Improvement of a Cr(VI) Extraction Method for Chromite Ore Processing Residue (COPR)-Contaminated Materials

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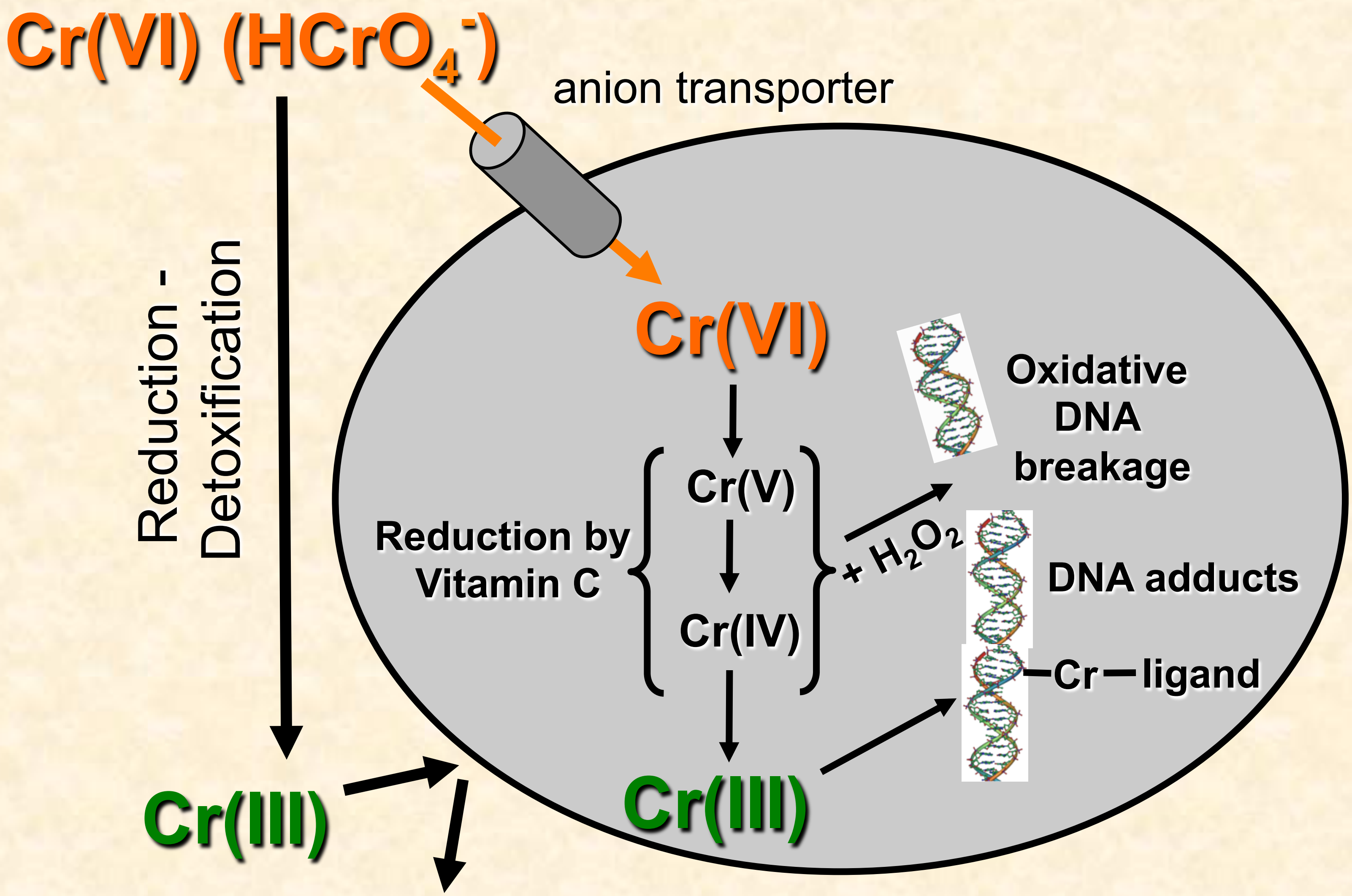
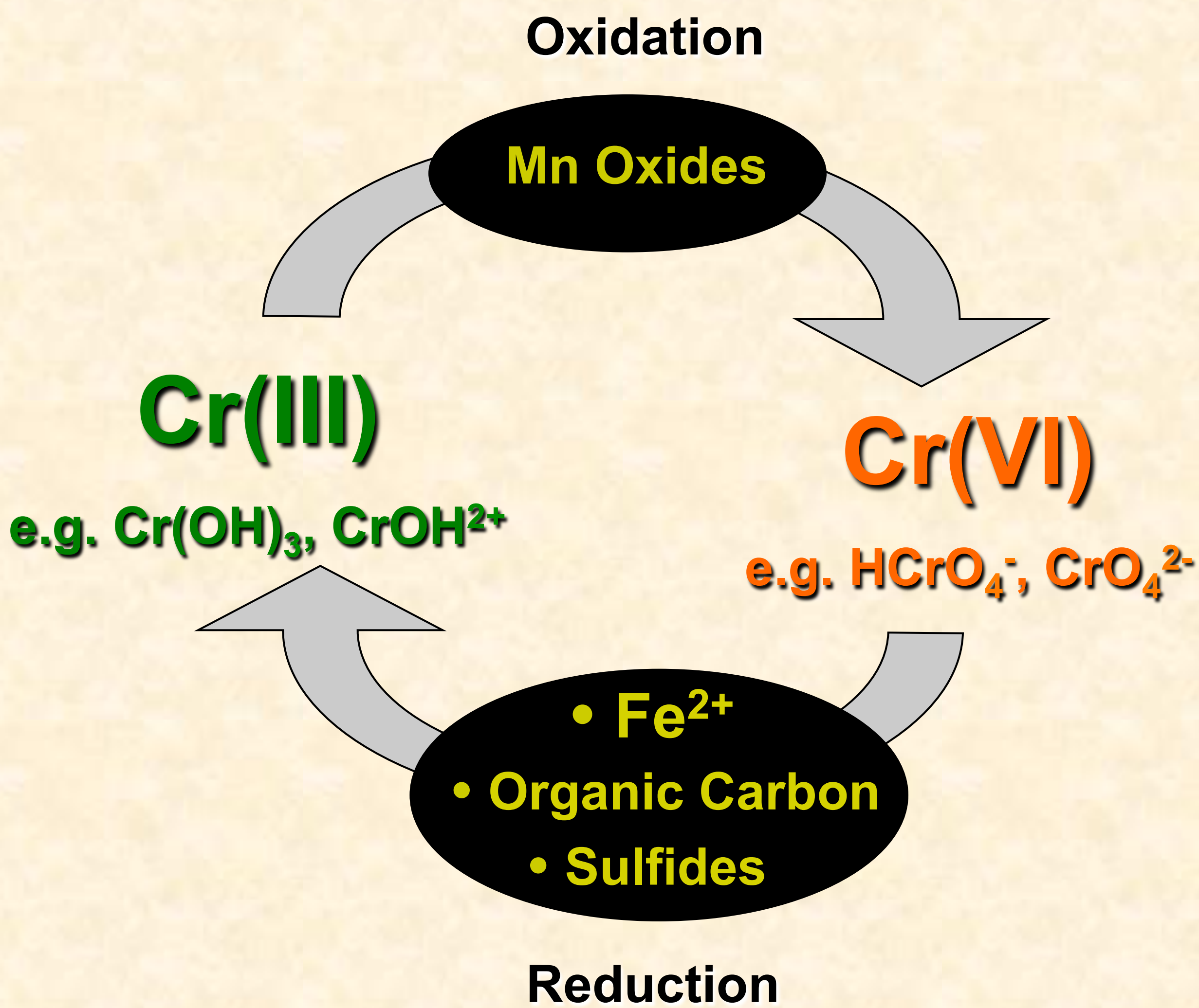
Toxicity and carcinogenesis of chromium



