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The High Energy Spallation Products of Copper*

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Nuclear reactions induced in elemental copper by irradiation with charged particles accelerated to energies in the hundred-Mev range have been studied, and the reaction products cover a range from the region of the target nucleus to a region which is removed from the target nucleus by as many as forty or more nucleons. The yields of the various products were measured, and the results show that a large majority of the products result from reactions in which only a fraction of the total energy of the incident particle is left with the nucleus. The distribution of the amounts of the reaction products is in agreement with a picture of high energy nuclear reactions involving nuclear transparency and the idea that the nuclear reactions involve excitation following collisions and energy transfers between the individual nucleons in the impinging particle and the individual nucleons in the target nucleus. The results include recent work on the nuclear reactions induced by 340-Mev protons and some earlier qualitative work on the nuclear reactions induced by 190-Mev deuterons and 190- and 380-Mev helium ions.

INTRODUCTION

THE acceleration of charged particles to energies in the hundreds of Mev range by the Berkeley 184-inch cyclotron has made it possible to study nuclear reactions in which the reaction products cover a range from the region of the target nucleus to a region which is removed from the target nucleus by as many as forty or more nucleons.[1] The term "spallation" has been suggested to describe this type of transformation in which the excitation of the nucleus is degraded by emission of small nuclear fragments such as neutrons, protons, deuterons, and alpha-particles.

Some of the results of spallation reactions induced with high energy deuterons and alpha-particles have been reported previously.[1–5] The present study consists of the determination of the radioactive products formed by the irradiation of elemental copper with 340-Mev protons. The data also include the results of a cursory investigation of the products formed by the irradiation of copper with 190-Mev deuterons and 190- and 380-Mev helium ions.

The observed spallation products include some 35 nuclides from sodium through zinc and the distribution of the amounts of the reaction products formed is in general agreement with the picture of high energy nuclear reactions described by Serber.[6] The observed yields show the effects of nuclear transparency and are consistent with Serber's idea that the nuclear reactions involve excitation following collisions and energy transfers between the individual nucleons in the impinging particle and the individual nucleons in the target nucleus. As would be expected on this picture, the products which are formed by reactions requiring small amounts of excitation occur most frequently.

The spallation data from the deuteron and helium ion irradiations of copper represent the results of some early qualitative work done in 1947 and 1948. At the present time this laboratory is not planning any immediate further investigations of these spallation distributions, and the data are published here for qualitative consideration only.

Preliminary results are included which show that secondary reactions are induced in copper by nuclear fragments emitted from copper nuclei excited by bombardment with 340-Mev protons. The results show conclusively that gallium isotopes, and inconclusively that germanium isotopes, are produced by the nuclear fragments.

PROCEDURE

Irradiations with the high energy particles were carried out in the circulating beam of the 184-inch frequency modulated cyclotron. The targets consisted of 6- and 10-mil copper foil about 15 mm long and 10 mm wide. The copper strips were clamped in target holders which could be attached to the movable probe head of the cyclotron, and the bombarding energies were adjusted by fixing the radial distance of the leading edge of the target strip from the origin of the beam. Since the degradation of the energy of the high energy particles in passing through the 10-mil copper foil is small, the targets could be considered as thin targets.

Because of the fluctuations in intensity of the circulating beam, the exact amount of the irradiation of the copper target could not be determined directly. The amount of the nuclide Cu^{61} formed during any given irradiation of the copper was determined and by relating the amounts of the other nuclides formed to the amount of Cu^{61} produced, relative yields of nuclides from any series of proton, deuteron, or helium ion irradiations could be compared.

The length of the irradiations varied from ten minutes to one hour depending on the half-lives of the nuclides

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* This work was performed under the auspices of the AEC.

[1] Cunningham, Hopkins, Lindner, Miller, O'Connor, Perlman, Seaborg, and Thompson, Phys. Rev. **72**, 739, 740(A) (1947).

[2] Miller, Thompson, and Cunningham, Phys. Rev. **74**, 347 (1948).

[3] H. H. Hopkins, Jr., Phys. Rev. **77**, 717 (1950).

[4] M. Lindner and I. Perlman, Phys. Rev. **78**, 499 (1950).

[5] Bartell, Helmholz, Softky, and Stewart, Phys. Rev. **80**, 1006 (1950).

[6] R. Serber, Phys. Rev. **72**, 1114 (1947).

which were to be studied. One approximately 30-hour proton bombardment, and one approximately 15-hour deuteron bombardment were done to determine the yields of the nuclides with very long half-lives.

An absolute cross section for the formation of the Cu^{61} from copper irradiated with 340-Mev protons was determined by irradiating a piece of 10-mil copper foil in the external beam of the 184-inch cyclotron. The beam intensity was measured directly by means of a faraday cup arrangement. In the case of the deuteron irradiation, the absolute cross section for the formation of Cu^{61} was calculated using an estimated value of one microampere for the deuteron beam intensity.

After the target was irradiated, it was dissolved and measured amounts of carriers were added to the target solution. The elemental fractions were separated by the chemical separation procedures to be discussed in the section of "Chemical Separation Procedures." For the proton irradiations, the amount of carrier remaining after the chemical separation of an elemental fraction was determined by chemical analysis and the percent of the carrier recovered was taken as a measure of the percent of the radioactive atoms of the element recovered. No correction was made for losses during the chemical separations in the cases of the deuteron and helium ion irradiations, but usually duplicate experiments were performed in the case of the deuteron study, and the higher yields were given greater statistical weight in the final average value of the yields.

Counting of the activities was done on an end-window, alcohol-quenched, argon-filled Geiger counter tube with a mica window of $\sim 3\text{-mg/cm}^2$ thickness used in conjunction with a scale of 64 counting circuit. The nuclides were characterized by half-life determinations, absorption measurements, and sign of particulate radiation emitted.

A crude beta-ray spectrometer was used in the determination of the sign of the beta-particles and was especially useful where it was necessary to resolve nuclides with similar half-life but differing in sign of particulate radiation emitted.

The counting data were corrected for window and air absorption, and in the cases where the yields are based on the counting of K x-rays, corrections were made for the fluorescence yields of the x-rays. Backscattering corrections were made only in the case of the determination of the absolute cross section for the formation of the Cu^{61} from the proton irradiation of the copper. The samples from the proton irradiations were mounted on thin cover glasses or 5-mil aluminum disks, and the backscattering corrections for such backings are essentially equal and constant for the energy range of the beta-particles observed. The samples from the deuteron and helium ion irradiations were mounted on stainless steel and platinum plates, and although the backscattering corrections are not equal, no correction was applied, since the correction is not too serious and the deuteron and helium ion data are presented for qualitative consideration only. No correction was made for self-absorption and self-scattering, since the weights of the samples counted were almost negligible in all instances.

RESULTS

A. Radioactive Nuclides Identified

The characteristic activities of the nuclides discussed in this section were observed in the elemental fractions separated from the irradiated copper target. References for most of the nuclides characterized may be found in the 1948 edition of "Table of Isotopes" by Seaborg and Perlman.[7] Only in the cases where information on the nuclides was published in the literature subsequent to the data given in "Table of Isotopes" will references be cited. All activities identified in the elemental fractions are discussed below and include the results from all bombardments (190-Mev deuterons, 190- and 380-Mev helium ions, and 340-Mev protons). A check of Figs. 3, 4, and 5 and the results for 190-Mev helium ions listed in part B of this section will show which individual activities were identified in each of the elemental fractions from the different bombardments.

Germanium Fraction

The activities observed in the germanium fraction from the copper irradiated with 340-Mev protons were characteristic of the light germanium isotopes. The characteristic decay periods[8] of Ge^{69} and Ge^{67} were easily resolved, and the amount of long-lived activity remaining after the shorter lived periods had decayed was comparable with that expected for the 250-day Ge^{68}. There was also a small amount of activity which showed the characteristic decay periods of Ge^{66} and its daughter Ga^{66}. Because of the limited amounts of activity formed the nuclides were characterized solely by decay periods and chemical behavior.

