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FeMnOx-1: A new microanalytical reference material for the investigation of Mn–Fe rich geological samples

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ABSTRACT

Suitable Mn–Fe rich microanalytical reference materials (MRMs) as calibration material for laser ablation–inductively coupled plasma mass spectrometry (LA-ICPMS) have not been available. The United States Geological Survey (USGS) in collaboration with the Max Planck Institute for Chemistry has prepared a synthetic MRM, FeMnOx-1, with elevated mass fractions of MnO (25 g/100 g), Fe_2O_3 (8.5 g/100 g) and high mass fractions of 25 trace elements varying between 200 and 5000 mg/kg. This new MRM has been designed as calibration material for a wide range of different Mn–Fe deposits, such as desert/rock varnish, ocean crusts and nodules as well as Mn accumulations in soils and lakes. Small-scale and large-scale homogeneity of FeMnOx-1 were tested with three LA systems (200 nm femtosecond, and 193 nm and 213 nm nanosecond lasers) using different spot sizes and fluences. Our results demonstrate that FeMnOx-1 is homogeneous in the pg to μg and nm to μm range and therefore well suited for microanalytical applications. The relative standard deviation (RSD) values obtained from repeated measurements are about 2–3% for test portion masses of 5–100 ng, and are comparable to those of the homogeneous NIST SRM 610 and USGS GSE-1G reference glasses. Homogeneity of FeMnOx-1 was also verified for a test portion of 0.1 ng. Seven laboratories using five different bulk and microanalytical techniques were involved in the characterization of FeMnOx-1. Small amounts of this MRM can be obtained on request from the authors.

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1. Introduction

Manganese–Fe-rich materials are of great economic and scientific interest. Of special interest are natural deposits, such as desert/rock varnish (e.g., Dorn, 1998), manganese nodules in lakes (e.g., Dean et al., 1981), hydrogenetic, diagenetic and hydrothermal Mn–Fe ocean nodules and crusts (e.g., Bau et al., 2014) as well as marine primary sedimentary manganese ore deposits (e.g., Frakes and Bolton, 1992). Recently, also the Mars Science Laboratory Curiosity pictured and characterized varnish-like shiny, black covers on Martian rocks that exhibit high contents of Mn (Lanza et al., 2015). Furthermore, anthropogenic-associated accumulations like roadside soil and plants with elevated levels of Mn from gasoline exhausts (Lytle et al., 1995) or black manganiferous crusts on buildings also referred to as urban varnish have been investigated (Grissom et al., 2014).

Microanalytical work has been performed on manganese nodules (e.g., Garbe-Schönberg and McMurtry, 1994; Bau et al., 2014) and rock varnish (e.g., Wayne et al., 2006; Goldsmith et al., 2014; Macholdt et al., 2015). In particular, the small <200 μm thin Mn-rich layers of varnish on desert rocks are important samples for paleoclimate research (e.g., Liu and Broecker, 2013 and references therein). For geochemical investigations, microanalytical techniques, such as LA-ICPMS, have been employed to determine element mass fractions in manganese nodules and in varnish layers (Macholdt et al., 2015) on rocks. These techniques, however, need MRMs for instrument calibration to avoid inaccuracies owing to different bulk composition of reference material and sample. In contrast to rock RMs, where homogeneity investigations were performed in the mg–g range, MRMs have to be homogeneous in the pg to μg or nm to μm scale. Because of possible matrix effects on sample analysis, it is preferable that MRMs are matrix-matched and contain high trace element mass fractions. Unfortunately, no such

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MRMs exist yet for Mn–Fe rich materials. Researchers therefore use mainly the certified NIST SRM 610 and SRM 612 silicate glasses (Hlawatsch et al., 2002; Nowinski et al., 2010), where mass fractions are well known (Jochum et al., 2011) or glasses with a basaltic composition, such as the MPI-DING glasses (Wayne et al., 2006) or the USGS GSE-1G glass (Macholdt et al., 2015). These glasses have the advantage that they are homogeneous for most elements in the nm–μm range and are well characterized (see GeoReM database http://georem.mpch-mainz.gwdg.de; Jochum et al., 2005a). However, they have low Mn (NIST SRM 610: 444 mg/kg, USGS GSE-1G: 590 mg/kg) and low Fe (NIST SRM 610: 458 mg/kg) contents compared with a typical varnish (Mn = 7–38 g/100 g, Fe = 0.7–7 g/100 g; Macholdt et al., 2015). Because of low Mn and Fe contents of the reference glasses, some authors use pressed powder pellets of natural manganese nodule RMs (e.g., USGS NOD A-1 and NOD P-1) for calibration. However, Macholdt et al. (2015) and others (Hoffmann et al., 1997; Hirata et al., 2013) showed that such samples are heterogeneous at the μm scale and that the mass fraction of many trace elements is too low and not well enough known to perform an accurate calibration. This means that the use of powdered manganese nodule RMs is severely limited for microanalytical work.

