

fresh air. After passage of 5000 liters of air (comparable to 10 hours of human breathing) through the filter, the filter had turned a deep grey with a visibly thick deposit. It is the trace elements, possibly introduced into the atmosphere by only a few specific sources, that may well provide the tag for studying motion and sources of air masses and the more abundant atmosphere pollutants.

Because this analytic technique is basically nonchemical, sample handling is greatly reduced. This decreases the likelihood of sample contamination. The directness of this analytic technique permits confidence limits of the observed data to be estimated accurately from the counting data.

The sensitivity of neutron activation and good resolution gamma-ray spectroscopy for determining, in mixtures

of elements, the abundance of even those elements present in trace concentrations immediately makes evident further applications of this tool in fields seemingly far removed from gamma-ray spectroscopy.

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#### Notes

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## Rubidium-Strontium Age of the Bosumtwi Crater Area, Ghana, Compared with the Age of the Ivory Coast Tektites

**Abstract.** *Rocks from the vicinity of Bosumtwi crater, Ghana, and a representative collection of Ivory Coast tektites have been analyzed mass spectrometrically for rubidium, strontium, and strontium isotopic composition. The data from the rocks of the crater area yield an age of  $1.97 \times 10^9$  years ( $\lambda_{Rb} = 1.47 \times 10^{-11}$  year $^{-1}$ ). The data for the Ivory Coast tektites fall on this isochron. This identity of age values for the Ivory Coast tektites and the Birrimian basement rocks of West Africa strongly supports the hypothesis of terrestrial formation for these tektites. The evidence available at present suggests that the Ivory Coast tektites are most probably the fusion products of meteoritic impact at the Bosumtwi crater site.*

The purpose of this study was (i) to determine if the Ivory Coast tektites fall on the 400-million-year isochron which has been suggested (1) for tektites from the other three major geographic localities, namely, Australasia, Czechoslovakia, and North America; and (ii) to compare the rubidium, strontium, and strontium isotopic compositions of the Ivory Coast tektites with those of the rocks at the Bosumtwi crater in Ghana. Maclaren (2) first suggested, in 1931, that the Bosumtwi, or Ashanti, crater was formed by meteoritic impact. The discoveries of coesite (3) and shatter cones (4) at the crater support this theory. Cohen (5) suggested that the Ivory Coast tektites, which occur approximately 300 km to the west of the crater, might have been produced by the impact. Since then, K-Ar analyses of Ivory Coast tektites (6) and Bosumtwi glass (7) have yielded the same age, within rather large

experimental uncertainty, of  $1.3 (\pm 0.3) \times 10^9$  years. Recently, fission track dating (8) has supported this agreement between the time of melting of the crater glass and the Ivory Coast tektites.

All but two of the tektites analyzed, GSFC Nos. 3 and 4, were from a group of 75 samples recently obtained from the Ivory Coast. Details of this collection, such as specimen locality, weight, density, and so forth, are in preparation for later publication. The samples analyzed were chosen to cover the specific gravity range of the collection and to cover the range of Rb/Sr ratios, which were estimated from rough x-ray fluorescence measurements. All of the tektites, except GSFC No. 4, are from the approximately 45- by 80-km strewn-field area described by Lacroix (9). Tektite GSFC No. 4 was found in 1963 in a prospecting pit 2 km south of Adzopé; this is approximately

100 km to the south of the previously defined strewn-field.

The rubidium, strontium, and strontium isotopic compositions for the tektites are given in Table 1; those for the rocks of the Bosumtwi crater area, in Table 2. The rubidium and strontium determinations are by stable isotope dilution techniques, while the isotope ratio analyses are on unspiked strontium. The basic analytical procedures have been previously described (1). Precision of the rubidium and strontium isotope dilution analyses, as demonstrated by replicate analyses, is approximately  $\pm 2$  percent. The strontium isotopic ratios reported in Tables 1 and 2 were determined on four different mass spectrometers of similar design (12-inch radius of curvature, 60° sector, single focusing) at the Massachusetts Institute of Technology, the Goddard Space Flight Center, and the National Bureau of Standards. Most of the samples were analyzed on at least two of the machines; only the average values for each sample are reported in the tables. No systematic bias was observed between the machines; the average difference between  $(Sr^{87}/Sr^{86})_N$  analyzed on the same sample was less than 0.1 percent for samples analyzed repeatedly on the same mass spectrometer and for samples analyzed on different machines.

