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Volcanic degassing necessary to produce a $CaCO_3$ undersaturated ocean at the Triassic–Jurassic boundary

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Abstract

Carbon cycle model calculations have been conducted to test the idea that the entire ocean became undersaturated or nearly undersaturated with respect to calcium carbonate at the Triassic–Jurassic (T–J) boundary. A low degree of saturation at this time has been cited to explain the relative lack of carbonate sediments, especially those that originally contained the more soluble minerals, aragonite and highly magnesian calcite. Sensitivity analysis indicates that only extreme conditions of massive and short-lived degassing of CO_2 and SO_2 from CAMP volcanism could have led to an undersaturated ocean. With total degassing of 21,000 GtC as CO_2 and 57,000 GtS as SO_2, an undersaturated ocean with respect to all calcium carbonate minerals could have persisted for 20–40 ka, but only if the volcanic degassing lasted for no longer than 50–100 ka. With half this amount of total degassing over 100 ka a very low degree of supersaturation, possibly stabilizing only low magnesian calcite, could have been maintained for 20 ka.

Keywords: Volcanic gases; Acidic ocean; Carbonate dissolution; Carbon cycle; T–J boundary

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1. Introduction

One of the five largest mass extinction events during the Phanerozoic Eon (Sepkoski, 1996) occurred near the boundary between the Triassic (T) and Jurassic (J) periods, ~ 200 million years (My) ago (Pálfy et al., 2000). (However, for an alternative interpretation of the evidence see Tanner et al., 2004.) Accompanying the extinctions of marine and terrestrial biota were a number of dramatic changes in the global carbon cycle including widespread igneous activity in the Central Atlantic Magmatic Province (CAMP) (Marzoli et al., 1999; Cohen and Coe, 2002; Marzoli et al., 2004), and perhaps a meteorite impact (Olsen et al., 2002). In particular, palaeobotanical evidence has revealed a sudden increase in the level of atmospheric CO_2 across the boundary (McElwain et al., 1999, Beerling, 2002; Beerling and Berner, 2002), while a sharp negative decrease in the carbon isotopic composition ($\delta^{13}C$) of marine carbonates and the organic remains of terrestrial and marine biota has been identified from a worldwide set of T–J boundary localities (McRoberts et al., 1997; McElwain et al., 1999; Pálfy et al., 2001; Ward et al., 2001; Hesselbo et al., 2002).

We have attempted to account quantitatively for the increase in CO_2 and decrease in $\delta^{13}C$ using a geochemical model of the long-term carbon cycle for the end-Triassic 'greenhouse' world that considers volcanic degassing, methane hydrate decomposition, biological storage of carbon, chemical weathering of Ca silicate and carbonate

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rocks and carbonate precipitation in a one-box homogeneous ocean (Beerling and Berner, 2002). The reasoning behind the study was that, due to very extensive eruptions of CO_2, accompanying the extrusion of CAMP basalts (Marzoli et al., 1999), atmospheric CO_2 rose and global greenhouse warming occurred which should have been deleterious to many organisms, especially land plants. However, volcanic degassing alone was found to be insufficient to account for both the increase in CO_2 recorded in fossil leaves and negative $\delta^{13}C$ excursion in organic matter. To reproduce the isotopic and CO_2 excursions, it was postulated that greenhouse warming by the excess volcanogenic CO_2 led to the thermal decomposition of methane hydrates in sediments resulting in the release to the atmosphere and oceans of CH_4, oxidation of the CH_4 to CO_2, and a further increase in atmospheric CO_2. The release of methane led to the addition of isotopically light carbon to the global carbon cycle, which produced a consistent and coherent explanation for the sharp drop in $\delta^{13}C$ of organic matter found at the boundary.

