

## PALAEOCEANOGRAPHY

## Seeing changes in a changing sea

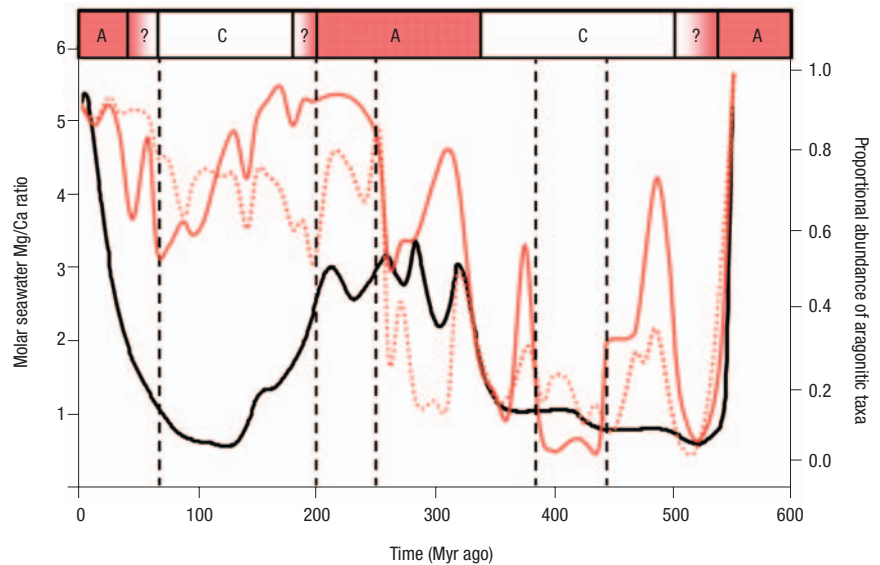
The ratio of magnesium to calcium in sea water is thought to have influenced the skeletal mineralogy of certain marine calcifiers throughout the Phanerozoic eon. A fresh look at old data suggests that mass extinctions may have also played a role.

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Fluctuations in the ratio of magnesium to calcium in ancient sea water have fascinated geoscientists for nearly half a century. This is because this ratio plays a critical role in determining which form of abiotic calcium carbonate — aragonite or calcite — will precipitate out of sea water. High ratios of magnesium to calcium have favoured production of aragonite whereas low ratios have favoured production of calcite<sup>1–5</sup>. Whether shifts in this ratio have also influenced the mineral make-up of biogenic calcium carbonate, secreted by many marine organisms for the production of calcareous shells and skeletons, is currently the subject of intense inquiry. On page 527 of this issue, Kiessling and colleagues<sup>6</sup> offer compelling evidence that mass extinction events may have also triggered changes in the predominant form of calcium carbonate produced by marine calcifiers.

During the Phanerozoic eon, which roughly spans the last 540 million years, the world's oceans have oscillated between states favouring the precipitation of aragonite/magnesium-rich calcite and magnesium-poor calcite (Fig. 1)<sup>1</sup>. A previous examination of the impact of these oscillations on marine calcifiers revealed that the form of calcium carbonate produced by the major reef-building and sediment-producing marine organisms of this time varied in temporal synchronicity with the ratio of magnesium to calcium (Mg/Ca) in sea water<sup>7</sup>, such that the abundance of aragonite-producing (aragonitic) calcifiers increased following a shift to aragonite-favouring seas. However, this study focused on highly productive marine calcifiers, known as hypercalcifiers, on the premise that these organisms probably use most of their energy to induce precipitation of calcium carbonate, rather than to control specific ionic ratios at their



**Figure 1** Changes in the proportional abundance of fossilized aragonite-producing marine organisms throughout the Phanerozoic eon. Changes in the proportional abundance of all aragonite-producing marine organisms (dotted red line) correspond to mass extinction events (vertical dashed lines) and not to changes in the ratio of magnesium to calcium in sea water (black line). Oceanic state (aragonite, A; calcite, C) is depicted along the top of the figure. Only the proportional abundance of aragonitic reef-building organisms (solid red line) varies in concert with changes in the magnesium to calcium ratio of sea water, as evidenced by synchronized reductions from 550 to 520 Myr ago and 210 to 120 Myr ago, and by synchronized increases from 440 to 320 Myr ago and 65 Myr ago to present time. The magnesium/calcium ratios were derived from refs 2 and 10; oceanic states were derived from ref. 1.

site of calcification. Such organisms would probably be particularly vulnerable to unfavourable changes in the Mg/Ca ratio of sea water.

