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Skeleton Crystals[1]

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KEYWORDS

Amorium, archaeology, Brushite, Byzantine, microchemistry, spindle stage

ABSTRACT

During the 2007 excavation season at the Byzantine city of Amorium located in central west Turkey, a burial place in the atrium of the lower city basilica was examined. It was noted by the archaeologists that the skeletal material of one of the occupants had developed tiny crystals on the surface. A small piece of the skull with the crystals present and some loose bone fragments were collected and submitted to the McCrone Research Institute for analysis. Initial observations were made using a stereomicroscope. Single crystals were examined using the polarized light microscope (PLM). Based on initial observations of the optical properties of these crystals, various microchemical tests were conducted. These crystals were found to contain calcium and phosphates. To determine the precise identity of the material, a single crystal was mounted on a spindle stage. By rotating the crystal around two axes we were able to determine the optic axial angle as orientations and magnitudes of the alpha, beta and gamma refractive indices.

INTRODUCTION

Amorium is a medieval city of the Byzantine Empire located in central western Turkey about 8 hours by bus from Istanbul. Some sources believe that it was once the largest and most important city in Anatolia (most of modern Turkey). It has been a city since the at least the 1st century B.C. The excavation project began in 1988 and is directed towards revealing the nature of post classical Amorium, i.e. this city bridges a gap between the mid 7th and late 11th centuries a poorly documented period in history. This is the time between the Christian Anatolia dark ages and the middle Byzantine period. Additional information about the excavation is available from the Amorium Excavation Project (1).

A small piece of skull with adhering crystals and some loose bone fragments were collected from area AM07, A21, Tomb 21 during the 2007 excavation season at the at the Amorium excavation site and submitted to the McCrone Research Institute for analysis (Figures 1,2). Stereomicroscopy was used to assess the sample and the PLM was used in conjunction with other microtechniques to determine the identity of the crystals.

MATERIALS AND METHODS

Microscopy

Preliminary observations were made using a stereomicroscope. The sample contained a mass of large crystals which were off white in color (Figure 3).

Using a tungsten needle, a small sub-sample was mounted in n=1.66 refractive index liquid for analysis by PLM. The crystals were euhedral, tabular, colorless, anisotropic, biaxial and displayed oblique extinction (Figures 4, 5). It should be noted that the extinction of these crystals appears nearly symmetrical due to the fact that the interfacial angle is 45° and the extinction angle is 18° (Figure 6). Conoscopy was used to determine the orientation of the beta (β) refractive index and the Becke line immersion method was used to measure the value of β. These crystals were also positively elongated and had a positive optic sign.

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Figure 1: Left, excavated burial place in the atrium of the lower city basilica.

Figure 2: Right, close up showing area where samples were taken.

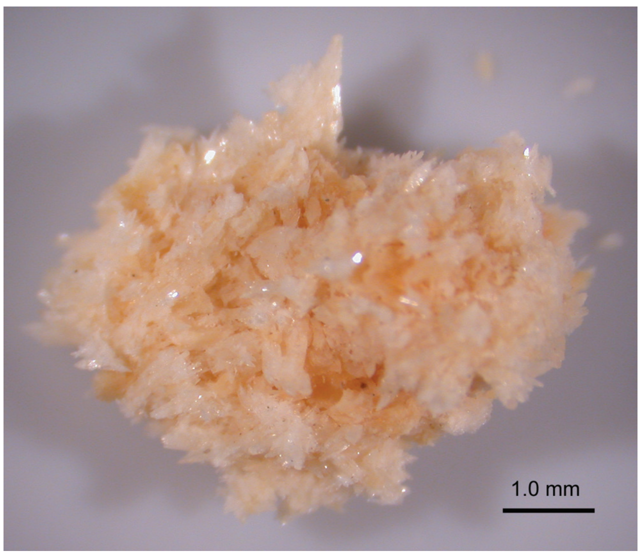

Figure 3: Large cluster of crystals from bulk sample.

Figure 4: Brushite crystal from Amorium sample mounted in n=1.66 refractive index liquid, plane polarized light.

Microchemistry

The crystals were found to be insoluble in water but soluble in dilute HCl, H_2SO_4 and HNO_3. Using preliminary β refractive index data the identity of the crystals was narrowed down to a small list of possible substances (2). Since these crystals were found on bone we theorized that they would likely contain the main components of bone; calcium and phosphates. To further narrow down the possibilities various microchemical tests were performed to test for the presence of specific elements and polyatomic ions. Both positive and negative control samples were also tested along with our test substance. Control samples are a necessity in microchemistry due to the small nature of samples and sensitivity of techniques.

A microchemical test for calcium was performed by taking a small amount of sample, acidifying it with 1:1 HCl and evaporating the solution to dryness. A 5% solution of H_2SO_4 was then added. The formation of long, slender colorless needles of $CaSO_4 \bullet 2H_2O$ confirmed the presence of calcium as seen in Figure 7.

