



# Chemical processes for the extreme enrichment of tellurium into marine ferromanganese oxides

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## Abstract

Tellurium, an element of growing economic importance, is extremely enriched in marine ferromanganese oxides. We investigated the mechanism of this enrichment using a combination of spectroscopic analysis and adsorption/coprecipitation experiments. X-ray Absorption Near-Edge Structure (XANES) analysis showed that in adsorption/coprecipitation systems, Te(IV) was oxidized on  $\delta$ -MnO<sub>2</sub> and not oxidized on ferrihydrite. Extended X-ray Absorption Fine Structure (EXAFS) analysis showed that both Te(IV) and Te(VI) were adsorbed on the surface of  $\delta$ -MnO<sub>2</sub> and ferrihydrite via formation of inner-sphere complexes. In addition, Te(VI) can be structurally incorporated into the linkage of Fe octahedra through a coprecipitation process because of its molecular geometry that is similar to the Fe octahedron. The largest distribution coefficient obtained in the adsorption/coprecipitation experiments was for the Te(VI)/ferrihydrite coprecipitation system, and it was comparable to those calculated from the distribution between natural ferromanganese oxides and seawater. Our XAFS and micro-focused X-ray fluorescence ( $\mu$ -XRF) mapping of natural ferromanganese oxides showed that Te was structurally incorporated as Te(VI) in Fe (oxyhydr)oxide phases. We conclude that the main process for the enrichment of Te in ferromanganese oxides is structural incorporation of Te(VI) into Fe (oxyhydr)oxide phases through coprecipitation.

This mechanism can explain the unique degree of enrichment of Te compared with other oxyanions, which are mainly enriched via adsorption on the surface of the solid structures. In particular, the great contrast in the distributions of Te and Se is caused by their oxidized species: (i) the similar geometry of the Te(VI) molecule to Fe octahedron, and (ii) quite soluble nature of Se(VI). Coexisting Mn oxide phases may promote structural incorporation of Te(VI) by oxidation of Te(IV), although the surface oxidation itself may not work as the critical enrichment process as in the case of some cations. This enrichment mechanism also means that ferromanganese oxides mainly scavenge dominant Te(VI) species from seawater and do not affect its species distribution in seawater, as described in a previous model. The variation in Te abundances and the correlation of Te concentration with the growth rate of natural ferromanganese oxides are consistent with the coprecipitation mechanism.

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## 1. INTRODUCTION

Ferromanganese oxides are important materials in the marine geochemistry of trace elements. They are aggregates of amorphous Fe (oxyhydr)oxides and Mn oxides and are

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widely present in forms such as crusts, nodules, and precipitate particles. Their large surface area and strong affinity for many elements make them efficient scavengers of trace metals from seawater. Some types of ferromanganese oxides are considered potential resources of valuable metals. It is well known that hydrogenetic ferromanganese crusts have traditionally been called cobalt (Co)-rich crusts. They often cover the surface of seamounts in the form of extended sheets and strongly accumulate many metals of economic interest, including Co, relative to the Earth's crust (e.g., Halbach et al., 1989; Hein et al., 2000).

From an economic viewpoint, ferromanganese crusts could properly be called “tellurium (Te)-rich crusts” (Hein et al., 2003). Tellurium is a metalloid located between Se and Po in the p-block of the periodic table. It exhibits certain metallic and non-metallic properties supporting recent development of a wide range of high-tech industries (e.g., Brown, 2000; Wachter, 2004; Deng et al., 2007; Ikeda et al., 2009; Graf et al., 2009; Zhang et al., 2009; Hein et al., 2010). Interestingly, Te is extremely enriched in hydrogenetic ferromanganese oxides (e.g., Hein et al., 2003, 2010; Lakin et al., 1963). While other elements including Co are enriched by 100–250 times over their Earth's crustal values, the enrichment of Te is ~55,000 times, the largest among all reported elements in ferromanganese oxides (Hein et al., 2000, 2003, 2010). Because Te is not mined as a primary ore anywhere in the world, its high concentrations in ferromanganese oxides could be a potential resource for meeting growing Te demands.

