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A PRELIMINARY INVESTIGATION INTO THE USE OF AN ELEMENTAL ANALYSIS IN THE CORRELATION OF SEDIMENTS FROM LAKE RUDOLF, KENYA

BY

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ABSTRACT

Eighteen elements were determined in several sedimentary strata layers using Instrumental Neutron Activation Analysis (INAA) and Atomic Absorption Spectroscopy (AAS). Proceedures for the trace elemental analysis were developed and applied to both a bulk sample analysis and an analysis of selected size fractions from these samples. Care was exercised in the handling of samples to minimize contamination and losses associated with trace element analysis.

The strata studied were selected from the plio-pleistocene sediments of Lake Rudolf, Kenya. This region is currently under extensive archeological and paleontological observation. Samples consisted of several sand and clay paleosol units and a number of volcanic tuffaceous horizons. It was of interest to determine the feasibility of using an elemental analysis as a stratagraphic correlation method for this region.

Determination of seventeen elements was made by INAA. Four of these, Sodium, Aluminum, Vanadium, and Manganese, were accomplished by a short irradiation and thirteen others by a long irradiation. Manganese and magnesium were determined by AAS, after a hydrofluoric acid decomposition.

The concentrations determined show differences in the samples. Volcanic tuff units show variation in their degree of weathering, which may lead to a correlation based on their change from primary magma. Sand and clay paleosols tend toward more regional relationships rather than individual horizon correlations. Additional correlative conclusions must wait until a more extensive study can be made. The current investigation indicates that such an elemental determination will aid in the geological study of this region and when integrated with other methods will help to determine relationships in the stratigraphy.

ACKNOWLEDGEMENT

This work is dedicated to Jeffrey Paul Hammock. His original conception and initiation of this research enabled its development. His efforts will allow the progress of this project to continue in the future. With this work I wish to thank him for his personal inspiration, and most of all for his friendship.

I wish to also express my deepest love for my wife, Cheryl, who endured the trials, and tribulations of the typing and editing of this manuscript, in addition to putting up with her crazy husband.

PREFACE

This thesis is presented in manuscript form. The first paper describes the analysis of 18 elements in paleosol sediments from Lake Rudolf, Kenya. The determination of 15 elements from volcanic horizons in the same region is presented in the second paper. The first appendix is an introduction to the thesis. The second appendix describes the experimental techniques of this research. The third appendix is a further discussion of the data. The last appendix is an entire bibliography of this thesis.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

Figure Page

The Elemental Composition of Paleosol Sediments from Lake Rudolf, Kenya.

A Preliminary Investigation of the Elemental Composition of Tuffs from Lake Rudolf, Kenya.

Appendix I.

Appendix II.

Appendix III.

THE ELEMENTAL COMPOSITION OF PALEOSOL SEDIMENTS FROM LAKE RUDOLF, KENYA

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ABSTRACT

The rapid non-destructive analysis for a large number of components can be achieved with relative simplicity in geochemical research with the use of Instrumental Neutron Activation Analysis (INAA). Several sand and clay sediments from the Lake Rudolf region of Kenya, Africa, have been analyzed for seventeen elements, both as major and trace components, employing this technique. The elements include : Na, Al, V, Mn, Sc, Cr, Fe, Co, Rb, Zr, La, Eu, Tb, Yb, Lu, Hf, and Ta. Magnesium was also determined by Atomic Absorption Spectroscopy. Results show similarities in these sediments over lateral displacements in addition to vertical differences between strata layers. These elemental abundance levels demonstrate the usefulness of this technique in geochemical studies of the area.

The discovery and analysis of fossiliferous remains and other archeological finds makes it necessary to catagorize them as completely as possible. R.E.F. Leakey, M.D. Leakey, and the Lake Rudolf expedition (1-4) have uncovered many specimens, including several complete hominid craniums, in the Lake Rudolf basin of Kenya, Africa. (fig.1) Over 600 specimens of vertebrate fossils have been reported by Vincent J. Maglio (5) from the regions near the lake.

Lake Rudolf's structure is associated with the tectonic relief of the East African Rift System. The sedimentology consists of over 300 meters of fluvial deltaic and lacustrine sediments distributed on late Miocene and Pliocene volcanics as described by Vondra and Bowen (6). Initial geological studies of the area were conducted by Behrensmeyer (7) in 1970. Since this preliminary work Vondra, Johnson, Bowen, and Behrensmeyer (8) have shown the sedimentology to consist of various pleistocene sedimentary beds ranging from coarse sands and pebble conglomerates to fine silts and clays in both fluvial and lacustrine environments. The complexity of correlation is evident from these stratagraphical studies. Correlation has depended primarily upon similar lithologies, bed thicknesses , field relationships, and measurements to key marker beds which could be traced laterally. These key marker beds, consist of volcanic sediments, which have been studied and dated to some extent by the research group of Fitch and Miller (9). The analysis of a selected number of these tuffaceous samples has been accomplished by Luedtke, Fasching, and Hammock and is reported elsewhere (10). The primary concern of this work was to investigate the elemental composition of several sand and clay paleosol units from the area.

The use of NAA in the study of geochemical systems and specimens is expanding continually. Scintillation counters have been successfully used in several analyses of rocks and soils as is demonstrated in reviewing the investigations of Thorenson (11), Brunfelt and Steine (12), and others. More recent analysis has taken advantage of the lithium-drifted germanium gamma-ray detectors whose importance and application are shown by Prussin, Harris, and Hollander (13). Gordon (14) has employed the use of these high-resolution detectors to determine 23 elements in a variety of igneous rocks with instrumental neutron activation. A routine instrumental determination of twenty-two elements on both rocks and sediments has also been reported by Das and Zonderhuis (15). Buenafana (16), in the study of basaltic soils, exploited this non-destructive method to analyze for twenty-five elements. Due to the higher resolution and the increased accuracy of peak location along with the simplicity of sample preparation, this investigation used Instrumental Neutron Activation Analysis (INAA).

The collection of the samples was undertaken by P.

Abell during the expedition season of 1972. Samples were taken by exposing the underlying sediment and then encapsulating a portion of this unexposed region in a large polyethylene vial, which had been previously leached in 12 N nitric acid and washed with distilled deionized water in order to remove contamination. The samples were then stored individually in sealed plastic bags which were crated for transport. Once in the laboratory sample handling was held to a minimum. All work was carried out in a clean bench. Two representative sub-samples were taken from each specimen, one weighing approximately 50 mg and the other 500 mg. Each was then sealed in a two dram polyethylene vial, that had previously been leached and washed with nitric acid and distilled deionized water. Attached to each 500 mg sample was a cobalt flux monitoring wire, used to correct for flux differences during a long irradiation.

Standards were liquid monitor solutions containing the elements being analyzed. Two solutions, one for short irradiations containing Na, Al, V, and Mn, and the other containing a combination of the long irradiation elements were made. These were prepared in the laboratory from available Dilute-It standards and oxides.

The irradiation procedures and elements analyzed are summarized in table 1. Four elements, Na, Al, V, and Mn, were determined from a short irradiation within ten minutes of activation. Another thirteen elements were analyzed after a seven hour irradiation with counts being taken at two and four week decay periods. These included Sc, Cr, Fe, Co, Rb, Zr, La, Eu, Tb, Yb, Lu, Hf, and Ta.

Standard photopeaks, as indicated by Gordon (14) and Morrison (17), were used in the determination of all the components. Samples were irradiated in the $4x10^{12}n/cm^{2}\bullet sec$ flux atomic reactor of the Rhode Island Nuclear Science Center. A 30 cm^3 Ge(Li) detection unit in conjunction with a 4096 channel Nuclear Data 2200 analyzer equipped with a magnetic tape output, collected the data. The data was then processed through an IBM 370/155 computer with the use of the program PIDAC (18). Accumulation of the results was recorded in parts per million of each element.

The spectra of a characteristic short and long irradiation are shown in figure 2. The major peaks of the short irradiation are the Na, Al, V, and Mn. The long spectrum is dominated by the Sc, Fe, Co, Ta, Eu, and Hf peaks. Many of the smaller peaks, including the Lanthanide series elements and other low energy emitters, are crowded into the first 800 Kev.

In table 2 the composition of a red clay strata along with overlying and underlying beds are shown. In reviewing this data many of the elements seem to be fairly consistant throughout the series, but there are some noteworthy exceptions. The Mn concentrations show a strong similarity between E-1, E-2, and E-3 with concentrations of about 1300 ppm. Sample E-4 appears slightly higher at 1900 ppm, and

E-5 had twice the concentration at 2600 ppm. When sample E-6 is observed, it drops back to a level of 1200 ppm, just below the first three. The Fe abundances may show a similar grouping. E-1, E-2, and E-3 are in the range of 2.5% to 2.8% , while E-4 and E-5 are now the same level of 2.2%Fe, and again E-6 is low at 1.8% . Lanthanum shows the same trend of Fe in that E-1, E-2, and E-3 are highest, with E-4 and E-5 being equal, and E-6 being low. Ta and Co also demonstrate a comparable correlation. The Mg variation is similar where E-1, E-2, and E-3 proved to be low at 560 ppm, and E-4 and E-5 higher in concentration at approxiamately 900 ppm and 1300 ppm respectively. The sample E-6 was low in concentration of Mg at 500 ppm. With the possible exception of Co, these elements also proved to show similar relationships when taken in a ratio to the aluminum concentration determined (table 3). The physical relationship of these samples is depicted in figure 3. From this representation the correlation is reasonable. E-1, E-2, and E-3 are from the top of the same stratagraphical unit at fifty foot lateral displacements. Sample E-4 is taken from the bottom edge of this same red strata. E-5 is from the overlying layer, and E-6 is from the stratum below. It is therefore reasonable to assume that E's 1-3 would show a strong similarity, but it is also significant that they exhibit this over a 100 foot lateral displacement. E's 4-6 are from different vertical localities and most likely have different mineralogies as well as different micro-environments.

The average values for two groups of sand paleosol and two groups of clay paleosol strata are given in table 4. Averages for locality one are different than locality two. The sands and clays of each locality are from a vertically oriented series. It is therefore interesting to note both the similarities of sand and clay from the same locality as well as similarities between clays of different localities and sands of different localities.

The Mn values for the clays are noticeably higher than those for the sands, and Yb may also show a close agreement between the two clay averages at 3.9 ppm and 3.7 ppm. The averages for sand #1 and clay #1 are in good agreement for Sc, Fe, Co, La, Eu, Tb, Lu, Hf, and Ta. In a similar manner, sand #2 and clay #2 are close. Thus, the bulk of the data tends toward a locality correlation rather than a paleosol type correlation. The major factor in such a correlation might be attributed to the differences in degree or type of weathering between the two regions.

CONCLUSIONS

1. Instrumental Neutron Activation Analysis proved to be a useful method in analyzing these samples for elemental abundances.

2. One can distinguish a degree of homogeneity within one of the paleosol units observed and one is also capable of distinguishing it from the surrounding strata.

3. There is a locality correlation between one verticle sand-clay series versus another.

4. It is believed that a particle size separation or mineral phase separation may help to develop more conclusive identification of these and other paleosol units found in the expedition site.

LIST OF FIGURES

LIST OF TABLES

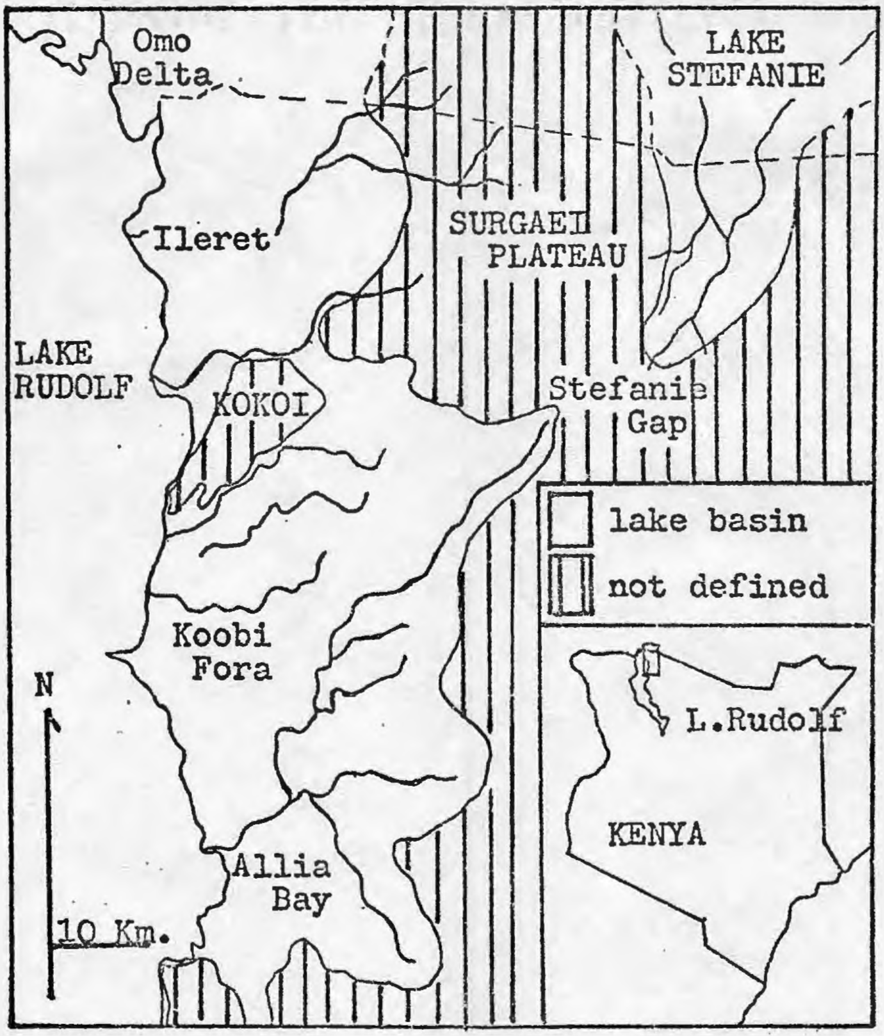
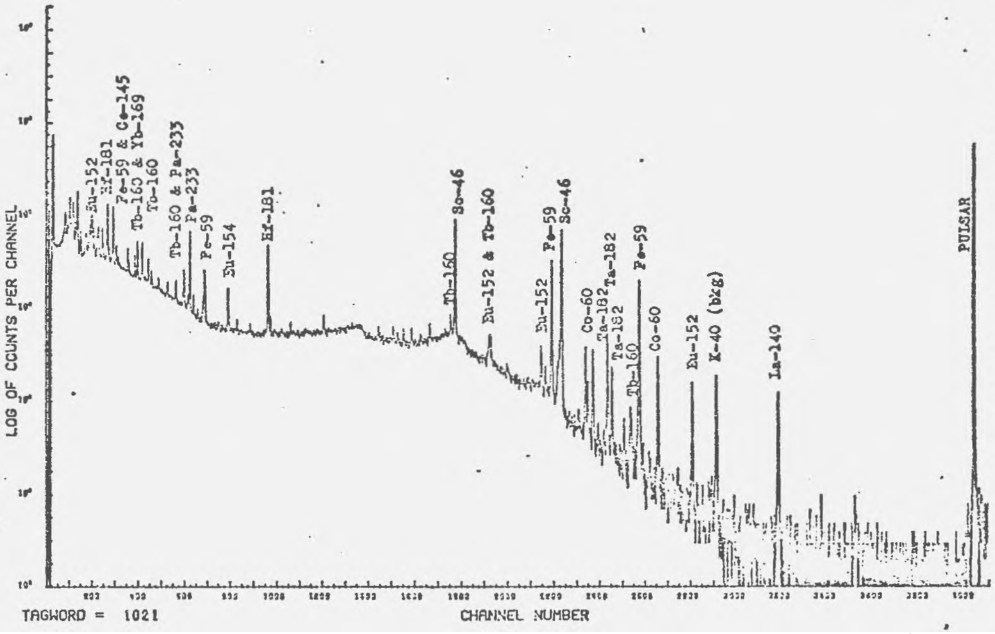


Fig. 1. Map detailing locations of major features mentioned in text.



