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Age-Dating of Volcanic Rocks: A Review

Andrew A. Snelling

Abstract

The problems with the unproven assumptions that underpin the radioisotope age-dating methods for volcanic rocks are well-documented in the conventional (uniformitarian) literature. Assumed initial conditions are violated by inheritance from mantle and crustal sources. The required closed-radioisotope, parent-daughter systems are violated regularly by open-system behavior—contamination, loss by diffusion, and weathering. And there is good experimental evidence of past accelerated-radioisotope decay in a recent catastrophic event. Thus, the millions-of-years ages for volcanic rocks and the age-dating radioisotope methods used to obtain them are totally unreliable. However, the inflated radioisotope ages often agree with the stratigraphic and biostratigraphic positions of the volcanic strata in the rock record, which is consistent with accelerated radioisotope decay during the recent global Genesis Flood cataclysm.

Key Words: radioisotope age-dating, volcanic rocks, assumptions, inheritance, contamination, open-system behavior, accelerated decay

Introduction

The successes of the radioisotope dating methods for obtaining ages for volcanic rocks that match their presumed ages based on their relative stratigraphic and/or biostratigraphic positions in the rock record are usually trumpeted as proving those age-dating methods work. However, sometimes these standard methods have proven futile because they produce erroneous ages, as documented in the literature (Snelling, 2000). And it is precisely where the methods fail that the unproven assumptions behind the methods are exposed. How serious this problem may really be is hard to gauge or quantify because it would seem that not all discrepant results are published, for obvious reasons. Nevertheless, if we use the Dalrymple (1969) study as a guide, he reported that about one-quarter of his results were anomalous (see below). At least he knew which samples gave anomalous results, but in other studies using other methods there are not always clear indications of which results might be anomalous apart from them not matching the expected target. This then could still be quite a serious widespread problem. That then raises the question—if these methods fail when the correct ages of the rocks are known, how can we trust these methods on rocks of unknown ages? After all, such failures are likely

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to be systematic, so that even when the methods provide ages compatible with the presumed ages, the compatibility may likewise be flawed.

The May 18,1980, volcanic eruption of Mount St. Helens may not have been the largest or most devastating historic eruption, but it was one of the most geologically significant. It provided a natural laboratory for geologists to witness the results of catastrophic geological processes.

Among the geological surprises was further confirmation that volcanic rocks cannot be accurately age-dated by radioisotope methods. Subsequent to the May 18, 1980, eruption, a new lava dome grew within the blasted-out crater. Austin (1996) collected a sample from it and submitted it to a recognized commercial laboratory for K-Ar dating. The whole-rock dacite sample yielded a K-Ar age of 350,000 years, while mineral concentrates separated from it yielded K-Ar ages up to 2.8 ± 0.6 Ma (million years). It was concluded that excess argon had been inherited from the volcanic gases trapped in the lava as it cooled and crystallized.

Stung by this result being used by a creationist geologist to discredit the K-Ar radioisotope dating method, opponents such as G. Brent Dalrymple (of the UC Berkeley Geochronology Laboratory) were vociferous in their efforts to accuse Steve Austin of incompetence and misapplying the K-Ar method to such a recent volcanic rock. However, the irony is that Dalrymple himself years before used the K-Ar method to date recent volcanic rocks (Dalrymple, 1969). Indeed, numerous other workers have also found the same problem that recent volcanic rocks inherit excess argon when they crystallize.

K-Ar Dating of Volcanic Rocks

Snelling (2000) provided a detailed overview with extensive documentation of this and other problems in age-dating volcanic rocks with the K-Ar method.

Critical to this method is the assumption that there was no radiogenic $^{40}\text{Ar}^{*}$ (the asterisk * denoting radiogenic ^{40}Ar as distinct from non-radiogenic ^{40}Ar) in rocks such as basalts when they formed, which is usually stated as being self-evident. For example, Geyh and 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 and Lanphere (1969, p.46) state:

> ...a silicate melt will not usually retain the ^{40}Ar that is produced, and thus the potassium-argon clock is not "set" until the mineral solidifies and cools sufficiently to allow the ^{40}Ar to accumulate in the mineral lattice.

And Dalrymple (1991, p.91) argued strongly:

> The K-Ar method is the only decay scheme that can be used with little or no concern for the presence of the daughter isotope. This is because ^{40}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}Ar escapes from the liquid.

Excess ^{40}Ar

However, that dogmatic statement is incompatible with Dalrymple's own earlier work on 26 historic subaerial lava flows, about 25% of which had non-zero concentrations of $^{40}\text{Ar}^{*}$ (that is, excess $^{40}\text{Ar}^{*}$) in violation of that key assumption of the K-Ar dating method (Dalrymple, 1969). The amounts of $^{40}\text{Ar}^{*}$ found in these historic lava flows were equivalent to the K-Ar ages listed in Table I. Furthermore, there are numerous other reported examples of excess $^{40}\text{Ar}^{*}$ in recent or young volcanic rocks equivalent to the excessively old K-Ar ages listed in Table II (Snelling, 2000).

Measurements of excess $^{40}\text{Ar}^{*}$ in lavas have been commonly reported. Fisher (1970) investigated submarine

Table I. Anomalous K-Ar ages for historic lavas calculated from their K-Ar analyses [Dalrymple, 1969].

Rock/Mineral Location	Historic Date	K-Ar Ages
Hualalai basalt, Hawaii	AD 1800–1801	1.6 ± 0.16 Ma and 1.41 ± 0.08 Ma
Mt. Etna basalt, Sicily	122 BC	0.25 ± 0.08 Ma
Mt. Etna basalt, Sicily	AD 1972	0.35 ± 0.14 Ma
Mt. Lasson plagioclase, California	AD 1915	0.11 ± 0.03 Ma
Sunset Crater basalt, Arizona	AD 1064–1065	0.27 ± 0.09 Ma and 0.25 ± 0.15 Ma

basalt from a Pacific seamount and found “the largest amounts of excess ^{4}He and ^{40}Ar ever recorded” (at that time). McDougall (1971) found “extraneous radiogenic argon present in three of the groups of basalt flows” on the young volcanic island of Reunion in the Indian Ocean. Significant quantities of excess ^{40}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., 1996b), and in samples from the Mid-Atlantic Ridge, East Pacific Rise, Red Sea, Galapagos Islands, McDonald Seamount, and Manus Basin (Staudacher et al., 1989; Marty and Humbert, 1997). Patterson et al. (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) confirmed that the excess ^{40}Ar* was not from atmospheric contamination at all.