Ferromanganese oxides can also be key materials for understanding the geochemical behavior of Te in the surface environment, which is poorly known owing to the extremely low abundance and difficulty of analysis. Tellurium shows a scavenging-type vertical profile in typical seawater, with concentrations ranging from 0.4 to 1.9 pM (Lee and Edmond, 1985). Tellurium(VI) species predominate over Te(IV) species by factors of 2.0–3.5 in seawater, in which the dominant species are likely  $\text{TeO}(\text{OH})_5^-$  and  $\text{TeO}(\text{OH})_5^-$  (Lee and Edmond, 1985; Byrne, 2002). Some researchers have suggested that the distribution of Te species in seawater may be controlled by preferential uptake of Te(IV) species by ferromanganese oxides (Hein et al., 2003). Other researchers suggest that the anomalous Te abundance in ferromanganese oxides may be related to the input of interplanetary dust particles (Li et al., 2005). Although several studies have reported such higher Te concentrations in ferromanganese oxides (~205 ppm) than in any other geological samples (Koschinsky and Hein, 2003; Hein et al., 2003; Li et al., 2005; Baturin, 2007; Baturin et al., 2007), unsolved mechanisms of the extreme Te enrichment can raise controversial interpretation.

Here, we have to note first that the extremely large value of Te enrichment factor,  $[\text{Te}_{\text{Fe-Mn crust}}]/[\text{Te}_{\text{Earth's crust}}]$ , is partly attributed to the quite low abundance of Te in Earth's crust. To understand the Te abundance in ferromanganese oxides without any over/underestimation, it is necessary to reveal the enrichment mechanism of Te into ferromanganese oxides “from seawater”. The value of  $[\text{Te}_{\text{Fe-Mn crust}}]/[\text{Te}_{\text{seawater}}]$  is not as unique as the value of  $[\text{Te}_{\text{Fe-Mn crust}}]/[\text{Te}_{\text{Earth's crust}}]$ , but it still falls among the

most enriched group (Hein et al., 2003, 2010). Especially, the value of  $[\text{Te}_{\text{Fe-Mn crust}}]/[\text{Te}_{\text{seawater}}]$  ( $\sim 10^9$ ) is obviously much larger than those of other oxyanions ( $\sim 10^7$ ) (e.g., Takematsu et al., 1990). This emphasizes that an essential problem to be solved is the reason why Te shows unique enrichment into ferromanganese oxides from seawater compared with other oxyanions.

Tellurium is a redox-active oxyanion; thus, surface oxidation has been proposed as an explanation for the unique enrichment of Te into ferromanganese oxides from seawater (Hein et al., 2003). Oxidation reaction can be a trigger for efficient enrichment for some cationic elements such as Co, Ce, and Tl (Murray and Dillard, 1979; Manceau et al., 1997; Takahashi et al., 2007; Peacock and Moon, 2012). By analogy with these elements, oxidation can also be a controlling factor for Te, where Te(IV) in seawater is preferentially adsorbed onto Fe (oxyhydr)oxides and is subsequently oxidized to Te(VI) (Hein et al., 2003).

However, no evidence of the chemical state of Te in marine ferromanganese oxides has been published, yet. Without that information, it is difficult to know the chemical processes, for example, whether Te(IV) is preferentially incorporated into ferromanganese oxides and whether the oxidation reaction of Te(IV) can actually occur. Such fundamental information can be provided by a combination of adsorption/coprecipitation experiments and X-ray Absorption Fine Structure (XAFS) analysis to understand the unique behavior of Te at the seawater/ferromanganese oxide interface.

In this paper, we present new insights into mechanism of the extreme enrichment of Te into ferromanganese oxides. We investigated (i) the chemical state of Te in synthetic Fe (oxyhydr)oxides, Mn oxides, and natural ferromanganese oxides, and (ii) the macroscopic distribution of Te(IV) and Te(VI) on Fe (oxyhydr)oxides and Mn oxides, respectively. The findings on the chemical process at the seawater/ferromanganese oxide interface will develop understanding of the roles of marine ferromanganese oxides in the geochemical cycle of trace elements.

## 2. MATERIALS AND METHODS

### 2.1. Samples

Hydrogenetic ferromanganese oxides were collected from two sites in the Pacific Ocean: D535 in the South Pacific Ocean (13.0°S, 159.2°W, 5222 m depth), and AD14 around the Marshall Islands (14.1°S, 167.2°W, 1617 m depth) (Takahashi et al., 2000, 2007; Kashiwabara et al., 2008, 2009, 2010, 2011, 2013). These samples were air-dried, and a part of them were polished to make ca. 30- $\mu\text{m}$ -thick sections on glass slides for two-dimensional micro-focused X-ray fluorescence ( $\mu\text{-XRF}$ ) mapping. Another part of the samples was ground into powder using an agate mortar. Elemental concentrations were determined by ICP-MS (Agilent technologies, Agilent 7500). Among major elements, Mn was 27.9 wt% and 29.5 wt% and Fe was 16.4 wt% and 16.7 wt% for D535 and AD14, respectively. Concentrations of oxyanions, including Te, are summarized in Table 1. Chemical compositions of these

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