Redox Transformations in Wildfire Ashes Studied by micro X-ray Absorption Spectroscopy

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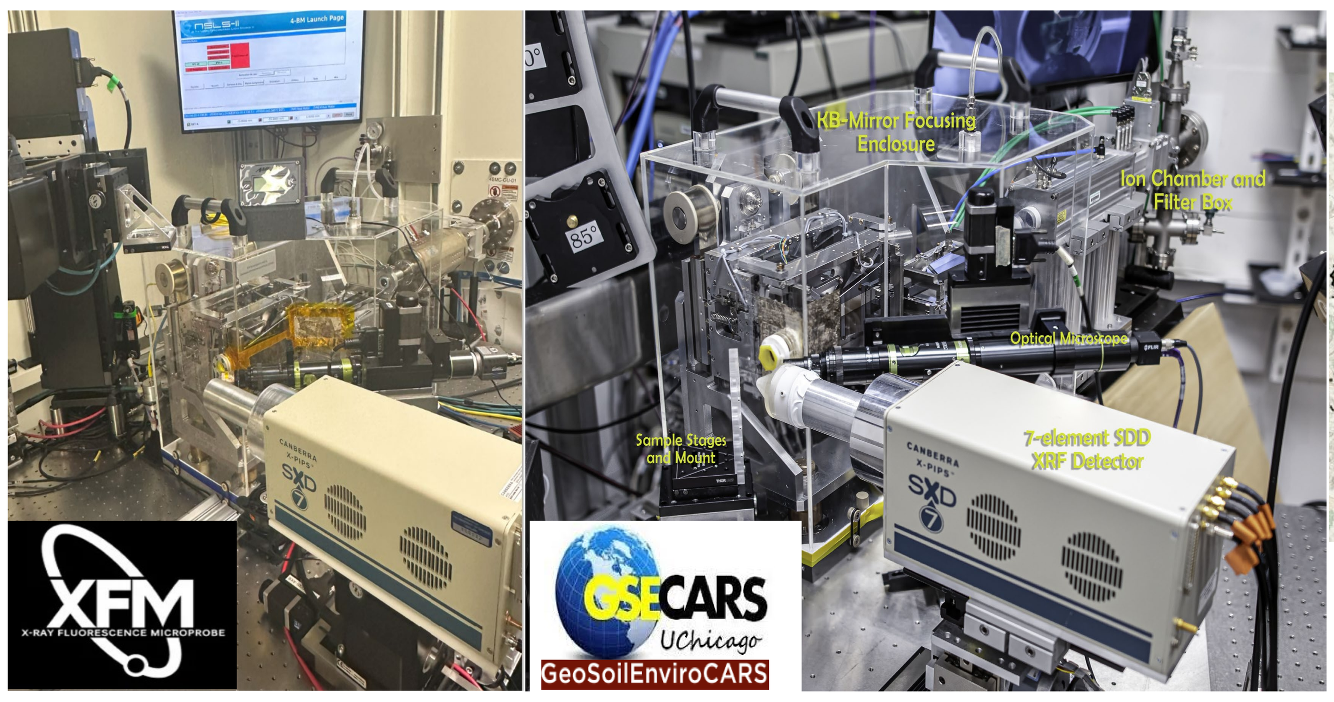
Background and Motivation

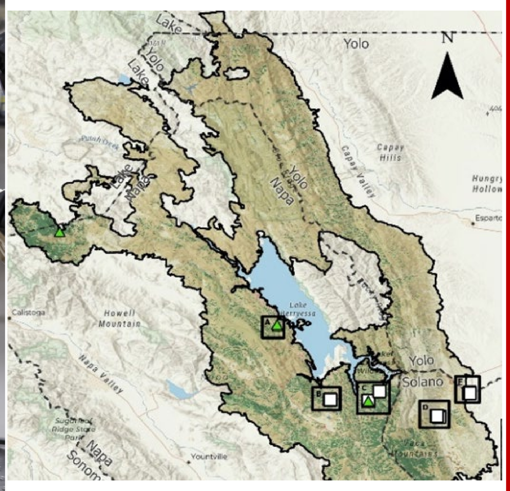
- Wildfires have increased in frequency, size, and severity, spreading into the wildland-urban interface (WUI) and emitting contaminants. Then, there is a need to understand the constituents of particulate matter emitted by WUI fires and their impact on environmental and human health with high spatial resolution.
- We performed experiments to evaluate oxidation state changes in metal(loid) (e.g., Cr, Mn, As, and Ti) to identify species and phase such as Magnéli titania (more toxic than anatase and rutile phases), Mn(IV) (highly reactive), As(III) (more mobile and toxic than As(V)) and/or Cr(VI) (more mobile and toxic than Cr(III)).