In Austin’s (1996) investigation of the 1986 dacite lava flow from the post-October 26, 1980, lava dome within the Mount St. Helens crater, he established that the 10-year-old dacite (when dated in 1996) yielded a whole-rock K-Ar model age of 0.35 ± 0.05 Ma due to excess ^{40}Ar* in the rock. He then produced concentrates of the constituent minerals, which yielded anomalous K-Ar model ages of 0.34 ± 0.06 Ma (plagioclase), 0.9 ± 0.2 Ma (hornblende), 1.7 ± 0.3 Ma (pyroxene), and 2.8 ± 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}Ar* responsible for the anomalous K-Ar ages was retained within the different constituent minerals in different amounts. Furthermore, the whole-rock age was very similar to the age of the plagioclase concentrate because plagioclase is the dominant constituent of the dacite.

Similarly, Snelling (1998) reported that andesite flows on New Zealand’s newest and most active volcano, Mt. Ngauruhoe in the Taupo Volcanic Zone, which produced andesite flows in 1949 and 1954, and avalanche deposits in 1975, yielded K-Ar model ages for five of these flows and deposits from <0.27 Ma to 3.5 ± 0.2 Ma. These dates could not be reproduced, even

Table II. Anomalous K-Ar ages for lavas with historic or expected recent ages [sources in Snelling, 2000].

Rock/Mineral Location	Historic/Expected Date	K-Ar Ages
Akka Waterfall Flow, Hawaii	Pleistocene	32.3 ± 7.2 Ma
Kilauea Iki basalt, Hawaii	AD 1959	8.5 ± 6.8 Ma
Mt. Stromboli, volcanic bomb	AD 1963	2.4 ± 2 Ma
Mt. Etna basalt, Sicily	AD 1964	0.7 ± 0.01 Ma
Medicine Lake Highlands obsidian, California	<500 years old	12.6 ± 4.5 Ma
Hualalai basalt, Hawaii	AD 1800–1801	22.8 ± 16.5 Ma
Alkali basalt plug, Benue, Nigeria	<30 Ma	95 Ma
Olivine basalt, Nathan Hills, Antarctica	<3 Ma	18.0 ± 0.7 Ma
Anorthoclase, Mt. Erebus, Antarctica	AD 1984	0.64 ± 0.03 Ma
Kilauea basalt, Hawaii	<200 years old	21.8 Ma
Kilauea basalt, Hawaii	<1000 years old	42.9 ± 4.2 Ma and 30.3 ± 3.3 Ma
East Pacific Rise basalt	<1 Ma	690 ± 7 Ma
Seamount basalt near East Pacific Rise	<2.5 Ma	580 ± 10 Ma and 700 ± 150 Ma
East Pacific Rise basalt	<0.6 Ma	24.2 ± 1.0 Ma

from splits of the same samples from the same flow, the explanation being variations in excess ^{40}Ar* content.

That the excess ^{40}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}Ar*, as did the olivine and clinopyroxene phenocrysts in Quaternary flows from New Zealand volcanoes (Patterson et al., 1994). Similarly, Poths et al. (1993) separated olivine and clinopyroxene phenocrysts from young basalts from New Mexico and Nevada and then measured "ubiquitous excess argon" in them. Damon et al. (1967) reported several instances of phenocrysts with K-Ar ages 1–7 million years greater than that of the whole rocks, and one K-Ar date for olivine phenocrysts of greater than 110 Ma in a recent (<13,000-year-old) basalt. Damon et al. (1967) thus suggested that large phenocrysts in volcanic rocks contain the excess ^{40}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}Ar* with large phenocrysts or with any other petrographic parameter.

Thus, most investigators have concluded that the excess ^{40}Ar* had to obviously be present in the molten lavas when they were extruded, which then did not completely degas as they cooled, the excess ^{40}Ar* becoming trapped in 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, with olivine retaining 0.34 ppm ^{40}Ar* (Broadhurst et al., 1990, 1992). It was concluded that the argon is held primarily in lattice vacancy defects within minerals.

However, from whence came the excess ^{40}Ar*, because it is argon which cannot be attributed to atmospheric contamination or in situ radioactive decay of ^{40}K? It is not simply "magmatic" argon. Funkhouser and Naughton (1968) found that the excess ^{40}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, and was sufficient to yield ages of 2.6 Ma to 2960 Ma. Thus, since the ultramafic xenoliths and the basaltic magmas came from the mantle, the excess ^{40}Ar* must initially reside there, to be transported to the Earth's surface in the magmas.

Many studies confirm the mantle source of excess ^{40}Ar*. Hawaiian volcanism is typically cited as resulting from a mantle plume. Most investigators now concede that excess ^{40}Ar* in the lavas, including those from the active Loihi and Kilauea volcanoes, is indicative of the mantle source area from which the magmas came (Patterson et al., 1990; Honda et al., 1993). Considerable excess ^{40}Ar* measured in ultramafic mantle xenoliths from Kerguelen Archipelago in the southern Indian Ocean likewise is regarded as the mantle source signature of hotspot volcanism (Valbracht et al., 1996a). Indeed, data from single vesicles in mid-ocean ridge basalt samples dredged from the North Atlantic suggest the excess ^{40}Ar in the upper mantle may be almost double previous estimates, that is, almost 150 times more than the atmospheric content (relative to Ar) (Moreira et al., 1998). Another study on the same samples indicates the upper mantle content of Ar could be even ten times higher (Burnard et al., 1997).

The key issue is still where this excess ^{40}Ar has come from, and whether it has been derived from radioactive decay of ^{40}K. One possibility is that the excess ^{40}Ar can be accounted for by radioactive decay during long-term residence of magmas in chambers before eruption. Esser et al. (1997) discounted this option for the Mt. Erebus anorthoclase phenocrysts. Dalrymple (1969) found that whereas the Mt. Lassen (1915) plagioclase phenocrysts yielded excess ^{40}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. Surtsey is an island off the southern coast of Iceland that formed in a volcanic eruption that began in 1963 and lasted until 1967 when the island reached its maximum size of 2.7 km^2 (1.0 sq. mi.) (Decker and Decker, 1997). Because phenocrysts usually crystallize from lavas after eruption, they may arbitrarily trap excess ^{40}Ar during lava cooling, ^{40}Ar that will thus not be from in situ ^{40}K radioactive decay in the magma's mantle source.

