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# The Cause of Anomalous Potassium-Argon “Ages” for Recent Andesite Flows at Mt. Ngauruhoe, New Zealand, and the Implications for Potassium-Argon “Dating”

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## Abstract

New Zealand's newest and most active volcano, Mt. Ngauruhoe in the Taupo Volcanic Zone, produced andesite flows in 1949 and 1954, and avalanche deposits in 1975. Potassium-argon “dating” of five of these flows and deposits yielded K-Ar model “ages” from  $<0.27\text{Ma}$  to  $3.5\pm 0.2\text{Ma}$ . “Dates” could not be reproduced, even from splits of the same samples from the same flow, the explanation being variations in excess  $^{40}\text{Ar}^*$  content. A survey of anomalous K-Ar “dates” indicates they are common, particularly in basalts, xenoliths, and xenocrysts such as diamonds that are regarded as coming from the upper mantle. In fact, it is now well established that there are large quantities of excess  $^{40}\text{Ar}^*$  in the mantle, which in part represent primordial argon not produced by *in situ* radioactive decay of  $^{40}\text{K}$  and not yet outgassed. And there are mantle-crust domains between, and within, which argon circulates during global tectonic processes, magma genesis, and mixing of crustal materials. This has significant implications for the validity of K-Ar and  $^{40}\text{Ar}/^{39}\text{Ar}$  “dating.”

## Keywords

Andesite, 1949–1975 Flows, Mt. Ngauruhoe, New Zealand, Potassium-Argon Dating, Anomalous Model “Ages,” Excess  $^{40}\text{Ar}^*$ , Excess  $^{40}\text{Ar}^*$  in Rocks and Minerals, Upper Mantle, Geochemical Reservoirs, Mantle-Crust Domains, Crustal Mixing, Magma Genesis

## Introduction

Mt. Ngauruhoe is an andesite stratovolcano of 2291 m elevation, rising above the Tongariro volcanic massif within the Tongariro Volcanic Center of the Taupo Volcanic Zone, North Island, New Zealand (Figure 1) (Graham & Hackett, 1987; Williams, 1994). Though not as well publicized as its neighbor, Mt. Ruapehu (about 12 km to the south), Ngauruhoe is an imposing, almost perfect cone that rises more than 1000 m above the surrounding landscape. Eruptions from a central 400 m diameter crater have constructed the steep ( $33^\circ$ ), outer slopes of the cone (Hackett & Houghton, 1987; Williams).

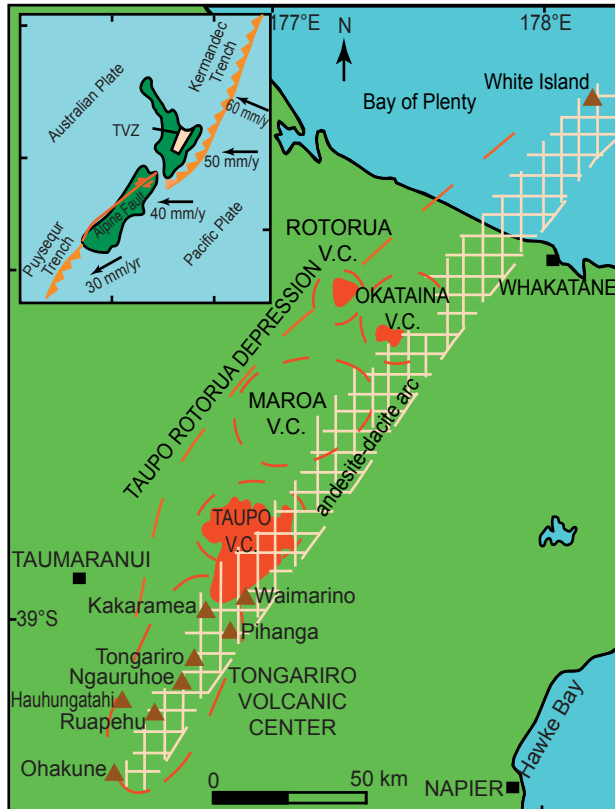
## Geologic Setting

The Taupo Volcanic Zone, a volcanic arc and marginal basin of the Taupo-Hikurangi arc-trench (subduction) system (Cole & Lewis, 1981), is a southward extension on the Tonga-Kermadec arc into the continental crustal environment of New Zealand's North Island. It has been interpreted as oblique subduction of the Pacific plate beneath the Australian

plate. The zone extends approximately 300 km north-northeast across the North Island from Ohakune to White Island (Figure 1) and is up to 50 km wide in the central part, narrowing northwards and southwards. This volcano-tectonic depression (Taupo-Rotorua depression (Grindley, 1960) comprises four rhyolitic centers (Rotorua, Okataina, Maroa, and Taupo), plus the calc-alkaline Tongariro Volcanic Center, part of a young ( $<0.25\text{Ma}$ ) andesite-dacite volcanic arc with no associated rhyolitic volcanism extending along the eastern side of the zone (Graham & Hackett, 1987).

The Tongariro Volcanic Center extends for 65 km south-southwest from Lake Taupo at the southern end of the Taupo Volcanic Zone (Figure 1) and consists of four large predominantly andesite volcanoes Kakaramea, Pihanga, Tongariro, and Ruapehu (Figure 2); two smaller eroded centers at Maungakatote and Hauhungatahi; a satellite cone and associated flows at Pukeonake and four craters at Ohakune (Figure 2) (Cole, Graham, Hackett, & Houghton, 1986; Hackett & Houghton, 1987).

Most vents lie close to the axis of a large graben in



**Figure 1.** The location of Mt. Ngauruhoe in the Taupo Volcanic Zone (TVZ), New Zealand, showing the main structural features. The shaded area is the andesite arc, and the inset shows the major components of the boundary between the Australian and Pacific Plates in the New Zealand region (arrows indicate relative motions). Solid triangles are basalt-andesite volcanoes (Graham & Hackett, 1987).

which Quaternary volcanic rocks overlie a basement of Mesozoic greywacke and Tertiary sediments (Gregg, 1960; Nairn & Wood, 1987). North-northeast-trending normal faults with throws up to 30 m cut the volcanoes within the graben. Nearly all vents active within the last 10 ka lie on a gentle arc which extends 25 km north-northeast from the Rangataua vent on the southern slopes of Ruapehu through Ruapehu summit and north flank vents, Tama Lakes, Ngauruhoe, Red Crater, Blue Lake, and Te Mari craters. None of the young vents lie on the mapped faults, which mostly downthrow towards the axis of the graben. The vent lineation lies above this axis, which is considered to mark a major basement fracture (Gregg, 1960; Grindley, 1965; Nairn & Wood) that allows the intrusion of andesite dikes.

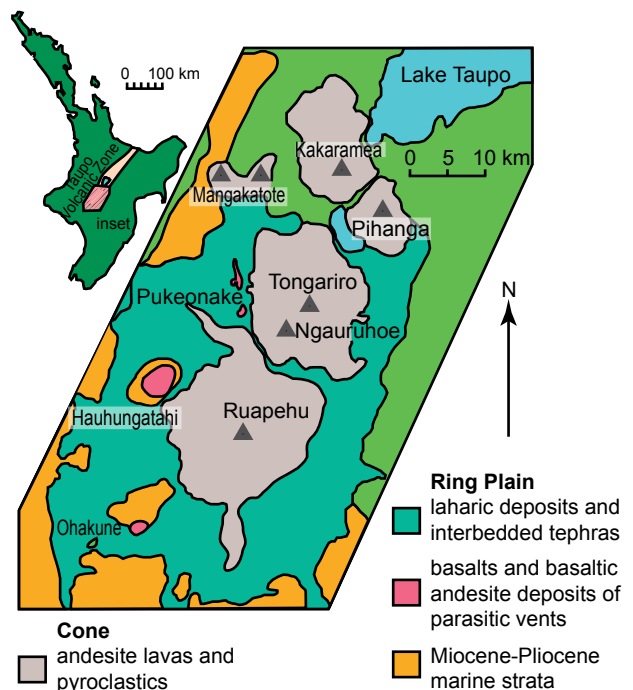
The Tongariro volcanics unconformably overlie late Miocene marine siltstones beneath Hauhungatahi, and a minimum age for the onset of volcanism is measured by the influx of andesite pebbles in early Pleistocene conglomerates of the Wanganui Basin to the south (Cole et al., 1986; Grindley, 1965). The oldest dated lavas from the Tongariro massif are hornblende

andesites exposed at Tama Lakes between Ngauruhoe and Ruapehu, at  $0.26 \pm 0.003$  Ma; from Ruapehu,  $0.23 \pm 0.006$  Ma; and from Kakaramea,  $0.22 \pm 0.001$  Ma (potassium-argon dates) (Stipp, 1968).

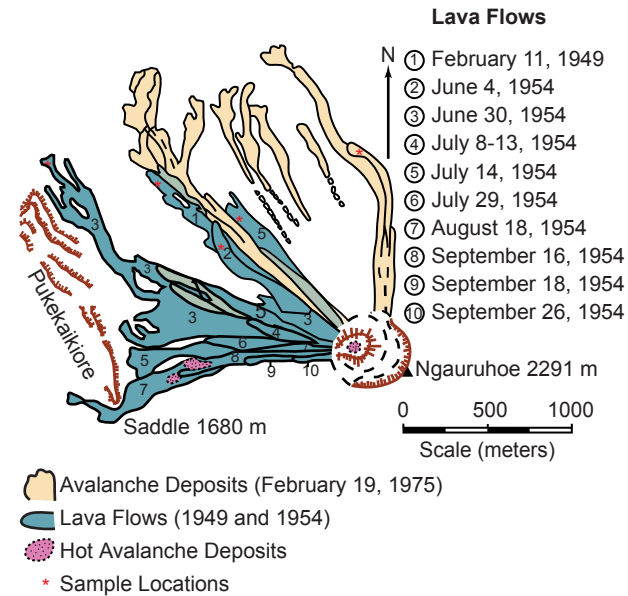
Tongariro itself is a large volcanic massif that consists of at least twelve composite cones, the youngest and most active of which is Ngauruhoe. A broad division has been made into older ( $>20$  ka) and younger ( $<20$  ka) lavas (Cole et al., 1986; Topping, 1973). There is a north-northeast alignment of the younger vents of Tongariro, particularly evident between Te Mari and Ngauruhoe.

### Ngauruhoe

Ngauruhoe is the newest cone of the Tongariro massif and has been active for at least 2.5 ka (Grindley, 1965; Nairn & Wood, 1987; Williams, 1994). It has been one of the most active volcanoes in New Zealand, with more than seventy eruptive episodes since 1839, when the first steam eruption was recorded by European settlers (Gregg, 1960; Nairn & Wood; Williams). Prior to European colonisation the Maoris witnessed many eruptions from the mountain (Gregg, 1960). The first lava eruption seen by European settlers occurred between April and August 1870, with two or three flows witnessed spilling down the north-western flanks of the volcano on July 7 (Gregg, 1960; Nairn & Wood). Following that event there have been pyroclastic (ash) eruptions every few years (Nairn & Wood), with major explosive activity in April–May 1948.



**Figure 2.** Location and deposits of the Tongariro Volcanic Center (Cole, Graham, Hackett, & Houghton, 1986; Hackett & Houghton, 1987).



**Figure 3.** Map of the north-western slopes of Mt. Ngauruhoe showing the lava flows of 1949 and 1954, and the 1975 avalanche deposits (Battey, 1949; Gregg, 1956, 1960; Nairn & Self, 1978; Nairn & Wood, 1987). The location of samples collected for this study are marked.

The next lava extrusion was in February 1949, beginning suddenly with ejection of incandescent blocks, and a series of hot block and ash flows down the north-western slopes on February 9 (Gregg, 1960; Nairn & Wood, 1987). The southern sub-crater filled with lava, which by late on February 10 had flowed over the lowest part of the rim and down the north-west slopes of the cone. By February 12 the flow had ceased moving, subsequent mapping placing its volume at about 575,000 m<sup>3</sup> (Figure 3) (Battey, 1949; Gregg, 1960). Further explosive pyroclastic (ash) eruptions followed, reaching a maximum about February 1921. The eruptions ended on March 3.