Materials and Methods

- Wildland-urban interface (WUI) fire ashes were collected from the 2020 LNU Lightning Complex Fire perimeter in Northern California, USA.
- Micro X-ray fluorescence (µXRF) imaging and micro X-ray absorption fine structure spectroscopic (µXAFS) experiments were performed at the beamlines 4-BM (XFM) at the National Synchrotron Light Source II (NSLS-II) in Brookhaven National Laboratory (BNL) and 13-ID-E (GSECARS) at the Advanced Photon Source (APS) in Argonne National Laboratory (ANL).



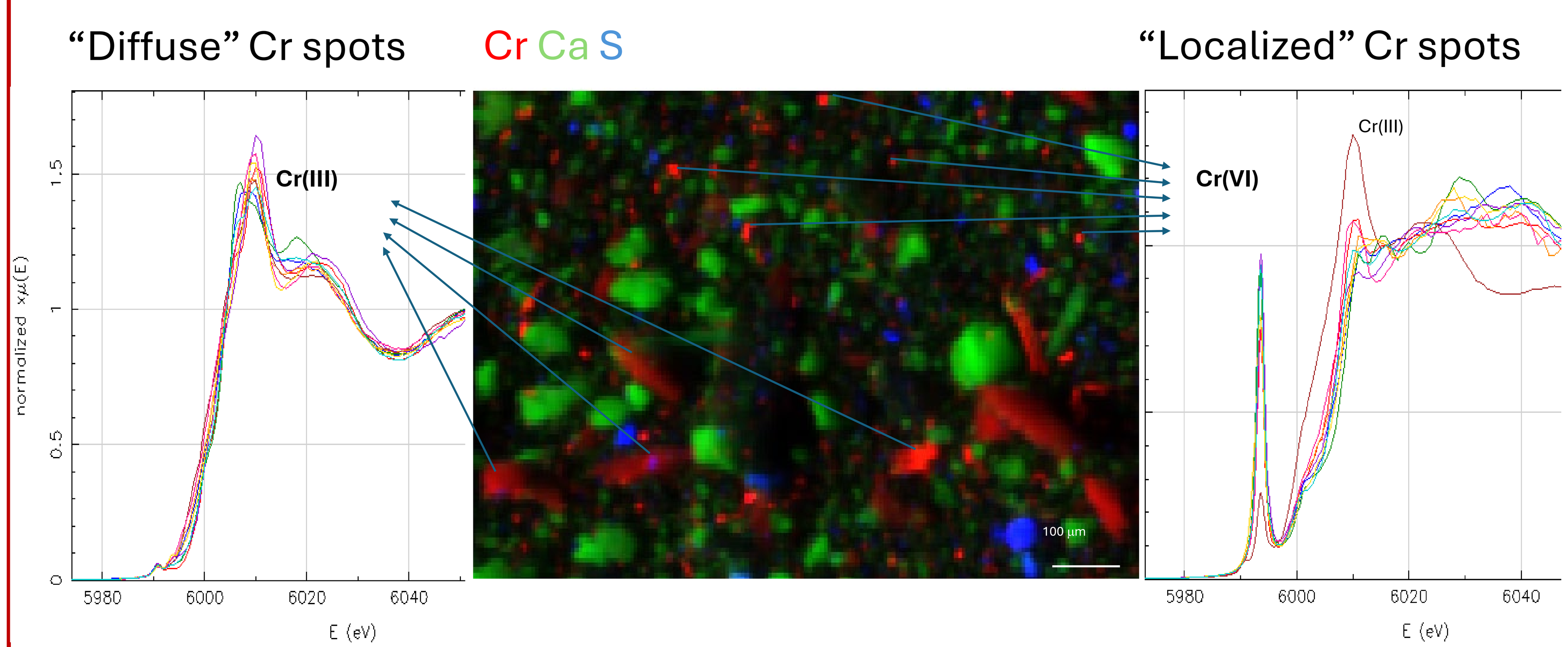
Caption: Schematic of (left) 4-BM XFM and (right) 13-ID-E GSECARS endstations at NSLS-II in BNL and APS in ANL respectively.



