

Determination of chromium valence over the range Cr(0)–Cr(VI) by electron energy loss spectroscopy

Tyrone L. Daulton^{a,*}, Brenda J. Little^b

^aMarine Geosciences Division, Naval Research Laboratory, Stennis Space Center, MS 39529, USA

^bOceanography Division, Naval Research Laboratory, Stennis Space Center, MS 39529, USA

Received 9 August 2005; received in revised form 31 January 2006; accepted 10 February 2006

Abstract

Chromium is a redox active 3d transition metal with a wide range of valences (−2 to +6) that control the geochemistry and toxicity of the element. Therefore, techniques that measure Cr valence are important bio/geochemical tools. Until now, all established methods to determine Cr valence were bulk techniques with many specific to a single, or at best, only a few oxidation state(s). We report an electron energy loss spectroscopy (EELS) technique along with an extensive suite of affined reference spectra that together, unlike other methods, can determine Cr valence (or at least constrain the possible valences) at high-spatial resolution (tens-of-nanometer scale) across a wide valence range, Cr(0)–Cr(VI). Fine structure of Cr-L_{2,3} edges was parametrized by measurement of the chemical shift of the L₃ edge and the ratio of integrated intensity under the L₃ and L₂ edges. These two parameterizations were correlated to Cr valence and also the dⁿ orbital configuration which has a large influence on L-edge fine structure. We demonstrate that it is not possible to unambiguously determine Cr valence from only one fine-structure parameterization which is the method employed to determine metal valence by nearly all previous EELS studies. Rather, multiple fine-structure parameterizations must be used together if the full range of possible Cr valences is considered. However even with two parameterizations, there are limitations. For example, distinguishing Cr(IV) from Cr(III) is problematic and it may be difficult to distinguish low-spin Cr(II) from Cr(III). Nevertheless, when Cr is known to be divalent, low- and high-spin dⁿ orbital configurations can be readily distinguished.

Published by Elsevier B.V.

PACS: 79.20.Uv; 68.37.Lp; 82.80.Dx; 82.80.Pv

Keywords: Electron energy loss spectroscopy; Chromium valence determination; L_{2,3}-adsorption edges; Transmission electron microscopy

1. Introduction

Chromium occurs in a variety of minerals [1] found in meteorites of all petrographic classes [2], lunar basalts [3], Martian rocks and the Earth, recording valuable information concerning geochemical conditions of mineralization and subsequent alteration. For example, many Cr-bearing minerals crystallize from basaltic magma where the valence of the mineralized Cr as well as the partitioning of Cr

between solids/liquid and metal/silicates is dependent on oxygen fugacity and temperature [3–5]. Although recently challenged [6], the similar depletions of Cr estimated for the Earth and the Moon (based on inferred Cr partitioning coefficients) with respect to the most primitive chondritic meteorites have been considered the strongest evidence for a terrestrial origin of the Moon [7]. In the terrestrial crust, Cr is a common constituent of ultramafic rocks, such as peridotite and their serpentines, e.g. chromite (Fe,Mg)-(Cr,Al,Fe)₂O₄ [8]. Natural weathering of Cr bearing minerals [9] and fallout of volcanic ash release Cr into the terrestrial environment. Furthermore, Cr compounds are widely used in numerous industrial processes [10] that can discharge Cr complexes in soils/sediments and surface/

*Corresponding author. Present address. Center for Materials Innovation, Washington University in St. Louis, St. Louis, MO 63130, USA. Tel.: +1 314 935 4537; fax: +1 314 935 6644.

E-mail address: tdaulton@physics.wustl.edu (T.L. Daulton).

ground waters, as well as the atmosphere in the form of aerosols. The geochemistry and toxicity of Cr in the environment are largely controlled by the valence of this redox active 3d transition metal. Chromium valence can be altered by microbes [11–13], green algae [14], higher plants [14,15] and mineral surfaces [16–19]. Therefore, techniques that determine Cr oxidation state are important biogeochemical tools.

Chromium has a wide range (–2 to +6, in rare cases –4 and –3 are reported) of possible oxidation states [20–24]. Of these, only two, trivalent Cr(III) and hexavalent Cr(VI), are stable in the majority of terrestrial surface and aqueous environments [25,26]. Thermodynamic calculations predict Cr(VI) is most stable form in oxygenated aqueous solutions (0.15×10^{-4} – 5.0×10^{-4} mol/L dissolved O_2) for $pH \geq 7$ while for $pH \leq 6$ Cr(III) is the most stable form [27]. Further, nearly all mineralized Cr in the terrestrial crust is trivalent presumably in disequilibrium with the atmosphere because of kinetic barriers [28].

