Oxidation of subducted organic matter buffered by marine carbonate rules the carbon isotopic signature of arc emissions

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Open ocean sediments consist mainly of inorganic biogenic calcite and organic matter, along with minor opal and clays. Once subducted, some carbon is removed from the slab and returns to the atmosphere as CO₂ in arc magmas, and its carbon isotopic signature is thought to reflect that of its subarc source region. We experimentally investigated the carbon isotopic exchange in aragonite + graphite metasediments interacting with water beneath the arcs at ≈ 100 km depth, relying on a redoxbuffered ($\Delta FMQ = +0.61$, where ΔFMQ is the difference expressed in log units relative to the reference fO_2 of the assemblage fayalite+magnetite+quartz) model isotopic system containing as end-members nearly pure ¹²C-graphite and ¹³Caragonite. We show that aqueous fluids with 16.6 mol% CO₂ are produced mainly by irreversible oxidation of graphite, which retains its initial isotopic composition. Conversely, the carbon isotopic composition of CO2 and of recrystallized carbonate converges within hours to the same ¹³C abundance, which declines exponentially with increasing CO2/aragonite ratio and it is independent of the absolute amount of graphite. Results suggest that CO₂ characterised by the global average isotopic composition of volcanic arc emissions can result from the interaction at subarc depth between water and a mixture of aragonite + graphite in any proportion, whenever oxidative processes bring the CO2/aragonite molar ratio to values close to 0.1. We present here a mathematical model based on our experimental data, showing that these conditions are met at relatively oxidizing conditions comprised between Δ FMQ +0.40 and +1.0, which agrees well with the natural record, and moderate fluid/rock molar ratios of 0.1-1.0, realistic at subarc depth where low dehydration regimes prevail.