Gallium Fraction

The characteristic activities of Ga^{68}, Ga^{67}, and Ga^{66} were observed in the gallium fractions separated from copper irradiated with 340-Mev protons. Cross sections were estimated for the formation of these nuclides from copper. It was assumed that Ga^{68} decays entirely by positron emission, Ga^{67} decays only by orbital electron capture (the counting efficiency of the x-rays was taken as 4 percent), and Ga^{66} decays 34 percent by orbital electron capture.[9] The cross section for the formation of Ga^{68} includes any Ga^{64} formed, since resolution of the two activities was not possible.

Zinc Fraction

The characteristic activities of Zn^{65}, Zn^{63}, and Zn^{62} were observed in zinc. The Zn^{65} was counted through

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[7] G. T. Seaborg and I. Perlman, Revs. Modern Phys. **20**, 585 (1948).

[8] McCown, Woodward, and Pool, Phys. Rev. **74**, 1311 (1948).

[9] L. M. Langer and R. D. Moffat, Phys. Rev. **80**, 651 (1950).

sufficient aluminum absorber to cut out completely the particulate radiation and x-rays, and the counting efficiency of the 1.1-Mev gamma-ray was taken as one percent. The Zn^{63} was characterized by its half-life and the nuclide was assumed to decay 93 percent by positron emission and 7 percent by orbital electron capture. The Zn^{62} was assumed to decay 10 percent by positron emission and 90 percent by K-capture[10] and was counted with the 10-minute Cu^{62} daughter in equilibrium.

Copper Fraction

The activities resolved in the copper were those of Cu^{64}, Cu^{62}, Cu^{61}, and Cu^{60}. The 12.8-hour Cu^{64} was the longest lived activity identified and was assumed to have a counting efficiency of 50 percent. The 10.5-minute Cu^{62} was the shortest lived activity identified, and the nuclide was considered as decaying completely by positron emission. Cu^{61} decays 66 percent by positron emission,[11] and 66 percent was taken as the counting efficiency of the nuclide. The 25-minute Cu^{60} was resolved with precision only in the copper fractions from the 190-Mev deuteron and 380-Mev helium ion irradiations.

Nickel Fraction

The only observable activities in nickel were the 2.6-hour Ni^{65} and the 36-hour Ni^{57}. The formation of the small amount of Ni^{65} from copper irradiated with protons is probably due to the reaction $Cu^{65}(n, p)Ni^{65}$ caused by secondary neutrons and will be neglected as a spallation product from 340-Mev protons. A counting efficiency of 50 percent was used for the Ni^{65} since the nuclide decays 50 percent by positron emission and 50 percent by orbital electron capture.[12]

Cobalt Fraction

The characteristic activities of Co^{61} and Co^{55} were identified in all elemental fractions of cobalt separated. The Co^{58} and Co^{56} were identified definitely in the proton irradiations and the characteristic 72-day half-life of these activities was observed in the cobalt fraction separated from the copper irradiated with 190-Mev deuterons. The Co^{61} decayed with the characteristic 1.75-hour half-life; and since it decays by negatron (negative beta-particle) emission, no correction was necessary for the counting efficiency. The Co^{55} was easily resolvable; and since no electron capture branching has been reported, the counting efficiency was taken as 100 percent.

The fact that the Co^{58} and Co^{56} decay with equal half-lives and are both positron emitters makes their resolution difficult. The resolution of the two activities was done only for the cobalt fraction separated from the copper irradiated with 340-Mev protons. The shape of the composite positron spectrum from the cobalt fraction was determined by means of a crude beta-ray spectrometer after the 18-hour Co^{55} had been allowed to decay. The shape of the positron spectrum for a sample of pure Co^{56} which had been determined under similar conditions was available, and by subtracting the contribution of the Co^{56} positron spectrum from the composite positron spectrum, the contribution of each isotope to the total activity was obtained. The counting efficiency of the Co^{58} was taken as 15 percent and that of the Co^{56} as 100 percent.

Iron Fraction

The characteristic activities of the radionuclides Fe^{59}, Fe^{55}, Fe^{53}, and Fe^{52} were probably present in all iron fractions separated from the copper irradiated with the protons, deuterons, and helium ions. All of these activities were identified definitely only in the iron fractions separated from the copper irradiated with 340-Mev protons. The Fe^{59}, Fe^{53}, and Fe^{52} were identified in the iron fractions from the copper irradiated with deuterons, and the only yield determined for the iron from 380-Mev helium ion irradiation was the Fe^{59}. The 2.9-year Fe^{55} was assumed to decay completely by orbital electron capture[13] and a counting efficiency of 10 percent was taken for the x-rays. The Fe^{53} was assumed to decay 100 percent by positron emission. The Fe^{52} was counted in equilibrium with its 21-minute Mn^{52} daughter. By determining the amount of 21-minute Mn^{52} in equilibrium with the Fe^{52} and milking the 5.8-day Mn^{52} which grows into the iron fraction, an estimation was made of the amount of positron emission and orbital electron capture branching for the Fe^{52}. It was found that the nuclide decays approximately 65 percent by positron emission and 35 percent by orbital electron capture.

Manganese Fraction

The radionuclides Mn^{56}, Mn^{54}, Mn^{52}, and Mn^{51} were identified in manganese. The Mn^{56} was assumed to decay completely by negatron emission. The Mn^{54} was counted through sufficient aluminum absorber to cut out all the particulate radiation and x-rays, and a value of 0.8 percent was assumed as the counting efficiency of the 0.8-Mev gamma-ray. Thirty-five percent was taken as the positron branching of the 5.8-day Mn^{52}, and the yield for manganese mass number 52 is reported on the basis of this activity. The Mn^{51} was assumed to decay completely by positron emission.

Chromium Fraction

The two activities identified in chromium were those of Cr^{51} and Cr^{49}. Since the Cr^{51} decays by orbital elec-

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[10] R. W. Hayward, Phys. Rev. **78**, 87(A) (1950).

[11] Owen, Cook, and Owen, Phys. Rev. **78**, 686 (1950).

[12] G. Friedlander and M. L. Perlman, Brookhaven National Laboratory Report 51 (1950), unpublished.

[13] G. L. Brownell, Massachusetts Institute of Technology Progress Report 37 (1949), unpublished.

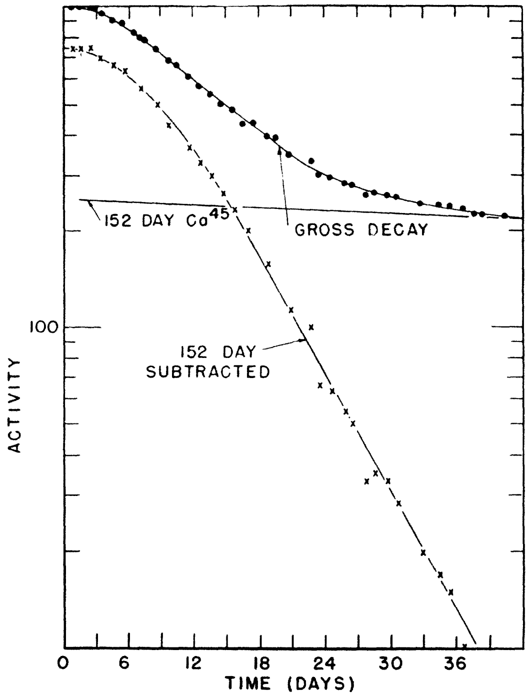

FIG. 1. Decay of calcium fraction separated from copper irradiated with 340-Mev protons.

tron capture and gamma-ray emission, the counting efficiency of this nuclide would have had to be estimated roughly, but it was possible to determine the counting efficiency directly by milking Cr^{51} from a known amount of Mn^{51} which had decayed. With the assumption that Mn^{51} decays 100 percent by positron emission, the Cr^{51} was found to have a counting efficiency of 2.6 percent when counted in a precipitate of barium chromate. The Cr^{49} was assumed to decay with no orbital electron capture branching.