The tektites in Table 1 are listed in order of increasing specific gravity. Thus they are probably listed in approximate order of decreasing SiO<sub>2</sub> content, as the inverse correlation between specific gravity and SiO<sub>2</sub> content has been demonstrated in several studies (10). The data in Table 1 suggest an inverse correlation between specific gravity and rubidium, but no correlation is evident between specific gravity and strontium.

The Ivory Coast tektites exhibit a rather restricted range in both rubidium and strontium, as has been observed for most elements in tektites. The strontium content in GSFC No. 4, however, is far outside the range of the other 12 samples. This value has been checked by two independent analyses, which agreed within  $\pm 1$  percent. The values for rubidium and strontium in Table 1 are in excellent agreement with the single reported analyses in an Ivory Coast tektite of 64 ppm Rb and 316 ppm Sr (by x-ray fluorescence techniques) by Gentner *et al.* (7). They also report rubidium and strontium in a Bosumtwi glass from the same

Table 1. Rb, Sr, and Sr isotopic composition of Ivory Coast tektites.

Sample No.*	Rb (ppm)	Sr (ppm)	Sr <sup>86</sup> /Sr <sup>88</sup>	Sr <sup>87</sup> /Sr <sup>86</sup>	(Sr <sup>87</sup> /Sr <sup>86</sup> ) <sub>N</sub> <sup>†</sup>	No. of analyses
T5702	75.3	289	0.1197	0.7224	0.7231	2
T5658	72.8	288	.1201	.7205	.7226	1
T5708	68.1	288	.1195	.7228	.7230	1
GSFC-4	63.6	399	.1197	.7178	.7187	3
T5704	66.5	303				
T5707	72.1	275				
T5709	65.4	325	.1195	.7221	.7224	2
T5663	67.6	277				
T5646	67.6	289	.1197	.7219	.7228	2
T5699	55.0	318				
T5673	67.5	287	.1201	.7196	.7217	2
GSFC-3	64.8	304	.1192	.7227	.7232	1
T5659	59.0	313	.1201	.7205	.7226	2

\*Samples listed in order of increasing density. †Measured Sr<sup>87</sup>/Sr<sup>86</sup> ratio normalized to a constant Sr<sup>86</sup>/Sr<sup>88</sup> ratio of 0.1194.

Table 2. Rb, Sr, and Sr isotopic composition of rocks and glass from the Bosumtwi Crater area, Ghana.

Sample No. and description	Rb (ppm)	Sr (ppm)	Sr <sup>86</sup> /Sr <sup>88</sup>	Sr <sup>87</sup> /Sr <sup>86</sup>	(Sr <sup>87</sup> /Sr <sup>86</sup> ) <sub>N</sub> <sup>*</sup>
No. 12. Phyllite from Obuom mine, south of Kumasi.	10 <sup>†</sup>	500 <sup>†</sup>	0.1181	0.7075	0.7036
No. 13. Graywacke, interbedded with sample No. 12.	35.5	625	.1194	.7044	.7044
No. 14 W.R. Granite, ½ mile from Ijisu, N.E. of crater. Whole rock fraction.	301	98.9	.1192	.9616	.9610
No. 14 C.F. Same granite as No. 14 W.R.; coarse fraction (+100 mesh).	344	85.9	.1187	1.0440	1.0409
No. 8. Suevite from Ata stream bed, Bosumtwi crater.	53.8	181	.1198	0.7255	0.7266
No. 10. Dark glass separated from suevite from Ata stream bed.	64.1	351	.1194	.7177	.7179

\*See second footnote to Table 1. †Estimates by x-ray fluorescence.