National Toxicology Program

Salnikow & Zhitkovich (2008) *Chem. Res. Toxicol.*

Chromium Redox Cycle



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Chromite Ore Processing Residue (COPR)

High Lime Process

Chromite ore, CaO, & Na_2CO_3 are heated at ~1100^o C in a rotating kiln

$$4FeCr_2O_4 + 8Na_2CO_3 + 7O_2 \longrightarrow 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2$$

$\downarrow$

water leach

China	**India**
Japan	**Pakistan**
UK	**USA**
	New Jersey
	Maryland

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Burke et al. (1991) *Environmental Health Perspectives*

Common Minerals in COPR

Chromite	$(Fe,Mg)Cr_2O_4$	Major host of Cr(III)
Brownmillerite	$Ca_2(Fe, Al)_2O_{10}$	Can host Cr(III) [Cr(VI)?]
Periclase	MgO	
Larnite	Ca_2SiO_4	
Brucite	$Mg(OH)_2$	
Calcite/Aragonite	$CaCO_3$	
Calcium silicate hydrate	CaH_2SiO_4	
Hydrogarnet	$Ca_3Al_2((Si/H_4)O_4)_3$	Can host Cr(VI)
Hydrocalumite	$Ca_4Al_2(OH)_{12}(OH)_2 \cdot 6H_2O$	Can host Cr(VI)
Hydrotalcite	$Mg_6Al_2(CO_3)(OH)16 \cdot 4H_2O$	Can host Cr(VI)
Ettringite	$Ca_6Al_2(OH)_{12}(SO_4)_3 \cdot 26H_2O$	Can host Cr(VI)

Geelhoed et *al*. (2002) *GCA*

Hillier et *al*. (2003) *STOTEN*

Mahlerbe et *al*. (2011) *ES&T*

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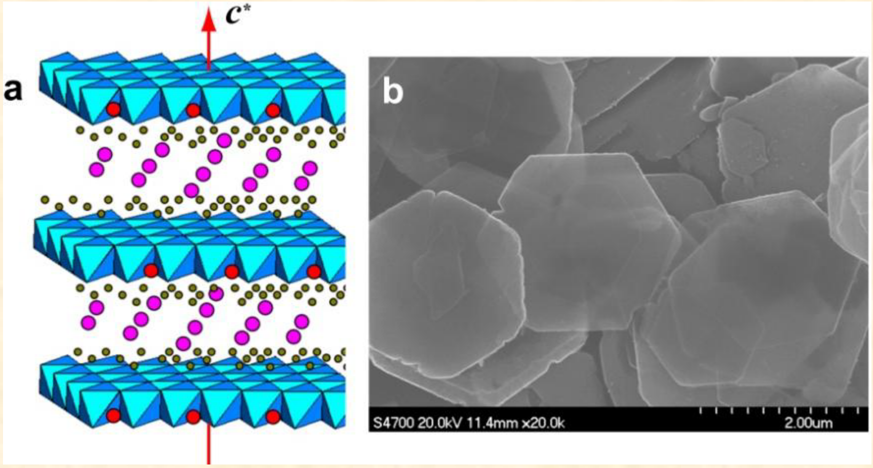
Layered Double Hydroxides (anionic clays)

$[M^{2+}_{1-x}M^{3+}_{x}(OH)_2]^{b+}\,[A^{n-}_{b/n}] \bullet mH_2O$

x usually between 0.2 and 0.33



Hydrotalcite

$Mg_6Al_2(OH)_{16}(CO_3) \bullet 4H_2O$

Hydroxy Hydrocalumite

$Ca_4Al_2(OH)_{12}(OH)_2 \bullet 6H_2O$

Sulfate Hydrocalumite (monosulfate)

$Ca_4Al_2\,(OH)_{12}SO_4 \bullet 6H_2O$

Cr(VI) Hydrocalumite

$Ca_4Al_2(OH)_{12}CrO_4 \bullet 6H_2O$

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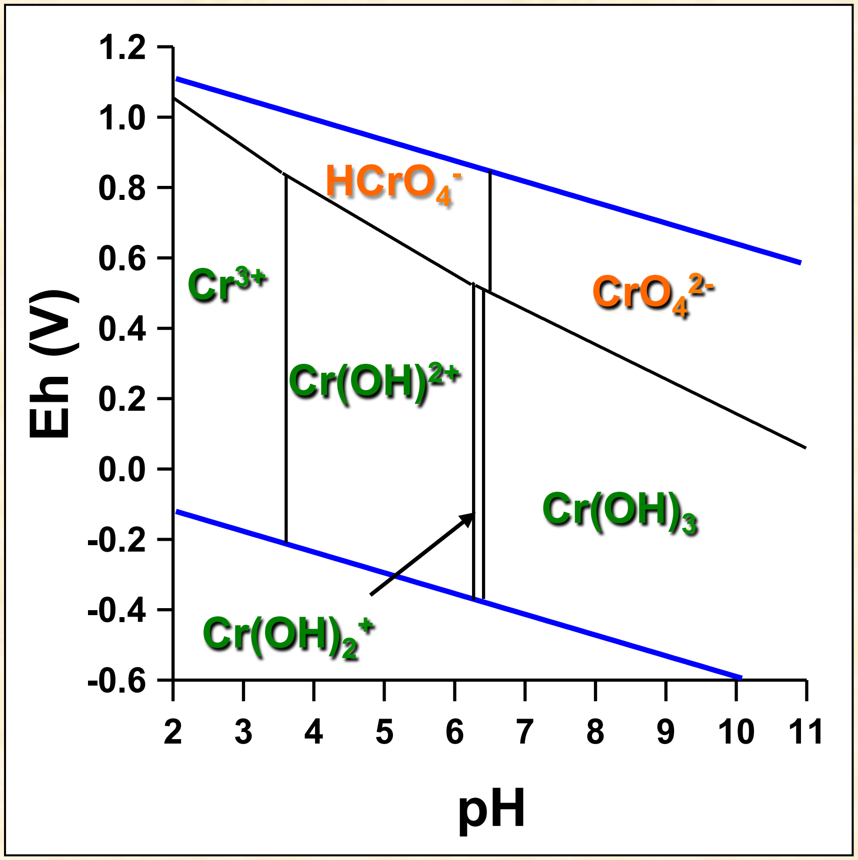
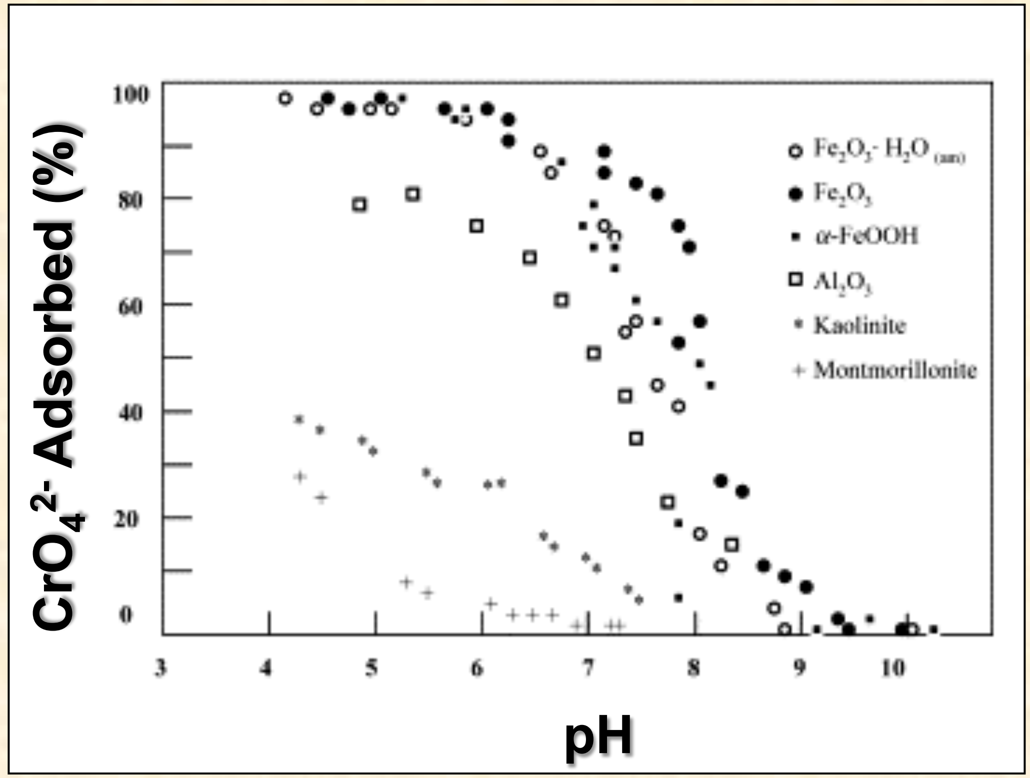
Kuang et *al*. (2010) *Materials*

