



The ratio of tellurium and selenium in geological material as a possible paleo-redox proxy



Thomas Schirmer*, Andrea Koschinsky, Michael Bau

Jacobs University Bremen, Earth and Space Sciences Program, Campus Ring, D-28759 Bremen, Germany

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ABSTRACT

Only few data for both tellurium and selenium in different geological materials including international reference materials have been available so far. In this study, the Te/Se ratio has been investigated in more detail to provide a better understanding of the correlation of these two elements in the geological environment. Nine international reference materials (IRMs) and 79 different geological samples spanning a wide range of formation times and conditions from the Paleoproterozoic to present were analyzed with quadrupole dynamic reaction cell (DRC)-ICP-MS. These samples include basalts, shales, river and beach sediments, loess, dolomites, a recent cold water coral, Precambrian manganese- and iron-formations and Cenozoic marine ferromanganese nodules and crusts. A wide range of concentrations between 0.01 and 1.5 $\mu\text{g/g}$ for Se and 0.01 and 90 $\mu\text{g/g}$ for Te was measured, and the most interesting feature was found to be the Te/Se ratio in the different geological matrices. While most rock and sediment samples fall within the range of Te/Se ratios typical of the average Earth's crust, a significant enrichment of Te over Se is evident for modern marine Mn-Fe oxide precipitates, with the most pronounced Te enrichment found for hydrogenetic ferromanganese crusts, which form under fully oxidizing conditions. The apparent positive trend of the degree of Te/Se fractionation with the redox potential of the formation environment suggests that the Te/Se ratio may represent a potential (paleo)proxy for redox environments.

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1. Introduction

Selenium (Se) and tellurium (Te) are two elements of scientific and economic interest, but especially for Te the concentration ranges in geological materials and its biogeochemical cycling are not very well known. The reason for this may be its complex geochemical behavior and the low concentrations in nature with the corresponding challenges for its analytic determination. The same applies to the ratio of these two elements. The complexity of the geochemical behavior of these two elements is related to their redox sensitivity. Stable oxidation states of Se and Te are -2 , 0 , $+4$, and $+6$. Typical chemical compounds are X^{2-} , $\text{X}(\text{s})$, XO_3^{2-} , and XO_4^{2-} (Kölbl, 1994). In nature, they commonly occur in sulfide ores, replacing S^{2-} (Pohl, 2011) in anoxic systems. In oxic environments, oxidation states $+4$ and $+6$ are found. In oxic solutions both elements can form anions of their respective oxo acids, whereas XO_2 or XO_3 is the oxidized solid form. They can be part of

other oxidic phases and are frequently found in iron oxides. Both are classified as toxic trace elements, but Se is also known to be an important essential element in biochemical processes in a restricted concentration range (Schwarz and Foltz, 1957). In industrial applications, both elements find increasing interest in modern technologies; Te is of importance primarily for steel finishing, but also for solar cell technology, while Se is used for photoactive cells, rectifiers and glass coloring agents, among other applications (Pohl, 2011).

Due to their increasing economic importance and environmental concern, and because of their manifold (bio) geochemical reactions in natural systems, the concentrations and behavior of these two elements are of high interest; however, knowledge of the distribution and the ratio of Se and Te in geological matrices, such as rocks, soils, sediments, and iron or manganese oxide precipitates, appears to be limited. The purpose of this paper is to help filling this gap using a simple and rapid simultaneous determination method with a sufficiently low limit of detection for Se and Te with DRC-ICP-MS and to present concentration data for Se and Te in different geological samples. Furthermore, we suggest the ratio of the two elements as a possible proxy for paleo-redox conditions during formation of oxidic phases in marine, and possibly other aqueous environments. An investigation of ferromanganese crusts, conducted by Hein et al. (2003) had shown an extreme enrichment of Te over the Earth's crust and seawater, but no comparable

* Corresponding author at: Clausthal University of Technology, Institute of Disposal Research, Adolph-Römer-Str. 2A, D-38678 Clausthal-Zellerfeld, Germany. Tel.: +49 5323 72 2917; fax: +49 5323 72 2810.

E-mail address: thomas.schirmer@tu-clausthal.de (T. Schirmer).

enrichment of the geochemically very similar element Se. This Te enrichment was related to a surface oxidation process of Te(IV) to Te(VI) on the Fe–Mn oxide surfaces, which apparently does not take place for Se(IV). Therefore, investigating the potential of the element pair Se and Te and its ratio as a paleo-redox proxy was a major goal of this study.

2. Occurrence of Se and Te in natural systems

The focus in this article will be on the ratio of Te and Se in different solid geological matrices. A comprehensive selection of Te and Se concentration data and Te/Se ratios calculated from these literature data of international reference samples (IRM, international reference material) for rocks, sediments, soils and coal in comparison for data for bulk silicate earth is presented in Figs. 1 and 2. For different geological reference materials Se values up to a few µg/g and in shale and bentonite up to 40 µg/g are quoted. Coal is often distinctively enriched in Se, being associated mainly with the organic and to a lesser extent with the sulfide fraction (U.S. National Committee for Geochemistry, 1980; Spears and Zheng, 1999; Lussier et al., 2003). Very high concentrations of Se are also found in sulfidic ores.

