

# A different ocean acidification hazard—The Kolumbo submarine volcano example

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Detailed knowledge of the geochemistry of CO<sub>2</sub>, the signature molecule of the 21<sup>st</sup> century, is a modern day requirement for almost all geochemists. Concerns over CO<sub>2</sub> driven contemporary climate change, its relationship to past climates in Earth history, skills required for geologic CO<sub>2</sub> sequestration, and the rapid emergence of ocean acidification as an environmental threat are all prime subject matter for the literate geoscientist today. In this issue of *Geology*, Carey et al. (2013, p. 1035) describe a new, interesting, and quite powerful natural example of the intersection of these concerns in describing the build-up of a large body of acidic, dense CO<sub>2</sub> rich sea water in the shallow crater of the Kolumbo volcano close to the Mediterranean island of Santorini. They present this finding in the context of a geochemical hazard to humans and as a natural test bed for CO<sub>2</sub> sequestration leakage from shallow injection. How real are these concerns, how similar are the situations to known threats, what strategies could be taken, and how useful an analog is this finding to the broad discussion over world-wide ocean acidification or the specific concerns over leakage from geologic CO<sub>2</sub> sequestration?

Kolumbo last explosively erupted in A.D. 1650, and ~70 people were killed by volcanic gases (Fouque, 1879) so plainly the potential is real. The build-up of CO<sub>2</sub> in the crater at the time of this earlier eruption is not known, but some significant concentration must surely have been present. The population of Santorini has likely increased since then, and thus some concern is clearly justified. But what would it take to destabilize the CO<sub>2</sub>-rich waters, how large is the chemical reservoir compared to known hazards, and how might this threat be detected?

The finding of submarine volcanos close to populated areas, and discussion of hazards from their eruptions, is not new, with the 2011–2012 eruption of El Hierro, Canary Islands (see the *Geology* Research Focus by Schmincke and Sumita [2013]) a prominent recent example. But Carey et al. focus not only on the sporadic eruptive events, but also on the physical stability of the large (2.0 × 10<sup>5</sup> m<sup>3</sup> STP; 395 metric tons) pool of excess CO<sub>2</sub> accumulated within the crater only 500 m below sea level, and draw attention to the similarity with the deadly abrupt release of CO<sub>2</sub> gas from the volcanic lakes Monoun and Nyos in Cameroon, Africa (Sigurdsson et al., 1987). Clearly there are some similarities: in both locations there is a crater-contained pool of CO<sub>2</sub>-enriched water made dense, and thus held in place, by the dissolution of the gas under hydrostatic pressure. This arises simply due to the fact that the partial molal volume of CO<sub>2</sub> in sea water (~30 ml/mol) is much less than its molecular weight (44 g/mol), so that dissolution creates a dense fluid. The effect is well known, and dense plumes of CO<sub>2</sub>-enriched water have been readily created in experimental investigations of deep seafloor CO<sub>2</sub> sequestration scenarios (Brewer et al., 2005).

But there are also significant differences between the Cameroon Lakes scenario and this finding. Lakes Monoun and Nyos are within a large caldera, with walls extending high into the atmosphere, locally confining the released dense CO<sub>2</sub> gas, thus exposing the human and animal populations. In the 21 August 1986 Lake Nyos event, 1700 people and 3500 livestock were asphyxiated. The Kolumbo crater walls do not extend above sea level, and are on average 150 m below the sea surface. Released gas therefore would not be confined, but exposed to the overlying water

column with its large capacity for dissolution. If transport overcomes this aqueous chemical sink—the bubble streams typically dissolve within ~10 m rise—the gas will be exposed to the atmosphere at the wind-swept open ocean surface.

There is also the matter of scale. The estimated 400 metric tons of dissolved CO<sub>2</sub> in the Kolumbo crater is far less than the 100,000–300,000 tons believed to have been released in the Lake Nyos event. Of course, we could be at an early stage of the CO<sub>2</sub> buildup, and over time, far larger quantities could accumulate. Carey et al. show that the local source is an extensive hydrothermal vent field, releasing almost pure CO<sub>2</sub> gas as bubble streams, beautifully imaged by the team. The deepest part of the crater is at ~500 m depth; pure CO<sub>2</sub> gas can become liquid at this depth under typical ocean conditions. But in the warm water of the Mediterranean, in this crater at 17 °C, this phase boundary is unlikely to be crossed. Liquid CO<sub>2</sub> venting has been observed in other, deeper and colder locations (Lupton et al., 2006), but this would make little difference in the long term. While liquid CO<sub>2</sub> is a much denser phase, it too is buoyant in sea water, and at depths down to ~2700 m it quickly dissolves as it rises through the water column (Brewer et al., 2002, 2006). The end result would be much the same— an accumulation of CO<sub>2</sub>-rich water within the crater.