Acidic Extraction is Not Possible





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Bradl (2004) *Journal of Colloid and Interface Science*

EPA Method 3060A

Objective

To quantify total Cr(VI) in a solid matrix, three criteria must be satisfied:

- the extracting solution must solubilize all forms of Cr(VI)
- the conditions of the extraction must not induce reduction of native Cr(VI) to Cr(III)
- the method must not cause oxidation of native Cr(III) contained in the sample to Cr(VI)

Extraction Procedure

- 2.5 g field-moist sample
- 50 mL digestion solution (0.5 M NaOH; 0.28 M Na_2CO_3; pH=13.4) (20 liquid:solid ratio)
- Optional if isotope dilution is used to correct for oxidation/reduction
  - 4 mmoles $MgCl_2$ – precipitates as $Mg(OH)_2$ or $MgCO_3$
  - 0.5 mmoles K_3PO_4 – interferes with HPLC separation
- Stir samples at 90-95^o C for 1 hour
- Filter (0.45 micron)
- Adjust pH to 7.5 with nitric acid
- Dilute to 100 mL

Analysis

- 7196A Visible Spectrophotometry of diphenyl carbazide complex
- 7199 Ion Chromatography with diphenyl carbazide detection
- 6800 Speciated Isotope Dilution Mass Spectrometry (SIDMS) – add $^{53}CrO_4$ and $^{54}Cr(III)$ spikes

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Initial Approach – Sample Grinding

- Mahlerbe et *al.* (2011, *ES&T*) indicated that increased grinding of NIST SRM 2701 did not change extraction efficiency
- Others found that intensive grinding did result in increased extraction efficiency and more Cr(VI) reduced by various remediation treatments[1,2]
- We investigated the effect of several different grinding regimes

1. Moon et *al*. (2008) *STOTEN*
2. Jagupilla et *al*. (2009) *J. Haz. Mat.*

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Our Sample Preparation, Extraction, and Analysis

- Micronize several grams of sample
  - Dry (10 min)
  - Water (10 min)
  - Methanol (10, 20, & 40 min)
- 500 mg subsample
- 190 mL of 0.5 M NaOH & 0.28 M Na_2CO_3 (pH=13.4)
- Shake in heated water bath at $95^{o}C$ for 2 hours
- Cool 1 hour on orbital shaker
- Filter (0.22 micron)
- Adjust to pH 7.5 with nitric acid
- Dilute to 250 mL
- 2 different analyses for Cr(VI)
  - Colorimetric (EPA 7196A)
  - HPLC – Dynamic Reaction Cell ICPMS

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NIST SRM 2701

- Soil heavily contaminated with chromite ore processing residue (COPR)
- Collected from Liberty State Park, Jersey City, NJ
- Prepared by Steve Wilson (USGS), Ball mill ground
- Total Cr 4.26% (42,600 mg kg^{-1}), pH = 9.6

Method	7196A[1]	7199[1]	6800[1]	XANES[2]	XANES[3] preliminary
Median Cr(VI) Concentration (mg kg^{-1})	365	390	551	3000-3400	1891-1973 3028-3339
Standard Deviation	74	72	16		2.3 (RSD) 4.8 (RSD)

Other studies show Method 3060A results in incomplete extraction of Cr(VI) from other COPR contaminated soils

- Ratio of Cr(VI) determined by XANES to 3060A = 1.5 to 3.9 (Dermatas et al., 2006, ES&T)
- XANES 7600 mg kg^{-1} and 3060A 4600 mg kg^{-1} (Wazne et al., 2007 J. Haz. Mat.)
- XANES 19,500 mg kg^{-1} and 3060 A 9,200 mg kg^{-1} (Yu et al., 2012 J. Haz. Mat.)

