

Thermobarometric implications of temporal and spatial variability in hydrothermal fluid SiO₂-Cl abundances through a full eruptive cycle at 9°50'N East Pacific Rise

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A persistent challenge to quantifying mass and heat flux to the oceans from mid ocean ridge hydrothermal systems lies in the translation of snapshots of fluid chemistry from transient systems to longer timescales. The hydrothermal field at 9°50' N in the East Pacific Rise provides an ideal natural laboratory to address the significant influence of an eruptive cycle on mass and heat contributions to the ocean. At this Ridge 2000 Integrated Study Site, approximately twenty vents have been sampled for high-temperature fluids in the last sixteen years. Extending earlier studies [1], we use fluid chloride and silica contents, coupled with thermodynamic data [e.g., 2, 3] to place constraints on the T, P conditions of fluid circulation. The fluid time-series includes samples with chloride contents greater than 1 molkg⁻¹ and silica contents greater than 20 mmolkg⁻¹. Generally, Cl and SiO₂ contents in all vents evolve non-monotonically with time, emphasizing that every vent represents a unique pathway but can contribute to a high resolution model of the spatially and temporally variable magma chamber dynamics. For example, in the case of M-vent, the thermobarometric model indicates P, T conditions suggesting a gradual shoaling with time until its extinction.

[1] Von Damm (2004), *Geophys. Monogr. Ser.* [2] Von Damm *et al.* (1991), *A. J. Science* **201** 977-1007. [3] Foustoukous and Seyfried, (2007) *Geochim. Cosmochim. Acta* **71** 186-201.

Marine aerosol and photochemistry

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The production of sea salt aerosol is, with dust, globally the strongest natural aerosol source. An important role of sea salt derived bromine for the photochemistry of the marine boundary layer (MBL) has long been suggested by model studies and recently been confirmed by field measurements at Cape Verde (Read *et al.*, 2008). Further recent measurements showed very high mixing ratios of ClNO₂ in polluted coastal areas (Osthoff *et al.*, 2008) and Cl₂ under clean conditions at Cape Verde (Lawler *et al.*, submitted) demonstrating that chlorine chemistry is not limited to the release of HCl from sea salt aerosol.

This presentation will briefly review the current state of the field and focus on model results for the role of sea salt aerosol in the oxidation of sulphur and of sea salt-derived halogens for the photochemistry in the MBL. Particularly the role of sea salt and halogens in the so-called CLAW hypothesis will be highlighted. BrO and Cl can oxidize dimethyl sulphide (DMS) very efficiently, albeit leading to different products. The fate of several intermediates of DMS breakdown is not entirely understood yet but several of these intermediates are highly soluble, taken up by aerosol particles and cloud droplets and therefore reduce the conversion efficiency of DMS to SO₂, the key H₂SO₄ precursor, required for new particle formation. In addition to these gas phase processes involving halogens, the hypohalous acids HOBr and HOCl (and dissolved O₃ under high pH conditions, typical of fresh sea salt) contribute to the production of sulphate in aqueous particles. The implications of these halogen-sulphur links are mainly a reduction in the formation of new cloud condensation particles but a growth in the size of the existing ones with important implications for the climate forcing of, e.g., stratocumulus clouds which are prevalent in the MBL.

Pollution from coastal megacities and ship plumes influence the chemistry of the MBL in large ocean regions and is expected to increase in the coming decades. The presence of high NO_x concentrations in the polluted MBL can result in transforming large ocean regions from areas in which net ozone destruction prevails to net ozone production areas. On the other hand, nitrogen oxides lead to an increase of halogen release (chlorine and bromine) from sea salt which increases ozone destruction. A first attempt at quantifying the net effect of these processes will be made.