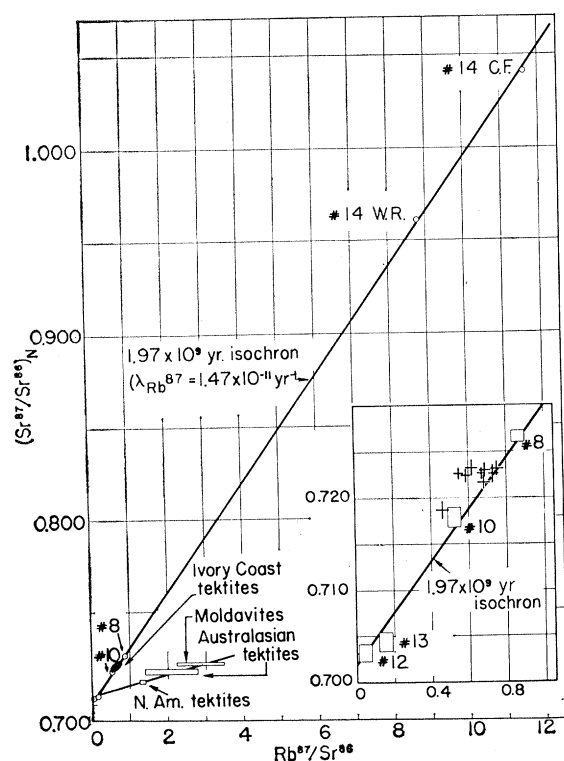


Fig. 1. Plot of Sr<sup>87</sup>/Sr<sup>86</sup> versus Rb<sup>87</sup>/Sr<sup>86</sup> for Bosumtwi crater rocks and Ivory Coast tektites. On the full plot the Bosumtwi rocks are shown as circles, while the field of Ivory Coast tektites is shown as a cross-hatched area. The Bosumtwi sample numbers correspond to the numbers in Table 2. The values covered by the other three groups of tektites (1, 13) are also shown on the full plot. In the large-scale inset, which refers to the lower left portion of the large diagram, the errors are shown, the Bosumtwi area rocks by boxes, and the individual Ivory Coast tektites by crosses.

general locality as glass No. 10 in Table 2. Their results (of 73 ppm Rb and 358 ppm Sr) are again in excellent agreement with our values.

The Bosumtwi area is underlain by rocks of the Birrimian System (Pre-Cambrian). Except for a small amount of recent clays and agglomerates, the rocks in the immediate vicinity of the crater are metamorphosed sediments of Birrimian age (predominately phyllites with interbedded graywackes and quartzites) and intrusive granites (11). We are unaware of any reported determinations of the absolute age of these rocks from the Bosumtwi area. However, numerous determinations have been made on very similar Birrimian rocks from the Ivory Coast. Approximately 80 mineral and whole-rock Rb-Sr age determinations have been made on the Birrimian rocks from the Ivory Coast (12), and they indicate an age for this system of between 1.9 and 2.0 × 10<sup>9</sup> years.

The analyses of the granite reported in Table 2 confirm the identification of the rocks of the Bosumtwi area as Birrimian. With the same decay constant for Rb<sup>87</sup> as was used in the Ivory Coast Birrimian calculations ( $\lambda_{\text{Rb}} = 1.47 \times 10^{-11} \text{ yr}^{-1}$ ), the granite data yield an age of 1.97 × 10<sup>9</sup> years.

The data in Tables 1 and 2 are plotted in Fig. 1. The phyllite and graywacke (samples Nos. 12 and 13) have Rb/Sr ratios that are so low they show almost no enrichment of Sr<sup>87</sup> even in 2 × 10<sup>9</sup> years. The glass and suevite (samples Nos. 10 and 8) lie on the 1.97 × 10<sup>9</sup> year isochron, despite the fact that the K-Ar analyses indicate they were formed approximately 1.3 × 10<sup>6</sup> years ago (7). The most logical interpretation is that they were produced by the mixing and fusion of the country rock of Birrimian age during the event that produced the crater, and merely reflect the Rb-Sr Birrimian age of their parent material. Calculations based on the Rb, Sr, and Sr isotopic composition of the phyllite, granite, and Bosumtwi glass indicate the glass could be a mixture of approximately 75 percent phyllite and 25 percent granite.

The Czechoslovakian, Australasian, and North American tektites are also plotted in Fig. 1, based on previously reported data (1). The 400-million-year isochron, through the average of each of these three groups, is shown. The Ivory Coast tektites definitely do not lie on this isochron, and thus the data

presented here on the Ivory Coast tektites do not clarify the significance of this isochron.

