Determination of Trace Metals in Individual Air Particulates Using Transmission Electron Microscopy

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Abstract

Ultramafic rocks, primarily serpentinite, in northern California contain high levels of Cr and Ni, both of which are known carcinogens. Due to weathering and land usage practices, these serpentinites are transported into the highly populated Sacramento Valley. There, Cr and Ni concentrate in soils. While Cr and Ni generally remain in refractory states in larger soil particles, soil samples of <2μm have been subjected to simulated gastric and lung fluids, and shown to readily dissolve. At this time, little is known about the fraction of soil that is small enough to be captured as airborne dust. Our research will investigate the nature of Cr and Ni in airborne dust, as well as Zn, As, Pb and asbestos fibers. We will use a 200kV transmission electron microscope (TEM) to analyze air filters supplied by the California Air Resources Board in order to determine the potential for inhalation risk of Cr and Ni.

Introduction

Ultramafic rocks in northern California contain elevated levels of Cr (1700 to 10,000 mg kg -1) and Ni (1300 to 3900 mg kg-1), as well as asbestiform minerals (Goldhaber et al., 2009). These materials are known to negatively affect human health, especially lung health. Chromium and Ni concentration in bulk soils range from 80 to 1420 mg kg-1 Cr and 65 to 224 mg kg-1 Ni. This is concentrated with respect to a U.S. mean of 37 mg kg -1 Cr and 13 mg kg-1 Ni. Chromium and Ni concentrations are substantially higher in finer grained fractions < 2μm.

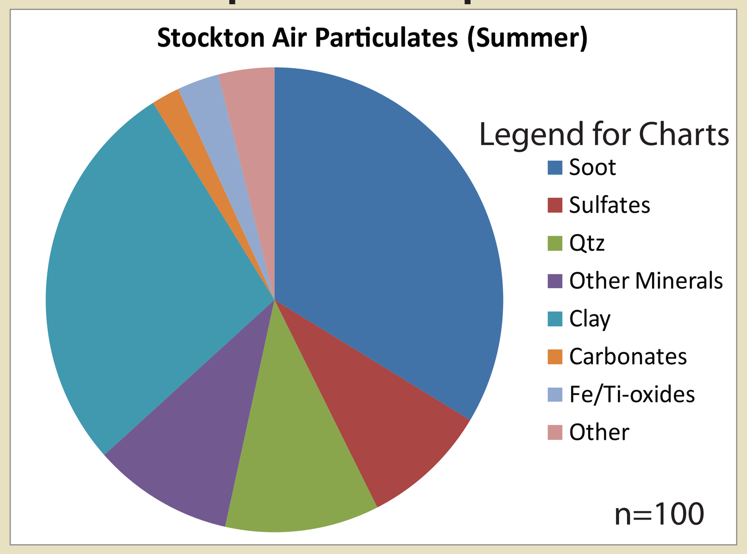
Soil sequential digestions from the central valley of California by J.M. Morrison during her dissertation research found that, while much of the Cr and Ni remains in refractory states in serpentinite and in the mineral chromite in coarse fractions (> 20μm) a significant amount has been weathered into sizes <2 μm. This fraction of the soils contains clays and iron oxide nanocrystalline particles that are considerably more concentrated in Ni (commonly up to 10,000ppm) and Cr (commonly up to 8000ppm). The nanocrystalline oxides are particularly bioaccessible as measured by digestions in simulated stomach and lung fluids.

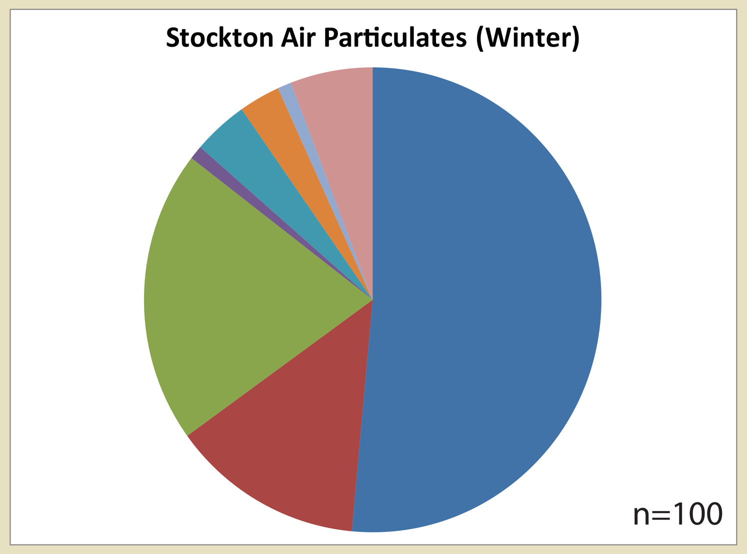
Higher trace element concentrations are associated with increased incidence of lung cancer in the study area and have resulted in the need for understanding the nature and distribution of these more bioaccessible forms. While soils characterization has been completed and is in the process of being submitted for publication little is currently known about the chemistry of the soil particles that become airborne dust.

