

Laboratory studies into sea-spray chemical speciation in plankton-enriched sea-water

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Marine aerosol enrichment by biogenic organic matter (OM) has been linked to phytoplankton activity [1], thus having a strong seasonal impact on both the Earth's albedo and climate. In addition to a seasonal cycle, sea-spray generation and its enrichment with OM is a very dynamic process producing regular OM plumes over N.E. Atlantic [2]. Plankton-enriched seawater contains a complex mixture of dissolved and particulate organic carbon components (POC and DOC) producing both water soluble and insoluble organic aerosol species [3, 4]; this warrants detailed laboratory studies aimed at establishing a link between observed ambient aerosol OM and its very primary form.

Laboratory studies using the microalgal species *Emiliania huxleyi*, *Leptocylindrus danicus* and *Cylindrotheca closterium* were performed using on-line and off-line analytical techniques, a sea spray production chamber and an ageing chamber with day-light and ozone. Under controlled conditions a sea spray highly enriched in OM was produced with levels similar to Facchini *et al.* [3]. HR-ToF-AMS, ¹HNMR and HTDMA techniques confirmed OM composition of highly hydrocarbon-like, water insoluble OM characteristic of unsaturated lipids exhibiting low hygroscopic growth factor. Freshly produced OM, while largely insoluble, was far less oxidised (less sugars) than the OM reported by Facchini *et al.* [3]. Processing with light and ozone continued to support primary origin of ambient OM.

[1] O'Dowd, C.D., *et al.* (2004) *Nature* **431**, 676-680. [2] Ovadnevaite, J., *et al.* (2011) *Geophys. Res. Lett.* **38**(2), L02807. [3] Facchini, M.C., *et al.* (2008) *Geophys. Res. Lett.* **35**(17), L17814. [4] Russell, L.M., *et al.* (2010) *P. Natl. Acad. Sci. USA* **107**(15), 6652-6657.

Mineralogy and geochemistry of zeolites of pyroclastic deposits in Northwestern of Tuzgölü Basin (Turkey)

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The Early Miocene volcanic rocks in the Kulu (Konya)-Haymana (Ankara) area were classified as andesitic-dacitic lavas and pyroclastics, and in some cases as trachytic and trachyandesitic. The zeolitic tuff layers are interbedded with bentonite layers and rarely silica lenses or thin layers. Plagioclase crystals, glass shards, and volcanic rock fragments altered to zeolites and smectite in tuff of the volcanic rocks. Clinoptilolite/heulandite, erionite/offlerite, analcime, and chabazite and rarely phillipsite and mordenite occur with other authigenic minerals, e.g. Fe- and Mg-rich smectite, K-feldspar. Gypsum, calcite, dolomite, and hexahydrate were also found in the some altered tuffs and clay layers. The zeolite minerals grow up as crypto- to microcrystalline aggregates after dissolved glass fragments in cavities and represent most of the matrix in the altered tuffs.

Nine K-feldspar, twelve plagioclase and sixty nine zeolite minerals were analyzed by microprobe. Zeolite analyses were made on single crystal and crystal clusters of heulandite, clinoptilolite, erionite, and chabazite. The structural formulae of the feldspar were calculated as $(\text{Si}_{2.98}\text{Al}_{1.03})(\text{K}_{0.67}\text{Na}_{0.27}\text{Ca}_{0.01})$ and $(\text{Si}_{2.67}\text{Al}_{1.31})(\text{K}_{0.05}\text{Na}_{0.60}\text{Ca}_{0.28})$, respectively, and the zeolite minerals as $[(\text{Si}_{28.7}\text{Al}_{7.3})(\text{Mg}_{1.5}\text{Ca}_{0.9}\text{Sr}_{0.1})(\text{K}_{1.0}\text{Na}_{1.3})]$, $[(\text{Si}_{29.6}\text{Al}_{6.4}\text{Fe}_{0.1})(\text{Mg}_{1.0}\text{Ca}_{1.0}\text{Sr}_{0.1})(\text{K}_{0.8}\text{Na}_{0.9})]$, $[(\text{Si}_{28.3}\text{Al}_{8.2})(\text{Mg}_{1.7}\text{Ca}_{0.3}\text{Sr}_{0.1})(\text{K}_{2.0}\text{Na}_{1.2})]$, and $(\text{Si}_{9.88}\text{Al}_{2.18}\text{Fe}_{0.01})(\text{Mg}_{0.2}\text{Ca}_{0.6}\text{Sr}_{0.03})(\text{K}_{0.3}\text{Na}_{0.17})]$, respectively. Clinoptilolites are mostly high-silica Ca-rich heulandites having intermediate composition between heulandites and clinoptilolites. Si/Al ratios of heulandites (3.70-4.20) and clinoptilolites (4.30-5.30) are similar to heulandite group minerals and their divalent/monovalent cation ratios range from 0.41 to 5.75 and 0.44 to 3.6, respectively. The structural (Na+K) content is higher than that of (Ca+Ba+Sr) in all heulandite group minerals and erionites. Mean Si/Al ratio of erionites is 3.40 and divalent/monovalent cation ratios are between 0.42 and 1.25. Zeolite minerals, e.g. analcime, chabazite, erionite, and phillipsite, and saline minerals such as gypsum, calcite, dolomite and hexahydrate were precipitated in a closed alkaline and saline environment. High proportions of alkali cations would indicate that highly alkaline pH values are likely in pore water in the tuff.