Indeed, diamonds and their microinclusions are a means of sampling the mantle because they are thermodynamically stable at the depths greater than 150 km where they formed, apparently in the Archean (Kirkley et al., 1992). When Zashu et al. (1986) obtained a K-Ar isochron age of 6.0 ± 0.3 Ga for ten Zaire diamonds, it was obvious excess ^{40}Ar* in the mantle was responsible, because the diamonds could not be older than the Earth itself. In a follow-up study Podosek et al. (1988) found that the ^{40}K present in these diamonds was in normal isotopic abundance, so the erroneous age had to be due to excess ^{40}Ar* not generated in situ but inherited or in trapped fluids from the mantle reservoir where the diamonds formed. Furthermore, Johnson et al. (2000) analyzed fluid inclusions in diamonds and found extremely high ^{40}Ar/^{36}Ar ratios and ^{40}Ar* poorly correlated with K indicative of mantle-derived excess ^{40}Ar* not produced by in situ decay of ^{40}K. Clearly, excess ^{40}Ar* is abundant in the mantle and can easily be transported up into the crust.

Thus, excess ^{40}Ar* migrating from the mantle is found in crustal rocks and minerals. Amounts of excess ^{40}Ar* in some CO_2-rich natural gas wells were found to exceed those in mantle-derived mid-ocean ridge basalts (Staudacher, 1987; Staudacher et al., 1989; Burnard et al., 1997; Moreira et al., 1998). It was also noted that the quantities of excess ^{40}Ar* in the continental crust can thus be as much as five times that found in mantle-derived, mid-ocean ridge basalts, strongly suggesting that excess ^{40}Ar* in crustal rocks and minerals could well be the norm rather than the exception.

Similarly, as Dalrymple (1991) commented, if a rock is heated or melted within the continental crust, then some or all the ^{40}Ar* may escape and migrate in the crust to be incorporated in other rocks and minerals as excess ^{40}Ar*. Thus, excess ^{40}Ar* has been recorded in many minerals in crustal rocks, some of which contain no ^{40}K, such as quartz, plagioclase, pyroxene, hornblende, biotite, olivine, beryl, cordierite, tourmaline, albite and spodumene in pegmatites, metamorphic rocks, and lavas (Damon and Kulp, 1958; Funkhouser et al., 1966; Laughlin, 1969).

Melton and Giardini (1986) found an ^{40}Ar/^{36}Ar value of 189 compared to a ratio of 294 for atmospheric argon in a diamond. Also, Melton and Giardini (1982) discussed models for the changes in Ar isotope contents of the mantle and the atmosphere over Earth history. Ozima (1975) gave a discussion of similar questions.

This crustal migration of ^{40}Ar* is thus known to cause grave problems in geochronology studies. For example, in the Precambrian Musgrave Block, northern South Australia, Webb (1985) found a wide scatter of K-Ar mineral ages ranging from 343 Ma to 4493 Ma due to inherited excess ^{40}Ar*, so that no meaningful interpretation could be drawn from the rocks. He concluded that the mafic magmas that formed the diabase dikes which gave anomalous ages "probably formed in or passed through zones containing a high partial pressure of ^{40}Ar*, permitting inclusion of some of the gas in the crystallizing minerals."

All this evidence clearly shows that excess ^{40}Ar* is ubiquitous in volcanic rocks when they cool and crystallize, and that the excess ^{40}Ar* was inherited from the mantle source areas of the magmas. This is not only true for recent and young volcanics, but for ancient volcanics such as the Middle Proterozoic Cardenas Basalt of eastern Grand Canyon (Austin and Snelling, 1998). The ^{40}Ar* intercept of their K-Ar isochron indicated there was some initial (inherited excess) ^{40}Ar* in those lava flows when they were extruded. Thus, in both the mantle and the crust, it has been repeatedly demonstrated that this ^{40}Ar predominantly represents primordial argon that is not derived from in situ radioactive decay of ^{40}K and thus has no age significance.

^{40}Ar Loss

While it is so evident that excess ^{40}Ar*, whether primordial or inherited, is a significant problem for age-dating of volcanic rocks, that is not the only encountered problem. For the K-Ar radioisotope method to work successfully, the ^{40}Ar* produced by in situ radioisotope decay of ^{40}K after the volcanic rocks are extruded has to be retained within them. Yet ^{40}Ar* loss from minerals is known to be a persistent problem. Because Ar is a noble (non-reactive) gas it does not form bonds with other atoms in crystal lattices of minerals, so no mineral phase preferentially takes up Ar (Dalrymple, 1991, p. 91). Rather, it is claimed that Ar can be readily lost from the minerals such as feldspar in volcanic rocks where it is produced. Ar also displays limited partition into fluids.

Faure (1986, p. 69) lists the causes in volcanic rocks to which Ar loss can be attributed:

- inability of mineral lattices to retain Ar even at low temperatures and atmospheric pressure,
- either partial or complete melting of rocks followed by crystallization of new minerals from the resulting melt (lava),
- increase in temperature from deep burial or contact metamorphism causing Ar loss from most minerals without producing any other chemical or physical changes in the rocks,
- metamorphism at elevated temperatures and pressures of volcanic rocks resulting in complete or partial Ar loss depending on the temperature and the duration of the event,
- chemical weathering and alteration by aqueous fluids, leading not only to Ar loss but also to changes in the K content of minerals,
- solution and redeposition of water-soluble minerals, and
- mechanical breakdown of minerals, radiation damage, and shock waves (even excessive grinding of rocks during their preparation for dating).

However, such explanations may often be resorted to in order to resolve conflicts between K-Ar dating results and expectations based on the evolutionary timescale, rather than being based on substantial experimental verification. Nevertheless, Ar is soluble in water (Mazor and Fournier, 1973; Mauger, 1977) and has a similar molecular diameter to water, so it can be removed from minerals and rocks by ground and thermal waters.

A very good demonstration of apparent ^{40}Ar* loss from different minerals in a thermal event is provided in the contact metamorphic zone associated with the Eldora granitic stock in the Colorado Front Range (Hart, 1964). The 54-Ma stock was intruded into Precambrian metamorphic rocks regarded as approximately 1350 Ma. It was found the K-Ar ages of biotite, hornblende, and K-feldspar in the host metamorphic rocks in close proximity to the intrusive contact decreased as a result of increasing losses of ^{40}Ar*, based on their presumed evolutionary age (Figure 1). That is, the fraction of ^{40}Ar* lost from each of the minerals decreased as a function of increasing distance from the contact and reflected the differing retentivities of these minerals for ^{40}Ar*. Whereas the coarse biotite lost almost all of its ^{40}Ar* at a distance of about 100 m (~300 ft.) from the contact, the effects of ^{40}Ar* loss could be traced for more than 2 km (1.2 miles) beyond that distance and the biotite K-Ar dates finally stabilized at a distance of about 4.25 km (2.6 miles) from the contact. The K-feldspar K-Ar dates increased somewhat erratically away from the contact and showed the effects of a substantial fraction of ^{40}Ar* loss even at a distance of almost 7 km (4.3 miles) from the contact. That distance is unlikely to be within the thermal aureole of the granitic stock but reflects the widely accepted view that K-feldspars may lose Ar by diffusion even at ambient temperatures (Dickin, 2005).