The eruption from May 13, 1954 to March 10, 1955 began with explosive ejection of ash and blocks, although red-hot lava had been seen in the crater five months previously (Gregg, 1960; Nairn & Wood, 1987). The eruption was remarkable for the estimated large volume of almost 8 million m<sup>3</sup> of lava that then flowed from the crater from June through September 1954, and was claimed to be the largest flow of lava observed in New Zealand (that is, by the European settlers) (Gregg, 1960; Williams, 1994). The lava was actually expelled from the crater in a series of seventeen distinct flows on the following dates (Gregg, 1956; 1960):

June 4, 30

July 8, 9, 10, 11, 13, 14, 23, 28, 29, 30

August 15 (?), 18

September 16, 18, 26

Figure 3 shows the distribution of those 1954 lava flows that are still able to be distinguished on

the north-western and western slopes of Ngauruhoe. All flows were of aa lava (as was the February 1949 flow), typified by rough, jagged, clinkery surfaces made up of blocks of congealed lava. The lava flows were relatively viscous, some being observed at close quarters slowly advancing at a rate of about 20 cm per minute (Gregg, 1956, 1960; Williams, 1994). The August 18 flow was more than 18 m thick and still warm almost a year after being erupted. Intermittent explosive eruptions and spectacular lava fountaining during June and July 1954 built a spatter-and-cinder cone around the south sub-crater, modifying the western summit of the mountain. Activity decreased for two months after the last of the lava flows on September 26, but increased again during December 1954 and January 1955 with lava fountaining and many highly explosive pyroclastic (ash) eruptions. The last ash explosion was reported on March 10, 1955, but red-hot lava remained in the crater until June 1955 (Gregg, 1956, 1960).

After the 1954–1955 eruption, Ngauruhoe steamed semi-continuously, with numerous small eruptions of ash derived from comminuted vent debris. Incandescent ejecta were seen in January 1973, and ash erupted in December 1973 contained juvenile glassy andesite shards (Nairn & Wood, 1987). Cannon-like, highly explosive eruptions in January and March 1974, the largest since 1954–1955, threw out large quantities of ash and incandescent blocks, one of which was reported as weighing 3000 tonnes and thrown 100 m (Nairn & Wood; Williams, 1994). Pyroclastic avalanches flowed from the base of large convecting eruption columns, down the west and north slopes of the cone, and the crater became considerably shallower (Nairn, Hewson, Latter, & Wood, 1976; Nairn & Wood).

A series of similar but more violent explosions occurred on February 19, 1975, accompanied by clearly visible atmospheric shock waves and condensation clouds (Nairn, 1976; Nairn & Self, 1978; Nairn & Wood, 1987; Williams, 1994). Ash and blocks up to 30 m across were ejected and scattered within a radius of 3 km from the summit. The series of nine, cannon-like, individual eruptions followed a 1.5 hour period of voluminous gas-streaming emission, which formed a convecting eruption plume between 11 km and 13 km high (Nairn & Self; Nairn & Wood; Williams, 1994). The explosions took place at 20–60 minute intervals for more than five hours. Numerous pyroclastic avalanches were also generated by fallback from the continuous eruption column, the avalanches consisting of a turbulent mixture of ash, bombs, and larger blocks which rolled swiftly down Ngauruhoe's sides at about 60 km per hour (Nairn & Wood; Williams). The deposits from these avalanches and the later explosions accumulated as sheets of

debris in the valley at the base of the cone, but did not extend beyond 2 km from the summit. It is estimated that a minimum bulk volume of 3.4 million m<sup>3</sup> of pyroclastic material was erupted in the seven-hour eruption sequence on that day (Nairn & Self). Figure 3 shows the location of these avalanche deposits.

There have been no eruptions since February 1975. A plume of steam or gas is still often seen above the summit of the volcano, as powerful fumaroles in the bottom of the crater discharge hot gases. However, the temperature of these fumaroles in the crater floor has steadily cooled significantly since 1979, suggesting that the main vent is becoming blocked.

### Sample Collection

Field work and collection of samples was undertaken in January 1996. The Ngauruhoe area was accessed from State Highway 47 via Mangateopopo Road. From the parking area at the end of the road, the Mangateopopo Valley walking trail was followed to the base of the Ngauruhoe cone, from where the darker-colored recent lava flows were clearly visible and each one easily identified on the north-western slopes against the lighter-colored older portions of the cone (Figure 3).

Eleven 2–3 kg samples were collected two each from the February 11, 1949, June 4, 1954, and July 14, 1954 lava flows and from the February 19, 1975 avalanche deposits, and three from the June 30, 1954 lava flows. The sample locations are marked on Figure 3. Care was taken to ensure correct identification of each lava flow and that the samples collected were representative of each flow and any variations in textures and phenocrysts in the lavas.

### Laboratory Work

All samples were sent first for sectioning one thin section from each sample for petrographic analysis. A set of representative pieces from each sample (approximately 100 g) was then despatched to the AMDEL Laboratory in Adelaide, South Australia, for whole-rock major, minor and trace element analyses. A second representative set (50–100 g from each sample) was sent progressively to Geochron Laboratories in Cambridge (Boston), Massachusetts, for whole-rock potassium-argon (K-Ar) dating first a split from one sample from each flow, then a split from the second sample from each flow after the first set of results was received, and finally, the split from the third sample from the June 30, 1954 flow.

At the AMDEL Laboratory each sample was crushed and pulverized. Whole-rock analyses were undertaken by total fusion of each powdered sample and then digesting them before ICP-OES for major and minor elements, and ICP-MS for trace and rare earth elements. Fe was analyzed for amongst the

major elements by ICP-OES as Fe<sub>2</sub>O<sub>3</sub> and reported accordingly, but separate analyses for Fe as FeO were also undertaken via wet chemistry methods. The detection limit for all major element oxides was 0.01%. For minor and trace elements the detection limits varied between 0.5 and 20 ppm, and for rare earth elements between 0.5 and 1 ppm.

The potassium and argon analyses were undertaken at Geochron Laboratories under the direction of Richard Reesman, the K-Ar laboratory manager. No specific location or expected age information was supplied to the laboratory. However, the samples were described as andesites that probably contained “low argon” and therefore could be young, so as to ensure the laboratory took extra care with the analytical work.

Because the sample pieces were submitted as whole rocks, the K-Ar laboratory undertook the crushing and pulverizing preparatory work. The concentrations of K<sub>2</sub>O (weight %) were then measured by the flame photometry method (Dalrymple & Lanphere, 1969), the reported values being the averages of two readings for each sample. The <sup>40</sup>K concentrations (ppm) were calculated from the terrestrial isotopic abundance using the measured concentrations of K<sub>2</sub>O. The concentrations in ppm of <sup>40</sup>Ar\*, the supposed “radiogenic” <sup>40</sup>Ar, were derived using the conventional formula from isotope dilution measurements on a mass spectrometer by correcting for the presence of atmospheric argon whose isotopic composition is known (Dalrymple & Lanphere). The reported concentrations of <sup>40</sup>Ar\* are the averages of two values for each sample. The ratios <sup>40</sup>Ar\*/Total Ar and <sup>40</sup>Ar/<sup>36</sup>Ar are also derived from measurements on the mass spectrometer and are also the averages of two values for each sample.

### Petrography and Chemistry

Clark (1960) reported that most of the flows from Ngauruhoe are labradorite-pyroxene andesite with phenocrysts of plagioclase (labradorite), hypersthene and rare augite in a hyalopilitic (needle-like microlites set in a glassy mesostasis) groundmass containing abundant magnetite. However, all lava, lapilli, and incandescent blocks that have been analyzed from eruptions this century also contain olivine; chemically they may be classed as low-silica (or basaltic) andesites (using the classification scheme of Gill, 1981). The published analyses in Table 1 show only trivial changes in composition between 1928 and 1975. In fact, the 1954 and 1974 andesites are so similar that Nairn et al. (1976) suggested that a solid plug of 1954-andesite was heated to incandescence and partially remobilized on top of a rising magma column in 1974. This plug was disrupted and blown from the vent as ejecta ranging in texture from solid blocks, through expanded scoria to spatter bombs.

**Table 1.** Whole-rock, major-element oxide analyses of recent lava flows at Mt. Ngauruhoe, New Zealand, as reported in the literature.

	1	2	3	4	5	6	7	8
SiO <sub>2</sub>	56.63	57.24	55.90	56.22	56.2	55.83	55.73	56.05
TiO <sub>2</sub>	0.81	0.81	0.76	0.76	0.8	0.76	0.77	0.84
Al <sub>2</sub> O <sub>3</sub>	16.71	16.75	16.90	16.63	16.6	17.03	17.23	16.08
Fe <sub>2</sub> O <sub>3</sub>	1.16	1.54	2.10	2.37	1.4	2.14	2.13	3.24
FeO	7.00	6.44	6.30	6.14	7.0	6.36	6.47	5.57
MnO	0.16	0.12	0.15	0.15	0.1	0.16	0.16	0.15
MgO	4.85	4.58	5.20	5.24	5.2	4.79	4.89	5.03
CaO	8.16	7.95	8.40	8.31	8.3	8.37	8.52	7.93
Na <sub>2</sub> O	2.85	2.74	2.60	3.14	3.1	2.93	2.86	2.82
K <sub>2</sub> O	1.16	1.49	1.00	1.14	1.2	1.20	1.08	1.23
P <sub>2</sub> O <sub>5</sub>	0.16	0.17	0.10	0.17	0.2	0.15	0.15	0.15
H <sub>2</sub> O	0.31	0.24	0.06	0.19	N/A	0.14	0.10	0.38
<b>TOTAL</b>	<b>99.95</b>	<b>100.07</b>	<b>99.47</b>	<b>100.46</b>	<b>100.1</b>	<b>99.86</b>	<b>100.09</b>	<b>99.47</b>

1. Ejecta from March 1928 eruption (Clark, 1960; Hackett & Houghton, 1987)
2. Lava from February 1949 eruption (Steiner, 1958; Clark, 1960; Hackett & Houghton, 1987)
3. Lava from June 30, 1954 flow (Steiner, 1958; Clark, 1960; Ewart & Stipp, 1968)
4. 1954 lava (VU 29250) (Graham & Hackett, 1987)
5. 1954 lava (VU 29250) (Cole, Graham, Hackett, & Houghton, 1986; Nairn & Wood, 1987)
6. Average of four lava flows from 1954 eruptions (Nairn, Hewson, Latter, & Wood, 1976; Hackett & Houghton, 1987)
7. Average of 5 blocks and bombs from January and March 1974 eruptions (Nairn et al., 1976; Hackett & Houghton, 1987)
8. Lapilli from February 19, 1975 eruption (Hackett & Houghton, 1987)

**Table 2.** Whole-rock, major-element oxide analyses of five recent lava flows at Mt. Ngauruhoe, New Zealand (Analyst: AMDEL, Adelaide; April 1996).

