

OPEN ACCESS

Not all chromates show the same pre-edge feature. Implications for the modelling of the speciation of Cr in environmental systems

To cite this article: J Dubrail and F Farges 2009 *J. Phys.: Conf. Ser.* **190** 012176

View the [article online](#) for updates and enhancements.

You may also like

- [Low-dimensional systems investigated by x-ray absorption spectroscopy: a selection of 2D, 1D and 0D cases](#)
Lorenzo Mino, Giovanni Agostini, Elisa Borfecchia et al.
- [Microbeam x-ray absorption spectroscopy study of chromium in large-grain uranium dioxide fuel](#)
C Mieszczyński, G Kuri, J Bertsch et al.
- [An x-ray absorption spectroscopy study of Ni–Mn–Ga shape memory alloys](#)
V G Sathe, Aditi Dubey, Soma Banik et al.

ECS
The
Electrochemical
Society
Advancing solid state &
electrochemical science & technology

DISCOVER
how sustainability
intersects with
electrochemistry & solid
state science research

Not all chromates show the same pre-edge feature. Implications for the modelling of the speciation of Cr in environmental systems.

J DUBRAIL¹, F FARGES^{2,3}

¹ *Laboratoire des géomatériaux, Univ. de Marne-la-Vallée/Paris-Est, Marne-la-Vallée, France*

² *Laboratoire de Minéralogie et de Cosmochimie du Muséum, CNRS UMR 7202, Muséum
National d'Histoire Naturelle, Paris, France*

³ *Department of Geological and Environmental Sciences, Stanford University, USA*

farges [AT] mnhn [DOT] fr

Abstract. High-resolution XANES spectra for various chromates show that their pre-edge feature varies dramatically with Cr-polymerization. Ab-initio FEFF calculations reproduces those observed experimental trends. Those variations can be easily explained with Pauling's bond valence rules. As chromates are used to model the fraction of toxic Cr(VI) in samples of environmental importance (among others), a careful choice of the chromate model compound is essential for a reliable model of the Cr-speciation in "unknown" samples.

1. Introduction

The speciation of chromium is often used to evaluate the amount of toxic, mobile, carcinogenic Cr(VI) in materials (soils, glasses, aqueous solutions)[1-12]. In contrast, Cr(III) is considered as less mobile and consequently much less toxic. We studied a variety of compounds showing those environments such as ruby, emerald, Cr-spinel, chromite for Cr(III) while a series of chromates were also studied. Like silicates and phosphates, chromates exhibit a variety of polymerization, from monomeric orthochromates (such as sodium chromate) to fully-polymerized "chromic acid" (CrO₃). Therefore, one can expect large variations in the XANES spectra as a function of the Cr-polymerization.

2. Experimental

Five chromates were investigated. CrO₃ is a fully polymerized chromate while ZnCrO₄, K₂CrO₄ and Na₄CrO₄·4H₂O are monomeric. Potassium dichromate has an intermediate Cr-polymerization (dimeric). To help compare those chromates, model compounds include a synthetic Cr(II)-acetate dihydrate and a natural Cr-spinel from Burma (5000 ppm Cr). Other models include natural uvarovite garnet (from Otokumpu, Finland, Ca₃Cr₂(SiO₄)₃), chromite (from Gassin, South France, FeCr₂O₄), eskolaite (synthetic, Cr₂O₃), Cr-K "alum" (synthetic, KCr(SO₄)₂) and Cr(III)-nitrate (synthetic, Cr(NO₃)₃·9H₂O).