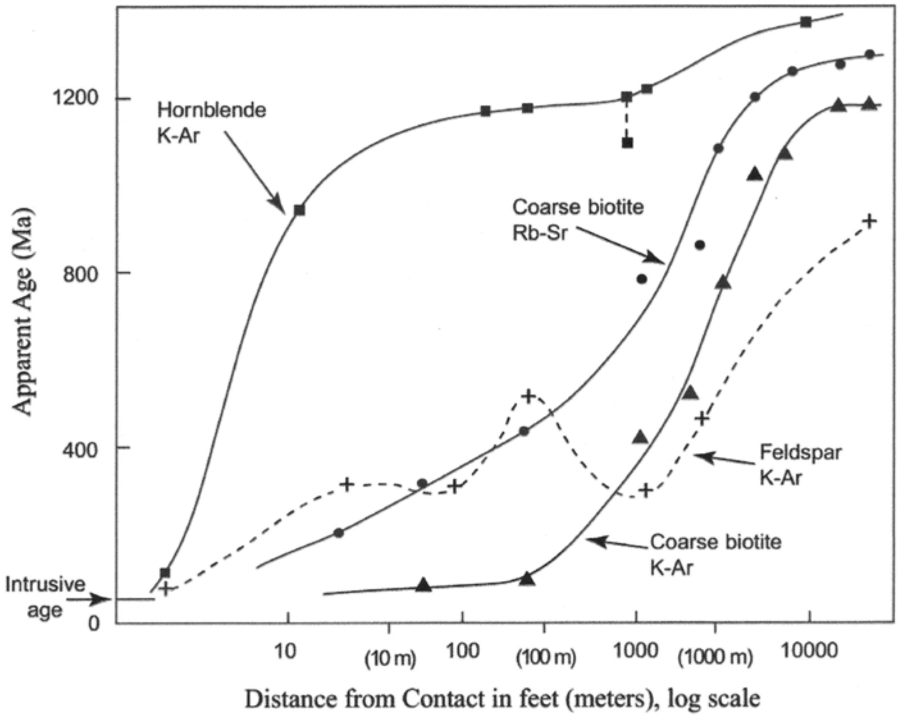

Figure 1. Plot of apparent mineral ages in Precambrian metasediments and metavolcanics against outward distance from the contact of the Tertiary Eldora granite stock, Colorado [after Hart, 1964].

It has been found that when a K-bearing mineral is heated, the ^{40}Ar* that has accumulated in it escapes by diffusion into intergranular space (Dalrymple, 1991, pp. 91, 115). Harrison (1981) experimentally measured the ^{40}Ar* loss from two compositionally contrasting hornblendes to determine the rate of ^{40}Ar* diffusion. To be assured that the ^{40}Ar* was released by diffusion, he heated the hornblendes under hydrothermal conditions at different temperatures and calculated the diffusion coefficients for Ar from the fraction of ^{40}Ar* released as a function of temperature. Harrison et al. (1985) conducted similar experiments to measure ^{40}Ar* loss from hydrothermally treated biotite and found that ^{40}Ar diffusivity in biotites is strongly dependent on the Fe/Mg ratio. They thus predicted that Fe-rich biotite was significantly less retentive of ^{40}Ar* than biotites of intermediate Fe/Mg compositions, a prediction confirmed by Grove and Harrison (1996). However, Fechtig and Kalbitzer (1966) found from extensive experimentation that diffusion at room temperatures is always so small that no appreciable Ar losses occur.

Nevertheless, K-Ar dating of ancient lava flows confirms that while they may have inherited excess ^{40}Ar* when they cooled and crystallized, with time they exhibit a net ^{40}Ar* loss. Austin and Snelling (1998) found that the Middle Proterozoic Cardenas Basalt of eastern Grand Canyon yielded a K-Ar isochron age of only 516 Ma, which is the same as the conventional Cambrian age of the overlying sedimentary strata, but less than half the published Rb-Sr isochron age of 1100 Ma (Larsen et al., 1994). They rejected that K-Ar isochron age, citing the conventional explanation was resetting of the K-Ar age due to Ar leakage and loss in the time since these lava flows were buried under other rock layers.

Similarly, Mankinen and Dalrymple (1972) rejected a 1.6 ± 0.1 Ma K-Ar date for the glassy matrix of a basalt because its plagioclase phenocrysts yielded a K-Ar age of 7.4 ± 0.2 Ma. Even though the glassy matrix constituted 75% of the rock and also contained plagioclase laths, and the rock's K content is almost entirely concentrated in the glass, which was described as unaltered, this age discrepancy was blamed on ^{40}Ar* loss from the glass. In contrast, Evernden et al. (1964) analyzed several devitrified volcanic glasses of "known" conventional ages and all yielded K-Ar ages that were too young, some being virtually zero ages, so they attributed this to ^{40}Ar* loss due to devitrification. So, how could ^{40}Ar* be equally lost from unaltered glass and devitrified (altered) glass?

The reality is that there is a steady loss of ^{40}Ar* from crustal rocks to the atmosphere (Drescher et al., 1998), which is a result of degassing of primordial ^{40}Ar and ^{40}Ar* from radioactive decay of ^{40}K in the mantle and crust. Although it has been amply demonstrated that this ^{40}Ar* flux produces a buildup of excess ^{40}Ar* in both mantle-derived volcanic and crustal rocks, ^{40}Ar* loss can clearly be a problem locally and regionally, resulting in anomalous K-Ar ages. Therefore, when the ^{40}Ar* contents of volcanic rocks and their minerals are measured, there is no way of determining categorically whether there has been ^{40}Ar* loss, even when the calculated ages are compatible with other radioactive dating systems or the expected conventional ages. This renders K-Ar dating as questionable at best.

Ar-Ar Dating of Volcanic Rocks

The Ar-Ar method is now routinely used, often in preference to the K-Ar method, and depends on the diffusion of ^{40}Ar* as minerals are heated in the dating laboratory. However, the method also depends on the irradiation of the ^{40}K in the rock and its minerals to convert it to ^{39}Ar. The ^{40}Ar/^{39}Ar ratios can then be more easily measured in single analyses in a mass spectrometer, rather than the ^{40}K and ^{40}Ar* contents being analyzed by separate techniques. But since the irradiation of the samples to convert the ^{40}K to ^{39}Ar is undertaken in nuclear reactors, there are fluctuations in the neutron fluxes of different reactors during the procedure. Thus, samples of known ages called fluence monitors are added to every batch of samples of unknown ages and those known ages are then used in the equation to solve for the ages of the unknown samples. Therefore, the Ar-Ar dating method depends on the accuracy of whatever radioisotope methods were used to establish the known ages of the fluence monitors. So, it is not an independent dating method, as is often claimed, nor is it any more reliable that the methods used to date the known ages of the fluence monitors. Ironically, for the dating of young volcanic rocks, the known ages of the fluence monitors have usually been dated by the K-Ar method!

