A potassium-rich zeolite in soil development on Danian chalk

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Abstract

A zeolite found in a soil profile developed in Danian chalk was studied. The results showed that it is a heulandite, temperature-stable to above 600°C with a Si/Al ratio of 2.88 and almost completely K-exchanged. The mineral probably formed under burial diagenetic conditions in the chalk formation.

KEYWORDS: zeolite, heulandite, soil, chalk, Denmark

Introduction

DURING a study of the clay-rich B horizons, developed in soils on Danian chalk in Denmark (Nørnberg et al., 1985; Nørnberg and Dalsgaard, 1985), a zeolite was found in the fine silt fraction. Zeolites have never before been reported from Danish soils or chalk formations, and are generally rare in soils (Ming and Dixon, 1986a). Clinoptilolite, a temperature-stable heulandite seems to be the most abundant zeolite in soils over a wide variety of pH conditions, from slightly acidic to strongly alkaline (Ming and Dixon, 1986b). However, it seems to be a matter of definition whether a zeolite with the heulandite structure is called a heulandite or a clinoptilolite. Mumpton (1960) suggested a compositional gap between the minerals heulandite (Si/Al ratio 2.75–3.25) and clinoptilolite (Si/Al ratio 4.25–5.25), clinoptilolite being temperature-stable to above 600°C. However, Boles (1972), in a broad study of previous research, determined the Si/Al ratio for a group of 60 zeolites with the heulandite structure and found that a number fell into this gap. Boles (1972) proposed a three-group classification of heulandites based on temperature stability. Similar results were reached by Alietti (1972) who classified a number of previously studied zeolites of heulandite structure in almost the same three groups based on temperature. Type 1 which is destroyed after heating to between 400 and 550°C. Type 2 which is not completely destroyed after the same heating treatment and the clinoptilolites which are resistant to heating at 750°C. Zeolites are known from Jurassic, Cretaceous and Palaeocene sediments in south-east England where Brown et al. (1969) found silt-size crystals of similar structure as the mineral described in this paper. Zeolites are also known from Upper Cretaceous formations in the Ukraine, USSR (Shumenko, 1962); from the Upper Cretaceous in Alberta, Canada (Morton and Smith 1987); and clinoptilolite is known as a replacement of foraminifera from the Upper Selandian non-calcareous greensand in Denmark (Hansen and Andersen, 1969). The zeolite in the present study was part of the residue after chalk dissolution, found as silt-size particles with a maximum edge length of 20 μm.

Materials

The zeolite was found in the fine silt fraction, 38–2 μm, of the B23- and C horizons of three mollisol profiles (Nørnberg et al., 1985). The soils have developed in a shallow moraine on top of residue from the chalk, the underlying material being lower Danian bryozoan chalk. The location was Sangstrup Klint, Denmark, see Fig. 1. The chalk, on average, contains 30% bryozoan fragments in a fine-grained matrix (Thomsen, 1976) and about 90% of the material is carbonates. The residue contains about 70% material $<2\,\mu m$, which is mostly smectite. The fraction 38–2 μm makes up about 25%. The silt consists of quartz, feldspar, mica, the zeolite and traces of cristobalite, tridymite and an amphibole.

Experimental

The C-horizon material has been used for further study. Destruction of organic material and
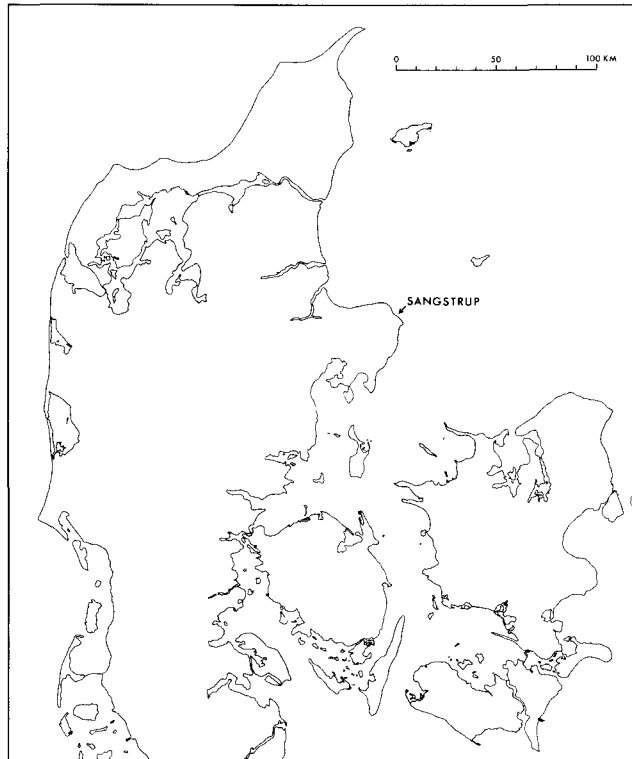
FIG. 1. Location of the study area, Sangstrup, Denmark.

