

NOTE

OCCURRENCE OF SILHYDRITE IN A SODA LAKE ON THE BOLIVIAN ALTIPLANO

The mineral silhydrite  $[3\text{SiO}_2 \cdot \text{H}_2\text{O}]$  was first found at the Trinity County, California (Gude & Sheppard, 1972). These authors showed that silhydrite could be formed from magadiite  $[\text{NaSi}_7\text{O}_{13}(\text{OH})_3 \cdot 3\text{H}_2\text{O}]$  by leaching Na out by surface or near-surface water. We found silhydrite at Cachi Laguna, a soda lake in the southern Bolivian Altiplano. The origin of the mineral,

however, appeared to be different from that in California and this paper describes the properties and occurrence of the silhydrite from Cachi Laguna.

*Geological setting, materials and methods*

The southern Bolivian Altiplano has been markedly affected by a strong acid volcanism

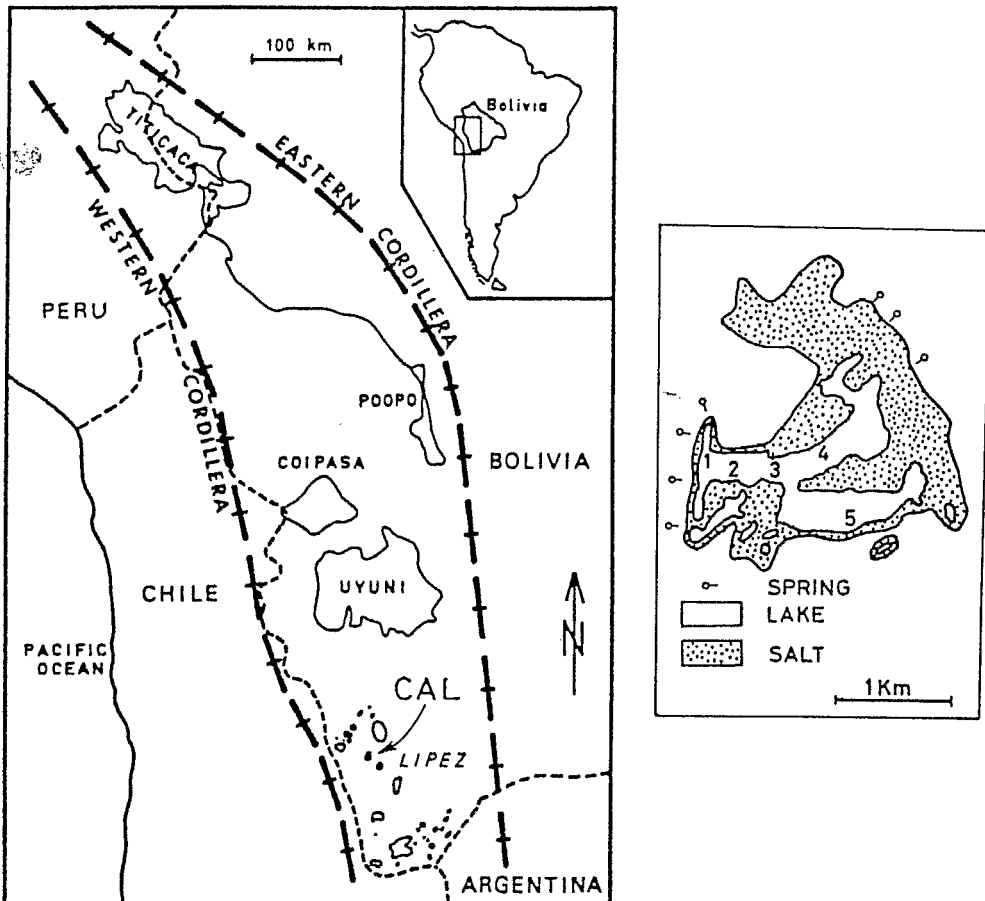


Fig. 1. Location of Cachi Laguna (CAL) and the samples listed in Table 1.

