A PHOSPHATE ANALYSIS OF SOILS FROM FOUR ARCHEOLOGICAL SITES IN NORTHERN GREECE

JULIA F. DALY
DEPARTMENT OF GEOLOGY
CARLETON COLLEGE
NORTHFIELD, MN 55057

INTRODUCTION

Soils associated with human occupation often have high concentrations of phosphorus as several forms of phosphate. Phosphate exists in all living beings in an organic form, and as these organisms die and decompose, this phosphorus is gradually converted to an inorganic form (Eidt, 1977). The inorganic phosphorus is insoluble, and will continue to accumulate in soil as long as a source for it exists. Within the soil, the phosphorus (as phosphate) bonds with aluminum, iron, calcium, and a small part of it becomes part of the soil solution (see fig. 1; Chang, 1957). Background phosphorous might exist in low concentrations most likely because of the presence of apatite in the parent material of the soil. Because the concentrations of phosphate produced by human occupation will be so much higher than those produced naturally, they can be detected and distinguished fairly readily (Eidt, 1977). Field and laboratory tests have been developed to qualitatively and quantitatively measure phosphate concentrations, and I have employed one of each of these methods in my research.

The project was a multi-purpose endeavor, involving not only evaluation of methods of phosphate analysis, but also the application of phosphate testing to examining landscape evolution and human interaction with the landscape in an area. Because Grevena is being surveyed for more extensive archeological research in the future, determining the lateral and vertical extent of soils which are believed to be in situ is important in evaluating potential sites. However, because we were also interested in learning more about the landscape evolution of the area, examining the colluvial fills near the landscape seemed a logical way of approaching the question of the relationship between human occupation and hill slope erosion. The close examination of these fills also provided an opportunity to test the phosphate detection and quantification methods, since they have been used primarily on in situ soils in the past.

METHODS

Because each of the four sites surveyed - Potamia, Agia Paraskevi, Paleogla, and Agios Nikolaos - posed different questions, soil samples were collected from different kinds of areas (surface, auger, vertical exposure) at each area. However, the field test performed with each sample was identical. This qualitative test, as described by Eidt (1977), involves applying an acid-molybdate solution to a small soil sample in order to form molybdophosphoric acid. This acid is reduced to a molybdenum-blue complex by ascorbic acid. The test is performed on filter paper, and as the molybdenum-blue complex is produced, a blue ring forms. In order to insure a fair comparison, the reaction is stopped after two minutes by washing the filter paper with citric acid; if this wash is not performed, the blue will eventually spread over the entire filter paper. The blue ring can be qualitatively evaluated for the intensity/darkness of the blue color (Eidt, 1977). I developed a five value scale: pale, light, medium, dark, and deep blue. Number values 1-5 have been assigned to these intensities for analysis purposes (see fig. 2). The filter papers were labeled and preserved for future reference. The consistency of the results seems to be most sensitive changes in the sample size; slight variations of the volume of the reagents applied, slight changes in concentration (due to possible evaporation), and the presence of calcium carbonate do not seem to affect the intensity of the blue in the ring (Daly, 1993). Qualitative comparisons of phosphate concentration could be made between sites based on the results of the field tests. This field test was also useful for determining the lateral and vertical extent of a site, whether or not soil from a particular horizon or fill was anthropogenically related, and to re-confirm or further explore areas that had shown up as magnetic or resistive anomalies.

In order to quantify the concentration of phosphorus, and perhaps determine land use (as in Overstreet et al, 1985), a soil fractionation technique was performed in the lab. The fractionation procedure is based on that outlined by Eidt (1977), and the colorimetry procedures are those described by Murphy and Riley (1962) and Watanabe and Olsen (1961) (see Fig. 3). The fractionation procedure results in the production of three fractions.

1. The first fraction is produced by two separations which extract that phosphate which is loosely bound Al-P, Fe-P, that which is resorbed by $CaCO_3$, and the very small amount already in the soil solution. NaOH and sodium citrate-sodium bicarbonate reagents (in separate steps) are used to remove these types of phosphate; the product is known as the NaOH+CB fraction.

2. The second separation uses sodium citrate - sodium bicarbonate - sodium dithionite to extract "tightly bound or occlusive phosphate absorbed by diffusive penetration or by incorporation with aluminum and iron oxides and hydrous oxides" (Eidt, 1330, 1977). This is known as the CBD fraction.

