Coupled change in ocean CO₂ chemistry and global climate in the Palaeozoic

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The Ordovician and Silurian periods were times of major environmental and biological change, including the Great Ordovician Biodiversification Event (GOBE) and the oldest of the five major mass extinctions (the end-Ordovician), which occurs at the culmination of major long-term cooling and glaciation followed by biological, and climatic, recovery in the early Silurian. However, the drivers of environmental change in this interval remain debated. CO₂ estimates are sparse and vary by almost an order of magnitude, and non-CO2 drivers, including volcanic aerosols and meteoritic debris, have also been proposed. Here we present the first reconstruction of ocean pH, and thereby ocean-atmosphere CO₂ chemistry, for the Ordovician and Silurian using the boron isotope composition of well-preserved fossilised brachiopods. These data show a substantial rise in ocean pH and an associated fall in atmospheric CO₂ coincident with the large cooling trend and major radiation in biodiversity through the Ordovician. CO₂-driven cooling thus sets the stage for the glaciation thought to trigger the end-Ordovician extinction event, while rising CO₂ in the early Silurian would have driven climatic recovery. Our findings demonstrate persistent coupling of CO2 and climate on geological timescales and the pervasive influence of CO2 on the Earth system and biospheric evolution.