The estimated total rate of seafloor degassing from all vents in the crater was not quantified by Carey et al., but as this venting continues, the key question would be whether the rate of release from the seafloor is balanced by diffusive loss at the upper boundary. If the release rate exceeds this, then continued buildup occurs. The data provided by Carey et al. do not show a sharp density boundary between the two fluid layers, as occurs in much more strongly stratified hot brine pools (Swallow and Crease, 1965). Even for these highly stable interfaces, significant diffusive losses occur. For example, at the large, highly stable, saline Orca Basin brine lake in the Gulf of Mexico, the diffusive input of salt matching the loss to the overlying water is estimated as some 0.5 million tons per year (Pilcher and Blumstein, 2007).

The preliminary nature of the finding of this CO<sub>2</sub>-rich pool did not allow for detailed examination of the physical stability of the gradients at the upper boundary, and an only rudimentary density profile shows density increasing from  $\sigma_t$  of 28.7 at 100 m depth to 29.2 at 500 m. While a turbid zone was found at ~250 m depth, no very sharp density boundary was observed. One must assume that vertical mixing processes occur, so that CO<sub>2</sub> losses to the upper ocean must be ongoing. It remains to be seen whether this situation can revert to a self-stabilizing regime, in which the CO<sub>2</sub> build up gradually increases the stability of the interface. The challenge of observing the density gradients is real. The standard oceanographic technique of profiling with a conductivity-temperature-pressure (CTP) unit to obtain the in-situ densities via the normal equation of state becomes flawed in these chemically altered waters (Brewer and Bradshaw, 1975). For small CO<sub>2</sub> and pH perturbations, the effect of added CO<sub>2</sub> gas is to consume carbonate ion and create bicarbonate—and the partial equivalent conductances of these species are well known, allowing for accurate corrections. But by pH 6, only 50% of the CO<sub>2</sub> present is as bicarbonate ion, and 50% as the un-ionized dissolved gas

molecule, markedly reducing the conductivity of the solution and introducing large errors into the estimate of the density gradient.

The observations of the deep Kolumbo crater water show a pH of ~5 at the bottom, and thus ~90% of the dissolved CO<sub>2</sub> must be in the un-ionized form, far outside the bounds of the standard equations. Carey et al. were clearly aware of this problem and made a useful first approximation to correct the derived densities. But the short duration of the mission and the early form of the observations prevent a full analysis that allows fluxes through the upper boundary to be calculated.

The pH observations are of great interest, as are careful measurements of the dissolved CO<sub>2</sub> in the recovered samples. The combination of the exsolved gas on recovery, plus the remainder in the 1-atm saturated solution, shows a maximum in-situ concentration of 50 mmol kg<sup>-1</sup>. If we combine this with the observed pH values and the known physical chemistry of sea water, we can estimate at what point (depth) this quantity of dissolved gas will spontaneously convert to the gas (bubble formation) phase. This is a critical quantity for the hazard calculation, because the large density change associated with the degassing step suddenly creates a rapidly rising plume. With the observed temperature of 17 °C, and assuming an alkalinity of 2300 μmol kg<sup>-1</sup>, I find that the in-situ *p*CO<sub>2</sub> is 1.35 atm, so that bubble formation will not occur until the fluid is transported (possibly displaced by a landslide, but without mixing) to 3.5 m depth. This seems unlikely to occur.

It thus appears that a Lake Nyos-type threat is unlikely at this time, but the finding is still of keen interest. The question of whether continued buildup can occur, and whether this can be self-stabilizing with a growing density contrast, yet remains. The site is remarkable as an example of extreme ocean acidification and its challenge to marine life. The observations clearly show marked corrosiveness to carbonate shells as the pH declines, and more complex forms of marine life are absent at depth in the crater. The lack of a sharp upper boundary and the more gradual decline of pH provide an elegant natural laboratory for ocean acidification research, complementing the opportunities at vents in other Mediterranean locations (Hall-Spencer et al., 2008) by providing gradients over a greater depth range. Carey et al. do not provide dissolved oxygen measurements, but the combination of high CO<sub>2</sub> and lower O<sub>2</sub> provides a powerful challenge to marine life and the O<sub>2</sub> gradients would be of great interest.

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