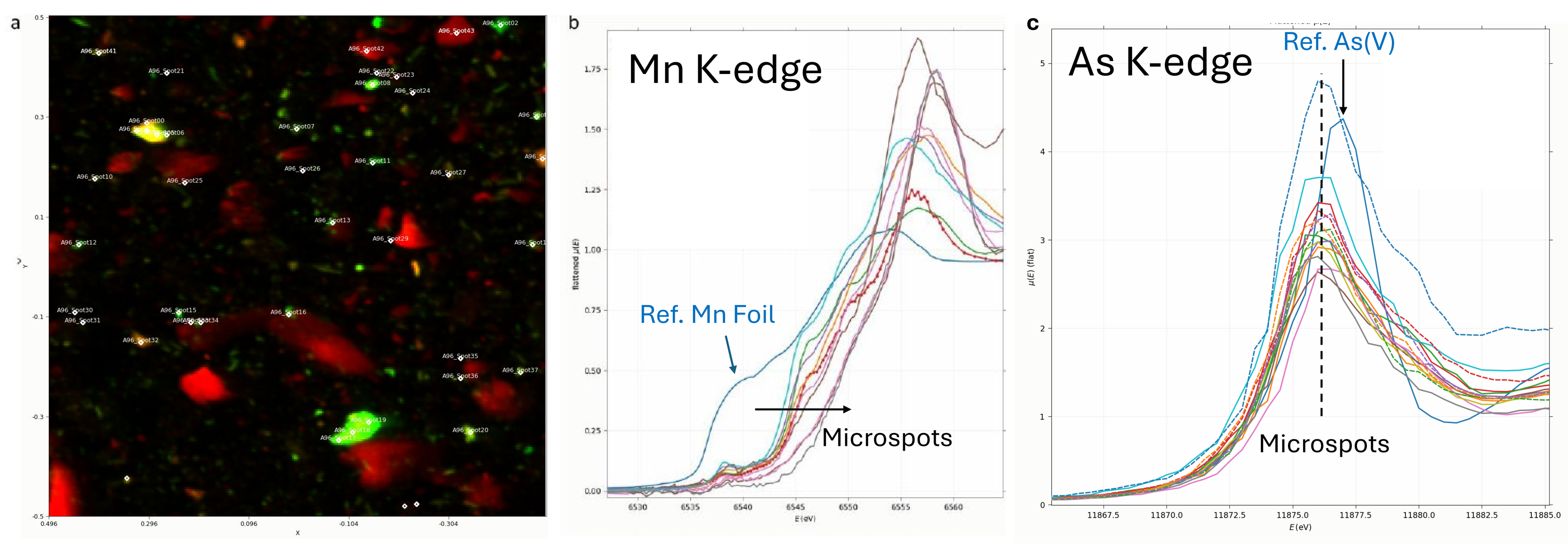
Caption: LNU Lightning Complex fire in California USA and locations of ash samples collected.

Initial Findings

We have found that not only the combustion of chromated copper arsenate (CCA) treated wood leads to the formation of incidental nano-materials (INMs) containing toxic and carcinogenic hexavalent chromium Cr(VI) detected in the ashes but also the whole combustion process. Mixed Cr(III) and Cr(VI) signals were detected.