Overman (2010) evaluated the Ar-Ar method and also exposed these and other problems. Among them he discussed how Dalrymple et al. (1993) performed an ^{40}Ar-^{39}Ar analysis of the Beloc Formation, Haiti, and pointed out some inconsistencies in the equations they used in this method.

Thus, the Ar-Ar method also suffers from the same problems as the K-Ar method, namely, excess ^{40}Ar* and ^{40}Ar* loss. So, the same examples of these issues from the conventional literature with respect to the failures of the K-Ar method also apply to the Ar-Ar method. However, a few additional examples confirm this.

The same ten Zaire diamonds for which Zashu et al. (1986) obtained a K-Ar isochron age of 6.0 ± 0.3 Ga (billion years), Ozima et al. (1989) found they produced an Ar/Ar age spectra yielding a ~5.7 Ga isochron. They also discovered that just as there was an excellent correlation between those diamonds' K contents and ^{40}Ar/^{36}Ar ratios, there was a correlation between their Cl contents and ^{40}Ar. They thus concluded that the ^{40}Ar was an excess component which has no age significance and is found in tiny inclusions of mantle-derived fluid.

Pickles et al. (1997) obtained 128 isotopic Ar analyses from ten profiles across biotite grains in an amphibolite-granulite facies metamorphic rock and ^{40}Ar-^{39}Ar ages within individual grains ranged from 161 to 515 Ma (Figure 2). They concluded that these observations could not be solely due to radiogenic buildup of ^{40}Ar* but must be due to incorporation by diffusion into the grains of excess ^{40}Ar* from an external source, namely, excess ^{40}Ar* from the mantle and in other crustal rocks and minerals.

In a detailed ^{40}Ar-^{39}Ar dating study of high-grade metamorphic rocks in the Broken Hill region of NSW (Australia), Harrison and McDougall (1981) found evidence of widely distributed excess ^{40}Ar*. Step-heating ^{40}Ar-^{39}Ar age spectra for plagioclases in mafic granulites (metamorphosed volcanic rocks) yielded unacceptable ages of up to 9.588 Ga, produced by excess ^{40}Ar* released at temperatures of 350–650°C and/or 930–1380°C. They suggested that the excess ^{40}Ar* is held in sites within the mineral lattice, such as structural holes, edge dislocations, and lattice vacancies. Thus, their study showed that at crustal temperatures, excess ^{40}Ar* will always be retained in those trapping sites, thus rendering ^{40}Ar-^{39}Ar dating questionable.

Rb-Sr Dating of Volcanic Rocks

The Rb-Sr isochron method is widely used for age dating, because most crustal rocks and minerals within them contain sufficient Rb and Sr (10–1000 ppm) to make their chemical separation and then mass spectrometry relatively straightforward. However, the results of Rb-Sr geochronology have not always been easy to interpret because it is claimed that both Rb and

Sr are mobile elements, so that the isotopic system may be readily disturbed either by influx of fluids or by a later thermal event (Rollinson, 1993, pp. 226–227; Rollinson and Pease, 2021, p. 190). On the other hand, Hanson and Gast (1967) stated that significantly no one had been able to thermally induce radiogenic ^{87}Sr to leave host minerals commensurable with ^{40}Ar loss under reasonable geological conditions, even though it was not uncommon to find biotites which had lost both ^{40}Ar and ^{87}Sr due to a thermal event.

Indeed, the previously cited contact metamorphic zone associated with the Eldora granitic stock in the Colorado Front Range is a classic example (Hart, 1964). The 54-Ma stock was intruded into Precambrian metamorphic rocks regarded as approximately 1350 Ma. The coarse biotites in the Precambrian amphibolites and schists showed even greater disturbance of the Rb-Sr system than the K-Ar system (Figure 1). Hart (1964) calculated that the coarse biotite only 20 feet (~6 m) from the contact with the granitic stock had lost 88% of its radiogenic ^{87}Sr, while the loss at 14,100 feet (~4.3 km) was essentially zero.

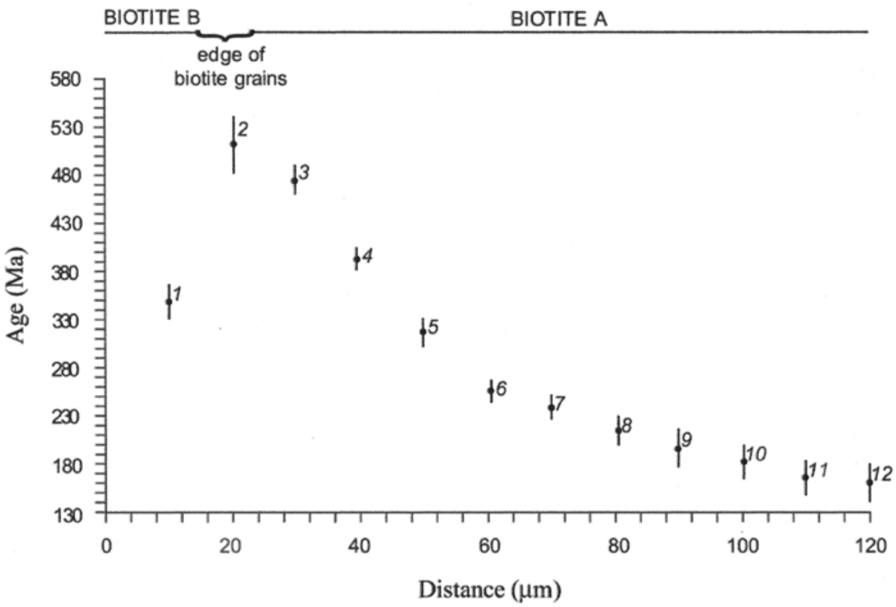

Figure 2. Apparent age versus distance profile across adjacent biotite grains in an amphibolite-granulite facies metamorphic rock from the Italian Alps [after Pickles et al., 1997—their profile 8 across sample 85370]. This high spatial resolution profile is along a "trench" produced by the beam from an ultraviolet laser ablation microprobe which is parallel to the biotite cleavage and perpendicular to the grain boundary. Apparent ages range from 515 ± 27 Ma at the edge of biotite A to 161 ± 19 Ma 100 μm in from the edge of biotite A. The high apparent ages at the grain boundary cannot be attributed to alteration because scanning electron microscope (SEM) images discount it.