μ XRF and μ XANES spectra were collected in 2006 at the Cr K-edge using the 11-2 beamline (SSRL), operating at 3.0 GeV and 100 mA currents. Harmonics were rejected using Ti-coated mirrors. Flux on the sample is 3×10^{12} ph/s at 400 mA injected currents and 6 keV. We used a Si(220) double crystal monochromator and reduced vertical slits before and after the monochromator (0.3 mm) to

enhance energetic resolution (~ 0.7 eV at the Cr K-edge). Samples powders were set in the transmission mode and Cr K-edge XANES spectra were collected with a Cr-foil (2nd transmission) to monitor energy calibration at ± 0.1 eV. XANES spectra were collected every 0.05 eV (2 s/point) in the pre-edge region (0.2 eV in the main edge region). Cr K-edge spectra were normalized following standard procedures using the XAFS3 package [13]. Pre-edges were modeled using PeakFit.

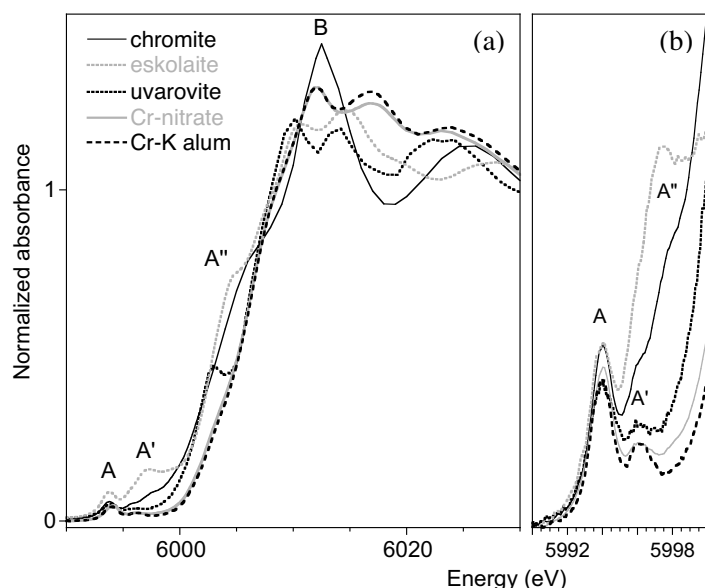


Figure 1 – (a) Cr K-edge XANES spectra for selected models of Cr(III), with a detail on the pre-edge feature (b).

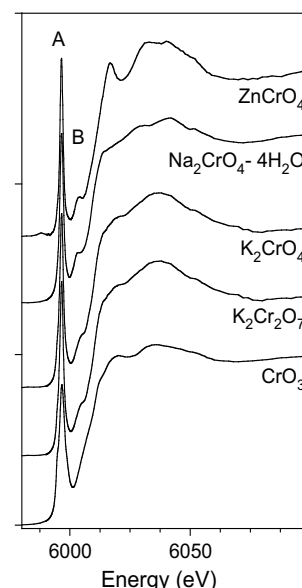


Figure 2 – Cr K-edge XANES spectra for models of Cr(VI).