A microchemical test for phosphates was also performed. A small portion of the sample was acidified in dilute HNO_3. A small drop of ammonium molybdate was prepared by acidifying it with HNO_3. These two drops were drawn together using a glass rod. The

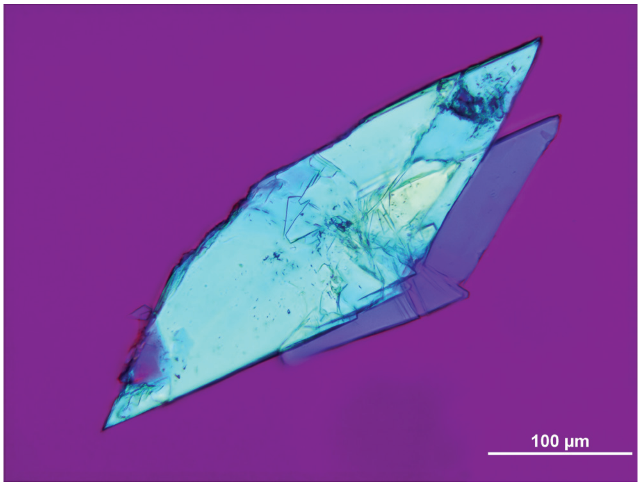

Figure 5: Brushite crystal from Amorium sample mounted in n=1.66 refractive index liquid, crossed polars with 530nm compensator, crystal is positively elongated.

formation of yellow "lemon drop" shaped crystals of ammonium phospho-molybdate confirmed the presence of phosphates in the sample as seen in Figure 8.

Spindle Stage

A detent spindle stage (Figure 9) was used to determine the optic axial angle (2V) as well as the alpha (α), beta (β) and gamma (γ) refractive index orientations. To obtain crystallographic data using the spindle stage, a single crystal was mounted on the end of a needle using nail polish as an adhesive. This needle was then fitted into the shaft of the spindle stage. After preparing the sample the spindle stage was then mounted on the stage of the PLM. The stage of the microscope was set to 0° and the spindle stage was attached to the microscope stage with the spindle axis in the E-W orientation. The spindle axis was set to 0° and a small fluid cell containing refractive index liquid was carefully slid into position so that the crystal