removal of carbonates were carried out in a solution containing 6% H_2O_2 and in a 1N CH_3COOH–CH_3COONH_4 buffer at pH 4.5, respectively. The residue was washed four times with distilled water in a centrifuge and dispersed at pH 9 with NaOH. It was then sieved through a 38 μm sieve and the <2 μm fraction siphoned off by repeated mixing and sedimentation cycles. The silt fraction was then separated at 2.28 g/cm^3 in bromoform twice, using the method of Ming and Dixon (1987). The structural and chemical studies were carried out by X-ray diffraction, electron microprobe and TEM, and the morphological studies by SEM and TEM. The water content was determined as loss between 110 and 1000 °C. The quartz content in the heavy liquid separated sample was determined by the standard addition method in powder diffraction.

Results

From the powder X-ray traces of the 38–2 μm <2.28 g/cm^3 fraction (Fig. 2) it is seen that the sample consists almost completely of zeolite and quartz. The X-ray pattern of the zeolite is in

agreement with Mumpton's (1960) data for clinoptilolite, as the mineral is stable on heating to 600 °C.

To determine the quartz content in the light fraction of the sample three different amounts of pure quartz were added to the sample and, from the I_k/I_z addition ratio curve (Fig. 3), the quartz content of the original sample was calculated as 7.3%. This content was used as a correction factor in calculation of the loss on ignition as the quartz was assumed not to add to the loss.

Scanning micrographs were taken of the zeolite crystals, (Fig. 4) and electron-diffraction (TEM) was used to confirm their identifications.

The crystals were impregnated with polyester resin before thin sections were made for electron-microprobe analysis. Five analyses on three different crystals were carried out and shown in Table 1 and are in good agreement. There was no Mg or Ca in the mineral. The totals are near 100%, indicating that the water must have evaporated, probably during the 200 seconds of analysis time in the electron beam. The analyses are recalculated to include the stoichiometric anion content as oxygen in the five analyses and an average
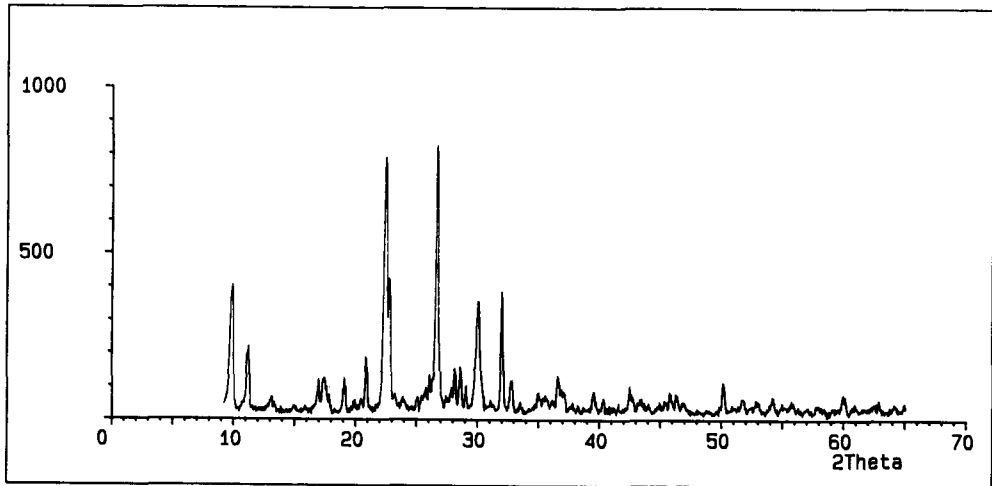
FIG. 2. X-ray diffraction trace of the 2–38 µm fraction $<2.28\,\text{g/cm}^3$, Cu-$K\alpha$.
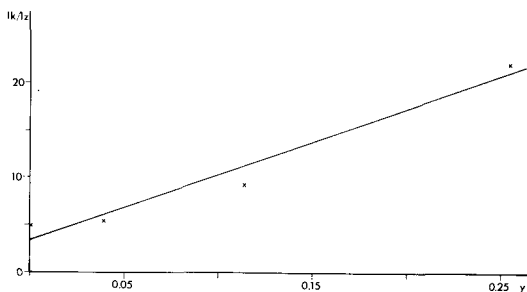

FIG. 3. Standard addition line for determination of quartz content.

of the five is recalculated to 72 oxygens in Table 1. The Si/Al molar ratios are in all cases very close and the charge of (Na + K) is close to the theoretical value taken as Al, though in all cases slightly too high.