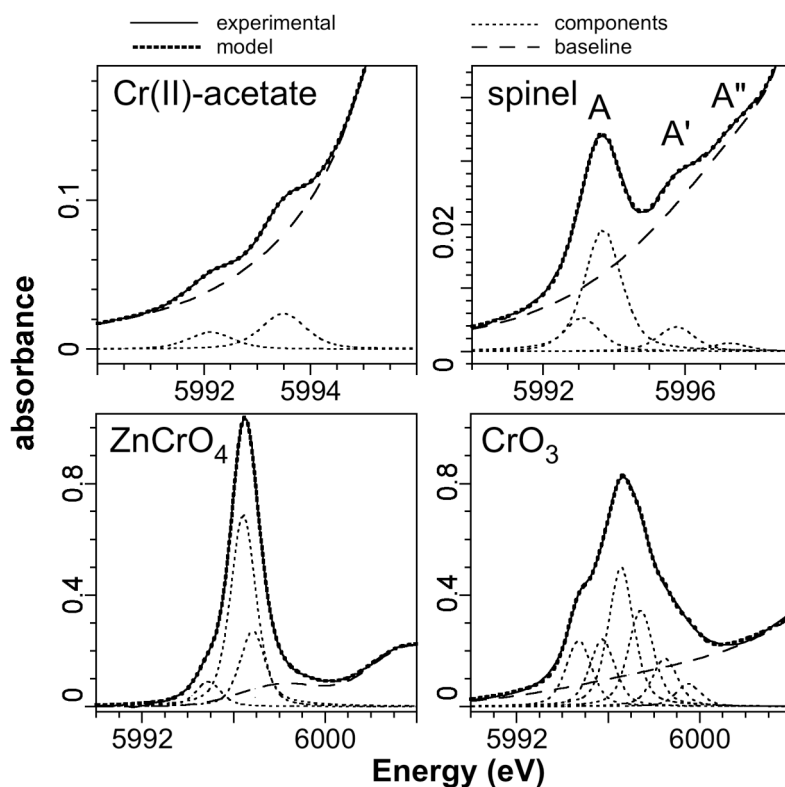


Figure 3 – Normalized pre-edge features for Cr(II)-acetate dihydrate, a Cr(III)-bearing spinel and two selected chromates. Cr(II)-acetate is used to determine the width and shape of transitions that could be resolved with XANES spectroscopy (here, 2). Then, the pre-edge shape obtained for Cr(II) is applied to Cr(III) and Cr(VI). We do not say that those transitions have a physical significance but they correspond to components that could be spectroscopically resolved. This strategy also minimizes the number of variable parameters (only area and position were allowed to vary).

3. Results

Figures 1 and 2 shows the normalized Cr K-edge spectra collected for the selected models of Cr(III) and the chromates of that study. Figure 3 shows the model of the pre-edge feature for 4 selected models of Cr(II), Cr(III) and two representative chromates (monomeric and polymeric). Figure 3 also give details on the way the pre-edge models were modeled.

Monomeric Cr(VI) is the most often used model for Cr(VI). Then, the largest error arises when polymeric Cr(VI) is modeled with monomeric Cr(VI). In that case, the side contributions of polymeric Cr(VI) (near 5995 and 5997 eV) might be partially hidden by the absorption of Cr(III) and by the edge jump. Then, the modeled amount of Cr(VI) will be lower than in reality. However, the resulting fit will be bad because the widths of the pre-edge for monomeric and polymeric Cr(VI) are so different.

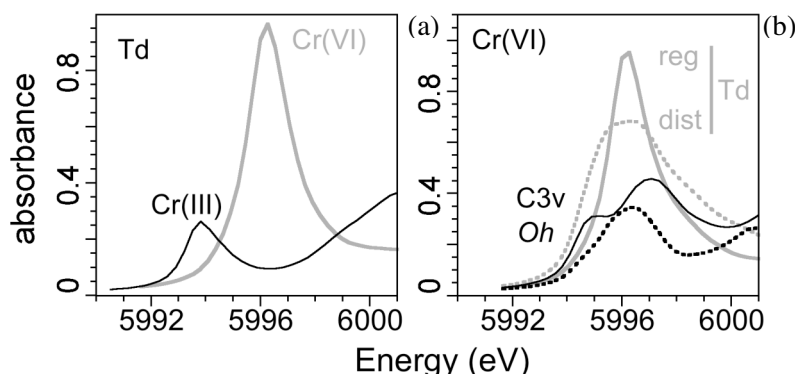


Figure 4 – FEFF 8.4 calculations of the pre-edge feature, simulating the experimentally observed variations in the pre-edge feature: (a) Cr(III) vs. Cr(VI) (with a Td symmetry); (b) Cr(VI) with various symmetries: Oh, C3v and two Td's, regular and distorted.

4. Discussion

The studied pre-edges for Cr(III) show similar features, with features A and A' (see Figures 2 and 3). Only a transition is sometimes observed on the high energy side of the pre-edge (see A'' on Figures 2 and 3). In contrast, the pre-edge width for Cr(VI) increases by ~ 50% from monomeric sodium chromate to polymeric CrO₃, Ab-initio XANES calculations (FEFF8.4) [14], using default conditions, confirms those trends (Figure 4) : shift of ~ 3 eV from Cr(III) to Cr(VI) and a increase of the pre-edge intensity from Oh to Td and an increase in pre-edge width with tetrahedral distortion.