TABLE 1. Chemical analyses of the brines of Cachi Laguna (density in  $\text{g/cm}^3$ ; alkalinity in  $\text{mEq/l}$ ; total dissolved solids: TDS in  $\text{g/l}$ ; others in  $\text{mg/l}$ ).

|                                    | 1    | 2     | 3     | 4     | 5     |
|------------------------------------|------|-------|-------|-------|-------|
| Temperature ( $^{\circ}\text{C}$ ) | 21   | 21    | 21.5  | 21    | 25    |
| Density                            | 1    | 1.001 | 1.014 | 1.029 | 1.238 |
| pH                                 | 9.65 | 10.50 | 10.50 | 10.38 | 10.05 |
| Alkalinity                         | 3.20 | 8.33  | 137   | 355   | 2500  |
| Cl                                 | 9.94 | 94.1  | 2080  | 4540  | 57200 |
| $\text{SO}_4$                      | 22.3 | 103   | 1980  | 3710  | 35800 |
| B                                  | 1.10 | 6.07  | 93.9  | 143   | 2500  |
| $\text{SiO}_2$                     | 76.5 | 146   | 215   | 345   | 432   |
| Na                                 | 66.2 | 246   | 4490  | 10600 | 92000 |
| K                                  | 17.4 | 80.9  | 1470  | 2850  | 35600 |
| Li                                 | 0.56 | 1.92  | 29.3  | 54.1  | 848   |
| Ca                                 | 5.77 | 3.21  | 2.2   | 2.5   | 6.0   |
| Mg                                 | 2.11 | 4.67  | 0.29  | 0.15  | 2.9   |
| TDS                                | 0.29 | 0.85  | 15.2  | 35.7  | 335   |

(Fernandez *et al.*, 1973). The lava isolated several small basins now occupied by saline lakes and playas (Risacher & Fritz, 1991). Cachi Laguna, a soda lake about 20 cm in depth, is found in such a basin. Sediments contain volcanic detritus and diatom frustules. Five samples of sediments were collected from the dilute spring zone towards the centre of the lake which contains the most concentrated brines (Fig. 1). The chemical compositions of the brines in contact with the studied samples are given in Table 1.

The  $<2 \mu\text{m}$  fractions were separated from the sediments using centrifugation techniques and investigated by X-ray diffraction using a Philips 1120/90 X-ray diffractometer (Ni-filtered  $\text{Cu-K}\alpha$ , 40 kV, 20 mA), scanning electron microscope (Jeol JSM 840) and scanning transmission electron microscope (Philips CM 12) equipped with an energy-dispersive X-ray spectrometer (EDAX PV 9900).

## Results

**Scanning electron microscopy.** The SEM observations of the samples 1, 2, 3 and 4 showed the presence of aggregates of silhydrite a few  $\mu\text{m}$  in size (Fig. 2). The morphology of these crystals is similar to those of the silhydrite studied by Gude & Sheppard (1972) from Trinity County in California. Magadiite is only found in contact with the most concentrated brine (sample 5) and silhydrite is absent.

**X-ray diffraction.** X-ray diffraction analysis was performed on non-oriented and oriented crystals of silhydrite and magadiite after treatments with organic compounds and after heating. The measured values obtained from the X-ray patterns of non-oriented crystals of silhydrite are compared with those of the silhydrite identified by Gude & Sheppard (1972) in Table 2. Figure 3 is a diffractogram showing the basal spacing ( $d_{001}$ ) of the silhydrite before and after treatment with hydrazine and after heating at  $490^{\circ}\text{C}$  for 4 h. The variations in the basal spacings of all silhydrite specimens and magadiite after the treatments are summarized in Table 3. The table shows that

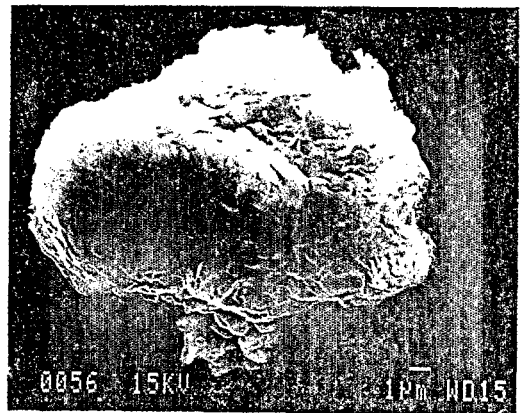


Fig. 2. Scanning electron micrograph of an aggregate of silhydrite.