Katie Donnelly used geophysics to locate buried structures at three sites. She coordinated magnetic and resistivity surveys at Aghia Paraskevi, Asprokambos, Paleogla, Dasaki and Aghios Nikolaos, Emilianos. Surveys over exposed walls at Paleogla will help Katie interpret the geophysical results at the other two sites, which have no structures exposed at the surface. Katie's geophysical results will also help determine the geophysical signature of the site geology.

Mary Greene described and measured the physical properties of soil materials in vertical sections at three sites. She described soil profiles at Potamia, Knidi/Itea, Paleogla, Dasaki, and Aghia Paraskevi, Asprokambos. In the field, Mary also measured the resistivity of soil layers in vertical sequence. In the lab, she measured the magnetic susceptibility of many of these same layers. Her results should help Katie Donnelly interpret the surface geophysical anomalies at the sites. She will also be able to determine some of the factors that control the geophysical properties of archaeologically significant layers.

Julia Daly measured qualitatively the phosphorus content of soil horizons and colluvial layers in described sections at all four sites. At many archaeological sites, phosphate increases with the intensity of human use. Julia has also determined how much occupation soils can be diluted by mixing with sterile colluvium and downslope movement and still retain an "occupation" phosphate signature. During this year, Julia has tested many of her samples in the lab to determine the specific form of the phosphorus. She and Mary Greene hope to test whether there is a correlation in archaeological materials between high magnetic susceptibility and high phosphate content.

Elizabeth Russell's project involves reconstructing the topography at the time of occupation at two sites, Potamia, Knidi/Itea and Aghios Nikolaos, Emilianos. At Aghios Nikolaos, topography on part of the site has been severely eroded (into badlands forms). At Potamia, the lower part of the site has been filled in with artifact-rich colluvium since occupation. In the field, Elizabeth mapped both sites with an automatic level and did some resistivity profiling and sounding to determine the shape of the colluvium/bedrock contact at Potamia. During this year, she experimented with computer-assisted design programs to come up with a picture of the landscapes at the time of occupation and of the sequence of changes that have brought them to their present condition.

Two projects focused solely on the site of Potamia, Knidi/Itea:

Bob Wilson is studying the evolution of the landscape in an area upstream of the large landslide. He has mapped alluvial terraces, determined their relative elevations, and described the soils on and within the terrace sequence in order to determine a chronology of erosion and deposition. There are a number of paleosols in the terrace sequences that may represent periods of landscape stability. Most of the terraces have a colluvial cover, so hillslope events will also be part of Bob's chronology. Bob collected some soil samples for lab analysis and charcoal from one colluvial unit that will help tie his chronology to absolute time. Bob's landscape history can be related to multiple occupations of the site, since some of the colluvial units contain artifacts (probably Early Medieval) and one of the alluvial sections contained Early Neolithic pottery.

Julie Williams is studying landscape evolution downstream of Bob Wilson's section. She also has mapped alluvial terraces, determined their elevations and described soils on and in the terraces. However, Julie's sections appear to be more alluvial (less colluvial) and she has collected three samples of charcoal for radiocarbon dating. Her study area is downslope and downstream from a large part of the site that was occupied in Hellenistic times; the obvious components of pottery and charcoal in parts of the alluvium may come from this site.

SUMMARY

The 1993 Keck projects gave students an opportunity to explore the interfaces between geology and archaeology. All project results will help us better understand the evolution of physical environment that humans inhabited and the effects of human habitation on the landscape.

3. The final extraction is the removal of occluded calcium phosphate and apatite by HCl, known as the HCl fraction.

Each o f the extractions produces an aliquot. Murphy-Riley colorimetry is performed on Aliquots A and G, while Watanabe-Olsen colorimetry is performed on Aliquots C and E (see fig. 3). Murphy-Riley colorimetry involves reagents similar to those used by Eidt in his field test procedure. An acidified solution of ammonium molybdate with ascorbic acid and a small amount of antimony (as potassium antimonyl tartrate) reacts with phosphate ions in the aliquot to form the phosphomolybdenum blue compound. The transmission (T) of the solution is measured at the absorption maximum of phosphomolybdenum blue in the presence of antimony, 882 mμ (Murphy, 1962). In order to determine the concentration of the phosphate from the transmittance values that I had obtained for each sample, I used Beer's Law, which says that $\log(1/T) = \varepsilon bc$, where T= transmittance, ε= molar absortivity, b= pathlength of the beam through the sample, and c= the concentration of absorbing atoms (West, 266-7).