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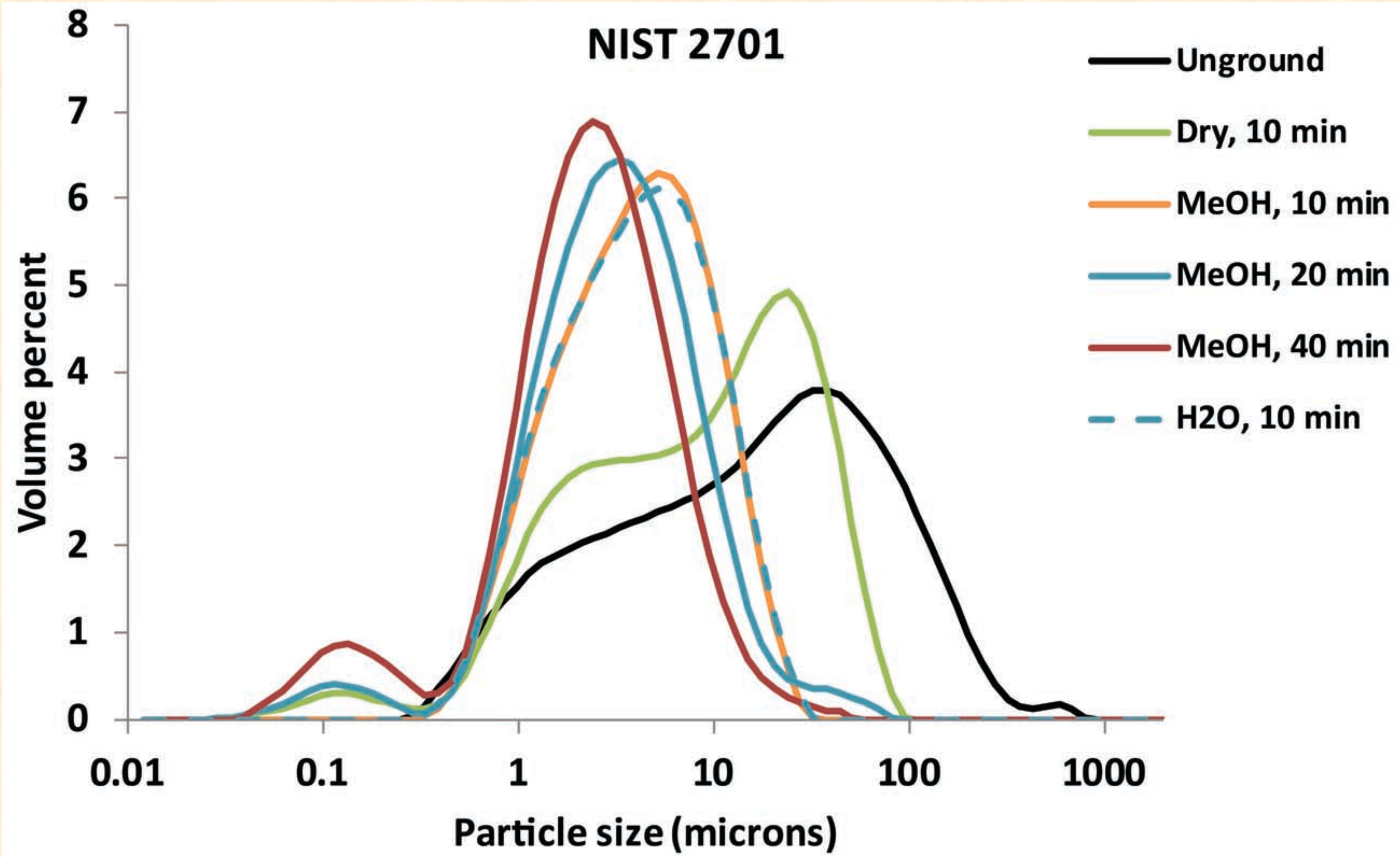
1. NIST Certificate revised 13 Sept 2013
2. Mahlerbe et al. 2011 ES&T
3. This study – performed at SLAC

Effect of Micronization on Particle Size – 2701



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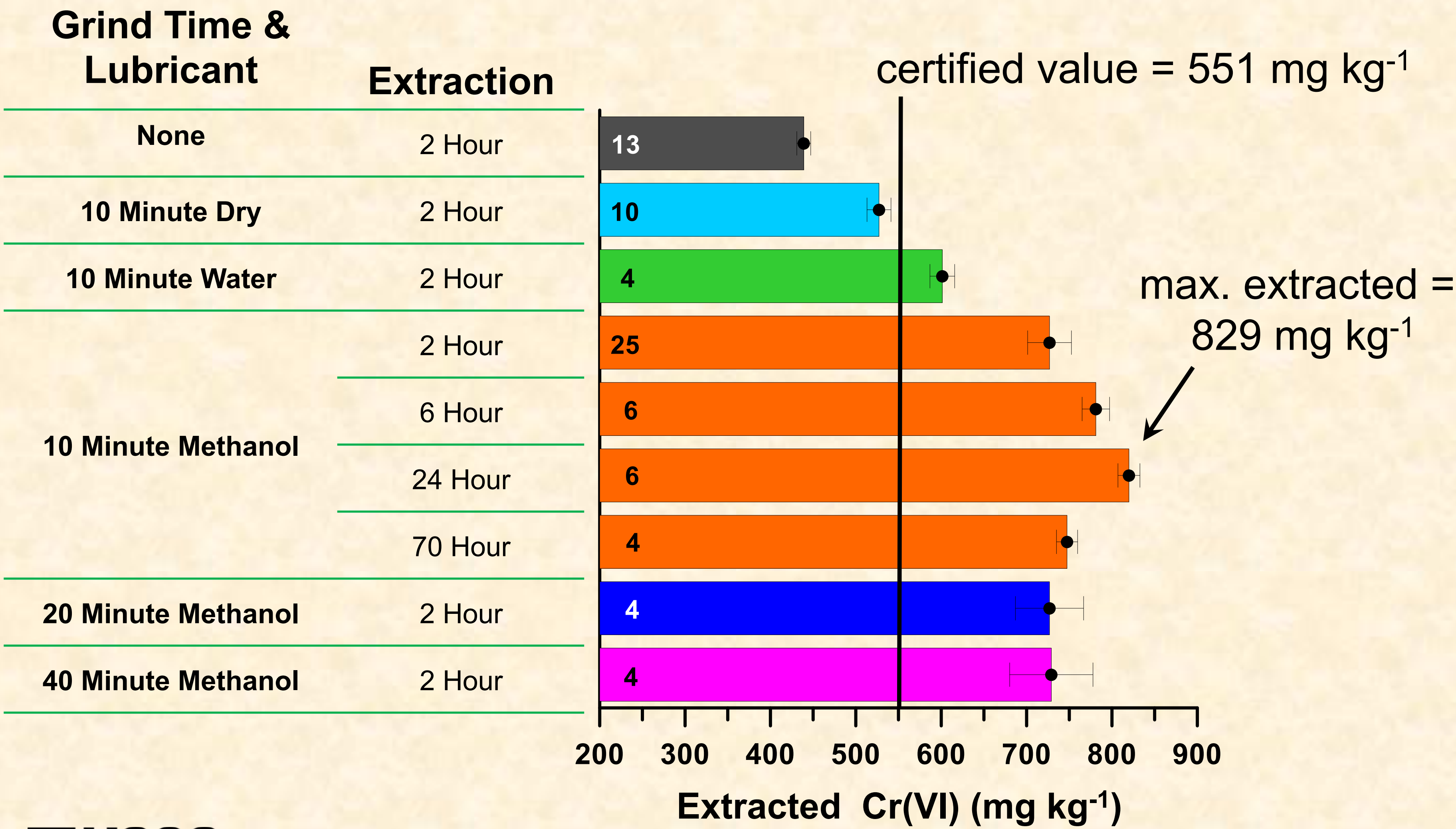
Extraction Results for NIST SRM 2701