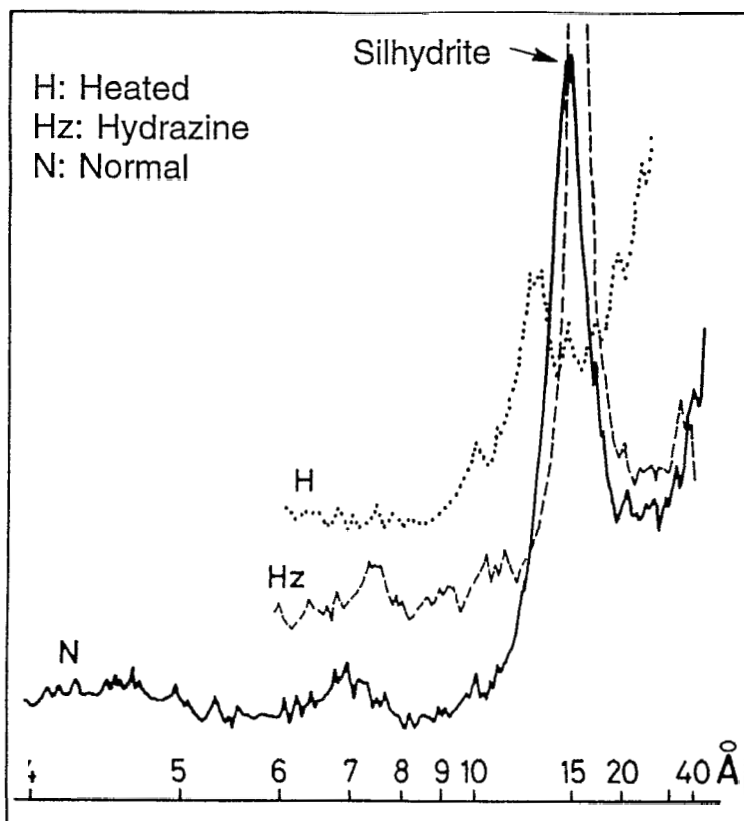


FIG. 3. X-ray diffraction pattern from oriented crystals of silhydrite showing its basal spacing ( $d_{001} = 14.5 \text{ \AA}$ ) and the results of treatment with hydrazine (Hz) and heating to  $490^\circ\text{C}$  (H).

TABLE 2. X-ray diffraction data for the silhydrite studied compared with those of silhydrite identified by Gude & Sheppard (1972).

| This work                     |     | Gude & Sheppard (1972)        |     |
|-------------------------------|-----|-------------------------------|-----|
| $d(\text{obs}) \text{ (\AA)}$ | $I$ | $d(\text{obs}) \text{ (\AA)}$ | $I$ |
| 14.48                         | 100 | 14.52                         | 100 |
| —                             | —   | 9.40                          | 10  |
| 7.32                          | 38  | 7.34                          | 22  |
| —                             | —   | 7.07                          | 21  |
| —                             | —   | 5.31                          | 16  |
| 3.65                          | 37  | 3.63                          | 27  |
| 3.56                          | 40  | 3.539                         | 25  |
| 3.42                          | 81  | 3.42                          | 82  |
| —                             | —   | 3.143                         | 35  |
| 1.84                          | 8   | 1.834                         | 9   |
| —                             | —   | 1.827                         | 13  |
| —                             | —   | 1.789                         | 6   |
| —                             | —   | 1.758                         | 5   |
| 1.72                          | <5  | 1.704                         | 5   |
| 1.68                          | <5  | 1.672                         | 5   |

silhydrite ( $14.3 < d_{001} < 14.6 \text{ \AA}$ ) might be transformed into a compound ( $15.8 < d_{001} < 16 \text{ \AA}$ ) similar to the magadiite ( $d_{001} = 15.6 \text{ \AA}$ ) identified in sample 5 after saturation by sodium citrate (Fig. 4). The behaviour of magadiite after treatments with hydrazine, ethylene glycol and heating (Fig. 5) is similar to that of magadiite taken from Lake Tchad (Maglione, 1976). The increase in the basal spacing of silhydrite after treatment with ethylene glycol or hydrazine is less than that of magadiite. This is probably due to the presence of small amounts of organic material between the layers of silhydrite which impede interlayer expansion by intercalation of guest molecules (Lagaly *et al.*, 1975; Beneke & Lagaly, 1977).

