刘卫国论文题目：沉积环境中的硼、氯同位素地球化学

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摘　要

本论文在对前人进行硼、氯同位素地球化学研究较系统的总结的基础上，开展了对沉积环境中的硼、氯同位素样品的测定方法、同位素组成和环境地球化学意义的研究，揭示了硼、氯同位素体系的应用前景。论文涉及的主要内容为：

1　　硼、氯同位素地球化学的发展历史和研究现状

对近十余年来硼、氯同位素各种测定方法的特点进行了对比，概述了它们在硼、氯同位素地球化学的研究中所起到的作用。硼同位素地球化学研究开展较多，已有的研究结果表明硼同位素的分馏主要是由 B（OH）3 和 B（OH）3 的分配比例所决定。硼同位素地球化学的研究在示踪成岩物质的来源、海相和陆相沉积环境的差异、古海洋环境的变化、以及环境污染的程度等方面取得了极大的进展。氯同位素地球化学研究更多的是在认识自然界氯同位素的分馏机理、组成变化的规律及隐含的地球化学意义。

2　硼同位素测定方法的深入研究

由于硼同位素地球化学研究的深度和广度的增加，促使硼同位素测定方法的不断完善。天然样品的硼含量一般较低，并且随着对测定精度和灵敏度要求的提高，对硼同位素样品的化学分离和提取以及测定过程的环境本底要求也在不断提高。对海洋生物碳酸盐、石盐、黄土中硼的化学分离处理方法的研究和建立可行的实验流程对高精度测定这些样品的硼同位素组成是重要的。来自 NO3 对热电离质谱硼同位素测定离子的同质异位素的干扰尽管较小，但其产生原因和对硼同位素测定干扰程度的研究表明：避免在样品中引入 NO3- 和有机物（特别是在化学处理过程和涂样试剂中）是降低硼同位素同质异位素干扰的关键。

3　盐湖沉积环境的硼、氯同位素地球化学

氯在盐湖卤水和盐类矿物中相对富集。柴达木盆地河水、地下水、盐湖卤水和石盐矿物氯同位素组成的结果表明：河水的 δ 37Cl 值最高，卤水的 δ 37Cl 值最低，盐湖卤水的氯同位素组成是与卤水的 pH 值、盐度及氯离子含量有关；昆特依盐湖钻孔石盐沉积的氯同位素组成变化，是与盐湖蒸发古环境变化有关。氯同位素地球化学特征有可能为盐湖古环境演化提供新的启示。

目前，人们对盐湖卤水和富硼的硼酸盐矿物的硼同位素分馏研究较多。然而，对石盐中的硼同位素组成的研究很少，而且对硼在石盐中的赋存状态尚不完全清楚。通过对人工合成卤水和盐湖卤水的蒸发实验，证实流质包体是石盐硼的主要来源。石盐中的硼同位素组成是与石

盐结晶时卤水的硼同位素组成相近，随蒸发卤水的 pH 值降低和 Ca 含量的增加，石盐与卤水之间的硼同位素分馏相对增大。

盐湖卤水的硼、氯同位素相关性结果表明：盐湖卤水的硼、氯同位素组成均与卤水的的蒸发和补给水的同位素组成有关。然而，卤水的硼同位素组成主要受补给水的硼同位素组成控制，而卤水的氯同位素组成则更多的取决于卤水的蒸发程度。

4　珊瑚礁的硼同位素组成及古环境意义

海洋生物碳酸盐硼同位素组成变化是与海洋生物活动环境变化有关，

因而引起人们对珊瑚礁硼同位素研究的兴趣。我国南海过去 7000 年以来珊瑚礁的硼同位素组成变化为 22.7-24.8‰,对应于海水的 pH 值变化为 8.10－8.41。珊瑚礁的硼同位素组成可能是古海平面变化新的代用指标。

5　黄土钙结核的硼同位素组成的初步探讨

采用酸溶样品和负热电离质谱测定黄土钙结核的硼含量和硼同位素组成结果表明：酸溶的硼主要是来自钙结核中的碳酸盐，其较大的硼同位素组成变化与 87Sr/86Sr 的比值有正相关关系，这是黄土沉积物后期风化淋滤环境变化的反映。

关键词：硼和氯同位素，测定方法，沉积环境，地球化学

Abstract

Boron and chlorine have two stable isotopes respectively, 11B and 10B, 37Cl and 35Cl. In this thesis The stable isotopes geochemistry of boron and chlorine in sedimentary environment including ocean, salt lake and loess deposit. have been investigation by using thermal ionization mass spectrometry (TIMS) in this thesis , A further discussion for the determination of boron isotopes based on PTIMS or NTIMS.is also described.