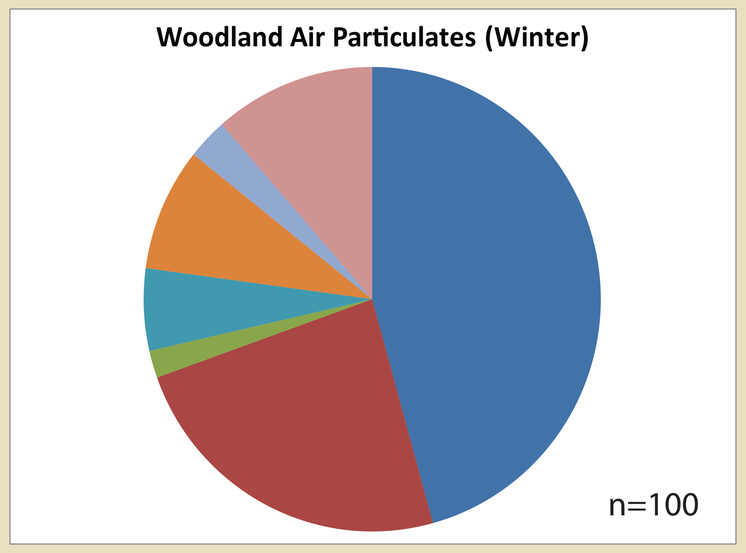
Methods

Samples were prepared using an agate mortar and pestal to remove dust particles from filters immersed in ethanol. Drops of the solution were dried on copper mesh grids coated with lacey carbon. Samples were then analyzed using a Jeol 2010 200kV analytical TEM with count times of 300 seconds per particle.