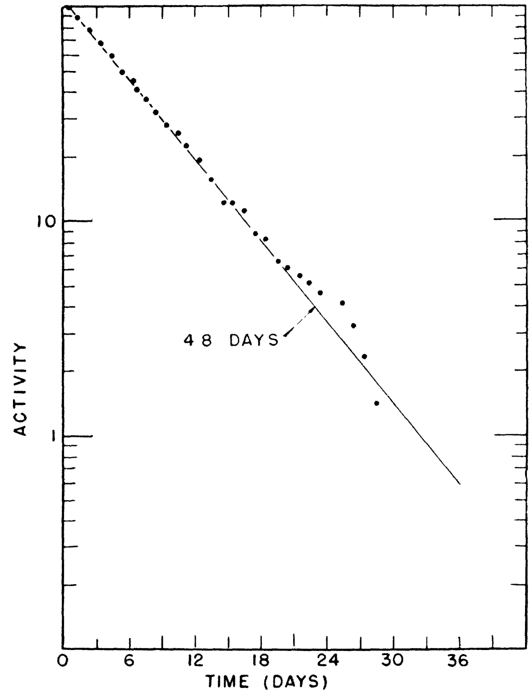

FIG. 2. Decay of calcium fraction separated from copper irradiated with 340-Mev protons counted through sufficient absorber to cut out the beta-particles of Ca^{45} and the Sc^{47} daughter.

Vanadium Fraction

The yield for vanadium is based on V^{48} which was assumed to decay 58 percent by positron emission.

Titanium Fraction

The only activity identified in titanium was that of the 3.08-hour Ti^{45} and the yield was calculated on the basis of the nuclide decaying entirely by positron emission.

Scandium Fraction

Several activities were observed in the scandium fraction separated from the copper irradiated with 340-Mev protons, and these activities were identified as belonging to Sc^{48}, Sc^{47}, Sc^{46}, Sc^{44m}, and a mixture of the 3.9-hour Sc^{44} and Sc^{43}. The 3.9-hour and 85-day activities were easily resolvable from the decay curves, but the resolution of the 2.44-day Sc^{44m}, the 3.4-day Sc^{47}, and the 44-hour Sc^{48} was more difficult. The contribution of the 2.44-day Sc^{44m}, with its 3.92-hour positron daughter in equilibrium, to the total activity was resolved approximately with the crude beta-ray spectrometer. With the positron activity resolved, the remaining activity was almost entirely that of the 3.4-day Sc^{47}, and the small amount of Sc^{48} activity resolved was so uncertain that the yield of this nuclide is not reported. The yield for Sc^{43} includes the 3.9-hour Sc^{44}, and these nuclides were assumed to decay completely by positron emission. The yield for Sc^{44} was calculated on the basis of the 2.44-day isomer.

Calcium Fraction

Only two activities were observed in the calcium fraction separated from the copper irradiated with 340-Mev protons. One was the 150-day Ca^{45} and the other was a 4.8±0.2-day beta-emitter with an energy of about 1.2 Mev as determined by an aluminum absorption measurement. This activity is probably the 5.8-day calcium activity reported as Ca^{47} by Matthews and Pool.[14] The growth of a 3.4-day scandium was observed in the decay of the calcium fraction and the scandium daughter was milked from the fraction. The aluminum absorption measurement of this 3.4-day scandium daughter showed it to be the activity assigned to Sc^{47}. The decay curve of the calcium fraction is shown in Fig. 1, and Fig. 2 shows the decay of the calcium fraction counted through sufficient aluminum absorber to

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[14] D. E. Matthews and M. L. Pool, Phys. Rev. **72**, 163 (1947).

cut out the beta-particles of the Ca^{45} and the Sc^{47} daughter. Thus, the decay sequence is

$$Ca^{47} \xrightarrow[4.8\text{ days}]{\beta^-} Sc^{47} \xrightarrow[3.4\text{ days}]{\beta^-} Ti^{47}.$$

Chlorine Fraction

The characteristic activities of Cl^{39} and Cl^{38} were identified in all the chlorine fractions separated from the irradiated copper, but Cl^{34} was identified only in the chlorine fraction separated from the copper irradiated with 340-Mev protons. The resolution of the Cl^{38} and Cl^{34} was accomplished by determining the relative amounts of positrons and negatrons present by means of the crude beta-ray spectrometer. The Cl^{39} was resolved directly from the gross decay curve. The Cl^{39}, Cl^{38}, and Cl^{34} were assumed to have counting efficiencies of 100 percent.

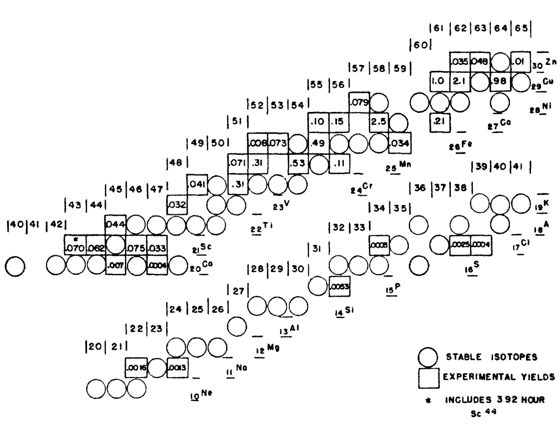

FIG. 3. Experimental yields from copper irradiated with 340-Mev protons. Yields are relative to Cu^{61}.

Phosphorus Fraction

The only activity observed in phosphorus was that of the 14.3-day P^{32}.

Sodium Fraction

Two activities were observed in the sodium fraction. The 14.8-hour Na^{24} was definitely identified, but the 2.6-year Na^{22} could be identified only on the basis of the decay during a 120-day period.

B. Yields of Spallation Products

Plots of the observed yields of the spallation products are shown in Figs. 3, 4, and 5. The yields are given relative to Cu^{61} which was arbitrarily assigned a yield of 1.0. The numbers listed for the various nuclides represent the ratios of the numbers of atoms of the particular nuclides to the number of atoms of the Cu^{61} formed in the irradiated copper, and hence the numbers represent the ratios of the cross sections for formation from elemental copper. The cross section for the formation of Cu^{61} from elemental copper irradiated with 340-Mev protons is 2.3×10^{-26} cm^2 as determined by a bombardment of copper in the external proton beam where the beam intensity was accurately measured. The cross section for formation of Cu^{61} from copper irradiated with 190-Mev deuterons is about 6×10^{-26} cm^2. This value is an average value of about six different deuteron irradiations, and the value was obtained by using an estimated value (one microampere) for the beam intensity. The cross sections for the formation of Cu^{61} from copper irradiated with 190-Mev and 380-Mev helium ions were not estimated since only one bombardment was done at each energy.

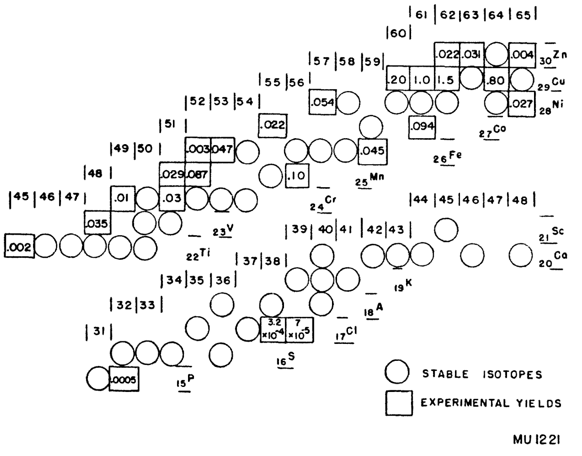

FIG. 4. Experimental yields from copper irradiated with 190-Mev deuterons. Yields are relative to Cu^{61}.

