



Contribution ID: 76

Type: not specified

Synchrotron radiation study of a 200 year-old Gaylussite ($\text{Na}_2\text{Ca}(\text{CO}_3)_2 \cdot 5\text{H}_2\text{O}$) specimen from Lagunillas-Mérida, Venezuela, and comparison with a specimen from Lake Magadi, Kenya.

Tuesday, 15 November 2022 18:30 (15 minutes)

1. Introduction

The mineral gaylussite, $\text{Na}_2\text{Ca}(\text{CO}_3)_2 \cdot 5\text{H}_2\text{O}$, was first identified from samples obtained in 1823 during an expedition to Colombia and Venezuela by the French chemist Jean-Baptiste Boussingault and the Peruvian mining engineer and chemist Mariano de Rivero [1]. The mineral samples were collected from Laguna de Urao, a salt lake in Lagunillas, Mérida state, Venezuela, from which some minerals had been previously studied by the German naturalist A. von Humboldt and the Venezuelan patriot, naturalist, and diplomat Manuel Palacio Fajardo. The new mineral, the first discovered in Venezuelan territory, was named by Boussingault gaylussite, in honor of the eminent French chemist. The thermal and hydration/dehydration behavior of gaylussite has been the subject of different studies, aimed at understanding the chemical and crystallographic relationship with other naturally occurring carbonates. Besides the fascinating historical context of the discovery of gaylussite, conflicting reports on the formation of the intermediate hydrate pirssonite, $\text{Na}_2\text{Ca}(\text{CO}_3)_2 \cdot 2\text{H}_2\text{O}$, the low temperature (orthorhombic) and high temperature (hexagonal) anhydrates nyerereite, $\text{Na}_2\text{Ca}(\text{CO}_3)_2$, carried out mostly on synthetic samples, sparked our interest in studying natural gaylussite. Preliminary results are reported here.

1. Results

The gaylussite specimen ENSMP 37496 (collected in 1823 by Boussingault) was an irregular cylinder-like grey fragment of 1.5x0.5 mm approximately. A white, powdery material easily disintegrated from the fragment upon handling. It was gently ground in an agate mortar and used to fill a 1.0 mm borosilicate capillary. High resolution X-ray powder diffraction patterns were collected at the ID22 beamline of ESRF. A Search/Match analysis using the PDF-4+ database [2] and a subsequent Rietveld analysis with TOPAS-Academic [3] indicated the presence of aragonite (29.2%), calcite (2.6%) and, surprisingly, sodium acetate trihydrate (67.9%). A small amount of quartz (0.3%) was also identified. These results prompted the examination of an inner section of the specimen which was carefully scrapped to eliminate material deposited on the surface. The analysis of this sample indicated a 46.5% of aragonite, 42.3% of $\text{Na}(\text{CH}_3\text{COO}) \cdot 3\text{H}_2\text{O}$, 0.3% of quartz, and 10.9% of gaylussite. It must be noted that calcium acetate efflorescence (as $\text{Ca}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ or $\text{Ca}(\text{CH}_3\text{COO})_2 \cdot 1/2\text{H}_2\text{O}$) has been extensively reported in calcareous museum objects stored for long periods of time [4,5] due to emission of acetic and formic acid from wood (particularly oak) cabinets [6]. However, $\text{Na}(\text{CH}_3\text{COO}) \cdot 3\text{H}_2\text{O}$ efflorescence has been reported mainly for glass objects. Upon heating at 650 °C, the Mérida sample shows decomposition to the high temperature phase of nyerereite, $\text{Na}_2\text{Ca}(\text{CO}_3)_2$, which is hexagonal. Upon cooling to ambient temperature, the low temperature orthorhombic form of nyerereite is obtained. For comparison, a study of specimen ENSMP 53763 from Lake Magadi (Kenya) indicated that this sample is almost pure gaylussite. No sodium or calcium acetate efflorescence is observed. The thermal decomposition was followed in situ by registering powder diffraction patterns every 10 °C from 20 to 650 °C. Pirssonite ($\text{Na}_2\text{Ca}(\text{CO}_3)_2 \cdot 2\text{H}_2\text{O}$) forms at approximately 120 °C, low-temperature nyerereite forms at 300 °C, and high-temperature nyerereite starts to form at around 430 °C. Above 450 °C only HT-nyerereite is present and, upon cooling, LT-nyerereite forms and remains at ambient temperature.

1. References

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Acknowledgements: We are grateful for the support of LAAAMP through a FAST Team award and to the STREAMLINE Insight Programme at ESRF. We also thank Dr. E. Gaillou and Musée de Minéralogie MINES Paris for providing the gaylussite specimens ENSMP 37496 (Venezuela) and ENSMP 53763 (Kenya) for this study.

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Session Classification: AfLS Contribution

Track Classification: AfLS