	1A	1B	2A	2B	3A	3B	3C	4A	4B	5A	5B
SiO <sub>2</sub>	56.7	56.2	55.3	55.8	56.3	55.9	55.6	56.1	55.6	56.0	55.4
TiO <sub>2</sub>	0.79	0.85	0.74	0.77	0.76	0.75	0.74	0.75	0.84	0.79	0.78
Al <sub>2</sub> O <sub>3</sub>	17.2	17.3	16.5	17.3	17.0	16.9	16.7	16.9	17.5	17.0	16.5
Fe <sub>2</sub> O <sub>3</sub> *	9.10	9.63	9.26	9.23	9.11	9.17	9.59	9.29	9.61	9.25	9.43
MnO	0.15	0.16	0.15	0.15	0.15	0.15	0.16	0.15	0.16	0.15	0.16
MgO	4.28	3.84	5.21	4.71	4.75	5.00	5.09	4.71	3.84	4.31	5.27
CaO	7.61	7.93	8.22	8.29	7.95	8.16	8.17	8.00	8.17	7.83	8.56
Na <sub>2</sub> O	3.08	3.19	2.91	3.03	3.06	2.98	2.95	3.02	3.11	3.08	2.86
K <sub>2</sub> O	1.15	1.01	1.05	1.00	1.10	1.08	1.06	1.12	1.04	1.10	1.09
P <sub>2</sub> O <sub>5</sub>	0.13	0.13	0.12	0.12	0.13	0.13	0.13	0.13	0.13	0.14	0.14
LOI	0.42	0.48	0.51	0.37	0.38	0.50	0.53	0.62	0.42	0.70	0.41
<b>TOTAL</b>	<b>100.51</b>	<b>100.72</b>	<b>99.97</b>	<b>100.77</b>	<b>100.69</b>	<b>100.72</b>	<b>100.72</b>	<b>100.79</b>	<b>100.42</b>	<b>100.35</b>	<b>100.60</b>

\*Total Fe as Fe<sub>2</sub>O<sub>3</sub>

1. February 11, 1949 flow, samples A and B
2. June 4, 1954 flow, samples A and B
3. June 30, 1954 flow, samples A, B, and C
4. July 14, 1954 flow, samples A and B
5. February 19, 1975 flow, samples A and B

Table 2 lists the whole-rock major element analyses of the eleven samples collected in this study. Comparison of the data for each flow with the corresponding data in Table 1 indicates that in their bulk chemistries all the samples analyzed (and thus all the flows) are virtually identical to one another, the trivial differences being attributable to the statistics of analytical errors, sampling and natural variations. Thus it is not unreasonable to conclude that these basaltic andesites are cogenetic, coming from the same magma and magma chamber, even as they have been observed to flow from the same volcano.

Nevertheless, Nairn et al. (1976) suggested that even though the 1949 and 1954 lavas were both olivine-bearing andesite, the chemical analyses (Table 1) showed the 1954 lava to be slightly more basic than the 1949 lava, with slightly higher MgO, CaO and total iron oxides, but lower SiO<sub>2</sub> and alkalis. However, these trends are not duplicated with any statistical significance by the analytical results of this study (Table 2). At least they found that their analyses of the 1974 lava blocks and bombs were identical within the limits of error with the 1954 lava (Table 1), which was also substantiated in this study with respect to the 1975 avalanche material and the 1954 lava (Table 2).

Clark (1960) and Cole (1978) recognized five lava types in the Tongariro Volcanic Center based on the modal proportions of the phenocryst minerals. Graham (1985) modified this scheme to six types based on a combination of mineralogy and chemistry, but given their uniform bulk chemistry and petrology, these Ngauruhoe lava flows group together as plagioclase-pyroxene andesite within Graham's "Type 1." Cole

et al. (1986) have described Type 1 lavas as volumetrically dominant within the Tongariro Volcanic Center and as exhibiting coherent chemical trends with increasing silica content. They are relatively Fe-rich and follow a typical calc-alkaline trend on the AFM diagram.

Adapting the terminology of Gill (1981), the Ngauruhoe lavas are described as basic andesites (53–58 wt% SiO<sub>2</sub>) (Cole et al.). Their designation as plagioclase-pyroxene andesites is based on the predominant phenocrysts present, with plagioclase greater than or equal to pyroxene. Two modal analyses are listed in Table 3 which very closely resemble the samples collected for this study.

All samples of the five lava flows examined in this study exhibited a porphyritic texture, with phenocrysts (up to 3mm across) consistently

**Table 3.** Modal analyses of two recent lava flows at Mt. Ngauruhoe, New Zealand, as reported in the literature.

Component	1	2
Plagioclase	22.6	21.6
Augite	2.6	2.6
Orthopyroxene	6.0	5.8
Olivine	0.2	0.2
Iron Oxide	—	g*
Xenoliths	2.6	4.5
Groundmass	66.0	65.3
<b>TOTAL</b>	<b>100.0</b>	<b>100.0</b>

g\* in groundmass

- Ngauruhoe VU 29250 (Cole, Graham, Hackett, & Houghton, 1986), a 1954 flow.
- Olivine-bearing low-Si andesite, June 30, 1954 Ngauruhoe flow (Cole, 1978).

amounting to 35–40% by volume. The phenocryst assemblage is dominated (2:1) by plagioclase, but orthopyroxene and augite (clinopyroxene) are always major components, while olivine and magnetite are only present in trace amounts. This POAM phenocryst assemblage is a typical anhydrous mineralogy (Cole et al., 1986). The groundmass consists of microlites of plagioclase, orthopyroxene, and clinopyroxene, and is crowded with minute granules of magnetite and/or Fe-Ti oxides. Small amounts (9–10%) of brown transparent (acid-residuum) glass are also present, and the overall texture is generally pilotaxitic.

Steiner (1958) stressed that xenoliths are a common constituent of the 1954 Ngauruhoe lava, but also noted that Battey (1949) reported the 1949 Ngauruhoe lava was rich in xenoliths. All samples in this study contained xenoliths, including those from the 1975 avalanche material. However, many of these aggregates are more accurately described as glomerocrysts and mafic (gabbro, websterite) nodules (Graham et al., 1995). They are 3–5 mm across, generally have hypidiomorphic-granular textures, and consist of plagioclase, orthopyroxene, and clinopyroxene in varying proportions, and very occasionally olivine. The true xenoliths are often rounded and invariably consist of fine quartzose material. Steiner also described much larger xenoliths of quartzo-feldspathic composition and relic gneissic structure.

The plagioclase phenocrysts have been reported as ranging in composition from An<sub>89</sub> to An<sub>40</sub> (andesine to bytownite), but in Ngauruhoe lavas are usually labradorite (An<sub>68-55</sub>). They are subhedral and commonly exhibit complex oscillatory zoning with an overall trend from calcic cores to sodic rims (Cole, 1978; Cole et al. 1983, 1986). Thin outer rims are usually compositionally similar to groundmass microlites. Twinning and hourglass structures are common.

Orthopyroxene predominates (>2:1) over clinopyroxene. Subhedral-euhedral orthopyroxene

is typically pleochroic and sometimes zoned. Compositions range from Ca<sub>4</sub>Mg<sub>74</sub>Fe<sub>22</sub> to Ca<sub>3</sub>Mg<sub>47</sub>Fe<sub>50</sub> (Cole et al. 1983, 1986), but representative bulk and partial analyses of Ngauruhoe orthopyroxenes (Cole, 1978; Ewart, 1971; Graham & Hackett, 1987) indicate a hypersthene composition predominates, which is confirmed by optical determinations (Clark, 1960; Cole). Euhedral-subhedral clinopyroxene is typically twinned and zoned, but compositions show a restricted range of Ca<sub>43</sub>Mg<sub>47</sub>Fe<sub>10</sub> to about Ca<sub>35</sub>Mg<sub>40</sub>Fe<sub>25</sub>, all of which is augite (Cole et al., 1986; Graham et al., 1995).

The olivine present is strongly magnesian, analyses indicating some compositional zoning from Fo<sub>88</sub> to Fo<sub>78</sub>. The magnetite present in the groundmass is titanomagnetite, judging from the amount of TiO<sub>2</sub> present in whole-rock analyses (Tables 1 and 2), but some ilmenite is likely to occur sporadically in association with it (Cole et al., 1986; Graham et al., 1995).

### K-Ar Results

All analytical results received from Geochron Laboratories are listed in Table 4, grouped in chronological order according to the historic date of each flow. The <sup>40</sup>Ar\* quantity refers to the amount of radiogenic <sup>40</sup>Ar measured in each sample. All other quantities are self-explanatory, some of them being calculated from the analytical results supplied by the laboratory.

The “age” of each sample is calculated from the analytical results using the general model-age equation (Faure, 1986; Dickin, 1995):—

$$t = \frac{1}{\lambda} \ln \left[ \frac{D_t - D_o}{P_t} + 1 \right] \quad (1)$$

where:

$t$  = the “age”

$\lambda$  = the decay constant of the parent isotope

$D_t$  = the number of daughter atoms in the rock presently

$D_o$  = the number of daughter atoms initially in the rock

$P_t$  = the number of parent atoms presently in the rock

To date a rock,  $D_t$  and  $P_t$  are measured, and Equation 1 can then be used if an assumption about the original quantity of daughter atoms ( $D_o$ ) is made. Applied specifically to K-Ar dating, Equation 1 thus becomes:-

$$t = \frac{1}{5.543 \times 10^{-10}} \ln \left[ \frac{1}{0.1048} \frac{{}^{40}\text{Ar}^*}{{}^{40}\text{K}} + 1 \right] \quad (2)$$

where:

$t$  = the “age” in Ma (millions of years)

$5.543 \times 10^{-10}$  = the current estimate for the decay

- constant of  $^{40}\text{K}$   
 0.1048 = the estimated fraction of  $^{40}\text{K}$  decays producing  $^{40}\text{Ar}$   
 $^{40}\text{Ar}^*/^{40}\text{K}$  = the calculated mole ratio of radiogenic  $^{40}\text{Ar}$  to  $^{40}\text{K}$  in the sample

It should be noted that to make Equation 2 equivalent to Equation 1,  $^{40}\text{Ar}^*$  is assumed to be equal to  $(D_t - D_o)$ , which thus means the  $^{40}\text{Ar}^*$  measurement has included within it an assumption concerning the initial quantity of  $^{40}\text{Ar}$  in the rock, namely, no radiogenic argon is supposed to have existed when the rock formed (that is,  $D_o = 0$ ). Thus Equation 2 yields a “model age” assuming zero radiogenic argon in the rock when it formed.

The model ages listed in Table 4 range from <0.27Ma to  $3.5 \pm 0.2\text{Ma}$ . However, it should be noted that the samples, one from each flow, that yielded model ages of <0.27Ma and <0.29Ma (that is, below the detection limits of the equipment for  $^{40}\text{Ar}^*$ ) were all processed at the K-Ar laboratory in the same batch, suggesting the possibility of a systematic problem with the analytical procedure and equipment (in particular, the gas extraction “line”). When this question was raised with the laboratory manager, Richard Reesman, he kindly rechecked his equipment and then re-ran several of the samples, producing similar results and thus ruling out a systematic laboratory “error.”

However, an independent blind check was then made, by submitting to the K-Ar laboratory duplicate splits from two samples already analyzed, to establish if results really were reproducible. The samples chosen were the A and B samples of the June 30, 1954

flow, because their first splits had produced the lowest and highest model ages, <0.27Ma and  $3.5 \pm 0.2\text{Ma}$  respectively. The results of these additional analyses are shown in Table 4 as A#2 and B#2, and yielded model ages of  $1.3 \pm 0.3\text{Ma}$  and  $0.8 \pm 0.2\text{Ma}$  respectively. Clearly, reproducibility was not obtained, but this is not surprising given the analytical uncertainties at such low to negligible levels of  $^{40}\text{Ar}^*$ , which are at the detection limits of the laboratory's equipment (Reesman, 1997, 1998).

## Discussion

In spite of the wide variations in model “ages” obtained between and within these recent lava flows, and of the difficulties obtaining analytical reproducibility, it is apparent that the cause of the anomalous K-Ar model “ages” is excess argon in the lavas, that is, non-zero concentrations of radiogenic argon ( $^{40}\text{Ar}^*$ ). This of course is contrary to the assumption of zero radiogenic argon in Equation 2 for calculating the model “ages.” When analyzed the oldest of the lavas was less than 50 years old, so there has been insufficient time since cooling for measurable quantities of  $^{40}\text{Ar}^*$  to have accumulated within the lavas due to the slow radioactive decay of  $^{40}\text{K}$ . Thus the measurable  $^{40}\text{Ar}^*$  can't be from in situ radioactive decay since cooling, and therefore must have been present in the molten lavas when extruded from Mt. Ngauruhoe.