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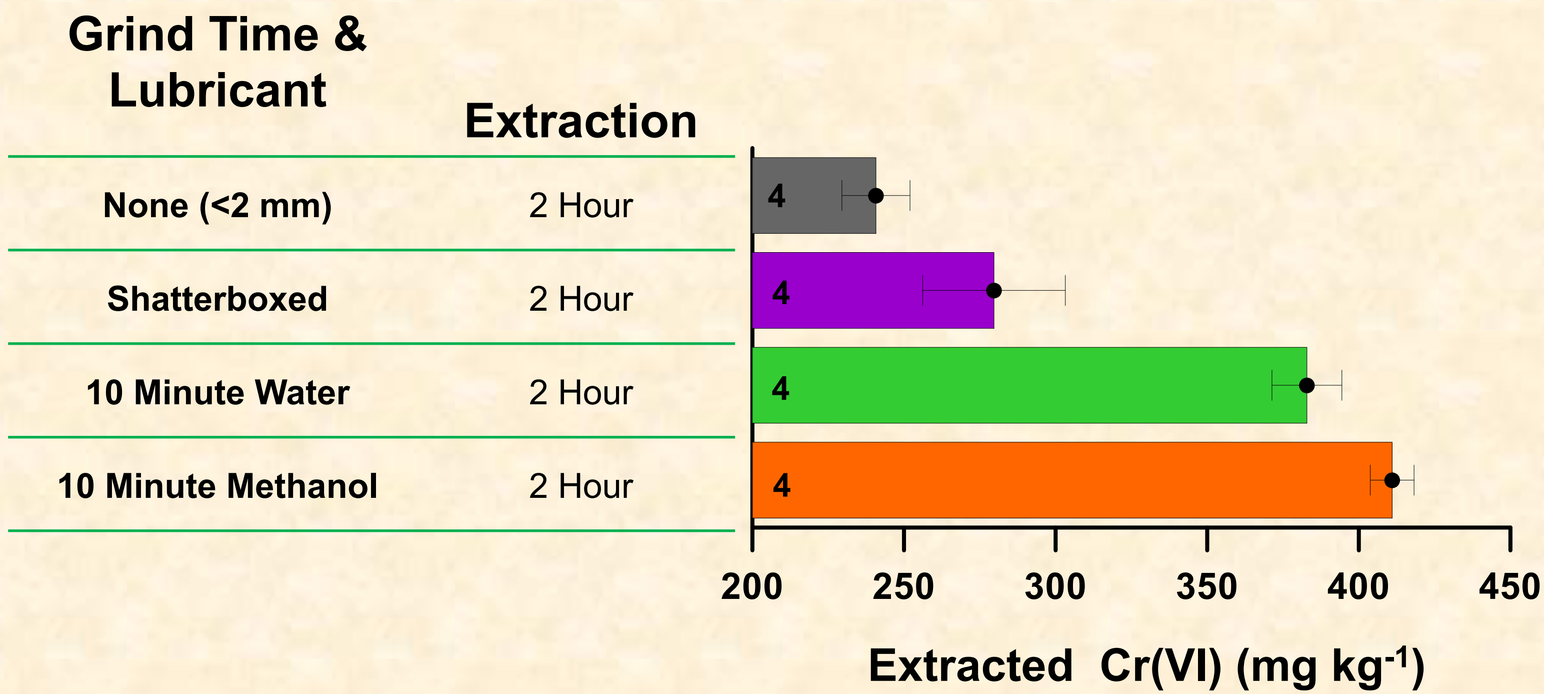
Extraction Results for 2B



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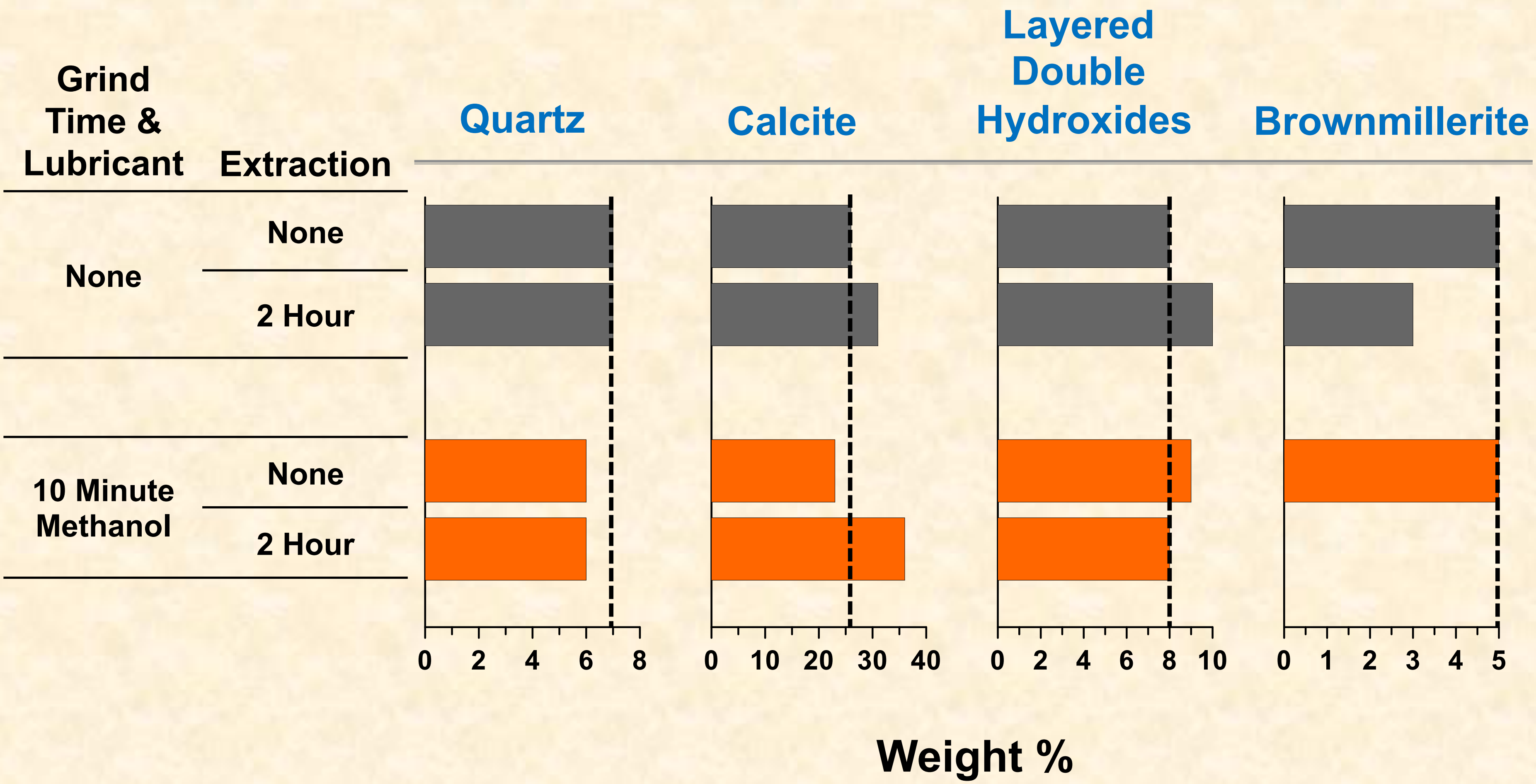
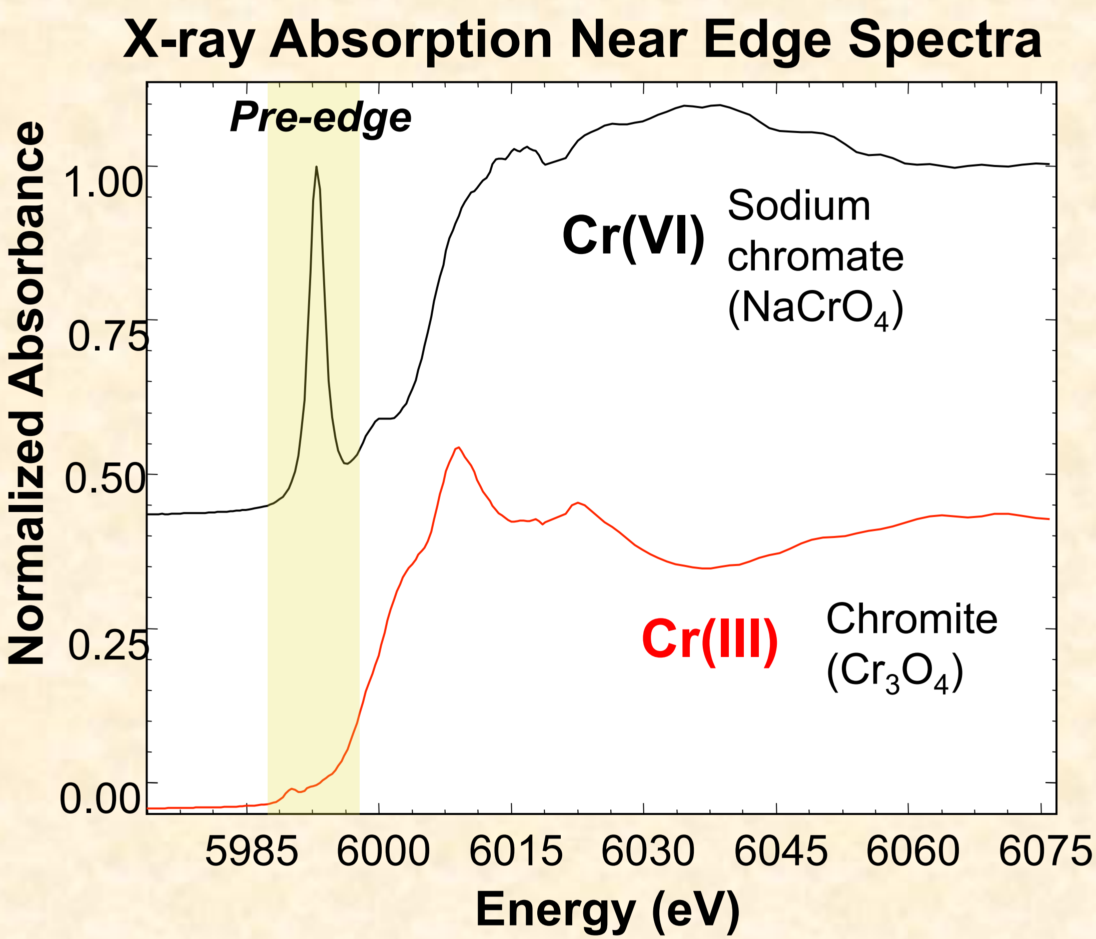
2701 Mineralogy (XRD preliminary results)



