

Potassium-argon age study of Deccan trap
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POTASSIUM-ARGON AGE STUDY OF DECCAN TRAPS, INDIA

A THESIS SUBMITTED TO THE GRADUATE DIVISION OF THE
UNIVERSITY OF HAWAII IN PARTIAL FULFILLMENT
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By

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ABSTRACT

The age of the Deccan traps has been debated for about a century. The volcanic activity represented by them is believed to be due to the breaking up of Gondwanaland. Controversy rages over the question: Are the traps Upper Cretaceous or Tertiary in age? Palaeomagnetic evidence on the traps has been marshalled in support of the continental drift hypothesis.

The K-Ar ages obtained in this study range from 46 to 91 million years. Due to high air argon contamination (about 90%) from the samples, plus errors from other sources, there is an uncertainty of $\pm 11.09\%$ in the age calculation. These results support the field evidence that the volcanic activity commenced in the Upper Cretaceous.

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CHAPTER I

INTRODUCTION

Statement of the problem

The age of the Deccan traps has been debated for about a century since Blanford, in 1867, on stratigraphic evidence, challenged their Tertiary age based on the fossil evidence. Controversy has raged over whether the first and major outburst of the volcanic activity represented by the traps commenced during Eocene, as maintained by one school on fossil evidence, or during Upper Cretaceous, as held by another school of thought on stratigraphic evidence. Currently, it is believed that the volcanic activity commenced in Upper Cretaceous and continued into Eocene, and even later, punctuated by long intervals of quiet. However, the time of commencement of volcanic outbursts and their duration is not accurately known; this calls for fresh thinking on the stratigraphic and other field relations of type areas, and above all, requires the elucidation of age relationships by radiometric age determination methods.

This is particularly important because the age of the Deccan traps has a bearing on the continental drift theory. It is believed that India experienced this stupendous outburst of volcanic activity as a result of the breaking up of the continental mass of Gondwanaland. Palaeomagnetic work on the traps suggests that India has drifted northwards through 50° of latitude and rotated 25° counter-clockwise, from southern to northern hemisphere (Deutsch et al., 1959), and

Bombay has moved 5,000 kms northwards since Cretaceous times (Holmes, 1965). However, preliminary K-Ar work on the age of the Deccan traps done by the Geophysical Laboratory, Carnegie Institution, Washington, D.C., does not justify detailed use of palaeomagnetic evidence in support of the drift theory.

Objectives and their significance

The purpose of this project is to find the age of the Deccan traps. Also, it is hoped that the work will shed some light on the continental drift theory as applied to India. It should be found to what extent it confirms the earlier age comparisons between great basaltic formations of India, South America, South Africa, and Australia (Du Toit, 1927; Maack, 1952; and Pascoe, 1964). This is of especially great significance as it relates to the theory of the evolution of continents.

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CHAPTER II

GEOGRAPHICAL SETTING

General

The Deccan traps extend continuously from south of Belgaum (lat. $15^{\circ}50'$ N.) to Goona (lat. $24^{\circ}30'$ N.), and from Bombay (long. $72^{\circ}50'$ E.) to Umurkuntuk (long. $81^{\circ}50'$ E.) covering an area of approximately 512,000 sq kms, and as much as 1.12 million sq kms if the outlying areas such as those at Rajahmundry and Sind, and the trap areas now faulted under the Arabian Sea, are considered to have once been connected (Fig. 1).

The Deccan traps are named after a Sanskrit word "Dakshun," meaning "south," (the traps are really in Central and Western India). The word "trap" comes from the Swedish word "trapp," meaning "step," or "stairway," because of their step-like topography. The term "Deccan traps" was first used by W. H. Sykes in 1883.

Stratigraphy

The traps unconformably overlies the Bagh beds, Lameta beds and Archaean rocks. Stratigraphically, they are classified as follows (Krishnan, 1960):

Upper traps	Abundant volcanic ash beds and sedimentary intertrappean beds of Bombay; thickness 1,500 ft.
-------------	--

Middle traps	Intertrappean beds are absent; few ash beds at the base but become numerous towards the top; thickness, 4,000 ft.
Lower traps	Intertrappean beds at Nagpur, Narbada Valley, etc.; ash beds are rare; thickness, 500 ft.
	Unconformity.
Lameta or Bagh beds or Archaean rocks	20 - 100 ft thick (thickness of Archaean rocks unknown).

Mode of occurrence

The traps were erupted subaerially through many scattered fissures, one flow piled up over another in an almost horizontal disposition. The formation ranges in thickness from as little as 100 ft in the east to a maximum thickness of about 10,000 ft towards the west, near Bombay. The average thickness is about 2,000 ft. The individual flows average 40 to 80 ft in thickness, and as many as 48 successive flows have been recorded in Madhya Pradesh by West (1958). It is believed that the general direction of migration of the volcanic activity was from east to west. The volcanic activity was initially quiet, but became a little more violent in the period of eruption of the Middle traps, as attested by a few interlayered ash beds, and finally reached its greatest violence during the eruption of the Upper traps, as shown by numerous ash beds. During quiescent periods between eruptions of successive flows of the Lower and Upper traps, subaerial erosion cut valleys in the lava terrain which were dammed by successive flows and became the site of numerous

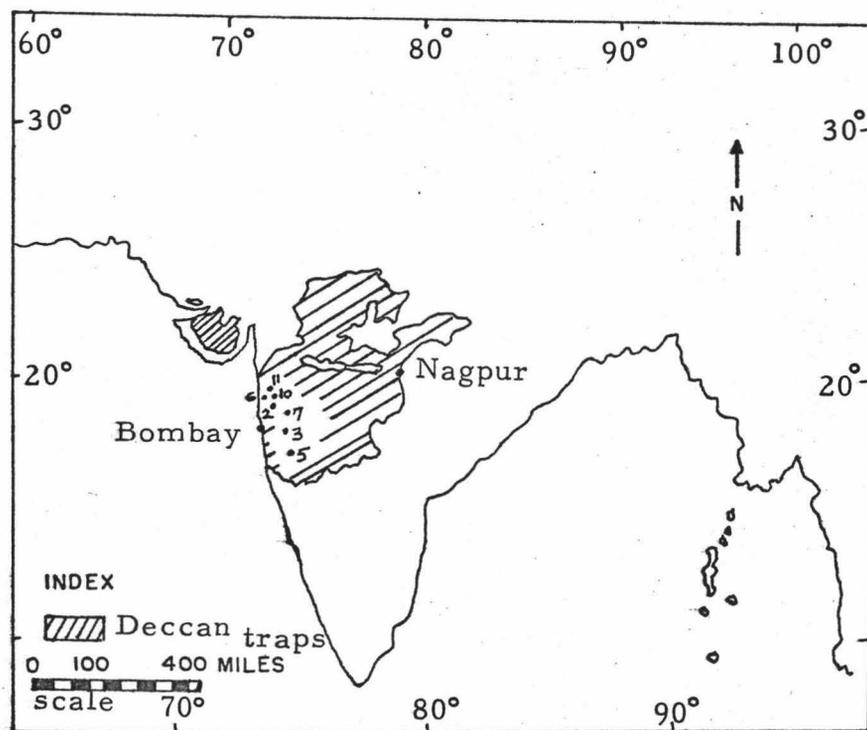


FIGURE 1. SKETCH MAP OF INDIA SHOWING
DISTRIBUTION OF DECCAN TRAPS.

1. Nagpur	(48 m.y.)
2. Palasdari	(68 m.y.)
3. Poona	(91 m.y.)
5. Karad	(69 m.y.)
6. Andheri	(46 m.y.)
7. Alandi	(113 m.y.)
10. Neral	(66 m.y.)
11. Badalpur	(67 m.y.)

lakes. The increasing evolutionary stages of the flora and fauna and presence of red clay or bole, coupled with the thickness of the intertrappean sedimentary beds laid down in these fresh-water lakes, suggest long pauses in the volcanic activity in India, besides throwing light on the age problem.

Dikes and sills of dolerite, varying in thickness from a few feet to 200 feet, are numerous in some areas, and a few have been traced laterally for 30 miles.

The traps have not been subjected to tectonic movements except locally, where they dip steeply and are folded and faulted. In general, they are almost horizontal. Along the west coast they have a gentle dip toward the Arabian Sea.

Petrography and petrology

The traps, belonging to the plateau basalts of Washington (1922), are uniform in megascopic and microscopic characters. The most common rock is black or brownish dark grey basalt or diabase, which, under a microscope, shows fine-grained ophitic to subophitic texture. The mineral composition consists of labradorite (approximately $Ab_1 An_2$), augite (also in some cases pigeonite, especially in the groundmass), iron ores such as magnetite and ilmenite, and apatite. Olivine may or may not be present, and glass content varies from 0 to 20%. Glass is altered to palagonite, chlorophaeite, and chabazite. Secondary minerals such as quartz, amethyst, agate,

chalcedony, opal, zeolites, and calcite, are very abundant in amygdales. The petrography of the Deccan traps has been described by Fermor (1925), Fox and Fermor (1916), Krishnan (1926), Prasad (1957), and West (1958).

At scattered places like Pavagad Hill (Gujarat) and Bombay, the traps have undergone differentiation (Mathur, 1934; Vemban 1946). In addition to the most common rock type, basalt or diabase, Mathur (1934) has described: (a) silicic types such as granophyre, trachyte, rhyolite, felsite, etc.; (b) syenite, diorite, monchiquite, and lamprophyres from the central mass of Mt. Girnar; and (c) olivine-bearing rocks such as olivine gabbro, olivine diorite, oceanite, peridotite, limburgite, etc., from Linga, Pavagad, Kutch, and Kathiawar.

The petrography of the samples analyzed for this report is given in Appendix A.

Chemical characters

The Deccan traps, whether basalt or diabase, show great uniformity in chemical composition. They are characterized by higher iron and titanium content and lower magnesia and alkali content, as compared to the abundance of these constituents in basalts of the central eruption type. The average potassium content increases from the lower traps ($K_2O = 0.51$ to 0.68%) to the Upper traps ($K_2O = 0.95\%$) (Washington, 1922). Sukeshwala and Poldervaart

(1958) have compiled all the chemical analyses made on the traps until 1958. One of their typical analyses (p. 1487) is as follows:

SiO ₂	50.35%	Na ₂ O	2.57%
Al ₂ O ₃	13.55%	K ₂ O	0.64%
Fe ₂ O ₃	3.11%	TiO ₂	2.51%
FeO	11.23%	P ₂ O ₅	0.21%
MgO	5.27%	MnO	0.14%
CaO	10.42%		

CHAPTER III

HISTORICAL SURVEY OF AGE PROBLEM

Although the fossils from the Deccan traps were first described by Voysey in 1819, it was in 1837 that J. G. Malcolmson, with the help of J. de C. Sowerby, assigned Tertiary age to them based on the evidence of the fossils discovered from the intertrappean beds between Nagpur and Hyderabad. Carter, according to Crookshank (1937) suggested that the Bombay intertrappean flora is younger than the coal-field flora, and also pointed out the association of traps with the Nummulitic (Eocene) beds in Rajpipla Hills. Hislop (1853) considered the Madhya Pradesh and Bombay traps to be homotaxial, and suggested the identity of the Lameta (Cretaceous) beds with the intertrappean beds. In 1855 he correlated the intertrappean fauna and flora with those of the London Clay, Great Britain, and of Riley, Belgium.