## No Radiogenic Argon Assumption Violated by Many Anomalous “Ages”

The assumption of no radiogenic argon ( $^{40}\text{Ar}^*$ ) when

**Table 4.** K-Ar analytical results and model ages for five recent lava flows at Mt. Ngauruhoe, New Zealand (Analyst: Geochron Laboratories, Boston; July 1996, December 1996, September 1997 and January 1998.) Constants used:  $^{40}\text{K}/\text{K} = 1.193 \times 10^{-4}\text{g/g}$ ; Fraction of  $^{40}\text{K}$  decays to  $^{40}\text{Ar}^* = 0.1048$ ; Decay constant of  $^{40}\text{K} = 5.543 \times 10^{-10}\text{yr}^{-1}$ ; Atmospheric  $^{40}\text{Ar}/^{36}\text{Ar} = 295.5$

Flow Date	Sample	$\text{K}_2\text{O}$ (wt%)	$^{40}\text{K}$ (ppm)	$^{40}\text{Ar}^*$ (ppm) $\times 10^{-4}$	$^{40}\text{Ar}^*$ (%)	$\frac{^{40}\text{Ar}^*}{\text{Total } ^{40}\text{Ar}}$	Total $^{40}\text{Ar}$ (ppm)	$\frac{^{40}\text{Ar}}{^{36}\text{Ar}}$	$^{36}\text{Ar}$ (ppm $\times 10^{-5}$ )	$\frac{^{40}\text{Ar}^*}{^{40}\text{K}}$	Model Age (Ma)	Uncertainty (Ma) (1 $\sigma$ )
February 11, 1949	A	1.066	1.272	<0.2	—	—	—	296	—	<0.000016	<0.27	—
	B	1.057	1.261	0.75	3.75	0.0375	0.0020	310	0.645	0.000059	1.0	0.2
June 4, 1954	A	1.034	1.234	<0.2	—	—	—	288	—	<0.000016	<0.27	—
	B	1.087	1.297	1.10	3.00	0.030	0.00367	308	1.192	0.000085	1.5	0.1
June 30, 1954	A#1	1.074	1.281	<0.2	—	—	—	285	—	<0.000016	<0.27	—
	A#2	0.977	1.166	0.87	2.75	0.0275	0.00316	306	1.033	0.000075	1.3	0.3
	B#1	0.944	1.126	2.28	4.05	0.405	0.00691	311	2.222	0.000202	3.5	0.2
	B#2	0.995	1.186	0.56	1.70	0.017	0.00329	304	1.082	0.000047	0.8	0.2
	C	1.097	1.308	0.93	3.75	0.0375	0.00248	311	0.798	0.000071	1.2	0.2
July 14, 1954	A	1.033	1.232	0.69	3.40	0.034	0.00203	301	0.675	0.000056	1.0	0.2
	B	1.004	1.198	<0.2	—	—	—	283	—	<0.000017	<0.29	—
February 19, 1975	A	1.128	1.346	0.79	2.55	0.0255	0.00310	307	1.010	0.000059	1.0	0.2
	B	1.048	1.250	<0.2	—	—	—	291	—	<0.000016	<0.27	—

the rocks formed is usually stated as self-evident. For example, Geyh & Schleicher (1990, p. 56) state:

What is special about the K-Ar method is that the daughter nuclide is a noble gas, which is not normally incorporated into minerals and is not bound in the mineral in which it is found.

Similarly, Dalrymple & Lanphere (1969, p. 46) state: a silicate melt will not usually retain the  $^{40}\text{Ar}$  that is produced, and thus the potassium-argon clock is not “set” until the mineral solidifies and cools sufficiently to allow the  $^{40}\text{Ar}$  to accumulate in the mineral lattice.

Dalrymple (1991, p.91) has recently put the argument more strongly:

The K-Ar method is the only decay scheme that can be used with little or no concern for the initial presence of the daughter isotope. This is because  $^{40}\text{Ar}$  is an inert gas that does not combine chemically with any other element and so escapes easily from rocks when they are heated. Thus, while a rock is molten the  $^{40}\text{Ar}$  formed by decay of  $^{40}\text{K}$  escapes from the liquid.

However, these dogmatic statements by Dalrymple are inconsistent with even his own work on historic lava flows (Dalrymple, 1969), some of which he found had non-zero concentrations of  $^{40}\text{Ar}^*$  in violation of this key assumption of the K-Ar dating method. He does go on to admit that “Some cases of initial  $^{40}\text{Ar}$  remaining in rocks have been documented but they are uncommon” (Dalrymple, 1991), but then refers to his study of 26 historic, subaerial lava flows (Dalrymple, 1969). Five (almost 20%) of those flows contained “excess argon,” but Dalrymple still then says “that ‘excess’ argon is rare in these rocks!” The flows and their “ages” were (Dalrymple, 1969):

Hualalai basalt, Hawaii (A.D. 1800–1801)	1.6±0.16Ma
	1.41±0.08Ma
Mt. Etna basalt, Sicily (122 B.C.)	0.25±0.08Ma
Mt. Etna basalt, Sicily (A.D. 1792)	0.35±0.14Ma
Mt. Lassen plagioclase, California (A.D. 1915)	0.11±0.03Ma
	0.27±0.09Ma
Sunset Crater basalt, Arizona (A.D. 1064–1065)	0.25±0.15Ma

Far from being rare, there are numerous examples reported in the literature of excess  $^{40}\text{Ar}^*$  in recent or young volcanic rocks producing excessively old whole-rock K-Ar “ages” as shown in Table 5.

Other studies have also reported measurements of excess  $^{40}\text{Ar}^*$  in lavas. Fisher (1970) investigated submarine basalt from a Pacific seamount and found “the largest amounts of excess  $^4\text{He}$  and  $^{40}\text{Ar}$  ever recorded” (at that time). McDougall (1971) not only found “extraneous radiogenic argon present in three of the groups of basalt flows” on the young volcanic island of Réunion in the Indian Ocean, but “extraneous argon” was also “detected in alkali feldspar and amphibole in hyperbyssal drusy syenites that are exposed in the eroded core of Piton des Neiges

**Table 5.** Examples of excess  $^{40}\text{Ar}^*$  in recent or young volcanic rocks producing excessively old whole-rock K-Ar “ages.”

Akka Water Fall flow, Hawaii (Pleistocene)	32.3±7.2Ma (Krummenacher, 1970)
Kilauea Iki basalt, Hawaii (A.D. 1959)	8.5±6.8Ma (Krummenacher, 1970)
Mt. Stromboli, Italy, volcanic bomb (September 23, 1963)	2.4±2Ma (Krummenacher, 1970)
Mt. Etna basalt, Sicily (May 1964)	0.7±0.01Ma (Krummenacher, 1970)
Medicine Lake Highlands obsidian, Glass Mountains, California (<500 years old)	12.6±4.5Ma (Krummenacher, 1970)
Hualalai basalt, Hawaii (A.D. 1800–1801)	22.8±16.5Ma (Krummenacher, 1970)
Rangitoto basalt, Auckland, New Zealand (<800 years old)	0.15±0.47Ma (McDougall, Polach, & Stipp, 1969)
Alkali basalt plug, Benue, Nigeria (<30Ma)	95Ma (Fisher, 1971)
Olivine basalt, Nathan Hills, Victoria Land, Antarctica (<0.3Ma)	18.0±0.7Ma (Armstrong, 1978)
Anorthoclase in volcanic bomb, Mt. Erebus, Antarctica (1984)	0.64±0.03Ma (Esser, McIntosh, Heizler, & Kyle, 1997)
Kilauea basalt, Hawaii (<200 years old)	21±8Ma (Noble & Naughton, 1968)
Kilauea basalt, Hawaii (<1000 years old)	42.9±4.2Ma (Dalrymple & Moore, 1968) 30.3±3.3Ma (Dalrymple & Moore, 1968)
East Pacific Rise basalt (<1Ma)	690±7Ma (Funkhouser Fisher, & Bonatti, 1968)
Seamount basalt, near East Pacific Rise (<2.5Ma)	580±10Ma (Funkhouser, Barnes, & Naughton, 1966) 700±150Ma (Fisher, 1972)
East Pacific Rise basalt (<0.6Ma)	24.2±1.0Ma (Dymond, 1970)

volcano.” Significant quantities of excess  $^{40}\text{Ar}^*$  have also been recorded in submarine basalts, basaltic glasses and olivine phenocrysts from the currently active Hawaiian volcanoes, Loihi Seamount and Kilauea, as well as on the flanks of Mauna Loa and Hualalai volcanoes, also part of the main island of Hawaii (Honda et al., 1993; Valbracht et al., 1996), and in samples from the Mid-Atlantic Ridge, East Pacific Rise, Red Sea, Galapagos Islands, McDonald Seamount and Manus Basin (Marty & Humbert, 1997; Staudacher et al., 1989). Patterson, Honda, & McDougall (1990) claimed that some of the initial



Loihi analytical results were due to atmospheric contamination of the magma either during intrusion or eruption, but subsequent work (Honda et al., 1993; Valbracht et al., 1996b) has confirmed that the excess  $^{40}\text{Ar}^*$  is not from atmospheric contamination at all.

### **Excess $^{40}\text{Ar}^*$ Occluded in Minerals**

Austin (1996) has investigated the 1986 dacite lava flow from the post-October 26, 1980 lava dome within the Mount St. Helens crater, and has established that the 10-year-old dacite yields a whole-rock K-Ar model “age” of  $0.35 \pm 0.05$  Ma due to excess  $^{40}\text{Ar}^*$  in the rock. He then produced concentrates of the constituent minerals, which yielded anomalous K-Ar model “ages” of  $0.34 \pm 0.06$  Ma (plagioclase),  $0.9 \pm 0.2$  Ma (hornblende),  $1.7 \pm 0.3$  Ma (pyroxene), and  $2.8 \pm 0.6$  Ma (pyroxene ultra-concentrate). While these mineral concentrates were not ultra-pure, given the fine-grained glass in the groundmass and some Fe-Ti oxides, it is nonetheless evident that the excess  $^{40}\text{Ar}^*$  responsible for the anomalous K-Ar “ages” is retained within the different constituent minerals in different amounts. Furthermore, the whole-rock “age” is very similar to the “age” of the plagioclase concentrate because plagioclase is the dominant constituent of the dacite.

That the excess  $^{40}\text{Ar}^*$  can be occluded in the minerals within lava flows, rather than between the mineral grains, has been established by others also. Laughlin et al. (1994) found that the olivine, pyroxene, and plagioclase in Quaternary basalts of the Zuni-Bandera volcanic field of New Mexico contained very significant quantities of excess  $^{40}\text{Ar}^*$ , as did the olivine and clinopyroxene phenocrysts in Quaternary flows from New Zealand volcanoes (Patterson, Honda, & McDougall, 1994). Similarly, Poths, Healy, & Laughlin (1993) separated olivine and clinopyroxene phenocrysts from young basalts from New Mexico and Nevada and then measured “ubiquitous excess argon” in them. Damon, Laughlin, & Precious (1967) have reported several instances of phenocrysts with K/Ar “ages” 17 million years greater than that of the whole rocks, and one K/Ar “date” on olivine phenocrysts of greater than 110 Ma in a recent (<13,000 year old) basalt. Damon et al. thus suggested that large phenocrysts in volcanic rocks contain the excess  $^{40}\text{Ar}^*$  because their size prevents them from completely degassing before the flows cool, but Dalrymple (1969) concluded that there does not appear to be any correlation of excess  $^{40}\text{Ar}^*$  with large phenocrysts or with any other petrological or petrographic parameter.