Watanabe-Olsen colorimetry is a modification of the Pons and Guthrie method, where the phosphomolybdenum blue complex is produced by mixing the aliquot with a molybdate-sulfuric reagent, producing the phosphomolybdate complex is removed to isobutyl alcohol, then reduced with stannous chloride. The transmission of the solution is measured at 660 mμ. Beer's Law is applied to determine the concentration of phosphate (Watanabe, 1962).

RESULTS AND DISCUSSION

Agia Paraskevi, Asprokambos: Was the site occupied continuously? What is the difference between this material, which is anthropic in situ material, and anthropic colluvium? The lateral and vertical extents of the site were measured through a combination of sampling along a transect line (see fig. 4), sampling from contemporary topographic boundaries, sampling from a vertical in situ section, and sampling from two different auger holes. Because the site is currently being cultivated, a plow pan exists in the soil between 40 and 50 cm, possibly complicating some of the results. The vertical extent of the site is inconclusive based on the results of the survey; the concentration of phosphate between the surface and as deep as 80-100cm is consistent enough to indicate that the site has been related to human occupation continuously for as long as we are able to tell. The transect line was not a very effective way of trying to determine lateral extent, perhaps because of the plow pan. Tests performed at topographic boundaries were also inconclusive (ring values of 3 - medium blue). When quantitative results are determined in the lab, it may be possible to speculate on the use of the land in the past. The main difference between this in situ material and colluvial anthropic material is that this is more likely to have a higher phosphate concentration, because the soil has not been disturbed or mixed with other non-anthropic soils.

Agios Nikolaos: How does the phosphate level correlate to the magnetic anomalies detected at the site? How was the site used? Has material associated with the period of occupation eroded away from the site? The lateral extent was difficult to constrain, but random sampling of the surface soil in the main field produced higher concentrations of phosphate in an area that was found to be a magnetic anomaly (Donnelly, 1994), (see fig. 5). An auger at this spot showed that the soil as for down as 80 cm was associated with human occupation, not only because of high phosphate concentrations, but also because between 50-80cm bits of decomposed pottery or roof tile were found in the soil. Downslope of the site the field test produces a medium to dark blue ring, suggesting that, although the area does not appear to have been part of the original site, material associated with human occupation has been eroded away from the site. Quantitative data relating to the use of the site is not yet available.

Potamia: How is the phosphate concentrated in colluvial fill around the site? What are the differences between colluvium associated with human occupation and sterile colluvium? Can the field test produce accurate results for colluvium? What is the relationship between the beginning of erosional processes near the site and human occupation? Phosphate seems to exist in anthropogenic concentrations in colluvial fills all around the site; finding a colluvial fill that did not seem to be anthropogenically related yet still could have been derived from the same site was extremely difficult. I thought I had located a sterile colluvium (there were no pieces of pottery or charcoal, and the field test indicated that it had slightly lower concentrations of phosphate than anthropogenic fills), however, the preliminary quantitative results of the soil fractionation process show that several of the supposedly non-anthropogenically related horizons seem to have a higher concentration of phosphate than the anthropogenic horizons (see fig. 6). Because some of the horizons from the "sterile" fill have much lower concentrations of phosphate, one possible explanation for the unexpectedly high concentrations of phosphate in some horizons might be that the samples were somehow contaminated. Anthropogenic colluvium from other areas of the site suggest that much of erosion is very closely tied to human occupation; in two of the fills, MS5 and MS6 (Doyle and Savina, 1989) all of the material in the fills indicated high phosphate concentrations in the field test.

Paleogla: Which horizons/fills are associated with human occupation? How was the site used? Was human occupation continuous? What are the differences in anthropic horizons, and why are there these differences? I located five different colluvial fills which may be related to human occupation. From profile OB28 (Doyle and Savina, 1989), a few of the horizons have been quantitatively analyzed for phosphate, yielding much higher concentrations than any of the other horizons analyzed. The field test was also helpful at this profile for confirming that all of the horizons were anthropic. There were numerous differences in anthropic horizons and profiles. At least two of the fills contained discreet charcoal layers; however, most of the fills are quite distinct from each other because they are derived from different areas of the hill. We also know that human occupation on the site involved some earth moving, which may also have influenced the character of the colluvial fills.

