

The anthropogenic contribution to carbon dioxide dissolved in seawater

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Emissions of anthropogenic CO₂ not only enhance greenhouse effects in the atmosphere and contribute toward global warming. Atmospheric CO₂ also reacts with surface ocean waters and causes ocean acidification, to an extent that marine organisms may face difficulty in sequestering CaCO₃ to build their shells. To assess how far the rate of acidification may progress in the future, reliable forecasts are needed as for the future emissions of CO₂. In addition, it must be known how much CO₂ is being exchanged across the atmosphere/seawater interface at any given pCO₂, in order to define the proportion of inorganic carbon stored in the ocean water that is anthropogenic in origin.

Exchange experiments between atmosphere and seawater are reported to quantify how much CO₂ can be exchanged between the Earth's atmosphere and ocean surface water at any given CO₂ partial pressure. The seawater came from the Aegean sea. Its total alkalinity was determined at 2698 ± 24 µmol/kg. The gases to simulate the Earth's atmosphere were commercial N₂-O₂ (4:1) gas mixtures with CO₂ ranging from < 10, 200, 280, 390, 1000, 2,000, 5,000, 20,000 and 100,000 µatm CO₂. At the present atmospheric level of CO₂ (400 µatm) about 18% of the inorganic carbon (DIC) inventory dissolved in surface seawater is due to direct exchange across the water-atmosphere interface. By far the largest proportion of the DIC in seawater, i.e. more than 80%, is derived from sources other than the atmosphere, and the concentration in seawater of this fraction is independent of short-term (human-scale) variations in pCO₂. The human contribution to the DIC of ocean surface water is defined as the carbon content that may be exchanged across the water-atmosphere interface between 280 and 400 µatm CO₂. It is quantified at ~ 115 ± 18 µmol carbon per kg seawater, or 4.5% of the total present-day DIC of surface ocean water.

That concentration is a higher than the anthropogenic contribution in mid-latitude Atlantic surface water (~ 60 µmol kg⁻¹), but (1) Aegean seawater is more alkaline than Atlantic water hence more capable of absorbing CO₂ via hydrolysis reaction; (2) the 60 µmol kg⁻¹ C dates from 1994, when the pCO₂ was only 355 µatm; and (3) any DIC derived from direct measurements of natural surface ocean waters may be a steady-state rather than an equilibrium concentration.

Secular variations in seawater chemistry controlling water-rock interaction in shallow reflux systems

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Secular variations of seawater composition influence both the primary mineralogy of marine non-skeletal carbonates and also the dolomitization potential of seawater-derived fluids. Using 1D reactive transport modelling we explore the role of seawater composition in controlling early carbonate diagenesis during reflux of brines, contrasting aragonitic and calcitic seawaters based on modern and Mississippian with Mg/Ca of ~5 and ~2 respectively.

Dolomite forms from reflux of modern brines by replacement of calcite, increasing the porosity. When replacement is complete, dolomite can continue to form as primary cement ("overdolomitization") and porosity is reduced. Increasing evaporative concentration in the brine pool enhances reaction rate independent of the effect on enhanced density-driven flow. Reflux of brines formed from Mississippian seawater leads to synchronous primary dolomite cementation and replacement of calcite, with net porosity occlusion. Release of Ca²⁺ by replacement dolomitization drives gypsum precipitation from both modern and Mississippian brines of >150‰ salinity, particularly at higher temperatures, further occluding porosity.

Temperature is an important control on dolomitization kinetics even at relatively low temperatures, with complete replacement of calcite occurring within 130 ky at 35°C, more than twice the rate at 30°C. Fine-grained calcitic sediments characteristically have a high effective surface area and may dolomitise at rates >10 times those of coarse-grained sediments. However, this effect may be offset by the lower permeability of finer sediments which limits rates of fluid flow for a given density head drive. The effect of microbial processes appears to be critical in generating nucleation sites ("seed dolomite"), as well as altering fluid chemistry. Neither secular variations in seawater chemistry associated with changing atmospheric pCO₂, nor biological induced alkalinity variation, appear to significantly influence dolomitization.