The data for the spallation products from copper irradiated with 190-Mev helium ions are not plotted since only a few values were determined. The relative yields were Cu^{61}, 1.0; Cu^{64}, 0.84; Cl^{38}, 0.0006; and no Cl^{34} was found.

The sum of the yields for the nuclides Co^{56} and Co^{58} from copper bombarded with 190-Mev deuterons was estimated to be about 1.0 on the basis of a counting efficiency of about 15 percent for the combination of

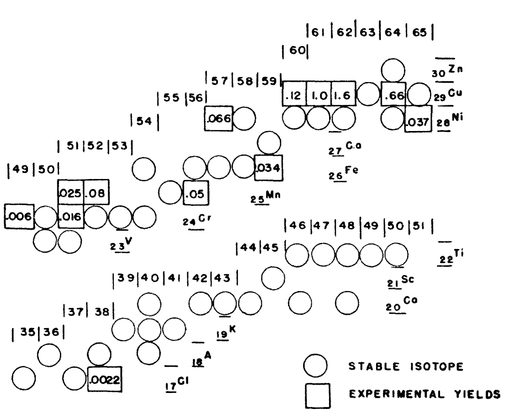

FIG. 5. Experimental yields from copper irradiated with 380-Mev helium ions. Yields are relative to Cu^{61}.

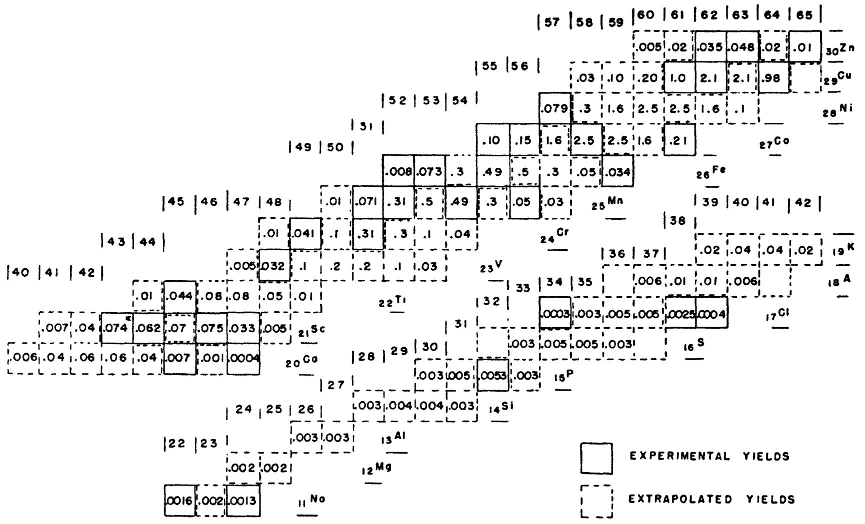

FIG. 6. Experimental, interpolated, and extrapolated yields from copper irradiated with 340-Mev protons. Yields are relative to Cu^{61}.

the activities. This is consistent with assuming that the activity is essentially all Co^{58}.

It should be emphasized that the yields for 340-Mev protons are in no way relative to the yields for 190-Mev deuterons, 190-Mev helium ions, or 380-Mev helium ions, since the cross section for formation of Cu^{61} from elemental copper is known with accuracy only in the case of the 340-Mev proton irradiations.† Many of the values for the reported relative yields are very dependent upon the counting efficiencies assumed (e.g., orbital electron capture), and when these efficiencies are better known the yields can be recalculated.

C. Yields of Secondary Reactions

The over-all or composite cross sections for formation of the gallium isotopes are as follows; Ga^{68} approximately 1×10^{-29} cm², Ga^{67} about 6×10^{-30} cm², and Ga^{66} approximately 1×10^{-29} cm².

The cross section for formation of Ge^{67}, Ge^{68}, and Ge^{69} are lower than those for the formation of the gallium isotopes, and it is estimated that these are all of the same order of magnitude, about 10^{-31} cm².

DISCUSSION

A. General Observations

The wide distribution and large number of radionuclides formed as spallation products of copper are immediately apparent from a study of Figs. 3, 4, and 5. The identification of Cu^{64}, Co^{58}, Mn^{54}, and Sc^{46}, shielded from formation by decay, is good evidence for believing that the observed nuclides are mainly primary products from the splitting up of the excited nuclues. The radionuclides with the largest neutron deficiencies or neutron excess are formed in lowest yield, and the yield for a given Z rises for the nuclides nearest the region of stability. Extrapolation of this effect to the region of stability indicates that the stable nuclides are formed in high yield. Thus the emission of almost exclusively neutrons (or protons) from a moderately excited nucleus, followed by a series of rapid positron (or negatron) decays, is a relatively rare event.

This picture of high energy nuclear reactions induced in copper is consistent with the results of studies of the spallation of arsenic[3] and antimony[4] with high energy particles. The observation that the radionuclides with the largest neutron deficiencies or neutron excess are formed in lowest yield may seem to be inconsistent with the results from studies of the spallation products from antimony irradiated with high energy particles. Lindner and Perlman[4] found that the yields of neutron deficient nuclides are larger than the yields of nuclides with an excess of neutrons. The results are consistent, however, when consideration is given to the fact that the probability of emission of charged particles from an excited nucleus is a function of the potential barrier, and is therefore a function of atomic number. The ratio of the probability of neutron emission to the probability of charged particle emission should increase with atomic number, and hence the yields of neutron deficient nuclides should rise as the atomic number of the target increases. As would be expected, however, the yields of isotopes with an excess of neutrons becomes higher than the yields for the neutron deficient isotopes of an element whenever it becomes energetically possible to form the element only by the emission of alpha-particles (or larger fragments) from the target nucleus.

The majority of the observed yield is found in the region of the target nucleus, indicating that reactions requiring much less than the maximum amount of

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† *Note added in proof:* Recent work by W. B. Hutchins of this Laboratory has yielded fairly accurate values for the yield of Cu^{61} with 190-Mev deuterons (3.8×10^{-26} cm²) and with 380-Mev helium ions (about 5.2×10^{-26} cm²).

excitation available to the nucleus are more probable; this is discussed in some detail in the next section.

It should be possible, knowing the general distribution of spallation products for a given Z, to extrapolate and interpolate yields for the nuclides not directly observed as spallation products of copper. The data from the spallation of copper irradiated with 340-Mev protons have been treated in this manner, as shown in Fig. 6. It was assumed that the most probable yield for a given Z is a region 2 mass units wide and that the yields 1 mass unit on either side of this region are formed in yields about 1.5 times lower than the values in the region of the maximum yield, that spallation yields 2 mass units removed are about ten times lower than the maximum, and that yields 3 mass units removed are about a factor of 20 lower than the maximum.

A summation of these extrapolated and interpolated yields for 340-Mev protons gives a total yield relative to Cu^{61} of about 30, and using the measured value of 2.3×10^{-26} cm^2 for the cross section for formation of the Cu^{61}, the total spallation cross section for copper is about 0.7×10^{-24} cm^2. The geometrical cross section for copper is about 0.94×10^{-24} cm^2.

The difference between the observed total cross section and the geometrical cross section for copper is largely the result of the nuclear transparency for 340-Mev protons. The mean free path in nuclear matter for 340-Mev protons has been estimated to be about 4×10^{-13} cm (see part B of this section). The nuclear transparency for a given mean free path can be calculated on a geometrical basis, and if the value $R=1.37A^{\frac{1}{3}}\times 10^{-13}$ cm is used for the nuclear radius (the constant 1.37 is used since this constant was used in estimating the mean free path) the calculated nuclear transparency of copper for 340-Mev protons is 20 percent. The observed transparency is 30 percent. The discrepancy between the observed and calculated transparencies probably can be explained by the approximate nature of the estimation of the total reaction cross section.