Long Irradiation

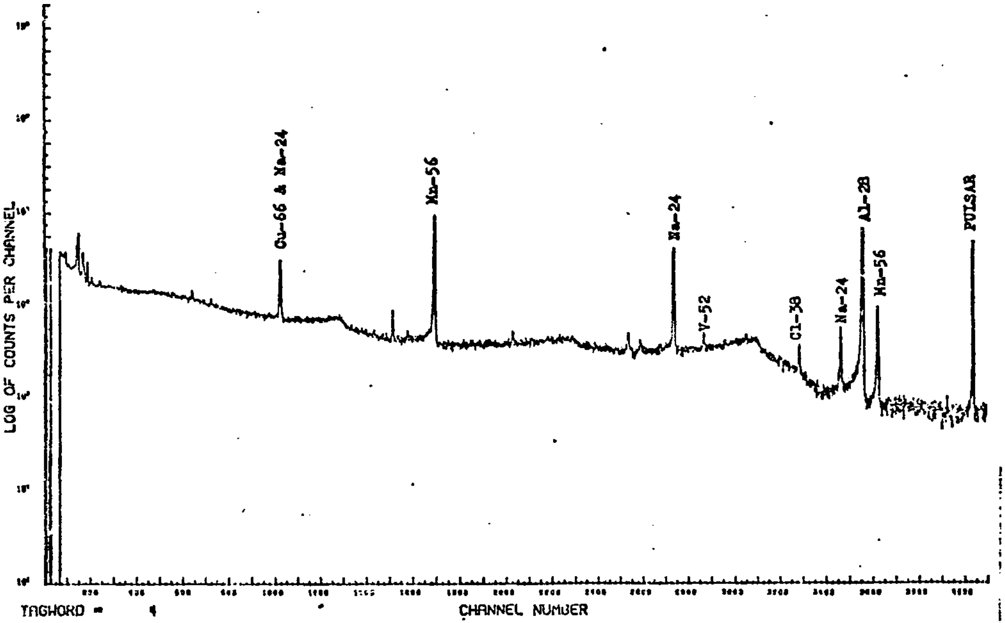


Fig. 2

Short Irradiation

E-SERIES

REB BED STRATUM

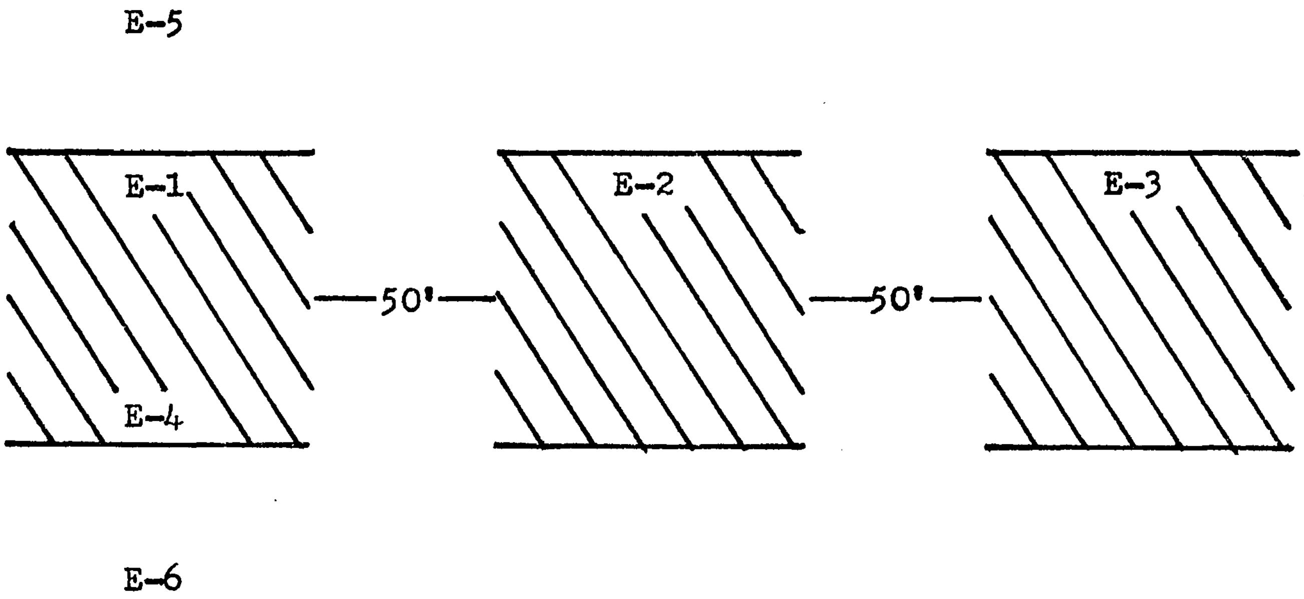


Fig. 3.

Table 1.

Irradiation Conditions

Type of Analysis	Irradiation Time	Decay Time	Measuring Time	Elements Determined
INAA	30 s	10 m	400 s	Na, Al, V, Mn
INAA	7 h	7, 15 d	4000 s	Sc, Cr, Fe, Co,
				Rb, Zr, La, Eu,
		30 d		Tb, Yb, Lu, Hf,
				Ta
AAS				Mg

Table 2.

E- Series Concentrations*

Element	E-1	±s	E-2	±s	E-3	±s	E-4	±s	E-5	±s	E-6	±s
Mg	540	11	557	11	587	12	1260	25	944	19	504	10
Na	4.8	0.6	5.6	0.7	4.1	0.5	3.9	0.5	3.1	0.4	5.1	0.6
Al	8.2	0.4	7.8	0.5	8.3	0.4	7.7	0.4	8.0	1.1	8.2	0.2
Sc	11.6	0.7	10.8	0.8	12.4	1.0	11.2	1.1	10.1	0.3	9.9	0.6
Cr	49.	4.	53.	5.	57.	5.	43.	4.	59.	5.	49.	4.
V	96.	6.	92.	11.	115.	14.	98.	6.	107.	21.	101.	6.
Mn	0.13	0.01	0.15	0.02	0.15	0.01	0.19	0.01	0.26	0.01	0.12	0.01
Fe	2.8	0.9	2.5	0.8	2.7	0.9	2.2	0.7	2.2	0.7	1.8	0.6
Co	28.2	2.5	24.4	2.2	27.6	2.7	23.0	1.9	23.3	1.9	19.0	1.5
Rb	55.	26.	47.	22.	58.	28.	39.	19.	69.	33.	47.	22.
Zr	2.0	0.6	---	---	2.6	0.5	2.0	0.5	2.9	0.9	2.6	0.5
La	38.	4.	34.	4.	35.	4.	26.	3.	25.	3.	23.	3.
Eu+	1.4	0.1	1.5	0.2	1.4	0.2	1.2	0.1	1.3	0.2	1.2	0.1

Table 2. E- Series Concentrations (cont.)

Element	E-1	±s	E-2	±s	E-3	±s	E-4	±s	E-5	±s	E-6	±s
Tb	1.5	0.2	1.5	0.1	1.5	0.2	1.3	0.1	1.1	0.2	1.3	0.1
Yb	2.8	0.3	4.0	0.4	3.5	0.3	2.5	0.3	2.6	0.3	3.2	0.3
Lu	0.52	0.02	0.47	0.02	0.55	0.02	0.50	0.02	0.45	0.02	0.45	0.01
Hf	9.8	0.2	10.3	0.8	11.8	0.8	8.2	0.8	10.2	0.5	8.4	0.5
Ta	2.5	0.3	2.1	0.4	2.7	0.2	1.8	0.4	1.8	0.2	1.6	0.2

* Ppm except for Na, Al, Mn, and Fe which are in percent.

+ Concentrations x10^{-3}.

Table 3.

Aluminum Ratios of E-Series Paleosols

Ratio	E-1	E-2	E-3	E-4	E-5	E-6
Mg / Al $\times 10^{-3}$	7.2	7.8	7.5	16.8	13.7	6.3
Mn / Al $\times 10^{-2}$	1.6	1.8	1.8	2.5	3.5	1.4
Fe / Al $\times 10^{-1}$	3.7	3.5	3.5	2.9	3.2	2.3
Co / Al $\times 10^{-4}$	3.4	3.0	3.2	2.8	3.1	2.2
La / Al $\times 10^{-4}$	4.6	4.4	4.2	3.4	3.1	2.8
Ta / Al $\times 10^{-5}$	1.7	1.9	1.7	1.6	1.6	1.5

Table 4.

Average Sand Clay Concentrations*

Element	Locality #1				Locality #2			
	Sand 1 (4-samples)		Clay 1 (4-samples)		Sand 2 (2-samples)		Clay 2 (2-samples)	
	value	±s	value	±s	value	±s	value	±s
Al	8.1	0.4	7.6	0.4	6.0	0.3	8.0	0.4
Sc	13.7	1.0	13.8	1.0	11.8	0.8	13.0	0.9
Cr	-	-	-	-	55.	6.	58.	6.
V	116.	9.	89.	7.	39.	3.	80.	6.
Mn	0.13	0.01	0.17	0.01	0.12	0.01	0.20	0.01
Fe	4.7	1.4	4.9	1.5	1.6	0.5	2.5	0.8
Co	35.	3.	32.	3.	18.	1.	25.	2.
La	55.	6.	63.	6.	46.	5.	46.	5.
Eu+	1.5	0.1	1.6	0.1	-	-	-	-
Tb	1.5	0.1	2.1	0.1	2.1	0.1	1.7	0.1
Yb	3.0	0.4	3.9	0.5	5.2	0.6	3.7	0.5
Lu	0.6	0.1	0.8	0.1	0.9	0.1	0.7	0.1
Hf	10.6	0.6	10.2	0.6	15.0	0.9	10.3	0.6
Ta	2.5	0.3	2.7	0.3	1.5	0.2	2.3	0.2

* Ppm except for Na, Al, Mn, and Fe which are in percent.

\+ Concentrations $x10^{-3}$.

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A PRELIMINARY INVESTIGATION OF THE ELEMENTAL COMPOSITION OF TUFFS FROM LAKE RUDOLF, KENYA

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ABSTRACT

Instrumental Neutron Activation Analysis (INAA) was used to measure the abundance of fourteen elements in volcanic tuff horizons from Lake Rudolf, Kenya. This rapid non-destructive analysis included determinations of Na, Al, Sc, V, Mn, Fe, Co, Zr, Eu, Tb, Yb, Lu, Hf, and Ta. In addition Mg and Mn were analyzed by Atomic Absorption Spectroscopy. Averages for elemental concentrations of the samples studied indicate a variation in composition. This variation may show differences in initial source vents, or differences in degree of weathering.

The East Rudolf Research Expedition, under the auspices of the National Museum of Kenya, which began in 1968 and includes investigators from a variety of disciplines, is currently engaged in an extensive investigation of the geological and paleontological history of the area east of Lake Rudolf in northwestern Kenya (figure 1). A variety of important fossil specimens have been discovered in this region. R.E.F. Leakey and M.D. Leakey (1-3) report the uncovering of several remains, including several complete crania, from both surface sites and in-situ locations of dated horizons. The discovery of these artefacts and other archeological finds in geological horizons, where a correlation can be confirmed, is of utmost significance. The extraordinary badland area, in which these remains are now being discovered, is offering a most challenging problem in correlation.

Structural characteristics of the lake have been associated with the tectonic relief of the East African Rift System by A.K. Behrensmeyer (4). More recent investigations by Vondra, Johnson, Bowen, and Behrensmeyer (5) have shown that the sedimentology consists of over 300 meters of fluvial deltaic and lacustrine sediments interspersed with lenses of both semi-continuous and discontinuous volcanic tuffs. These tuffaceous units currently serve as local stratagraphic markers. This sedimentary terrain is separated by the Kokoi Horst and Surgaei Plateau structures as shown in figure 1. In addition a degree of north-south faulting and east-west folding has occurred.

The tuffaceous lenses, as proposed by Findlater (6), are deposited from an aqueous medium (the lake). The initial source vents are believed to be outside the immediate lake vicinity with a re-deposition of these tuffs onto the lake bottom occurring as a result of stream erosion. Findlater (6) characterizes the basal deposits as exhibiting the highest degree of purity, with a very fine or fine grained texture, and ranging from bluish-grey to white in color. Bowen and Vondra (7) indicate the bulk of these tuffs to consist of glass shards incorporating a limited amount of sanadine, hornblende, biotite, quartz, and pumice fragments, with a considerable formation of secondary calcite in some areas.

The tuff facies have been separated into four general catagories based primarily upon the K/Ar dating of Fitch and Miller (8). They consist of the KBS tuff, the BBS or Koobi Fora tuff, the Tula Bor tuff, and the Karari or Chari tuff. The KBS seems to be the most continuous and recognizable and is indicated by Bainbridge (9) to be well preserved in a variety of environments. It was also one of the first to be dated by the Fitch and Miller group (8) at 2.6±0.26 m.y. This date was corroborated by the faunal succession determination of Maglio (10).

The sedimentary terrain of east Rudolf, as was stated, is separated by the Kokoi Horst and Surgaei Plateau structures and correlation between the two areas is a present difficulty. This study has dealt with the elemental analysis of a few of the volcanic tuffaceous sediments in the area of the expedition. It is the authors' opinion that with the knowledge of both the major and trace elemental compositions of the tuffs additional information can be gained concerning the geological correlation of them across the erosional gaps.

Elemental composition studies have proved helpful in similar studies of volcanic samples from the northwestern United States and Canada. Early chemical analysis of volcanic ash by Powers and Wilcox (11) indicated general differences between Mount Mazama ash and Glacier Peak ash. The use of neutron activation analysis (NAA) for cascade pyroclastics by Theisen, Borchardt, Harward and Schmitt (12) proved very promising in distinguishing pumice and volcanic ash soils from different sources. Additional investigations by Borchardt, Harward, and Schmitt (13), with NAA, were able to distinguish elemental differences between ashes from separate eruptions of St. Helens.

This study has incorporated the use of instrumental neutron activation analysis (INAA) for its analytical technique. A.A. Smales (14) indicated that INAA allows a high degree of sensitivity, gives freedom from reagent blanks, has a high degree of specificity, and removes the need for chemical operations. The successful use of the scintillation counting technique, by Brunfelt and Steine

(15) indicates some of the possibilities afforded to elemental abundance determinations by INAA to geological materials. Investigations by Gordon and co-workers (16) made measurements of twenty-three elements by non-destructive methods employing a Ge(Li) detection system. The increased resolution of the Ge(Li) crystals over the NaI detectors enabled Filby, Haller, and Shah (17) to determine thirty-two elements by both destructive and non-destructive techniques. In addition, several of the related studies already mentioned employed this technique. Consideration of the successes of INAA made it an obvious choice in this work.

Tuff samples were collected from selected sites in the area of the Karari escarpment. Nine samples were taken from a variety of facies and outcropings in the vicinity. Some of these outcrops are believed to be of different origin. Others have been designated in particular tuff unit groupings.