History of boron and chlorine isotopic geochemistry

Since 1980s, the variations of boron and chlorine isotopes in nature have been evidenced with some high precise methods of determining boron and chlorine isotopes by using PTIMS and NTIMS

Many significant works about boron and chlorine isotopic geochemistry have been done in oceans, salt lakes, groundwater, evaporated sediment and hydrothermal fluids. This chapter gives a brief summary of including analytical methods and application to earth science.

Further investigation of boron isotopic measurement

The positive thermal ionization mass spectrometry (PTIMS) has been widely used to determine the isotopic composition of the boron and chlorine in geological samples. However, it is very important that the boron and chlorine compounds must be a pure form, separated from the natural samples for isotopic measurement of boron and chlorine by PTIMS. Further, it is more difficulty to separate boron from halite, coral and carbonate of loess, due to its low boron concentration. A complete precedure of experimental technology is described for separating the boron or chlorine speues from the sedimentary minerals and natural water. In addition, a further discussion of the boron and chlorine isotopic measurement is also described.

An isobaric interference for boron isotopic measurement by negative thermal ionization mass spectrometry (NTIMS) has been studied. The result shows that the CNO- is not only from the organic material, but also from nitrate in loading reagent in NTIMS. Monitoring the mass 43 ion intensity and 43/42 ratio of blank are necessary for the boron isotopic measurement in NTIMS, other than is only boron content.

Boron and chlorine geochemistry in salt lakes

The isotopic compositions of chlorine in salt lake brine coexisting with halite, oil-field water and river water from the Qaidam Basin (Qinghai, China) have been examined using High-precision measurement of chlorine isotopes based on thermal ionization mass spectrometry of the Cs2Cl+ ion. The variation of theδ37Cl value in these salt lakes is mainly associated with brine evaporation, halite precipitation and the hydrochemistry of input water. The chlorine isotopic composition may reflect the evaporative degret of the salt lake brine.

The δ37 Cl values of salt deposits in the Kunteyi are reduced with the upward and appear in

the eight cycls. This variation is controlled by paleoclimate condition. The systematic variation in δ37Cl of sale deposits are an useful indicafor for the study of paleoclimate of salt deposits in drought and stronger evaporated condition (chapter 5).

The mechanism of incorporating boron into halite during evaporation of salt lake brines is subject to dispute, and there are few studies of the boron concentrations and isotopic compositions during this process due to low boron concentration in halite. A set of evaporation experiments from artificial solutions and salt lakes brines have been analyzed in this study. The results of boron concentration and isotopic composition analyses demonstrate that the boron in halite comes mainly from fluid inclusions. These values are controlled by the boron isotopic composition of the boron sources, pH values and Na/Ca ratios in the salt lake brines. The variation of boron isotopes in halite may be used to trace the hydrochemical evolution and paeleoevaporation environment in salt lakes.

A relation of the boron and chlorine isotopes to the hydrochemistry of the salt lake brine has been investigated. The results show that the variations of the boron and chlorine isotopic composition are associated with evolution of salt lake brines. The boron isotopic composition of brine is under control of source water and Ca concentration of the brine. The chlorine isotopic composition is controlled by brine evaporated. A negative relation between the boron and the chlorine isotopic composition is given.

Composition of boron isotopes in coral from South China Sea

Boron isotopic composition and concentration in the corals from South China Sea have been investigated by using thermal ionization mass spectrometry. A discussion is given for the relation among boron isotopic composition, pH value, boron concentration and age .The results indicate that boron isotopic composition of the corals varies in a range of 22.7 to 24.8%, and appears in the positive relation with the boron concentration. The pH values of ancient seawater in last 7000 years are calculated based on the correlative equation between boron isotopic composition and pH value. Preliminary study shows that boron isotopic composition of coral may become a tracer of the sea level change.

Composition of boron isotopes of carbonate nodule in loess

Boron isotopic composition of nodule has been determined by NTIMS. The result show that there is a positive relationship betweenδ17B and 87Sr/86Sr. Boron isotopes of nodule in loess may trace the weathering process.

Key words:

boron and chlorine isotopes, measurement method, sedimentary environment, geochemistry