The data in Fig. 6 show that about 80 percent of the spallation yields are concentrated in the elements copper, nickel, and cobalt. Outside the immediate region of the bombarded nucleus, the yield values in the region of most probable yield for a given Z are a decreasing function of Z indicating that nuclear reactions requiring very high excitations of the nucleus are much less probable than reactions requiring perhaps some 25 to 50 Mev of excitation.

B. Mechanisms of High Energy Spallation

The accepted and experimentally supported theory of nuclear reactions at low energies (<40 Mev) involves the formation of a compound, excited nucleus;[15] the incident particle is captured by the target nucleus to form a compound nucleus with an excitation energy equal to the kinetic energy plus the binding energy of the incident particle. The excitation is then dissipated as a separate step by the evaporation of nucleons to form the product nucleus. Using only this picture of the compound nucleus, one would expect that bombardment with particles of several hundred Mev of energy would lead to very low yields of nuclides which are within a few mass units of the target nucleus, since emission of a large number of particles from the highly excited compound nucleus would be much more probable. On the contrary, however, the data presented in the preceding sections show that a large majority of the reactions induced in copper irradiated with 340-Mev protons, 190-Mev deuterons, and 190- and 380-Mev helium ions lead to products which differ from the target nucleus by a loss of only several nucleons.

Serber has suggested a mechanism which very satisfactorily explains the observed facts.[6] Irradiation with high energy protons, deuterons, and helium ions can be considered on essentially the same basis, since bombardment with 190-Mev deuterons or with 190- and 380-Mev helium ions can be regarded as a simultaneous bombardment by the several individual nucleons (neutrons and protons) making up the incident particle. The binding of the nucleons in the incident particle is important mainly in giving a spatial correlation between them. Serber points out that the collision time between a high energy incident nucleon and a nucleon in the nucleus is short compared to the time of collision of the nucleons in the nucleus, suggesting that collisions between incident nucleons and the individual nucleons in the nucleus are of primary importance.

Since the individual nucleon-nucleon collisions are important, the high energy nuclear reactions can be interpreted in terms of the high energy scattering between nucleons. Consideration of high energy scattering leads to two conclusions. First, at sufficiently high energies the nucleus becomes partially transparent to the bombarding particles, and second, the incident particle loses only a fraction of its energy in the collisions. Serber estimated that the mean kinetic energy transfer to the struck particle by a 100-Mev nucleon is about 25 Mev and that the mean free path for this 100-Mev nucleon traversing nuclear matter is about 4×10^{-13} cm. Since the struck particles have a shorter mean free path than the incident one, they will usually distribute their energy to other nucleons through collisions, but it is possible that these struck nucleons can escape from the nucleus with little or no energy loss. The subsequent behavior of the excited nucleus can be described in terms of an evaporation model, with the excitation energy dissipated by boiling off particles with several Mev of kinetic energy each.

The high spallation yields in the immediate region of the target nucleus are probably formed by reactions in which only single nucleon-nucleon collisions take place. In the case of the deuteron and helium ion yields, this means that only one of the incident nucleons undergoes a collision in these reactions. The minimum energy

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[15] N. Bohr, Nature **137**, 344 (1936).

transfer from a single nucleon-nucleon collision would take place when such a collision occurs near the edge of the nucleus, and the struck nucleon escapes from the nucleus with little or no energy transfer to the nucleus.

A larger portion of the energy of the incident particle may be left with the nucleus if multiple nucleon-nucleon collisions take place. Both of the nucleons in the deuterons may undergo nucleon-nucleon collisions (or, in the case of the helium ion, two or three or four of its constituents may undergo such collisions), and each of these impinging nucleons after such collisions may either escape or collide with additional nucleons in the target nucleus. This would lead in the extreme to products resulting from nuclei excited to almost the full energy of the impinging proton, deuteron, or helium ion, amounting essentially to the formation of a compound nucleus in the ordinary sense. Thus the target may receive excitation energy from about zero up to the full energy of the projectile.

It is difficult to estimate the energetic requirements for formation of spallation products such as Cl^{38} and Na^{24}. It is apparent from energetic considerations that Cl^{38} cannot be produced in copper irradiated with 190-Mev deuterons by a reaction in which only single nucleons (neutrons and protons) are emitted. The threshold for formation of Cl^{38} from copper by the reaction $Cu^{63}(p, pn6\alpha)Cl^{38}$ in which the maximum number of alpha-particles is emitted is roughly 110 Mev, but recent experimental results indicate that fragments larger than alpha-particles are emitted among the competitive products of nuclear reactions,[16–18] and the energetic requirements for these reactions are even lower than for a series of alpha-particle emissions. The observed yield for any given spallation product of copper probably actually represents the sums of the yields of several types of nuclear reactions which form the given nuclide. The fact that the observed yields for Cl^{38} from 190-Mev deuterons and 190-Mev helium ions are about a factor of six lower than those from 340-Mev protons and 380-Mev helium ions (the relative yields for chlorine from the copper irradiated with deuterons and helium ions should be accurate to at least a factor of two) indicates that nuclides in the region of Cl^{38} are probably formed mainly by reactions which require an appreciable part of the entire energy of the whole incident particle.

It is not difficult to visualize, in terms of an average energy loss of about 25 Mev per nuclear collision and a mean free path (4×10^{-13} cm) of about $\frac{3}{4}$ the nuclear radius for copper (6×10^{-13} cm) or equal to the nuclear radius as suggested by Goldberger,[19] mechanisms by which the 190-Mev deuterons, and 190- and 380-Mev helium ions might impart large portions of their total energy to the copper nucleus. It is difficult, however, to understand how a 340-Mev proton could impart large amounts of excitation to the nucleus with a fair probability if it transfers in a single nucleon-nucleon collision an average kinetic energy of only 25 Mev as would be predicted by Serber and has a mean free path about equal to the nuclear diameter for copper as estimated by Yamaguchi.[20]

In the light of some recent results of high energy scattering experiments,[21,22] it is possible to actually estimate the mean free path of 340-Mev protons in nuclear matter and to estimate the average kinetic energy loss of a 340-Mev proton in one individual collision with a nucleon in a copper nucleus and to see if the values estimated for the average kinetic energy loss and mean free path are more in line with high energy transfers having a fair probability.

The experimental data on proton-proton scattering at 340 Mev[21] show that the scattering cross section does not follow an expected $1/E$ dependence, and that the cross section is considerably higher than would be expected if it varied as $1/E$. Also the results indicate that the cross section is practically isotropic between 0° and 90° in the laboratory system. This means that high energy transfers in single proton-proton collisions have a relatively high probability. By extrapolating the data from neutron-proton scattering with 260-Mev neutrons[22] to 340 Mev and averaging the cross sections and energy transfers for $n-p$ and $p-p$ scattering over the different scattering angles, it is possible to estimate a mean energy loss for the 340-Mev protons of about 70 Mev per collision in a copper nucleus. On the basis of these scattering data the mean free path of a 340-Mev proton in nuclear matter has been estimated to be about the same as that for a 95-Mev nucleon,[23] about 4×10^{-13} cm. With the mean kinetic energy transfer per single nucleon-nucleon collision being about 70 Mev, it is not difficult to understand how large amounts of excitation are imparted to the nucleus. Incidentally, averaging in a similar manner for $n-p$ scattering with 90-Mev neutrons[24] and $p-p$ scattering with 105-Mev protons[25] gives an average energy loss for $\sim$100-Mev protons of about 20 Mev per collision in a copper nucleus.