Most investigators have come to the obvious conclusion that the excess  $^{40}\text{Ar}^*$  had to have been present in the molten lavas when extruded, which then did not completely degas as they cooled, the excess

$^{40}\text{Ar}^*$  becoming “trapped” in the constituent minerals, and in some instances, the rock fabrics themselves. Laboratory experiments have tested the solubility of argon in synthetic basalt melts and their constituent minerals near  $1300^\circ\text{C}$  at one atmosphere pressure in a gas stream containing argon (Broadhurst, Drake, Hagee, & Benatowicz, 1990, 1992). When quenched, synthetic olivine in the resultant material was found to contain 0.34 ppm  $^{40}\text{Ar}^*$ . Broadhurst et al. (1990) commented that “The solubility of Ar in the minerals is surprisingly high,” and concluded that the argon is held primarily in lattice vacancy defects within the minerals.

In a different experiment, Karpinskaya, Ostrovsky, & Shanin (1961) heated muscovite to  $740^\circ\text{--}860^\circ\text{C}$  under high argon pressures (2800–5000 atmospheres) for periods of 3 to 10.5 hours. The muscovite absorbed significant quantities of argon, producing K/Ar “ages” of up to 5 billion years, and the absorbed argon appeared like ordinary radiogenic argon ( $^{40}\text{Ar}^*$ ). Karpinskaya (1967) subsequently synthesized muscovite from a colloidal gel under similar argon pressures and temperatures, the resultant muscovite retaining up to 0.5 wt% argon at  $640^\circ\text{C}$  and a vapor pressure of 4000 atmospheres. This is approximately 2,500 times as much argon as is found in natural muscovite. These experiments show that under certain conditions argon can be incorporated into minerals and rocks that are supposed to exclude argon when they crystallize.

### **Applications to the Mt. Ngauruhoe Andesite Flows**

Therefore, the analytical results from the very recent (1949–1975) andesite flows at Mt. Ngauruhoe, New Zealand, that yield anomalous K-Ar model “ages” because of excess  $^{40}\text{Ar}^*$ , are neither unique nor an artifact of poor analytical equipment or technique. This realization that the presence of the excess  $^{40}\text{Ar}^*$  in these rocks is both real and measurable, and has not been derived from radioactive decay of  $^{40}\text{K}$  in situ, leads to the obvious questions as to whether there is any pattern in the occurrences of excess  $^{40}\text{Ar}^*$ , and from whence came this excess  $^{40}\text{Ar}^*$ ?

It is clear that the excess  $^{40}\text{Ar}^*$  was in the lavas when they flowed from the Mt. Ngauruhoe volcano and were trapped in the andesite as it cooled. That there were gases in the lavas is readily evident from the copious “frozen” bubble holes now in the rock, implying that much of the gas content escaped as the lavas flowed and cooled. When choosing samples, care was taken to select pieces from each flow that were different from one another (for example, copious “frozen” gas bubble holes compared with virtually no such holes). It is hardly surprising, therefore, that the  $^{40}\text{Ar}^*$  measurements on four of the five flows were

consistent with such differences the samples from each flow which had very few or virtually no “frozen” gas bubble holes yielded excess  $^{40}\text{Ar}^*$  and thus anomalous K-Ar model “ages,” whereas the other samples from each of these flows which contained copious “frozen” gas bubble holes failed to yield detectable  $^{40}\text{Ar}^*$  (<0.27Ma and <0.29Ma in Table 4).

The exception was the June 30, 1954 flow—not only was this expected relationship between excess  $^{40}\text{Ar}^*$  and lack of “frozen” gas bubble holes not duplicated, but analyses on duplicate splits off the same samples yielded widely divergent results (<0.27Ma versus  $1.3\pm 0.3\text{Ma}$  and  $3.5\pm 0.2\text{Ma}$  versus  $0.8\pm 0.2\text{Ma}$ , see Table 4). Thus the presence (or absence) of excess  $^{40}\text{Ar}^*$  must also depend on which portion of a rock sample is being analyzed, which in turn implies dependence on the mineral constituents present, including the glass in the groundmass. As already noted, Austin (1996) found widely different amounts of excess  $^{40}\text{Ar}^*$  in the mineral separates concentrated from Mount St. Helens 1986 dacite, while numerous other studies (Laughlin et al., 1994; Patterson et al., 1994; Poths et al., 1993; Valbracht et al., 1996b) have located excess  $^{40}\text{Ar}^*$  in phenocrysts.

### **Cooling Rates, Pressures, and Potassium Alteration**

Another factor is the rate of cooling of lavas. Dalrymple & Moore (1968) found that the 1 cm thick glassy rim of a pillow in a Kilauea submarine basalt had greater than forty times more excess  $^{40}\text{Ar}^*$  than the basalt interior just 10 cm below. The glassy pillow rim is, of course, produced by rapid quenching of the hot basalt lava immediately it contacts the cold ocean water, so the excess  $^{40}\text{Ar}^*$  in the lava is rapidly trapped and retained. Dymond (1970) obtained similar results on four deep-sea basalt pillows from near the axis of the East Pacific Rise. Dalrymple & Moore (1968) also found that the excess  $^{40}\text{Ar}^*$  contents of the glassy rims of basalt pillows increased systematically with water depth, leading them to conclude that the amount of excess  $^{40}\text{Ar}^*$  is a direct function of both the hydrostatic pressure and the rate of cooling. In a parallel study, Noble & Naughton (1968) reported K-Ar “ages” from zero to 22Ma with increasing sample depth for submarine basalts probably less than 200 years old, also from the active Kilauea volcano.

Seidemann (1977) has reported yet another intriguing relationship. He analyzed deep-sea basalt samples obtained from DSDP drillholes in the floor of the Pacific Ocean basin and found K-Ar “ages” increased with increasing K contents of the basalts, a relationship he noted also appeared in similar data published by DSDP staff (Seidemann, Figure 1). In basalt pillows the K content increases from the margin to a maximum at an intermediate distance

into the pillows, whereas holocrystalline basalts show a decrease of K inward from the margin (Hart, 1969). Seidemann concluded, as had others before him, that submarine weathering adds K to the basalts, as does alteration at the time of formation, whereas the glassy pillow margins are largely impervious to seawater. The net result, however, is unreliable K-Ar “dates,” because the measured  $^{40}\text{Ar}^*$  was probably not derived by radioactive decay of the measured  $^{40}\text{K}$  contents. Seidemann also determined that sediment cover is not a significant barrier to the diffusion of K into basalt.

It is possible that some of these factors are relevant to the pattern of excess  $^{40}\text{Ar}^*$  measured in the samples from the recent Mt. Ngauruhoe andesite flows. For example, the surfaces of the flows would have cooled more rapidly to crusts on top of the still molten flow interiors, which would certainly have been the case with the August 18, 1954 flow that was reported as being 18 m thick. Furthermore, the overburden pressure within the deep interiors of such thick flows would likewise inhibit degassing of the lava as it cooled. However, so long as the crusts on the tops of the flows remained unbroken and intact they would have sealed in the molten lava and its contained gases, including excess  $^{40}\text{Ar}^*$ . But this sealing was probably short-lived, because today the flows mostly outcrop as piles of pieces of andesite that look like rubble (typical aa lavas). The continued flow of the lavas down the sides of the volcano would have broken up the crusts as soon as they congealed, as would contraction with cooling, thus enabling the molten interiors to degas as they cooled. So the speed of cooling was likely the most relevant factor, and this would have varied laterally and vertically within the flows, even at localised scales of a few centimeters.

Any effects of weathering on the K contents of these flows can be discounted. On the one hand these are subaerial flows that do not appear to have been subjected to leaching or addition of K, or to any K-rich alteration for that matter, while on the other they have very uniform K contents (see Tables 1, 2, and 4). This is not unexpected, given the fact they flowed from the same magma source/chamber close together timewise. The K-Ar data in Table 4 do not reveal any discernible relationship between K contents and K-Ar model “ages” of these flows, unlike the negative correlation found in the Middle Proterozoic Cardenas Basalt upper member flows in Grand Canyon, Arizona (Austin & Snelling, 1998).

Perhaps the key issues, though, are where this excess  $^{40}\text{Ar}^*$  has come from, and whether it has been derived from radioactive decay of  $^{40}\text{K}$ . One possibility is that the excess  $^{40}\text{Ar}^*$  can be accounted for by radioactive decay during long term residence of magmas in chambers before eruption. Esser,

McIntosh, Heizler, & Kyle (1997) discounted this option for the Mt. Erebus anorthoclase phenocrysts. Dalrymple (1969) found that whereas the Mt. Lassen (1915) plagioclase phenocrysts yielded excess  $^{40}\text{Ar}^*$  and an anomalous K-Ar model “age,” a plagioclase from the 1964 eruption of Surtsey only had argon whose isotopic composition matched that of air. Because phenocrysts usually crystallize from lavas after eruption, they may arbitrarily trap excess  $^{40}\text{Ar}^*$  during lava cooling,  $^{40}\text{Ar}^*$  that will thus not be from in situ  $^{40}\text{K}$  radioactive decay.

### **Negative K-Ar Model “Ages” and Atmospheric Argon**

Another relevant consideration bearing on these issues is the observation noted by Dalrymple (1969) that some modern lava samples actually yield **negative** K-Ar model “ages,” apparently due to excess  $^{36}\text{Ar}$ . Air has an  $^{40}\text{Ar}/^{36}\text{Ar}$  ratio of 295.5, but some of Dalrymple’s samples had ratios less than 295.5 (and hence negative “ages”). Some of the Mt. Ngauruhoe samples in this study also yielded  $^{40}\text{Ar}/^{36}\text{Ar}$  ratios less than 295.5 (see Table 4). According to the straightforward interpretation of the K-Ar dating methodology, this should be impossible. Dalrymple was not willing to attribute these anomalous ratios to experimental error, and neither was Richard Reesman of Geochron Laboratories.

Dalrymple (1969) suggested three possible explanations that might account for the excess  $^{36}\text{Ar}$ :

1. incorporation of “primitive argon,”
2. production of  $^{36}\text{Ar}$  by the radioactive decay of  $^{36}\text{Cl}$ ,  
or
3. fractionation of atmospheric argon by diffusion.

He rejected the possibility of significant  $^{36}\text{Ar}$  formation in situ from nuclear reactions (option 2) because the Cl content of basalts and the production rate of  $^{36}\text{Cl}$  by cosmic-ray neutrons both are too low to account for any significant amount of  $^{36}\text{Ar}$ . Instead, Dalrymple seemed to favor option 3, that when atmospheric argon diffused back into lavas as they cooled,  $^{36}\text{Ar}$  diffused in preferentially. However, he also recognized the weakness of this argument—it is difficult to explain why some lavas are enriched in  $^{36}\text{Ar}$  while others are not (as at Mt. Ngauruhoe also). To be consistent, if fractionation of atmospheric argon occurred during diffusion, then this would mean that even supposedly “zero age” lavas actually have an apparent age, and that most lavas do not degas upon eruption. In fact, depending on how strong the fractionation of  $^{36}\text{Ar}$  was during diffusion, it could even be that all lavas do not completely degas.

This only leaves Dalrymple’s option 1, that the lavas with the anomalously high  $^{36}\text{Ar}$  come from areas of the mantle (and perhaps also the crust) which have primordial argon that has not been

diluted with radiogenic  $^{40}\text{Ar}$ , and have not completely degassed. However, this means that there is no reason to assume that lavas whose argon matches that in the atmosphere have degassed either, because they may have simply started with argon which matches atmospheric argon. Nevertheless, Dalrymple is convinced that “much of the volatile juvenile content may still be present in volcanic rocks quenched on the ocean floor” (Dalrymple & Moore, 1968). Indeed, Dalrymple has specifically defined excess  $^{40}\text{Ar}^*$  as  $^{40}\text{Ar}$  that is not attributed to atmospheric argon or in situ radioactive decay of  $^{40}\text{K}$  (Dalrymple & Lanphere, 1969). Krummenacher (1970) is more cautious, attributing anomalous  $^{40}\text{Ar}/^{36}\text{Ar}$  ratios and excess  $^{40}\text{Ar}^*$  to the “mass fractionation effect on argon of atmospheric isotopic composition” trapped in the lavas, as well as to the presence of “magmatic” argon different in isotopic composition.

