

Formation of iron nanoparticles during dust cloud processing

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The large variations in pH of natural cloud water may lead to changes in phases of the iron (Fe) minerals in the dust. The speciation and reactivity of the Fe phases in dusts incorporate into clouds are however, not known. In this study, we investigated the changes in Fe speciation during simulated cloud processing of two Saharan soil samples using traditional Fe sequential extraction techniques and modern ultrahigh resolution microscopic and diffraction techniques.

The variations in pH within natural clouds were simulated experimentally by adding H₂SO₄ to pH=2 and then NH₄OH to pH=5-6 to pre-sieved (< 20 μm) Saharan soil solutions (30 mg L⁻¹) and reacting them for 24 hours. Imaging and diffraction analyses of the processed samples indicated that the simulated processing induced the neo-formation of Fe-rich nanoparticles, which were not found in the non-processed soils. The reactive Fe content (nanoparticulate and amorphous Fe) in the two processed Saharan soils were higher than those in the corresponding non-processed soils, providing a means of determining quantitatively the amount of newly formed nanoparticles produced as a result of the 'cloud' processing.

Fe-rich nanoparticles were also observed in a natural sample of Saharan dust collected from a rain event in the western Mediterranean, but neither present in dry deposited Saharan dust from the eastern Mediterranean nor the Saharan soils. The observed nanoparticles in the western Mediterranean samples were similar in composition to those formed in the experimentally 'cloud' processed Saharan soils. These findings were also confirmed by the higher reactive Fe contents of the 'wet' western Mediterranean Saharan dust sample compared to those in the non-processed Saharan soils or in the 'dry' eastern Mediterranean dust sample.

These results suggest that 'cloud' processing of mineral dust could result in the formation of chemically more reactive Fe-rich nanoparticles.

Middle Archean CO₂ flux into oceanic crust from ocean

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We estimated CO₂ flux from ocean to oceanic crust at Archean mid-ocean ridge based on hydrothermal carbonatization of Archean mid-ocean ridge basalt in the 3.0-3.2 Ga Cleaverville area located in the north western part of the Pilbara Craton, Western Australia.

The stratigraphically upper part of the Cleaverville area is composed mainly of sedimentary rocks of bedded chert, banded iron formation, and clastic rocks of sandstone, mudstone and minor conglomerate (Cleaverville Formation), whereas the lower part comprises at least 4 km-thick basaltic greenstones with volcanic structures of pillow lava, pillow breccia and sheeted flows (Regal Formation). Because of the low metamorphic grade that ranges from sub-greenschist to greenschist facies at low-pressure condition [1], the greenstones well preserve original igneous texture such as intersertal, intergranular and hyaloophitic textures.

The carbonate minerals occur primarily as matrix minerals that replace igneous phases such as glass, plagioclase and clinopyroxene, which suggest that the carbonate minerals were formed by the first hydration event, namely mid-ocean ridge hydrothermal alteration. The greenstones show various extent of carbonatization but volume concentration of the carbonate minerals in the greenstones decreases stratigraphically downward, which most likely reflect the geothermal gradient of ancient oceanic crust because carbonate minerals become unstable with increasing temperature in the basalt-H₂O-CO₂ system. Stable carbon and oxygen isotope ratios of carbonate minerals indicate that the CO₂ in hydrothermal fluid was derived mainly from seawater and that magmatic contribution of mantle-derived CO₂ was quite small. These results revealed that CO₂ flux from ocean to upper oceanic crust at Archean mid-ocean ridge was extremely higher than modern equivalent. It is therefore concluded that the Archean hydrothermal carbonatization of upper oceanic crust had a great potential to change CO₂ level in the atmosphere-ocean.

[1] Shibuya *et al.* (2007) *J. Metamorphic Geol.* **25**, 751-767.