

## Challenges Involved In X-Ray Microanalysis Of The Mineral Kernite [Na<sub>2</sub>B<sub>4</sub>O<sub>6</sub>(OH)<sub>2</sub>·3H<sub>2</sub>O]

Edward P. Vicenzi<sup>\*,\*\*</sup>, Douglas Meier<sup>\*\*</sup>, and Jeffrey Davis<sup>\*\*</sup>

\* Smithsonian Institution, Museum Conservation Institute, Suitland, MD 20746

\*\* National Institute of Standards and Technology, Surface and Microanalysis Science Division, Gaithersburg, MD 20899

Borate minerals are the source for many industrial applications from early civilizations' use of borax [Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>·10H<sub>2</sub>O] as a flux for metal working (1) to trace B doping in semiconductors circuitry. Over 200 varieties of borate minerals are found in nature, yet kernite [Na<sub>2</sub>B<sub>4</sub>O<sub>6</sub>(OH)<sub>2</sub>·3H<sub>2</sub>O], the subject of this study, is among a short list of borates whose deposits are commercially mined today. We have examined kernite from Boron, CA using wavelength and energy dispersive spectrometry as well as variable pressure-scanning electron microscopy and X-Ray diffractometry.

**Phase stability**– Kernite surfaces were found to contain a discontinuous film of a presumably more hydrous Na borate phase, and in places were decorated with dissolution pits (Figures 1A and 1B). Large (multi-centimeter sized) translucent single crystals of kernite were observed to transform to a milky white colour under high vacuum (HV) conditions in the electron microprobe (~2 x 10<sup>-4</sup> Pa). This observation, coupled with X-ray diffraction patterns taken of powdered samples subjected to UHV conditions, suggests kernite undergoes a profound phase transition with decreasing total pressure and/or P<sub>H<sub>2</sub>O</sub> (Figure 2). Low angle peaks either disappear or are much diminished after UHV treatment, which is in contrast to a previously reported metastable phase produced under low vacuum conditions (2).

**EPMA quantification** – Analysis of boron by EPMA-WDS requires attention to both chemical shifts and crystallographic orientation (3) (Figure 3). Low yields for boron are partly ameliorated by use of a B<sub>4</sub>C/Mo multilayer diffractor. Calculations performed using CalcZAF for stoichiometric kernite indicate a >90% absorption correction for B X-ray intensity owing to large mass absorption by O and Na (MACs: ~16k and ~43k respectively). Differences in carbon film thickness between the kernite specimen and the standards are important given the large absorption of B and O X-rays by C (MACs: ~6k and ~11.5k respectively). The magnitude of these absorption effects can result in very large uncertainties in the measured kernite composition. Quantitative analyses suggest an excess of B (relative to stoichiometric kernite) of >30% using the peak intensity method, or just <3% relative using the peak integral method (Table 1). A defocused beam 50 μm in diameter was used, and where possible, the time dependency of X-ray count rates were evaluated and compensated for. Despite these efforts, Na concentrations are low by ~67% (again relative to stoichiometric kernite) suggesting a migration of Na under the electron beam on a time scale shorter than our ability to measure time dependency of the X-ray signal (Figure 4). Further evidence for electron beam-induced Na migration is revealed by the lack of a Na peak in Auger electron spectra of kernite's surface (4). Our EPMA results are most consistent with kernite having lost some waters of hydration, but not structurally bound water.

1. D. E. Garrett, *Borates: Handbook of Deposits, Processing, Properties, and Use* (Academic Press, San Diego, CA, 1998), pp. 470.
2. N. A. Sennova *et al.*, *Crystal Technology and Research* **40**, 563 (2005).
3. G. F. Bastin, H. J. M. Heijligers, *Journal of Solid State Chemistry* **154**, 177 (2000).