### **The Role of Xenoliths**

Is the excess  $^{40}\text{Ar}^*$  simply “magmatic” argon, that is, argon that collects in the magma and then is inherited by the lavas from it? Funkhouser & Naughton (1968) found that the excess  $^{40}\text{Ar}^*$  in the 1800–1801 Hualalai flow, Hawaii, resided in fluid and gaseous inclusions in olivine, plagioclase, and pyroxene in ultramafic xenoliths in the basalt. The quantities of excess  $^{40}\text{Ar}^*$  were sufficient to yield K-Ar model “ages” from 2.6Ma to 2960Ma. However, Dalrymple (1969) subsequently only used the presence of the ultramafic xenoliths and their excess  $^{40}\text{Ar}^*$  contained in inclusions to explain partly the excess  $^{40}\text{Ar}^*$  and anomalous K-Ar model “ages” he obtained from the same 1800–1801 Hualalai flow, suggesting instead that the large single inclusions are not directly responsible for the excess argon in the flows and that the  $^{40}\text{Ar}^*$  is distributed more uniformly throughout the rocks. Nevertheless, those K-Ar and Ar-Ar geochronologists who are concerned about the excess  $^{40}\text{Ar}^*$  in their samples undermining their “dating” are careful to check for xenoliths and xenocrysts. Esser et al. (1997) did so and discounted xenocrystic contamination.

Xenoliths are present in the Ngauruhoe andesite flows (Table 3), but they are minor and less significant as the location of the excess  $^{40}\text{Ar}^*$  residing in these flows than the plagioclase and pyroxene phenocrysts, and the much larger glomerocrysts of plagioclase, pyroxene, or plagioclase and pyroxene that predominate. The latter are probably the early-formed phenocrysts that accumulated together in the magma within its chamber prior to eruption of the lava flows. Nevertheless, any excess  $^{40}\text{Ar}^*$  they might contain had to have been supplied to the magma from its source. The xenoliths that are in the andesite flows have been described by Steiner (1958) as gneissic, and

are therefore of crustal origin, presumably from the basement rocks through which the magma passed on its way to eruption.

### **Noble Gases from the Mantle**

With the advent of the necessary technology, the isotopic concentrations and ratios of noble gases (including argon) in rock and mineral samples are now obtainable. Honda et al. (1993) have reported such analyses on submarine basalt glass samples from Loihi Seamount and Kilauea, Hawaii, and concluded that helium and neon isotopic ratios in particular, being uniquely different from atmospheric isotopic ratios, are indicative of the mantle source area of the plume responsible for the Hawaiian volcanism rather than from atmospheric contamination of the magma (Patterson et al., 1990). The  $^{40}\text{Ar}/^{36}\text{Ar}$  ratios are consistent with excess  $^{40}\text{Ar}^*$  having also come with the magma from the mantle. A subsequent study (Valbracht et al., 1996b), in which a larger suite of basalt glass samples, and also samples of olivine phenocrysts, from the same and additional Hawaiian volcanoes were analyzed, concluded that the isotopic systematics indicate that the helium and neon have been derived from the mantle and have not been preferentially affected by secondary processes. Consequently, the excess  $^{40}\text{Ar}^*$  also in these samples would have been also carried from the upper mantle source area of these basalts by the magma plume responsible for the volcanism. Moreira, Kunz, & Allègre (1998) have suggested, based on new experimental data from single vesicles in mid-ocean ridge basalt samples dredged from the North Atlantic, that the excess  $^{40}\text{Ar}^*$  in the upper mantle may be almost double previous estimates (Staudacher et al., 1989) (that is, almost 150 times more than the atmospheric content relative to  $^{36}\text{Ar}$ ), and represents a primordial mantle component not yet outgassed. Burnard, Graham, & Turner (1997) obtained similar results on the same samples, but maintained that because some of the  $^{36}\text{Ar}$  is probably surface-adsorbed atmospheric argon, the upper mantle content of excess  $^{40}\text{Ar}^*$  could be even ten times higher.

Similar results (Valbracht et al., 1996a) have been obtained from ultramafic mantle xenoliths in basalts from the Kerguelen Archipelago in the southern Indian Ocean, and the considerable excess  $^{40}\text{Ar}^*$  measured concluded to be a part of the mantle source signature of this hotspot volcanism. However, it has not only been the suboceanic mantle that has thus been sampled for its excess  $^{40}\text{Ar}^*$  via such magma plumes. Matsumoto, Honda, McDougall, & O'Reilly (1997) have reported high  $^{40}\text{Ar}/^{36}\text{Ar}$  ratios in spinel-lherzolites from five eruption centers in the youthful (<7Ma) Newer Volcanics of southeastern Australia. These anhydrous lherzolites have

compositions representative of the upper lithospheric mantle, and the significant excess  $^{40}\text{Ar}^*$  in them indicates the presence of a subcontinental mantle reservoir with a very high  $^{40}\text{Ar}/^{36}\text{Ar}$  ratio, and thus substantial excess  $^{40}\text{Ar}^*$ , similar to that found in mid-ocean ridge and plume/hotspot basalts. Another example is the Cardenas Basalt and associated diabase (Middle Proterozoic) of eastern Grand Canyon, regarded as part of the pervasive mafic mid-continental magmatism of the southwestern United States and thus also sourced from the subcontinental mantle. Austin & Snelling (1998) have found that the  $^{40}\text{Ar}/^{36}\text{Ar}$ - $^{40}\text{K}/^{36}\text{Ar}$  isochrons for fourteen and six samples of these rocks respectively yield initial  $^{40}\text{Ar}/^{36}\text{Ar}$  ratios of  $787\pm 118$  and  $453\pm 42$ , indicative of some initial excess  $^{40}\text{Ar}^*$ .

### **Sampling the Mantle with Diamonds and their Inclusions**

Another means of "sampling" the mantle is the study of diamonds and their micro-inclusions. It is now firmly established that diamonds are thermodynamically stable in the pressure-temperature regime in the mantle at depths greater than 150km, and their origin is believed to extend back to the Archean and the early crust of the earth (Kesson & Ringwood, 1989; Kirkley, Gurney, & Levinson, 1992). Diamonds are formed in a number of processes associated with two rock types, eclogite and peridotite, xenoliths of which are also brought up into the upper crust with diamonds from the upper mantle below continental Precambrian shields (cratons) by kimberlite and lamproite "pipe" eruptions (Gurney, 1986, 1990; Kirkley et al., 1992). Even though the host kimberlite or lamproite may be relatively young (even in conventional terms), many diamonds date back to the Archean and thus the early history of the earth (Kirkley et al., 1992; Richardson, Gurney, Erlank, & Harris, 1984). To account for all this evidence, it is postulated that the formation of most diamonds was closely associated with subduction of the Archean oceanic crust into the mantle (Kesson & Ringwood, 1989; Kirkley et al., 1992), the required carbon, which was originally thought to be primordial carbon already in the mantle, now believed to derive from sedimentary marine carbonates and biogenic carbon from bacteria/algae in the sediments subducted with the oceanic crust (Eldridge et al., 1991; Kirkley et al., 1991, 1992).

The noble gas contents of diamonds are consistent with their ancient and mantle origin, high helium isotopic ratios (290 times the atmospheric ratio) being regarded as primordial and rivalling those measured for the sun today (Gurney, 1986; Ozima & Zashu, 1983). Of significance here is the postulation that He, Ar, K, Pb, Th, and U are added to the convecting

upper mantle circulation, and the proportions and isotopic compositions are strongly determined by entrainment from the lower mantle (below 670 km) (Gurney, 1990; Harte & Hawkesworth, 1986). This is reflected in those Ar isotopic measurements that have been made on diamonds and their micro-inclusions.

Rather than focus on attempting to date only diamond micro-inclusions as others had done, Zashu, Ozima, & Nitoh (1986) carefully selected ten Zaire diamonds and examined them for purity before undertaking K-Ar dating analyses of the diamonds themselves. However, at the outset they noted that there had been almost no direct radiometric dating of diamonds except for conventional K-Ar dating, and the results had been questionable due to the possible presence of excess  $^{40}\text{Ar}^*$ . To avoid this problem, they used the K-Ar isochron dating method. Their experimental data showed good linear correlations, but these isochrons yielded an age of  $6.0 \pm 0.3$  Ga, which of course was unacceptable because these diamonds would be older than the earth itself. Mistakes in the experimental procedure were easily discounted, so they were forced to conclude that excess  $^{40}\text{Ar}^*$  was responsible, and that it needed to be in a fluid state to ensure the homogenization necessary to give such a constant  $^{40}\text{Ar}/\text{K}$  ratio. Alternately, they speculated that the diamonds might differ in K isotopic composition from common potassium, but this was discounted in a follow-up study (Podosek et al., 1988) in which it was found that  $^{40}\text{K}$  was present in these diamonds in normal abundance. Because  $^{40}\text{Ar}/^{39}\text{Ar}$  analyses yielded the same unacceptable “age,” it was concluded that the excess  $^{40}\text{Ar}^*$  was not generated in situ, but was an inherited or “trapped” component from the mantle reservoir when and where the diamonds formed.

These Zaire diamonds are not the only ones which have yielded excess  $^{40}\text{Ar}^*$ . Phillips, Onstott, & Harris (1989) used a laser-probe to  $^{40}\text{Ar}/^{39}\text{Ar}$  date eclogitic clinopyroxene inclusions in diamonds from the Premier kimberlite, South Africa, and found moderate  $^{40}\text{Ar}/^{36}\text{Ar}$  ratios indicative of much less excess  $^{40}\text{Ar}^*$  than in the Zaire diamonds. The “age” of these eclogitic diamonds was thus determined to be  $1.198 \pm 0.014$  Ga, much younger than the 3.3 Ga peridotitic diamonds at Kimberley and Finsch (Kirkley et al., 1992), also in South Africa, so Phillips et al. (1989) interpreted the moderate excess  $^{40}\text{Ar}^*$  as characteristic of mantle conditions prevailing at the time and in the region of Premier eclogitic diamond formation.

Zashu et al. (1986) postulated that the excess  $^{40}\text{Ar}^*$  in the Zaire diamonds needed to be in a fluid state. Though *Navon, Hulcheon, Rossman, & Wasserburg* (1988) did not analyze for argon when they investigated fluids in micro-inclusions in diamonds

from Zaire and Botswana, they found a high content of volatiles and incompatible elements in the uniform average composition of the micro-inclusions, with the amounts of water and  $\text{CO}_2$  (in carbonates) almost an order of magnitude higher than the volatile contents of kimberlites and lamproites (host rocks to diamonds). At 13 wt%, the chlorine levels were also much higher than those of kimberlites (<0.1%), although the bulk composition of the micro-inclusions, including the high  $\text{K}_2\text{O}$  content (up to 29.7 wt%), resembled that of such potassic magmas. They concluded that these micro-inclusions represent the volatile-rich (~40% volatiles) fluid or melt from the upper mantle in which the diamonds grew, and that because of the high volatile content in this hydrous mantle fluid, high levels of rare gases may also be expected and explain the high  $^{40}\text{Ar}/\text{K}$  ratios (the excess  $^{40}\text{Ar}^*$ ) and anomalous “ages.”

As a result of continued investigation of the Zaire cubic diamonds, which produced  $^{40}\text{Ar}/^{39}\text{Ar}$  age spectra yielding a ~5.7 Ga isochron, Ozima, Zashu, Takigami, & Turner (1989) discovered that just as there was an excellent correlation between their potassium contents and  $^{40}\text{Ar}/^{36}\text{Ar}$  ratios, there is also a correlation between their chlorine contents and  $^{40}\text{Ar}$ . They concluded from their data

that the  $^{40}\text{Ar}$  is an excess component which has no age significance, and that the  $^{40}\text{Ar}$  and its associated potassium are contained in sub-micrometer inclusions of mantle-derived fluid.

