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ORIGINAL ARTICLE

Detrital and authigenic(?) baddeleyite (ZrO_2) in ferromanganese nodules of Central Indian Ocean Basin

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Abstract Occurrence of baddeleyite (ZrO_2) which is a rare mineral has been recorded in ferromanganese nodules of Central Indian Ocean Basin (CIOB). The mineral occurs either as independent isolated sub-rounded to elliptical grains or in clusters forming fine subhedral crystals (<3 μm) within ferromanganese concretionary growth bands. The mode of occurrence, textural features and chemistry of the mineral suggest detrital and possibly an authigenic origin for baddeleyite. For authigenic origin it is proposed that zirconium might have got released either from the terrigenous sediments or the altered seafloor rocks forming halogen complexes and subsequently it has re-precipitated in the form of baddeleyite within manganese nodules under oxic to sub-oxic conditions.

1. Introduction

Baddeleyite (ZrO_2) is a rare mineral. In terrestrial environment it occurs mainly as an accessory mineral in alkaline, silica-undersaturated rocks such as sanidinites, kimberlites, carbonatites, and syenites, as well as in hydrothermal and alluvial deposits, altered pyroxenite and some metamorphic rocks (Keil and Fricker, 1974; Williams, 1978; Raber and Haggerty, 1979; Scatena-Wachel and Jones, 1984; Lorand and Cottin, 1987). The mineral has also been recorded from extra-terrestrial rocks such as lunar basalts, breccias, tektites, and meteorites (Bukovanská et al., 1997; Kuehner et al., 2007). However, the mineral has not been recorded from low-temperature environments. The first report of baddeleyite from marine manganese nodules (which forms under extreme low-temperature situations) from Central Indian Ocean Basin (CIOB) was made by the present authors (Nayak et al., 2009). In this paper we discuss the possible origin of baddeleyite in manganese nodules of CIOB which has hitherto not been reported from any other manganese nodule field.

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2. Materials and methods

Manganese nodule samples were originally collected by the National Institute of Oceanography (NIO), Goa from the first Generation Mine Site of Indian Ocean Nodule Field (IONF;

roughly bordered between 10° to 16°30′ S and 72° to 80° E; average water depth 5000 m) within the CIOB wherein the nodule abundance is >5 kg/m^2 and the bottom sediments are predominantly siliceous. Part of these manganese nodule samples were obtained by us at the National Metallurgical Laboratory (NML), Jamshedpur which were primarily meant for some metallurgical extraction processes. However, as a pre-requisite, the nodules were physically and mineralogically characterized to know their density and relative abundance of mineral phases including minor and trace phases during the current investigation. The manganese nodules investigated broadly show three types of morphologies: mono-nodules (with single nucleus), bi-nodules (with two nuclei) and poly-nodules (with three or more nuclei). A total of twenty nodules were investigated but nine nodules (three from each morpho-types) were mineralogically characterized. Though nodules can have varieties of nuclei (such as rock fragments, earlier nodule fragment, bones, shark teeth, pumice etc.), our investigated nodules had rock fragments and/altered basaltic material in the nucleus. Wet density was measured by conventional method using a Sartorius Balance (least count: 0.0001 g) with an attachment for measuring specific gravity. Polished mounts of the nodules were studied under plane polarized reflected light using Leica-make optical petrological microscope and also under scanning electron microscope (SEM, HITACHI S-3400N). Composition of the phases were determined by EDS (thermoelectron NSS-300) attached to the SEM. Bulk powder samples were also investigated by X-ray diffraction using a Seifert X-ray diffractometer (model: XRD 3003 PTS) with Cu-target.