The assignment of Tertiary age to the Deccan traps was challenged by Blanford (1867) who argued on stratigraphic evidence that the volcanic activity commenced in Cretaceous time and continued into the Eocene. Blanford found an unconformity between the traps and the Bagh beds at Bagh, and in Gujarat the intertrappean beds dip below the Middle Nummulitic (Eocene) beds which contain abundant trap debris. This suggests an important unconformity. Hence, the traps of Madhya Pradesh might be Middle Cretaceous, while those of Bombay might be oldest Tertiary. As pointed out by Crookshank (1937), the Cretaceous age was strongly supported by Fedden's

discovery of trap flows at Bor Hill in western Sind. Here, Blanford discovered a basalt flow between a bed containing Cardita beaumonti, a typical Cretaceous index fossil, and rocks of the Ranikot stage (Eocene). Other flows were also discovered in the Cretaceous beds 700 feet below the top of the Cretaceous beds. King, in 1880, according to Crookshank (1937), supported Blanford by pointing out a slight unconformity between fossiliferous marine infratrappean beds and the intertrappean beds containing estuarine fossils near Rajahmundry. In 1921 Matley discovered that in the Jabalpur area, the Gondwana beds pass upward into the lowest trap flows without any break. Since the age of the Saurian bones a few feet below the traps is Albian or Cenomanian (low middle Cretaceous) in the Jabalpur area, the traps must be Cretaceous. Holland (1926) concluded from the occurrence of Bullinus (Physa) prinsepii in the Maestrichtian of Baluchistan, that the Deccan traps are Cretaceous.

Meanwhile, beginning in 1906, palaeobotanical and palaeontological evidence had been gathered supporting the Tertiary age.

Bose's (1884) observation that in the Lower Narbada Valley, the Lameta beds overlie their so-called homotaxial Bagh beds with an unconformity, and pass upward into the ash beds of the lowest trap flows, led Crookshank (1937) to favor a Tertiary age, as the traps here are separated from Ariyalur (Upper Cretaceous) beds by an unconformity plus 40 ft of Lameta Limestone. The discovery of Cardita beaumonti from the Rajahmundry infratrappean beds by Hem Chander Das Gupta (Crookshank, 1937), combined with King's (1880)

find of an unconformity between the traps and the infratrappean beds would indicate a Tertiary age. Huene and Matley (Crookshank, 1937), after a study of more saurian bones, raised the age of the Lameta beds from Albian or Cenomanian to Turonian.

Sahni (1934, 1937, 1940) marshalled palaeobotanical evidence in favor of Tertiary age at a time when the Cretaceous age for the Deccan traps was officially accepted by the Geological Survey of India. Sahni gave three principal reasons: (1) among the angiosperms there is a marked preponderance of palms which, as a group, first appeared in Cretaceous time but reached its maximum abundance during the Tertiary; (2) the occurrence of Nipadites, which is an index fossil for the Tertiary; and (3) the occurrence of genus Azolla. The Hydropterideae family to which Azolla belongs, has never been found in rocks older than Tertiary. Rao et al. (1936) discovered foraminifera and chara fruits near Pungadi and Dudukur. The foraminifera (Miliolidae, Lagenidae, Rotalidae, etc.) are not important stratigraphically, but species of Chara: C. Wrightii Salter, C. helicteres Brong, C. Caelata Reid and Groves, etc., have definite Tertiary affinities; and so has an algae, Acicularia, belonging to the family Dasycladaceae. Rama Rao (1936) studied traps in the Nagpur-Chhindwara area which unconformably overlie the Bagh and Lameta beds; in the Surat and Broach areas where they are overlain by Nummulitic (Eocene) and underlain by Cretaceous and Archaean rocks; and in the Rajahmundry area where they unconformably overlie the marine infratrappean (Lameta) beds. He has shown that the

detailed analysis of the geology of each of the areas, plus the fact that there was a long interval of time between the lowest and topmost flows, favors a Tertiary age. In support of the evidence from plant remains, Woodward (1908) presented the evidence of Tertiary age furnished by fish remains from intertrappean beds of Dhamiri and Dangargaon in Madhya Pradesh. Hora (1938) described fish remains including Lepidosteus indicus, Pycnodus lametae, Easerranus hislopi, etc., and fish scales of Musperia and species of Clupea from intertrappean beds at Deothan and Kheri, Madhya Pradesh, favoring Lower Eocene age. Prakash (1960) has listed all the fossil plants discovered from intertrappean beds until 1960. Other intertrappean fossils of insects, frogs, tortoises, etc., are not of any stratigraphic value. Crookshank (1937) concluded that the present evidence favors a Tertiary age, but that field evidence is not strong.

Holmes (1931, p. 411) used a radioactive method of age determination and assigned an early Eocene age to the Pavagad traps, while the associated acid felsites of the plug on the Maugaja plateau appeared to have a Miocene age. Dubey (1934) dated acid felsites (not Deccan traps proper) which represent the last phase of volcanic activity, at 5 to 5.9 million years by the He method, thus supporting Holmes' earlier estimate of Miocene age for these acid lavas.

Sukeshwala (personal communication), during the period 1935 to 1938, used the U-Pb method, which indicated Cretaceous to Oligocene ages. In 1941 Kalapesi et al. obtained ages of 68.4 m. y. (Lower Eocene) to 45.6 m. y. (Oligocene) by the "lead ratio" method for two distinct

basalt flows at Bombay and Salsette Islands. Later, in 1944, Kalapesi and Sukeshwala, using the U-Pb method, obtained ages ranging from 98.8 m. y. (Upper Cretaceous) to 15.2 (Middle Miocene). The later age is that of a dike rock.

Not much radiometric age determination work has been done on the Deccan traps. In a preliminary investigation, the K-Ar method was used by the Carnegie Institution (1964). Those samples were dated which, according to palaeomagnetic data, gave the position of the Indian subcontinent in the southern hemisphere, at the equator, and in the northern hemisphere. Since the ages obtained did not systematically decrease going from the southern to the northern hemisphere, as they should if the drift hypothesis based on palaeomagnetic data is true, it was concluded that radiometric data forbid the use of palaeomagnetic evidence in support of continental drift.

From the foregoing discussion, it is obvious that the problem of the age of the Deccan traps must be tied to the stratigraphic relations between the lowest traps and the infratrappean beds, and between the uppermost traps and the overlying rocks. It should also be determined whether the lowest traps are of the same age in different parts of India.

CHAPTER IV

HISTORICAL SURVEY OF K-AR METHOD

General

Although potassium was discovered by Humphry Davy in 1807, it was not until 1906 that Campbell and Wood discovered its radioactivity. Weizsacker (1937) predicted the dual decay of potassium into Ar^{40} and Ca^{40} , which was proved by Thompson and Rowlands in 1943. After the confirmation by Smythe and Hemmendinger (1937) that K^{40} is a radioactive isotope of potassium, and the determination of its abundance by Nier (1935) as 0.001 ± 0.001 percent (redetermined as 0.019 ± 0.001 percent in 1950), Aldrich and Nier (1948) showed for the first time the relation between the $\text{Ar}^{40}/\text{K}^{40}$ ratio and the age of sylvite and langbeinite, thus heralding a new era in the quantitative measurement of geological time. Smits and Genter (1950) were the first to apply the method to an undated mineral. A milestone in the progress to precise and accurate measurement techniques was the introduction of the isotopic dilution technique by Inghram et al. (1950). By 1957 the technique of sample fusion with a flux which did not completely liberate argon was replaced by direct fusion of the sample without adding any flux (Guldner and Beach 1950; Carr and Kulp, 1957). Alpert (1953) developed techniques for measuring and achieving ultrahigh vacuum, and the design of a new mass spectrometer by Reynolds (1956) insured sensitivity and accuracy for the argon analysis.

Principle

The method is based on the principle that K^{40} , a natural radioactive isotope of potassium, disintegrates spontaneously into stable daughter products Ar^{40} and Ca^{40} at a certain rate, depending upon the decay constants. The decay scheme is shown in Fig. 2. The age of a mineral or a rock can be determined from the knowledge of the present ratio of Ar^{40}/K^{40} and the decay constants: λ_e , for electron capture; and λ_β for β -decay; and their branching ratio, $\frac{\lambda_e}{\lambda_\beta} = R$, provided the system has remained closed with respect to both K^{40} and Ar^{40} throughout its geological history. That is, (1) no argon was trapped at the time the mineral or rock was formed, and (2) neither argon nor potassium has been gained or lost. The criteria for a closed system are hard to evaluate exactly. Usually the agreement of ages determined on different co-existing minerals and by different methods is suggestive of a closed system.

Based on the decay scheme, the equation for argon accumulation time, or age of the mineral, is given by

$$t = \frac{1}{\lambda_e + \lambda_\beta} \ln \left[1 + \frac{Ar^{40}}{K^{40}} \left(\frac{1 + R}{R} \right) \right] \quad (1)$$

which on substitution of the values of the decay constants gives the following workable equation:

$$t_{m.y.} = 1887 \ln \left(1 + 9.130 \frac{Ar^{40}}{K^{40}} \right) \quad (2)$$

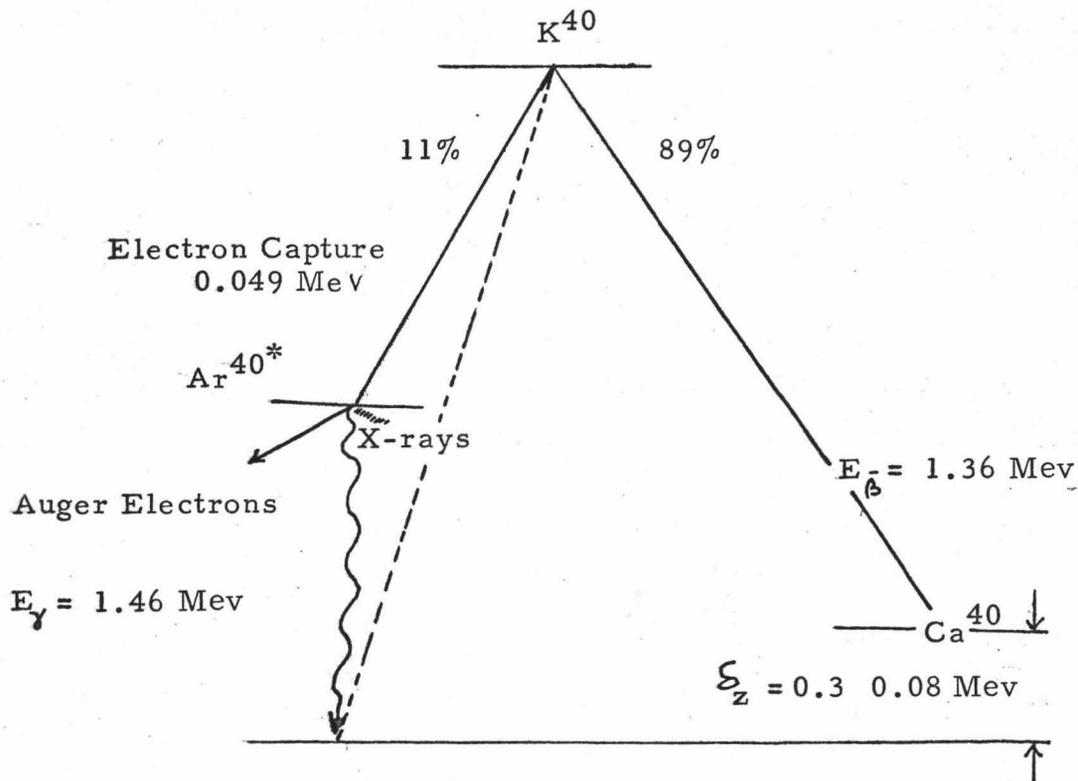


FIG. 2. DECAY SCHEME OF K^{40}

$$\lambda_e = 0.585 \times 10^{-10} \text{ yrs}^{-1}$$

$$\lambda_\beta = 4.72 \times 10^{-10} \text{ yrs}^{-1}$$

$$R = \frac{\lambda_e}{\lambda_\beta} = 0.124$$

$$T_{\frac{1}{2}} = 1.3 \times 10^9 \text{ yrs}$$

$$\frac{K^{40}}{K} = 0.000122 \pm 0.000001$$

Decay constants

The decay constants λ_e and λ_β , and hence the branching ratio, R, which determine the half life of K^{40} , are not accurately known. There is no good agreement between geologically determined values and those determined by counting techniques. About 89% of the decay of K^{40} takes place by the emission of 1.36 Mev β^- emission directly to the ground state of Ca^{40} , whereas about 11% is by electron capture to an excited state of Ar^{40} which further undergoes transition to ground state by the emission of x-rays and auger electrons. λ_β is determined from β^- activity while γ activity gives λ_e on the assumption that all of this decay passes through the excited state of Ar^{40} , a possibility which is still currently being investigated.

Aldrich and Wetherill (1958) have reviewed the present status of decay constants, and believe that the figure $\lambda_e = 0.585 \times 10^{-10} \text{ yrs}^{-1}$ is accurate within 5% of the true value. λ_β is more accurately known because β^- activity can be accurately measured (23 - 34 disintegrations per sec. per gm. K; 28.2 - 0.3 disintegrations per sec. per gm. K is a good value). For young rocks such as the Deccan traps the age is more dependent on λ_e ; for very young rocks a 5% error would be transferred to the resulting age because it varies directly with λ_e .

Validity of K-Ar method

The Rb^{87} - Sr^{87} method cannot be applied to the dating of the

traps because common strontium is very high in basalts; and to be dated with 10% accuracy the equation (Hart, 1966)

$$\frac{\text{Rb}}{\text{normal Sr}} \quad t = 2500 \quad (3)$$

where t is in million years, must be satisfied. Thus, common strontium swamps the ratio. This method is suited to older rocks, although rocks as young as 10 million years can be dated provided $\frac{\text{Rb}}{\text{Sr}} \approx 250$. The U-Pb, and Th-Pb methods may not be useful for volcanic rocks younger than Miocene (Kulp, 1963).

The $\text{K}^{40} - \text{Ar}^{40}$ method has been successfully used to date whole volcanic rocks (Erickson and Kulp, 1961; Funkhouser, 1966; McDougall, 1963, 1964; Dalrymple, 1963; and Amaral et al., 1966). Since the traps are mostly composed of calcic plagioclases, pyroxenes, iron ores, olivines and glass, each of these minerals will be considered for retentivity of argon.

Plagioclases from young diabases give good results, but those from old diabases show loss of argon (McDougall, 1963). However, Evernden and James (1964) argue that volcanic feldspars with less than 0.9% potassium should retain argon over a time equivalent to that from the Palaeozoic era to the present.

Pyroxenes from volcanic rocks have been found to contain excess argon (Hart and Dodd, 1962). However, chloritization of pyroxenes can lead to selective loss of argon (Evernden et al., 1964).

Altered olivines, especially those which have undergone

deuteric alteration to iddingsite, have been reported to have lost argon (Dalrymple, 1963). Samples of the Deccan traps do not contain much olivine, but those present do show some alteration, though not of deuteric nature.

Glass shows loss of argon on devitrification (Evernden et al., 1964; and Schaeffer et al., 1961) and on argillitic alteration (Bassett et al., 1964). The traps analyzed for this report do not contain much glass, and most of that present is unaltered except for one specimen.

Another source of excess argon is the fluid inclusions in minerals (Rama et al., 1964; Lippolt and Gentner, 1963; and Funkhouser, 1966). The analyzed specimens of traps do not show any fluid inclusions under the microscope.

Geological time scale

The geological time scale worked out on world-wide radiometric data by Kulp (1961) is given in Table I.

TABLE I. GEOLOGICAL TIME SCALE
(AFTER KULP, 1961)

ERA	PERIOD	EPOCH	BEGINNING OF INTERVAL	
CENOZOIC	QUATERNARY	Pleistocene	1	
	TERTIARY	Pliocene		13
		Miocene		25
		Oligocene		36
			Upper	45
			Middle	52
			Lower	58
		Eocene		58
		Paleocene		63
	MESOZOIC	CRETACEOUS	Maestrichtian	
Campanian			Upper	84
Santonian				
Coniacian				90
Turonian				
Cenomanian				110
Albian			Lower	120
Aptian				
Neocomian			135	
JURASSIC		Bathonian	Upper	166
			Middle	
		Bajocian	Lower	181
TRIASSIC			Upper	200
			Middle	
			Lower	(230)
PERMIAN		Upper		
		Middle	260	
		Lower	280	
PALEOZOIC	CARBON-IFEROUS	PENNSYLVANIAN		
		MISSISSIPPIAN		
		Visean		320
		Tournaisian		345
	DEVONIAN		Upper	(365)
			Middle	
			Lower	390
	SILURIAN			405
				(425)
	ORDOVICIAN	Trenton	Upper	445
			Middle	
		Lower	500	
CAMBRIAN		Upper	530	
		Middle		
		Lower	? ? 600	

CHAPTER V

EXPERIMENTAL TECHNIQUES

Sample selection

Since fine-grained basalts have been found by Erickson and Kulp (1961), McDougall (1963), and Amaral et al. (1966) to yield satisfactory results, fine-grained basalt specimens were selected for K-Ar dating in this study. None of the specimens has undergone weathering and alteration of minerals does not exceed 5%. The glass content is low.

Sample preparation

The rocks were scrubbed, washed, dried, and broken with a sledge hammer into small pieces. They were then transferred to the crusher and broken into small pieces of approximately 1-1/2" diameter. The broken samples were quartered. One quarter was ground to 200 mesh and used for potassium analysis. The other portion was ground in a steel mortar, sieved, and the portion retained in / 60 mesh was used for argon analysis. Some samples for argon analyses were ground to 32 mesh. Every care was taken to avoid contamination.

Chemical treatment of samples for potassium analysis

The following procedure was followed for taking the samples into solution for potassium analysis:

1. About 0.05 gm of the sample was accurately weighed into a platinum dish with a Mettler balance.
2. 15 ml of HF and 1 ml of dilute H_2SO_4 were added, and the solution was heated to "simmer" on the hot plate overnight. The HF was added occasionally until the sample was completely dissolved. It was evaporated to dryness, avoiding spattering.
3. 7 ml of concentrated HNO_3 and 20 ml of demineralized water were added to the residue and the solution was evaporated.
4. When the solution was dry and fumes of H_2SO_4 had ceased, the dry residue was taken into solution by adding 0.65N HCl.
5. The solution was transferred to a volumetric flask and diluted to 100 ml (or 250 ml, etc., as desired) in 0.65N HCl.
6. Blanks were prepared each time a sample was prepared, performing all steps without adding the sample.
7. (a) To prepare the solution for the mass spectrometric run by isotope dilution technique, an aliquot of the sample solution, containing the same amount of K as was present in the spike (e. g. , spike solution contained 9.8 ppm of K^{41} , and thus 1 ml of spike was mixed with

5 ml of a solution containing 2 ppm of K), was taken and mixed with the spike solution. The solution was heated in a silica dish at about 100°C. An infrared lamp was focused over the solution to avoid spattering; the dish was covered with a glass vessel to avoid contamination from the air.

- (b) About 2 cm of platinum wire of 0.008" thickness was cut and cleaned by alternate electrical heating and dipping in concentrated HCl. The wire (filament) was further cleaned for one hour by electrical heating at an amperage (6 amps) just below where it would burn out. The wire was then bent into a loop and coated with the sample by evaporating the sample solution on the loop. Once a uniform deposit was obtained by electrical heating, the filament current was raised to 3 amperes so as to condition it for 15 minutes. Meanwhile, the source from the mass spectrometer was removed and cleaned. The filament was inserted in the posts of the source and the source was replaced in the mass spectrometer.
- (c) The forepump was started. When the pressure was less than 40 microns (in about 15 minutes) the metal oil diffusion pump was switched on, and in another 30 minutes the pressure was around 2×10^{-6} torr. The

ion gauge was outgassed. The filament was again conditioned under vacuum at about 3 amperes for 4 hours.

Flame photometric analysis

Potassium analyses were made in duplicate and replicate using a Beckman D. U. Spectrophotometer, Model 2400, with a flame photometer attachment, and the intensity of emission was recorded on a Leeds and Northrup Speedomax recorder (Type 9) with a 20 mv. scale deflection. Spectral energy was recorded at oxygen pressure of 14 pounds per square inch (psi), hydrogen at 4.5 psi, with sensitivity at 0.1 setting, wavelength at 767 mm and slit width of 0.04 mm. The standards of various concentrations, already available, were prepared from Merck reagent grade K_2SO_4 dissolved in 0.65N HCl. In each run the wavelength selector was adjusted to obtain maximum emission, and peak heights were adjusted to 90% of full-scale deflection.

The peak height due to emission from the sample was always adjusted to lie between the peak heights of the two standards. The parts per million (ppm) of potassium in the samples were calculated by the following equation:

$$K_s \text{ (in ppm)} = K_h - K \left(\frac{\Delta h_1}{\Delta h_2} \right) \quad (4)$$

where K_s is potassium in ppm in the sample; K_h is the potassium in the more concentrated standard; ΔK is the difference in ppm of the

potassium content of the two standards; Δh_1 is the difference in the peak heights of the sample and the more concentrated standard; and Δh_2 is the peak height difference between the two standards. The percent of potassium was then calculated by

$$\%K = \frac{K_s \times \text{volume of the solution}}{10^6 \times \text{wt. of sample in gms}} \times 100 \quad (5)$$

The results obtained by flame photometry are given in Table I.

