AN X-RAY FLUORESCENCE STUDY OF LAKE SEDIMENTS FROM ANCIENT TURKEY USING SYNCHROTRON RADIATION

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DISCLAIMER

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Sediments from relic Lake Golbasi were analyzed by X-ray fluorescence with synchrotron radiation to determine changes in element concentrations over time with selected elements serving as proxies for environmental change. Increases in Ca and Sr suggest soil formation during a dry period, from ca. 4500 BC to ca. 200 AD at which point K, Rb, Zr, Ti, and Y increase, indicating the return of a wet environment. Soil erosion, represented by Cr and Ni, increases ca. 7000 BC, probably as a consequence of environmental change, prior to suggested exploitation of natural resources by the newly urbanized society of the third millennium BC.

INTRODUCTION

This paper presents synchrotron-radiation-based X-ray fluorescence (SR-XRF) data from lake sediments collected in the Amuq valley located in the Hatay province of southcentral Turkey. Of particular interest is the correlation between concentrations of elements and environmental change. The Amuq valley lies 80-100 meters above mean sea level. To the west lie the heavily forested Amanus Mountains composed of intrusive igneous formations in the south and sedimentary rock in the north (fig. 1). The uplands to the east and south of the valley consist of denuded limestone massifs and just to the northeast of the valley lie outcrops of vesicular basalt. Rainfall, which measures about 600-700 millimeters per annum, is sufficient for rain-fed cultivation yet is often enhanced by irrigation to increase crop yield [1]. Three rivers feed the Amuq valley: the Kara Su from the north, the Nahr al-Afrin from the east, and the Orontes from the south. The Orontes flows through a narrow gorge in the city of Antakya (ancient Antioch) before emptying into the Mediterranean Sea. Mankind has occupied the Amuq valley significantly for some 9000 years. In essence, the Amuq serves as a microcosm for the study of environmental change and human activity in the ancient Near East.