The samples were dislodged from their site with only the unexposed non-weathered pieces being selected. These were placed in polyethylene vials, which had been acid leached and washed in distilled deionized water in the laboratory. They were then individually placed in plastic bags and crated for transport.

Once in the laboratory, sample handling was kept to a minimum. Samples of fine grained glass fragments were selected and weighed into two dram polyethylene vials for irradiation. These vials were then heat sealed and a cobalt flux monitor was attached to each vial prepared for a long irradiation.

Standards consisted of two liquid monitor solutions. One was prepared for the elements of short half-life and the other for long half-life isotopes.

Irradiations were carried out in the Rhode Island Nuclear Science Center's 2 M.W. reactor at a neutron flux of $4x10^{12}n/cm^2 \cdot sec$. Two irradiations of each sample were done: the first for the short half-life isotopes of Na, Al, V, and Mn, the second for long half-life isotopes as indicated in table 1. In table 2, the isotopes measured and the peak energies used are shown for all the elements.

After irradiation, flux monitors were removed from the long irradiation samples. Sample containers were washed and spectra were obtained using the prescribed decay and counting times indicated in table 1.

Background activities and blank tests were run for induced activities in the polyethylene vials and in no case did the recorded activities interfere with the gamma-rays from the samples.

Measurements were accumulated on a 7% Ge(Li) detector with the use of a Nuclear Data 2200 4096 channel analyzer and a magnetic tape output. Flux monitors were counted by employing a NaI detection system. All the data was processed using an IBM-370/155 computer with the program PIDAC (18) to qualify and quantify the peaks.

Average results for the nine tuff samples analyzed are shown in table 3, along with values reported for volcanic ash from volcanic sites in the northwestern United States, and from Mount Suswa in southern Kenya. Lake Rudolf tuffs compare well with the values reported for Mount Mazama and Glacier Peak for the elements Na, Sc, Fe, Co, and Eu. They appear to be enriched in Tb, Hf, and Ta. Glass from Mount Suswa appears to be quite different than that from the tuff deposits. Mg, Fe, and Zr in the tuffs are very low in comparison. Na, Al, and Mn are also low but are only approximately one-half the concentrations reported for Mount Suswa.

In reviewing the errors associated with the nine samples average, it becomes apparent that these samples are not from compariable sources. Errors indicated in most cases are much higher than the counting statistics and higher than errors reported for the other works. It is believed that this may point to several sub-groupings of the tuffs into different units. If such a differentiation is to be accomplished a much larger number of well documented samples will have to be studied. Such and analysis with the use of a statistical method of comparison should enable a correlation of tuff layers and outcropings in the Lake Rudolf area.

CONCLUSIONS

1. Results show similar values to other INAA investigations on volcanic layers in the United States and Canada.

2. Standard deviations of the averages reported would indicate that there is a difference between the samples analyzed.

LIST OF FIGURES

LIST OF TABLES

1. Irradiation Conditions.
2. Nuclides and Photopeaks Observed.
3. Mean elemental composition of Lake Rudolf Tuffs compared to those of glassy fraction from other areas.

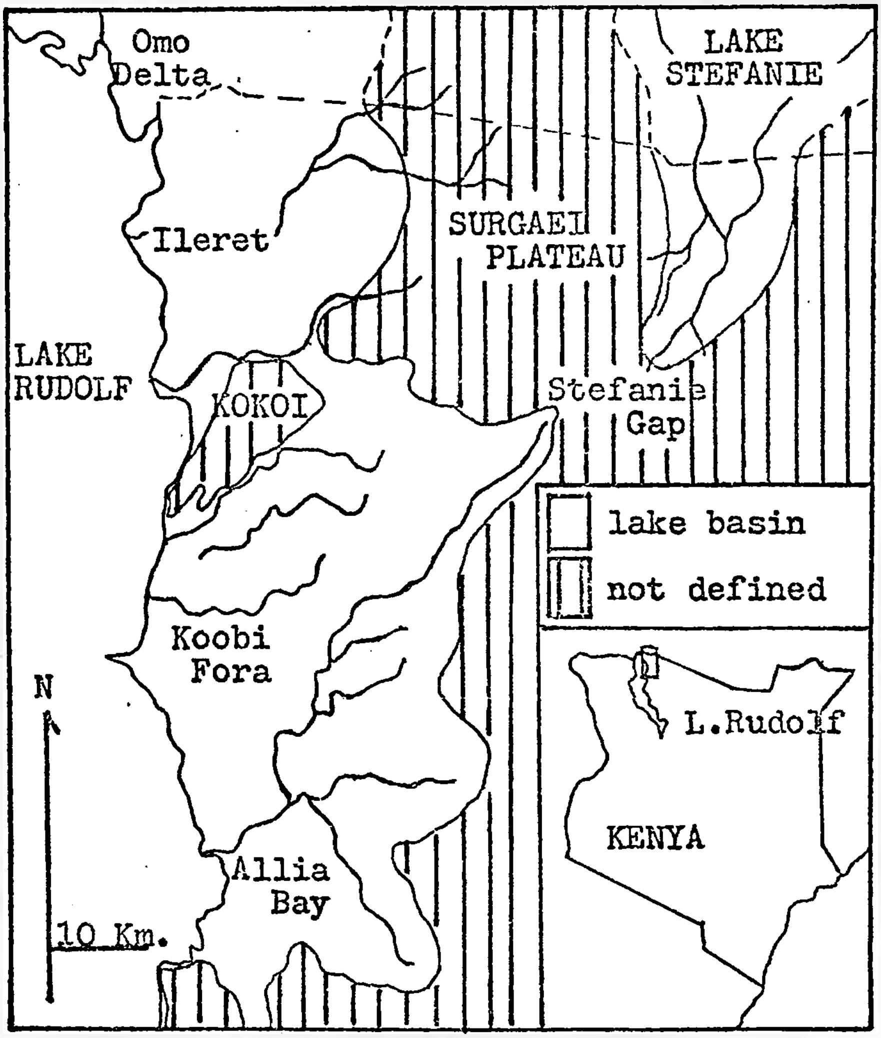
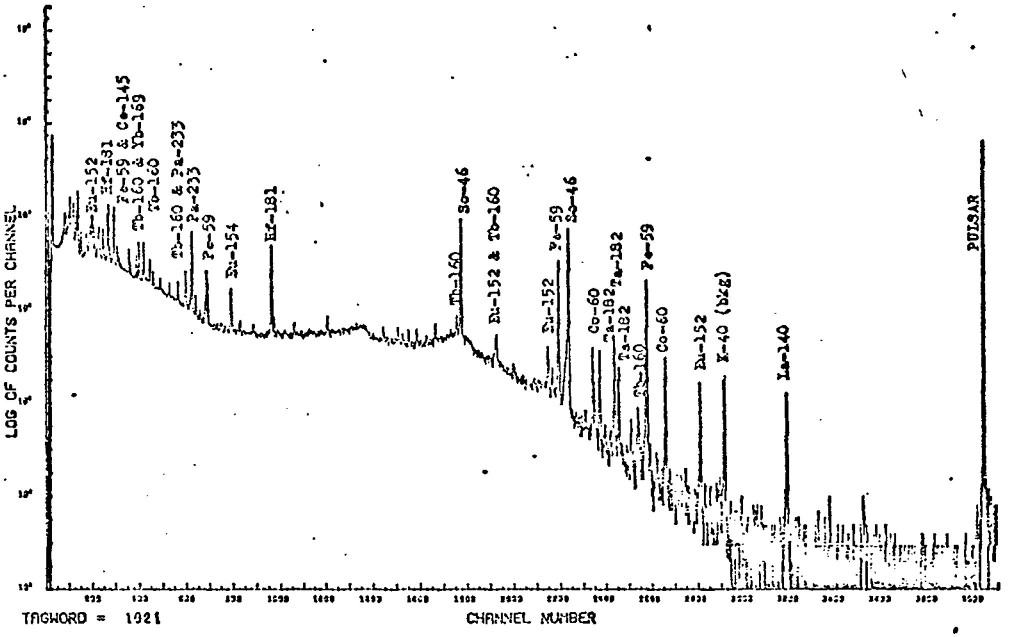


Fig. 1. Map detailing locations of major features mentioned in text.



Long Irradiation

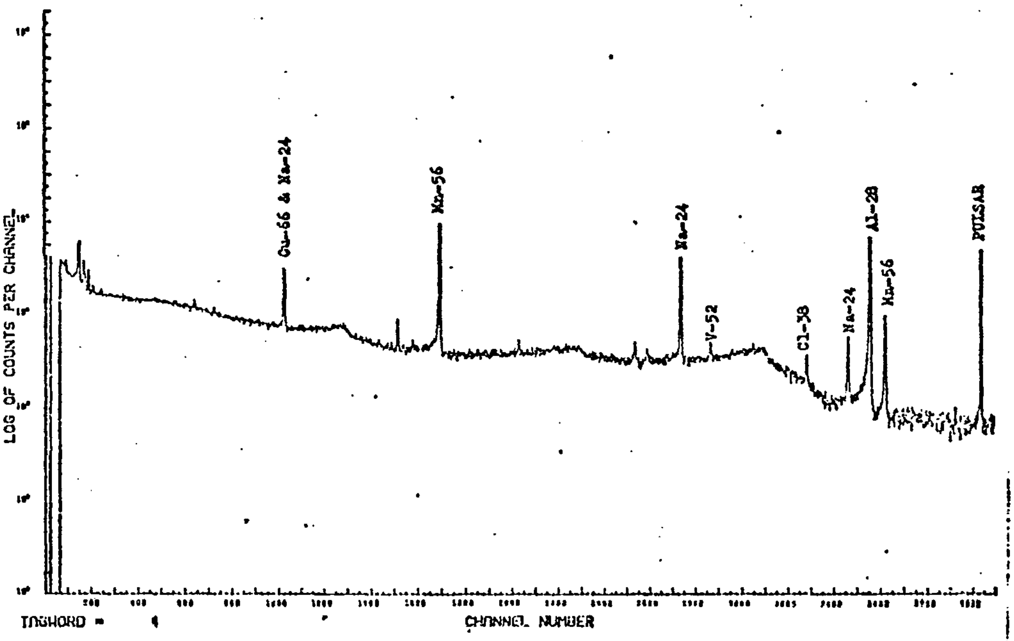


Fig.2

Short Irradiation

Table 1.

Irradiation Conditions

Type of Analysis	Irradiation Time	Decay Time	Measuring Time	Elements Determined
INAA	30 s	10 m	400 s	Na, Al, V, Mn
INAA	7 h	7, 15 d	4000 s	Sc, Fe, Co, Zr, Eu, Tb, Yb, Lu,
		30 d		Hf, Ta
AAS				Mg

Table 2.

Nuclides and Photopeaks Observed

Element	Product Nuclide	Half-Life	Photopeak(s) used in Determination (Kev)
Na	Na-24	15.0 h	1369,1732 (DE)
Al	Al-28	2.31m	1780
Sc	Sc-46	84.0 d	889, 1120
V	V-52	3.75m	1434
Mn	Mn-56	2.58h	847
Fe	Fe-59	45.0 d	1292
Co	Co-60	5.26y	1173, 1332
Zr	Zr-95	66.0 d	724
Eu	Eu-152	12.0 y	121, 248, 1408
Tb	Tb-160	72.0 d	298, 1311
Yb	Yb-175	4.2 d	285
Lu	Lu-177	160.0 d	208
Hf	Hf-181	42.5 d	134, 482
Ta	Ta-182	115.1 d	1221, 1231

Table 3.

Mean Elemental Composition of Lake Rudolf Tuffs Compared to Those of Glassy Fractions from Other Areas

Element	Lake Rudolf Tuff (9-samples)		Glass(19) Mount Suswa	Mount(13) Mazama C1 (4-samples)		Glacier(13) Peak (3-samples)	
	value*	±s	value*	value*	±s	value*	±s
Mg	0.03	0.02	0.36	-	-	-	-
Na	2.8	0.8	5.8	3.34	0.09	2.55	0.16
Al	6.1	1.2	9.3	-	-	-	-
Sc	3.4	1.3	-	6.6	0.5	3.7	1.1
V	25.	19.	-	-	-	-	-
Mn	0.12	0.04	0.23	-	-	-	-
Fe	0.63	0.17	6.2	1.51	0.11	1.17	0.3
Co	5.1	3.7	-	2.8	0.3	3.2	0.6
Zr	4.4	1.2	520.	-	-	-	-
Eu	1.5+	0.3	-	0.94	0.05	0.58	0.09
Tb	3.4	0.8	-	0.79	0.13	0.23	0.20
Yb	0.4 @		-	3.6	0.9	0.9	0.6
Lu	1.5 @		-	0.51	0.11	0.27	0.12
Hf	26.	7.	-	6.6	0.5	3.0	1.0
Ta	8.6	2.9	-	0.30	0.10	0.32	0.09

* Ppm except for Mg, Na, Al, Mn, and Fe which are in percent.

+ Concentrations x10^{-3}.

@ Indicates an upper limit for this value.

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APPENDIX I

INTRODUCTION AND REVIEW OF LITERATURE

INTRODUCTORY REMARKS

The objective of this study was to investigate the feasibility of using an elemental analysis as a stratagraphic correlation method in the Lake Rudolf Basin of Kenya, Africa. Several organizations are currently engaged in extensive archeological, paleontological, and geological studies of early man in this area. Selected plio-pleistocene samples include twenty-four sand and clay paleosol strata and an equivalent number of volcanic tuffaceous sediments. Analysis of both raw and prepared samples for as many as eighteen different elements was accomplished by employing Instrumental Neutron Activation Analysis (INAA) and Atomic Absorption Spectroscopy (AAS). It is believed that from the data accumulated, there are very definite indications that such a geochemical study will give a more conclusive correlation to the geology of the region.

Purpose of the Study

Prior to 1968 little was known about the area east of Lake Rudolf , with the primary source of information being an expedition in 1888 by Teleki and Von Hohnel. In 1935 another brief encounter with the terrain was made by Fuchs (V71). The National Museum of Kenya Expedition, which began in 1968, is headed by R.E.F. Leakey and includes investigators from a variety of disciplines. The Lake Rudolf Expedition has uncovered many important fossil specimens, including several hominid remains from the areas east of the lake. The hominid remains have been reviewed by Leakey (L70B, L71, L73). They are represented by well preserved crania and specimens found from both surface sites and in-situ locations in dated horizons. M. Leakey (L70) confirms the importance of the artefacts recovered in her study of a large series of fifty-one specimens from one site of the region. Additional studies of other vertebrate fossils from the Kubi Algi, Koobi Fora, and Ileret areas have been pursued by V. Maglio (M71) in his work on faunal remains. R. Leakey states the significance of the discovery of artefacts in geological horizons where correlations can by confirmed. Therefore, the discovery and analysis of fossiliferous remains and other archeological finds makes it desirous, if not imperative, that they can be catagorized as completely as possible. Elemental analysis of the sedimentary terrain incorporating these artefacts should aid in their characterization.

General Geology

The territory currently under study is bounded in the north by the Kenya-Ethiopian border and extends south approximately 100 kilometers. It is bounded in the west by Lake Rudolf and reaches eastward to the Surgaei Plateau some 50 kilometers. (figure 1)

Behrensmeyer (B70), in her preliminary investigations, reports the structural characteristics of Lake Rudolf to be closely associated with the tectonic relief of the East African Rift System and in particulary the Gregory Rift Valley. Additional investigations by Vondra and Bowen (V73) show that the sedimentology consists of over 300 meters of fluvial deltaic and lacustrine sediments distributed on late Miocene and Pliocene volcanics. These sediments receed gently toward the lake off the Surgaei Plateau in the east. This migration to the west during the Plio-Pleistocene eras is believed by Vondra and Bowen (V73) to record a general regression of the lake to its present shoreline. Except for occasional reversals due to faulting they report this pattern to be uninterupted. The faulting, as seen by Behrensmeyer (B70), exhibits no continuous major faults, but exists as several small series of parallel fractures one-half to three miles in length along a general north-south orientation line. A degree of folding also appears in an east-west direction perpendicular to the lake.