Pauling's second rule [15] explains how polymerization enhances polyhedral distortion that had a well-known direct effect on the pre-edge feature intensity but also on its width.

This result shows that extreme caution must be taken when simulating a mechanical mixture of Cr(III) and Cr(VI) as Cr-polymerization strongly affects the shape of the pre-edge feature to model to derive the desired respective amounts of Cr(III) and Cr(VI). The good news is that the width of the pre-edge feature for Cr(VI) can be easily used as an indicator of the Cr(VI)-polymerization. Then, this observation should be used to choose the appropriate model compound of Cr(VI) that can be used to derive reliable fractions of Cr(VI) relative to Cr(III) during the model of "unknown" samples.

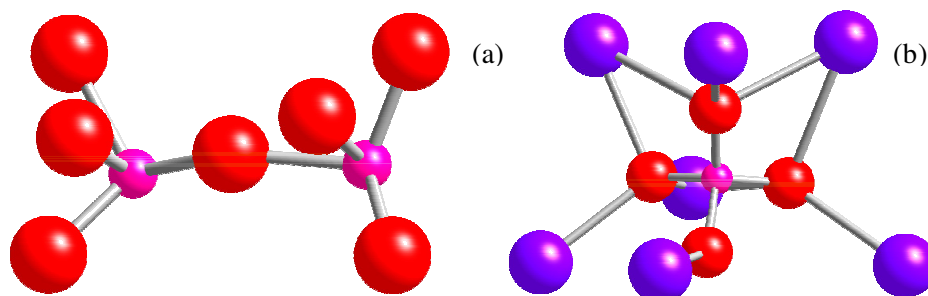
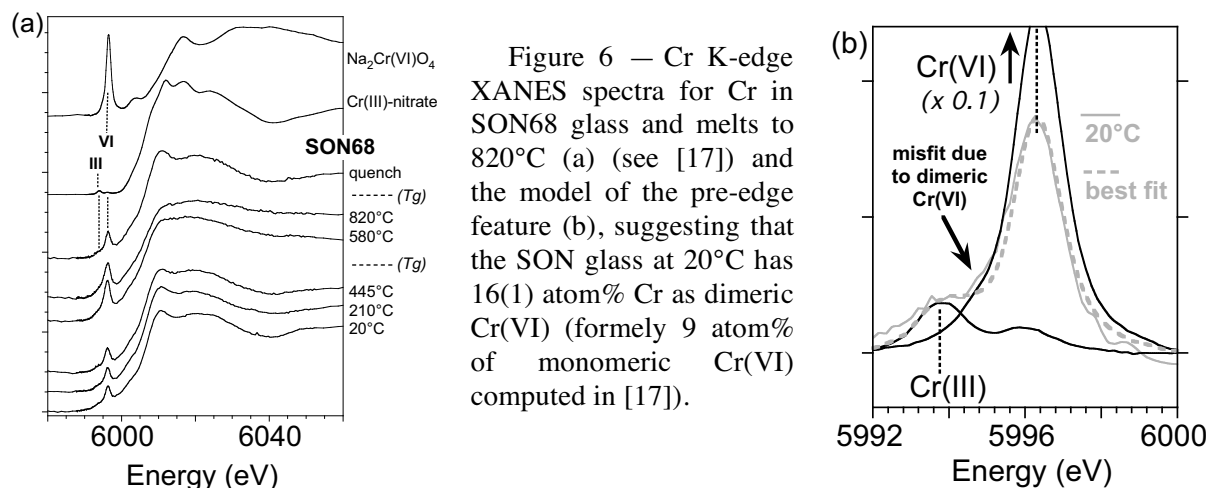


Figure 5 — Atomic clusters around Cr (pink) in CrO₃ (a) and K₂CrO₄ (b). Oxygens are in red and potassium in blue. Note the bridging oxygens in CrO₃, while oxygens are charge compensated by potassium in K₂CrO₄. Hence, tetrahedral distortion is much greater in CrO₃ (Cr-O distances varies from 1.58 to 1.75 Å) as compared to K₂CrO₄ (Cr-O distances varies from 1.64 to 1.66 Å).