CONCLUSION

Through the testing of both the field and the laboratory method of determining phosphate concentration, it seems that both of the methods are useful for identifying anthropic soils that are no longer in situ. Analysis of these soils seems to lead to the conclusion that human occupation was a factor which influenced landscape evolution in the area, since many of the colluviums near sites primarily contain anthropic/phosphate-rich material. The field test may continue to be an extremely useful device in the Grevena project, since it seems to yield reasonably reliable results, and will help to identify potential sites more easily. The preliminary results of the quantitative analysis indicate that, while seemingly inconsistent with the field test, it may still yield useful results, and may be used to detect phosphate in colluvium. Completion of the quantitative tests will lead to a better understanding of their usefulness.

REFERENCES

Bishop, E.; and Daly, J., 1993, unpublished data.

Chang, S.C.; and Jackson, M.L., 1957, Fractionation of Soil Phosphorus: Soil Science, vol. 84, pp. 133-144.

Donelly, K., 1994, this publication.

Eidt, R.C., 30 September 1977, Detection and examinationof anthrosols by phosphate analysis: Science, vol. 197, no. 4311, pp. 1327-1333.

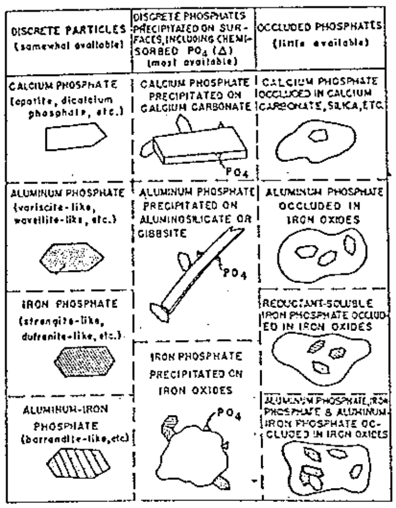
Murphy, J.; and Riley, J.P., 1962, A modified single solution method for the determination of phosphate in natural waters:Analytica Chimica Acta, vol. 27, pp. 31-36.

Overstreet, W.C.; Eidt, R.C.; Brinkmann, R.; Detra, D.E.; and Chao, T.T., 1985, Orientatio survey using phosphate fractionation to distinguish anthrosols from native sediments in the Wadi al-Jubah Archeological Area, Yemen Arab Republic: American Foundation for the Study of Man, 1984 -1985, vol. 4, pp. 121-154.

Savina, M.; and Doyle, R., 1989, unpublished soil description.

Watanabe, F.S.; Olsen, S.R., 1962, Colorimetric determination of phosphorus in water extracts of soil: Soil Science, vol. 93, pp. 183-188.

West, D.C., 1987, Essentials of Quantitative Analysis, New York: Mcgraw-Hill Book Company, 458p.



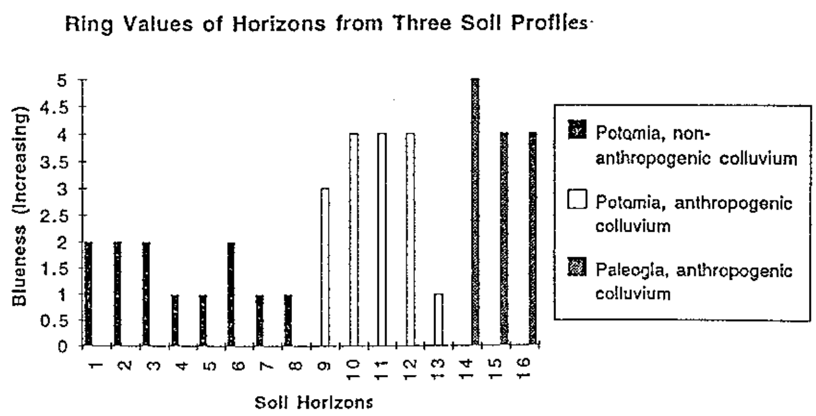
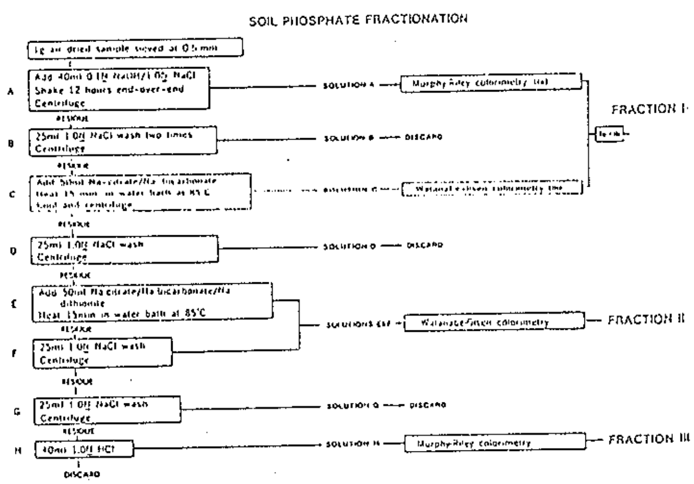


