NOTES

Ba-BEARING CLINOPTILOLITE FROM ODP LEG 127, SITE 795, JAPAN SEA

Abstract—Ba-bearing clinoptilolite (with >2 wt. % BaO) occurs in Neogene marine siliceous sediments from ODP Leg 127 Site 795 in the Japan Sea. Ba-bearing clinoptilolite is formed by reaction of volcanic glass and Ba-rich pore water during burial diagenesis.

Key Words—Analcime, Barium, Burial diagenesis, Clinoptilolite, Siliceous sediment.

INTRODUCTION

During burial diagenesis of silicic volcaniclastic sediments in thick marine sequences, silicic glass shards in sediments alter to clinoptilolite, which is then transformed into analcime (+/−) heulandite (Iijima, 1978). Burial diagenesis of volcanic glass in siliceous sediments or in tuffs with alternating siliceous layers tends to produce bentonite instead of zeolite. The reason for this difference appears to be that solution transfer of SiO_2 from the tuff to the siliceous layer occurred in the sediments during early diagenesis. Si concentration of pore water is one of the important controlling factors in zeolite formation. This study documents a rare occurrence of diagenetic zeolites in diatomaceous, siliceous sediment from ODP Leg 127, Site 795, Japan Sea. The clinoptilolite has an anomalously high Ba concentration (BaO > 2 wt. %), which is unusual also.

SAMPLES AND METHODS

This drillhole is located in the northern Japan Basin, 150 km northwest of Syakotan peninsula (Tamaki *et al.*, 1990). Figure 1, a lithostratigraphy of this site, shows the sediments range in age from middle Miocene to Quaternary. The basement, which occurs at a depth of 683.5 m consists of basalt, basaltic andesite, and basaltic breccias. The following sedimentary sequences of this site were divided into five units. (All depths in this article refer to depths below the sea floor.)

More than 60 samples of fine-grained diatomaceous sediment were collected at the interval of 10-50 m in the depth range of 280.0–683.7 m. Clinoptilolite was identified by powder X-ray diffractometer (XRD). Only the main peak (9.8° CuKα) could be detected for most samples due to the low concentration of clinoptilolite. The chemical composition of clinoptilolite was analyzed from a polished thin section by a scanning electron microscope (SEM) JEOL JSM-840 with EDS system. The beam current was 15 keV–0.5 nA; the beam scanning area was 2.2 × 2.9 μm to 3.3 × 4.3 μm; and the live time was 100 s. Bulk samples were chemically analyzed by X-ray fluorescence analysis (XRF) and the bulk BaO content was determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES).

OCCURRENCE OF ZEOLITES

Ba-bearing clinoptilolite occurs at 337.0–585.0 m, Ba-free clinoptilolite occurs at 667.6–683.7 m, and analcime occurs at 669.8 m. Both types of clinoptilolite were present as an alteration product of silicic glass, entirely or partly filling voids of dissolved glass shards. Most clinoptilolites show thin tabular crystals of 10–50 μm in length, depending on the size of the voids.

Ba-bearing clinoptilolite grown in the vesicle of a dissolved glass shard has sharp and straight crystal edges and an overgrowth of opal-CT lepisphere (Figure 2A). in contrast, the edges of the Ba-free clinoptilolite are rounded by dissolution (Figure 2B) because the clinoptilolite at this depth was unstable and began to dissolve and react to analcime, found at 669.8 m.

CHEMICAL COMPOSITION OF CLINOPTILOLITE AND CLINOPTILOLITE HOST SEDIMENT

Zoned crystals of clinoptilolite have not been observed from SEM; however, only single spot analysis was possible by EDS because of the small crystal size. The bulk composition of samples analyzed by XRF was normalized in dry base. The average chemical composition of clinoptilolite and bulk samples are shown in Table 1.

The framework compositions of all clinoptilolite found at this site are similar to each other and characterized by low Si. The Si/(Al + Fe) ratios of these clinoptilolites are in the range of 4.0–4.2.

Clinoptilolite at this site can be divided into two types by the differentiated extra framework cations. One type is Ca-clinoptilolite, which occurs from 667.6 to 683.7 m. This type is characterized by the absence of Ba and a higher number of alkaline earth cations compared to alkali cations. The second type is Ba-bearing Na-clinoptilolite, which is distributed from 337.0 to 585.0 m, and can be subdivided into two
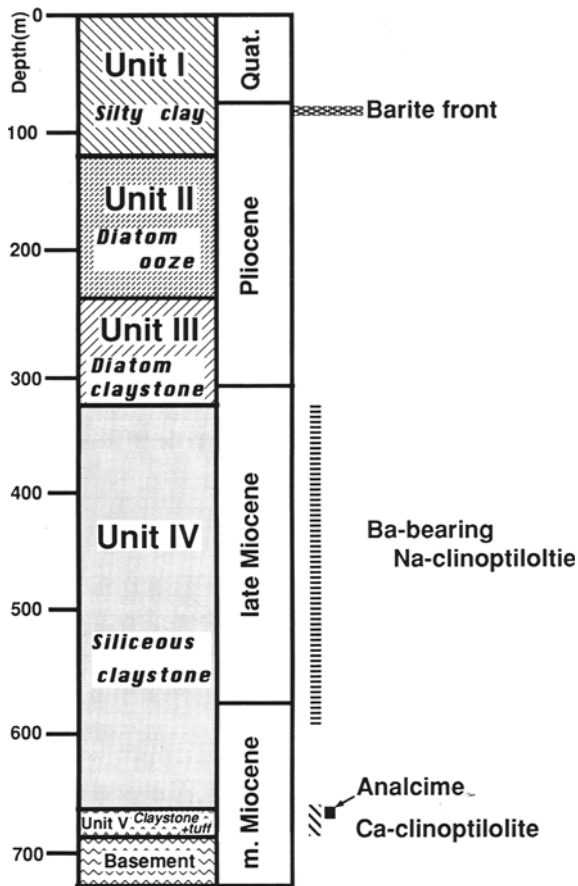
Figure 1. Stratigraphy (from Tamaki et al., 1990) and distribution of barite (from Brumsack et al., 1992) and zeolite at Site 795.