Direct Analysis - Chromium X-ray Absorption Near-Edge Spectra are sensitive to oxidation state



- Tetrahedral Cr(VI) has a diagnostic pre-edge feature
- Cr XANES line shape is related to molecular speciation

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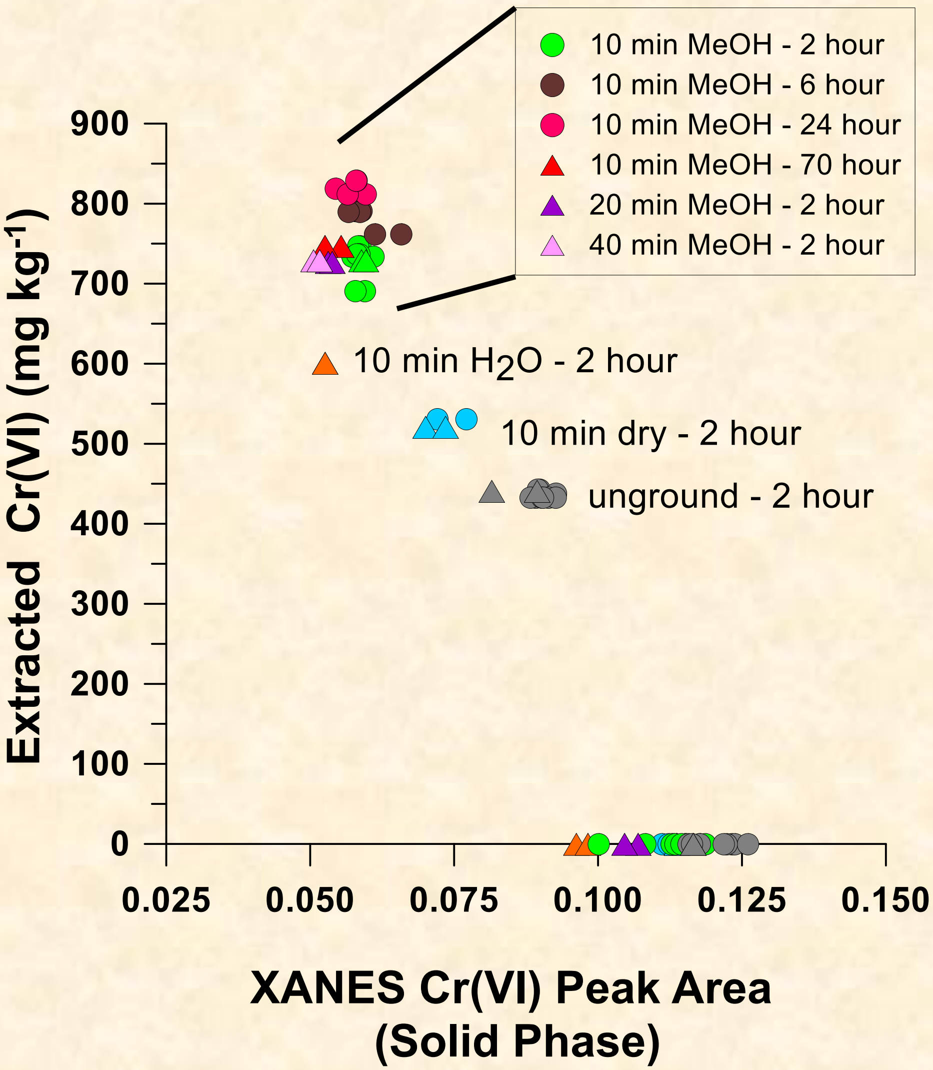
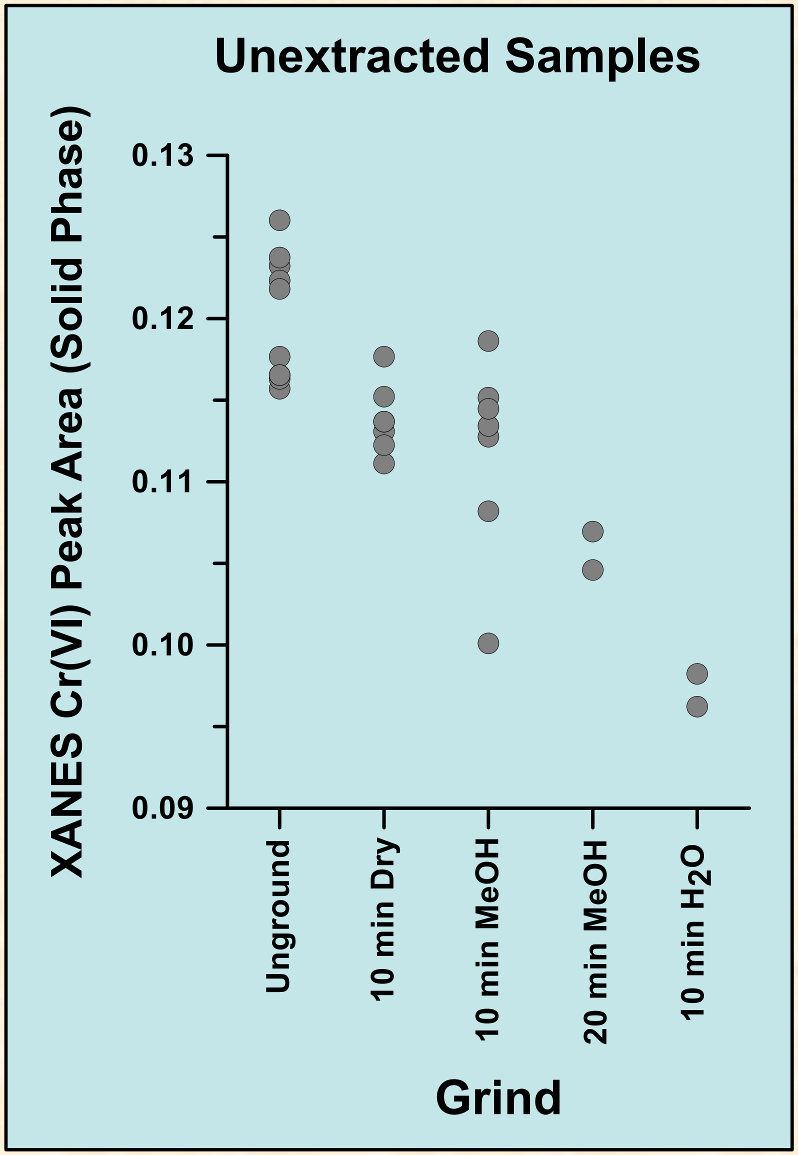
Extracted Cr(VI) versus Residual Cr(VI) by XANES





