

FTIR spectral analysis of PM₁₀ and PM_{2.5} particulate matter over the urban area of Palermo (Italy) during normal days and Saharan events

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The principal sources of particulate matter in Palermo urban area are gasoline and diesel-powered vehicles, domestic heating, resuspension of soil dust and a geogenic source which includes soil erosion, marine aerosol and sporadic Saharan events. Annual average PM₁₀ and PM_{2.5} concentrations result 27.8±9.8 and 21.3±5.1 µg/m³. The highest mass levels, 246 and 65 µg/m³ respectively for PM₁₀ and PM_{2.5}, were observed during Saharan events. For the present study, which uses the ATR-FTIR spectroscopy to provide insights on the chemical composition of airborne particulate matter, a total of 89 filters were collected: 13 PM₁₀ filters from a sub-urban background station, 36 PM₁₀ and 40 PM_{2.5} filters from a sampling site exposed to heavy traffic. ATR-FTIR spectra were acquired with a Tensor 27 (Bruker Optics) FTIR spectrometer operating in the infrared (370–7500 cm⁻¹) region. After correction for the background spectrum all the analyzed spectra showed vibrational frequencies at 616 and 1088, 813 and 1352, 1414 cm⁻¹, corresponding to SO₄²⁻, NO₃⁻ and NH₄⁺ ions, respectively. The simultaneous presence of these ions, confirmed by LC and UV-VIS techniques, suggests the formation of secondary particulate of ammonium nitrates and sulphates. The peak at 778 cm⁻¹ was attributed to geogenic CO₃²⁻ ions derived from erosion of local carbonate rocks. PO₄³⁻ ions, identified by the peak at 535 cm⁻¹, were detected in suburban samples as well as in urban samples and they are indicative of contamination from phosphate industries of North Africa although their origin from pollen grains cannot be ruled out. FTIR also identified several organic functional groups, although specific organic molecules could not be identified. The broad band in the aliphatic stretching region (2800–3000 cm⁻¹) with sharp peaks at 2850, 2920 and 2952 cm⁻¹, was attributed to aliphatic C-H vibrations. The urban filters exposed to SW and SE winds (from North Africa) are characterised by peaks at 913 cm⁻¹, 3620 and 3698 cm⁻¹, indicative of OH-stretching in clay and also peaks at 3404 and 3545 cm⁻¹ typical of gypsum.

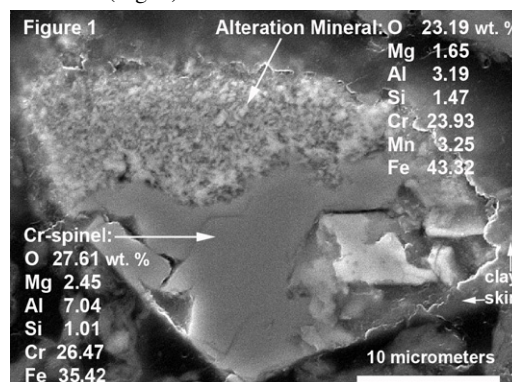
Weathering textures and chemical changes of Cr-bearing spinels, California

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Soils developed on ultramafic rocks contain elevated concentrations of Fe, Mg, Cr, and Ni. Weathering of ultramafic rocks (serpentinite) in the Coast Range and Sierra Nevada foothills of California enriched Cr and Ni in soils of the Sacramento Valley. We compare and contrast the *in situ* weathering of Cr- and Ni-bearing minerals in serpentinite from both source areas, as well as alluvial soils, to document mineralogic transformations that occur with respect to Cr and Ni. Cr-rich spinels, which contain non-toxic Cr (III), are relatively refractory; therefore Cr is not easily bioaccessible. Cr-spinels are the primary source of Cr in serpentinites, whereas Ni is primarily found in the serpentine minerals lizardite, antigorite, and chrysotile. Ni also occurs in trace amounts in spinel minerals.

Weathered Cr-bearing spinels examined by scanning electron microscopy and energy dispersive X-ray show that Coast Range Cr-spinels are Al-poor, whereas spinels from the Sierra Nevada are Al-rich. Although there are primary chemical differences, Cr-spinels from both provenances exhibit similar weathering textures of interpenetrative dissolution reaction fronts between the core grain and alteration minerals (Fig. 1). Secondary fine-grained alteration minerals commonly show a decrease in Mg, Al, Cr, and an increase in Fe content, which demonstrates the mobility of these metals (Fig. 1). Both authigenic clay platelets and illuvial clay skins around Cr-spinel grains in alluvial soils are enriched in Cr (Fig. 1).



The extensive weathering textures in the refractory Cr-spinels and decreased Cr concentrations are evidence that Cr has mobilized, potentially transforming to a more bioaccessible form adsorbed on surrounding clays or incorporated into Mn- and Fe-oxides. Importantly, the alteration products include Mn (Fig. 1), which can act as an oxidant for non-toxic Cr (III) in Cr-spinel to potentially toxic Cr (VI).