Regional scale OA oxidation observed over the Po Valley basin (Italy), at Mt. Cimone (2165 m asl)

M. RINALDI[1], S. GILARDONI[1], S. DECESARI[1], S. FUZZI[1], P. CRISTOFANELLI[1], P. BONASONI[1], S. FERRARI[2], V. POLUZZI[2] AND M.C. FACCHINI[1]

[1]Istituto di Scienze dell'Atmosfera e del Clima, Consiglio Nazionale delle Ricerche, Bologna, 40129, Italy (*correspondence: m.rinaldi@isac.cnr.it)

[2]Centro Tematico Regionale Aree Urbane, Arpa Emilia-Romagna, Bologna, 40138, Italy

High resolution time of flight aerosol mass spectrometer (HR-ToF-AMS) measurements have been performed, for the first time, at Mt. Cimone GAW station (44°12' N, 10°42' E, 2165 m asl) from 11 June to 9 July 2012, under the framework of the EU project PEGASOS and the Emilia-Romagna Region project SUPERSITO.

The peculiar character of the site allows the investigation of organic aerosol (OA) ageing occurring at regional scale over the Po Valley. In fact, particles sampled during the day are representative of the early stages of aerosol atmospheric oxidation, comprising processed primary OA and secondary OA formed in the Po Valley basin, being the site within the planetary boundary layer (PBL). During the night, the aerosol sampled at Mt. Cimone is representative of more processed conditions, as the site is in the free troposphere (FT), containing aerosols with an age from several hours to days.

Elemental analysis performed with high resolution mass spectra [1], revealed decreasing average H/C and increasing O/C ratio from PBL to FT samples. As a consequence, the OM/OC ratio passes from 1.83±0.05 in PBL, to 1.94±0.08 in FT samples.

These results evidence the progressive oxidation of OA over the Po Valley basin, from few hours after their emission/formation to one or more days of atmospheric processing. On a Van Krevelen space, the data produce a slope of ~ -1, suggesting that the observed regional scale oxidation processes occur mainly through the addition of carboxylic functional groups [2]. This is further confirmed by the analysis of the HR mass fragments, showing that, from PBL to FT samples, the average contribution of fragments containing carbon, hydrogen and more than one oxygen atom (CHO>1) passes from 25% to 33%, while both CH and CHO fragments decrease their contribution.

[1] Aiken *et al.* (2007) Anal. Chem. **79**, 8350-8358. [2] Heald *et al.* (2010) Geophys. Res. Lett. **37**, L08803.

Sr^{2+} and Mn^{2+} incorporation during $CaCO_3$ cementation on calcitic and aragonitic shells

T. RINDER[1]*, M. DIETZEL[2] AND A. DEDITIUS[2]

[1]GET/CNRS, 14 avenue Édouard Belin, 31400, Toulouse(*correspondence: rinder.thomas@gmx.net)

[2]TU Graz, Institute of Applied Geosciences, Rechbauerstr. 12, Graz, Austria

Precipitation of calcium carbonates may cause significant changes in the porosity, permeability and overall physical properties of sedimentary rocks. For instance in sandstone the loss of permeability and porosity negatively influences the potential quality of the hostrock as a hydrocarbon or groundwater reservoir [1]. In recent years more attention to cementation issues is received for the increasing efforts to reduce CO_2 emission into the atmosphere and the possibility of long term storage by means of underground fixation in carbonates [2].

In the present study flow through experiments were carried out to investigate carbonate cementation of primary unconsolidated shell material by investigation of the spatial distribution and trace element incorporation of the precipitated material. $NaHCO_3 – Na_2CO_3 – CaCl_2$ solutions supersaturated with respect to calcite were pumped through columns packed with shell fragments of a grain size between 0.5 and 1mm. Sr^{2+} and Mn^{2+} addition was used to trace the temporal and spatial evolution of newly formed precipitates in the pore space.

Overall distribution coefficients calculated from aqueous bulk solutions result in a D_{Sr} of 0.68 and D_{Mn} of 6.08 for the precipitated $CaCO_3$. These coefficients are in good agreement with literature values within the given proportions of precipitated calcite and aragonite. However, apparent measured distribution coefficients in the newly formed $CaCO_3$ solids derived from electron microprobe analysis are highly heterogeneous and results in a maximum D_{Sr} and D_{Mn} value of 18 and 163, respectively.

Alternating trace element rich and poor growth zones were discovered in our experiments carried out at a constant solution composition, temperature and flow rate. We suggest that the incorporation behaviour depicted by bulk ratios which serve as proxies for the reconstruction of environmental conditions during precipitation of $CaCO_3$ is not necessarily valid on the microscale. The actual locally occurring trace element incorporation into $CaCO_3$ can significantly exceed or fall below the average bulk incorporation.

[1] Taylor & Machent (2011),*Marine and Petroleum Geology* **28**, 1461-1474. [2] Matter *et al.* (2009), *Energy Procedia* **1**, 3641-3646.

DOI:10.1180/minmag.2013.077.5.18