The Kokoi Horst, as can be seen from the map in figure 1, separates the northern Ileret area from the Koobi Fora and Alia Bay regions in the south. In the Ileret, recent studies by Vondra, Johnson, Bowen, and Behrensmeyer (V71) have shown the lower fifty meters to be interspersed with two tuffs, which currently serve as local stratigraphic markers. This area has yielded many of the hominid specimens collected so far. The upper unit of this sequence, in the north, is a lacustrine and fluvial-deltaic sediment labeled the Galana Boi unit. The same study describes the lower unit of the Koobi Fora as deep water to littoral lacustrine claystone, siltstone, and sandstone. These claystones and siltstones were gypsiferous with veins of selenite and satinspar. This area is also reported by Vondra, Johnson, Bowen, and Behrensmeyer (V71) to contain channel sandstones with some siltstones and mudstones marked discontiuously with tuff lenses. They also record a very large tuff deposit in the upper member of the Koobi Fora, approximately twelve meters in thickness. The top part of the Koobi Fora unit retains isolated sections of sediments which are believed to match the Galana Boi beds of Ileret, according to these co-investigators.

Lenses of tuff occur throughout the sedimentary sequence. These, as proposed by Findlater (F73) show definite deposition from an aqueous medium. They are believed to have two sources. Findlater (F73) suggests they could originate within the lake basin from primary airfall, and then have been reworked by flood waters locally, or he believes the most probable source is from initial deposition sites upstream and redeposition from stream erosion onto the lake bottom. The time lapse from eruption to final sedimentation is considered by Findlater (F73) to be at the most a few years. Whichever mechanism of deposition occurred, subsequent knowledge of the initial source vent location of the ash should allow more positive theories to arise.

Findlater (F73) characterizes the basal deposits as showing a high degree of purity. This seems to suggest that source areas may have seen heavily choked drainage if source vents were outside the lake basin. The basal portion is reported as having parallel laminations with very fine or fine grained texture, while upper portions are more massive and show ripple marks. Frank's (F73B) investigation of the Koobi Fora formation ranges the tuffs from a bluish-grey in the relatively pure state, to very pale orange in the reworked or slightly altered state. In their stratigraphic studies Vondra and Bowen (V73) report the bulk of tuffs to consist of glass shards incorporating a limited amount of sanadine, hornblende, biotite, quartz, and pumice fragments. They do state that in some cases a considerable amount of secondary calcite formation is found due to the alkaline lake environment.

The tuff facies have been separated into four general sections, based primarily upon K/Ar dating and their believed presence in both Ileret and Koobi Fora areas. These are depicted in figure 2. The KBS tuff seems to be the most continuous and recognizable in the field. Bainbridge (B11), in studies of the Koobi Fora tuff indicates it has been preserved in a variety of environments with similar lithologies, thicknesses, and field relationships. The KBS tuff was one of the first to be dated by Fitch and Miller (F70B) at 2.61±0.26 m.y.. This date was determined in reference to the in-situ specimens of sanadine located within it by R. Leakey (L70B). The BBS or Koobi Fora tuff is located above the KBS. Frank (F73B) describes this as being found in sporadic outcrops, which tend into reworked tuffs of grayish-orange tuffaceous silts. Such short lateral extent makes correlation of these outcrops as a single tuff sequence difficult. The Tula Bor tuff, which appears below the KBS, exhibits lenses of relatively pure glass shards, to ones of very arenaceous tuff according to Bainbridge (B73). Their color ranges from white, to light grey, to grayish-green with well sorted and fine grained particles. The Karari of Chari tuff is believed to be the youngest as dated by Fitch and Miller (F72), and appears above the Koobi Fora and BBS tuffs.

The sedimentology of this region consists of various pleistocene sedimentary units, ranging from coarse sands and pebble conglomerates to fine silts and clays in both fluvial and lacustrine environments. Incorporated into these sedimentary structures, at a variety of intervals, are volcanic tuffaceous sediments, which at the current time appear to form the best marker beds.

Problems of Comparison

As was mentioned the sedimentary terrain of the East Rudolf is separated by the Kokoi Horst-Surgaei Plateau structures (figure 1). There exists at present difficulty in the stratigraphic correlation between the two areas. Vondra and Bowen (V73) have stated that the existence of this horst makes a physical trace of individual beds of the Ileret member to those of the Koobi Fora area impossible. There Vondra, Johnson, Bowen, and Bainbridge (V71) observe no regional trends of faulting which would seem to aid in the transition from one area to the other. Findlater (F73) finds that field characteristics of the tuffs and sediments show no unique features, either in gross aspect or petrography. The grey diatomaceous siltstones which cap the Ileret and the Koobi Fora-Alia Bay areas, mentioned by Bowen and Vondra (V73), show similar lithology and position, but exact lateral relationships are not yet fully known. Outcrops have shown little relief, as they have been covered with additional sediments and are quite discontinuous. The sandstones and conglomerates observed by Frank (F73B) are channel deposits which tend to migrate, thus correlations based on these may transgress time. Therefore, the physical aspects of individual tuffs or paleosol horizons has limited use in correlating isolated outcrops to one another. Due to this considerable difficulty in interrelating the sedimentary beds, the fossil materials uncovered are still referred to locality sections of the region.

The difficulty in relating outcrops of tuff and other sediments does not end with the depositional environment, the degree of faulting and folding, and the extensive physical erosion of the region. The tuffs, which appear to show the most promise of correlation, may exhibit other major difficulties. Findlater (F73) relates the inhomogeneity of temperature in primary magma before eruption, which may cause inhomogeneity of trace element distribution in the tuff. Upon eruption the magma may incorporate wall rocks form the source vent or from the flow area. Fitch and Miller (F72) state that since the tuffs are not primary air-fall or ash-flow they are open to contamination by older volcanic rock and bed rock which may have been coincidentally eroded with them. In conjunction, they suggest that there may be several different leaves of tuff which relate to the same volcanic action due to river capture or degree of seasonal rainfall.

Other factors may effect both tuffs and paleosol units. Contemporaneous weathering during transportation and after deposition may occur in varying degrees. Post depositional leaching by groundwater can include devitrification of the volcanic glass and lead to isotope and element fractionation according to Findlater (F73). A major interference is from the lake itself. The sodium-rich waters cause highly alkaline ground-water , resulting in increased secondary calcite formation.

Correlation Methods

Several correlative techniques are in progress to definitely distinguish which horizons can be matched with each other. Faunal studies related by R. Leakey (L73) have shown that regions of the Ileret and Koobi Fora areas overlap to some extent. However, only a gross correlation can be obtained from this type of evidence. This is due to the limits of resolution which can not differentiate horizons which are closer that 250,000 years. Findlater (F73) also points out that fauna do not appear in all facies, such as the lacustrine lithofacies.

Radiometric K/Ar dating of the tuff horizons has been carried out by the group of Fitch and Miller (F72). This method has been established for some time and has given the best information to the tuff ages and relationships. Vondra and Bowen (V73) report the matching of the Chari and

Karari tuffs along the Karari escarpment on this basis. In addition they show a similar correlation by the use of total elemental oxygen isotope ratio analysis of the glass shards in this area. Fitch and Miller (F72) have dates on sections of the four major tuffs ranging from the Karari tuff at 1.34 m.y., to the KBS tuff at 2.61 m.y.. The majority of the reliable dates have been achieved through the analysis of pure sanadine crystals. The possibility of finding these type crystals in each outcrop is low and inhibits accurate dating.

The use of paleomagnetic reversal has shown an excellent relation to the dating method. The most secure correlation, given by Brock and Isaac (B74), has been in the area between the KBS and Tula Bor tuffs, with other matches still being tentative.

Instrumental Neutron Activaton Analysis (INAA)

Neutron Activation Analysis has become a useful tool in geochemical analysis and it has been chosen here to conduct an elemental analysis of selected sediments from the Lake Rudolf Expeditionary site. It is believed that additional correlation can be achieved through integration of this and the other methods now being used and tested. Using the knowledge of both the major and trace elementary compositions of the tuffs and paleosols more information can be gained concerning the geological setting of the area.

Applications of INAA in geochemistry has greatly increased. Thorenson (T64), in his analysis of soils and rocks with the use of a NaI detector, was able to show concentration differences for nine separate elements. The analysis of standard rocks by Brunfelt and Steine (B66) also indicated the successful use of scintillation detection. However, the poor resolution of this type of detector limits the number of elements that can be determined non-destructively.

With the use of Ge(Li) detection systems it has become possible to analyze for many more elements, both with non-destructive and destructive methods. Prussin, Harris, and Hollander (P65) were some of the first to indicate the importance and application of these detectors. Work by Randale and Goles (R70) reveals that these detectors allow an increased number of elements to be determined in geologic samples, and in many cases improves the accuracy of the abundance measurement. The principle advantage of the Ge(Li) crystals over the NaI scintillation detectors is their higher resolving power. Due to this higher resolution, a marked simplification of complex gamma-ray spectra can be achieved. In the non-destructive analysis for a large number of elements this type of detection is significant.

Several studies show the analysis of standard rocks, a variety of classified minerals, sediments, and rare earth element mixtures to be very successful using this technique. Filby, Haller, and Shah (F70) give methods for the determination of up to thirty-two elements using both destructive and non-destructive techniques. Gordon and co-workers (G68) made determinations of twenty-three elements by non-destructive analysis. Of forty-five elements determined by Morrison (M69B), ten were accomplished through non-destructive methods. INAA has shown good results when used by Cojocaru and Ispas (C70) on several rock standards.

The use of an elemental analysis in geological studies is imperative. In studies similar to ours it has complimented and augmented other geologic data. Routine instrumental determination of twenty-two elements, in rocks and sediment, is reported by Das and Zonderhuis (D70). While utilizing primarily non-destructive techniques, Buenafana (B73B) has studied basaltic type soils of Uruguay.

A rather extensive use of NAA, on samples from northwestern United States and Canada, to distinguish between ash falls from several volcanic sites, has proved useful in the classification of the ashes. Early chemical analysis of these layers of volcanic ash by Powers and Wilcox (O64) indicated general differences between those of Mount Mazama and Glacier Peak. The use of neutron activation for cascade range pyroclastics of these and other sources was investigated by Theisen, Borchardt, Harward, and Schmitt (T68). It was determined by this investigation that NAA was very promising in distinguishing pumice and volcanic ash soils from different sources. In 1867 a study by Westgate and Dreimanis (W67) with the use of refractive indexes, minerology, and chemical composition, volcanic ash deposits in Canada were distinguished. They reported sites of Mazama Ash and the possibility of St. Helens Y-Ash. An indication of the significance of ash layers as stratigraphic markers, especially when widely distributed, was made. Borchardt, Harward, and Schmitt (B71), in a more extensive study of volcanic ash deposits determined INAA to be valuable in the detection of significant differences in elemental content of volcanic ash layers of the Pacific Northwest. They report that elemental abundances in glassy separates of unweathered ash were independent of the distance from the source. Not only were differences between ashes from several sources indicated, but variations in elemental content were observed for three separate eruptions of St. Helens; labeled as St. Helens-Y, -W, and -T.

Elemental abundance measurements have also been employed successfully on other Kenyan sites. Nash, Carmichael, and Johnson (N69), in studies of Mount Suswa in southern Kenya, differentiated between lavas of four distinct episodes on the basis of minerology and chemical composition. Relationships between elements of the Paka volcano have been reported by Sceal and Weaver (S71).

Of the analytical methods available for elemental measurements in geological materials, INAA has been one of the most sensitive and reliable. INAA both improves the time of analysis and the accuracy of determination of trace components of samples. It allows a high degree of sensitivity, gives freedom from reagent blanks, has a high degree of specificity , and removes the need for chemical operations on microgram quantities of samples, as related by A.A. Smales (S31).

Atomic Absorption Spectrophotometry

Atomic absorption spectroscopy (AAS) seems to offer the next most accurate and flexible tool in the elemental analysis of geochemical materials. A lithium metaborate fusion (LiBO) method has been used successfully in the analysis of thirteen elements by Medlin (M69). Applications or adaptations of this method are shown in the work done by Yule (Y69). A less complex method was developed by Langmyhr and Paus (L68, L68B, L69, L69B) , using hydrofluoric acid decompostion solution. This has proved applicable to all types of rocks for a variety of elements. Feldspars have been analyzed for Al, Fe, Mg, Ca, Na, K, Mn, and Ti by these investigators. Several types of silica materials, such as glasses, quartzite, sandstones, and sand, have also yielded to this technique quite readily, Analysis of reference rock samples have shown good agreement to other methods. Due to the relative ease and scope of the HF method, it proves to be a good comparison and complimentary method to INAA.

Summary

A definite correlation between the sediments of East Rudolf is not yet confirmed, particularly between the deposits of the Koobi Fora and Ileret areas. The best attempt at correlation to date has been accomplished with the K/Ar dating procedures on sanadine crystals in the tuffs examined by Fitch and Miller (F72). Even with these relationships, a more conclusive comparison of volcanics to sediments to fossil remains needs to be clarified. Hopefully a complete geochemical picture will come from an integration of K/Ar dating, oxygen-isotope analysis, paleomagnetic reversal chronology, and elemental analysis. The elemental abundances of as large a number of elements as possible in the same sample is necessary to establish a coherent picture. The elements should represent a large number of geochemical classes, and they should differ in their response to external forces. A presence in trace amounts will tend to maximize the effect of their response to such stimuli. INAA will allow the simultaneous measurement of a great number of elements. This method will allow both major and trace elements to be determined. The sensitivity and specificity of the technique will allow significant differences to be seen. In addition, the use of AAS will allow a complimentary and comparison method of analysis to insure accuracy. It is believed that this type of study will serve as an integral part in the correlation of the stratigraphy of the Lake Rudolf Expeditionary site.