Similarly, Hansen and Gast (1967) investigated the effects of thermal metamorphism on Rb-Sr ages of biotite, muscovite, and K-feldspar in a granitic stock in Minnesota near its contact with an intrusive gabbro and on Rb-Sr ages of biotite in an amphibolite in Wyoming intruded by a diabase dike. The apparent loss of ^{87}Sr from biotite had occurred at moderate temperatures near and out to 20 m from the Wyoming dike, but near and out to 5 km from the Minnesota gabbro.

Furthermore, Patel et al. (1999) found contrasting responses in the Rb-Sr radioisotope system between regional and contact metamorphism. Whereas the Rb-Sr isotopic data required that ^{87}Sr was redistributed during regional metamorphism on a scale of at least tens of meters, during subsequent contact metamorphism at an apparent higher temperature isotopic mobility was restricted to a centimeter-scale or less. They concluded that the regional metamorphism involved fluid transport which facilitated Sr isotopic resetting, whereas the contact metamorphism occurred in a relatively dry environment in which isotopic mobility was restricted. However, fluids facilitate isotopic mobility at all observational scales, particularly when their chemistry and temperature make them more reactive.

Consequently, the Rb-Sr method lost credibility in the 1980s as evidence of open-system behavior mounted (Dickin, 2005, p. 51). For example, Rb-Sr isochrons in metamorphic terrains yielded good linear arrays whose ages were meaningless. And Rb-Sr systems appeared disturbed and reset to give good-fit secondary isochrons even by relatively low-grade metamorphism when there was little field evidence and only relatively minor mineralogical alteration (Zheng, 1989).

Open-system behavior can occur at even lower grades of metamorphism in fine-grained, acidic volcanic rocks (i.e., silica-rich, "felsic" rocks). Such units are attractive for conventional "absolute" dating of the stratigraphic record because they are conformable with the enclosing sedimentary strata. Experience has shown they are particularly susceptible to radiogenic ^{87}Sr loss, because the mobility of ^{87}Sr is facilitated by its formation in situ into non-lattice positions, allowing the ^{87}Sr to easily migrate during any subsequent metamorphism. Thus, when the Stockdale rhyolite, England, yielded a 16-point Rb-Sr isochron age that was inconsistent with its presumed age based on biostratigraphy and other dating methods, it was argued that the whole unit had probably been disturbed by a postulated hydrothermal event after its extrusion and subsequent burial (Compston et al., 1982).

In reality, few mineral-rock systems are perfectly homogenized during any metamorphism (Zheng, 1989), the open-system Rb-Sr systematics in numerous environments discrediting Rb-Sr isochron dating (Dickin, 2005, pp. 48–52). Gain or loss of Rb and Sr from rocks can be so regular that a linear array can be produced on a conventional isochron diagram and biased isochron results give spurious ages and initial ^{87}Sr/^{86}Sr ratio estimates (Zheng, 1989). Zheng (1989) concluded that:

> As it is impossible to distinguish a valid isochron from an apparent isochron in the light of Rb-Sr isotopic data alone, caution must be taken in explaining the Rb-Sr isochron age of any geological system…an observed isochron does not certainly define a valid age information for a geological system, even if a goodness of fit of the experimental data points is obtained in plotting ^{87}Sr/^{86}Sr vs. ^{87}Rb/^{86}Sr. This problem cannot be overlooked in evaluating the numerical timescale.

Indeed, the Rb-Sr dating method relies on assuming samples from a cogenetic rock unit are the same age, have the same initial ^{87}Sr/^{86}Sr ratio, and acted as a closed system. The goodness of fit of the analytical data points in the plot of ^{87}Sr/^{86}Sr versus ^{87}Rb/^{86}Sr served as a check on these assumptions. However, when applied to an increasing number of geological situations, it soon became apparent that excellent-fitting linear relationships between ^{87}Sr/^{86}Sr and ^{87}Rb/^{86}Sr ratios could yield anomalous isochrons with no distinct geological or age meaning, as recognized by Zheng (1989).

For example, Sun and Hansen (1975) found that the Rb-Sr data for fourteen different, recently-erupted ocean island basalts when plotted on an isochron yielded a positive correlation with an ~2 Ga age. They also found that the basalts on individual ocean islands sometimes also yielded false isochrons, which they attributed to the Rb/Sr isotopic composition of the heterogeneous mantle sources of the magmas. Thus, Brooks et al. (1976a) used the term "mantle isochrons" for these apparent ages. And it is now well-known that basalt magmas will inherit the isotopic composition of their mantle source (Dickin, 2005, pp. 45–46).

Brooks et al. (1976b) extended the concept of mantle isochrons to continental igneous rocks in their Rb/Sr isotopic study of thirty "ancient" continental volcanic and plutonic rock suites. The resultant data for each of the rock suites formed pseudo-isochrons which they rejected as mixing lines produced by crustal contamination of the mantle-derived basalt magmas, instead interpreting them as representing the Rb/Sr isotopic chemistry of domains in the subcontinental lithosphere. Austin (1994) confirmed this when he found the Rb/Sr isotopic data for the recent Uinkaret Plateau lava flows in western Grand Canyon yielded an Rb-Sr isochron age of ~1.1 Ga, identical to the conventionally established Rb-Sr isochron age for the Precambrian Cardenas Basalt in eastern Grand Canyon (Larson et al., 1994). Both the recent and "ancient" basalt lavas had thus been derived from the same mantle source with the same Rb/Sr chemistry, and not age.

Another example of correlated ^{87}Sr/^{86}Sr and ^{87}Rb/^{86}Sr ratios was reported by Bell and Powell (1969) for lava flows in two volcanic centers 160 km apart in east Africa. These lavas are known to be quite young; some even having erupted in historic times. However, their ^{87}Sr/^{86}Sr ratios correlated positively with their ^{87}Rb/^{86}Sr ratios, yielding an isochron age of 773 Ma for these young lavas 160 km apart. This fictitious age was thus interpreted as due to a mixing process, and not due to radioactive decay of ^{87}Rb in the rocks after their formation. Snelling (2003) found there had been a similar isotopic mixing process as basalt magma was contaminated by wall-rocks on its passage from the mantle wedge source under New Zealand to erupt recently as andesite lava flows at Mt. Ngauruhoe.

Faure and Powell (1972, pp. 36–41) demonstrated that many apparently cogenetic suites of both oceanic and continental volcanic rocks have significant within-suite variations in their initial ^{87}Sr/^{86}Sr ratios, which violates a key assumption of Rb-Sr age dating. They suggested these variations were caused by either differences in the initial ^{87}Sr/^{86}Sr ratios of the source regions in the upper mantle and lower crust, or variable contamination of their parent magmas via bulk assimilation, wall-rock reactions, selective migration of radiogenic ^{87}Sr, and/or isotopic exchange and equilibration.