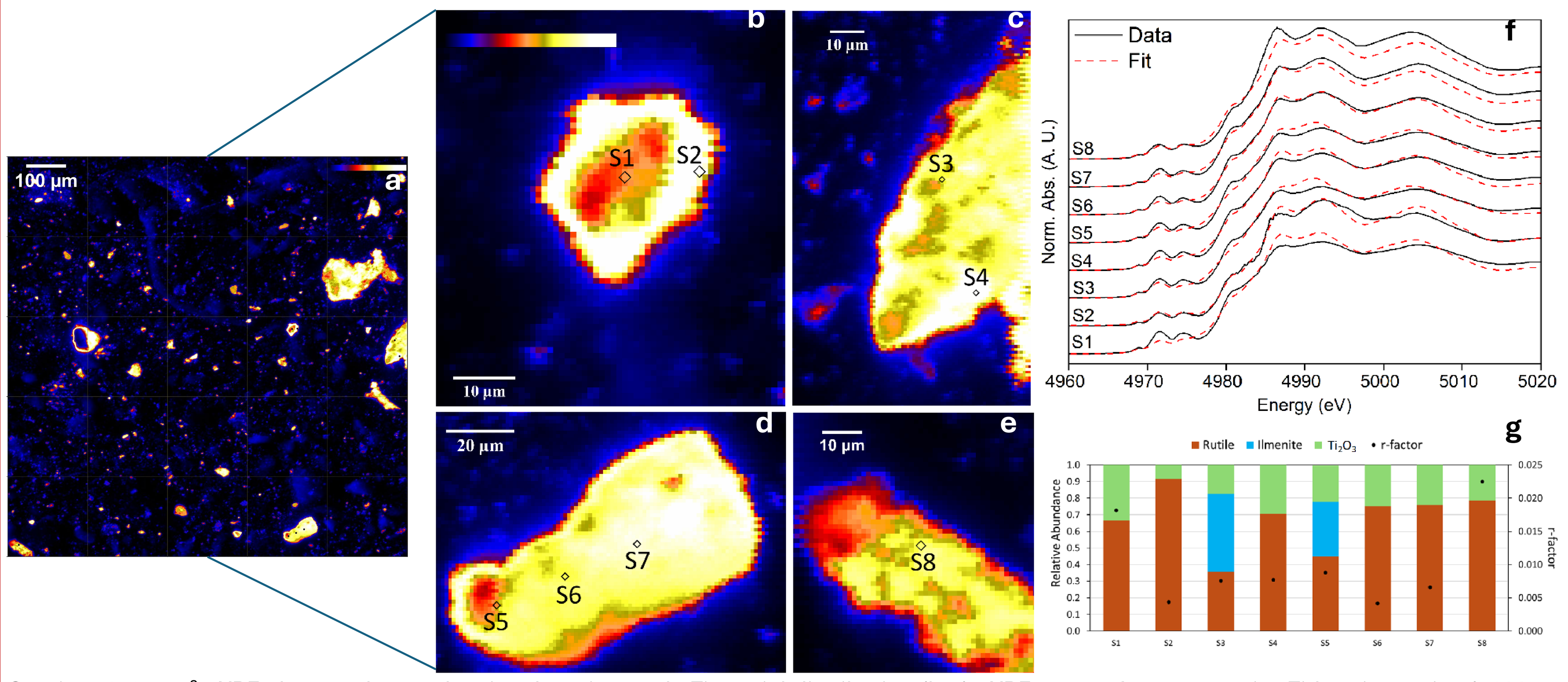


Caption: X-ray fluorescence images of Cr (red), Ca (green) and S (blue) in fire ash sample from chromated copper arsenate (CCA) treated wood; (left) Cr K-edge µXANES from "diffuse" areas showing predominance of non-toxic Cr(III) species (as expected for CCA wood); (right) Cr K-edge µXANES from discrete, localized spots showing predominance of toxic and carcinogenic Cr(VI) species. Scale bar is 100 microns.