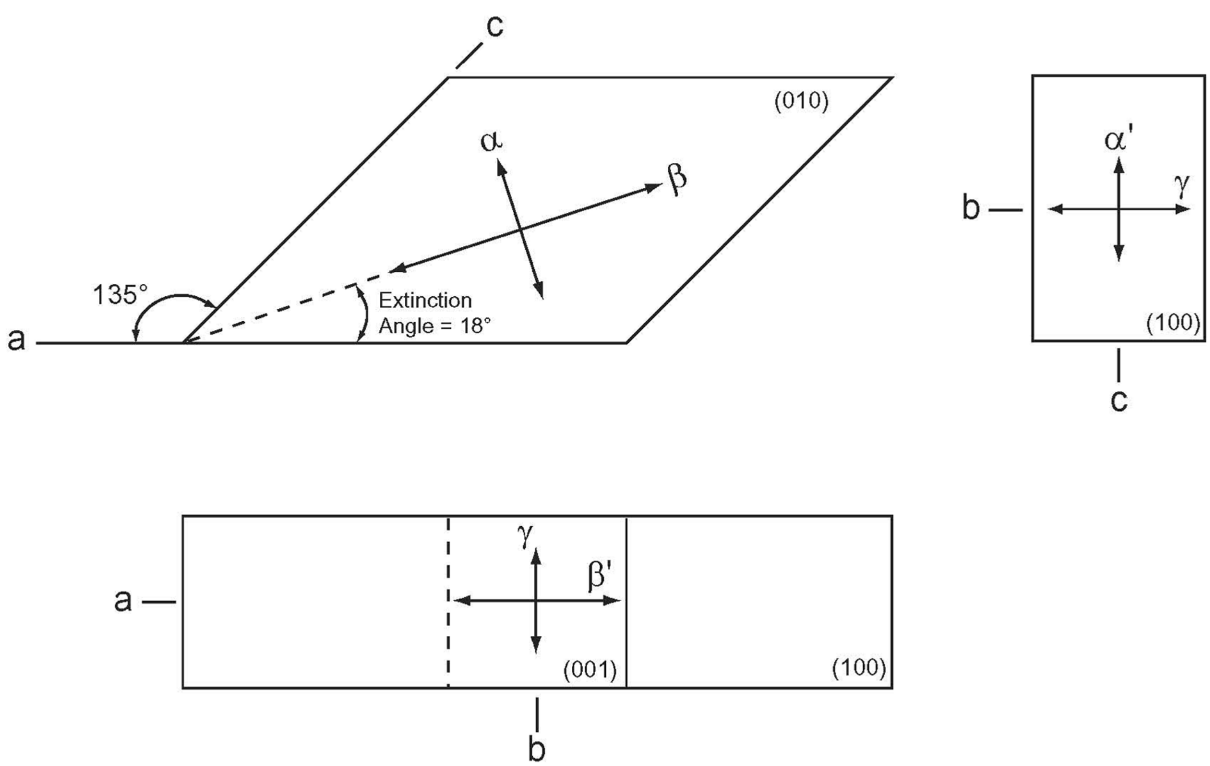

Figure 6: Orthographic projection of monoclinic brushite crystals (pinacoids 010, 100, 001).

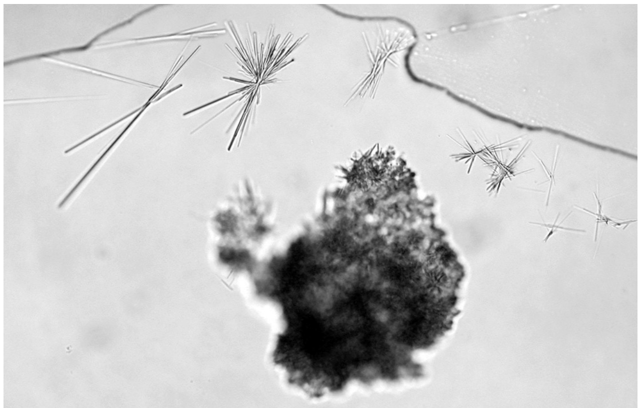

Figure 7: Results of a microchemical test for calcium. Sample was acidified with 1:1 HCl, then allowed to evaporate to dryness. A 5% solution of H_2SO_4 was then added the formation of long slender colorless needles of $CaSO_4 \bullet 2H_2O$ confirmed the presence of calcium.

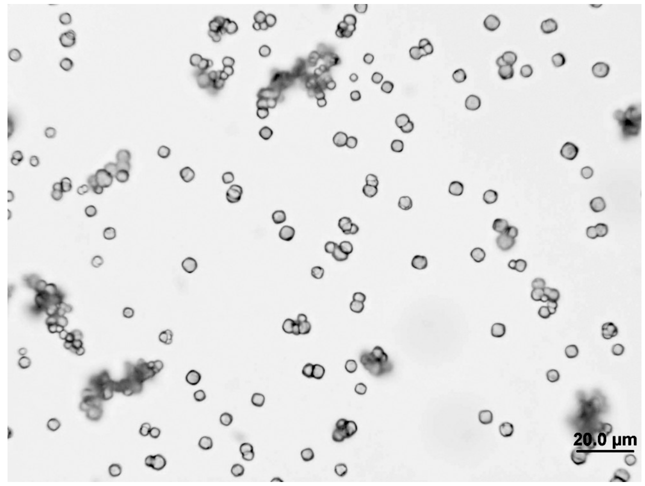

Figure 8: Results of a microchemical test for phosphates. Sample was acidified in dilute HNO_3. A small drop of ammonium molybdate which had been prepared in HNO_3 was drawn to the acidified sample. The formation of yellow "lemon drop" shaped crystals of ammonium phosphomolybdate confirmed the presence of phosphates.

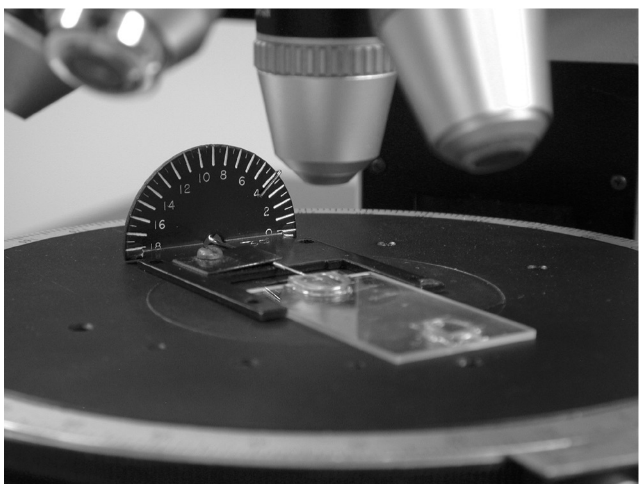

Figure 9: Detent spindle stage attached to Nikon Optiphot-Pol; fluid cell also shown.