Figure 2. SEM microphotographs of A) Ba-bearing clinoptilolite (404.5 m) and B) Ba-free clinoptilolite (676.7 m).

subtypes. Ba-Na-type I exhibits an equal mole ratio of alkali to alkaline earth cations, whereas Ba-Na-type II is Na dominant (Na $\gg$ K + Ca + Ba).

The major element composition of clinoptilolite does not depend on the bulk composition of zeolite hosted sediment, with the exception of Ba.

ORIGIN OF Ba-BEARING CLINOPTILOLITE

Ba enters marine sediments as plankton remains (Schmitz, 1987). After enrichment in the diatomaceous sediment, Ba migrates upward by diffusion from deeper layers (Brumsack, 1989). In contrast, sulfate diffuses downward into the sediments from sea water due to microbially induced SO_4^{2-} reduction. As a result of mixing of aqueous Ba^{2+} + SO_4^{2-}, authigenic barite precipitates at a distinct interface that is regarded as a "barite front" by Brumsack (1989) and Von Breyman et al. (1990). In a similar manner, Ba enrichment in tuffs is reported as replacement of volcanic glass by authigenic harmotone with or without barite precipitation at Site 799, southwestern end of Kita-Yamato
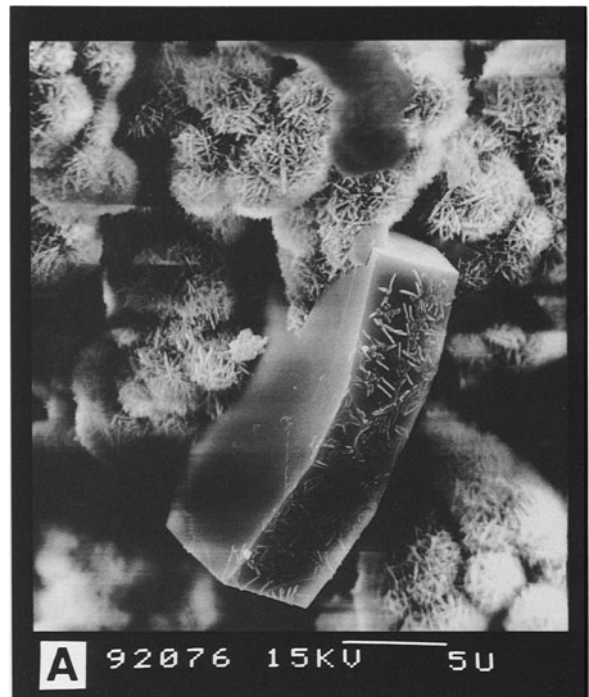
Trough, Japan Sea (Pouclet et al., 1992). At Site 795, diagenetic remobilization of biogenic Ba is remarkable (Masuzawa et al., 1992) and the "barite front" is found near 75 m (Brumsack et al., 1992).

Table 1. Average chemical composition of clinoptilolite and bulk samples at selected depths in Site 795.

Depth (m): Cation type:	404.5 Ba-Na-type I	414.5 Ba-Na-type II	683.7 Ca-type
Chemical composition of clinoptilolite			
SiO_2 (wt. %)	64.58	67.26	67.42
Al_2O_3	13.39	13.52	13.83
Fe_2O_3	0.26	0.22	0.17
MgO	0.59	0.40	0.17
CaO	1.79	0.29	3.75
BaO	2.29	1.20	0
Na_2O	2.59	6.08	2.75
K_2O	0.96	0.74	0.73
Total	86.43	89.70	88.82
$Si/(Al + Fe)$	4.04	4.18	4.11
Bulk composition of zeolite hosted sediment			
SiO_2 (wt. %)	65.90	82.48	72.81
TiO_2	0.90	0.39	0.32
Al_2O_3	18.08	8.36	10.99
Fe_2O_3	7.01	3.89	5.34
MnO	0.03	0.05	0.04
MgO	3.69	1.33	2.41
CaO	1.14	0.39	1.91
Na_2O	1.79	1.48	3.41
K_2O	1.41	1.59	2.73
P_2O_5	0.05	0.04	0.04
BaO (ppm)	2200	890	540

Volcanic glass typically begins to change to clinoptilolite at a temperature of 41°–55°C (Iijima, 1988). This temperature corresponds to 300–450 m in this site. Clinoptilolites occurring in this depth range are *in situ* clinoptilolites (clinoptilolites that precipitated at the present depth). These clinoptilolites form by the reaction of volcanic glass and Ba-rich pore water which migrated from a deeper layer, so the Ba content of clinoptilolites is anomalously high. Ba-bearing clinoptilolite occurring below this depth formed by the same mechanism during the time period when they were in the clinoptilolite formation interval. This mechanism of formation of Ba-bearing clinoptilolite is similar to the mechanism for harmotone formation at Site 799, but the depth of formation for clinoptilolite is consid-

erably deeper because harmotone formation could be found near the surface.

The layer which includes Ca-clinoptilolites directly overlies the basement rock, so it did not go through an interval of Ba-rich pore water at the clinoptilolite formation depth, and the clinoptilolites formed there were Ba-free. These Ca-clinoptilolites are unstable at the present depth, resulting in their dissolution and transformation to analcime.

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