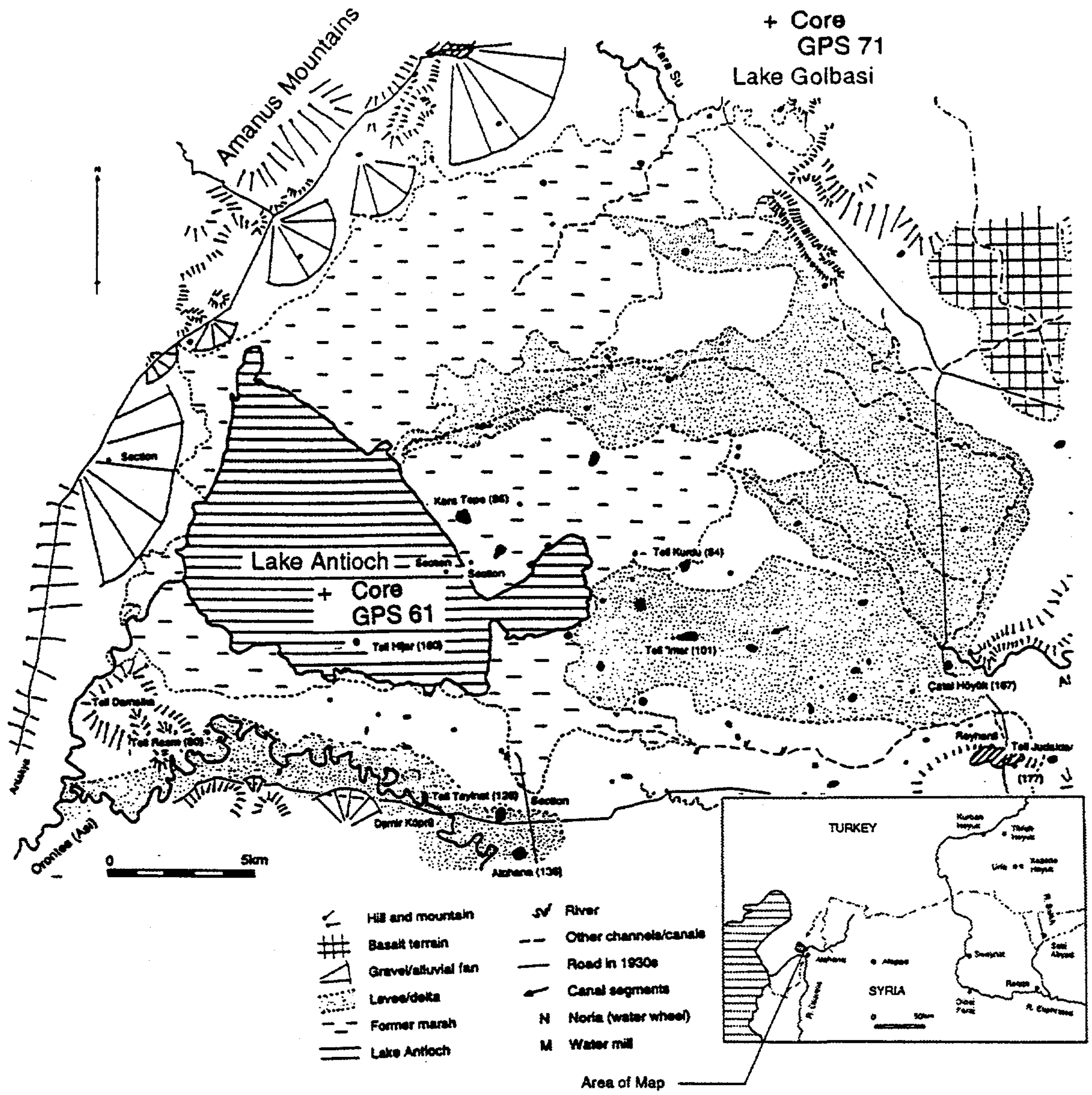

Fig. 1 Geomorphological sketch of the Amuq valley indicating the Lake of Antioch and the two main cores. Elemental analysis relates to core GPS 71. Inset shows the Amuq valley in its Near Eastern context.

The down-faulted Amuq basin is a well-watered and fertile plain, the floor of which has been occupied by several lakes and marshes at various times over the last 30,000 years. Between 5000 and 3000 BC the largest archaeological sites in the plain appear to have been in the center of the plain after which the main settlements developed along the southern edge. This was in the vicinity of a major east–west trade route that had connected Syria and Mesopotamia with the Mediterranean for several thousand years. Water sources in the form of springs, marshes, perennial rivers and episodic lakes provided abundant water, but these often, extensive bodies of water sometimes limited the amount of available agricultural land. One lake, the Lake of Antioch, which occupied the southern part of the plain, deposited shelly silts over archaeological sites dated between 3000 and 2500 BC, and can therefore be dated no earlier than the 2^{nd} half of the third millennium BC (GPS 61).

The sedimentary history of the Lake of Antioch suggests that the lake developed during the last 2000-3000 years as a result of episodic high-energy floods spilling over into flood basins, and the progressive choking of the basin outlet by aggradation of Orontes levees, possibly reinforced by tectonic movements. Flooding, partly a result of climatic fluctuations, human influences on basin vegetation (therefore runoff and flood peaks), and discharge of water from canals, may have contributed to lake growth as well. Lake Golbasi at the north end of the basin was cored by a team from Groningen University, Netherlands, to a depth of 15 meters in order to determine the sedimentary history of the lake and obtain samples for pollen analysis (GPS 71). The upper 6.4 m of the core was sampled for elemental analysis by synchrotron-radiation-based X-ray fluorescence (SR-XRF). The results of this assay were then compared with the better known sequence from the Lake of Antioch. The combined evidence for long-term changes in the local environment from these two cores could then be related to changes in human settlement.