*Scanning transmission electron microscopy.* Figure 6 is a transmission electron micrograph of an ultrathin section of a silhydrite aggregate previously embedded in an epoxy resin (Ehret *et al.*, 1986). The chemical microanalyses of these

TABLE 3. Variation in basal spacings of silhydrite and magadiite after treatments.

|                   | Basal spacing ( $d_{001}$ Å) |            |      |      | Magadiite<br>5 |
|-------------------|------------------------------|------------|------|------|----------------|
|                   | 1                            | Silhydrite |      |      |                |
|                   |                              | 2          | 3    | 4    |                |
| Without treatment | 14.6                         | 14.5       | 14.3 | 14.5 | 15.6           |
| Ethylene glycol   | 14.9                         | 14.5       | 14.3 | 14.5 | 17.8           |
| Hydrazine         | 15.1                         | 15.0       | 15.0 | 15.0 | 16.5           |
| Heated*           | 12.6                         | 12.5       | 12.5 | 12.5 | 10** and 13    |
| Na citrate        | 16.0                         | 15.8       | 16.0 | 15.9 | —              |

\* 490°C for 4 h. Results of heating after Na citrate treatment were identical.

\*\* low-intensity peak.

crystals confirm that they are silhydrite which is essentially silica with traces of Mg, Al, Ca, Fe, Na and K (Table 4). Silhydrite is not stable under the

electron beam and gives a diffuse electron microdiffraction pattern. Diatom frustules observed by TEM are severely corroded.

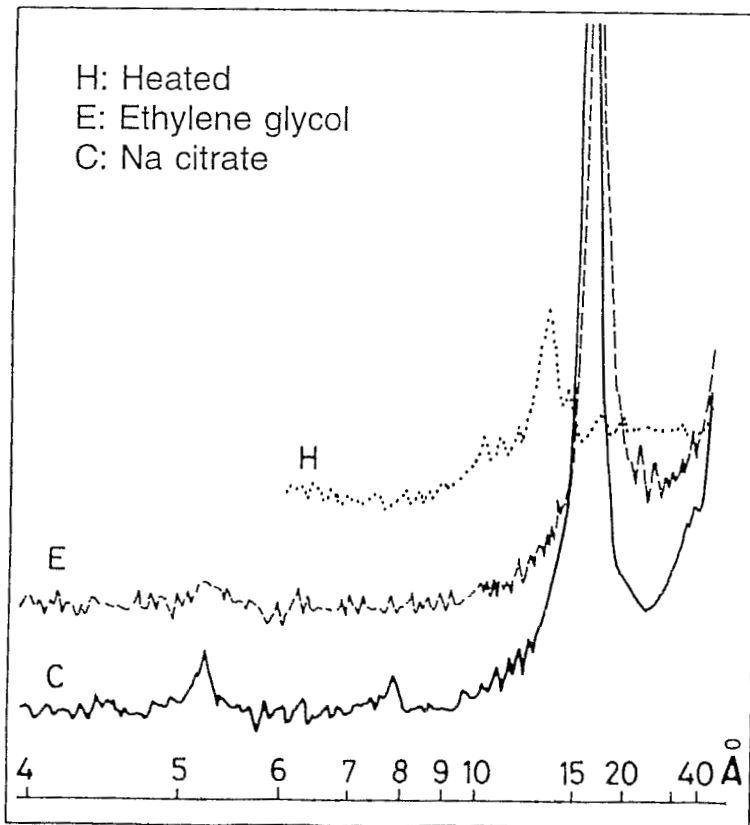


FIG. 4. X-ray diffraction pattern from oriented crystals of silhydrite after treatment with Na citrate (C) and subsequent treatment with ethylene glycol (E) and heating to 490°C. The basal spacing ( $d_{001} = 15.8$  Å) is compatible with magadiite.