Recent calculations based on an evaporation model for the emission of the particles from the excited nucleus indicate that the emission of alpha-particles from the excited nucleus should be a fairly probable occurrence and that the evaporation of particles should lead to products along the region of stability.[26,27] The observed spallation yields are in agreement with these calcula-

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[16] S. Wright, Phys. Rev. **77**, 742(A) (1950).

[17] L. Marquez and I. Perlman, Phys. Rev. **81**, 953 (1951).

[18] R. E. Batzel and G. T. Seaborg, Phys. Rev. **79**, 528 (1950); **82**, 607 (1951).

[19] M. L. Goldberger, Phys. Rev. **74**, 1269 (1948).

[20] Y. Fujimoto and Y. Yamaguchi, Prog. Theor. Phys. **5**, 141 (1950).

[21] O. Chamberlain and C. Wiegand, Phys. Rev. **79**, 81 (1950).

[22] Kelly, Leith, Segrè, and Wiegand, Phys. Rev. **79**, 96 (1950).

[23] S. Fernbach, private communication.

[24] Hadley, Kelly, Leith, Segrè, Wiegand, and York, Phys. Rev. **75**, 351 (1949).

[25] R. W. Birge, Phys. Rev. **80**, 490 (1950).

[26] K. J. Le Couteur, Proc. Phys. Soc. (London) **A63**, 259 (1950).

[27] Y. Yamaguchi, Prog. Theor. Phys. **5**, 142 (1950).

tions since the yields apparently do have a definite maximum of most probable yield for a given Z about 2 mass units wide and a line drawn along this region of most probable yield would be drawn through the region of stability. The very high yield of Mn^{52} compared to Fe^{52} for the isobaric pair $Fe^{52}-Mn^{52}$, apparent in both the 190-Mev deuteron and 340-Mev proton yields, indicates that there is a much larger difference in the yields than would be expected from the regular trends of the spallation yields, and it seems logical to explain the difference observed in terms of alpha-particles being boiled off from the excited target nucleus as suggested by Helmholz *et al.*[5] If the Fe^{52} and Mn^{52} are formed by reactions initiated by noncapture processes (processes in which the proton or the deuteron loses energy to the nucleus but is not retained by the nucleus) the reactions for the formation of Fe^{52} and Mn^{52} should, perhaps, be written $Cu^{63}(p, pp6n\alpha)Fe^{52}$ or $Cu^{63}(d, dp6n\alpha)Fe^{52}$ and $Cu^{63}(p, p3n2\alpha)Mn^{52}$ or $Cu^{63}(d, d3n2\alpha)Mn^{52}$. On this basis the yields indicate that the probability of emission of two alpha-particles plus three neutrons is much higher than that for the emission of one alpha-particle, six neutrons, and a proton. Although this effect shows up only in special cases like this where such direct comparisons can be made, it is probably a general phenomenon.

It is also possible on the basis of the spallation yields to say something about the probability of exchange reactions, for example, reactions in which the incident proton or the proton of the incident deuteron undergoes a charge exchange with a neutron in the copper nucleus and emerges as a neutron. The high yields of copper relative to the corresponding zinc isotopes indicate that these exchange reactions do not predominate.

The decreasing yields of individual nuclei far removed from the target nuclei are, of course, resulting in part from statistical considerations and the greater number of possibilities. A larger number of different combinations of emitted particles is possible from a highly excited nucleus than from a nucleus excited to a smaller extent. Thus, even if the probabilities of exciting a nucleus to say 200 and 100 Mev were the same, the yield of an individual product resulting from the higher excitation would be lower than one resulting from the lower excitation.

It is interesting to note that no observable yield of Cu^{67} was obtained from copper irradiated with 380-Mev helium ions. This nuclide can be formed only by an $(\alpha, 2p)$ reaction on Cu^{65}.

In the light of the foregoing discussion of the emission of fragments among the competitive products of spallation reactions it is possible to suggest mechanisms for the formation of the observed gallium and germanium activities. The mechanism for the formation of gallium is probably

$$_{29}\mathrm{Cu}+p\rightarrow \mathrm{fragments}+{}_{2}\mathrm{He}$$

$$_{29}\mathrm{Cu}+{}_{2}\mathrm{He}\rightarrow {}_{31}\mathrm{Ga}+xn,$$

and for the formation of germanium:

$$_{29}\mathrm{Cu}+p\rightarrow \mathrm{fragments}+{}_{3}\mathrm{Li}$$

$$_{29}\mathrm{Cu}+{}_{3}\mathrm{Li}\rightarrow {}_{32}\mathrm{Ge}+xn.$$

These mechanisms have been postulated[28, 17] previously to explain similar reactions.

CHEMICAL SEPARATION PROCEDURES

The irradiated copper foil was dissolved in hot concentrated nitric acid or hydrochloric acid and hydrogen peroxide, and milligram amounts of the elements calcium through zinc were then added to act as carrier for the elemental fractions. Known amounts of the elemental fractions to be separated were added so that a quantitative estimation of the amounts of the original carrier lost during the chemical separation procedures could be made in the case of the proton bombardment, and the macro amounts of the other elements were added to act as holdback agents. The chemical separation procedures included distillation, extraction, and precipitation operations, and these procedures were carried out usually with volumes of 5 to 15 ml.

In general the degree of radiochemical purification required depends on the relative spallation yield and the counting efficiencies of the radionuclides in the elemental fraction. If the nuclides are formed in high yield and have a high counting efficiency, the degree of radiochemical purification need not be too high, but if the spallation yields are low or the counting efficiencies are low, the degree of purification must be high.

Usually the particular elements to be investigated were separated successively from the entire dissolved target solution. Since different combinations of elements were removed in each investigation, the chemical separation procedures as a whole varied from bombardment to bombardment. The essential steps for the separation and purification of the elemental fractions were the same, and the over-all procedures differed only in the order in which the separations were used. For this reason only the important steps necessary for the chemical separation and purification of the various elemental fractions are discussed. The final precipitates, if the final step in the chemical separation procedure is a precipitation, were usually dissolved, and aliquots were taken from the solution for counting.

Germanium

The irradiated copper target was dissolved in a minimum amount of concentrated nitric acid, and 10 mg of germanium carrier was added to the solution. The solution was transferred to a glass still, and 20 ml of 6 N HCl was added. The hydrochloric acid solution was distilled until only 2 to 3 ml of solution remained in the still. The distillate was collected in a flask immersed

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[28] D. H. Templeton and I. Perlman, Abstracts of Papers (Meeting of Am. Chem. Soc., Portland, Oregon, September 13–17, 1948), pp. 55–60.

in an acetone dry ice bath. Hydroxylamine hydrochloride was added to the distillate to destroy any chlorine, and hydrogen sulfide was bubbled into the cold solution to precipitate germanium sulfide. The precipitate was washed with water and then dissolved in 0.5 ml of concentrated ammonium hydroxide. The ammoniacal solution was diluted to 10 ml and transferred to a clean glass still. Ten ml of concentrated hydrochloric acid was added, and the distillation of the germanium tetrachloride was repeated. The germanium was precipitated in the final form as the sulfide and transferred to a plate for counting.

Gallium

The solution of the copper target, with 5 mg each of iron and gallium carrier added, was adjusted to 7.75 N in hydrochloric acid. The gallium and iron were extracted from the hydrochloric acid solution with about 20 ml of isopropyl ether. The ether layer was washed four times with 6 ml portions of 7.75 N HCl, and the iron and gallium were extracted from the ether layer with water. The extract was then adjusted to 1 N in sodium hydroxide, and the ferric hydroxide precipitate was removed by centrifugation. Two to three mg of iron carrier was added and the ferric hydroxide precipitate again removed. The sodium hydroxide solution containing the gallium was adjusted to 7.75 N in hydrochloric acid, and the gallium was extracted with isopropyl ether. The ether layer was washed four times with 6 ml portions of 7.75 N HCl and the gallium was extracted from the ether layer with water. Two to three mg of iron carrier as ferric chloride was added to the extract and the solution was adjusted to 1 N in sodium hydroxide. The ferric hydroxide was removed by centrifugation, and the sodium hydroxide solution was adjusted to 7.75 N in hydrochloric acid. The ether extraction was repeated, and the gallium was reextracted into water. Gallium hydroxide was precipitated from the water extract by adjusting the pH of the solution to about 5.5 with sodium hydroxide.