In light of this archaeological framework, the objectives of this project were to try to recognize signals of environmental change by tracking diachronic trends in trace element concentrations. This is not a sedimentological study *per se* but rather an exploration of the use of the Advanced Photon Source in archaeology. We suggest that both environmental change [2] and human activity [3,4] contributed to environmental degradation and are represented by fluctuations in lake deposits. The implications of lake development and lake retreat are supported by the data produced herein.

EXPERIMENT

The experimental setup (fig. 2) includes a double-crystal Si (333) water-cooled monochromator that diffracts a monochromatic X-ray (i.e., with a single wavelength or energy). The X-ray fluorescence yield depends upon the incident X-ray energy that is selected by the monochromator. In this experiment 32 keV incident photons were used with a gas flow ionization chamber to count the X-ray flux. A silicon solid state detector was used for its ability to measure multiple elements simultaneously. The energy resolution of the Si(Li) detector is 0.2

keV (at 6.3 keV Fe Kα) - 0.3 keV (at 15.8 keV Y Kβ/Zr Kα). The regions of interest spanned 3 keV – 20 keV.

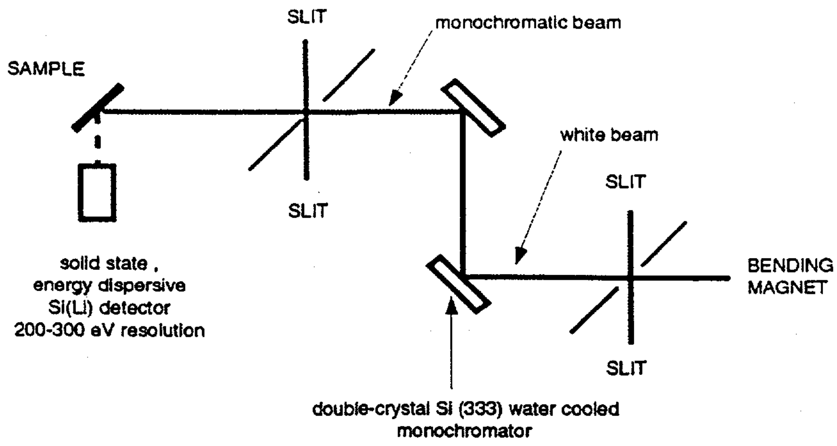

Fig. 2 Schematic diagram of experimental setup at SRI-CAT (2-BM) at the Advanced Photon Source, Argonne National Laboratory.

Spectra for each sample were collected in just ten minutes. We were able to detect the following elements: K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn, Pb, Bi, Rb, Sr, Y, Zr, and Nb. Some difficulties in interpretation arose due to peak overlap For example, the Y Kα line overlapped the Sr Kβ resulting in mixed intensities. However, since the Sr Kα line was clearly resolved and the emission energies are known, the Sr Kβ could be determined by the yield ratio of Sr Kα/S r Kβ. Once we obtained the Sr Kβ we then went back and determined the intensity of Y Kα.

The spectra of these elements are displayed as peaks characteristic of the emission energies for each individual element. The area covered by each peak was obtained by subtracting the background and then fitting a Gaussian function. Independent chemical analysis of two samples was conducted using inductively coupled plasma – atomic emission spectroscopy (ICP-AES), and instrumental neutron activation analysis (INAA). The measurements obtained by INAA on sample GPS71_60 were used as an internal standard against which our data was measured.

Table 1 displays the presence of the elements detected by SR-XRF in comparison with the ICP-AES and INAA data. The experiment did not allow for the measurement of the low-Z elements (Na, Mg, Al, Si), but they could be easily measured by SR-XRF if the samples and detector were placed in a helium filled environment to minimize absorption. Elements higher than atomic number 42 (molybdenum) are omitted from table 1 because they were not the focus of this project. Yttrium and niobium were detected by SR-XRF but not by ICP-AES or INAA.