Here we revisit this theme to investigate the suggestion that there was a worldwide lack of aragonite and high Mg calcite, and reduced low-Mg calcite deposition near the Triassic–Jurassic boundary (Hautmann, 2004). Hautmann (2004) has suggested that this global carbonate 'gap' in the stratigraphic record was due to excessive buildup of CO_2 in the atmosphere and oceans, the oceans then becoming undersaturated with respect to aragonite, high-Mg calcite and, to a less extent, low-Mg calcite. Under these conditions, biocalcifying organisms with aragonitic and high-Mg calcitic skeletons were in a competitive disadvantage compared with those that either secreted less soluble low-Mg calcite or were non-calcifying, with the result being that aragonite and high-Mg calcite secreting organisms were more prone to extinction (Hautmann, 2004). We examine the Hautmann (2004) hypothesis by calculating the effect of changes in the volcanic degassing rate of both CO_2 and SO_2 on $CaCO_3$ saturation state using a slight modification of the geochemical model used earlier to calculate atmospheric CO_2 levels and the $\delta^{13}C$ of organic matter (Beerling and Berner, 2002). To achieve this aim, we have varied the values and duration of CO_2 and SO_2 input fluxes to analyze how an undersaturated ocean might have been attained while still producing the independently measured, and previously calculated, rises in atmospheric CO_2 and drops in $\delta^{13}C$.

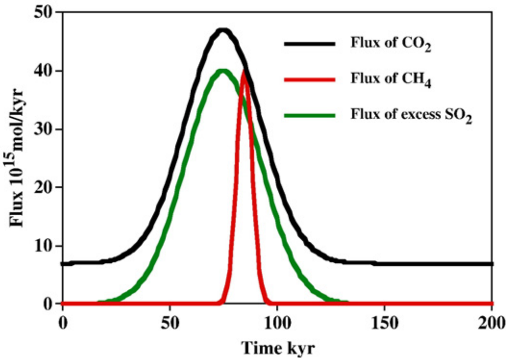

Fig. 1. Plots of rates of gas input to the atmosphere vs. time for the situation of total volcanic degassing of 21000 Gt C with molar $SO_2/CO_2=1$ and total CH_4 degassing from clathrates of 4300 Gt C.

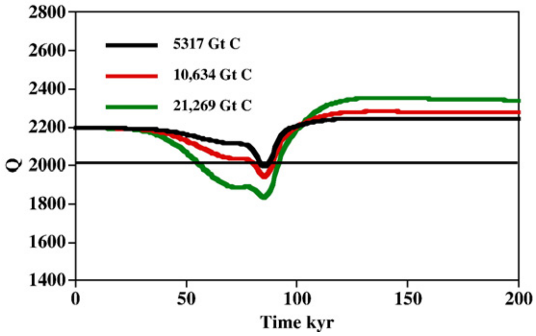

Fig. 2. Effect of changes in total degassing over a 100 kyr period on the degree of saturation Q of seawater with respect to $CaCO_3$ (see text for definition of Q). Total masses of degassed CO_2 (with molar $SO_2/CO_2=1$) are in Gt C. A value of $Q=2000$ (straight line) represents mean carbonate saturation ($Q=K$) for the entire ocean. Units for Q are $(10^{18}\text{ mol})^2$.

2. Methods

To track possible evidence of changes in the state of saturation for the whole ocean with respect to $CaCO_3$ the geochemical carbon cycle model of Beerling and Berner (2002) has been slightly modified. The changes are: (1) the expression for the rate of burial of $CaCO_3$ is changed to more realistically reflect the kinetics of carbonate precipitation under extreme CO_2 degassing. The new expression is:

$$F_{bc} = \mathrm{kpp}(Q - K) \tag{1}$$

$$Q = M_{\mathrm{Ca}} C_{\mathrm{w}}^2 / C \tag{2}$$

where:

F_{bc}	rate of $CaCO_3$ deposition from seawater
C	mass of CO_2 in the atmosphere (10^{18} moles)
C_{w}	mass of inorganic carbon in the oceans (10^{18} moles)
M_{Ca}	mass of dissolved calcium in the oceans (10^{18} moles)