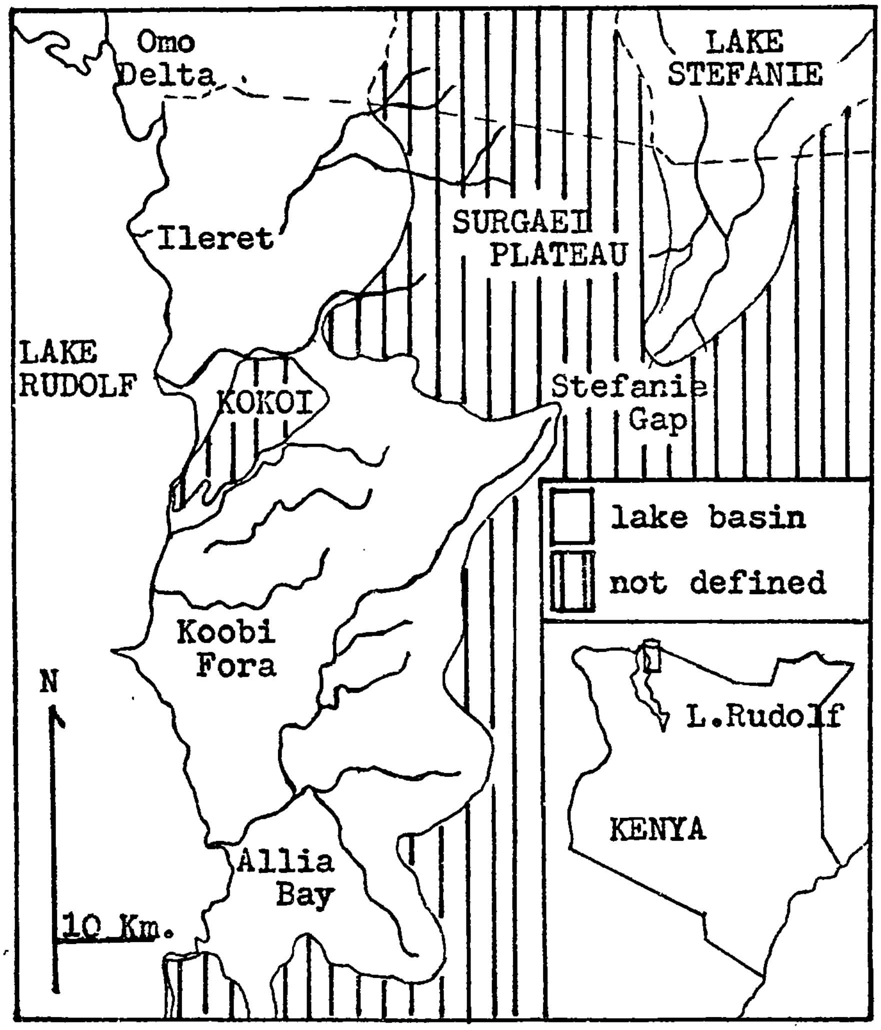
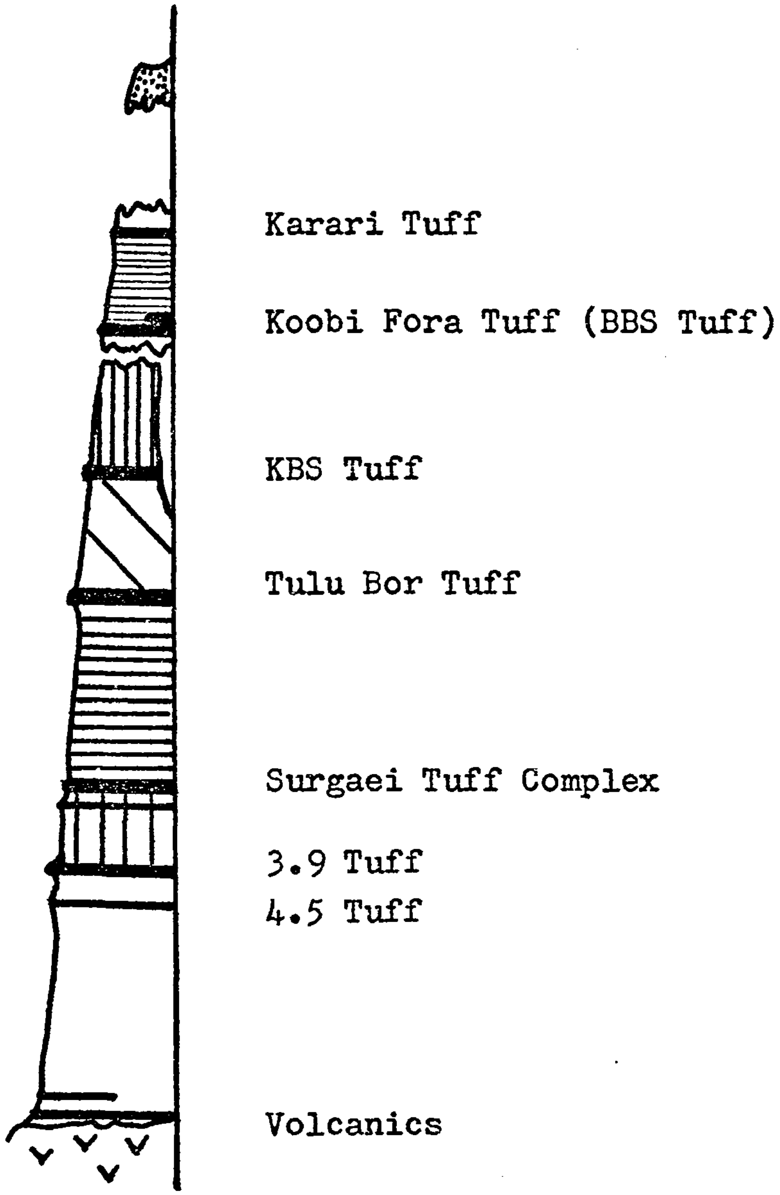


Fig. 1. Map detailing locations of major features mentioned in text.

Generalized Section Showing Tuff Horizons (9)



Total section approximately 300 meters thick.

Fig. 2.

APPENDIX II

EXPERIMENTAL APPARATUS, PROCEDURES AND DATA TREATMENT

Apparatus

The apparatus used in this investigation consisted primarily of the neutron-irradiation and gamma-ray counting equipment of the Rhode Island Nuclear Science Center. The neutron source was a 2 M.W. swimming pool reactor and samples were irradiated in a thermal neutron flux of $4x10^{12} n/cm^2 \bullet sec$. The samples were inserted and retrieved from a location near the core with the use of the pneumatic irradiation tube system available.

Samples were then counted with an Ortec 30 cm^3 Ge(Li) coaxial detector connected to a Nuclear Data Model 2200 4096 channel analyzer which was equipped with a computer compatible magnetic tape output. In conjunction with this detection system a similar Ortec Ge(Li) detector connected to a PDP 11/40 computer 4096 channel analyzer with a DEC disc storage and a computer compatible magnetic tape output was used.

The data, compiled on magnetic tape from the counting systems, was then processed on an IBM 370/155 computer by means of the University of Rhode Island PIDAQ Program (M72).

Elemental concentrations of a few elements were also determined by Atomic Absorption Spectroscopy (AAS). This was accomplished with the use of a Perkin Elmer Model 360 Atomic Absorption Spectrophotometer. Normal flame attachments and gases were employed in these evaluations.

This analysis was used to corroborate and augment results obtained from the INAA determinations.

The method of sample separation used in this study consisted of a polyethylene sieve apparatus. This was constructed from different polyethylene mesh sizes connected in series by polyethylene holders. The construction of this apparatus was preferable to the use of the conventional brass or stainless steel apparati used in standard geological sieving, because of trace element contamination problems.

Procedures

The primary concern in the preparation and analysis of the samples was to reduce handling and avoid contamination. Samples for both the long and the short irradiations were handled in the same manner. Samples were taken in the field by excavating the weathered face of the deposit. Thus exposing relatively undisturbed material below. Then a portion of this unexposed sediment was either scooped into or selected fragments were placed in a pretreated labeled polyethylene vial which was immediately placed in a zip-lock plastic bag. These were then crated for transport to the laboratory. The polyethylene vials had been previously acid leached with 12N HNO_3 and washed with distilled deionized water.

Once in the laboratory sample preparation was kept to a minimum. The strata, which were primarily clumps of particles, were agitated in the sampling vials until a majority of the sample was of small particle size.

Bulk analysis was accomplished by weighing out two fractions of the samll particles into two dram polyethylene vials. The first weight taken was a 50 mg sample to be used in the short irradiation. The long irradiation sample consisted of a 100 mg sample. The vials were then heat sealed to avoid opening of the container during irradiation. Long irradiation samples were also equipped with a Co flux wire, which was heat sealed to the exterior of each vial. Irradiation and counting times of the samples are shown in table 1, and the decay intervals and peak energies employed are shown in table 2. Post-irradiation procedures were reduced to washing the exterior of each vial with acid and distilled deionized water.

Standards used in this experiment were prepared from primary Dilute-It standards and oxide forms. The standard for the short irradiation consisted of appropriate concentrations of Na, Al, Mn, and V in order to obtain a similar dead time to that of the samples. A long irradiation standard was prepared in a similar manner for all the elements being determined.

Two separation techniques were attempted to evaluate the possibilities of analysis improvement. The first employed the use of a tilted shaker board. This apparatus was constructed from polyethylene materials and heat sealed together. Although it was initially believed this may provide an effective means of separation, the very small particle size and the friction of the polyethylene surface proved to be unacceptable. The method of separation selected made use of a similarily total polyethylene composition. It consisted of a number of polyethylene sieve mesh sizes placed in series with screw closures taken from the tops of wide mouth polyethylene bottles. This apparatus, shown in figure 1, provided discrete size fractionalization of the particles and in addition was acid washable between each sample separation. It is believed that this separation procedure gave us the quickest and most effective separation. Samplings and analysis of the fractions followed that of the bulk sample analysis.

AAS analysis was accomplished after a digestion of a 500 mg portion of the sample. The digestion procedure is outlined in figure 2. The sample was digested in 70 ml. of hydrofluoric acid and nitric acid solution, which consisted of 75% hydrofluoric acid and 25% nitric acid. This solution was heated for twenty-four hours and then taken to dryness. After being reconstituted in 10 ml. of boric acid, and 10 ml. of HNO_3, the solution was transferred and diluted to 100 ml. total volume. The solutions were then stored in polyethylene bottles and kept frozen till analysis. Standard instrumental procedures of the AAS unit were followed as indicated in the conditions manual of

Perkin-Elmer Corporation.

All samples analyzed were carried through the INAA procedures for bulk samples. Approximately half of these were then analyzed through the AAS procedure. Portions of the samples were then separated and the fractions were analyzed by INAA.

Data Treatment

Neutron Activtion Analysis was used to determine the compositions of elements in the samples. The ease of simultaneous determinations of both major and trace components made this technique convenient. The quantity of a particular element is related to its activity by equation (1):

$$(1)\quad A(o) = N\phi\sigma\,(1-e^{-\lambda t})$$

where:

N = number of atoms of the stable isotope

ϕ = thermal neutron flux (2×10^{12} n/cm^2•sec)

σ = thermal neutron capture cross-section

λ = $0.693/t_{1/2}$ ($t_{1/2}$ the half-life of the isotope produced)

t = the duration of the irradiation in the same units as $t_{1/2}$

$A(o)$ = the initial activity at the end of the irradiation.

The gamma-ray activity, A(t), of an isotope counted at time (t) after irradiation may be determined by equation (2):

$$(2)\quad A(t) = A(o)\, e^{-\lambda t}$$

therefore it follows:

$$A(o) = A(t) / e^{-\lambda t}$$

the gamma-ray activity of the standard, A(t)s, and the sample, A(t)x, are counted and corrected for their respective decay times by means of equation (3), producing A(o)s and A(o)x, the activities of standard and sample at the end of irradiation. Substitution into equation (1) gives:

$$(4)\quad A(o)s = N(s)\, \phi(s)\, \sigma(s)\, (1-e^{-\lambda_s t_s}) \quad \text{and}$$

$$(5)\quad A(o)x = N(x)\, \phi(x)\, \sigma(x)\, (1-e^{-\lambda_x t_x})$$

Since only one irradiation was used, it follows that:

$$\phi_s = \phi_x$$

$$t_s = t_x$$

Since the same isotope is measured in the standard and the sample it follows that:

$$\lambda_s = \lambda_x$$

$$\sigma_s = \sigma_x$$

Division of (4) by (5) and substitution of equalities yields:

$$(6)\quad A(o)s \;/\; A(o)x = Ns \;/\; Ns \qquad \text{or}$$

$$(7)\quad Nx = [\; Ns\ A(o)x \;] \;/\; A(o)s$$

The concentration of the isotope in the sample may be readily determined from equation (7), where Ns is the known number of atoms. A(o)s and A(o)x are calculated from the gamma activities of the standard and sample, $A(t)_s$ and $A(t)_x$, respectively.

This derivation assumes that the standard and the sample have identical geometric characteristics. Effects caused by geometric differences are minimized when the activity of a sample is increased and the distance from the detector is also increased during counting.

POLYETHYLENE SIEVE APPARATUS

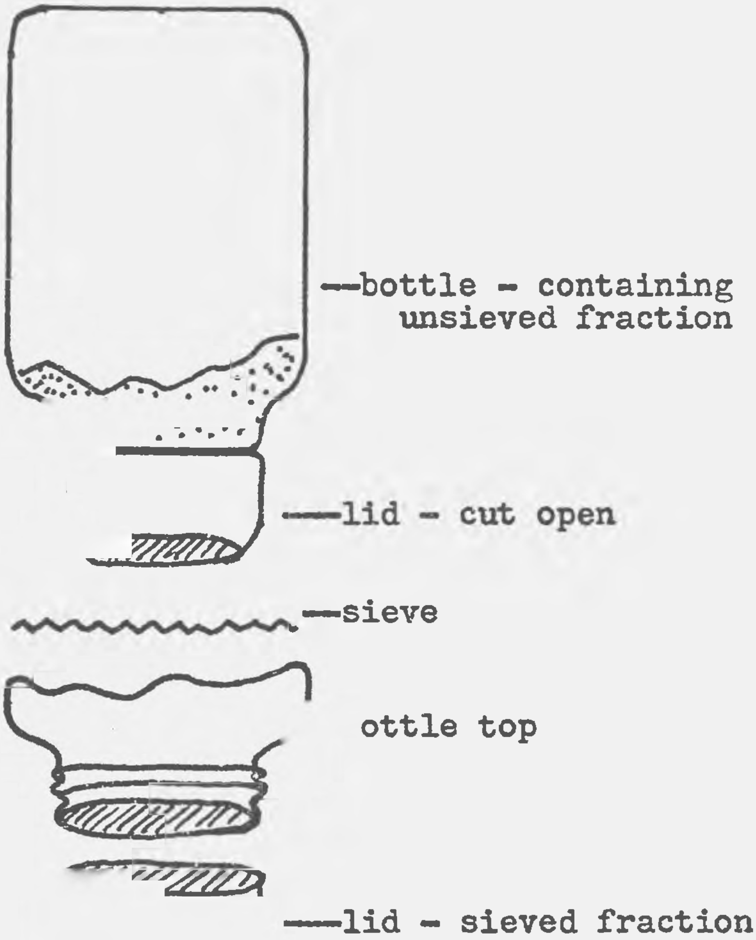


Fig. 1.

Atomic Absorption Digestion Procedure

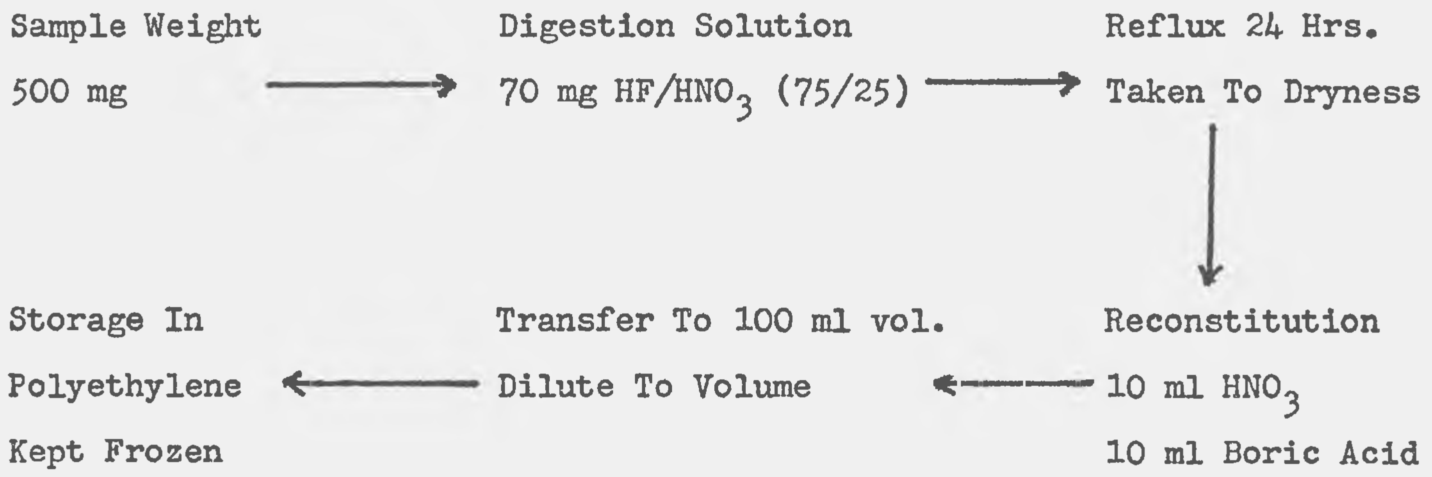


Fig. 2.