Elements	SR-XRF	ICP-AES	ICP-AES	INAA
	detected	GPS71_80	GPS71_160	GPS71_60
		%	%	ppm
Na		0.359	0.453	4195
Mg		3.18	3.32	
Al		4.54	4.04	6.153%
Si		24.9	23.3	
K	√	0.957	0.988	1.19%
Ca	√	3.05	4.95	2.15%
Sc				13.57
Ti	√	0.39	0.349	4010.1
V		0.014	0.012	97.85
Cr	√	0.062	0.053	764.65
Mn	√	0.129	0.106	1151.2
Fe	√	4.36	3.99	4.729%
Co		0.005	0.005	46.2
Ni	√	0.056	0.059	477.6
Cu	√	0.005	0.007	
Zn	√	0.005	0.004	77.3
As				10.12
Rb	√			63.05
Sr	√	0.03	0.028	169.1
Y	√			
Zr	√	0.005	0.004	118
Nb	√			

Table 1. Selected elements measured by SR-XRF, ICP-AES, and INAA.

Samples of sediments were taken at 20 centimeter intervals initiated at the surface of the relic lake bed down to a depth of 6.4 meters. According to radiocarbon dates, this 6.4 m segment of the core represents an estimated 13000 years of history. Correspondingly, the concentrations of elements are plotted as a function of depth. The increase or decrease in the concentrations of selected elements over time provides information on the ancient environment, changes that were induced through either environmental change and/or human activity.

The sample identification numbers represent the site identification number as well as the stratigraphic location of the sediment in question. For example, GPS71 is the site indicator for the Amuq archaeological survey as recorded by the Global Positioning System and _40 is the designation for the depth in centimeters below the surface from whence the sample came. Thus, GPS71_40 is a sample from 40 centimeters below the surface at Amuq site number 71, Lake Golbasi. The sediments from the Lake Golbasi core were dried and then pulverized with a mortar and pestle to induce homogeneity into the sample. A hydraulic press was used to form the sediment pellets. A pressure of 8 tons/cm^2 was applied. Each pellet contained about one gram of sediment and measured 13 millimeters in diameter and 3 millimeters thick.

X-ray fluorescence analysis can be performed using radiation produced from conventional X-ray tubes, rotating anode machines, or synchrotron radiation. The advantages of synchrotron radiation include tunability, polarization, intensity, and speed. The tunability of synchrotron radiation allows the wavelength of radiation most suitable for the problem at hand to be selected. Since synchrotron radiation is linearly polarized, observing the scattered radiation at 90° angle minimized the elastically scattered photons, preventing the incident radiation from saturating the solid state detector. This polarization cuts down the dead time of the detector and reduces the experiment time considerably. Although the high intensity of synchrotron radiation is very useful when it comes to small samples as demonstrated in this experiment, it is even more significant when applied to a large number of samples. It is not uncommon these days to have a detector that can handle over 10^6 counts per second thus enabling the high intensity of synchrotron radiation to be exploited. Higher quality spectra on these samples could be recorded in less than 30 seconds with a multi-crystal detector. Speed ultimately has an impact on the number of samples that can be measured in a reasonable time, and for systematic studies of this type where hundreds of samples are likely to be measured, speed is of the essence. Finally, we feel that the introduction of synchrotron-radiation-based X-ray fluorescence analysis into the domain of archaeology has significant benefits that go beyond the current problem. It is not insignificant that synchrotron radiation is non-destructive, making it a choice technique for objects of archaeological, historic, and artistic value.

RESULTS and DISCUSSION

The Lake Golbasi sediments are separated into five components represented by different groups of elements. The quartz sand fraction, the primary component of the sedimentary core, is represented by Zr, Ti and Y. The clay/silt fraction is represented by K and Rb, the calcium carbonates by Ca and Sr, and the heavy minerals by Cr and Ni [5]. Copper represents metal working, but unfortunately the copper peaks were not well resolved, thus preventing us from drawing any inferences about metal production at this time. Sample no. GPS71_260 is not included in the figures because it was unavailable for analysis.