Mass spectrometric analysis

The isotope dilution technique was used to determine potassium by using a solid source mass spectrometer (Fig. 3, Fig. 4, and Plate I) similar to the one developed by Marcley (1960) and Dewdney (1960). This is a simple single focusing, 90° sector mass spectrometer in which the ions are deflected by passage through the magnetic field along a radius r given by the equation

$$r = \left[\frac{m V}{e B^2} \right]^{1/2} \quad (6)$$

where $\frac{m}{e}$ is the mass to charge ratio; V is the accelerating voltage; and B is the magnetic induction. In this instrument r (= 4.5 cm) and B (= 3300 gauss) are fixed; and therefore the particular m/e ratio brought into path r is a function of V . It is obvious from equation (6) that m/e ratio is inversely proportional to V , which means high m/e ratio (K^{41} in this case) would appear before low m/e ratio (K^{39} in this case).

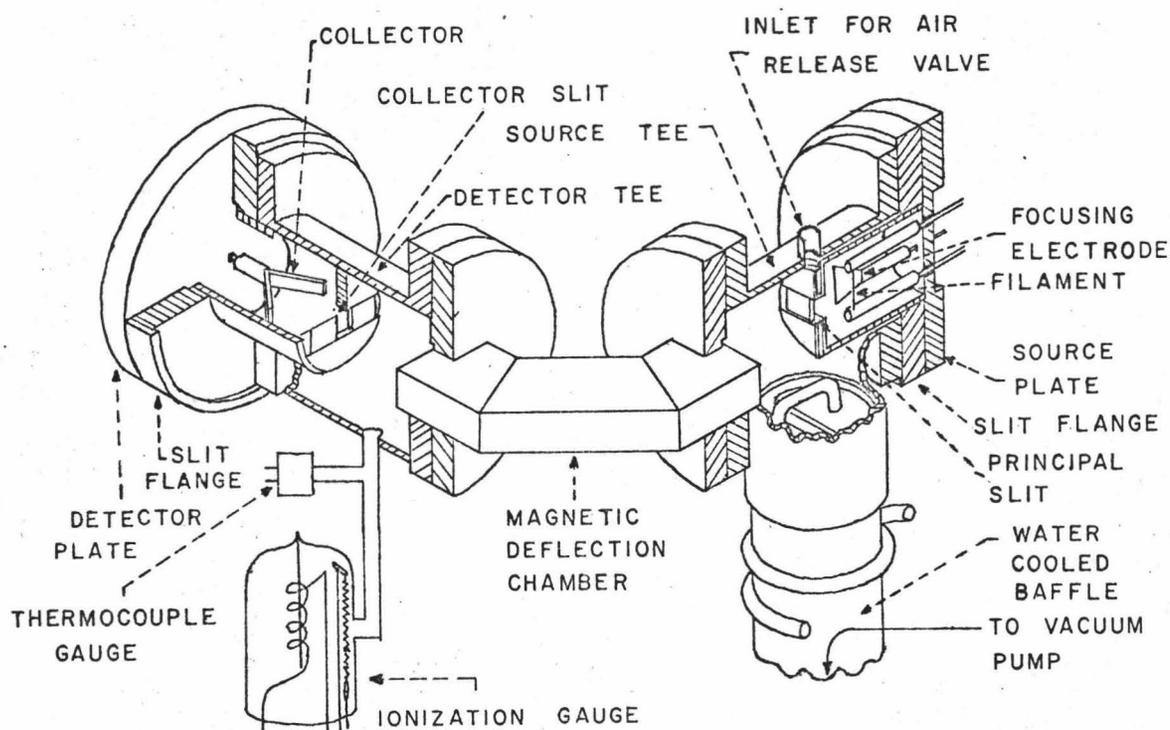


FIG. 3. SECTIONAL VIEW OF THE SOLID SOURCE MASS SPECTROMETER. MODIFIED AFTER MARCLEY (1960).

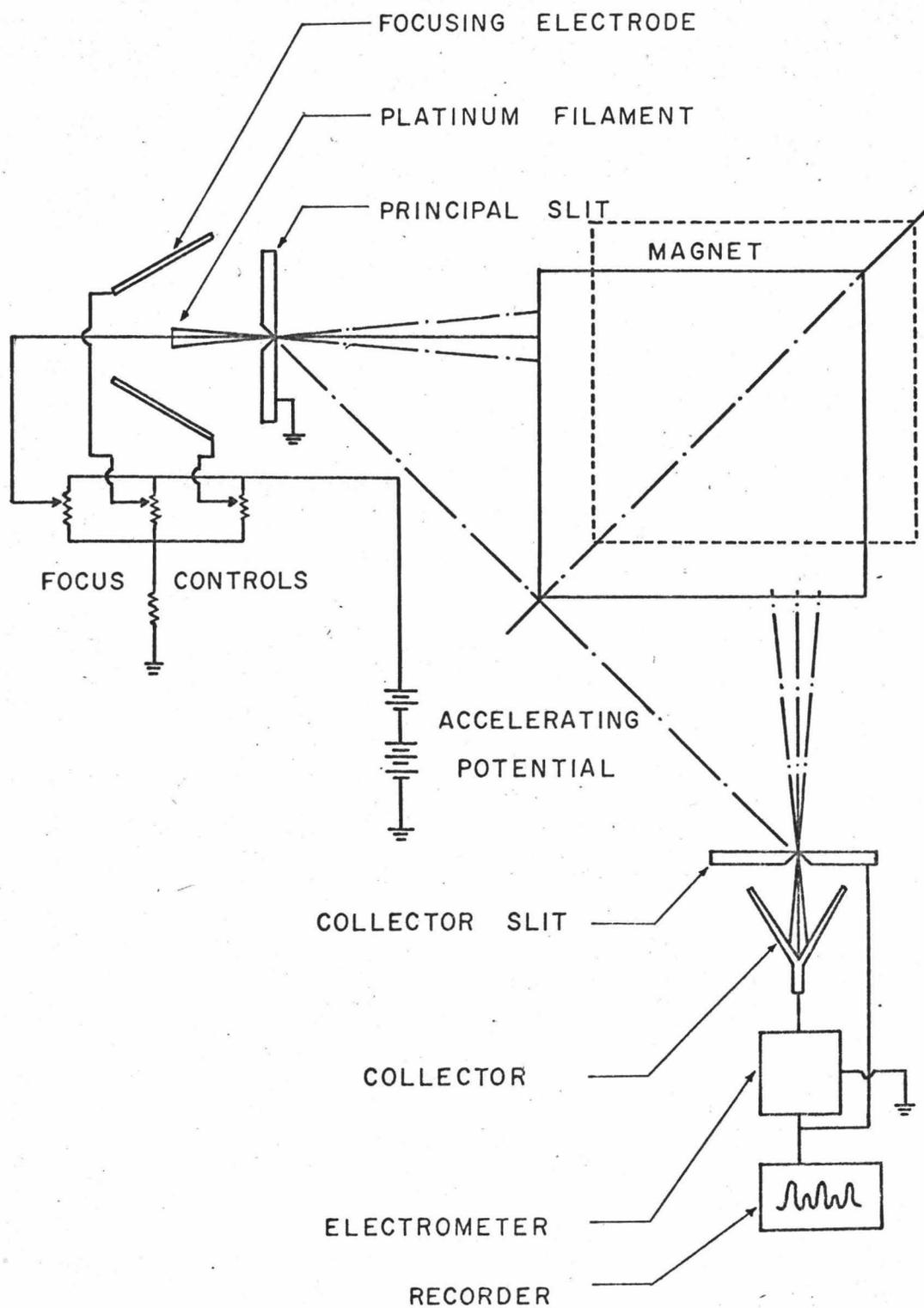


FIG. 4. SCHEMATIC DIAGRAM OF ION BEAM IN SOLID SOURCE MASS SPECTROMETER. MODIFIED AFTER MARCLEY (1960).

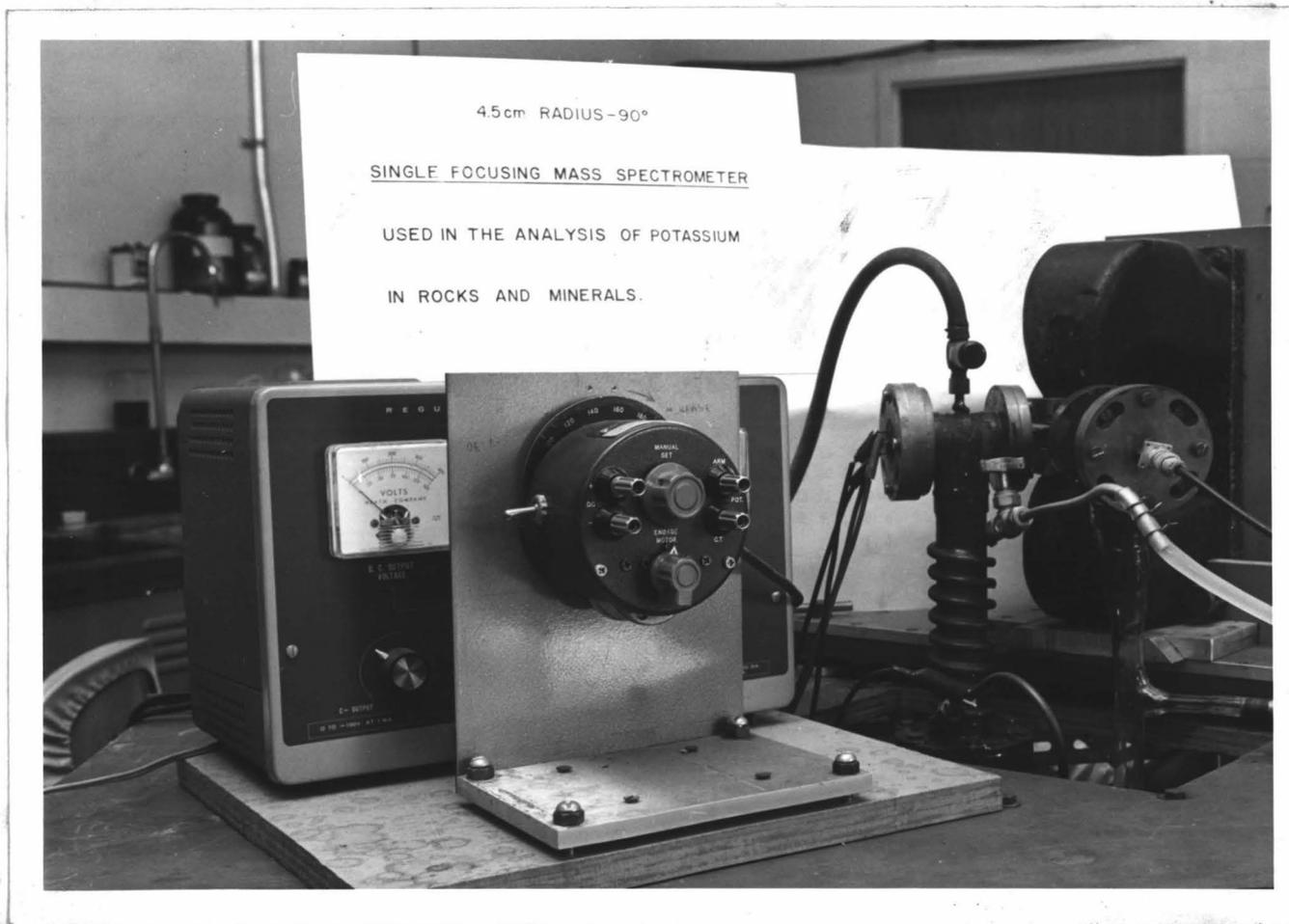


PLATE 1. VIEW OF THE SOLID SOURCE MASS SPECTROMETER

The ion beam produced at the source was passed through the source slit (0.4 mm in diameter), the magnetic field, and was collected on a Faraday cup-type detector. To achieve maximum signal, the ion beam was focused and the sensitivity was varied. The signal was fed to a General Radio, Type 1230A, D.C. Electrometer. The output from this was fed to a Varian Model G-10 Recorder. The accelerating voltage was varied by spectral type 860, 10 turn, control. A General Radio, Type 907-R-144, self-reversing dial drive mechanism was used for automatic scanning up and down the mass.