Air Sample Composition

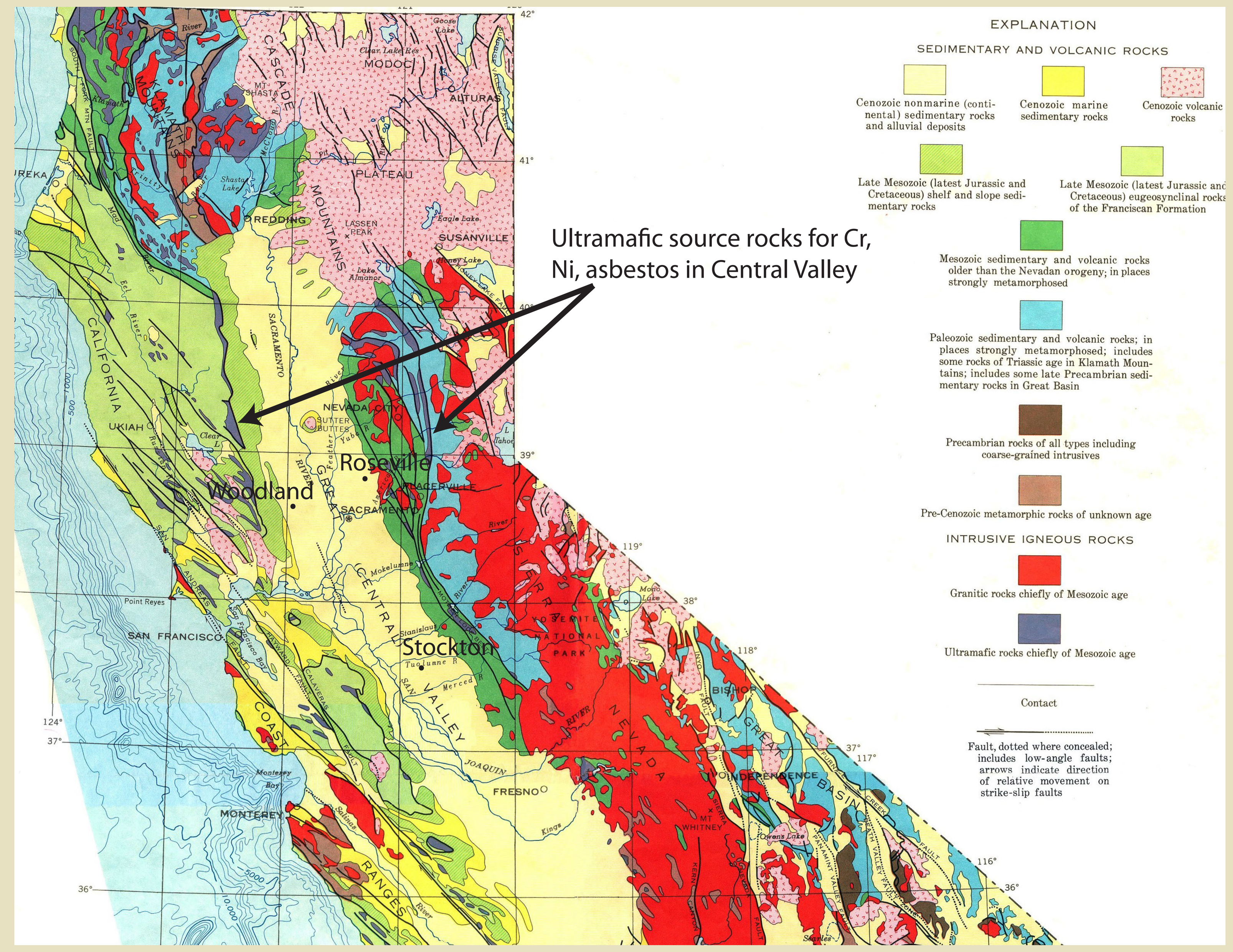






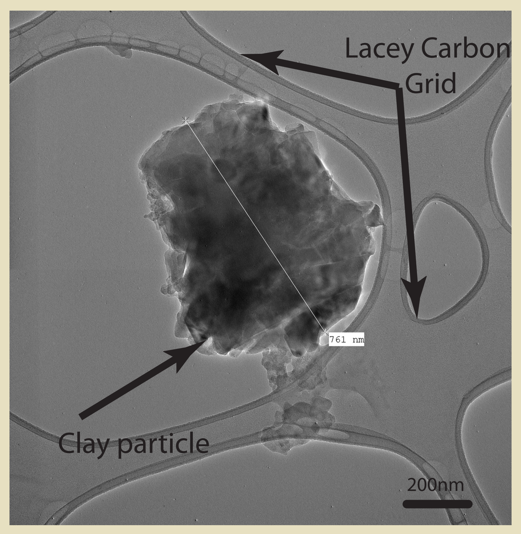
100 point counts show variations in dust components. Comparisons between locations, as well as seasonal differences reflect changes in dust composition and metal content. For example, summer air (dry season) has higher % of mineral dust.

Study Area



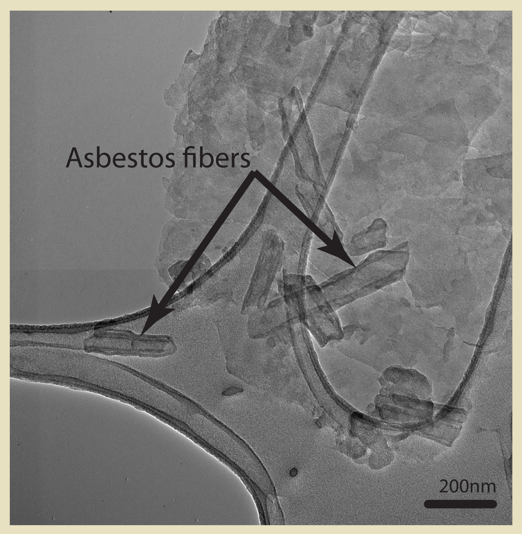
Air Particulates

Clay



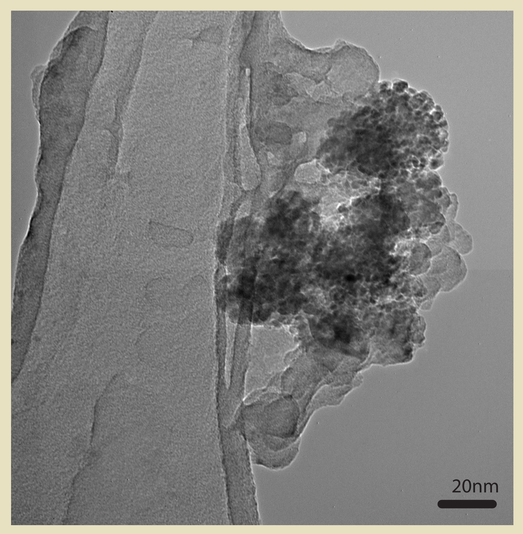
Trace metals Cr, Ni, Pb and As are frequently present in airborne clay particles.

