

## A STUDY OF ANALCIME MINERAL IN SOME SOILS OF WEST PAKISTAN

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Three out of a total of nine soil samples from West Pakistan showed unusually high (more than 100) exchangeable sodium percentage (ESP) when determined according to the conventional methods. But the pH of these soils ranged from 7.0 to 7.6. This was regarded as an unusual result. It was suspected that the high ESP in the soils may be due to "zeolitic sodium" released from analcime mineral. An intensive mineralogical investigation showed that there is no analcime mineral present in these soils. The high ESP in the soils was therefore not caused by analcime mineral. Low pH values (7.0-7.6) might be regarded as the main obstacle in the way of the synthesis of analcime in the soils under study.

### Introduction

Analcime is a silicate mineral of zeolitic type and has a three dimensional structural framework of linked  $(\text{Si,Al})\text{O}_4$  tetrahedrons with  $(\text{Si,Al})$  and  $\text{O}$  being present in the ratio of 1:2.<sup>10</sup> The mineral has a chemical composition of  $\text{NaAlSi}_2\text{O}_6 \cdot n\text{H}_2\text{O}$ . Deffeyes<sup>6</sup> regarded analcime as a secondary silicate mineral in sedimentary rocks formed by diagenesis. He noted that most of the sedimentary zeolites occur as extremely fine-grained aggregates which are usually impossible to identify in hand specimen and they are often too fine-grained for accurate optical measurements. The zeolites in the rocks, therefore, are most readily identified by X-ray diffraction analysis.

X-ray diffraction patterns for cubic analcime and noncubic analcime showed only cubic analcime as a diagenetic product.<sup>5</sup>

The mode of origin of analcime can be inferred partly from their occurrence in nature and partly from the results of laboratory experiments. The occurrence of authigenic analcime in the deep sea sediments shows that analcime can form below room temperature.<sup>6</sup> In a number of hydrothermal experiments the synthesis of zeolites have been attempted but in none of the experiments the stability fields of individual zeolite mineral are clearly defined.

Deffeyes<sup>6</sup> for the first time made an attempt to find the stability fields of different zeolites and indicated the stability fields of analcime.

Analcime was reported<sup>8</sup> in rhyolitic tuff and mudstone. It was found associated with other minerals as phillipsites, clay minerals and potas-

sium feldspars in the mudstone. The compositional range for analcime was from  $(\text{Na,Al})_{15.4}\text{Si}_{32.6}\text{O}_{20} \cdot n\text{H}_2\text{O}$  to  $(\text{Na,Al})_{12.6}\text{Si}_{35.4}\text{O}_{96} \cdot n\text{H}_2\text{O}$ .

In a system of  $\text{Na}_2\text{O}$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$  and  $\text{H}_2\text{O}$ , analcime forms quite easily outside its stability fields, thus indicating that at surface temperatures the kinetics of nucleation and of crystal growth are important in determining the products formed from the alteration of vitric ash.<sup>12</sup>

Ross<sup>17</sup> suggested as far back as 1928 that zeolites could be formed by the action of saline lake water on clay minerals. A synthesis of analcime was reported from the action of a strong  $\text{NaOH}$  solution on kaolinite at  $90^\circ\text{C}$  and atmospheric pressure. When kaolinite or halloysite reacts with  $\text{NaOH}$ , the original kaolin structure is broken and becomes amorphous.<sup>14</sup> The nucleus of analcime mineral forms in this amorphous state.

Laboratory data on the genesis of analcime indicate that the zeolites can form only in alkaline environments.<sup>11</sup> That the composition of saline lake water can influence the zeolite mineralogy is supported by the observation<sup>4</sup> that in the Green River Formation, alteration of volcanic material to analcime occurred before the sediments were compacted by diagenesis.

While studying the chemical properties of some saline and sodic soils of Fresno series in California, Schulz *et al.*<sup>13</sup> observed that some of these soils showed unusually high ESP results but plants were growing on them as usual. With the help of X-ray diffraction analysis they conclusively showed that the soils have about 35% analcime mineral  $[\text{NaAl}(\text{SiO})_2 \cdot n\text{H}_2\text{O}]$ , in addition to 35% illite, 15% montmorillonite, 5% vermiculite and 5% kaolinite.