Valence of Cr strongly affects many biogeochemical properties of Cr complexes including solubility, adsorption affinity and toxicity. All Cr(VI) species are soluble oxides, and the three main Cr(VI) species in solution are highly soluble chromate (CrO_4^{2-}), hydrochromate ($HCrO_4^-$) and dichromate ($Cr_2O_7^{2-}$) anions [29,30]. Hexavalent (as well as pentavalent) Cr species are strong oxidants which act as carcinogens, mutagens and teratogens in biological systems (for reviews, see Refs. [25,31,32]). The structural similarity of chromate anions (dominant Cr(VI) species at $pH < 6.1$, [30]) to biologically important inorganic anions, such as SO_4^{2-} and PO_4^{3-} , is likely responsible for their ability to readily transverse cell membranes, via the sulfate transport system, and be incorporated into cells (for reviews, see Refs. [32,33]). In contrast, most water soluble Cr(III) species do not occur naturally and are unstable in the environment [25]. Only under very acidic ($pH \leq 5$) or very basic ($14 \leq pH$) conditions will Cr(III) exhibit solubility above $10 \mu M$ concentration [34,35]. In solution, Cr(III) exists as the cations Cr^{3+} (aq) and hydroxo complexes $Cr_m(OH)_n^{(3m-n)+}$ [34]. However, Cr^{3+} (aq) and $Cr(OH)_n^{(3-n)}$ complexes can be removed significantly from solution through adsorption by organic carbon [36] and mineral surfaces [37–39]. Therefore, Cr(III) species have low toxicity, in part, because their bioavailability is limited by low solubility and the tendency to form strong complexes with organics and hydroxo complexes. In contrast, the high mobility (solubility), bioavailability (uptake) and toxicity of Cr(VI) make it a particular environmental concern.

Geochemical and microbiological processes of Cr oxidation/reduction can drive both precipitation–dissolution and ion adsorption–desorption reactions in the environment. The study of these reactions as well as the study of the Cr redox processes themselves has been hindered by the lack of an analytical technique that can determine the oxidation state of Cr at high-spatial resolution. For instance, little is known about the redox intermediates. Redox intermediates of Cr are unstable with

intermediate valence between the valences of the stable end member forms. Previous studies have suggested the existence of several Cr redox intermediates in the reduction of Cr(VI):Cr(V) [14,40–45] and Cr(IV) [46]. To fully understand the geochemistry of Cr in the environment it is necessary to identify redox intermediates and the associated pathways involved in the interconversion of the different forms of Cr. This requires a technique that can determine Cr valence over a wide range of valences.

Nearly all of the established methods to determine Cr valence are bulk techniques and many are specific to only a few oxidation states. The most widely used method for measuring Cr in the environment is the diphenylcarbazide colorimetric method that is assumed specific to Cr(VI) [25,47]. However, Cr(V), a possible redox intermediate in reduction of Cr(VI) to Cr(III) by bacteria [42,44,45] and green algae [14], reacts with diphenylcarbazide to form stoichiometric oxidation products that exhibit similar photon absorbance as reaction products of Cr(VI) [48]. Spectroscopic methods using element specific detectors combined with chromatographic separations have been used to detect a limited number of valences of select metals (e.g., Cr(III) and Cr(VI)). Such methods include: flame (F)- and electrothermal (ET)- atomic adsorption spectrometry (AAS); direct current plasma (DCP)- and inductively coupled plasma (ICP)- atomic emission spectrometry (AES); inductively coupled plasma mass spectrometry (ICP-MS); UV–vis spectrometry and thermal lens spectrometry (TLS) (for a review see Ref. [49]). Furthermore, valence of 3d or 4d transition metals can be analyzed by X-ray fluorescence spectrometry (XRS) [50], X-ray photoemission spectrometry (XPS) [51], X-ray absorption spectrometry (XAS) [3,52], electron paramagnetic resonance (EPR) (also known as electron spin resonance (ESR)) spectrometry [42,53,54], high-field (HF)- EPR spectrometry (for integer-spin “EPR-silent” transition metals) [55], Auger electron spectrometry (AES) [56], and Mössbauer spectrometry [57]. However, it has been reported that Mössbauer spectrometry cannot be applied to Cr because of the lack of suitable Cr isotopes for measurement [58]. None of these techniques can determine metal valence at the submicron level in the proper biological/petrological context necessary for understanding the environmental processes of Cr reduction/oxidation.

Electron energy loss spectrometry (EELS) using transmission electron microscopy (TEM) is capable of determining valence of metals at high-spatial (nm) resolution (e.g. see Refs. [59–62]). Further, it has been demonstrated that electron energy-filtered TEM imaging can produce valence specific maps of metals [63–65]. Determination of oxidation state by EELS (as well as XPS and XAS) is accomplished by analyzing valence-induced differences in the fine structure of absorption edges through the comparison of unknowns to standards of known oxidation state. Absorption edges result from excited electron transitions to unoccupied states such as in the valence band of a metal. For EELS valence determination of transition metals, the most often used absorption edges are the well-separated L_2 and L_3 (or

Download English Version:

<https://daneshyari.com/en/article/1678342>

Download Persian Version:

<https://daneshyari.com/article/1678342>

[Daneshyari.com](https://daneshyari.com)