K and Rb, which occur in direct proportion to the quantity of silt/clay deposited on the lakebed, provide a proxy indicator for pluvial conditions and lake development. On the other hand, a decrease in K and Rb suggests a period with a drier lake bed. SR-XRF of the Lake Golbasi sediments demonstrates that the amount of K and Rb increases in phases from 6.4 m to 3.0 m below the surface, at which point there is a marked decline suggesting the retreat of the lake (fig. 3a). This period lasts until about 1.2 m beneath the surface, at which point there is a slight rise in K and Rb indicating the return of a wet environment. The trends in the concentrations of the quartz sand fraction - Zr, Ti, and Y parallel the trends in the clay/silt fraction - K, Rb (fig. 3b).

The trends in calcium carbonates complement the quartz sand and clay/silt fraction. Ca and Sr increase in phases from 6.4 m to 3.4 m, at which point the concentrations suddenly plunge. After the severe decline, Ca and Sr slowly increase suggesting that the soil formation processes that produced the calcareous horizons returned, peaking at about 1.2 m below the surface (fig. 3c). In natural soils, an increase in Ca as calcium carbonate may indicate a period of aridity that causes lakes to recede. In consequence, the receding lake waters deposit calcium carbonate salts within lake floor soils. Thus, an increase in Ca and Sr between 3.4 m and 1.2 m may represent the development of a soil profile enriched in calcium carbonates. At 1.2 m the concentrations of Ca and Sr decline, while the concentrations of K and Rb rise. This supports our suggestion that an increase in K and Rb represents lake development, while an increase in Ca and Sr represents lake retreat. In both cases, the trends in these trace elements are representative of environmental change.

The heavy mineral component of the lake core, represented by Cr and Ni, derives most likely from the slopes of the Amanus Mountains that lie just to the north and west of the Amuq Valley. This range has extensive outcrops of serpentine, the parent rock of Cr and Ni, and is home to commercial chromite deposits [6]. The increased presence of Cr and Ni in the lake sediments strongly suggests environmental degradation. Concentrations of Cr and Ni are present from 6.4 m to 4.0 m beneath the surface, at which point they increase continuously up through the remainder of the core (fig. 3d).