Zinc

The dissolved target solution with carriers added was adjusted to 2 N in hydrochloric acid and the copper precipitated as the sulfide. The hydrogen sulfide was expelled and the solution neutralized with ammonium hydroxide. The solution was then adjusted to pH 3 with dilute sulfuric acid, and the zinc was precipitated as the sulfide. The precipitate was dissolved in dilute hydrochloric acid and the hydrogen sulfide expelled by boiling. Three milligrams of iron carrier was added and the solution adjusted to 1 N in sodium hydroxide. The ferric hydroxide was removed by centrifugation, and the ferric hydroxide precipitation was repeated. The solution was then adjusted to 1 N in hydrochloric acid and the zinc precipitated by adding 4 ml of a solution of ammonium mercuric thiocyanate prepared by adding 16 g of ammonium thiocyanate and 13.5 g of mercuric chloride to 250 ml of water. The zinc mercuric thiocyanate precipitate was washed with a solution containing ammonium mercuric thiocyanate and then transferred to an aluminum plate to be dried and weighed in this form.

Copper

The dissolved target solution with carriers added was adjusted to 2 N in hydrochloric acid and the copper precipitated as the sulfide. The sulfide precipitate was dissolved in hot concentrated nitric acid, the sulfide expelled or oxidized, and the nitrate destroyed by boiling with concentrated hydrochloric acid. The solution containing the copper was adjusted to 0.5 N in hydrochloric acid, sulfur dioxide bubbled through the solution to reduce the copper, and then sodium thiocyanate added to precipitate copper as the cuprous thiocyanate. The cuprous thiocyanate was washed with water and then dissolved in nitric acid. The nitrate was again destroyed by boiling with concentrated hydrochloric acid and the solution again adjusted to 0.5 N in hydrochloric acid. The copper was then precipitated in the final form as the cuprous thiocyanate.

Nickel

The solution remaining, after the copper had been removed as the sulfide, was boiled to expel the hydrogen sulfide and the iron oxidized with a few drops of nitric acid. The solution was then made alkaline with ammonium hydroxide and the precipitated hydroxides removed. The precipitate was washed with a hot solution of ammonium chloride and the wash combined with the supernate from the precipitation. Three mg of iron carrier was added and the ferric hydroxide removed by centrifugation. The solution was made slightly acid with acetic acid, and 2 ml of a 1 percent alcoholic solution of dimethylglyoxime was added to precipitate the nickel as nickel dimethylglyoxime. The precipitate was washed with water and then dissolved in concentrated hydrochloric acid. One to 2 mg portions of copper, cobalt, and manganese were added to act as holdback carriers, the solution neutralized with ammonium hydroxide, and then made slightly acid with acetic acid. Dimethylglyoxime was again added to make sure that the precipitation of the nickel dimethylglyoxime was complete, and the precipitate was washed with water. The nickel was weighed as the nickel dimethylglyoxime.

Cobalt

After the copper had been removed as the sulfide, the solution was boiled to remove the hydrogen sulfide and then neutralized with potassium hydroxide. The solution was adjusted to 3 N in acetic acid, and 3 to 4 ml of a saturated solution of potassium nitrite acidified with acetic acid was added to the hot solution containing the cobalt. The precipitate of potassium cobaltinitrite was allowed to settle in a steam bath, removed by centrifugation, and washed with a 5 percent potassium nitrite solution acidified with acetic acid. The precipitate was dissolved in hydrochloric acid, and holdback carriers for zinc, copper, nickel, and manganese were added. The solution was then neutralized with potassium hydroxide and the cobalt again precipitated as potassium cobaltinitrite. The cobalt was weighed as the potassium cobaltinitrite.

Iron

The solution of the copper target, with 5 mg of iron carrier added, was adjusted to 7.75 N in hydrochloric acid and the iron extracted with isopropyl ether. The ether layer was washed four times with 6 ml portions of 7.75 N HCl, and the iron was extracted from the ether layer with water. The solution was made alkaline with 1 N NaOH and the ferric hydroxide precipitate separated by centrifugation. The precipitate was dissolved in hydrochloric acid and the iron again extracted from 7.75 N HCl with isopropyl ether. The ether layer was again washed with 7.75 N HCl and the iron extracted from the ether layer with water. The iron was analyzed by a colorimetric method.

Manganese

The solution of the target, to which 5 mg of manganese carrier and holdback carriers for the other elements had been added, was adjusted to 2 N in hydrochloric acid and the copper removed as the sulfide. The supernate was made alkaline with ammonium hydroxide and the alkaline sulfides precipitated. The sulfide precipitate was dissolved in concentrated nitric acid and fuming nitric acid added to make the volume up to about 5 ml. Two or three crystals of potassium chlorate were added, and the solution was boiled gently for a few minutes to precipitate manganese dioxide. The precipitate was removed by centrifugation, washed with water, and then dissolved in one drop nitric acid and one drop of hydrogen peroxide. Holdback carriers for zinc, copper, nickel, cobalt, iron, and chromium were added and the manganese was again precipitated as manganese dioxide from concentrated nitric acid. The manganese was analyzed by weighing as manganese dioxide.

Chromium

The steps for the chemical separation of chromium were the same as those given for the separation of the manganese down to the point where the manganese was first removed as manganese dioxide. At this point the chromium was in the form of the chromate and remained in the supernate after the manganese dioxide was removed by centrifugation. The nitric acid solution containing the chromate was adjusted to 0.2 N in nitric acid and the solution cooled in an ice bath. Two to three drops of 30 percent hydrogen peroxide were added to form the blue peroxychromic acid, and the peroxychromic acid was extracted with diethyl ether. The ether layer was washed twice with 5 ml portions of water containing a drop of nitric acid. The peroxychromic acid was removed from the ether layer by adding a solution of 0.5 N NaOH which breaks down the peroxychromic acid and forms the chromate. The ether was removed by evaporation, and the excess hydrogen peroxide was destroyed by boiling the solution. The solution was made slightly acid with acetic acid, and the barium was precipitated as the chromate by adding 0.5 N $BaCl_2$ dropwise to the hot solution of the sodium chromate. The chromium was weighed as barium chromate.

Vanadium

The vanadium was usually separated just subsequent to the extraction of the chromium as the blue peroxychromic acid as described in the preceding section on chromium. The solution containing the vanadium was almost neutralized with sodium hydroxide and then was poured into 10 ml of a hot solution of 1 N NaOH. The hydroxide precipitate was removed by centrifugation and then washed with 4 ml of hot 1 N NaOH. Two mg each of iron and titanium carrier were then added to the solution and the hydroxides precipitated. The supernatant solution containing the vanadium was boiled to reduce the volume and then made slightly acid with acetic acid. Lead acetate was added to precipitate the vanadium as lead vanadate, and the precipitate was washed with a dilute solution of lead acetate made slightly acid with acetic acid. The lead vanadate was dissolved in nitric acid and the solution adjusted to 2 N in nitric acid. The lead was precipitated as the sulfide, and the sulfide was expelled by boiling the solution. Five mg of chromium carrier was added and sulfur dioxide was passed through the solution to reduce the vanadium and chromium. The solution was almost neutralized with sodium hydroxide and then poured into a boiling solution of 1 N NaOH to precipitate the chromium hydroxide. The chromium hydroxide was removed by centrifugation, and the vanadyl ion was oxidized to the vanadate state with hydrogen peroxide. Vanadium was then precipitated as lead vanadate from a solution slightly acid with acetic acid. The vanadium was analyzed colorimetrically.

