



Determination of trace elements in calcium rich carbonate rocks by Wavelength Dispersive X-ray Fluorescence Spectrometry for environmental and geological studies



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HIGHLIGHTS

- The WDXRF technique was developed for the sedimentary rocks with high Ca content.
- Infinitely thick samples were prepared.
- The calibration data were obtained using the sediment and rock reference materials.
- V, Cr, Co, Ni, Cu, Zn, Pb, Ba, La, Ce, Nd, Rb, Sr, Y, Zr, Nb were determined.
- Analytical figures of merit were found to be satisfactory.

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ABSTRACT

A simple, rapid and non destructive Wavelength Dispersive X-ray Fluorescence Spectrometry (WDXRFS) was developed for the determination of trace elements such as V, Cr, Co, Ni, Cu, Zn, Pb, Ba, La, Ce, Nd, Rb, Sr, Y, Zr, and Nb in carbonate rocks with high calcium content. Samples of marble, limestone, fluorite ore and carbonatite-like rocks were chosen as objects under investigation. These samples have wide ranges of major and trace element contents, and high concentration of calcite (70–98%) in calcium rich carbonates. The sample mass required for infinite thickness was calculated for each element. In order to determine V, Cr, Co, Ni, Cu, Zn, Ba, La, Nd, Ce, sample weighting 1 g was pressed with a pressure of 100 kN. For the determination of Rb, Sr, Y, Zr, Nb, Pb, the sample mass was increased up to 5 g. The calibration curves were constructed by employing the International Certified reference materials (ICRMs) and in-house standard reference materials (HSRMs) of various types of rocks and sediments, and the matrix effects were taken into account using the influence coefficients (α -correction equations). Analytical figures of merit have also been assessed. The calculated values of the instrumental limit of the detection were within the interval from 0.5 to 4.0 mg kg⁻¹. The repeatability and reproducibility were found to be satisfactory with the relative standard deviations lower than 5%. The accuracy was evaluated by the analysis of two reference materials and the comparison with the ICP-MS results. A good agreement was achieved between the reference and measured values with recoveries ranging from 85% to 115%. The relative disagreements between the XRF and ICP-MS results were less than 10%.

1. Introduction

A comprehensive study of geological and geochemical characteristics of carbonate sedimentary rocks usually involves the determination of chemical composition of samples studied. Obtained geochemical data about spatial distribution of different elements can be used for determining the origin of the carbonate rocks, understanding the nature of modern carbonates, interpreting processes and products of diagenesis, etc. (James and Jones, 2015; Letnikova, 2005; Sklyarov et al.,

2001). In geologic study carbonatite and carbonatite-like rocks, the major and trace elements can serve as an indicators of Late Riphean rifting, which took place in the Siberian craton (Savel'eva et al., 2014). Geoecological and geochemical investigations of sediments and sedimentary rocks are performed in (Santos et al., 2007; Zwolinski et al., 2007; Markov, 2011) to reconstruct paleo-geochemical conditions of the sedimentation and to identify the main factors controlling their accumulation.

In the present research, studied samples of the sedimentary rocks

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were collected from two areas: central part of the Republic of Buryatia and western shore of Lake Baikal (Russia). These samples have wide ranges of major and trace element contents, and high concentration of calcite: in carbonate samples the calcite content is from 90% to 98%, in carbonatite samples – 70–90%. Concentrations of the major oxides in various types of the carbonates, for instance, dolomite (Wheeler, 1999), limestone (Wheeler, 1999; Arriolabengoa et al., 2015; Babatunde and Ademola, 2014), magnesite (Jones and Wilson, 1991), and marl (Arriolabengoa et al., 2015), can be successfully determined using X-ray fluorescence (XRF) method. However, in geochemical and ecological studies the bulk chemical composition of the carbonate rocks is not fairly informative without experimental data about the accumulation and spatial distribution of the trace elements (Letnikova, 2005; Sklyarov et al., 2001). As is known, carbonate materials is characterized by low concentration levels of most of the trace elements (Revenko, 2002). In fact, usage of the WDXRF method can be limited due to the poor sensitivity for some elements. Moreover, there is a general lack of the International Certified reference materials (ICRMs) and the in-house standard reference materials (HSRMs) of the carbonate rocks suitable for analyzing the diversity of the trace elements (Revenko, 2002; Sliwinski et al., 2012; Sarbajna et al., 2013).

Main objective of our research is to develop WD X-ray fluorescence (WDXRF) technique, in particular, generate the best analytical strategy for the determination of the selected trace elements to study the genesis of the sedimentary carbonates and carbonatites. Within the investigation, we consider the following steps: (i) choice and performing the sample preparation procedure; (ii) analyzing carbonate, carbonatite (veined carbonated and carbonatic-siliciclastic rocks), and fluorite ore samples by the XRF spectrometry including the choice of optimal conditions of the measurement; (iii) computing concentrations of some trace elements (V, Cr, Co, Ni, Cu, Zn, Pb, Ba, La, Ce, Nd, Rb, Sr, Y, Zr, and Nb), which are indicators of the paleo-geochemical conditions of the sedimentation; (iv) performing the correction of the matrix effects; (v) validating analytical figures of merit for the developed XRF technique.

2. Methodology

2.1. Sample collection and processing

All studied samples were collected from two areas: central part of the Republic of Buryatia and western shore of Lake Baikal. Geographical setting of these areas is the following.