TABLE 4. Chemical microanalyses (STEM-EDX) of six particles of silhydrite.

|                                | 1    | 2    | 3    | 4    | 5    | 6    | Mean     |
|--------------------------------|------|------|------|------|------|------|----------|
| Na <sub>2</sub> O              | —    | —    | —    | 0.3  | 0.4  | 0.4  | 0.2±0.2  |
| Al <sub>2</sub> O <sub>3</sub> | —    | —    | —    | 1.1  | 0.4  | 0.7  | 0.4±0.4  |
| MgO                            | —    | 0.3  | 0.7  | 0.2  | 0.5  | 0.5  | 0.4±0.2  |
| SiO <sub>2</sub>               | 98.9 | 97.8 | 98.2 | 97.5 | 97.5 | 95.2 | 97.5±1.2 |
| K <sub>2</sub> O               | 0.3  | 0.9  | 0.8  | —    | 0.3  | 1.1  | 0.5±0.4  |
| CaO                            | 0.4  | 0.8  | —    | 0.4  | 0.7  | 1.2  | 0.6±0.4  |
| Fe <sub>2</sub> O <sub>3</sub> | 0.4  | 0.2  | 0.3  | 0.5  | 0.2  | 0.9  | 0.4±0.2  |

### Discussion on the origin of silhydrite

The primary precipitation of silhydrite near the spring is the result of the alkaline Si-rich and Na-poor state of the solution rather than the result of leaching of magadiite which is only found down-

stream in the most saline parts of Cachi Laguna. Under alkaline conditions, the solubility of amorphous and crystalline silica forms are enhanced by the formation of soluble silica polymers such as Si<sub>4</sub>O<sub>6</sub>(OH)<sub>6</sub><sup>2-</sup> (Markhasev & Sedletskii, 1964; Stumm & Morgan, 1970). The

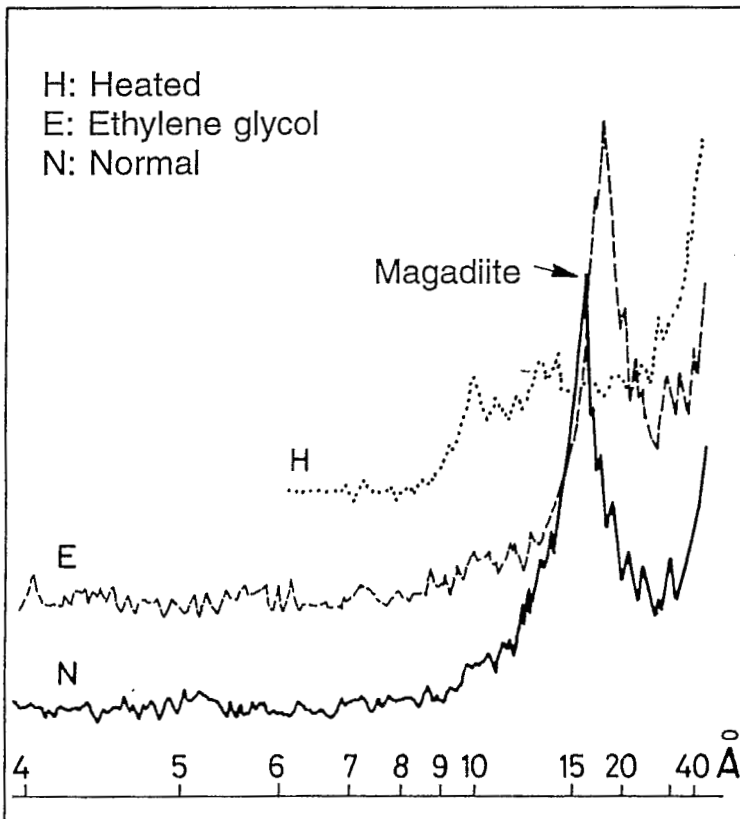


FIG. 5. X-ray diffraction pattern from oriented crystals of magadiite showing its basal spacing ( $d_{001} = 15.6 \text{ \AA}$ ) and the results of treatment with ethylene glycol (E) and heating to 490°C (H).



FIG. 6. Transmission electron micrograph of an aggregate of silhydrite.

dissolution of diatoms into these waters leads to the relative enrichment of silica over Na. The levels of solubility of amorphous silica and silhydrite are quite close, based on the thermodynamic data of Maglione (1976) and Woods & Garrels (1987). The precipitation of silhydrite, a hydrated crystalline form, should be favoured when hydrated polymers are the dominant soluble form. The low concentration of Na in these waters would favour silhydrite or other silica polymorphs in preference to magadiite. With increasing Na concentrations, such as are found near the centre of the lake, magadiite is the thermodynamically favoured mineral (Eugster, 1967; Bricker, 1969; Maglione, 1970).

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