Table 1.

Irradiation Conditions

Type of Analysis	Irradiation Time	Decay Time	Measuring Time	Elements Determined
INAA	30 s	10 m	400 s	Na, Al, V, Mn
INAA	7 h	7, 15 d	4000 s	Sc, Cr, Fe, Co, Zn, Rb, Zr, La,
		30 d		Tb, Eu, Yb, Lu, Hf, Ta
AAS				Mg, Mn

Table 2.

Nuclides and Photopeaks Observed

Element	Product Nuclide	Half-Life	Photopeak(s) used in Determination (Kev)
Na	Na-24	15.0 h	1369,1732 (DE)
Al	Al-28	2.31m	1780
Sc	Sc-46	84.0 d	889, 1120
Cr	Cr-51	27.8 d	320
V	V-52	3.75m	1434
Mn	Mn-56	2.58h	847
Fe	Fe-59	45.0 d	1292
Co	Co-60	5.26y	1173, 1332
Zn	Zn-69m	13.8 h	439
Rb	Rb-86	18.7 d	1078
Zr	Zr-95	66.0 d	724
La	La-140	40.2 h	328, 1597
Eu	Eu-152	12.0 y	121, 248, 1408
Tb	Tb-160	72.0 d	298, 1311
Yb	Yb-175	4.2 d	285
Lu	Lu-177	160.0 d	208
Hf	Hf-181	42.5 d	134, 482
Ta	Ta-182	115.1 d	1221, 1231

APPENDIX III

ADDITIONAL DATA DISCUSSION

The data in tables 1 and 2 indicates results of initial tuff analysis. This comparison of two tuff samples shows the reproducibility of the technique, and helps to predict the possible use of this type of analysis for correlation of the tuff layers.

The two samples were selected from large chunks of material collected by P. Abell during the 1971 field season. Sections were selected with approximately 50 grams of each being taken. Each was observed under a microscope and ascertained to be 90-95% volcanic glass fragments containing very little visible feldspar. Triplicate samples of each were taken and analyzed, as has been stated.

There is a considerable difference in abundances between the two samples. Tuff 7 may be considered a more mafic type rock and tuff 10 a more felsic rock. Tuff 10 has a higher Na concentration at 6.0% in comparison to 4.6% for tuff 7. Al was not determined for tuff 7, however, the values obtained for Al on tuff 10 compare favorably to the world averages for felsic rocks quoted by Krauskopf (K67).

The elements Cr, V, and Co all tend to confirm the hypothesis that tuff 7 is more mafic. These elements are all lower in concentration in tuff 10. Mn breaks this trend by increasing from tuff 7 to tuff 10 values. Sc, Zr, La, Eu, Yb, and Lu are of comparible levels in the two samples, while Hf and Ta decrease from tuff 7 to tuff 10.

This initial analysis shows similarities of some elements and differences for others. In most cases the data indicates a reproducibility of analysis within the sample. Tuff 7 was the most homogeneous showing a high of 10% error in the three Zr analyses, and a low of 1% for the Ta concentrations. Tuff 10 followed with a range of 10% to 1% deviation in values, although three higher deviations were recorded for Zr, Cr, and Eu, which can not be directly accounted for.

Homogeneity of samples is obtainable, provided a high degree of glass fragments are contained in the sample. Reproducibility with this technique can be obtained, generally to within ± 10% for the elements analyzed .
A further major conclusion of this initial work shows that a reasonable relationship for the data can be hypothesized.

Blank data, for empty polyethylene vials, handled in the same manner as the samples, is shown in table 3. All values stated are upper limits for the elements in question. It is clear from this data that the containers contributed no significant activity to the isotopes being analyzed.

It was of interest to determine the reproducibility of samples taken in the field. Duplicate field samples of each tuff were collected. Table 4 shows the Mn/Al ratios and V/Al ratios obtained for seven of these sample pairs. In all cases, except possibly for the V/Al ratios of F and Y tuffs, the data indicates a good agreement between duplicates, Differences between samples may also be evident especially for the Mn/Al ratio where tuffs E, F, D, Z, and FD are very similar. Tuff DD is half this amount, and tuff Y appears to have twice the concentration. It is difficult to see a similar type correlation from the V/Al ratio. This data indicates a degree of homogeneity in the samples taken, at least for their Mn, V, and Al content.

The results of our INAA analysis were cross-checked with the use of another method. AAS was chosen. Due to blank difficulties, occurring from reagents, only Mg and Mn analyses were obtained. The comparison data for the Mn analysis is shown in table 5. Of the samples analyzed all but four agree. AAS analysis of E-5 and E-6 are twice as high as values obtained by INAA. This would seem to indicate a contamination of these samples during digestion, or a geometry effect during INAA. The two discrepencies in the tuff analysis are lower for AAS. Again this may be due to a geometry effect, or it might occur if digestion were incomplete. Geometry effects are believed to be small in consideration of the high activity of samples and distance from detector during INAA. Thus it is believed that the AAS errors may account for the discrepancies. Comparison of the two methods is good, and data for Mn accumulated from either method is believed acceptable.

Bulk Sample Analyses

The elemental concentration data for four series of sand-clay strata are given in tables 6-9. Their corross-section relationships are shown in figures 1 and 2, and geographic localities are mapped in figure 3. The C and G series samples pertain to the sand and clay averages of location 1, in table 4, of paper I, reported earlier. Location 2 sand and clay averages are those of samples F-1 and F-3, and F-2 and F-4, respectively.

From our analysis the layers of locality 1 show good agreement in their composition. Manganese is one of the most variable elements, and may indicate a grouping of the sand layers at 1200 ppm.. The Mn content of clay strata is more variable, but of higher concentration. Other elements such as Co, Eu, and Tb show a good correlation between sand layers C-1, C-3, G-1, G-3, and H-1. Similarities may also be observed in the compositions of clays C-2 and G-2, and C-4 with G-4.

The F-series paleosol unit was more random in composition and proved to indicate no correlation even in the weakest sense. As was state previously, this series did show a locality relationship when compared to the other paleosol data.

The elemental concentrations for the nine tuffs, averaged in table 3 of manuscript 2, are given in table 10. Al-ratios of these samples are reported in table 11, along with the stratagraphical unit from which they came. These units are depicted in figure 2, of Appendix I , and their geographic al localities are mapped in figures 3 and 4.

From the Al-ratios of these tuffs it is difficult to determine any definite correlation of them, while they remain in the framework of the indicated groupings.

It may be possible to establish an order in degree of weathering for the samples. Tuff E-1 seems to be the least weathered. Its Al-ratios are considerably higher for many of the elements versus those of the other samples. DD-3 is the other outstanding sample because its ratios are very low. The remaining samples group in between these two. Y-5 gives a high Mn/Al value along with high Al-ratios for Tb, Zr, Fe, Ta, and Sc. This would indicate it to be the next least weathered sample following E-1. The individual concentrations in table 10, indicate the same high relationship of E-1 and Y-5, along with the low concentration exhibited by sample DD-3.

Size Fraction Determinations

It was of interest to determine if a particle size separation would enable a more conclusive representation of the data. Several samples were taken and separated in the sieve apparatus described earlier. Data for the E-series paleosol samples are shown in table 12, and their Al-ratios are given in table 13. The V and Mn ratios to Al, indicate the original hypothesis that E-1, E-2, and E-3 correlate well. E-4 and E-5 are considerably different from E's 1-3, E-6 is slightly lower. Each size fraction indicates this same corelation. It appears that there is an enrichment of the V and Mn in the smallest fraction in relation to the others. This small fraction gives a more pronounced difference in ratios for Mn. The V/Al ratios of this fraction show equivalent values for E-3 and E-4, but continue to report a difference between them and E-5. The V concentration and its Al ratio, determined for E-6, is substantially increased and reveals an increased difference from the others in the 88 micron fraction. This data gives a good arguement for size separation, in that these short analyses appear more consistant, and indicate a larger difference between these different stratigraphic units.

Size fractionalization of several tuffs was also accomplished, and the data is presented in tables 14 and 15. These concentrations and ratios would indicate a slightly different relationship than bulk analysis. Sample Y-5 is consistantly the highest in elemental ratios to Al. Tuffs DD-1 and 7 follow behind this sample. Again sample DD-3 is the lowest in concentrations and ratios. Samples Z-3, E-1, and F-1 fall in between Y-5 values and DD-3 values. This may start to indicate a degree of comparison to the existing units indicated. The most recent tuffs should be the closest to primary magma, and thus have in general, the highest values for the mobile type elements. Tula Bor, which is represented as the oldest tuff, is the most depleted in composition, as would be expected for an older, more weathered unit.

C–G–H–SERIES Paleosol Layers

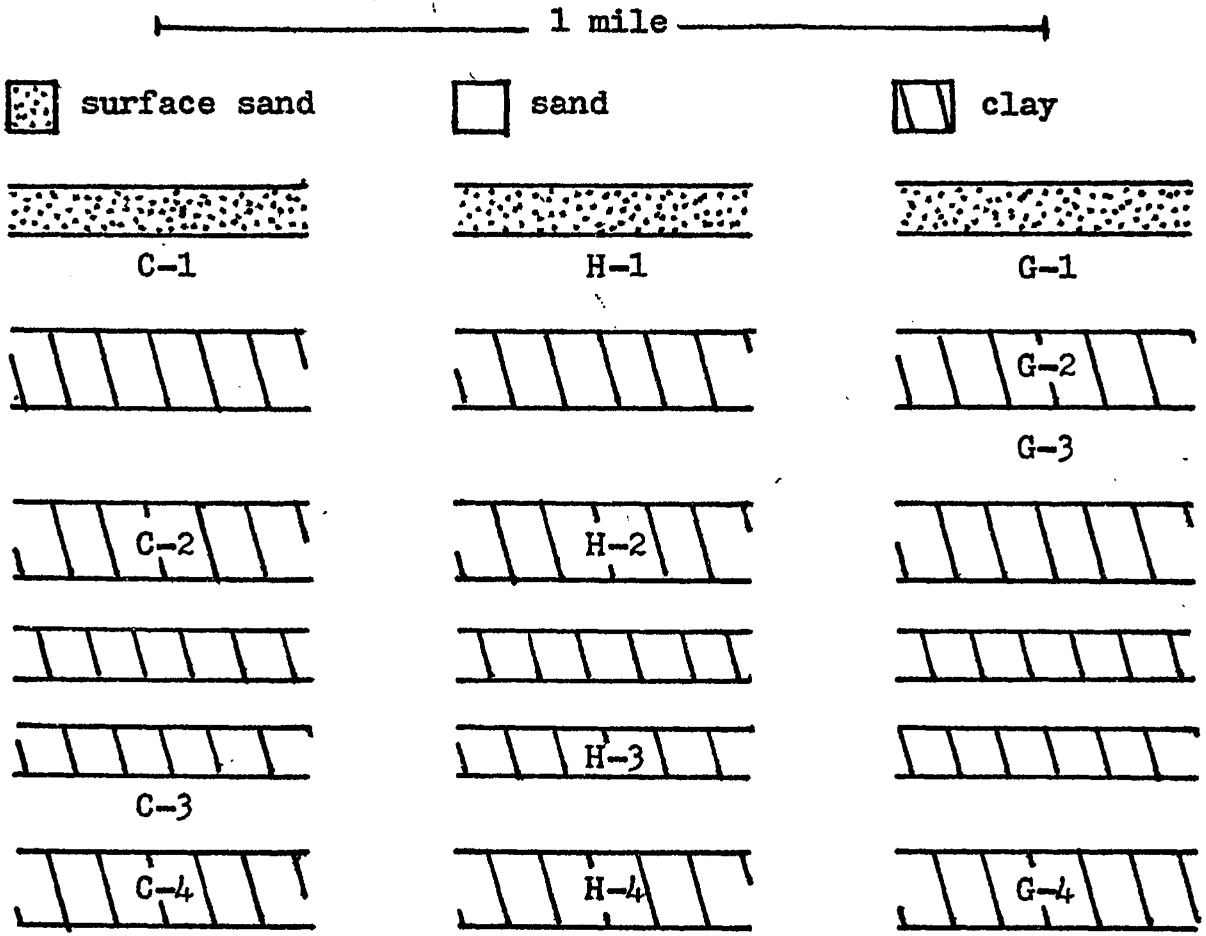


Fig. 1.

F-SERIES

Paleosol Layers

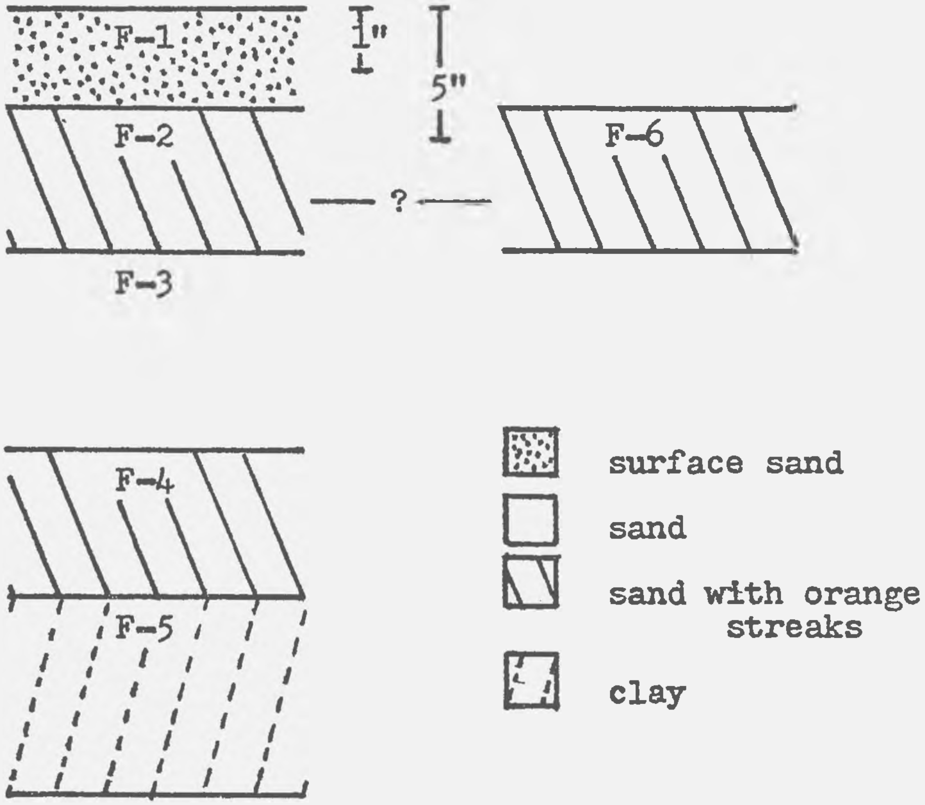


Fig. 2.