For instance, the modeling of the Cr K-edge pre-edge feature in borosilicate glasses and melts to 1200 K (SON68) [16,17] simulating those used for nuclear waste storage is shown on Figure 6. A close examination of the Cr(VI) component of those peculiar pre-edges show a misfit with monomeric chromates near 5995 eV, suggesting the presence of more polymerized chromates moieties in those glasses and melts. Therefore, the computed amounts of Cr(VI) in those systems were underestimated in [17]. A new model with Na-dichromate reports 16(1) atom% dimeric Cr(VI), about twice as in [17].



References

- [1] Charlet L and Manceau A 1992 *J Colloid Interface Sci* **148** 443
- [2] Brown G E Jr, Chambers S A, Amonette J E, Rustad J R, Kendelewicz T, Liu P, Doyle C S, Grolimund D, Foster-Mills N S, Joyce S A and Thevuthasan S (2001) Am Chem Soc Symp Ser 778, Nuclear Site Remediation - First Accomplishments of the Environmental Management Science Program (Eds. PG Eller and WR Heineman), pp 212-246, Am Chem Soc, Columbus, OH, USA.
- [3] Sutton S R, Jones K W, Gordon B, Rivers M L and Smith, J V 1993 *Geochim Cosmochim Acta*, **57** 461
- [4] Peterson M L, Brown GE Jr, Parks G A and Stein C L 1997 *Geochim Cosmochim Acta* **61** 3399
- [5] Gaudry E, Kiratisin A, Saintavit P, Brouder C, Mauri F, Ramos A, Rogalev A and Goulon J 2003 *Phys Rev B* **67** 094108
- [6] Pantelouris A, Modrow H, Pantelouris M and Hormes J 2004 *Chem Phys* **300** 13
- [7] Glatzel P, Bergmann U, de Groot FMF, Weckhuysen BM and Cramer SP 2005 *Phys. Scripta* **T115** 1032
- [8] Beale A M, Gradnjan D, Kornatowski J, Glatzel P, de Groot F M F and Weckhuysen BM 2006 *J Phys Chem B* **110** 716
- [9] Villain O, Calas G., Galois L, Cormier L and Hazemann J L 2007 *J. Am. Ceram. Soc.* **90**, 3578
- [10] Juhin A, Calas G, Cabaret D, Galois L and Hazemann J M 2008 *Amer. Mineral.* **93**, 800
- [11] Tromp M, Moulin J, Reid G and Evans J 2007 *AIP Conf Proc* **882** 699
- [12] Farges F 2009 *Phys. Chem. Mineral* (online first) DOI 10.1007/s00269-009-0293-3
- [13] Winterer M 1997 *J. Phys IV (France)* **7**, C2.243
- [14] Ankudinov A L, Ravel B, Rehr J J and Conradson S D 1998 *Phys Rev B* **58** 7565
- [15] Pauling L. 1929 *J. Amer. Chem. Soc.* **51**, 1010
- [16] Brown G E, Jr, Farges F and Calas G 1995 In: "Structure, dynamics, and properties of silicate melts" (Eds. J.F. Stebbins, D.B. Dingwell, et P.F. McMillan, Reviews in Mineralogy, Vol. 32, The American Society of America, pp. 317-410.
- [17] Farges F, Brown G E, Jr. 2006 Proceedings of the XAFS-13 meeting (available here: www.slac.stanford.edu/econf/C060709/papers/055_TUPO80.PDF); *AIP Conf. Proc.* **882**, 44