However, the plotted points for the Ivory Coast tektites lie essentially on the Birrimian-age isochron of  $1.97 \times 10^9$  years. Only three of the tektite points fall exactly on the isochron; the others all occur, at varying distances, slightly to the left of the line. This selective scatter to the left of the line can be ascribed to fractional volatilization of Rb relative to Sr during the fusion process which formed the tektites. Several recent studies suggest that selective volatilization of Rb relative to Sr took place during the fusion process that produced tektites (13) and, further, that the  $\text{SiO}_2$  content decreases (hence the density increases) with increasing volatilization (14). The tektites listed in Table 1 (in order of increasing specific gravity) could be considered, therefore, as being listed roughly in order of increasing degree of volatilization and increasing loss of rubidium relative to strontium. There is an inverse correlation of rubidium with density, and a direct correlation of density with the distance of the points to the left of the line. That is, the samples at the top of the table, which according to the referenced studies should have suffered the least fractionation, lie on the line, while samples with increasing density (that is, less  $\text{SiO}_2$  and more volatilization) fall, in general, further to the left of the isochron.

The age relationships presented here for the Ivory Coast tektites and the Birrimian rocks support the hypothesis of terrestrial origin for these tektites. The probability that these tektites, if extraterrestrial, would have just the right combination of rubidium, strontium, and strontium isotopic composition to lie on the isochron of the country rock on which they fell seems rather remote. Because much of the basement of West Africa is approximately  $2 \times 10^9$  years old, this age value does not point unequivocally to the Bosumtwi crater as their place of formation. However, chemical similarities between the Ivory Coast tektites and glass from the Bosumtwi crater support this hypothesis of common origin. Gentner *et al.* (7) report the close similarity between the Bosumtwi crater glass and the Ivory Coast tektites for seven trace elements. Our Rb, Sr, and strontium isotopic analyses support this close similarity between the two types of materials. In addition, preliminary

chemical analyses of these samples show a close similarity for the major elements examined: Fe, Ti, Ca, Mg, K, Na, and Mn (15). The concentrations of all these elements, except Ca, in the one piece of Bosumtwi glass available, lie within the rather restricted range of the 11 analyzed Ivory Coast tektites.

These three lines of evidence—the Rb-Sr age correlation (age of parent material), the K-Ar age correlation (age of fusion), and the chemical correlation—strongly support the hypothesis that the Ivory Coast tektites are related to the phenomenon that formed the Bosumtwi crater.

*Note added in proof.* An independent Rb-Sr isotopic study of three Ivory Coast tektites and five Bosumtwi crater glasses has recently been completed by Lippolt and Wasserburg (*Z. Naturforsch.*, in press). Their data and conclusions are essentially in agreement with this paper.

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## Imidonitrogen in *Chlorella* "Polyphosphate"

**Abstract.** "Polyphosphate" and fragments isolated from acid hydrolysis of polyphosphate have an infrared absorption band at  $1400\text{ cm}^{-1}$ , which is characteristic of imidodiphosphate linkages. Complete hydrolysis of purified "polyphosphate" releases 1 to 2 moles of phosphate per mole of ammonia. The polymer must contain subunits which are cyclic and which contain both imidodiphosphate linkages and phosphate anhydride linkages.

The polyphosphate in *Chlorella* is not a simple phosphate anhydride polymer (1-3); nor is it, because of its stability in water, one of the many polymers containing phosphorus which are unstable in water. The properties of trimetaphosphoimide (4) prompted a study to determine whether metaphosphoimide groups occur within the material of high molecular weight commonly designated as polyphosphate. Imidodiphosphate linkages have not been reported in natural products.

Sodium trimetaphosphoimide was synthesized (5) in order to study its properties in more detail. Its specific metachromasy (2) is 0.3 compared to 0.0 for trimetaphosphate. Thus metaphosphoimides are more metachromatic than metaphosphates. This is significant because *Chlorella* polyphosphates have been reported to have very high specific metachromasies, which could not be explained if the polyphosphate contained only anhydride linkages (2). Trimetaphosphoimide re-