

Grain scale pressure heterogeneity produced through volume change associated with mineral reaction

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Recent work on melting, corona textures and phase precipitation developed in high metamorphic-grade rocks has focused on the chemical potential relationships that account qualitatively for the spatial and chemical relationships involved. There are two related ways in which this work can be advanced. The first involves using or devising diffusion coefficients to move towards quantitative modelling. The second, more critical step is to realize that mineral reaction cannot take place independently of the strength of its immediate environment. We will consider various aspects of this, on the basis that the diffusional relaxation modifies the elastic state of the material and affects its mechanical properties. As the induced stress may have a profound effect on diffusion in a solid, the elastic and chemical response of the material must be taken into account simultaneously. In geomaterials, only limited information exists on reactions that involve chemical transport combined with reaction-induced stress, but the mechanical feedback of volume change that is involved in chemical reaction in rocks may significantly control the progress of reaction. Pressure variations that existed at the grain scale during decompression and cooling of higher-pressure rocks are likely to have influenced the final microstructure. Our data based on numerical modelling show that pressure variations may be generated and maintained on a geological time scale as a result of the mechanical feedback of the rock during metamorphic reactions which take place in a restricted space.

Decrease of the potential of oxalic acid and other organic acid aerosols as cloud condensation nuclei by the complex formation with metal ions

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Secondary organic aerosols (SOA) play a key role on the solar radiation balance in troposphere, since SOA can act as cloud condensation nuclei (CCN) due to its high hygroscopic nature. Oxalic acid is one of the most dominant components of SOA, which has cooling effects of the earth by acting as CCN. However, it is uncertain whether the oxalic acid can exist as free oxalic acid or metal-oxalate complexes in aerosols, even if there is a large difference in their solubilities into water. Consequently, XAFS measurement was conducted to demonstrate the presence of metal-oxalate complexes.

Size fractionated aerosol samples were collected in Tsukuba (located at northeast about 60 km from Tokyo) using a low-volume Andersen-type air sampler. The sampler had eight stages and a back-up filter. The sampling was conducted during winter and summer in 2002.

Calcium oxalate was observed in finer particles in each period from Ca K-edge XANES, and its fractions among total Ca were approximately 20%. Similarly, Zn oxalate was also detected in finer particles from Zn K-edge XANES and EXAFS. The [Zn-oxalate] / [Zn]total ratio in each period clearly increased with the decrease in the particle diameter. This result revealed that Zn-oxalate was formed in the aqueous phase at particle surfaces or in cloud processing. In other words, Zn-oxalate was abundant at the particle surface, resulting from the increase in the [surface]/[bulk] ratio with decreasing particle size. Based on (i) total concentrations of oxalate, Ca, and Zn determined by ion-chromatography and ICP-AES analyses and (ii) Ca- and Zn-oxalate fractions obtained by XAFS, we determined the fraction of metal-oxalate complexes among total oxalate in aerosols. In winter, Ca- and Zn-oxalate fractions reached about 60% of total oxalate in the ranges of 1.1-2.1 μm and 0.65-1.1 μm , while the value was about 60-80% in the same particle size range in summer. On the other hand, Ca- and Zn-oxalates are highly insoluble, showing that the complexes cannot act as CCN. Therefore, the ability of oxalic acid as CCN is needed to be reconsidered, because most of oxalic acid in aerosols exists as metal-oxalate complexes as shown by XAFS spectroscopy in this study. Moreover, the formation of stable metal-oxalate complexes at particle surface can inhibit the chance of the particle's activation to produce other chemical species.

References

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