In spite of the low pressure of about 6×10^{-7} torr, the precision of the peak heights was not very good; standard deviations of about 6% were common. This may be due to lack of sufficient controls such as exist in a versatile mass spectrometer.

Isotope dilution technique (theory)

If x atoms of normal potassium are mixed with y atoms of K^{41} spike, and K^{39}/K^{41} ratio is called R , then

$$R = \frac{93.08 \ x \ + \ 1.28 \ y}{6.91 \ x \ + \ 98.72 \ y}$$

$$\text{or } x = y \frac{98.72R - 1.28}{93.08 - 6.91 R}$$

Replacing atoms by weights of the normal and spike; i. e., x and y , respectively, we get

$$\begin{aligned}
 x &= y \frac{98.72R - 1.28}{93.08 - 6.91 R} \times \frac{\text{at. wt. of normal K}}{\text{at. wt. of spike}} \\
 &= y \frac{98.72R - 1.28}{93.08 - 6.91 R} \times \frac{(6.91)(41) \mp (93.08)(39)}{(1.28)(39) \mp (98.72)(41)} \\
 &= 13.64 y \frac{R - 0.013}{13.47 - R}
 \end{aligned}$$

Since y and R are known, hence x can be calculated.

Results of potassium analyses

The results of potassium analyses are given in Table II. The mass spectrometric determinations using isotope dilution technique and flame photometric determinations agree within 4.5%.

The precision is a measure of reproducibility. Standard deviation, σ , according to Youdon (1951), is given by $\sqrt{\frac{\sum d^2}{2n}}$, where n = 16 is the number of pairs of solutions on which single photometric determinations were made; d is the percent difference between the pairs. In the case of replicate analyses the consecutive pairs of determinations were chosen. Thus, for the whole analyses, $\sigma = 0.367\%$. The standard deviation of the mean = $\sqrt{\frac{d^2}{n(n-1)}}$ = 0.135%, and the 95% confidence interval is $\frac{12.71 \times 0.0367}{2} = 3.31\%$.

The accuracy of the results can be judged by comparison to standards. NBS #99 gave a value of 0.327% K by flame photometry and 0.340 by isotope dilution technique using mass spectrometry against the accepted average value of 0.34% K. Thus, it is believed that the accuracy of potassium determinations is better than $\pm 4.5\%$.

TABLE II. POTASSIUM DETERMINATIONS

SAMPLE NUMBER	FLAME PHOTO-METRIC		%K, MASS SPECTRO-METRIC
1	0.236 0.235	0.236	0.239
2	0.628 0.630	0.629	0.637
3	0.515 0.521	0.518	0.520
4	0.221 0.222	0.222	0.206
5	0.240 0.239 0.240 0.233	0.238	0.239
6	0.603 0.605 0.610	0.606	0.630
7	0.312 0.309	0.306	
8	0.279 0.274	0.276	
9	0.216 0.220	0.218	
10	0.600 0.596	0.598	
11	0.860 0.865 0.880	0.868	
12	0.395 0.390	0.392	
NBS #99	0.327		0.340

In the interpretation of accuracy for potassium analysis, it should be pointed out that Yamashiro (1965) obtained results by the isotope dilution technique agreeing within 2% with flame photometric determinations. For potassium greater than 3% the relative difference was 1.63 to 1.91%, for K greater than 1.5% the relative difference was 3.4 to 4.2%, for K a little less than 1% it was 6.49 to 9.96%, and the relative difference was 30.3% for rocks containing less than 0.5% K. For low potassium rocks such as W-1 (diabase or dolerite) the interlaboratory precision was 2.6% standard deviation.

Dalrymple and Hirooka (1965) found that in a young basalt (2.6% K, 3 million years old) the precision of ten replicate analyses by flame photometry was 0.35% with a total spread of 1.16%. They have established that heterogeneity of a sample can cause a wide spread. According to them, interflow variations are even larger.

Argon analysis

The determination of Ar^{40} derived from the disintegration of K^{40} consists of the liberation of the gases by the fusion of the whole rock sample, purification of the evolved gases, mixing and equilibration with an Ar^{38} spike, and the ultimate mass spectrometric analysis using isotope dilution technique.

Preparation of Ar^{38} and air argon spikes

The system for spike preparation is shown schematically in Figure 5. Three flasks, whose volumes were measured accurately

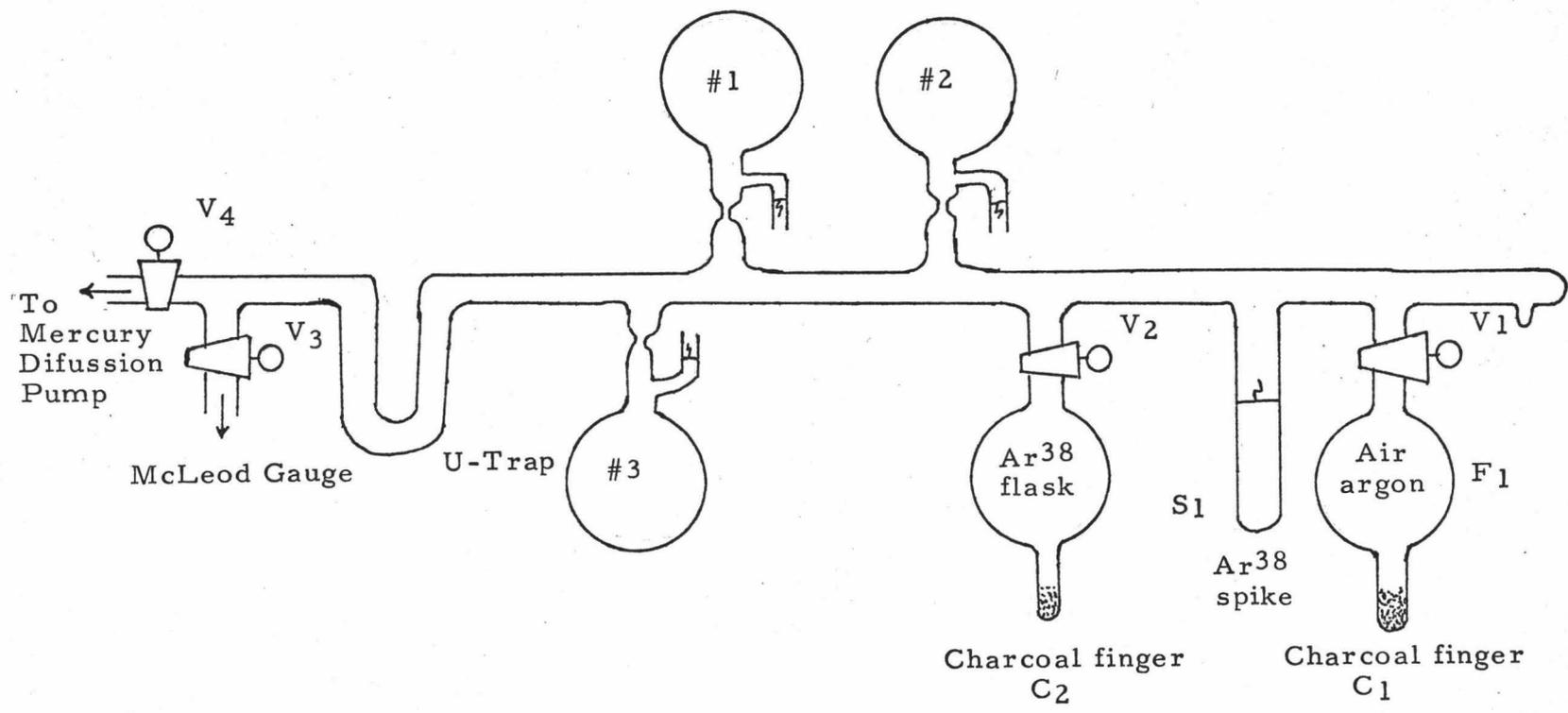


FIG. 5. SCHEMATIC DIAGRAM OF Ar^{38} AND AIR ARGON SPIKE PREPARATION SYSTEM

by filling with distilled water and weighing, were put on the system. They had capillary necks and were numbered as #1, #2, and #3. A tube, S_1 , containing Ar^{38} spike, and a flask, F_1 , containing air argon were also connected to the system. The air argon flask and the flask for the collection of Ar^{38} spike had activated charcoal fingers C_1 and C_2 , respectively, to absorb the spikes when cooled with liquid nitrogen.

The system was pumped by a mercury diffusion pump backed by a Welch fore pump. When the pressure was less than 1×10^{-7} torr, the valves V_1 , V_2 , and V_4 were closed and valve V_3 was opened. The break-seal tip in the tube S_1 containing Ar^{38} spike was broken by manipulating an iron nail with a magnet. After half an hour of equilibration of isotopes the pressure was measured in the CVC McLeod gauge. If the pressure was higher than the desired pressure, liquid nitrogen was put around the charcoal finger C_2 after opening the valve V_2 . After half an hour, the valve V_2 was closed, and the pressure was noted. If it was still too high, the valve V_3 was closed, and gases were pumped away by opening the valve V_4 to the pumping system. Then the valve V_4 was closed, and V_3 was opened to note the pressure again. If the pressure was still too high, the cycle was repeated until the desired pressure was obtained. The flasks #1, #2, and #3 were removed by torch and stored. One flask containing Ar^{38} spike was put on the argon extraction and purification system.

Air argon spikes were also prepared in the same way.

Spike calibration

Ar³⁸ spike was calibrated against the USGS muscovite P-207 standard containing 1.267×10^{-9} moles/gm of Ar⁴⁰. A known volume of Ar³⁸ spike was mixed and equilibrated with the gases evolved by the fusion of the standard. The gases were cleaned in the purification unit and then analyzed in the Reynolds-type mass spectrometer as described later. A scale factor in terms of moles/gm per millivolt was calculated from the data so obtained.