Turner, Burgess, & Bannon (1990) also used the  $^{40}\text{Ar}/^{39}\text{Ar}$  technique through correlations with K, Cl, and  $^{36}\text{Ar}$  to unscramble the mixtures of radiogenic and parentless (excess) Ar components in fluid inclusions in “coated” Zaire diamonds and in olivine from an East African mantle xenolith. Their results proved conclusively that  $^{40}\text{Ar}$  is present in a widespread chlorine-rich component, which implies the existence of  $\text{H}_2\text{O}/\text{CO}_2$ -rich phases with  $^{40}\text{Ar}/\text{Cl}$  ratios that are “remarkably uniform over large distances,” with enrichments of these two incompatible elements by almost four orders of magnitude relative to bulk upper-mantle values. Clearly, excess  $^{40}\text{Ar}^*$  is abundant in the mantle and can be easily transported up into the crust.

### **Crustal Excess $^{40}\text{Ar}^*$**

Is there only evidence for excess  $^{40}\text{Ar}^*$  in the mantle, gleaned from rocks (basalts and ultramafic xenoliths) and minerals (olivine, pyroxene, plagioclase, and diamonds) that were formed in, or ascended from, the mantle? Patterson et al. (1992) envisage noble gases from the mantle (and the atmosphere) migrating and circulating through the crust, so there should be evidence of excess  $^{40}\text{Ar}^*$  in crustal rocks and minerals. In fact, noble gases in  $\text{CO}_2$ -rich natural gas

wells support such migration and circulation—that is, the isotopic signatures clearly indicate a mantle origin for the noble gases, including amounts of excess  $^{40}\text{Ar}^*$  in some  $\text{CO}_2$ -rich natural gas wells exceeding those in the mantle-derived mid-ocean ridge basalts (Ballentine, 1997; Burnard et al., 1997; Moreira et al., 1998; Staudacher, 1987; Staudacher et al., 1989). Staudacher also notes that the quantities of excess  $^{40}\text{Ar}^*$  in the continental crust can be as much as five times that found in such mantle-derived mid-ocean ridge basalts (Staudacher et al., 1989), strongly suggesting that excess  $^{40}\text{Ar}^*$  in crustal rocks and their constituent minerals could well be the norm rather than the exception, thus making all K-Ar (and Ar-Ar) dating questionable.

It has now been established that some diamonds can form in the crust during high-grade metamorphism (Dobrzhinetskaya et al., 1995; Sobolev & Shatsky, 1990) and via shock metamorphism during meteorite or asteroid impact (Hough et al., 1997). The pressures and temperatures of high-grade metamorphism had been regarded as insufficient to produce diamonds, but the key ingredient was found to be volatile  $\text{N}_2$ - $\text{CO}_2$ -rich fluids. Noble gas data on these diamonds are not yet available, due to their size and rarity, but such data have been definitive in establishing the crustal origin of carbonado diamonds (Ozima, Zashu, Tomura, & Matsuhisa, 1991). Nevertheless, they still contain excess  $^{40}\text{Ar}^*$ .

Dalrymple (1991), referring to metamorphism and anatexis of rocks in the crust, commented, “If the rock is heated or melted at some later time, then some or all the  $^{40}\text{Ar}$  may escape and the K-Ar clock is partially or totally reset.” In other words,  $^{40}\text{Ar}^*$  escapes to migrate in the crust where it may then be incorporated in other minerals as excess  $^{40}\text{Ar}^*$ , just as  $^{40}\text{Ar}^*$  degassing from the mantle does. Thus, for example, excess  $^{40}\text{Ar}^*$  has been recorded in many minerals (some of which contain no  $^{40}\text{K}$ ) in crustal rocks, such as quartz, plagioclase, pyroxene, hornblende, biotite, olivine, beryl, cordierite, tourmaline, albite, and spodumene (Funkhouser, Barnes, & Naughton, 1966; Laughlin, 1969) in pegmatites, metamorphic rocks, and lavas. And it is not just K-Ar dating analyses that detect excess  $^{40}\text{Ar}^*$ , as Lanphere & Dalrymple (1976) used the  $^{40}\text{Ar}/^{39}\text{Ar}$  method to confirm the presence of excess  $^{40}\text{Ar}^*$  in feldspars and pyroxenes. Indeed, in a recent study (Pickles, Kelley, Reddy, & Wheeler, 1997), 128 Ar isotopic analyses were obtained from ten profiles across biotite grains in amphibolite-granulite facies metamorphic rocks, and apparent  $^{40}\text{Ar}/^{39}\text{Ar}$  “ages” within individual grains ranged from 161 to 514 Ma. The investigators concluded that these observations cannot be solely due to radiogenic build-up of  $^{40}\text{Ar}^*$ , but must be the result of incorporation by diffusion of excess  $^{40}\text{Ar}^*$  from an external source, namely,

$^{40}\text{Ar}^*$  from the mantle and other crustal rocks and minerals. Indeed, Harrison & McDougall (1980) were able to calculate a well-defined law for  $^{40}\text{Ar}$  diffusion from hornblende in a gabbro due to heating. They also found that the excess  $^{40}\text{Ar}^*$  which had developed locally in the intergranular regions of the host gabbro reached partial pressures in some places of at least  $10^{-2}$  atm.

This crustal migration of  $^{40}\text{Ar}^*$  is known to cause grave problems in attempted regional geochronology studies. In the Middle Proterozoic Musgrave Block of northern South Australia, Webb (1985) found a wide scatter of K-Ar mineral ages ranging from 343 Ma to 4493 Ma due to inherited (or excess)  $^{40}\text{Ar}^*$ , so that no meaningful interpretation could be drawn from the rocks (granulite, gneiss, pseudotrachylite, migmatite, granite, and diabase). Of the diabase dikes which gave anomalous ages, he concluded that

The basic magmas probably formed in or passed through zones containing a high partial pressure of  $^{40}\text{Ar}^*$ , permitting inclusion of some of the gas in the crystallizing minerals.

Likewise, when Baski & Wilson (1980) attempted to argon date Proterozoic granulite-facies rocks in the Fraser Range (Western Australia) and Strangways Range (central Australia), they found that garnet, sapphirine, and quartz in those rocks contained excess  $^{40}\text{Ar}^*$  that rendered their argon dating useless because of “ages” higher than expected. They also concluded that the excess  $^{40}\text{Ar}^*$  was probably incorporated at the time of formation of the minerals, and their calculations suggested a partial pressure of  $\sim 0.1$  atm Ar in the Proterozoic lower crust of Australia, which extends over half the continent.

In a detailed  $^{40}\text{Ar}/^{39}\text{Ar}$  dating study of high-grade metamorphic rocks in the Broken Hill region of New South Wales (Australia), Harrison & McDougall (1981) found evidence of widely distributed excess  $^{40}\text{Ar}^*$ . The minerals most affected were plagioclase and hornblende, with step heating  $^{40}\text{Ar}/^{39}\text{Ar}$  “age” spectra yielding results of up to 9.588 Ga. Such unacceptable “ages” were produced by excess  $^{40}\text{Ar}^*$  release, usually at temperatures of 350–650 °C and/or 930–1380 °C, suggesting the excess  $^{40}\text{Ar}^*$  is held in sites within the respective mineral lattices with different heating requirements for its release. There are three principal trapping sites for Ar in solids structural holes, edge dislocations, and lattice vacancies. (Argon is also known to be held sometimes in some minerals in fluid inclusions.) Clearly, this study shows that at crustal temperatures, which are less than 930 °C, some excess  $^{40}\text{Ar}^*$  will always be retained in those trapping sites in minerals where it is obviously “held” more tightly, thus rendering K-Ar and  $^{40}\text{Ar}/^{39}\text{Ar}$  dating questionable. Harrison & McDougall (1981) were only able to produce a

viable interpretation of the data because they made assumptions about the expected age of the rocks and of a presumed subsequent heating event (based on Pb-Pb and Rb-Sr dating), the latter being the time when they conjecture that accumulated  $^{40}\text{Ar}^*$  was released from minerals causing a significant regional Ar partial pressure of  $\sim 3 \times 10^{-4}$  atm to develop.

### **Mantle-Crust Domains and Excess $^{40}\text{Ar}^*$**

Harte & Hawkesworth (1986) have identified domains within the mantle and crust and described the interaction between them, all of which is relevant to the migration and circulation of argon (and thus excess  $^{40}\text{Ar}^*$ ) from the lower mantle to the crust and to lavas extruded on the earth's surface. The six domains are physically distinct units which show wide differences in average physical and chemical properties, as well as apparent age, structure, and tectonic behavior. They are the lower mantle (below 670 km), upper mantle, continental mantle lithosphere, oceanic mantle lithosphere, continental crust, and oceanic crust, and each is a distinct geochemical reservoir. Each domain may provide material for magmatic rocks, and particular geochemical features of magmas may be associated with particular domains. Thus the convecting upper mantle which comes to the surface at mid-ocean ridges may be identified as the source of most geochemical features of mid-ocean ridge basalts, including their excess  $^{40}\text{Ar}^*$  content. Similarly, the convecting lower mantle is regarded as the primordial or bulk earth geochemical reservoir, which may also contribute excess  $^{40}\text{Ar}^*$  to mid-ocean ridge basalts, but is more important for its contribution to ocean island basalts (for example, Hawaii) and other plume-related basalts (continental alkali basalts and continental flood basalts). However, considerable complexity may be added to the deeper mantle geochemical structure as a result of localized accumulation of subducted oceanic lithosphere.

Porcelli & Wasserburg (1995) have proposed a steady-state upper mantle model for mass transfer of rare gases, including argon. The rare gases in the upper mantle are derived from mixing of rare gases from the lower mantle, subducted rare gases, and radiogenic nuclides produced in situ. Porcelli & Wasserburg claim that all of the  $^{40}\text{Ar}$  in the closed-system lower mantle has been produced by  $^{40}\text{K}$  decay in the lower mantle, but this claim is based on the assumption of a 4.5 Ga earth. In any case, they contradict themselves, because they also state (Porcelli & Wasserburg, 1995, p. 4924), "The lower mantle is assumed to have evolved isotopically approximately as a closed system with the in situ decay of  $^{129}\text{I}$ ,  $^{244}\text{Pu}$ ,  $^{238}\text{U}$ ,  $^{232}\text{Th}$ , and  $^{40}\text{K}$  adding to the complement of initial rare gases." In other words, they admit that some of the  $^{40}\text{Ar}$  must be primordial and not derived

from radioactive  $^{40}\text{K}$ . They then go on to claim that in the upper mantle,  $^{40}\text{K}$  decay further increases the radiogenic  $^{40}\text{Ar}$  from the lower mantle by a factor of  $\sim 3$ , but again this presupposes a 4.5 Ga earth and doesn't allow for primordial  $^{40}\text{Ar}$  that could well be also in the upper mantle if its admitted to be in the lower mantle.

In the case of the continental and oceanic lithospheric domains, the lack of convective stirring means that different geological processes and events may implant in each domain a variety of geochemically distinct materials which will remain isolated from one another. Therefore, these domains do not have a single set of geochemical characteristics; thus identification of geochemically defined "sources" with particular physically defined crust-mantle domains is complex, and the geochemical definition of particular reservoirs cannot be regarded as simply definition of major physical entities. Nevertheless, excess  $^{40}\text{Ar}^*$  will be added to these domains by the passage of basaltic magma plumes from the upper mantle to the earth's surface.

Furthermore, the processes of oceanic lithosphere formation from the convecting upper mantle in association with mid-ocean ridge activity mean that its isotopic characteristics everywhere will be largely similar to those of the convecting upper mantle and mid-ocean ridge basalts, including the addition of excess  $^{40}\text{Ar}^*$ . The corollary to this is that the oceanic crust is formed as part of these same processes. However, the oceanic crust generally has a thin veneer of sediments over it, and thick wedges of sediments adjacent to the domains of continental crust, whereas sections of oceanic crust are hydrothermally altered. The compositions of these components of the oceanic crust may, therefore, include a considerable contribution from continental detritus and ocean water, so that this oceanic crustal material may give rise to a distinct geochemical reservoir, the fate of which during subduction back into the upper mantle becomes critically important if it contributes to island arc volcanics, plume-related intra-place magmas, and mantle-derived xenoliths.