Analcime is a very common and characteristic authigenic mineral in saline and sodic soils of the

\* The experimental work was done by M.S.H. at the United States Salinity Laboratory at Riverside, California, in 1966. The soil samples were collected by S.A.

arid region.<sup>16</sup> It can form only in those soils which have a pH value of 9.0 and above.

In the present paper an attempt to identify analcime mineral in some salt-affected soils of West Pakistan will be discussed.

### Materials and Methods

In 1966 nine salt-affected soils from the western side of the Indus River near Ghulam Muhammad Barrage in West Pakistan were collected. These were all surface soils from open fields. After the chemical analysis by the conventional methods<sup>3,15</sup> it was observed that three out of the nine soils showed impossible exchangeable sodium percentage (ESP) of more than hundred. ESP was calculated using Bower and Hatcher's formula.<sup>3</sup>

$$\frac{\text{Exchangeable Na}^+}{\text{CEC}} \times \frac{100}{1} = \text{ESP}$$

To account for the high ESP an intensive mineralogical investigation of the sand, silt and clay fractions of these soils was carried out. A very high amount of some unusual minerals like analcime was suspected. It was known that analcime has comparatively weak and unstable crystal structure<sup>16</sup> and the structure might even break down during the pretreatments of the soils. X-ray diffraction analysis was, therefore, made on soils before pretreatment. In a separate experiment the soil samples were pretreated by Barshad's method.<sup>2</sup> The inorganic fraction of soils was then separated into  $>50\mu$ ,  $50-2\mu$  and  $<2\mu$  fractions. Each separate fraction was investigated by X-ray diffraction analysis using a Phillips X-ray diffraction unit with a Geiger counter and chart recorder.

### Results and Discussion

Schulz *et al.*<sup>13</sup> noted that the most important diagnostic X-ray peak for analcime mineral occurs at  $5.59 \pm 0.02$ .

An examination of X-ray diffraction charts showed that there was no trace of any analcime mineral in the soils under study. This was testified by the absence of any of the diagnostic peaks<sup>13</sup> of analcime in the X-ray diffraction charts. Other minerals present in the soils included mica, quartz, feldspar, pyroxene, amphibole and a small amount of montmorillonite. In addition, some salt minerals such as sodium chloride, sodium sulphate, calcium chloride and magnesium chloride were identified in the soils.

Analcime mineral has the unique property of fixing  $\text{Na}^+$  somewhere in its structure in a difficultly exchangeable to nonexchangeable position.<sup>1,13</sup> This  $\text{Na}^+$  may be gradually released from that position with increasing washings of the mineral. Washing out of this "fixed sodium," called "zeolitic sodium",<sup>13</sup> results in the higher ESPs of these soils which have considerable amount of analcime mineral.

The high ESP of the soils from West Pakistan could not be explained by the X-ray analysis. There is no analcime mineral in these soils, and it is not known if any other mineral has this sodium-fixing capacity.

The reason for not forming any analcime mineral in the soils under study may be their low pH values and possibly low  $\text{Na}^+$  activity. Although a large amount of salt is present, the pH values of the soils range from 7.0 to 7.6. Analcime usually forms in soils having pH values of 9.0 and above,<sup>16</sup> and such high pH is found only in the sodic soils and not in the saline soils. Three soils under study have been designated as "saline-sodic" according to the definition of USSL staff.<sup>15</sup>

At a pH value of 7.6 the secondary layer silicates such as montmorillonite and kaolinite are stable minerals.<sup>9</sup> Analcime was synthesized by causing kaolinite to react with NaOH at pH around 10.0. After the reaction, the kaolinite structure breaks down, the whole mass becomes amorphous and analcime crystals nucleate and grow.<sup>14</sup>

The absence of analcime in the present soils from West Pakistan indicates that the soil environment is not suitable for the synthesis of this mineral.

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