

Possible rôle of internally mixed crustal materials in the enrichments in sulphur of supermicrometric Antarctic coastal aerosol particles

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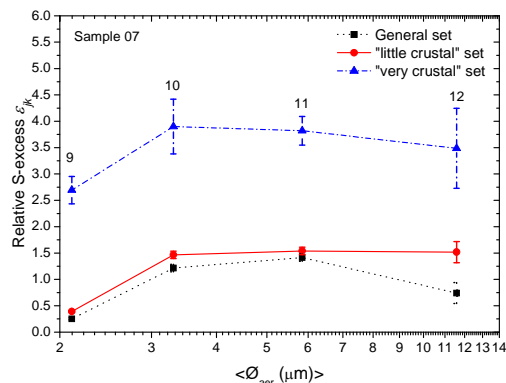
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The interactions of gaseous sulphur compounds with supermicrometric sea-salt particles may play an important rôle (1, 2) in the fluxes of such compounds out of the atmosphere at the Antarctic coastal site Baia Terra Nova (Lat. 74°42'43"S, Long. 164°06'58"E). Indirect evidences suggest a possible rôle of internally mixed crustal materials in those interactions (1,2). Here we try to face this last problem by means of microPIXE single particle analysis of three size-segregated coastal aerosol samples, collected (2002/03 campaign) at BTN, in the framework of a multiannual experiment. An SDI 12-stage impactor was used; bulk PIXE analysis covered the full SDI size range, whereas microPIXE concerned only the first four SDI stages ($12. > \langle \text{O}_{\text{aer}} \rangle > 1.6 \mu\text{m}$). The elemental masses (fg) of up to 9 elements (Na, Mg, Al, Si, S, Cl, K, Ca, Fe) were measured in 2800 particles. Elements Na and Cl were detected in (virtually) all particles; Si in roughly 60% and S in 90% of the particles. The results of a Principal Component Analysis, "PCA", of the multielemental data, concerning separately each size-segregated subsample and several distinct groups of elements, were published elsewhere (3). Depending on the particular group of considered elements (and on the corresponding set of particles), only one Principal Component, "PC", (interpreted as "sea-salt"), or, alternatively, two PC's ("sea-salt" and "crustal") satisfactorily explain the data. Elements Na and Si are convenient quantitative signatures of the two PC's. An "Internal Mixing", "IM", of crustal and sea-salt materials is present in those particles containing, at least, Si. Element S doesn't fit the PCA framework.

We can now face the initially mentioned problems by considering only the behaviour of elements Na, S, Si. We characterize each particle i by means of: $m_{\text{Na}}^i, m_{\text{S}}^i, m_{\text{Si}}^i$, respectively its Na, S, Si masses; $R_s^i = (m_{\text{S}}^i / m_{\text{Na}}^i)$, its S vs Na mass ratio; $E^i = (R_s^i / R_{\text{sw}})$, its "S-enrichment factor", R_{sw} being the sea-water S/Na density ratio; $e^i = (E^i - 1)$, its relative "S-excess", which corresponds to the individual $nssS/ssS$ (non-sea-salt/sea-salt) ratio. m_{S}^i vs m_{Na}^i scatterplots conveniently describe the situation for each size-segregated subsample jk of sample k . It is found that: almost always $e^i \geq 0$, (an indication of the overall quality of the results); the values of e^i are widely dispersed (thus explaining the impossibility of fitting PCA). The quantity

$$\varepsilon_{jk} = \left[\left(\frac{\sum_i m_{\text{S}}^i}{\sum_i m_{\text{Na}}^i} \right) / R_{\text{sw}} - 1 \right] = (nssS / ssS)_{jk}$$

is the overall relative S-excess of subsample jk . Furthermore, we evaluate the individual relative amount of crustal materials by means of R_{Si}^i , the Si/Na mass ratio, and subdivide the particles into distinct sets, depending on whether their R_{Si}^i value is larger ("very crustal set") or smaller ("little crustal set") than a convenient cut value (the same for all subsamples). A further set, "general set", contains all the particles. We can thus evaluate for each subsample jk , three distinct values of ε_{jk} , corresponding respectively to the "little crustal set", the "general" set and the "very crustal set", in an order of increasing relative amounts of crustal materials. The figure displays the situation for sample 07. $\langle \text{O}_{\text{aer}} \rangle$ is the geometric mean value of the aerodynamic diameter of each SDI stage. The values of ε_{jk} corresponding to the "very crustal" set are found to be much larger than the others. The other samples display similar results. The above is evidence that large mass fractions of crustal materials in the particles favour increased gas-particle interactions. More convenient sets, based on the presence, or the absence, of Si, are going to be used soon.



References

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