The complexity of continental crustal material is well known through direct observation, and the mantle lithosphere attached to it may be expected to show a similar complexity. Nevertheless, it is evident that excess  $^{40}\text{Ar}^*$  also resides in the continental mantle lithosphere, as indicated by xenoliths (Matsumoto et al., 1997). Likewise, there is evidence of excess  $^{40}\text{Ar}^*$  in crustal magmatic rocks (for example, gabbros, Harrison & McDougall, 1980; pegmatites Laughlin, 1969), migrating through metamorphic terrains (Baksi & Wilson, 1980; Harrison & McDougall, 1981; Webb, 1985), and in natural gas in sedimentary reservoirs (Staudacher, 1987).

### **Mt. Ngauruhoe in its Tectonic Framework**

The presence, therefore, of excess  $^{40}\text{Ar}^*$  in the recent andesite flows at Mt. Ngauruhoe is to be expected. The Taupo Volcanic Zone is a volcanic arc and marginal basin of the Taupo-Hikurangi arc-trench system (see Figure 1 again), which is a southward extension of the Tonga-Kermadec arc into the continental crustal environment of New Zealand's North Island (Cole & Lewis, 1981). Geophysical investigations indicate that the Pacific Plate is being obliquely subducted beneath the Australian Plate on which most of New Zealand's North Island sits, and that the volcanoes of the Taupo Volcanic Zone, including Ngauruhoe in the Tongariro Volcanic Center, are about 80km directly above the subducting Pacific Plate, a zone of earthquakes revealing where the movement is taking place (Williams, 1994). Friction along the plane of contact is believed to cause melting to produce pockets of magma, which then feed via conduits to the volcanoes above. Thus the recent andesite flows at Mt. Ngauruhoe are calc-alkaline island arc volcanics.

The tectonic and geochemical framework of the Ngauruhoe andesite flows within the mantle-crust domains of Harte & Hawkesworth (1986) is that of subducting oceanic crust (derived from the convecting upper mantle), carrying with it the wedge of continental sedimentary detritus which has accumulated at the continental margin and in the adjacent trench to the east of the coastline. Attached beneath the subducting oceanic crust is its associated oceanic mantle lithosphere, and together they are being thrust downwards into the upper mantle. Above the subducting plate are the continental crust and continental mantle lithosphere of the overriding plate, the continental crust being at the contact plane at shallow depths near the trench, and then the attached continental mantle lithosphere beneath at a depth of about 35km (Graham & Hackett, 1987). Thus the geochemical reservoir from which the Ngauruhoe andesite magma has been drawn is potentially a mixture of melted oceanic crust, continental sedimentary detritus and continental crust, and possibly continental mantle lithosphere, or even upper mantle.

### **Genesis of the Mt. Ngauruhoe Andesite Magma and its Excess $^{40}\text{Ar}^*$**

One of the easier investigations of the petrogenesis of these volcanic rocks of the Taupo Volcanic Zone was that of Stipp (1968), and Ewart & Stipp (1968). They analyzed samples that had been systematically collected, including not only the lavas and the pyroclastics, but also the Permian to Jurassic interbedded greywackes, siltstones, and shales (the potential crustal source rocks) which are spatially

related to, and underlie, the volcanics. Of primary interest were Sr, Rb, and K contents, and  $^{87}\text{Sr}/^{86}\text{Sr}$  and  $^{87}\text{Rb}/^{86}\text{Sr}$  ratios. Three possibilities for the origin of the calc-alkaline andesite magma were under investigation fractional crystallization of a basalt magma under oxidizing conditions; some form of hybridization between basaltic and acidic magmas, possibly followed by fractional crystallization; and derivation of a primary andesite magma from the upper mantle. Ewart & Stipp (1968) regarded their Sr isotopic data as more consistent with the production of the andesites by partial assimilation of sedimentary material by basaltic magma (derived from the upper mantle), the adjacent greywackes, siltstones, and shales being the most likely sedimentary material, and the unassimilated gneissic xenoliths probably representing the basement rocks to those sediments. However, they admitted that the data did not exclude the possibility of a primary andesitic magma derived directly from the upper mantle, provided that some assimilation of crustal material modified it prior to eruption.

Subsequent investigations by Cole (1978) favored the alternate petrogenetic model of a primary andesitic magma. He suggested that the subducting oceanic crust assimilated the greywacke-siltstone-shale and overlying sediments east of the Taupo Volcanic Zone to produce amphibolite, which subsequently broke down to produce phlogopite eclogite below 90km. This in turn partially melted at 150–200km, and the resultant magma fractionated in the upper mantle or lower crust to produce andesite. However, based on rare-earth element geochemistry, Cole, Cashman, & Rankin (1983) modified that petrogenetic model, suggesting that while the andesite magma genesis was probably associated in the upper mantle with the downgoing slab and some crustal contamination occurred, the andesite does not appear to have had an eclogite parent. This would then suggest that the melting associated with the subducting slab to generate the andesite magma occurred at a depth of less than 90km.

Graham & Hackett (1987) agreed with this conclusion, demonstrating from geophysical evidence that the top of the subducting slab is at a depth of about 80km below Ngauruhoe, and that the crust there is probably less than 20km thick. Thus the upper mantle wedge between would consist only of plagioclase-peridotite and spinel-peridotite. At 80km depth the hydrated amphibolite assemblage of the upper portion of the subducting slab of oceanic crust and oceanic mantle lithosphere would have started to dehydrate, thus liberating water and possibly other volatile constituents into the overlying upper mantle wedge, significantly lowering its melting point. Graham & Hackett then showed that the



geochemical evidence requires the andesite magma for the Ngauruhoe lava flows to have been generated from an original low-alumina basalt magma produced in the upper mantle wedge by anatexis of the asthenosphere (uppermost mantle) and/or subcontinental mantle lithosphere probably catalyzed by hydrous, metasomatic fluids from the subducting slab.

Some specific geochemical enrichment then appears to have occurred as a result of this mantle metasomatism and continental crustal contamination during ascent and storage of the magma. Graham & Hackett (1987) used least squares geochemical modeling to show how the andesite magma could be generated from such a parent basalt magma by a process of combined assimilation of crustal material (addition of 6% assimilant) and fractional crystallization (30% removal of crystals). Furthermore, the presence of xenoliths in the Ngauruhoe andesite flows, particularly the vitrified meta-greywacke and gneissic xenoliths, indicate conclusively that the assimilant was most likely a partial melt of gneiss, originally the adjacent greywacke-siltstone-shale sediments (Graham & Hackett, 1987; Graham et al., 1995).

These processes responsible for the generation of the andesite magma did not diminish the excess  $^{40}\text{Ar}^*$  content of the resultant flows. Though the amount of excess  $^{40}\text{Ar}^*$  is not high when compared with that found in mid-ocean ridge basalts, it is nonetheless significant that the excess  $^{40}\text{Ar}^*$  was still present in the lavas upon eruption and cooling. The evidence indicates that the parent basaltic magma was generated in the upper mantle where the excess  $^{40}\text{Ar}^*$  in the geochemical reservoir is now known to be upwards of 150 times more than the atmospheric content, relative to  $^{36}\text{Ar}$ . The subsequent crustal contamination and fractional crystallization to form the andesite magma during ascent, and the degassing of the magma during eruption and lava flow and cooling, did not remove all the excess  $^{40}\text{Ar}^*$ , a small portion of which was left to be trapped in the congealed lava and its constituent minerals.

This model for the generation of the andesite magma in the post-Flood world is, of course, based on the plate tectonics model for global tectonics through earth history. Even though the postulated plate movements today are extremely slow, and thus extrapolated back over millions of years by uniformitarians, a catastrophic model for plate tectonics in the context of the Flood is entirely compatible with both Scripture and the scientific data (Austin et al., 1994). Plate movements are regarded as occurring catastrophically during the Flood and then rapidly slowing down to today's rates in the post-Flood era.

## Conclusions

The fact that there is even some excess  $^{40}\text{Ar}^*$  in these recent andesite flows, and that it appears to have ultimately come from the upper mantle geochemical reservoir, where it is regarded as leftover primordial argon not yet fully expelled by the process of outgassing that is supposed to have occurred since the initial formation of the earth, has very significant implications.

First, this is clearly consistent with a young earth, where the very short time scale since the creation of the earth has been insufficient for all the primordial argon to be released yet from the earth's deep interior. Furthermore, it would also seem that even the year-long global catastrophic Flood, when large-scale convection and turdecer occurred in the mantle (Austin et al., 1994), was insufficient to expel all the deep earth's primordial argon.

Second, this primordial argon is, in part, "excess"  $^{40}\text{Ar}^*$  not generated by radioactive decay of  $^{40}\text{K}$ , which has then been circulated up into crustal rocks where it may continue migrating and building up to partial pressure status regionally. Because the evidence clearly points to this being the case, then when samples of crustal rocks are analyzed for K-Ar "dating" the investigators can never really be sure that whatever  $^{40}\text{Ar}^*$  is in the samples is from in situ radioactive decay of  $^{40}\text{K}$  since the formation of the rocks, or whether some or all of it is from the "excess  $^{40}\text{Ar}^*$ " geochemical reservoirs in the lower and upper mantles. This could even be the case when the K-Ar analyses yield "dates" compatible with other radioisotopic "dating" systems and/or with fossil "dating" based on evolutionary assumptions. And there would be no way of knowing because the  $^{40}\text{Ar}^*$  from radioactive decay of  $^{40}\text{K}$  cannot be distinguished analytically from primordial  $^{40}\text{Ar}$  not from radioactive decay, except of course by external assumptions about the ages of the samples.

Therefore, these considerations call into question all K-Ar "dating," whether "model ages" or "isochron ages," and all  $^{40}\text{Ar}/^{39}\text{Ar}$  "dating," as well as "fossil dating" that has been calibrated against K-Ar "dates." Although seemingly insignificant in themselves, the anomalous K-Ar "model ages" for these recent andesite flows at Mt. Ngauruhoe, New Zealand, lead to deeper questions. Why is there excess  $^{40}\text{Ar}^*$  in these rocks? From where did it come? Answers to these questions in turn point to significant implications that totally undermine such radioactive "dating" and that are instead compatible with a young earth.

## Future Research

Further research is very definitely warranted. The most pressing need is to attempt to quantify how much primordial  $^{40}\text{Ar}$  there is today in the upper mantle. Also, how much has circulated into crustal

rocks, how much is in natural gas reservoirs, and how much might have escaped into the atmosphere during 6,000–7,000 years, including accelerated rates during the Flood. It might then be possible to quantify how much primordial  $^{40}\text{Ar}$  there was in the mantle at the time of the earth's creation. From these calculations and associated modelling exercises there might develop quantifiable evidence for the earth's youthfulness.

Additionally, further research is needed to quantify how much “excess  $^{40}\text{Ar}^*$ ” is in all the crustal rocks and minerals that have been, and are, subject to K-Ar and  $^{40}\text{Ar}/^{39}\text{Ar}$  “dating.” This would include what are regarded as mantle xenoliths and xenocrysts (for example, diamonds). It is helpful to show on the one hand that such “dating” is questionable, but on the other hand there are still many “dates” that are concordant, that is, they agree with other uniformitarian dating systems and schemes. So ultimately we need to explain why that happens when other “dates” are discordant and anomalous. There may, in fact, be some pattern or systematic way in which “excess  $^{40}\text{Ar}$ ” has been trapped in rocks and occluded in minerals at different levels (depths and relative ages) in the geological record. If so, then K-Ar and  $^{40}\text{Ar}/^{39}\text{Ar}$  “dating” would irrevocably be discredited.

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