was surrounded by refractive index liquid as shown in Figure 9. The first measurement was then taken by rotating the PLM stage until the crystal became extinct; this angle was recorded. The PLM stage was then returned to the 0° position. The spindle axis was rotated to 10°, and the extinction data collected. This was repeated for spindle axis positions from 20° to 180° in 10° increments. More detailed accounts of spindle stage use have been published by Bloss (3) and Gunter (4). The data obtained from the spindle stage were then entered into EXCALIBRW, a free software program which calculates the coordinates of the acute bisectrix (AB), obtuse bisectrix (OB), optic normal (ON) and 2V (Figure 10). An orthographic projection of brushite is shown in Figure 6. The spindle and microscope stage can then be aligned as determined by EXCALIBRW in order to orient the crystal for refractive index measurements. The fluid cell refractive index liquid can

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                         Figure 10 Excalibr data brushite
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 EXCALIBR       Bartelmehs, Bloss, Downs, and Birch; Z. Krist (1992)
 Windows Detent Spindle Stage Version 8.19.00(downs@geo.arizona.edu)
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McRI - Amorium, crystals on bone


 Experimental Treatment ID number = 999.0
 Refined Reference Azimuth, Mr =    0.50

 Clockwise Stage
 Number of iterations(100 max.) =  11
 R-squared =  0.97635


      S         Ms        Es    CALC(Es)  Es-CALC(Es)
     0.00     30.00    150.50    150.63     -0.12
    10.00     31.10    149.40    149.41     -0.01
    20.00     30.50    150.00    149.94      0.06
    30.00     28.10    152.40    153.16     -0.75
    40.00     19.10    161.40    159.69      1.71
    50.00     13.00    167.50    168.46     -0.96
    60.00      4.30    176.20    176.54     -0.33
    70.00     88.20     92.30     92.36     -0.05
    80.00     84.30     96.20     96.28     -0.08
    90.00     80.50    100.00     99.06      0.94
   100.00     79.10    101.40    101.26      0.14
   110.00     77.60    102.90    103.22     -0.31
   120.00     75.80    104.70    105.15     -0.44
   130.00     73.00    107.50    107.20      0.31
   140.00     71.60    108.90    109.45     -0.55
   150.00     67.80    112.70    111.93      0.77
   160.00     66.60    113.90    114.57     -0.67
   170.00     63.30    117.20    117.18      0.02
   180.00     60.70    119.80    119.37      0.43

 Optic Axial Angle, 2V (ese) =  86.351 (1.540)


  Computed Cartesian Coordinates
              x     (ese)          y     (ese)           z     (ese)
 OA1       0.4140 (0.0116)     -0.6534 (0.0101)      0.6338 (0.0100)
 OA2      -0.7801 (0.0092)      0.0151 (0.0149)      0.6255 (0.0115)
 AB       -0.2510 (0.0056)     -0.4376 (0.0149)      0.8634 (0.0090)
 OB        0.8726 (0.0027)     -0.4885 (0.0049)      0.0061 (0.0052)
 ON        0.4191 (0.0076)      0.7549 (0.0081)      0.5045 (0.0154)

  Spindle Stage Coordinates to measure refractive indices.
             S    (ese)        Es   (ese)              Ms
 OA1      135.87 ( 0.83)    65.54 ( 0.73)
 OA2       88.62 ( 1.36)   141.27 ( 0.84)   (e-w polr.)  (n-s polr.)
 AB       116.88 ( 1.03)   104.54 ( 0.33)     75.97       165.97
 OB       179.29 ( 0.62)    29.24 ( 0.32)    151.26       241.26
 ON        33.75 ( 1.08)    65.22 ( 0.48)    115.28       205.28

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 EXCALIBR       Bartelmehs, Bloss, Downs, and Birch; Z. Krist (1992)
 Windows Detent Spindle Stage Version 8.19.00(downs@geo.arizona.edu)
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Figure 10: Data obtained from EXCALIBRW

be easily changed and the Becke line test performed for accurate refractive index determinations.

RESULTS AND DISCUSSION

Optical and crystallographic data were obtained by using the spindle stage to determine optical orientation and the Becke line technique to determine refractive index. The refractive indices of these biaxial crystals were α=1.539, β=1.548, γ=1.551 and 2V=87°. By careful application of the right microtechniques and appropriate reference texts (2, 5, 6) the sample collected at the Amorium site was identified as the mineral brushite $CaH(PO_4)\bullet 2H_2O$ (2). In 2002, graves of similar construction were also excavated in the narthex of the church. Remains found in these graves also exhibited this crystal formation on the bone surface. There have been other documented occurrences of brushite found on bone (6, 7).

CONCLUSIONS

The crystals formed on the skeletal remains were the mineral, brushite. This mineral can be formed by the breakdown of $CaPO_4$ and $CaCO_3$ in the presence of water. Other standard reference samples of brushite did not contain crystals as large or well formed as those recovered from Amorium but refractive index measurements and microchemical analysis were consistent. This supports the conclusion that the burial place at Amorium exhibited ideal conditions for this type of mineral growth and was likely undisturbed for a long period of time.

ACKNOWLEDGMENTS

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