DETERMINATION OF TRACE ELEMENTS IN CARBONATES BY INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS

S. OHDE,** N. OHTA,* K. TOMURA**

*Department of Chemistry, Faculty of Science, Tokyo Metropolitan University, Setagaya-Ku, Tokyo (Japan)
**Institute for Atomic Energy, Rikkyo University, Yokosuka (Japan)

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A systematic non-destructive determination of eighteen trace elements (F, Na, Cl, Sc, Mn, Zn, Br, Sr, I, Ba, La, Ce, Sm, Eu, Tb, Yb, Th and U) in carbonate samples by thermal neutron activation analysis was developed. Three 0.2-0.5 g samples were irradiated for 15 sec (in the case of determination of F), for 3 min (in the case of Na, Ca, Mn, Sr and I) and for 60 hrs (in the case of Sc, Zn, Br, Ba, La, Ce, Sm, Eu, Tb, Yb, Th and U) in the TRIGA MARK II Reactor at a thermal neutron flux of $5 \cdot 10^{14} \text{ n} \cdot \text{cm}^{-2} \cdot \text{sec}^{-1}$ (15 sec and 3 min irradiation) and $1.5 \cdot 10^{13} \text{ n} \cdot \text{cm}^{-2} \cdot \text{sec}^{-1}$ (60 hrs irradiation), respectively. According to the half life of the nuclides formed, the activities were measured with a Ge(Li) spectrometer as follows, $^{20}$F : 15 sec counting after 20-25 sec cooling, $^{24}$Na, $^{38}$Cl, $^{56}$Mn, $^{87}$Sr and $^{128}$I : 600 sec counting after 30-120 min cooling, $^{85}$Br, $^{160}$La, $^{153}$Sm, $^{173}$Yb and $^{239}$Np (daughter of $^{239}$U) : 3000 sec counting after 1 week cooling, $^{46}$Sc, $^{65}$Zn, $^{131}$Ba, $^{141}$Ce, $^{152}$Eu, $^{160}$Tb and $^{233}$Pa (daughter of $^{233}$Th) : 5000 sec counting after 1 month cooling. The errors due to the fluctuation of the neutron flux and the counting geometry were minimized by the use of calcium determined previously with EDTA-titration as an internal standard. The interferences from $^{24}$Mg(n, p)$^{24}$Na and $^{235}$U(n, fission) reactions were corrected by the activities produced by the reactions in unit weight of magnesium and uranium, and their concentrations in samples measured experimentally. The data of Na, Mn, Zn and Sr were compared with the results obtained by atomic absorption analysis.

Introduction

The analysis of trace elements in carbonate samples is important for the studies of the sedimentary environment and the diagenetic process of sedimentary carbonates. The determination of several trace element contents have been performed hitherto mainly with a spectrochemical method.1-3 There have been few reports based on activation analysis.4-8 The neutron activation analysis seems to be a favorable method for the simultaneous and sensitive determination of trace elements.

*Present address: Water Research Institute, Nagoya University, Chikusa-Ku, Nagoya, Japan.
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in carbonate samples. In this paper, the authors report the systematic determination of eighteen trace elements in carbonate samples by non-destructive neutron activation analysis using an internal standard.

Experimental

Sample

The samples used in this study were collected from Minami-Daito-Jima (an emerged atoll in the Pacific Ocean), Okinawa Prefecture, Japan. These samples contain limestone, dolostone, coral and speleothem.

Standard

A reference standard of fluorine (2500 and 5000 µg F) was prepared by mixing calcium fluoride and calcium carbonate powders. Reference standard of sodium, chlorine, scandium, manganese, zinc, bromine, strontium, iodine, barium, thorium and uranium were prepared separately as follows: a 10 µl of standard solution containing Na (10 and 100 µg), Cl (15, 150), Scs(4.4, 44), Mn (1.0, 10) Zn (500), Br (100), Sr (10, 1000), I (1.0, 100), Ba (100), Th (3.6, 36) and U (10, 50) was pipetted onto a small piece of filter paper and evaporated under a heating lamp. The U.S. Geological Survey standard rock diabase W-1 and granite G-2 were used as the standard of rare earth elements (La, Ce, Sm, Eu, Tb and Yb).

Irradiation

About a 0.2–0.5 g powdered or block sample was sealed in a polyethylene bag (15 sec or 3 min irradiation) or wrapped in an Al-foil (60 hrs irradiation). The samples and reference standards were irradiated in the TRIGA MARK II Reactor of Rikkyo University as shown in Table 1.

Counting

After appropriate cooling, the γ-ray measurements were performed for 15 to 5000 sec as shown in Table 1 using an ORTEC Ge(Li) detector (effective volume: 50 ml, resolution for 1.332 MeV peak of 60Co: 2.1 keV) and a 4096 channel pulse height analyzer (GEOSCIENCE Corp.).

Results and discussion

The abundances of eighteen trace elements in carbonate samples were obtained by non-destructive neutron activation analysis. The abundance of each element was calculated by comparing the best photopeak activity of a sample with that of the