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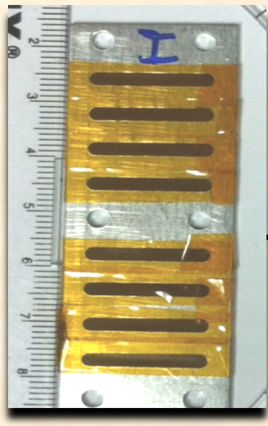
Alternative Techniques Employed

Direct determination of Cr(VI) in solids

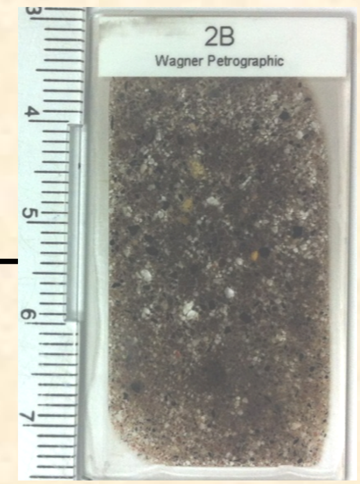
Identification of Cr(VI) mineral residence

Synchrotron lightsource



Bulk XANES spectroscopy

μ-XANES
μ-XRF Mapping



Bulk Raman spectroscopy

μ-Raman

Laboratory instrument

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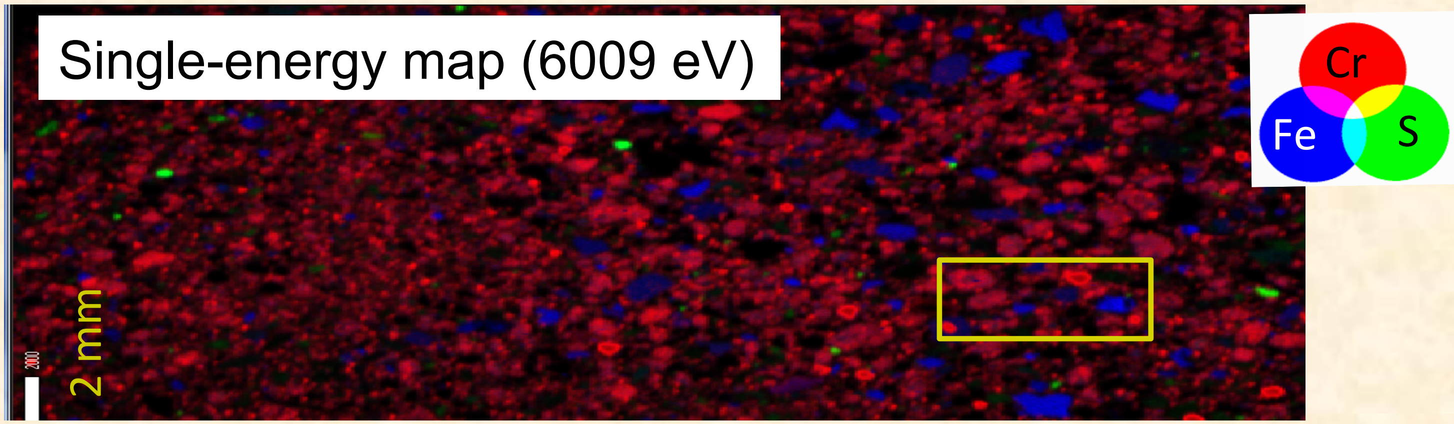
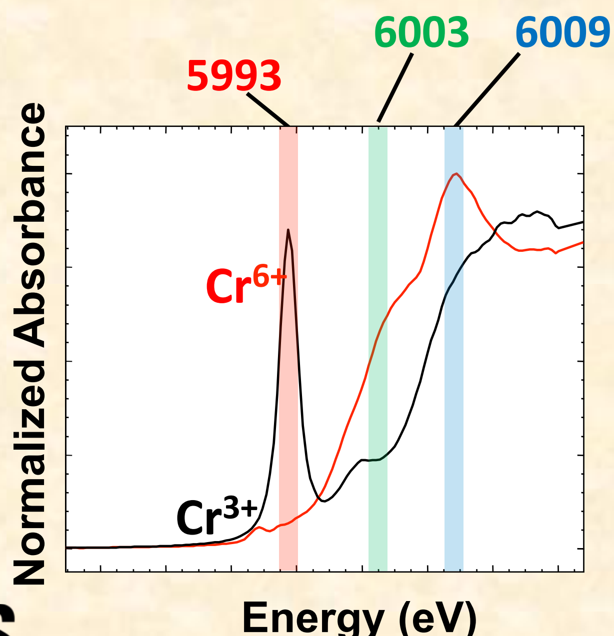
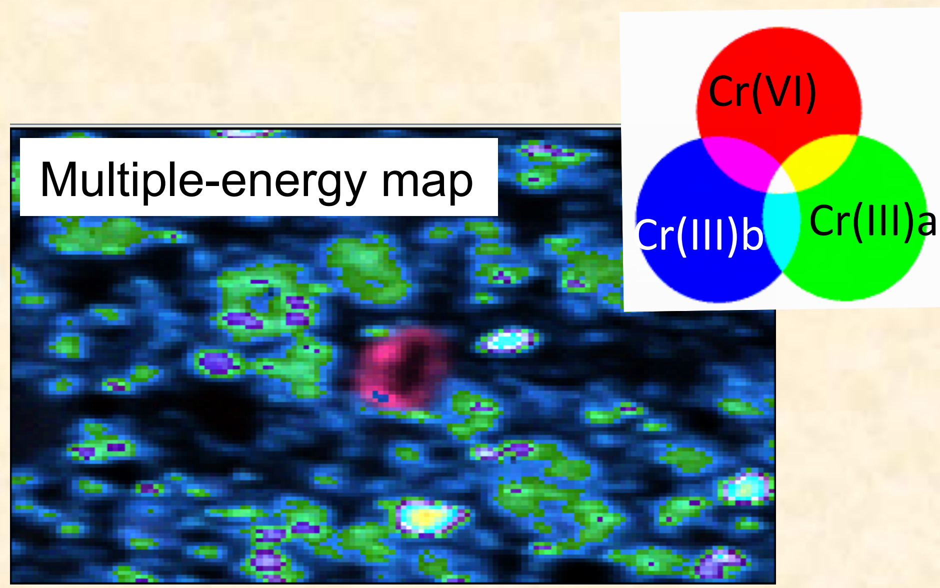
Micro-X-ray Fluorescence Mapping – 2 Types of Info

