

Carbon dioxide degassing and estimation of thermal energy release from White Island volcano, New Zealand

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Accurate quantification and mapping of the total carbon dioxide (CO₂) emitted from a variably permeable volcano still remains a challenge. We used high resolution measurements of CO₂ flux and heat flow within the crater floor of White Island to characterise the mass (CO₂ and steam) and heat released. White Island is an andesite stratocone and New Zealand's most active volcano. Frequent phreatic, phreatomagmatic and magmatic eruptions have occurred throughout the 19th and 20th century. White Island's most recent magmatic explosive eruption occurred in 2000. Currently, the hydrothermal system is manifested by localised vigorous fumarolic activity, mud pools and mounds, and an acidic (pH ≈ -0.4) 200 m diameter crater lake, and diffuse degassing through the crater floor.

CO₂ flux degassing and thermal budget

In 2011, we performed 691 measurements of CO₂ flux using the accumulation chamber method. CO₂ flux values measured were ranged between of 0.1 – 29,896 g m⁻² d⁻¹. Total CO₂ emission rate estimated by stochastic simulation was 116 ± 2 td⁻¹ within the crater floor (0.31 km²). The δ¹³C range (-10 and -2‰) reflects the spatial variance in magmatic CO₂ contribution. Based on CO₂ flux data and a mean H₂O/CO₂ wt ratio of 15.3, the flux of thermal energy released from the crater floor totals 54 ± 1 MW. The associated rate of steam condensation is 1760 ± 25td⁻¹. The spatial distribution of surface heat flow, soil gas δ¹³C, surface hydrothermal features and CO₂ flux indicates high gas and thermal permeability at old crater margins, and breaks in slope (crater floor/wall, crater floor/mound). We suggest that areas of high degassing are associated with advective gas transport adjacent to persistent fumarole pathways. Areas of low permeability are associated with sulphur/anhydrite and iron oxide-silica precipitation crusts which limit gas diffusion to the surface. In addition, we explore the influence of sea water and meteoric water influx into the hydrothermal system.

Evidence of paleo sulfate methane transition zone in marine sediments

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The sulfate methane transition zone (SMTZ) denotes a redox interface within the anoxic sediment column where pore water sulfate and methane concentration profiles intersect and are depleted to non detectable concentrations. This depletion in sulfate and methane concentrations are attributed to the anaerobic oxidation of methane (AOM) performed by a syntrophic consortium of CH₄-oxidizing archaea and sulfate-reducing bacteria [1]. AOM causes marked enrichment in H₂S and HCO₃⁻ ion concentrations in the porewaters within the SMTZ, resulting in precipitation of Fe-sulfides, Ca-Mg-carbonates. Sulfate concentration profile, depth to SMTZ and thickness of SMTZ depend on the methane flux. High methane flux results in linear sulfate concentration gradient and shallow SMTZ and vice versa. In the Krishna-Godavari (K-G) basin, Bay of Bengal, seismic data [2] show regional presence of gas hydrates manifested in the form of a bottom simulating reflector (BSR). Sediment cores for the study were collected on-board Marion Dufresne and JOIDES Resolution as part of the gas hydrate exploration program in the K-G basin offshore. Our results show multiple carbonate bearing zones in the sediment with pronounced carbon isotopic depletion typical of AOM. Biogenic methane with δ¹³C ranging from -80 to -100‰ (VPDB) have earlier been reported [3] from K-G basin. In contrast, we have not recorded any appreciable barium front in any of the cores. The barium front possibly disappeared whenever the SMTZ moved up across an existing Ba front. However carbonate layers are not subject to such dissolution. The zones with depleted carbon isotope ratios are enriched in pyrite with heavy sulfur isotope ratios suggesting Rayleigh fractionation in a closed system. The sharp rise in ³⁴S_{CRS} indicate focussed sulfate reduction in SMTZ. In the long core NGHP-01-10D several such zones with heavy sulfur isotope ratios have been noted indicating paleo SMTZ transition zones. We propose that content and stable isotope ratios of authigenic carbonate and pyrite in marine sediments may serve as an ideal tool to detect fossil sulfate methane transition zone in the absence of barium front.

[1] Boetius et al. (2000) *Nature*, **407**, 623– 626.

[2] Ramana et al. (2004) *International Jour. Environmental Studies* **64**, 675-693.

[3] Mazumdar et al. (2009) *Geophy. Geochem. Geosys.*, **10**, 1-15.