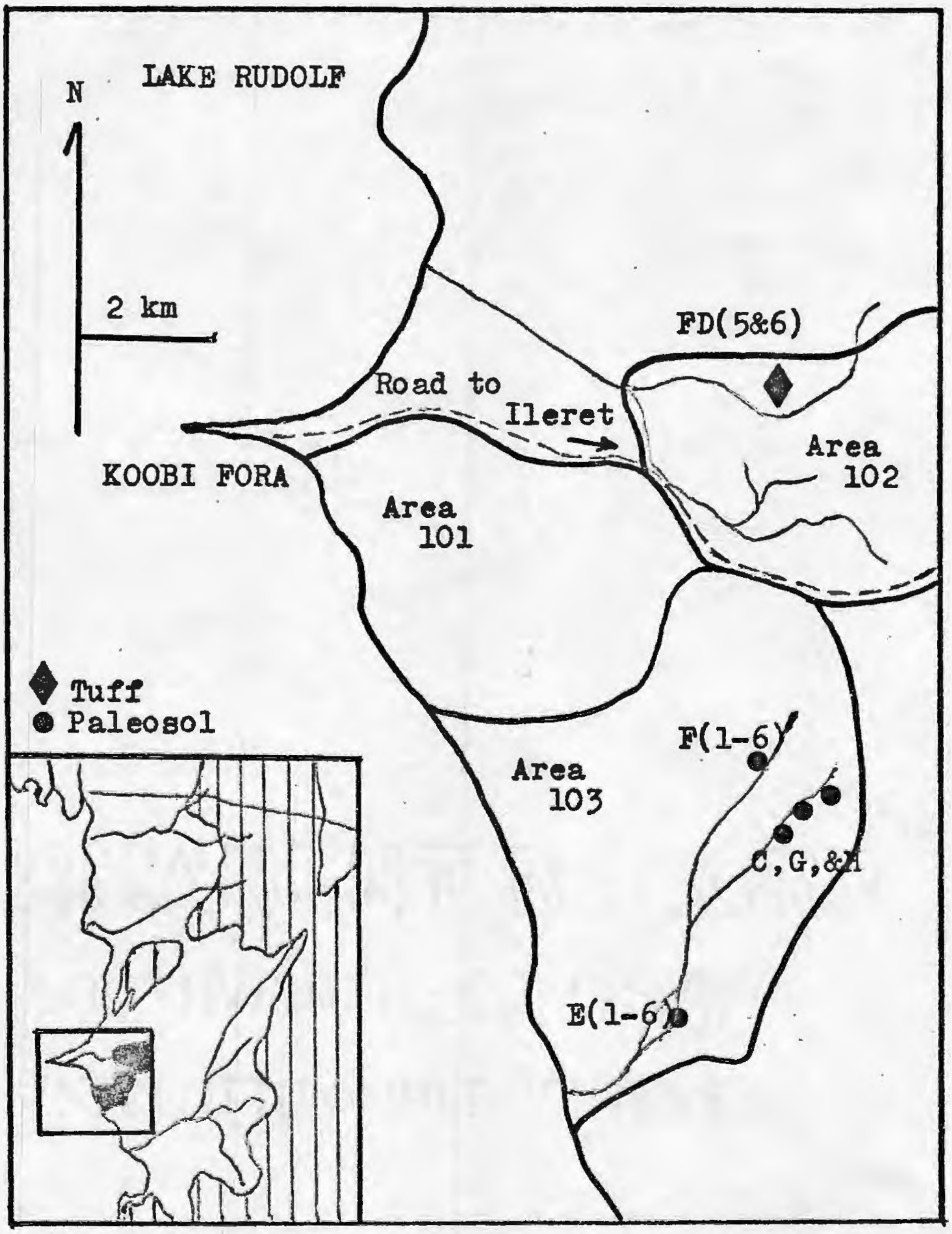


Fig3 General Sample Locations in Areas 101, 102, and 103.

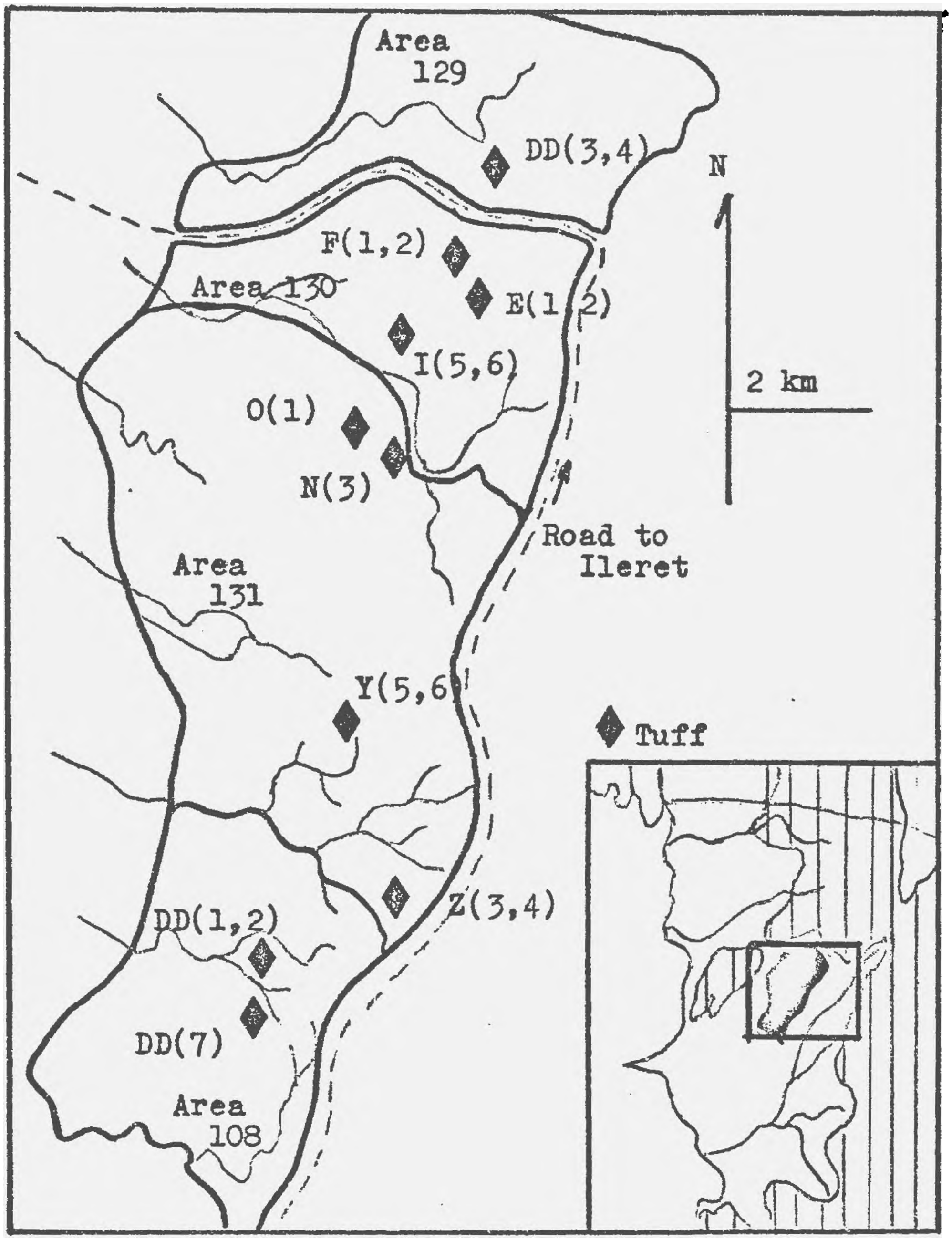


Fig 4. General Sample Locations In Areas 108, 131, 130, and 129.

Table 1.

Triplicate Analysis of Tuff #7*

Element	Sample			Ave.	Error	% error
	#1	#2	#3			
Na	4.8	4.9	4.1	4.6	0.3	7
Al	-	-	-	-		
Sc	0.50	0.52	0.48	0.50	0.02	3
Cr	7.9	7.1	8.1	7.7	0.5	6
V	220.	212.	217.	216.	3.	1
Mn	0.074	0.068	0.074	0.072	0.003	4
Co	1.3	1.4	1.1	1.3	0.1	8
Zr	2.3	2.2	2.8	2.4	0.3	10
La	43.	41.	44.	43.	1.	3
Eu+	1.1	1.2	1.4	1.2	0.1	8
Tb	3.2	2.9	3.1	3.0	0.2	5
Yb	6.05	5.83	5.80	5.89	0.06	1
Lu	0.93	0.82	0.87	0.87	0.05	6
Hf	23.2	21.1	21.9	22.1	0.9	4
Ta	6.01	6.08	5.95	6.01	0.05	1

* Ppm except for Na and Mn which are in percent.

+ Concentration x10^{-3}.

Table 2.

Triplicate Analysis of Tuff #10*

Element		Sample		Ave.	Error	% error
	#1	#2	#3			
Na	5.8	-	6.2	6.0	0.2	3
Al	7.1	7.6	7.4	7.4	0.2	3
Sc	0.53	0.48	0.57	0.52	0.04	7
Cr	3.2	3.5	5.4	4.0	0.9	23
V	90.	97.	92.	93.	3.	3
Mn	0.10	0.12	0.10	0.11	0.01	10
Co	1.4	1.3	1.6	1.4	0.1	9
Zr	1.9	1.8	2.6	2.1	0.3	16
La	38.	34.	36.	36.	2.	4
Eu+	1.2	1.8	1.4	1.5	0.3	20
Tb	3.8	3.6	3.6	3.7	0.1	2
Yb	5.67	5.31	5.46	5.48	0.15	3
Lu	0.88	0.87	0.85	0.87	0.01	1
Hf	18.5	16.9	17.7	17.7	1.2	7
Ta	4.9	4.3	4.7	4.6	0.3	6

* Ppm except for Na, Al, and Mn which are in percent.

\+ Concentration x10^{-3}.

Table 3.

Blank Data

Short Irradiation*

Element	1	2	3	4	5
Na	11.	32.	n.d.+	62.	n.d.+
Al	4.	11.	69.	25.	16.
V	0.01	0.01	0.32	0.18	0.03
Mn	0.04	0.10	0.14	0.19	0.13

Long Irradiation

None of the elements determined in quantities high enough to interfere with sample concentrations.

* All values are upper limit determinations.

\+ Indicates no detection of that element.

Table 4.

Mn and V Aluminum Ratios for Duplicate Field Samples of Tuffs

Sample	Mn/Al ($\times10^{-2}$)	V/Al ($\times10^{-4}$)
E-1	2.0	6.3
E-2	1.9	5.8
F-1	2.2	2.3
F-2	1.7	3.7
DD-1	1.5	-
DD-2	1.6	1.3
Z-3	2.2	5.1
Z-4	2.3	4.8
DD-3	0.8	1.3
DD-4	0.9	1.4
FD-5	2.2	2.7
FD-6	2.0	2.8
Y-5	3.5	2.0
Y-6	3.7	1.3

Table 5.

Comparison Mn Data

Sample	INAA		AAS	
Paleosol	Content	±s*	Content	±s*
E-1	1280	80	1270	50
E-2	1450	200	1300	50
E-3	1500	100	1290	50
E-4	1900	100	2160	90
E-5	2600	100	4630	190
E-6	1200	70	2150	90
Tuff				
E-1	860	50	970	40
F-1	1230	70	1110	40
DD-1	950	50	1120	40
DD-3	580	30	530	20
DD-7	1540	90	1460	60
Z-3	1240	70	890	40
FD-5	1450	80	1100	70
Y-5	1840	90	1800	70

* s is one standard deviation.

Table 6.

Elemental Concentrations of Paleosol C-Series*

Element	C-1		C-2		C-3		C-4	
	value	±s	value	±s	value	±s	value	±s
Al	8.7	0.4	7.8	0.4	8.5	0.4	7.3	0.4
Sc	13.5	0.1	13.3	0.1	14.6	0.2	-	-
Cr	170.	60.	140.	50.	190.	70.	120.	40.
V	114.	8.	89.	6.	128.	9.	76.	7.
Mn	0.12	0.01	0.13	0.01	0.12	0.01	0.24	0.01
Co	33.	1.	31.	1.	33.	1.	31.	1.
Zr	4.0	1.4	-	-	5.8	2.4	5.0	1.7
La	1.5 @		1.5 @		1.3	0.2	2.3	0.2
Eu+	1.6	0.1	1.4	0.1	1.6	0.1	1.8	0.1
Tb	1.5	0.2	1.8	0.2	1.3	0.2	2.3	0.2
Lu	0.8	0.1	0.8	0.1	0.6	0.1	1.0	0.2
Hf	10.0	0.6	11.2	0.7	10.8	0.7	9.1	0.7
Ta	2.7	0.3	2.1	0.3	2.1	0.3	3.3	0.4

* Ppm except for Al and Mn which are in percent.

@ Indicates these are an upper limit for detection.

+ Concentration x10^{-3}.

Table 7.

Elemental Concentrations of Paleosol G-Series*

Element	G-1		G-2		G-3		G-4	
	value	±s	value	±s	value	±s	value	±s
Al	7.8	0.4	7.5	0.4	7.6	0.4	8.1	0.5
Sc	13.4	0.1	11.9	0.1	14.2	0.1	16.0	0.1
Cr	67.	6.	51.	4.	71.	6.	71.	5.
V	114.	7.	93.	8.	108.	8.	97.	8.
Mn	0.17	0.01	0.12	0.01	0.11	0.01	0.16	0.01
Fe	4.8	1.2	4.5	1.1	4.6	1.2	5.2	1.3
Co	35.0	0.9	30.4	0.8	36.3	0.9	31.6	0.9
Zr	4.1	0.8	3.7	0.9	2.0	0.6	2.7	0.6
La	52.	6.	56.	6.	57.	6.	69.	7.
Eu+	1.6	0.1	1.4	0.1	1.5	0.1	2.0	0.1
Tb	1.68	0.08	1.70	0.09	1.61	0.08	2.63	0.12
Yb	3.1	0.3	2.3	0.3	2.9	0.3	5.5	0.5
Lu	0.59	0.02	0.45	0.02	0.56	0.02	0.95	0.03
Hf	10.4	0.3	8.9	0.3	11.2	0.4	11.6	0.4
Ta	2.1	0.2	2.5	0.2	3.0	0.2	2.8	0.2

* Ppm except for Al, Mn, and Fe which are in percent.

+ Concentration $x10^{-3}$.

Table 8.

Elemental Concentrations of Paleosol H-Series*

Element	H-1		H-2		H-3		H-4	
	value	±s	value	±s	value	±s	value	±s
Al	8.3	0.4	8.7	0.3	8.1	0.4	8.2	0.4
Sc	14.7	0.2	12.8	0.1	14.0	0.2	14.5	0.2
V	108.	8.	112.	7.	107.	7.	93.	8.
Mn	0.11	0.01	0.15	0.01	0.16	0.01	0.13	0.01
Co	33.	1.	34.	1.	33.	1.	34.	1.
La	1.5 @		1.3 @		3.4	1.5	1.7	1.0
Eu+	1.6	0.1	1.8	0.1	1.6	0.1	1.7	0.1
Tb	1.75	0.18	1.97	0.17	1.75	0.19	2.00	0.19
Lu	1.1	0.2	0.5	0.1	0.9	0.2	1.0	0.2
Hf	9.1	0.6	8.5	0.6	9.4	0.7	9.0	0.6
Ta	3.1	0.4	2.9	0.3	2.9	0.4	2.5	0.3

* Ppm except for Al and Mn which are in percent.