The Ar³⁸ spike used in this study was purchased from the Institute of Physical Chemistry, University of Zürich, Switzerland. It had the following isotopic composition: Ar⁴⁰, 0.015%; Ar³⁸, 99.982%; Ar³⁶, 0.003%.

Argon extraction

Argon was extracted by direct fusion of the samples without adding any flux (Guldner and Beach, 1950; and Carr and Kulp, 1957).

The extraction and purification system is shown schematically in Fig. 6, and Plate 2 shows part of the purification system.

About 1 gm of the whole rock sample was wrapped in Kaiser aluminum foil, marked for identification, weighed in a Mettler balance, and placed in the arm of the fusion furnace. As many as eight samples could be placed in this manner. The fusion furnace consisted of an air-cooled quartz tube about 3.5 cm in diameter and about 30 cm in length. A molybdenum crucible 2 cm in diameter

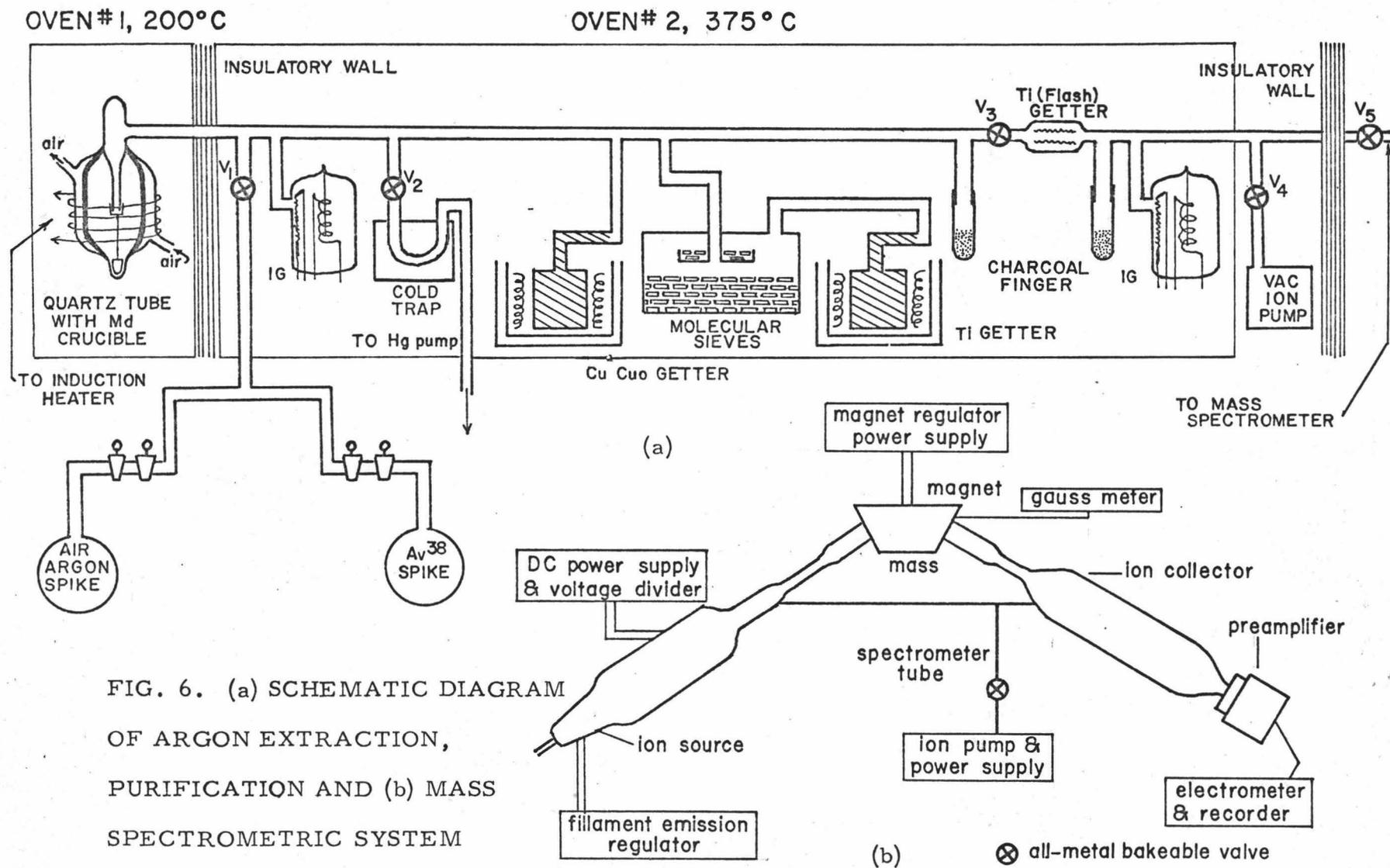


FIG. 6. (a) SCHEMATIC DIAGRAM OF ARGON EXTRACTION, PURIFICATION AND (b) MASS SPECTROMETRIC SYSTEM

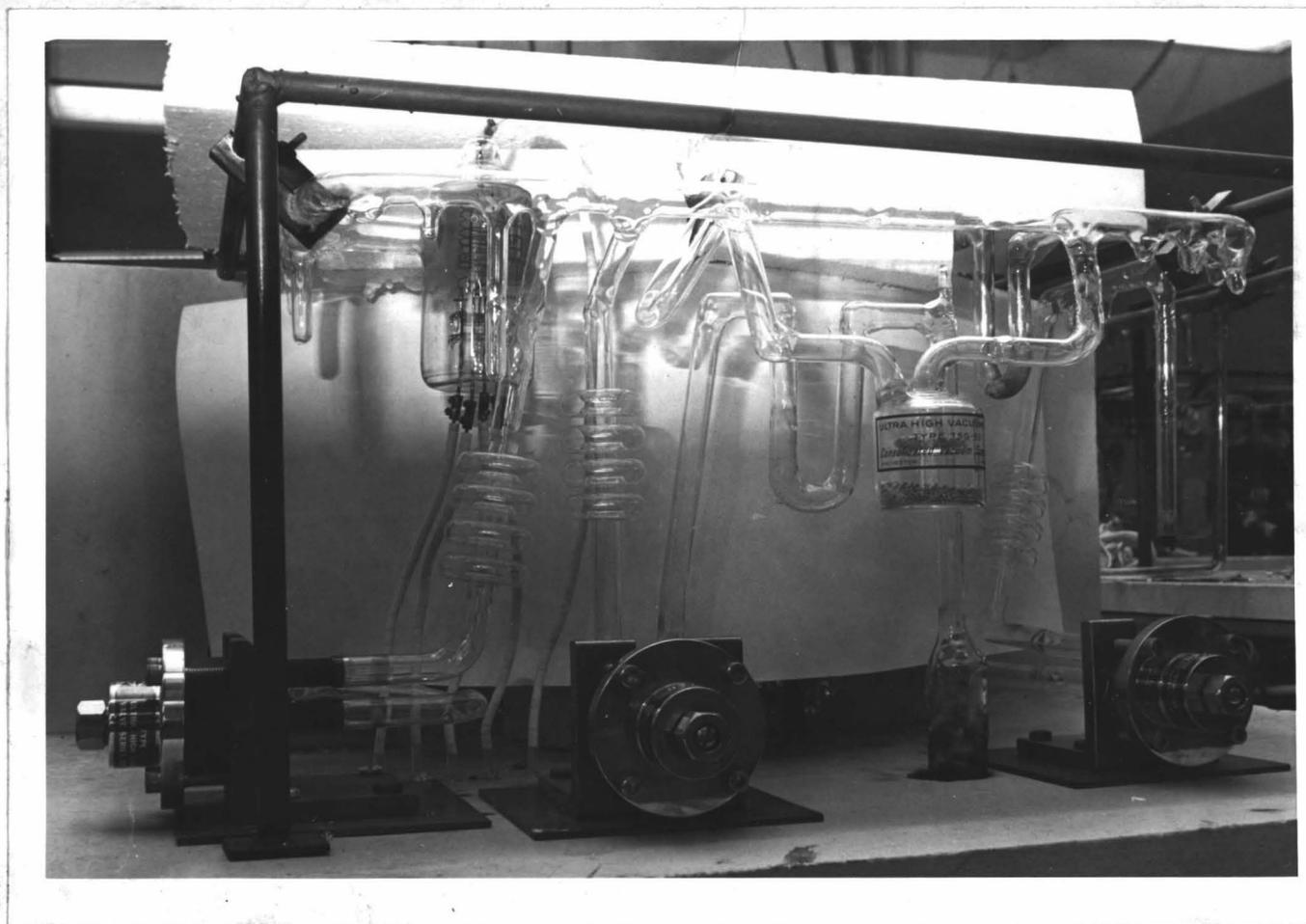


PLATE 2. VIEW OF PART OF THE ARGON PURIFICATION SYSTEM

ASBESTOS ABANDONED IN THE WOODS

and 9.3 cm in length was inserted in the quartz tube. The lip of the crucible was flattened against the walls of the quartz tube to avoid arcing at the sharp edges. The crucible rested on a molybdenum sheet stand.

The sample was fused by induction heating with a 5 KW Lepel radio-frequency generator which has a water-cooled primary coil of 10 turns, and the molybdenum crucible acted as the secondary. During the fusion of the sample, the quartz furnace was air cooled by passing air at 6 psi. The temperature of the furnace was slowly raised at intervals of 5 minutes until the highest temperature of 1400°C was achieved. To liberate all the argon additional heating for 15 minutes was continued at 1400°C.

Argon purification

The purification unit consisted of 10-15 gm of Linde molecular sieves, 1/16" pellets of 13 X type, enclosed in a pyrex bulb; a titanium getter made of 10 gm of -10 to +24 mesh titanium sponge and two 3 x 24" strips of 8 mil titanium metal; a titanium flash getter made of titanium and tantalum entwined wires wrapped over a tungsten filament, and a Cu-CuO getter composed of 50-100 gm of 20 mesh CuO rolled up in copper screens. Hydrogen and carbon monoxide were oxidized to water and carbon dioxide by the Cu-CuO getter; the water was absorbed by molecular sieves; while nitrogen was removed by the titanium getter.

Plate 2 shows part of the purification system.

Procedure

The sample and purification units were pumped by a mercury diffusion pump backed by a Welch Duoseal mechanical oil pump. The sample end near the mass spectrometer and the mass spectrometer tube itself were pumped by VacIon pumps.

After the installation of the molybdenum crucible in the furnace and putting in the samples, Unit #1 was baked at 390°C, the purification section, Unit #2, was baked at 390°C, and the charcoal in charcoal finger C₂ was outgassed at 350°C. After cooling the units, the Bayard-Alpert ionization gauge was degassed. The titanium getter, T₁, was degassed at 850°C. The Cu-CuO getter was raised to a temperature of 350°C. Finally, the titanium getter, T₁, was switched off.