In contrast, Kiessling and colleagues<sup>6</sup> examined the mineralogical composition of all varieties of calcifying organisms throughout the Phanerozoic eon and found no correlation between the proportional abundance of aragonitic organisms and oceanic state (Fig. 1). Even when they limited their analysis to calcifiers that they suggest are unable to physiologically buffer chemical changes in sea water — such as corals, hypercalcifying sponges, bryozoans, rhynchonelliform brachiopods and epifaunal bivalves — there remained little correspondence between the proportional

abundance of aragonitic organisms and oceanic state (Fig. 1). Only when they constrained their analysis to the major reef-building organisms of the time did a robust correspondence emerge, in line with earlier palaeontological and experimental investigations (Fig. 1)<sup>7,8</sup>.

For newly evolved skeletons, however, transitions between oceanic states do appear to matter. In a recent comparably broad analysis of early marine calcifiers spanning the late Ediacaran and Ordovician periods (around 550–444 million years ago), the mineralogies of newly evolved skeletons mirrored the transition between aragonitic and calcitic oceanic states purported to occur around this time<sup>9</sup>. Together these studies suggest that although the Mg/Ca

ratio of sea water may have dictated the mineralogy of these calcifiers when they first evolved skeletons, subsequent changes in oceanic state appear to have had little influence on the ultimate fates of these groups.

Of potentially greater import, however, is the identification by Kiessling and co-workers of statistically significant changes in the proportional abundance of aragonitic organisms across several mass extinction events, including the Ordovician–Silurian 444 Myr ago, the Permian–Triassic 251 Myr ago, the Triassic–Jurassic 200 Myr ago, and the Cretaceous–Paleogene 65 Myr ago (Fig. 1). Importantly, changes in the abundance of aragonitic organisms following mass extinction events were predominantly driven by selective recovery (which rarely entailed

the evolution of new skeletons) — rather than selective extinction — of organisms using either the aragonitic or calcitic forms of calcium carbonate. However, the direction of change in skeletal mineralogy across mass extinction events was not always towards the form favoured by coeval seawater chemistry. This final observation begs the question why groups of marine organisms using the unfavoured form of calcium carbonate would sometimes recover more quickly from mass extinctions than organisms using the favoured form.

Kiessling and colleagues raise a question whose exploration should advance our understanding of how marine calcifiers recover from mass extinctions, and elucidate the role that skeletal mineral compatibility with sea water plays in such recoveries. Amid growing

concern that ocean acidification, global warming, pollution and habitat loss will cause widespread extermination, if not extinction, of many marine calcifiers in the modern ocean, such an understanding appears particularly worthy of pursuit.

## References

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## VOLCANOLOGY

# Molten carbonate eruptions



SPRINGER

Oldoinyo Lengai, Masai for ‘Mountain of God’, in the East African Rift Valley is a volcano with a difference. It is the only active volcano on Earth that expels molten carbonate rich in sodium and calcium instead of the more usual silica-rich lavas, and it also spews highly alkaline ash. Past explosive eruptions have been reported to have caused health problems to the local Masai people and their livestock as well as wildlife through contamination of the water sources in the area.

A phase of effusive eruption of Oldoinyo Lengai in 2006, spanning late March and early April, was the longest active period recorded so far. During this time, almost a million cubic metres of natrocarbonatite lava extruded from the volcano, allowing Matthieu Kervyn and colleagues to investigate the shallow

magmatic system of this unique volcano (*Bull. Volcanol.* doi:10.1007/s00445-007-0190-x; 2008). They reconstructed the sequence of eruptive events by using satellite data and eyewitness accounts, and by characterizing the morphology of the various lava features in detail.

The main crater area of the volcano is marked by the presence of a number of rather curious-looking volcanic constructs called hornitos. This group of sharply conical features formed after 2001 as a result of localized, mildly explosive eruptions that piled up partially solidified lava fragments. Kervyn and colleagues suggest that during the 2006 eruption, lava first effused from the flanks of hornitos.

Withdrawal of lava from beneath the hornitos rendered them unstable and some collapsed. There were numerous phases of collapse at Oldoinyo Lengai,

suggesting that lava was derived from shallow interconnected reservoirs rather than a single reservoir. Some of the lava filled up the southern part of the crater, whereas much of the rest flowed down the western flank of the volcano through a gully. Upon reaching gentler slopes, the lava flow had grown to a thickness of over 10 metres and a length of over a kilometre.

Analysis of the chemical composition of the lava flows revealed less than 4% of silica (by weight), a much lower proportion than the tens of percent found in lavas from most terrestrial volcanoes. Nevertheless, the morphology of the lava flows, as well as features within the crater such as the hornitos, are very similar to that of more typical volcanoes.

The region around the volcano is sparsely populated and the risk to the local population appears to be limited. However, the volcano and its vicinity are a tourist attraction. Effusive events and instability resulting from the collapse of hornitos can be dangerous to visitors. During the initial stages of the 2006 eruption, dust plumes due to collapse were incorrectly reported in the international media as ash plumes attributed to an explosive eruption. Such reports may scare off tourists that the region needs badly. Accurate information on the health risks at Oldoinyo Lengai is therefore all the more important.

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