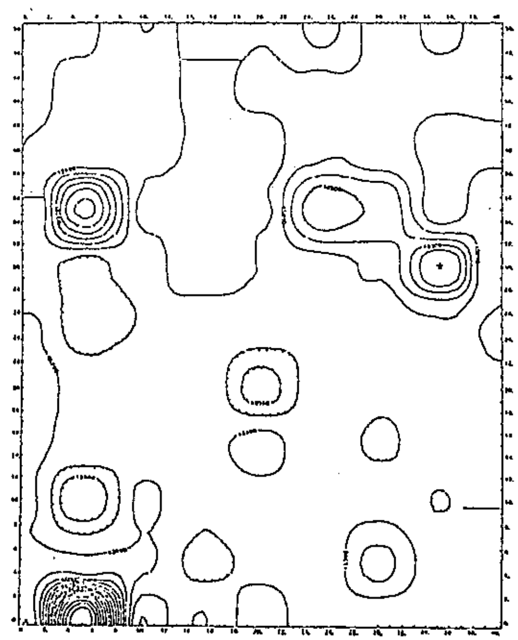
Figure 1. (left) Representation of the physical distribution of chemical forms of inorganic phosphates present in soils (from Chang and Jackson, 1957).

Figure 2. (right) Ring values for selected horizons from the three soil profiles which have been partially quantitatively analyzed thus far. Zero indicates that no blue color was produced in the field test of the sample, meaning that the sample has a very low phospahte concentration.



Asprokambos	Ring value	Agios Nikolaos	Ring value	Potamia	Ring value	Paleogla	Ring value
In situ	3	Auger 1	4	MS 6	3	OB28	n/a
vert. profile	4	(see fig. 5)	4		4	(also known	n/a
(horizons	5		4		4	as PG1...)	n/a
1-8)	4		5		4		4
	5	Below site	3		1		4
	5		4		0		5
	5		2	MS5	4		4
	3		2		4		3
Augor 1	4	On site	3		4		4
(at 3rd	4	(NE cornor of	4		3		4
transect pt.)	3	site)	3		3		4
	4		4		4		5
Auger 2	3		4	Off-site fill	2		
	4		3		2		
	3		5		2		
	3	(Auger 1)	4		1		
	4		4		1		
Transect	2				2		
(N-S, 45m,	3				1		
5m intervals)	4				1		
	3				1		
	3						
	3						
	2						
	2						
	1						
	1						

Figures 3-6 (clockwise from upper left). 3. Flow chart of soil fractionation procedure outlined and developed by Eidt (1977). 4. Chart of qualitative values collected at each of the four sites through Eidt's rapid field test. Zero indicates a low phosphate concentration, while five indicates a very high phosphate concentration. 5. Magnetic survey map of Emilianos (agios Nikolaos); the star indicates the site of Auger 1.
6. Chart of preliminary quantitative values collected for two horizons at Potamia (MS5 and osc) and one at paleogla (PG1). Zeroes indicate that testing has not been completed.



Horizon		con. frac 1a	#1a+#1b	conc. #2	conc. #3	Total
MS5	1	6.4833E-08	9.6574E-08	0	2.7702E-08	0
	2	1.5431E-07	1.7399E-07	3.8975E-09	0	1.7789E-07
	3	9.0611E-08	9.8425E-08	0	1.9686E-08	0
	4	1.5431E-07	0	0	5.6427E-08	0
	5	1.4488E-07	0	0	-3.5571E-06	0
osc	2.	1.4488E-07	0	0	6.0619E-08	0
	2.2	1.6385E-07	0	0	9.9397E-08	0
	2.3	1.0828E-07	1.0828E-07	0	6.4833E-08	0
	2.4	2.447E-07	0	0	8.1923E-08	0
	2.5	6.0619E-08	6.0619E-08	0	9.9397E-08	1.6002E-07
	2.6	8.1923E-08	0	0	9.0611E-08	0
	2.7	2.7733E-07	2.7733E-07	0	6.9071E-08	0
	2.9	2.0322E-07	0	0	6.4833E-08	0
pg	1.6	1.3333E-06	1.3451E-06	0	4.8111E-08	0
	1.7	6.3835E-07	0	0	5.6427E-08	0
	1.9	7.1246E-07	0	0	7.8146E-09	0