Thus, Cortini and Hermes (1981) documented variations in the initial ^{87}Sr/^{86}Sr ratios for suites of young lavas from a single volcano, demonstrating that the assumption of a well-defined initial ^{87}Sr/^{86}Sr ratio for many suites of volcanic rocks is violated. Obviously, the state of the Rb-Sr system at the time of formation of a rock is of crucial importance in understanding the meaning of an isochron. Yet even samples that do not have identical ages and initial ^{87}Sr/^{86}Sr ratios can be fitted to isochrons (Köhler and Müller-Sohnius, 1980; Haack et al., 1982). Furthermore, the interpretation of Rb-Sr isotope data is influenced by factors external to the actual Rb-Sr radioisotope system, such as the rotation of an isochron to describe the perceived distortion of the Rb-Sr system in German volcanics due to presumed post-magmatic processes (Schleicher et al., 1983).

Hedge and Walthall (1963) and Allègre (1987) agreed that variations in initial ^{87}Sr/^{86}Sr ratios may have resulted from Rb/Sr fractionation (differentiation), since Rb is an alkali metal and Sr an alkaline-earth metal. Therefore, Zheng (1989) maintained that the three variables ^{87}Rb, ^{87}Sr, and ^{86}Sr are not independent of each other and thus the measured ^{87}Sr/^{86}Sr and ^{87}Rb/^{86}Sr ratios are not necessarily two independent variables on the Rb-Sr isochron diagram. Furthermore, he argued cogently that because geological systems cannot have a homogeneous ^{86}Sr distribution, and because ^{86}Sr is used as a common variable in the conventional isochron equation, the observed isochronous correlations in ^{87}Sr/^{86}Sr vs. ^{87}Rb/^{86}Sr plots are enhanced and induced due to the function of ^{86}Sr as the common denominator. Thus, Rb-Sr dating of both young and ancient volcanic rocks is unreliable.

U-Th-Pb Dating of Volcanic Rocks

Due to the documented problems with the K-Ar, Ar-Ar, and Rb-Sr methods, the U-Pb, Th-Pb, and especially Pb-Pb methods have become the "must use" geochronological tool. However, the same inherent problems with the other age-dating methods have also been documented to plague the U-Th-Pb methods.

Of major concern is open-system behavior as the U-Pb and Th-Pb systems rarely stay closed due to the mobility of Pb, Th, and especially U, under conditions of low-grade metamorphism and superficial weathering (Dicken, 2005). Indeed, U can be lost from samples with no discernible effects of alteration, so it has been suggested that leaching of U from surficial rocks might be a universal phenomenon, and elemental mobility is possible to depths of several hundred meters (Stuckless, 1986), which thus also perturbs the daughter Pb. The identified factors that control U and/or Pb mobility include lattice sites in minerals for U and its daughter products, access of groundwater to those sites, and the volume and chemistry of the circulating groundwater.

In practice, therefore, the mobility of U, Th, and Pb renders their use for U-Pb isochron dates very limited (Dickin, 2005), this open-system behavior largely invalidating U-Pb dating of rocks. This is why the focus has shifted to using the U-Th-Pb dating methods on minerals, such as zircon ($ZrSiO_4$), making that the most widely-regarded benchmark radioisotope-dating methods currently in use, including for age-dating volcanic rocks. In zircon, similar-sized U^{4+} ions substitute in its lattice for Zr^{4+} whereas larger Pb^{2+} ions do not fit into the zircon lattice. So it is claimed that when zircon crystallizes, no Pb is incorporated into its lattice, and thus all the Pb now measured in zircon is due to subsequent in situ radioisotope decay of the U that was incorporated in the zircon lattice when it crystallized.

However, the fundamental problems inherent in the radioisotope dating methods due to the underlying assumptions still apply to the U-Th-Pb methods, even to minerals such as zircon. Snelling (2017a, b, 2018, 2019) reported in detail these problems, documenting them from the conventional literature. These are respectively the inability to precisely determine the ^{238}U and ^{235}U decay rates, the incorporation at crystallization of common Pb that also includes non-decay-derived ^{206}Pb and ^{207}Pb, the mobility of U and Pb, and the mass fractionation of U and Pb isotopes both naturally and during analyses.

Wasserburg (1963) and Wetherill (1963) derived equations to describe steady Pb loss by diffusion resulting from radiation damage to crystal lattices. Goldrich and Mudrey (1972) argued that radiation damage of U-rich mineral lattices as a result of the α-decay of U, Th, and their daughters formed micro-capillary networks which became fluid-filled, the fluids dispersing the non-bound Pb diffusing from those crystal lattices. Meldrum et al. (1998) confirmed that radiation damage drastically increases the rate of Pb diffusion. Furthermore, while the diffusion rate is slow, higher temperatures induce faster diffusion, as dramatically demonstrated by Davis et al. (1968). In the same contact metamorphic zone of Precambrian metamorphic rocks intruded by the Eldora granitic stock in the Colorado Front Range, in which the K-Ar and Rb-Sr isotope systems had been perturbed in several minerals (Figure 1), within 50 feet of the contact the ^{238}U ages of zircon crystals dropped from 1405 Ma to 220 Ma while the ^{207}Pb concentration dropped from 150 ppm to 30 ppm (Figure 3).

Zircon crystals are often zoned, reflecting growth during crystallization, but both zoned and unzoned crystals may be found in the same rock. Pidgeon (1992) demonstrated that unzoned crystals can be the result of recrystallization of zoned crystals accompanied by loss of U, Th, and Pb, and resetting of the U-Pb ages. With the advent of ion microprobes with their very narrow ion beams able to target 2 μm-wide spots, different growth zones within crystals can be dated. Utilizing the SHRIMP (sensitive high-mass resolution ion microprobe), Compston (1997) found that radiogenic Pb varied within most tested zircon grains on a 20 μm spatial scale. Some spots were characterized by huge excesses of ra-