Asbestos

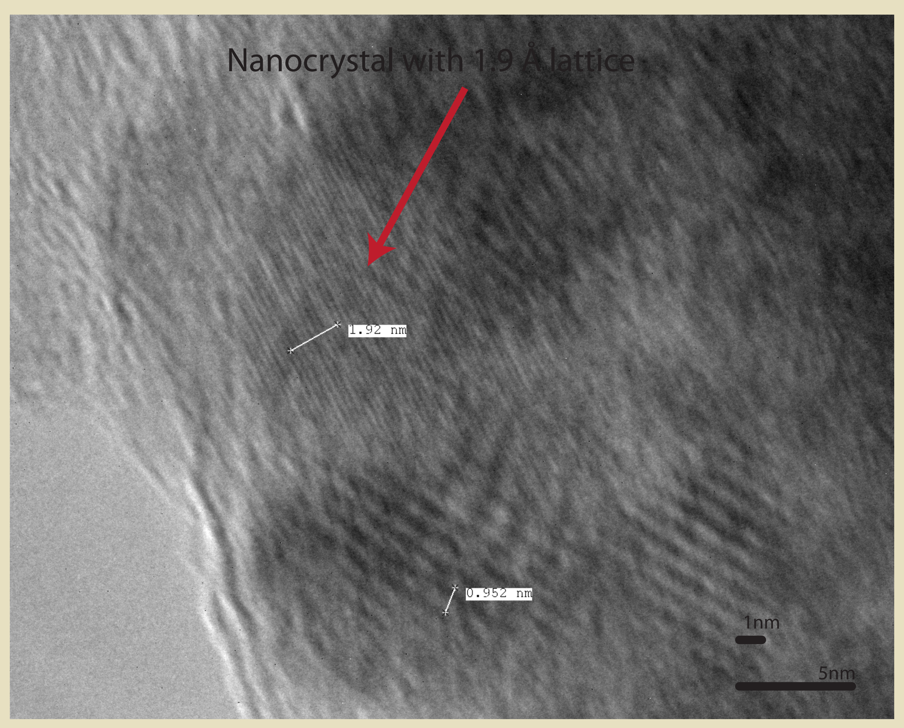


Asbestos particles found in airborne dust from the Sacramento Valley, CA

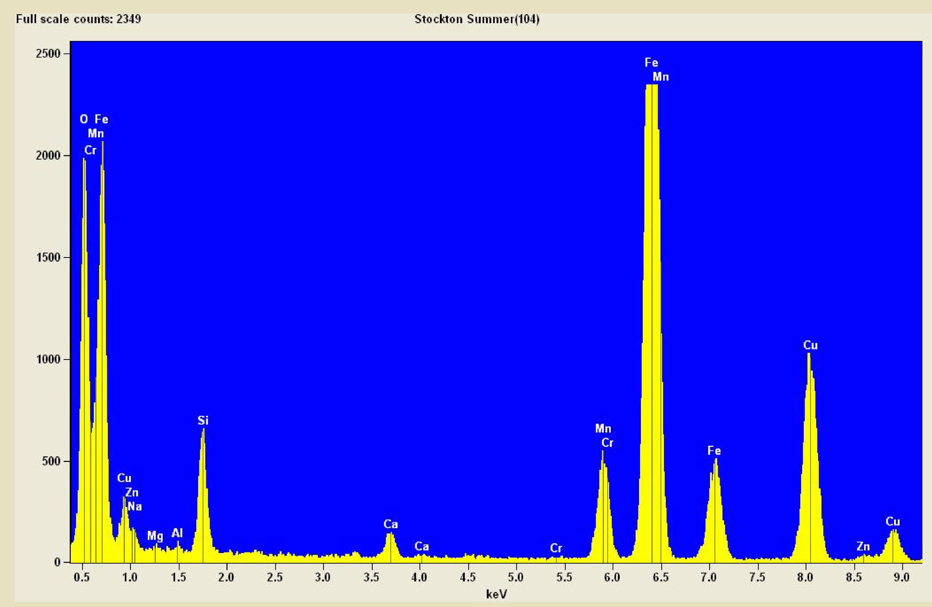
Fe-Oxides



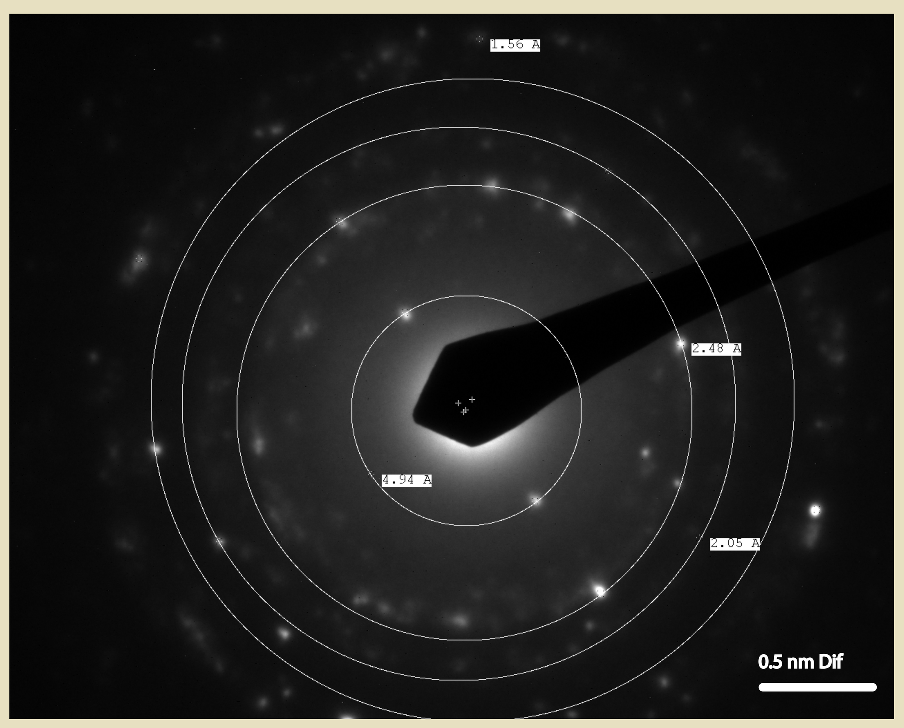
Overview of Fe-oxides "clumps." These nanoparticles often contain Cr and Ni which can cause lung cancer if inhaled.



Lattice imaging in Fe-oxide nanoparticles show nanocrystalline nature of Fe-ox. Small