From X-ray powder data taken with a STOE powder transmission diffractometer the unit cell parameters were calculated in the monoclinic system as a 7.405, b 17.885, c 15.821 Å, α 90.00°, β 91.39°, γ 90.00° and V = 2095Å^3.

Discussion

The X-ray spacing and unit cell parameters are very similar to those reported by Wise *et al.* (1969) and Koyama and Takeuchi (1977). The Si/Al ratio of 2.88 is characteristic for group 1 heulandites according to the classification of both Boles (1972) and Alietti (1972) and also for the group of natural Ca-rich clinoptilolites reported by Alietti *et al.*

(1977). However, the cation contents are different from natural heulandites of the clinoptilolite type.

The zeolite is temperature-stable above 600 °C and was therefore first considered to be a clinoptilolite. The high-temperature stability of heulandite was found by Shepard and Starkey (1966) for K-exchanged types. A K-form (23-K) with Si/Al ratio of 3.17 was reported from Iceland by Alietti *et al.* (1974) and it might be possible that a nearly total K-exchange could take place over a long time in a soil environment. End-members of Na- and K-clinoptilolite are reported from syntheses in the laboratory, but no Si/Al ratios are given (Cheng-Hang Chi and Sand, 1983).

As the lower Danian chalk where the zeolite was found has no evidence of volcanic material, the zeolite was probably formed under burial diagenetic conditions. Biogenic silica has formed flint layers in the formation and cristobalite–tridymite are important minerals in the coarser fraction of the residue from the dissolved chalk. The zeolite is thought to have formed during the late phase of diagenetic transformation of silica compounds, when the Si/Al ratio in the formation water was sufficiently low. The zeolite will from the Si/Al-ratio be defined as a K-exchanged heulandite of group 1.

Acknowledgements

Table 1. Chemical composition. Form calculated without water
and recalculated on the basis of 72 oxygens.

Sample	1	3	3a	4	4a	Average	Average incl. water
Na_2O	0.87	0.91	0.95	0.89	0.74	0.87	0.77
Al_2O_3	18.93	18.88	18.66	18.14	18.40	18.60	16.49
SiO_2	64.24	63.77	63.44	61.38	62.26	63.02	55.87
K_2O	16.77	16.46	16.41	15.93	16.34	16.38	14.52
H_2O							11.35
	100.81	100.02	99.46	96.34	97.74	98.87	99.00

Ions recalculated

O	11.077	11.088	11.080	11.078	11.084
Na	0.108	0.114	0.119	0.115	0.094
Al	1.424	1.432	1.423	1.428	1.430
Si	4.101	4.104	4.104	4.100	4.103
K	1.366	1.351	1.354	1.357	1.377
Si/Al	2.88	2.87	2.88	2.87	2.87
Na + K	1.474	1.465	1.473	1.472	1.471

Average of 1-4a recalculated on basis of 72 oxygens:
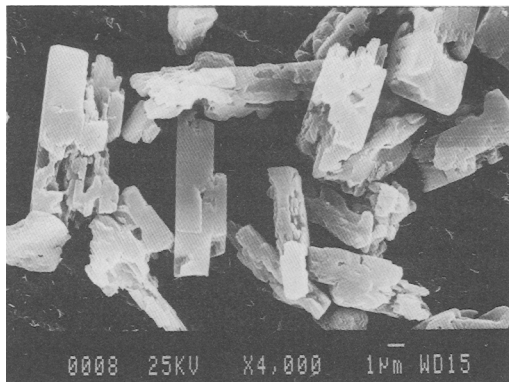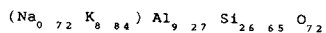
$(Na_{0.72} K_{8.84}) Al_{9.27} Si_{26.65} O_{72}$

FIG. 4. Scanning electron micrograph of heulandite crystals.

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