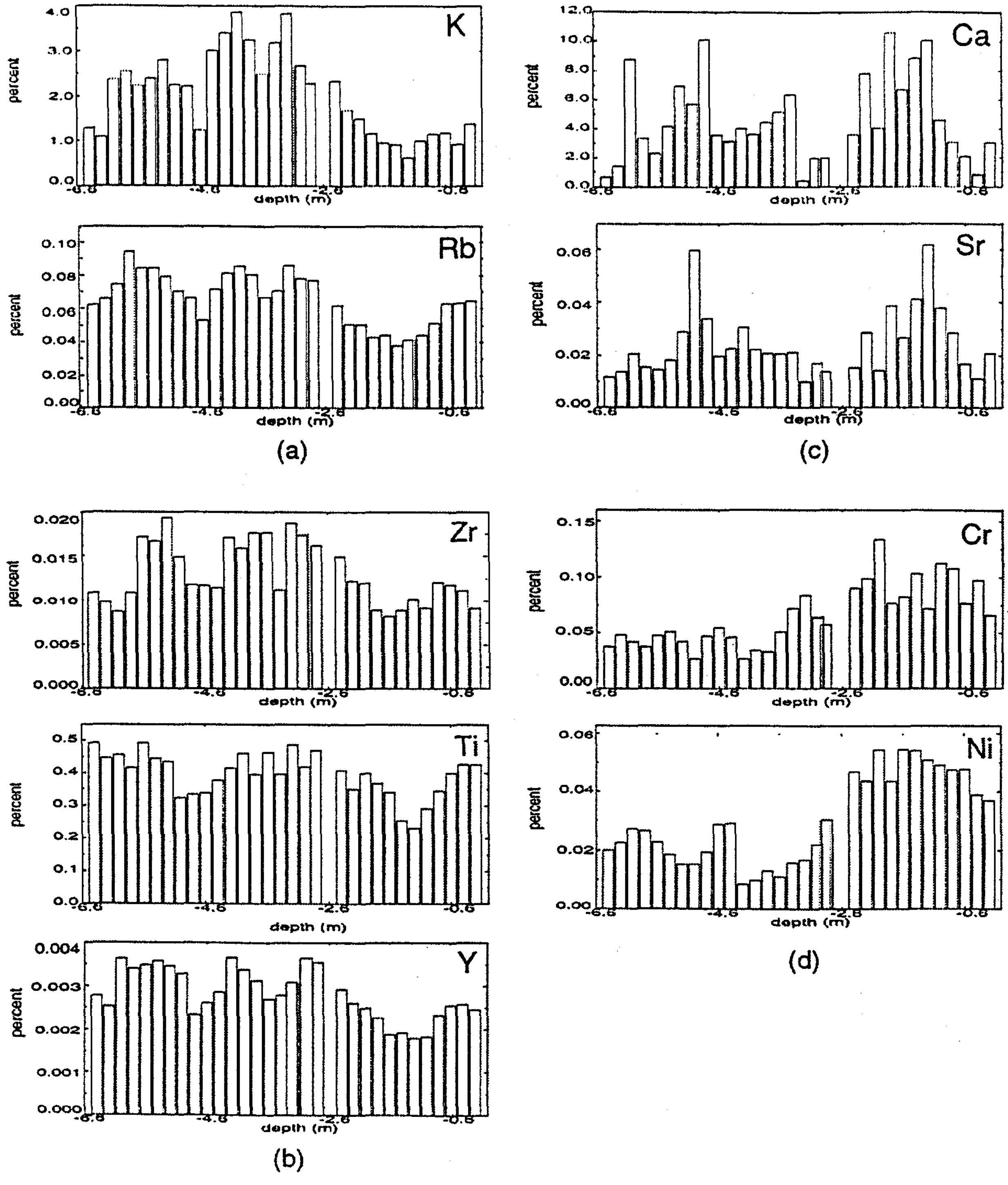

Fig. 3 Trends in concentrations of elements over time.
Deepest samples to the left.

CONCLUSION

Trends in elemental composition through time suggest that erosion of the Amanus mountains, indicated by Cr and Ni, increased above 4.0 m depth (after ca. 7000 BC). Lake sediments, indicated by K and Rb, accumulated prior to this increase in erosion. The lake then retreated. In the upper 0.60-0.80 m of the core a slight rise in the level of the lake is indicated. This later rise correlates closely with the redevelopment of the Lake of Antioch, which suggests that the growth and retreat of both lakes were influenced by the same processes. Finally the development of calcium-rich accumulations, indicated by Ca and Sr, suggest soil formation and drying out of the lake floor in the period between ca. 3600 and 0 BC, that is approximately when the Lake of Antioch retreated. The elemental analysis therefore suggests that the growth and decline of Lake Golbasi was approximately synchronous with that of the Lake of Antioch.

Soil erosion and deposition transform the landscape but it is often difficult to determine if the causes are anthropogenic, environmental, or a combination of both. We suggest that the process of erosion in the Amuq Valley began as a result of environmental change prior to any serious human impact in the region. It appears that the exploitation of natural resources to satisfy the fuel demands of the larger urban settlements of the third millennium BC may have aggravated these processes. Moreover, the data demonstrate changing levels of lakes which themselves may have had a radical effect on the development of human settlements. In conclusion, SR-XRF makes possible not only the identification of individual elements, but, more importantly, it provides the means for recognizing trends in element concentrations over time that serve as proxies of environmental change.

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