Sample 2B (unground, unextracted)







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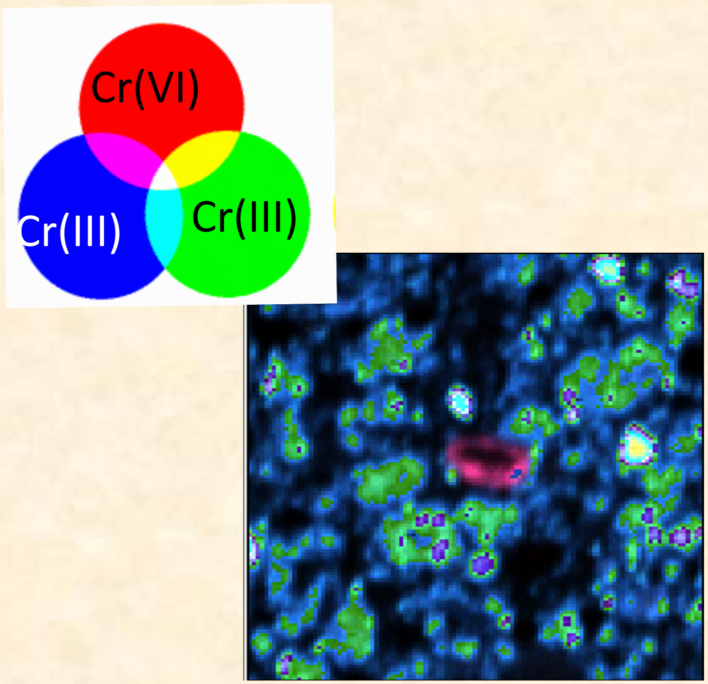
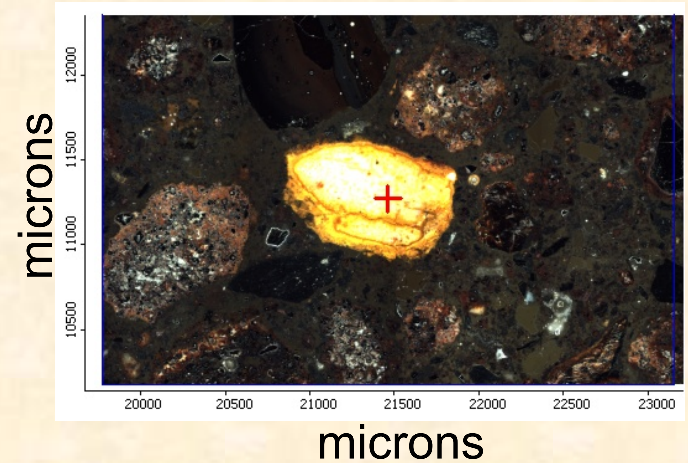
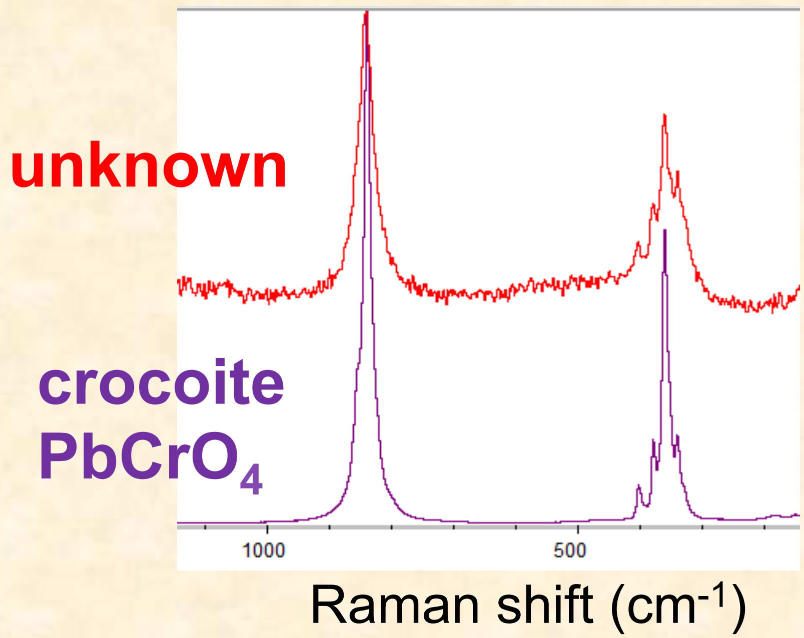
μ-Raman sensitive to Cr(VI)-rich grain in COPR

μ-XRF Map



μ-Raman





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Conclusions

- Micronization of NIST 2701 results in more Cr(VI) extracted than ever before reported for the standard
- Still getting <30% of total Cr(VI) as determined by XANES as reported by Malherbe
- USGS XANES results for NIST 2701 vary depending on how constrained the peak fitting routines are used to perform quantitative analysis by XANES
- Substantial dissolution of layered double hydroxides does not appear to occur during extraction - principal mineralogical residence of Cr(VI) is maintained

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