution of carbonaceous materials

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Subducted organic matter plays a key role in the production of COH fluids and volcanic arc gaseous emissions. Assessing how its intrinsic heterogeneity affects its redox dissolution is fundamental to develop more accurate models of the deep organic carbon cycle. To this purpose, we experimentally investigated at 550 °C, 1 GPa and fO_2 buffered from $\Delta FMQ \approx +4$ to -7 the solubility of synthetic analogues of carbonaceous material (CM) characterized by peculiar structural, textural and compositional features, i.e., graphite (crystalline $C(sp^2)$; O <1 at%), mesoporous carbon (poorly ordered porous $C(sp^2)$; O <1 at%; oxygenated functional groups, OFGs, ~2%), glass-like and Vulcan® carbon (disordered sp^2 -rich C; $C(sp^3)$ <30 at%; up to ~8 at% O; OFGs <30 at%), graphite oxide (partly ordered $C(sp^3)$; $C(sp^2)$ <2 at%; O ~31 at%; OFGs ~41 at%). Graphite and mesoporous carbon are quite inert ($CM_{dissolved}$ <0.4%), glass-like and Vulcan® carbon are more soluble at extreme redox conditions ($CM_{dissolved}$ ~1% at $\Delta FMQ \approx +4$ and >1% at $\Delta FMQ \approx -7$), graphite oxide reacts extensively at all redox conditions ($CM_{dissolved}$ >2%). In the fluid CO_2 and CO are the dominant volatile carbon species at $\Delta FMQ \approx -5$; CH_4 prevails at $\Delta FMQ \approx -7$ in all the runs except that with graphite oxide. Low crystallinity, high content of $C(sp^3)$, O and OFGs appear to increase CM solubility. In particular, a high content of O heteroatoms and OFGs promotes CO_2 release, while the formation of H- and O-bearing surface complexes probably accompanies the production of CO as reaction intermediate. Hydrogen adsorption on active sites seems to reduce graphite and mesoporous carbon reactivity at $\Delta FMQ \approx -5$ and -7 ; a similar process likely hinders methane formation in the runs at $\Delta FMQ \approx -5$, where a pure CH_4 fluid would be expected from thermodynamics. These results can indicate that immature CM (poorly crystalline, $C(sp^3)$ - and O-rich) is more prone to dissolution at the onset of dehydration reaction in forearcs and may give a fundamental contribution to the organic carbon flux. Moreover, the high stability of some H- and O-bearing functional groups may be associated with a previously neglected flux of hydrogen and oxygen associated with CM subduction.