Caption: (a) µXRF elemental map showing Mn (Red) and As (Green) concentrations. (b) Mn K-edge µXANES spectra showing a high variability of species (e.g., $MnSO_4$, MnS, Mn_3O_4, MnO_2, Mn_2O_3) on selected microspots. (c) As K-edge µXANES show a slight reduction point to have some As(III) nanoparticles (blue spectrum As(V) as reference).

- Oxidation of Mn(II) or Mn(III) during high-temp O_2-rich combustion and complex redox chemistry from synthetic materials could lead to microscopic Mn(IV) expected to be found as as pyrolusite.
- Analyzed microspots from As K-edge µXANES shows an slight energy shift to lower energy than As(V), this point to some As(III) in WUI ashes which likely reflects submicrometric As(III) particles formation, which usually requires low-oxygen or smoldering zones.
- µXRF mapping revealed Ti-rich particle aggregates (~20-50 µm) which could contain reduced phases due to potential reducing microenvironments with high-temperature conditions.
- Ti K-edge µXANES linear combination fitting analysis suggests that WUI fire ash sample contain a mixture of anatase, rutile, ilmenite, and Ti_2O_3. The Ti_2O_3 (which never appeared pure) is attributed as a component of the Magnéli phases (e.g., a mixture of TiO_2 and Ti_2O_3)



Caption: 1x1 mm[2] µXRF elemental map showing the microscale Ti spatial distribution (b-e) µXRF maps of representative Ti-bearing grains (<100 µm size) with a series of microspots (S1 to S8) used for Ti K-edge µXANES; (f) linear combination fits of Ti K-edge µXANES spectra of S1 to S8 microspots, and (g) the relative abundance of the identified Ti-phases in the analyzed microspot using the reference spectra (rutile, ilmenite and Ti_2O_3).

Table. Relative abundance of each Ti phase (fitting window = -20 to 30) in the spots measured by µXANES

Spectrum number	Ti_2O_3	Rutile	Anatase	Ilmenite	Error Ti_2O_3	error Rutile	error Anatase	error Ilmenite	r-factor	chi-square
38	0.082	0.918	0.000	0.000	0.008	0.092			0.004	0.204
41	0.294	0.706	0.000	0.000	0.047	0.010			0.008	0.344
68	0.249	0.751	0.000	0.000	0.008	0.051			0.004	0.200
69	0.241	0.759	0.000	0.000	0.010	0.039			0.007	0.345
72	0.214	0.786	0.000	0.000	0.024	0.020			0.022	1.334
40	0.174	0.355	0.000	0.471	0.053	0.032		0.037	0.008	0.309
66	0.217	0.045	0.000	0.336	0.054	0.035		0.040	0.009	0.367
18	0.000	1.000	0.000	0.000					0.007	0.297
30	0.000	1.000	0.000	0.000		0.000			0.008	0.375
39	0.000	1.000	0.000	0.000		0.000			0.010	0.476
23	0.000	1.000	0.000	0.000					0.009	0.476
56	0.000	1.000	0.000	0.000		0.000			0.018	0.855
3	0.000	0.000	1.000	0.000			0.000		0.009	0.514
20	0.000	0.000	1.000	0.000					0.014	0.835
58	0.000	0.000	1.000	0.000			0.062		0.017	0.976

Concluding Remarks

- Cr K-edge µXANES localized spots point to submicron Cr(VI)-rich particles found from the combustion of chromated copper arsenate and/or Cr_2O_3-contained pigments, paints, and coatings leading to INMs.
- Even Mn(IV) is less bioavailable, we have detected potential signatures of its presence by Mn K-edge µXANES, which could have been favored by high-temperature and oxygen-rich combustion conditions.
- As from WUI fires could contain traces of As(III) in submicrometric level.
- Evidence of Magnéli Phases has been found, which are formed by the thermal reduction of TiO_2 at 800–1200°C in low-oxygen (reducing) microenvironments. µXAFS is an essential tool for their detection.
- Semi-quantitative analyses (e.g., LCFs and/or PCAs) are still needed (e.g., to support As(III) detection).

Relevant References

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