Zaigraevskii area is located in central part of the Buryatia Republic (109°15'N and 52°50'E). Area of the Zaigraevskii district is equal to 6603 km². It borders with the Baikal region (Ulan-Ude town) in the north and Zabaikal'skii area in the south (Zaigraevskii area, 2015). Biliutinsky deposit is a part of the Zaigraevskii district and located 80 km north of the Ulan-Ude town. Nowadays, chemically pure limestones of the Biliutinsky deposit are used for the production of different types of chemical materials such as carbide of calcium and silicon, acetylene, lime chloride, and others. Also these limestones are applied in metallurgy, paper-pulp and building industry (Mineral resources of the Republic of Buryatia, 2015). The representative limestone, marble, carbonate and fluorite ore samples were collected by S.I. Shtel'makh from a bottom part of dikes of granite-porphry, andesite, trachyte composition of the Biliutinsky deposit.

The carbonatite-like rocks are appearing along the western shore of the Lake Baikal, a south part of the Siberian craton. The carbonatite rocks occur in the form of veins a few centimeters thick and fragments up to 10 cm among gneisses and granites. The rocks are yellow-gray or brown-colored and consist of carbonate 70–90% (Savel'eva et al., 2014). The carbonatite-like samples weighing about 15 kg were collected from calcitic and dolomitic veins at three sampling sites located approximately 10 km away from each other.

The cone and quartering sample preparation was applied for the obtaining a representative sample. The sample preparation has been

performed with requirements given in (OST, 2004). The collected samples were manually grinded and homogeneously mixed in an agate mortar for 10 h. For the elimination of a particle aggregation during the milling process a few drops of an ethyl hydroxide of high purity were added. Particle sizes of the powdered samples were defined using a laser particle-size analyzer “Analysette 22” COMPACT (FRITSCH, Germany). The determined sizes of the particles are in the range from 10 to 61 μm. Then the weighing procedure was conducted as follows. For the determination of Rb, Sr, Y, Zr, Nb, Pb each sample powder weighing 5 ± 0.001 g and wax weighing 1 ± 0.001 g as a binding agent was taken using an analytic balance of AB-series (St. Petersburg, Russia). Then these components were mixed and thoroughly shaken for two minutes. For the determination of the V, Cr, Co, Ni, Cu, Zn, Ba, La, Ce, Nd contents, each sample powder weighing 1 ± 0.001 g was also taken using the analytic balance. Prepared samples were pressed on the basis with boric acid using a HERZOG HTP-40 semiautomatic press with a pressure of 100 kN.

2.2. WDXRF set-up

All measurements were carried out in a vacuum condition using a WDXRF spectrometer S8 TIGER (Bruker AXS, Germany). This instrument is equipped with a 4 kW power X-ray tube with a rhodium anode and a beryllium window of 75 μm thickness. Detailed information about the WDXRF-spectrometer features can be found elsewhere (Service Manual, 2007). Listed in Table 1 are the instrumental measuring conditions used.

To select the optimal crystal, we measured the intensities of peaks and backgrounds for the analytical CrK_α-, LaL_α-, and Sr K_α- lines using LiF(200) and LiF(220) crystals and a 0.23° collimator. The comparison of the intensity levels of the peaks and backgrounds for these elements and the calculated WDXRF spectrum contrast (peak-to-background ratio) values of their spectra for the LiF(200) and LiF(220) crystals was carried out (Table 2, Figs. 1–3). It can be seen, that for our WDXRF spectrometer, S8 TIGER, with a comparable contrast on the LiF(200) and LiF(220) crystals, measurements on the LiF(200) crystal provide higher count rate by 1.3–2 times. In our opinion, this is due to the fact that in this wavelength region the scattered bremsstrahlung of the X-ray tube is not the dominant background component for our spectrometer. For all measurements, the authors applied an universally usable crystal of LiF(200) which has higher reflectivity, rather than LiF(220), and can be used for the elements with atomic number 19 (K) onwards (Schlotz, 2006). LiF(220) has lower reflectivity but higher resolution than LiF(200) (Schlotz, 2006). Thus, our choice of the LiF(200) crystal for determining the V, Cr, Co, Ni, Cu, Zn, Pb, Ba, La, Ce, Nd, Rb, Sr, Y, Zr, and Nb contents was responsible for the above arguments and the obtained experimental data.

Measurement time of the analytical line and the background from each element was 60–100 s and 30–60 s, respectively. Processing the X-ray spectra, numerical peak separation, and the correction of the matrix effects were performed using the software SPECTRA^{plus} (SPECTRA 2010) linked to the equipment.

2.3. Reference materials

The analytical quality control and construct of calibration curves were carried out using the ICRMs and HSRMs of different types of rocks and sediments with high content of calcium (more than 25%): carbonatite Bronnitsky (4390-88), fluorite FM (2979-81), GPOS301 and GPOS302 (dolo limestones), GPOS303 (feldspar dolo limestone), OOPE401 (calcareous ooze) (Arnautov, 1990; Govindaraju, 1994).

The available ICRMs and HSRMs only partially cover possible variations of the concentrations of the elements determined. The possibility of the usage of the ICRMs and HSRMs of the different composition rocks in a single calibration set was showed in (Revenko, 2002) to provide wide range of the element contents determined. Thus, the rock

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