3. Results

The manganese nodules investigated are porous and their specific gravity varies around 2.0 g/cm^3. Optical microscopy, SEM and XRD studies revealed that the nodules predominantly consist of todorokite with subordinate δ-MnO_2. The todorokite recorded is of two types having its strongest peak (dÅ) at 9.50 or 9.65 (Fig. 1; very close to 10 Å manganate described in literature, Roy, 1981). The other phases associated with the nodule are iron oxy-hydroxide, quartz, amorphous silica, amorphous Fe-Mn oxides, and clays. These associated phases are not very clearly detectable in XRD but they have been identified from their compositions determined by EDAX. Clay mineral compositions within the concentric growth bands of the nodules resemble with kaolinite, illite, chlorite and montmorillonite. In most nodules the core is found to consist of altered basaltic material. Conventional chemical analysis of the core material of one mono-nodule revealed $w(SiO_2)$ − 40.03%, $w(Al_2O_3)$ − 15.33%, w(FeO) − 12.20%, w(MgO) − 2.53%, w(MnO) − 2.17%, $w(TiO_2)$ − 1.47%, w(CaO) − 0.96%, $w(Na_2O)$ – 2.88%, and w(K_2O) – 3.07%. In addition to these, some trace mineral phases (e.g., Fe-oxides, Ti-oxides, Fe-Ti oxides, barite etc.) were recorded. Most importantly we noted the occurrence of baddeleyite in three instances under the scanning electron microscope. The three occurrences were in three different nodules (two mono-nodules and one bi-nodule). In two cases the mineral occurs as single isolated sub-rounded/eliptical grains within somewhat porous and ill-defined layer (Fig. 2). In the other case which is a mono-nodule, baddeleyite occurs as clusters of very fine tabular crystals (<3 μm) with partial to distinct crystal outline within a dense layer (Fig. 3). In back scattered mode baddeleyite shows high atomic contrast with respect to the ferromanganese matrix (Figs. 2b and 3a). Fig. 3b reveals the subhedral nature of the crystals that appear as if these have grown in a cluster authigenically. X-ray elemental maps for Mn and Zr are presented in Fig. 3c and d, respectively. Because of the fine size and low abundance, baddeleyite grains could neither be studied under optical petrological microscope nor could be detected through X-ray diffraction. However, the composition of baddeleyite has been confirmed by EDS analysis. The isolated baddeleyite grains in Fig. 2 revealed presence of zirconium and oxygen in the composition (Table 1) whereas clustered grains in Fig. 3 revealed significant quantity of manganese in addition to zirconium and oxygen (Fig. 4; Table 1). Though EPMA could have been a better option for determination of absolute composition on ~1 μm size spots we could not opt for it considering the availability of smaller grains of baddeleyite (<3 μm) and the chances of contamination from the oxide matrix. Keeping our limitations in mind, we have analyzed the grains by EDS with utmost care keeping the spot size at 100 nm so that the excited area for X-rays would be small and therefore do not expect any contamination in our analysis.

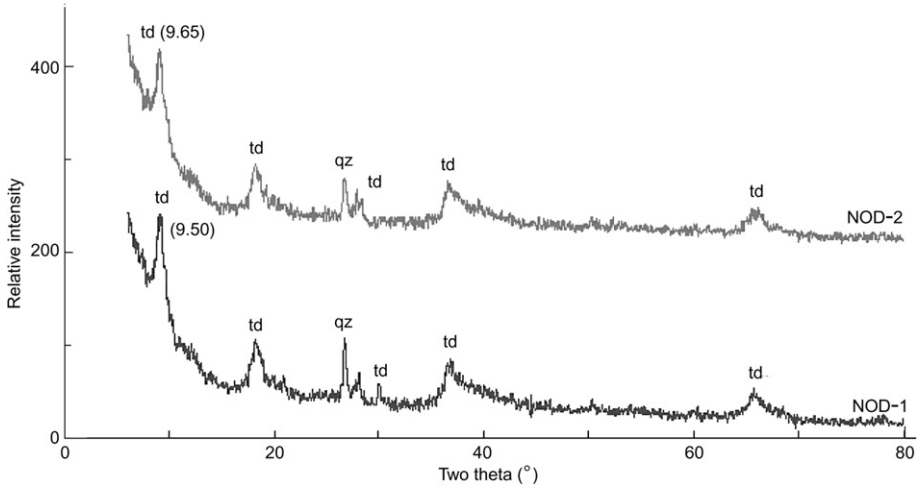

Figure 1 X-ray diffraction (XRD) pattern of two nodule samples (NOD-1 and NOD-2) from CIOB showing dominantly the peaks of todorokite (td); the major peaks are 9.50 dÅ and 9.65 dÅ, respectively. qz = quartz.