Owing to these disadvantages the USGS in collaboration with the Max Planck Institute for Chemistry has produced a synthetic Mn–Fe-rich MRM, which is designed to be homogeneous in the nm–μm or pg–μg range, contains trace element mass fractions in the upper hundred mg/kg range (Fig. 1), and is available in sufficient supply (100 g) to satisfy the needs of many microanalytical laboratories. The aim of this paper is to present information on this new MRM, FeMnOx-1, to demonstrate homogeneity and to report mass fractions of 37 major and trace elements using different bulk and microanalytical techniques.

2. Analytical

2.1. Sample preparation

A detailed description of the sample preparation is given in Supplementary Tables S1 and S2. All chemicals used in the preparation of FeMnOx-1 were commercially available reagent grade and used without further purification. The target mass for this initial preparation was 100 g. Matrix elements were prepared using either chloride and nitrate salts (Al, Ca, Fe, Mg, Mn, Ti) or hydroxides and phosphate salts (Na, P, K, Si). A total of 27 trace elements were added to the cation solution using aliquots of commercially available 1000 or 10,000 mg/L single element standard solutions.

The cation and anion solutions were combined in a 2 L beaker which resulted in the formation of a dark brown precipitate after vigorous mixing using a glass stir rod. A 20 mL aliquot of commercial grade sodium hypochlorite (8% m/m) was then added to the beaker converting the material to a black/dark brown precipitate by oxidation of Mn^{2+} to Mn^{4+}. The precipitate was mixed for an additional hour and then allowed to equilibrate overnight. After settling the colorless supernatant was decanted and the solid material transferred to a series of 125 mL polyethylene bottles. Starting conductivity and pH measurements on the supernatant solution yielded values of 130 mS and ~13, respectively. The bottles were transferred to an International Equipment Company (IEC) low speed (5000 rpm) centrifuge and spun for a period of 20 min. After centrifuging the supernatant was decanted and deionized water added to the bottles. The solid phase was resuspended with vigorous hand shaking and the bottles centrifuged for an additional 20 min. This washing process was repeated (10–13×) until the supernatant conductivity was 300 μS or less. After centrifugation, aliquots (10 g) of the precipitate were micronized in deionized water, for 7 min, using agate grinding media and a Macrone micronizing mill. When micronizing was complete the material was transferred to a beaker and dried overnight at 110 °C. The dried material was ground in an Angstrom agate shatter box (model TE110) for 10 min. The total mass of dried material prepared in this manner was 93.23 g. As Fig. 2 shows, pressed pellets can be produced from the powdered sample for microanalytical purposes (see Supplementary data for details).

2.2. Techniques

2.2.1. Bulk techniques

Major and several trace element mass fractions were determined in two different laboratories by XRF. At the Institute for Geosciences of the University of Mainz FeMnOx-1 was analyzed by XRF using a 2002 model Philips MagXPRO X-ray spectrometer with a Rh-X-ray-tube and a maximum excitation of 3.2 kW for major and 3.6 kW for trace elements. For major element analyses 0.4 g of powder were mixed with 5.2 g of lithium meta-tetra borate (LTB) (1:14) to produce fused glass beads. Pressed powder pellets were produced using 6 g of undiluted material for trace element determinations. In addition, the loss on ignition (LOI) was determined by a stepwise heating process. The wavelength dispersive X-ray fluorescence (WDXRF) method at the commercial laboratory SGS in Canada was a standard LTB fusion followed by WDXRF analysis.

Major and trace element analyses were also performed by solution ICPMS, isotope dilution (ID)-ICPMS and ICP-atomic emission spectroscopy (ICPAES) in different laboratories. At SGS laboratory, Canada, the

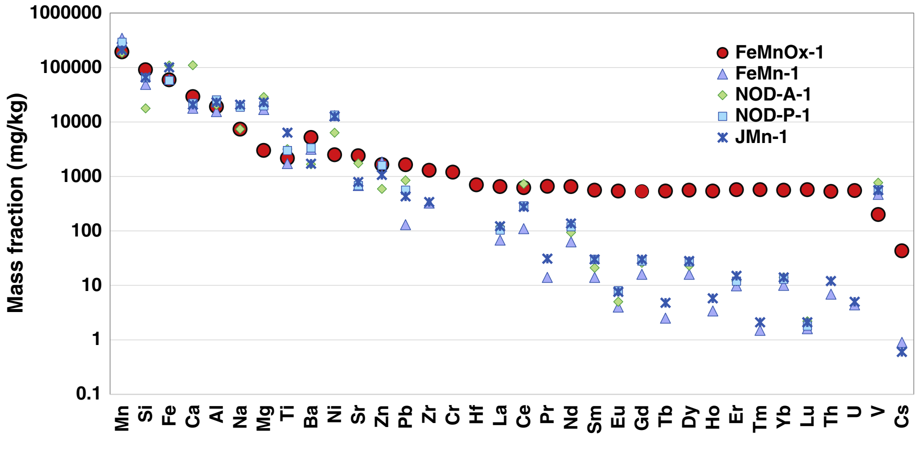

Fig. 1. Mass fractions of major and trace elements for the nodule RMs FeMn-1, NOD-A-1, NOD-P-1 and JMn-1 (data from the GeoReM database). Elements are arranged according to their increasing contents in FeMnOx-1. Mass fractions are compared with the new MRM FeMnOx-1 (Table 1). Note the high trace element content of FeMnOx-1, which is suitable for calibration of trace elements.

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