Tellurium data sets for IRMs are mostly available only from analytical publications and compilations, presenting a wide concentration range from <0.001 µg/g up to >100 µg/g (Fig. 1), but do not represent certified values. High concentrations in Te have been reported especially for

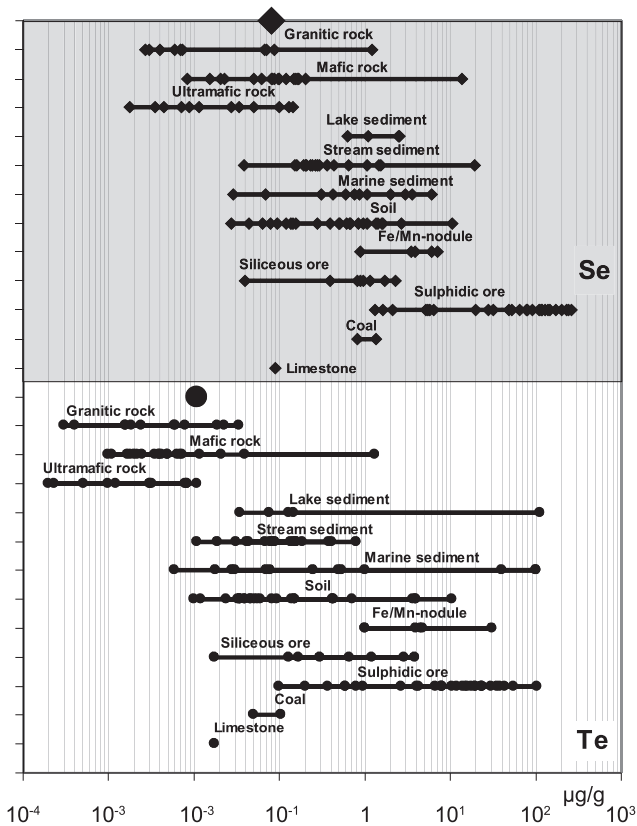


Fig. 1. Te and Se concentrations for international reference materials divided up into different reservoirs. Big black dots on top of the sections: bulk silicate earth (Wang and Becker, 2013). Data set from Jochum et al. (2005) (averages) and Govindaraju (1994), Makishima and Nakamura (2009), Matusiewicz and Krawczyk (2009), König et al. (2012), Yi et al. (2000), Wang and Becker (2013), Savard et al. (2009), Lorand and Alard (2010), Jenner et al. (2012), Hamlyn et al. (1985), Forrest et al. (2009), Floor and Román-Ross (2011), and Dare et al. (2010).

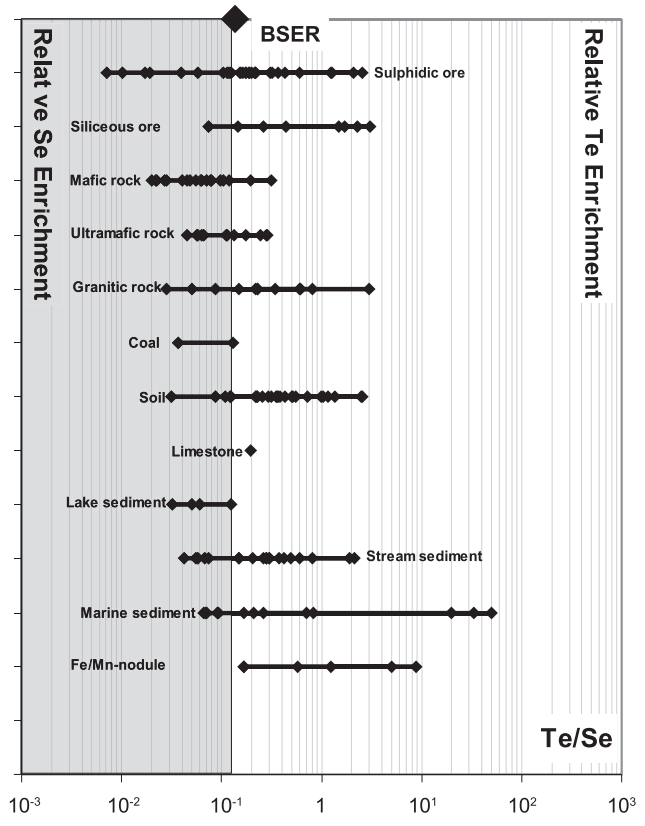


Fig. 2. Te/Se ratios for international reference materials, references see Fig. 1. Big black mark above data sets: bulk silicate earth ratio (BSER).

marine sediments and ferromanganese nodules. Coal and sulfidic ores are slightly enriched in Te compared to bulk silicate earth. Ultramafic rocks have the lowest concentrations in Te and Se. A reason for this could be that these elements do not fit into the crystal lattices of the typical ultramafic minerals (olivine, pyroxene, plagioclase and oxides).

Using the data from Wang and Becker (2013), the average Te/Se ratio for bulk silicate earth can be calculated to be about 0.14. Distinctly higher ratios with respect to this ratio occur in sediments, especially from marine environments and in marine ferromanganese nodules. The explicit enrichment of Te in these environments has been explained with surface oxidation processes (Hein et al., 2003). Because of very high enrichment of Se in some sulfides, sulfidic ores can have the lowest Te/Se ratio. This can be due to exchange of the crystallographically similar S with Se. Due to the fact that – compared with the BSER – Te as well can be distinctively enriched over Se a similar behavior can be assumed for Te, depending on the available quantities of Se and Te and the conditions of formation.

3. Overview of Se and Te determination methods

The determination of Se and Te poses a number of problems, depending on the analytical technique used and the speciation present in the sample material or required for determination. The critical steps include digestion and – if required – separation or preconcentration, and the measurement itself.

During (pressurized) acid digestion, Se is volatile to a certain extent when using temperatures above 80 °C and/or acid mixtures containing HCl (Layton-Matthews et al., 2006). The reason is that in the reduced state (Se(IV)) this element forms volatile hydrides. The classic pressurized acid digestion procedures therefore have to be adapted to lower

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