@ Indicates these are an upper limit for detection.

\+ Concentration $x10^{-3}$.

Table 9.

F- Series Concentrations*

Element	F-1	±s	F-2	±s	F-3	±s	F-4	±s	F-5	±s	F-6	±s
Al	5.9	0.2	8.7	0.5	6.1	0.3	9.9	0.5	7.5	0.4	7.5	0.3
Sc	10.1	0.1	13.6	0.1	21.4	0.2	13.9	0.1	14.3	0.1	13.1	0.1
Cr	47.	4.	68.	6.	80.	7.	51.	4.	62.	5.	47.	4.
V	38.	3.	91.	7.	38.	3.	120.	10.	89.	7.	76.	6.
Mn	0.25	0.01	0.17	0.01	0.12	0.01	0.41	0.02	0.16	0.01	0.24	0.01
Fe	1.6	0.4	2.6	0.7	3.0	0.8	2.8	0.7	-	-	2.4	0.6
Co	10.7	0.4	23.1	0.7	31.0	0.2	10.0	0.8	-	-	27.6	0.7
Zr	6.8	1.0	2.0	0.6	-	-	-	-	1.2	0.6	1.6	0.6
La	46.	5.	55.	6.	97.	11.	36.	4.	56.	6.	49.	5.
Eu+	1.4	0.1	1.4	0.1	3.0	0.3	1.5	0.1	1.5	0.1	1.4	0.1
Tb	2.1	0.1	1.5	0.1	2.7	0.3	1.8	0.1	1.9	0.1	1.6	0.1
Yb	5.2	0.3	3.6	0.4	6.5	1.0	3.8	0.3	3.8	0.3	3.3	0.3

Table 9. F- Series Concentrations (cont.)

Element	F-1	±s	F-2	±s	F-3	±s	F-4	±s	F-5	┘	F-6	±s
Lu	0.88	0.02	0.70	0.02	1.10	0.10	0.72	0.02	0.69	0.02	0.58	0.02
Hf	18.2	0.5	10.6	0.4	18.0	1.0	10.0	0.3	11.8	0.4	9.9	0.3
Ta	1.5	0.2	2.2	0.2	-	-	2.4	0.2	2.5	0.2	2.0	0.2

* Ppm except for Al, Mn, and Fe which are in percent.

+ Concentrations x10^{-3}

Table 10A.

Bulk Analysis for KBS Tuff Samples*

Element	E-1	±s	I-5	±s	N-3	±s	O-1	±s
Mg	630	30	-		-		-	
Na	2.1	-	-		-		-	
Al	4.3	0.2	8.4	0.3	5.7	0.2	6.3	0.2
Sc	4.53	0.04	5.65	0.05	3.29	0.03	2.81	0.03
V	27.	4.	31.	6.	22.	5.	73.	6.
Mn	0.09	0.01	0.18	0.01	0.10	0.01	0.11	0.01
Fe	0.88	0.10	0.53	0.05	0.68	0.08	0.66	0.08
Co	8.5	0.2	13.0	0.3	5.5	0.2	3.4	0.1
Zr	5.6	0.4	3.6	0.4	4.4	0.3	5.4	0.4
Eu+	1.39	0.05	2.29	0.06	1.31	0.04	1.27	0.05
Tb	4.00	0.08	2.91	0.06	3.81	0.07	4.39	0.08
Yb @	0.4		0.3		0.4		0.5	
Lu @	1.7		2.4		1.7		1.5	
Hf	33.3	0.9	19.5	0.5	31.1	0.8	34.7	0.9
Ta	11.1	0.4	5.8	0.2	10.6	0.3	11.5	0.4

* Ppm except for Na, Al, Mn, and Fe which are in percent.

\+ Concentration $x10^{-3}$.

@ Values are upper limits for these elements.

Table 10B.

Bulk Analysis for Karari, BBS, and Tula Bor Tuff Samples

Element	DD-1	±s	Z-3	±s	Y-5	±s	DD-3	±s	FD-5	±s
	KARARI				BBS		TULA BOR			
Mg	264	30	156	7	146	7	52	3	285	14
Na	2.5	-	4.0	-	1.7	-	3.1	-	3.3	-
Al	6.0	0.2	5.7	0.2	5.1	0.2	7.0	0.2	6.5	0.2
Sc	1.42	0.02	3.24	0.03	3.64	0.03	1.41	0.02	4.90	0.04
V	4.	2.	29.	4.	10.	3.	9.	3.	18.	3.
Mn	0.09	0.01	0.13	0.01	0.18	0.01	0.06	0.003	0.15	0.01
Fe	0.55	0.06	0.57	0.07	0.68	0.08	0.26	0.03	0.83	0.09
Co	2.3	0.1	3.3	0.1	2.1	0.1	1.0	0.1	6.9	0.2
Zr	4.7	0.3	4.1	0.3	4.9	0.3	1.7	0.2	5.5	0.4
Eu+	1.86	0.05	1.88	0.05	1.47	0.05	0.68	0.03	1.18	0.05
Tb	3.59	0.06	2.67	0.05	3.58	0.06	1.69	0.04	3.48	0.08
Yb @	0.3		0.8		0.4		0.2		0.5	

Table 10B. Bulk Analysis for Tuff Samples (cont.)

Element	DD-1	±s	Z-3	±s	Y-5	±s	DD-3	±s	FD-5	±s
	----------KARARI-----------				----BBS----		---------TULA BOR----------			
Lu @	1.2		1.2		1.4		0.8		1.6	
Hf	26.3	0.7	20.0	0.5	29.9	0.8	10.6	0.3	25.1	0.7
Ta	7.4	0.3	4.7	0.2	11.4	0.4	4.1	0.2	10.4	0.4

* Ppm except for Na, Al, Mn, and Fe which are in percent.

+ Concentration $x10^{-3}$.

@ Values are upper limits for these elements.

Table 11.

Bulk Analysis Al-Ratios for Nine Tuffs

Ratio	DD-1	Z-3	Y-5	E-1	I-5	N-3	O-1	DD-3	FD-5
	---KARARI----		BBS	-------------KBS-------------				--TULA BOR---	
Mg/Al x10^{-3}	4.4	2.7	2.9	15.0	-	-	-	0.7	4.4
Na/Al x10^{-1}	4.2	7.0	3.3	3.4	-	-	-	4.4	5.1
Sc/Al x10^{-5}	2.4	5.7	7.1	10.5	6.7	5.8	4.5	2.0	7.5
Mn/Al x10^{-2}	1.5	2.2	3.5	2.0	2.1	1.8	1.7	0.8	2.2
V/Al x10^{-4}	0.7	5.1	2.0	6.3	3.7	3.9	11.6	1.3	2.7
Fe/Al x10^{-1}	0.9	1.0	1.3	2.1	1.2	1.1	0.8	0.4	1.3
Co/Al x10^{-4}	0.4	0.6	0.4	2.0	1.5	1.0	0.5	0.1	1.1
Zr/Al x10^{-5}	7.8	7.2	9.6	13.0	4.3	7.7	8.6	2.4	8.5
Eu/Al x10^{-8}	3.1	3.3	2.9	3.2	2.7	2.3	2.0	0.9	1.8
Tb/Al x10^{-5}	6.1	4.7	7.0	9.9	3.4	6.5	6.8	2.4	5.3
Hf/Al x10^{-4}	4.4	3.5	5.9	7.7	2.3	5.5	5.5	1.5	3.9
Ta/Al x10^{-4}	1.2	0.8	2.2	2.6	0.7	1.8	1.8	0.6	1.6

Table 12.

Size Fraction Concentrations for E-Series Paleosols*

Element	E-1	±s	E-2	±s	E-3	±s	E-4	±s	E-5	±s	E-6	±s
----------SIZE FRACTION >177 MICRON----------												
Na	4.3	0.6	6.7	1.4	3.9	0.8	3.3	0.5	2.3	0.5	-	
Al	9.7	0.2	7.4	0.2	7.3	0.2	5.0	0.1	4.0	0.1	-	
V	121.	5.	92.	4.	93.	4.	40.	4.	36.	3.	-	
Mn	0.16	0.01	0.13	0.01	0.17	0.01	0.43	0.01	0.71	0.02	-	
----------SIZE FRACTION 125-177 MICRON----------												
Na	6.6	0.9	5.3	0.6	3.9	0.5	5.0	0.6	4.9	0.8	5.1	0.6
Al	9.3	0.2	8.8	0.2	8.8	0.2	8.1	0.3	9.3	0.3	9.4	0.3
V	103.	4.	80.	4.	93.	5.	69.	7.	51.	7.	101.	6.
Mn	0.15	0.01	0.13	0.01	0.13	0.01	0.20	0.01	0.30	0.01	0.14	0.01

Table 12. Size Fraction Concentrations E-Series (cont.)

Element	E-1	±s	E-2	±s	E-3	±s	E-4	±s	E-5	±s	E-6	±s
----------SIZE FRACTION 88-125 MICRON----------												
Na	4.3	0.8	4.9	0.9	3.7	0.7	4.0	0.7	2.9	0.5	-	
Al	8.0	0.2	7.3	0.2	8.2	0.2	8.6	0.3	7.3	0.2	-	
V	103.	5.	90.	4.	124.	5.	101.	8.	50.	3.	-	
Mn	0.15	0.01	0.14	0.01	0.17	0.01	0.19	0.01	0.16	0.01	-	
----------SIZE FRACTION <88 MICRON----------												
Na	4.0	0.6	5.5	0.7	4.7	0.7	3.2	0.5	2.1	0.3	-	
Al	8.9	0.2	9.1	0.2	9.0	0.2	6.4	0.2	6.3	0.2	7.8	0.2
V	131.	8.	134.	5.	155.	6.	110.	5.	123.	5.	206.	7.
Mn	0.18	0.01	0.19	0.01	0.20	0.01	0.25	0.01	0.36	0.01	0.21	0.01

* Percent except for V which is in ppm.

Table 13.

Aluminum Ratios for E-Series Size Fractions

Ratio	E-1	E-2	E-3	E-4	E-5	E-6
----- Size Fraction >177 Micron-----						
Na/Al	0.44	0.91	0.53	0.66	0.58	-
V/Al*	1.25	1.24	1.27	0.80	0.90	-
Mn/Al+	1.61	1.76	2.26	8.60	17.8	-
----- Size Fraction 125-177 Micron-----						
Na/Al	0.71	0.60	0.44	0.62	0.53	0.54
V/Al*	1.11	0.91	1.06	0.85	0.55	1.07
Mn/Al+	1.58	1.49	1.42	2.41	3.23	1.52
----- Size Fraction 88-125 Micron-----						
Na/Al	0.54	0.67	0.45	0.47	0.40	-
V/Al*	1.29	1.23	1.51	1.17	0.68	-
Mn/Al+	1.88	1.88	2.12	2.26	2.21	-
----- Size Fraction <88 Micron-----						
Na/Al	0.45	0.60	0.52	0.50	0.33	-
V/Al*	1.47	1.47	1.72	1.72	1.95	2.64
Mn/Al+	2.00	2.09	2.21	3.86	5.76	2.69

* Values x10^{-3}

\+ Values x10^{-2}

Table 14.

Tuff Concentrations for Size Fraction 88 Microns*

Element	DD-1	±s	Z-3	±s	DD-7	±s	Y-5	±s	E-1	±s	F-1	±s	DD-3	±s
	------KARARI------				--------BBS--------				--------KBS--------				TULA	BOR
Na	2.5	0.5	4.0	1.2	-		1.7	0.5	2.1	0.4	2.0	0.4	3.1	0.7
Al	5.5	0.2	5.6	0.2	4.9	0.1	5.5	0.2	6.7	0.2	6.7	0.2	5.7	0.2
Sc	0.48	0.01	0.40	0.01	0.29	0.01	1.22	0.02	0.52	0.01	0.29	0.01	0.24	0.01
Cr	2.1	0.4	0.7	0.1	1.5	0.2	1.9	0.3	2.0	0.2	1.0	0.1	0.4	0.1
V	10.	2.	21.	2.	11.	2.	6.	2.	27.	2.	4.	1.	6.	1.
Mn	0.94	0.03	1.39	0.04	1.33	0.04	2.10	0.06	0.88	0.03	1.01	0.03	0.51	0.01
Fe	0.17	0.04	0.07	0.02	0.14	0.03	0.23	0.05	0.10	0.02	0.41	0.20	0.04	0.01
Co	0.60	0.07	0.21	0.03	0.29	0.04	0.41	0.05	0.80	0.05	0.13	0.02	0.17	0.02
Zn	0.69	0.13	0.08	0.01	0.20	0.03	0.26	0.10	0.16	0.04	0.21	0.03	0.15	0.03
Zr	1.41	0.23	0.81	0.11	1.33	0.16	2.60	0.30	0.79	0.12	1.02	0.11	0.42	0.08
Eu+	4.6	0.3	1.8	0.1	2.0	0.1	4.4	0.3	1.5	0.1	1.2	0.1	0.9	0.1
Hf	7.5	0.3	2.6	0.1	5.0	0.2	11.2	0.3	4.2	0.1	4.5	0.1	1.8	0.1

Table 10B. Bulk Analysis for Tuff Samples (cont.)

Element	DD-1	±s	Z-3	±s	DD-7	±s	Y-5	±s	E-1	±s	F-1	±s	DD-3	±s
	KARARI				BBS				KBS				TULA BOR	
Lu	3.91	0.10	1.38	0.03	2.48	0.05	5.55	0.10	1.56	0.04	1.62	0.04	1.10	0.03
Ta	2.2	0.2	0.5	0.1	1.4	0.1	3.8	0.2	1.4	0.1	1.6	0.1	0.7	0.1

* Ppm except for Na, Al, and Fe which are in percent.

¤ Value x10^{1}.

+ Concentration x10^{-3}.

Table 15.

Al-Ratios for Tuff 88 Micron Fraction

Ratio	DD-1	Z-3	DD-7	Y-5	E-1	F-1	DD-3
	----KARARI-----		-----BBS-------		-----KBS------		TULA BOR
Na/Al $x10^{-1}$	4.5	7.1	-	3.1	3.1	3.0	5.4
Sc/Al $x10^{-5}$	8.7	7.1	5.9	22.1	7.7	4.3	4.2
Cr/Al $x10^{-4}$	3.8	1.3	3.1	3.5	3.0	0.1	0.7
V/Al $x10^{-3}$	1.8	3.8	2.2	1.1	4.0	0.6	1.1
Mn/Al $x10^{-2}$	1.7	2.5	2.7	3.8	1.3	1.5	0.9
Fe/Al $x10^{-1}$	3.1	1.3	2.9	4.2	1.5	6.1	0.7
Co/Al $x10^{-4}$	1.1	0.4	0.6	0.7	1.2	0.2	0.3
Zn/Al $x10^{-5}$	12.5	1.4	4.0	4.7	2.3	3.1	2.6
Zr/Al $x10^{-4}$	2.5	1.4	2.7	4.7	1.2	1.5	0.7
Eu/Al $x10^{-4}$	8.4	3.2	4.1	8.0	2.2	1.8	1.6
Hf/Al $x10^{-4}$	13.6	4.6	10.2	20.0	6.3	6.7	3.2
Lu/Al $x10^{-5}$	7.0	2.5	5.1	10.1	2.3	2.3	1.9
Ta/Al $x10^{-4}$	3.8	1.1	2.4	6.4	1.6	1.9	1.1

APPENDIX IV

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