4. D. C. Meier *et al.* (this volume)

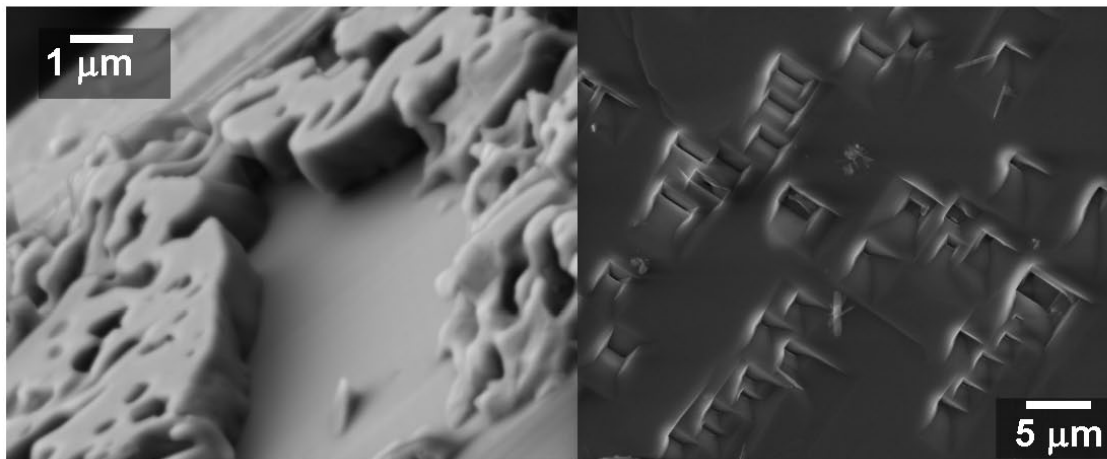


Figure 1 A) VP SEM image of kernite crystal incompletely coated with a submicrometer thick film of a presumably more hydrated Na borate phase. (HV=5 kV, gaseous SE,  $P_{H_2O} = 1.1 \times 10^2$  Pa).

Figure 1 B) VP SEM image of the surface of kernite decorated with dissolution pits. (HV=10 kV, gaseous SE,  $P_{H_2O} = 7.9 \times 10^1$  Pa).

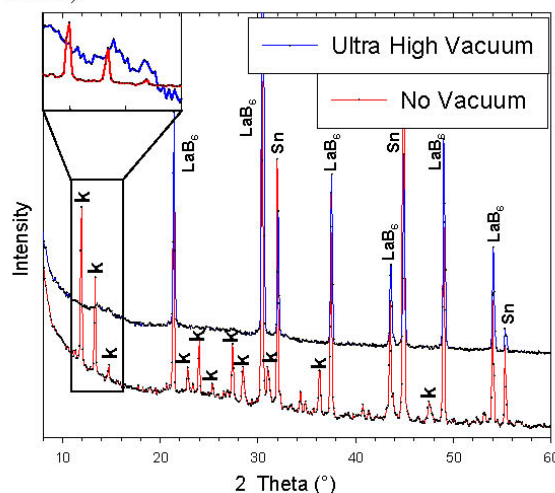


Figure 2 X-ray diffraction patterns for kernite/ $LaB_6$  powder on Sn using Cu radiation at ambient P (red) and subjected to UHV ( $1.0 \times 10^{-6}$  Pa) for 116 hours (blue). Inset: low angle peaks.

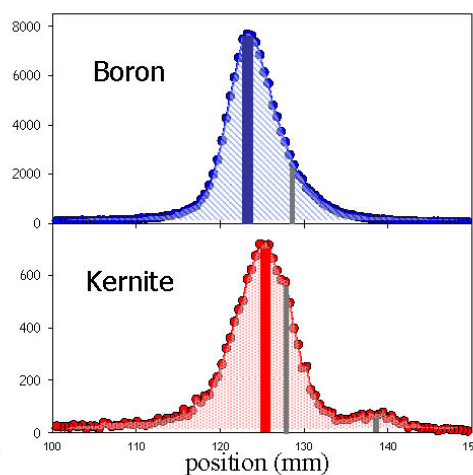


Figure 3 Boron  $K_{\alpha}$  wavelength dispersive spectra for boron metal and kernite.

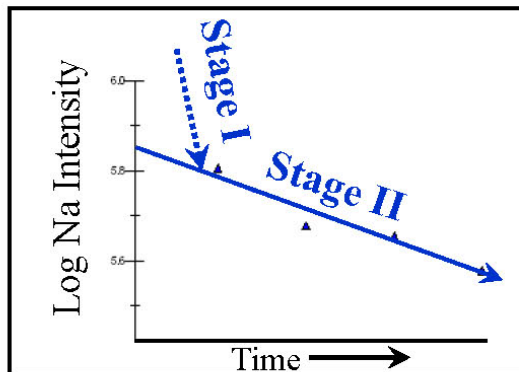


Figure 4 Time dependent Na  $K_{\alpha}$  signal of kernite under the electron beam (solid arrow: regression of 4 data points for 32 seconds; dashed arrow: proposed short-term loss).

Table 1. Representative EPMA-WDS analyses of kernite using two approaches to quantify B. (HV=5 KV at high vacuum,  $\sim 1 \times 10^{-4}$  Pa).

	wt%	wt%	at%	at%
	peak intensity	integral	peak intensity	integral
<b>B</b>	20.66	16.91	27.63	28.4
<b>O</b>	59.98	59.32	68.01	67.3
<b>Na</b>	5.44	5.45	4.36	4.31
<b>Totals</b>	86.08	81.68	100.00	100.01