When the pressure was around 2×10^{-6} torr, the valves V₂ and V₃ were closed. The pipette, with a volume of 2.41 cc, was filled with Ar³⁸ spike by closing the stopcock to the purification system and opening the stopcock to the spike reservoir. After 10 minutes the stopcock leading to the spike reservoir was closed and spike was pulled over the charcoal finger, C₁, by cooling it with liquid nitrogen. The sample was then inserted into the molybdenum crucible by manipulating an iron slug with a magnet. The titanium getter was switched on, while the Cu-CuO getter was already at 350°C. The valve V₁ was closed. The sample was fused at 1400°C by induction heating with a radiofrequency generator. When the titanium getter

was at 850°C, the liquid nitrogen around the charcoal finger C₁ was removed, and thus the Ar³⁸ spike and the gases evolved by the fusion of the sample were allowed to mix and getter for about half an hour. Then the valve V₄ leading to VacIon pump was closed, and the argon was pulled over the charcoal finger, C₂, cooled with liquid nitrogen, by opening the valve V₃. Twenty minutes were allowed for this operation. The valve V₂ was closed and the liquid nitrogen was removed. The charcoal finger was warmed to liberate argon. The pressure in the system was momentarily checked by switching on the Bayard-Alpert ionization gauge, and if it was higher than 9 x 10⁻⁵ torr, the titanium getter, T₂, was flashed for 30 seconds or more by passing a current of 22 amperes to lower the pressure to a low 10⁻⁵ torr range. The valve V₆ leading to the VacIon pump in the mass spectrometer tube was closed. The argon was allowed to enter the mass spectrometer by opening the valve V₅. Before introduction of argon the background was scanned, and the settings were left where the Ar⁴⁰ peak was observed. After the introduction of argon when the first ion of argon hit the filament, the point was marked "zero-time," and growth of Ar⁴⁰ peak was watched. When it leveled off, the valve V₅ was closed. The Ar³⁶, Ar³⁸, and Ar⁴⁰ peaks were scanned automatically and manually under static conditions by varying the current in the electromagnet, and by monitoring the magnetic flux by an RFL Gaussmeter using a Hall effect indium-arsenide probe tied to the lower plate of the magnet. The Ar³⁶, Ar³⁸, and Ar⁴⁰ peaks were recorded at 3.68 KG, 3.78 KG, and 3.88 KG, respectively. A constant voltage transformer was used to regulate the voltage as to

reduce fluctuations in the filament emission, DC power supply, magnetic power supply, and vibrating reed electrometer.

The mass spectrometer (Plate 3) is a glass, 4.5", 60° sector, single-focusing Reynolds-type mass spectrometer. It has been fully described by Funkhouser (1966). The operating parameters of the mass spectrometer were as follows:

trap current	25 a
filament current	3.9 a
case voltage	36 V
case current	0.99 ma
trap voltage	147 V

The ion collector had been coated with a black graphite paint and enclosed in a grounded steel box to prevent stray currents from contributing to the background. The background of Ar³⁶ and Ar⁴⁰ were 0.1 mv and 0.45 mv, respectively.

The ion current was measured by a Cary vibrating reed electrometer, Model 31, and its output was fed to a Leeds and Northrup recorder.

To compensate for memory effect and mass discrimination in the mass spectrometer, the peak heights were plotted against time, and extrapolated to "zero time." The zero time values were used for calculation of age.

Since hydrogen seems to contribute to the Ar³⁶ peak, it was

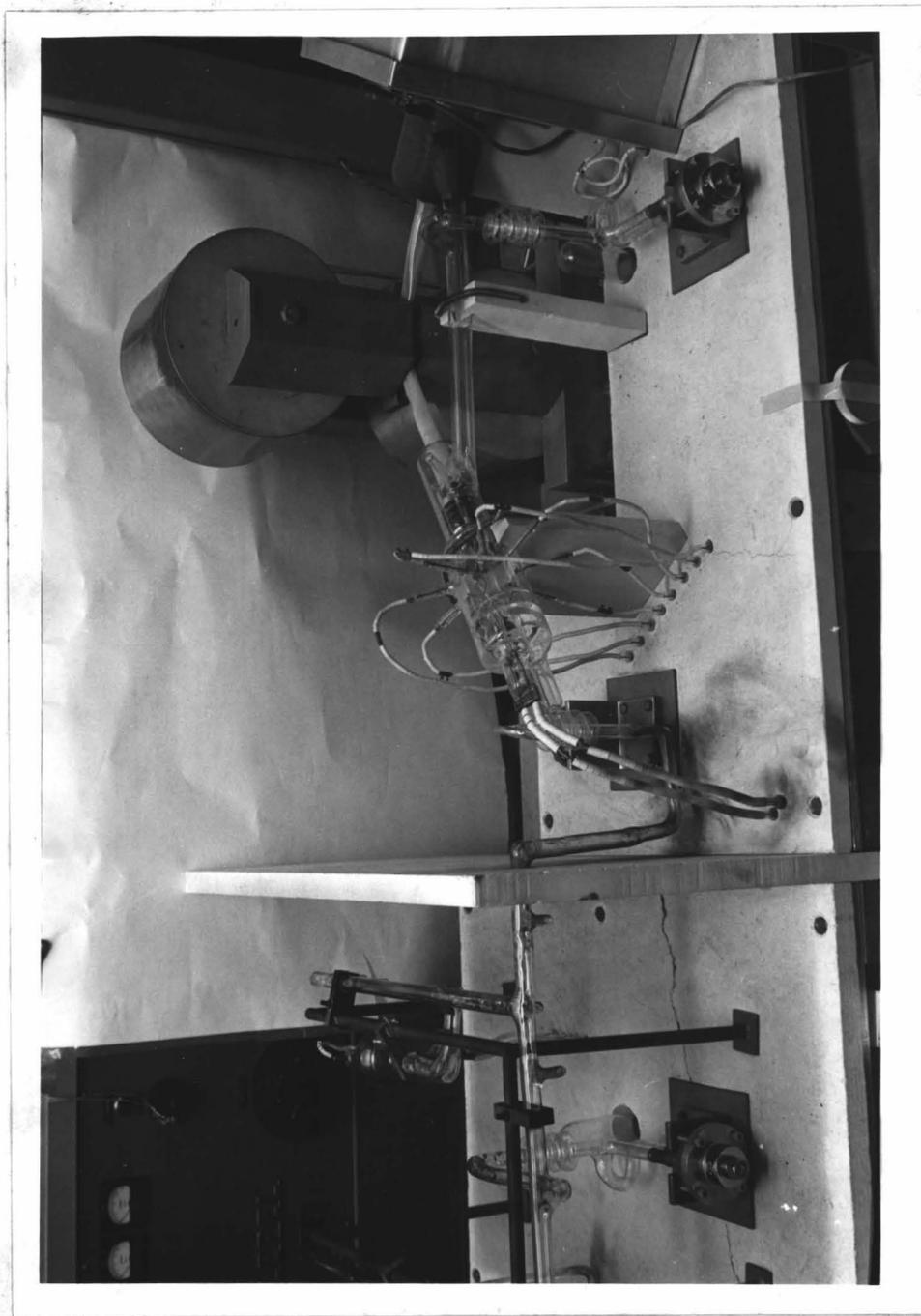


PLATE 3. VIEW OF GAS SOURCE MASS SPECTROMETER

also monitored by scan. It was less than 0.01 mv. Therefore, its contribution to Ar³⁶ peak is negligible.

CHAPTER VI
RESULTS AND DISCUSSIONS

The detailed results of K^{40} - Ar^{40} age determinations are given in Table III. To evaluate the confidence to be attached to these results, it is necessary to discuss the various sources of error.

1. Air argon contamination

Air argon consists of 99.6% Ar^{40} , 0.003% Ar^{38} , and 0.387% Ar^{36} . There is no way to distinguish between the radiogenic argon and the atmospheric argon. However, it is known that in air the ratio $\frac{Ar^{40}}{Ar^{36}} = 295.5$. Thus, the correction is made by measuring the total Ar^{40} and subtracting from it the product of the quantity of Ar^{36} and 295.5; i. e.,

$$\text{Corrected } Ar^{40} = \text{total } Ar^{40} - 295.5 \times Ar^{36}$$

It is obvious that a small error in the measurement of Ar^{36} is magnified by 295.5. A one percent error in the air correction at 80% air argon contamination introduces a $\pm 5\%$ error in the calculated age; the error increases to $\pm 10\%$ if the air argon contamination is 90% (McDougall, 1964, p. 110). The percent error, E, in the radiogenic argon due to the error in Ar^{36}/Ar^{40} can be calculated from the following equation (Lipson, 1958):

$$E = \frac{ef}{100 - f}$$

where e is the percent error in the Ar^{36}/Ar^{40} ratio, and f is the percent of atmospheric argon in the sample.

TABLE III. POTASSIUM - ARGON AGE RESULTS ON DECCAN TRAPS

SAMPLE NUMBER	LOCALITY	AVERAGE POTASSIUM (Wt.%)	K ⁴⁰ (MOLES/GM)(X10 ⁻⁸)	Ar ^{40*} MOLES/GM(X10 ⁻¹¹)	ATMOS-PHERIC Ar (%)	$\frac{Ar^{40*}}{40 X K}$ (X10 ⁻³)	CALCULATED AGE (MILLION YRS)(Figures rounded)
1	Nagpur	0.236	0.998	2.883	89	2.850	48
2	Palasdari	0.629	1.900	7.605	90	4.003	68
3	Poona	0.518	1.580	8.513	90	5.388	91
5	Karad	0.238	0.726	2.981	90	4.106	69
6	Andheri	0.606	1.848	4.769	91	2.580	46
7	Alandi	0.306	0.933	6.344	95	6.800	113
10	Neral	0.598	1.824	7.113	88	3.900	66
11	Badalpur	0.868	2.647	10.590	90	4.000	67

It is important that the air argon which may have been absorbed on the surface of the samples or absorbed by the rock from the air at the time of crystallization (McDougall, 1964) should be reduced as much as possible. This is done by heating the samples to 200°C for several hours under vacuum. It was shown by Armikhanov *et al.* (1961) that the air argon is liberated by heating the samples at 200°C without any loss of radiogenic argon. The use of tracers has been suggested (Naughton, 1963), and Naughton has even used vacuum crushing.

In the present study the samples analyzed have air argon of about 90% which means there is an error of $\pm 10\%$ in the determination of argon from this factor alone. In sample #7 the air argon is 95% of the total argon, involving error of about $\pm 40\%$.

2. Mass spectrometry

Replicate analyses of air have given results of $\text{Ar}^{40}/\text{Ar}^{36}$ agreeing within 1% of the values reported by Nier (1950). Thus the mass spectrometric error, $\sigma_{\text{m.s.}}$, is $\pm 1\%$.

3. Argon-38 spike calibration

The spikes were calibrated against the USGS-muscovite standard, P-207. Since only a scale factor was found in terms of moles/gm mv, the error is difficult to evaluate. Assuming that the liberation of argon from the standard and samples was complete, the error due to calibration, σ_s , should be negligible.

4. Error in potassium determinations

As discussed earlier the potassium determinations are believed to have an accuracy of better than $\pm 4.5\%$.