lattice measures 1.9 Å. Small particles represent neocrystallites.
(Note: Single Fe^{2+} atoms have diameters of approx. 1.54Å.)

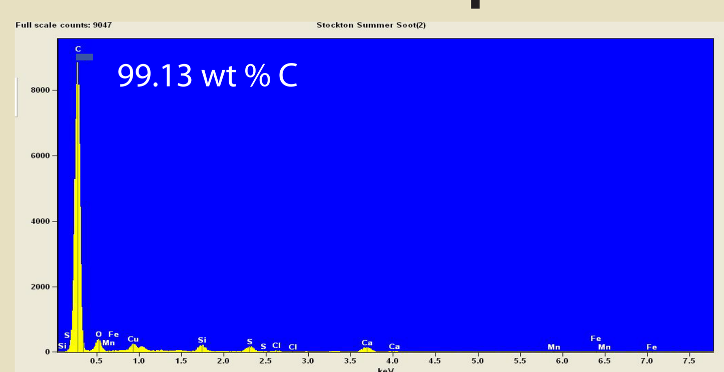


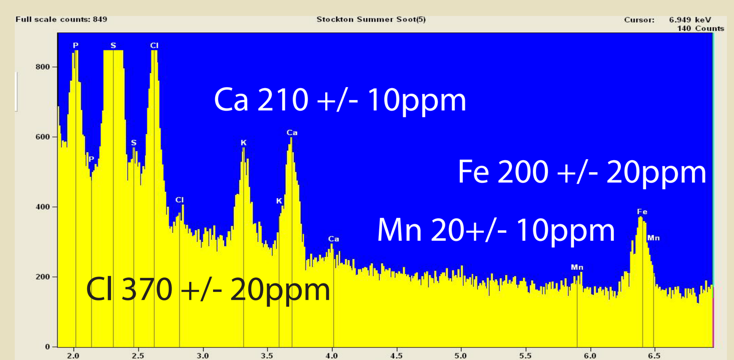
- Spectrum for Fe-oxide nanocrystals
- Particle has sequestered trace amounts of Zn, Ti and Cr



Diffraction pattern from Fe-oxide nanoparticle. Fuzzy reflections are typical of disordered neo-crystallites.