Titanium

After the copper had been removed as the sulfide, the solution with the carriers added was boiled to remove the hydrogen sulfide, and the solution was made alkaline with ammonium hydroxide to precipitate the hydroxides of iron, scandium, and titanium. The precipitate was washed with hot, dilute ammonium hydroxide and then dissolved in hydrochloric acid. The solution was then adjusted to 0.5 N in hydrochloric acid and scandium precipitated as the fluoride by adding 0.3 ml of 27 N HF. After allowing the precipitate to settle for ten minutes on a steam bath, the scandium fluoride was removed by centrifugation, and the supernatant was made alkaline with ammonium hydroxide. The combined titanium and ferric hydroxide precipitate was removed, dissolved in nitric acid and adjusted to 1.6 N in nitric acid. Five ml of a solution of potassium iodate was added and the titanium separated as potassium titanium iodate. The precipitate was washed with a dilute solution of the potassium iodate. The iodate was destroyed by bubbling sulfur dioxide into the precipitate mixed with a few ml of dilute hydrochloric acid. Ammonium hydroxide was added to precipitate the titanium hydroxide; the precipitate was removed by centrifugation and then dissolved in hydrochloric acid. Five mg of scandium carrier was added, and the scandium was precipitated as scandium fluoride from a 0.5 N solution of hydrochloric acid as before. The titanium was again precipitated as the hydroxide and the precipitate dissolved in nitric acid. The solution was again adjusted to 1.6 N in nitric acid and the potassium titanium iodate again precipitated. The titanium was analyzed colorimetrically.

Scandium

The steps in the separation procedure for scandium are the same as those for titanium down to the point where the scandium fluoride is removed. The fluoride precipitate was washed with 0.5 N HCl containing one drop of 27 N HF. Sulfuric acid was used to dissolve the scandium fluoride and the fluoride ion was removed by fuming the scandium solution with a small amount of concentrated sulfuric acid. The sulfuric acid solution was made alkaline with ammonium hydroxide and the scandium hydroxide precipitate removed by centrifugation. The hydroxide was dissolved in hydrochloric acid and the solution adjusted to 0.5 N in hydrochloric acid. Scandium fluoride was then precipitated by adding 0.3 ml of 27 N HF, and the precipitate was allowed to settle on a steam bath. The precipitate was again dissolved in sulfuric acid, the hydrogen fluoride distilled, and scandium hydroxide precipitated from an alkaline ammonium hydroxide solution. The scandium was weighed as scandium oxide.

Calcium

After the copper had been removed, the solution containing 5 mg of calcium carrier and carriers for the other elements was made alkaline with ammonium hydroxide, and the alkaline sulfides and hydroxides were precipitated. Carriers for zinc through scandium were again added, and the alkaline sulfides and hydroxides were again precipitated. This last step was again repeated, and the solution was then boiled to remove the hydrogen sulfide. The solution was made slightly acid with oxalic acid, and 5 ml of 4 percent ammonium oxalate was added to precipitate calcium oxalate. The precipitate was allowed to settle on a steam bath for ten minutes, was removed by centrifugation, and washed with water containing oxalic acid and ammonium oxalate. The calcium oxalate was dissolved in concentrated nitric acid, and a few crystals of potassium chlorate were added to oxidize the oxalic acid. Three mg of iron carrier was added, and the solution was made alkaline with ammonium hydroxide. The ferric hydroxide was removed by centrifugation and the solution made acid with oxalic acid. Four ml of a solution 4 percent in ammonium oxalate was added to precipitate calcium oxalate as the final purification step, and the precipitate was allowed to settle on a steam bath. The calcium was weighed as calcium oxalate.

Chlorine

The copper was dissolved in nitric acid and 5 mg of chlorine in the form of sodium chloride was added. The solution was boiled to distill the hydrogen chloride and the gas was caught in a solution containing two to three drops of nitric acid and sufficient silver nitrate to precipitate the chlorine as silver chloride. The solution was heated almost to boiling to coagulate the precipitate, and it was removed by centrifugation. The precipitate was washed with dilute nitric acid and then dissolved in dilute ammonium hydroxide. The solution was then acidified with nitric acid and additional silver nitrate added to make sure that the precipitation of the silver chloride was complete. The chlorine was weighed as silver chloride.

Phosphorus

The copper target was dissolved in nitric acid and 5 mg of phosphorus as phosphate ion was added to the solution. Holdback carriers were also added for the other elements zinc through calcium. The solution was adjusted to 1 N in nitric acid and 10 ml of ammonium molybdate[29] was added to the warmed solution to precipitate ammonium phosphomolybdate. The precipitate was allowed to settle for 15 minutes, removed by centrifugation, and washed with a solution of 1 percent nitric acid. The precipitate was dissolved in ammonium hydroxide containing citrate ions to complex titanium which otherwise would form an insoluble phosphate. Hydrochloric acid was added until the precipitate that formed during neutralization dissolved with difficulty: this assured that sufficient acid had been added. Five mg each of vanadium and titanium carrier were added, and sulfur dioxide was bubbled through the solution to reduce all the vanadium to the vanadyl state. Two ml of a cold magnesium chloride mixture[30] was added, and the solution was allowed to stand for five minutes. Concentrated ammonium hydroxide was then added

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[29] W. F. Scott, *Standard Methods of Chemical Analysis, I*, edited by N. H. Furman (D. Van Nostrand Company, Inc., New York, 1939), fifth edition, p. 697.

[30] Reference 29, p. 695.

equal to one-quarter of the original volume and the precipitate of magnesium ammonium phosphate was allowed to settle for 15 minutes. The precipitate was removed by centrifugation and then washed with 3 N NH_4OH. The precipitate was dissolved in 1 N HNO_3, and the phosphorus was again precipitated as the ammonium phosphomolybdate. The phosphorus was weighed as the ammonium phosphomolybdate.

Sodium

The copper was dissolved in concentrated hydrochloric acid and hydrogen peroxide, and 5 mg of sodium as sodium chloride was added as carrier. Carriers for the elements zinc through potassium were added, the solution adjusted to 2 N in hydrochloric acid and the copper precipitated as the sulfide. The solution was boiled to dryness to remove the excess acid, the residue dissolved, and then the solution made alkaline with ammonium hydroxide. Hydrogen sulfide was added and the sulfides and hydroxides were precipitated. Additional 3 mg portions of carriers zinc through scandium were added and precipitated. This scavenging process was repeated twice. Excess hydrochloric acid was added to the alkaline sulfide solution, the acidified solution boiled to dryness, and the ammonium chloride driven off. The residue was dissolved in water, the solution checked to make sure it was neutral, and the sodium precipitated as the sodium zinc uranyl acetate by the addition of a solution of zinc uranyl acetate.[31] Two 5-ml portions of zinc uranyl acetate were used to wash the precipitate, and the precipitate was then dissolved in absolute alcohol saturated with hydrogen chloride gas. The resulting mixture was cooled in an ice bath and the sodium chloride separated by centrifugation. The sodium chloride precipitate was washed with a 5-ml portion of an alcohol-hydrogen chloride solution. The sodium chloride was dissolved in water and the solution neutralized with potassium hydroxide. Zinc uranyl acetate was added to precipitate the sodium, the precipitate removed by centrifugation, and then washed with additional zinc uranyl acetate. The precipitate was dissolved in absolute alcohol saturated with hydrogen chloride, the mixture cooled in an ice bath, and the sodium chloride removed by centrifugation. The sodium chloride was washed with an additional portion of the ethyl alcohol-hydrogen chloride solution. The sodium was weighed as sodium chloride.

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[31] Reference 29, p. 879.