MAGNETIC AND ELECTRICAL RESISTIVITY SURVEYS OF ARCHAEOLOGICAL SITES IN GREECE

Kathleen E. Donnelly
Trinity University

Introduction

Archaeologists are increasingly turning to geophysical methods to improve their understanding of archaeological sites. Ideally, geophysical methods allow the archaeologist to view the subsurface without destroying the site. Geophysical measurements can also aid in efficient excavations, revealing if and where excavations will be advantageous. The two geophysical methods used in this survey are magnetics and electrical resistivity. They are two of the most frequently used geophysical methods in archaeology (Weymouth, 1986).

Magnetic surveys are perhaps the most efficient geophysical method (Aitken, 1961). The proton precession magnetometer has enabled a relatively large area to be measured in a short amount of time. One problem with magnetic measurements is that a variety of sources, such as geologic or recent human activity, can cause the same anomaly as an archaeological feature. To solve this problem, magnetic measurements are often combined with electrical resistivity measurements (Weymouth, 1986; Young and Droege, 1986; Pattantyus, 1986). Resistivity surveys are more time-intensive than magnetic surveys, and therefore, are less efficient. Another problem with resistivity measurements is that they are strongly affected by the water content in the ground. Thus, an arid climate like Greece is ideal for resistivity surveys. Besides these specific problems, the overall success of both magnetic and resistivity surveys depends on the contrast of physical properties of the archaeological feature and its surrounding material (Young and Droege, 1986).

Three archaeological sites are included in this study: Aghios Nikolas, Emilianos; Paleogla, Dasaki; and Aghia Paraskevi, Asprokambos. The data presented below are selections chosen from the total data collected.

Methods

Two EG&G Geometrics proton precession magnetometers were used to take magnetic measurements. One magnetometer was used in gradiometer mode with the top sensor at a height of 3m and the bottom sensor at a height of 1m. It was discovered after the data were collected that the top sensor was too high to resolve archaeological features. Therefore, only the total field data from the bottom sensor were used. The other magnetometer was reserved to take base station readings at regular time intervals. These base station readings were used to correct for diurnal variation of the earth's magnetic field.

The magnetic data were dumped into a computer after each field day. The program, Magpac, was used to apply diurnal corrections to each measurement and for preliminary analyses. Surface III software was used to grid data at 1m intervals using either slope projections or scaled inverse distance squared projections and to produce final contour maps.

A Bison Instruments earth resistivity system, model 2350, was used to measure apparent resistivities. Collection of resistivity measurements is more time-intensive than collection of magnetic measurements; thus, resistivity measurements were not taken along every magnetic line. Four probes were used in a Wenner array with an A-spacing of 1m. In addition to profiles, two soundings were also measured: one at Emilianos and one at Paleogla.

Results by Site

Aghios Nikolas, Emilianos

The first magnetic measurements were taken on a 40m x 50m grid. The lines were oriented north-south with 5m spacing between points and lines. To define an observed linear anomaly in greater detail a smaller grid (10m x 20m) with a spacing of 2m between data points was measured over a portion of the anomaly. The data from the coarse and finer surveys were combined and gridded in Surface III, using slope projection. A contour map of the data shows the linear anomaly of 25 gammas (Figure 1).

Apparent resistivity readings were also measured over the linear magnetic anomaly. The data points were taken at a 5m spacing. A contour map of the data shows a strong anomaly with a dramatic increase in apparent resistivity (Figure 2). The center of this anomaly is approximately 5m north of the magnetic anomaly's center. Daly (1994) used an auger to dig a hole at x=35m, y=30m. Small fragments of pottery and pieces of charcoal were found in the upper 10cm, and at depths of 50-80cm a red layer was present, possibly the remains of decomposed pottery or roof tile (Daly, 1994).

Both the magnetic and electrical resistivity surveys reveal an anomaly with centers along the north-south profile, x=35m. The magnetic anomaly center is shown to be at y=30m, while the resistivity anomaly center is 5m to the north of this (Figures 1 and 2). The positive peak would be expected to be displaced to the south of