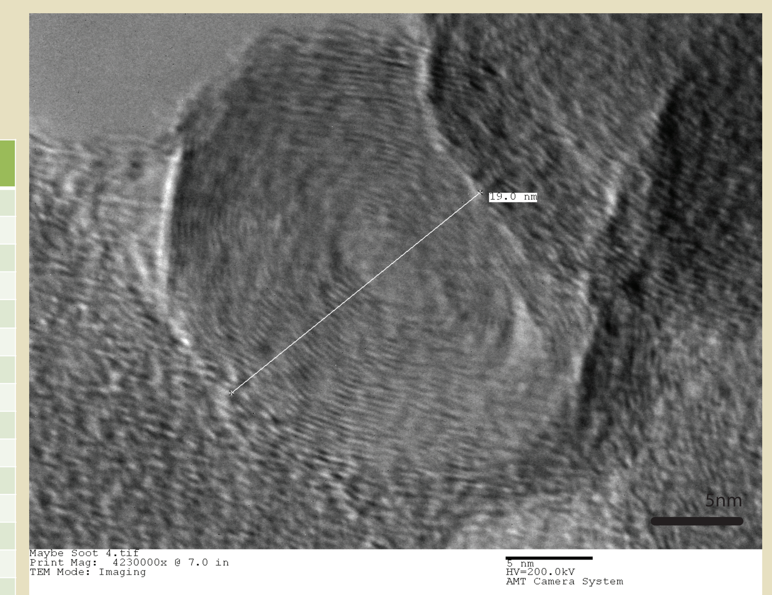
Soot Nanoparticles





Element	Net Counts	Net Counts Error	K-Factor	Weight %	Weight % Error	Compnd %	Norm. Compnd%
C	1417842	+/- 6131	12.5099	99.193	+/-0.429	99.193	99.193
Na	16524	+/- 473	1.4594	0.135	+/-0.004	0.135	0.135
Mg	7056	+/- 180	1.1981	0.047	+/-0.001	0.047	0.047
Al	4944	+/- 280	1.0939	0.030	+/-0.002	0.030	0.030
Si	52623	+/- 412	1.0000	0.294	+/-0.002	0.294	0.294
P	3732	+/- 163	1.0247	0.021	+/-0.001	0.021	0.021
S	26747	+/- 364	1.0296	0.154	+/-0.002	0.154	0.154
Cl	6648	+/- 278	0.9980	0.037	+/-0.002	0.037	0.037
K	3285	+/- 239	0.9367	0.017	+/-0.001	0.017	0.017
Ca	4095	+/- 125	0.9026	0.021	+/-0.001	0.021	0.021
Cr	181	+/- 108	1.0126	0.001	+/-0.001	0.001	0.001
Mn	409	+/- 126	1.0574	0.002	+/-0.001	0.002	0.002
Fe	3335	+/- 275	1.0703	0.020	+/-0.002	0.020	0.020
Ni	259	+/- 131	1.1387	0.002	+/-0.001	0.002	0.002
Zn	2317	+/- 199	1.3140	0.017	+/-0.001	0.017	0.017
Pb	441	+/- 158	3.0172	0.007	+/-0.003	0.007	0.007
Total				100.000		100.000	100.000

Soot is a product of the combustion of carbonaceous materials. It appears as small spheres 25 -45nm) of single layer carbon atoms (graphene) around a central core. Light concentric lines in the image represent single atoms of carbon.



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Results and Conclusions

- Airborne particles in the Sacramento Valley contain trace amounts of Cr, Ni, As and Pb in bioavailable nanoparticulates
- Larger clays (~ 1μm) contain up to 400ppm Cr, 850ppm Ni
- Fe-oxides contain large metal loads (2940ppm Cr, 1820ppm Ni, 2620ppm Pb), and occur primarily as nanocrystallites

Future Research

- Continue with data collection to obtain a detailed statistical profile of each location
- Determine relationships between dust content, location of collection, and season of collection
- Continue to analyze amporphous phases, Fe-oxides, organics and minerals to better understand the nature of metal-sequestering phases

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