5. Error in decay constants

The decay constants used in the $K^{40}-Ar^{40}$ age equation are known to be accurate within 5%. However, this error is not considered because all workers use the same constants. This error affects only the absolute age but does not affect the comparison between ages. Hence, error due to decay constants, $\sigma_{d.c.}$, is neglected.

Total Error

Assuming that the various sources of error outlined above do not mutually contribute to each other, the total error in the age calculation is given by

$$\sigma_{total} = \sqrt{\sigma_{air}^2 + \sigma_{m.s.}^2 + \sigma_s^2 + \sigma_{d.c.}^2 + \sigma_K^2}$$

Neglecting σ_s and $\sigma_{d.c.}$ as explained above, the final equation for total error is

$$\begin{aligned} \sigma_{total} &= \sqrt{\sigma_{air}^2 + \sigma_{m.s.}^2 + \sigma_K^2} \\ &= \sqrt{(10)^2 + (1)^2 + (4.5)^2} \\ &= 11.09\% \end{aligned}$$

Example of an age calculation

An example of an age calculation is given below:

A. Calculation of scale factor:

Results of USGS Muscovite P-207 standard

Weight of standard = 0.4725 gm

Peak heights:

$$\text{Ar}^{36} = 25.86 \text{ mv}$$

$$\text{Ar}^{38} = 80.5 \text{ mv}$$

$$\text{Ar}^{40} = 10650 \text{ mv}$$

$$\text{Air Ar}^{40} = 25.86 \times 295.5 = 7641.6 \text{ mv}$$

$$\text{Radiogenic Ar}^{40*} = 10650 - 7641.6 = 3008.4 \text{ mv}$$

$$\text{Amount of Ar}^{40*} \text{ per gm} = \frac{3008.4}{0.4725} \text{ mv}$$

Now 1 gm of P-207 gives $\text{Ar}^{40*} = 1.267 \times 10^{-9}$ moles

or $\frac{3008.4}{0.4725}$ mv of P-207 corresponds to 1.267×10^{-9} moles/gm

or 1 mv of P-207 corresponds to $\frac{1.267 \times 10^{-9}}{3008.4} \times 0.4725$

$$= 1.989 \times 10^{-13} \text{ moles gm}$$

B. Calculation of age of sample #2

(a) Weight of sample for potassium analysis = 0.7057 gm

Amount of potassium in the sample = 0.629%

$$\begin{aligned} \text{Amount of K}^{40} \text{ in the sample} &= \frac{(1.22 \times 10^{-4})}{40} \times (0.629 \times 10^{-2}) \\ &= 1.9 \times 10^{-8} \end{aligned}$$

$$\text{where } \frac{\text{K}^{40}}{\text{K}} = 1.22 \times 10^{-4}$$

(b) Weight of sample for argon analysis = 1 gm

Peak heights:

$$\text{Ar}^{36} = 4.58 \text{ mv}$$

$$\text{Ar}^{38} = 80.5 \text{ mv}$$

$$\text{Ar}^{40} = 1488 \text{ mv}$$

$$\text{Air Ar}^{40} = 4.58 \times 295.5 = 1353.4 \text{ mv}$$

$$\text{Radiogenic Ar}^{40*} = 1488 \times 1353.4 = 134.6 \text{ mv}$$

Amount of radio-
genic Ar^{40*} in
the sample

$$\begin{aligned} &= 134.6 \times 5.65 \times 10^{-13} \\ &= 7.605 \times 10^{-11} \text{ moles/gm} \end{aligned}$$

(c) Percent of air correction = 90.9%

$$(d) \text{ Ratio of } \text{Ar}^{40}/\text{K}^{40} = \frac{7.605 \times 10^{-11}}{1.9 \times 10^{-8}} = 4.003 \times 10^{-3}$$

$$\begin{aligned} (e) \text{ Age, } t &= 1887 \ln \left(1 + 0.130 \frac{\text{Ar}^{40}}{\text{K}^{40}} \right) \\ &= 1887 \ln \left(1 + 9.130 \times 4.003 \times 10^{-3} \right) \\ &= 67.6 \text{ million years} \end{aligned}$$

Discussion

It must be emphasized here that the exact stratigraphic horizons of analyzed samples are not known. It is, therefore, impossible to make a detailed interpretation of the age data. The following discussion is, therefore, of a general nature.

The range of ages from 46 to 91 million years, disregarding the age of 113 million years which is in error of more than 40% because of 95% air contamination, suggests that India witnessed the beginning of volcanic activity during Cretaceous time, and that the activity continued through the Eocene epoch. Hence, the radiometric data supports the stratigraphic evidence of Upper Cretaceous age for the first eruptions.

Sahni's (1940) suggestion that the volcanic activity represented by the Deccan traps in India commenced and ended in the Eocene epoch is contradicted by this study. On the contrary, the volcanic activity lasted much longer, as is shown by the range of ages obtained. This is also indicated by numerous intertrappean beds, clay or bole layers sandwiched between the traps, and further by the contrasted evolutionary stages of the intertrappean fauna and flora from different stratigraphic levels. However, it must be pointed out that the number of samples dated for such a vast geological formation is extremely small. An extensive detailed study of a large number of Deccan trap samples is needed to establish the span of time embraced by them, and the general direction of migration of volcanic activity.

The hypothesis that volcanic activity was contemporaneous in India, South Africa, South America, Australia, and Antarctica, has been ruled out by the radiometric age determinations by McDougall (1961, 1963, and 1966) and Amaral et al. (1966). According to McDougall, dolerites of Antarctica are mid-Upper Jurassic (147 to 163 m. y.) and the South African (Karoo) dolerites are mid-Lower Jurassic (154 to 190 m. y.). Thus, dolerites were emplaced in South Africa during the early Jurassic and continued into Middle Jurassic. They were also emplaced at this time in Antarctica and Australia. However, it has been recently shown by Amaral et al. (1966) and McDougall and Ruegg (1966) that the South American basaltic rocks are Cretaceous in age (100.5 m. y. to 161 m. y.). It is interesting to point out here that the age of the Rajmahal traps of the Damodar Valley and Assam, India, which are very similar to the Deccan traps in mineral composition, ranges from Lower to Middle Jurassic. Thus, the Rajmahal traps may be roughly correlated with the South African dolerites. The hypothesis that the eruption of vast volumes of basaltic magma in different parts of the world was due to the breaking up of the Gondwanaland continent is not necessarily invalidated by the fact that the eruptions were not everywhere of exactly the same age. Since the disintegration of Gondwanaland must have been a slow process and zones of tension were developed at different times at different places during the process, it is reasonable to assume that resulting volcanic activity may have varied in time from place to place. It may have commenced in one area before it did in another, with some overlapping times of activity.

Summary

1. The volcanic activity represented by the samples of the Deccan traps studied began during the Upper Cretaceous time and continued into the Eocene, with some activity as late as Miocene.
2. The volcanic activity in the continents of Asia (India), South Africa, South America, Antarctica, and Australia was overlapping in time.
3. Much detailed work on type sections of the Deccan traps should be done to estimate the duration of the volcanic activity and its general trend of migration. The radiometric dating of the Rajmahal traps should throw additional light on the relation of continental drift and volcanism in the Gondwana continents.

APPENDIX A

PETROGRAPHIC DESCRIPTION OF SAMPLES

A brief petrographic description of the samples is given below.

Sample #1 Location: Nagpur (Lat. $21^{\circ} 8'$, Long. $79^{\circ} 3'$)

Texture

The rock section shows porphyritic texture with phenocrysts of labradorite, augite, and olivine in a fine-grained matrix of plagioclases, pyroxenes, olivine, and glass. The texture is locally glomeroporphyritic.

Mineral Composition

Plagioclases: mostly labradorite, some bytownite; lath shaped, showing albite and Carlsbad twinning; altered slightly to sericite along cleavages and cracks; carry inclusions of glass and magnetite.

Pyroxenes: mostly augite, there appears to be pigeonite in the matrix; anhedral grains with cleavage; extinction angle about 44° .

Olivine: anhedral grains with irregular cracks; some grains completely altered to serpentine and to xylotile - a rather rare mineral of the serpentine group.

Xylotile: Opaque; greenish brown and fibrous.

Magnetite and a little ilmenite are present. The glass does not show devitrification.

The average length of plagioclases in phenocrysts is about 0.5 mm and in the groundmass 0.09 mm.

Sample #2 Location: Palasdari (Lat. $18^{\circ} 53'$, Long. $73^{\circ} 19'$)

Ophitic texture with phenocrysts of plagioclase and augite in a groundmass of glass, plagioclase, and pyroxene. The mineral composition consists of fresh labradorite (altered a little along cleavages and cracks), augite, olivine, xylotile, magnetite and ilmenite. The glass is not devitrified. Average length of plagioclase in phenocrysts is about 2.5 mm and in the groundmass 0.07 mm.

Sample #3 Location: Poona (Lat. $18^{\circ} 34'$, Long. $73^{\circ} 52'$)

Same as #2; in this the labradorite laths, with polysynthetic twinning, show greater alteration to sericite. The glass appears to be devitrified. The plagioclase phenocrysts average 1.1 mm, and the plagioclase grains in the matrix are about 0.07 mm long.

Sample #5 Location: Karad (Lat. $17^{\circ} 17'$, Long. $74^{\circ} 11'$)

Porphyritic texture; labradorite phenocrysts have inclusions of glass and are a little altered; anhedral grains of augite and olivine altering to xylotile are present; magnetite is an accessory mineral. The average length of plagioclase is 1.1 mm in

phenocrysts and 0.19 mm in the groundmass.

Sample #6 Location: Andheri (Lat. $19^{\circ} 5'$, Long. $72^{\circ} 50'$)

Similar to #5 except that plagioclase laths show greater alteration; the glass is not devitrified. The average length of plagioclase grains is about 0.58 mm in phenocrysts and about 0.16 mm in the groundmass.

Sample #7 Location: Alandi (Lat. $18^{\circ} 42'$, Long. $73^{\circ} 50'$)

Porphyritic texture; labradorite phenocrysts are altered along the margins; augite and pigeonite are fresh; olivine alters to xylotile though relatively fresh anhedral grains are also present; plagioclases average 2.5 mm in phenocrysts and 0.13 mm in the groundmass.

Sample #10 Location: Neral (Lat. $19^{\circ} 2'$, Long. $73^{\circ} 19'$)

Ophitic texture; labradorite crystals with inclusions of glass and magnetite are quite fresh; augite crystals with two sets of cleavages are present, extinction angle varies from 28° to 41° ; olivine, which is present in much less quantity than in other samples, is at places only slightly altered, while at other places it is completely altered to xylotile; magnetite and ilmenite are present; the glass is a little devitrified. Plagioclases average 1.56 mm in phenocrysts and 0.07 mm in the groundmass.

Sample #11 Location: Badalpur (Lat. $19^{\circ} 9'$, Long. $73^{\circ} 1'$)

Porphyritic texture; labradorite is sericitized and has inclusions of glass and magnetite; olivine shows alteration to xyloite; augite, magnetite and ilmenite are present; the glass shows devitrification. The average length of plagioclases is 1.5 mm in phenocrysts and 0.07 mm in the groundmass.

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