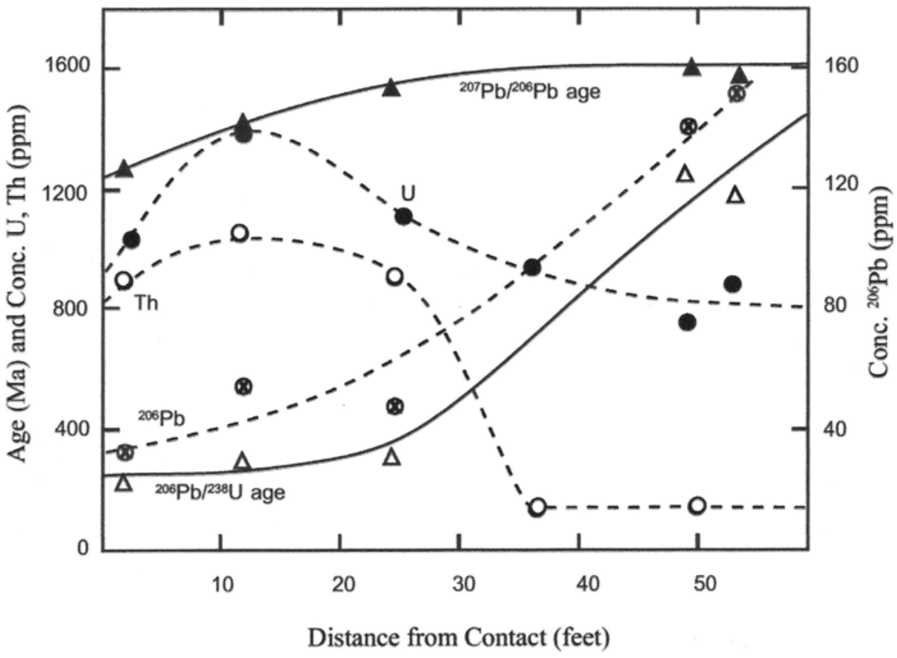

Figure 3. Change in ^{206}Pb/^{238}U and ^{207}Pb/^{206}Pb ages and in concentrations of U, Th, and ^{206}Pb in zircons in Precambrian metasediments and metavolcanics as a function of distance from the contact with the Tertiary Eldora granite stock, Colorado [after Davis et al., 1968].

diogenic Pb up to 30 times the expected values. Furthermore, Wingate and Compston (2000) demonstrated that there were pronounced reproducible differences in ^{206}Pb/^{238}U ratios and thus ages between four differently-oriented faces of a large baddeleyite (ZrO_2) crystal as well as correlated variation in ^{208}Pb/^{206}Pb with ^{232}Th/^{238}U (Figure 4a, b). And in a second experiment, isotopic ratios were measured on the same crystal faces of 47 baddeleyite crystals but at different orientations with the SHRIMP's beam over a 180° range, the results revealing a striking, approximately sinusoidal, variation in ^{206}Pb/^{238}U ages with orientation (Figure 4c). Also, ^{208}Pb/^{206}Pb and ^{232}Th/^{238}U both varied with orientation in zircon and monazite ([Ce, La, Th] PO_4) crystals.

Another significant problem for zircon U-Pb dating are zircon crystals in some granitic rocks that yield much older ages than the accepted ages of the rocks. These older zircons are usually interpreted as being inherited from the source rocks that melted to produce the magmas (Williams et al., 1983; Chen and Williams, 1990). However, Davis et al. (1968) demonstrated that similar temperatures had a dramatic effect on zircon U-Pb ages (Figure 3). In some published studies, the supposedly inherited zircon grains are 5–10 times older than those matching the accepted ages of the granites—up to 1753 Ma in a 21 Ma, Himalayan granite (Parrish and Tirrul, 1989), up to 3500 Ma in a 426-Ma, south-east Australian granodiorite (Williams, 1992), and up to 1638 Ma in a 370-Ma, New Zealand granite (Muir et al., 1996). Furthermore, a 20-Ma, Himalayan granite contained zircon grains yielding U-Pb ages up to 1483 Ma and monazite grains yielding negative U-Pb ages, such as -97 Ma (Parrish, 1990)!

Deciding on whether anomalous zircon U-Pb ages are due to open-system behavior (such as Pb loss) or whether the zircon grains have been inherited thus depends on the ages expected by the investigators. Indeed, if Pb is lost from some mineral grains, which can be accelerated by heat, water, radiation damage, and even weathering, then it can be inherited by other crystals, such as the Pb presumably lost from the monazite in the 20-Ma, Himalayan granite (above) probably being inherited by its zircon grains. Williams et al. (1984) found unsupported (excess) radiogenic Pb in a zircon crystal in an Antarctic gneiss, which thus produced anomalously high ages. Similar situations also result in ages hundreds of millions of years more than expected and are interpreted as due to excess radiogenic Pb, the origin of which is either explained as mixing from older source materials which melted to form magmas, and/or due to subsequent migration as a result of fluids, temperature, and pressure (Copeland et al., 1988; Zhang and Schärer, 1996). This begs the question—should anomalously old zircons be interpreted as inheritance of the zircon crystals, or of the excess radiogenic Pb in the crystals?

Now Pb is widely distributed throughout the Earth, and thus the isotopic composition of Pb varies within wide limits, from the highly radiogenic Pb in supposedly very old U-bearing minerals to the common Pb in minerals such as galena (PbS) that have low U/Pb and Th/Pb ratios. Lead is also a trace element in most rocks, its isotopic composition being a record of the chemical environments in which the Pb may have resided, including within the Earth's mantle. Thus, the Pb isotopic compositions in rocks display complex patterns of variation that supposedly reflect their particular geologic histories, all of which is relevant to Pb-Pb dating.

The Earth's mantle is increasingly being recognized as the key component of the Earth's make-up, mantle convection not only being the driving force behind plate tectonics but the means by which rocks, minerals, elements, and isotopes are mixed and differentiated into different reservoirs. Isotopic analyses of ocean island basalts were first used to demonstrate mantle heterogeneity. Gast et al. (1964) found significant differences in Pb isotope ratios within suites of volcanic rocks on Gough and Ascencion Islands in the Atlantic Ocean. Subsequently, Tatsumoto (1966) found variations between the Pb isotopic compositions of mid-ocean ridge and ocean island basalts. Many subsequent studies of the Pb isotopic compositions of ocean island basalts found they define a series of linear arrays that are Pb-Pb isochrons corresponding to Pb-Pb ages of between 1 Ga and 1.5 Ga for what are only recently-erupted lava flows (Sun, 1980). The differences in Pb isotopic ratios among volcanic rocks from different islands in the Atlantic and Pacific Oceans indicate the apparent heterogeneity of the upper mantle is a worldwide phenomenon and is not restricted to one or two anomalous islands.

These Pb-Pb isotopic linear arrays or false Pb-Pb isochrons for ocean island basalts can be interpreted as resulting from discrete mantle differentiation events or as the products of two-component mixing processes (Faure, 1986; Dicken, 2005, p.149). Indeed, the presence of Pb with different isotopic compositions in the heterogeneous upper mantle permits mixing to occur during the formation of basalt magmas (Sun and Hansen, 1975). Therefore, the significance of false Pb-Pb isochron data arrays for mid-ocean ridge and ocean island ba-

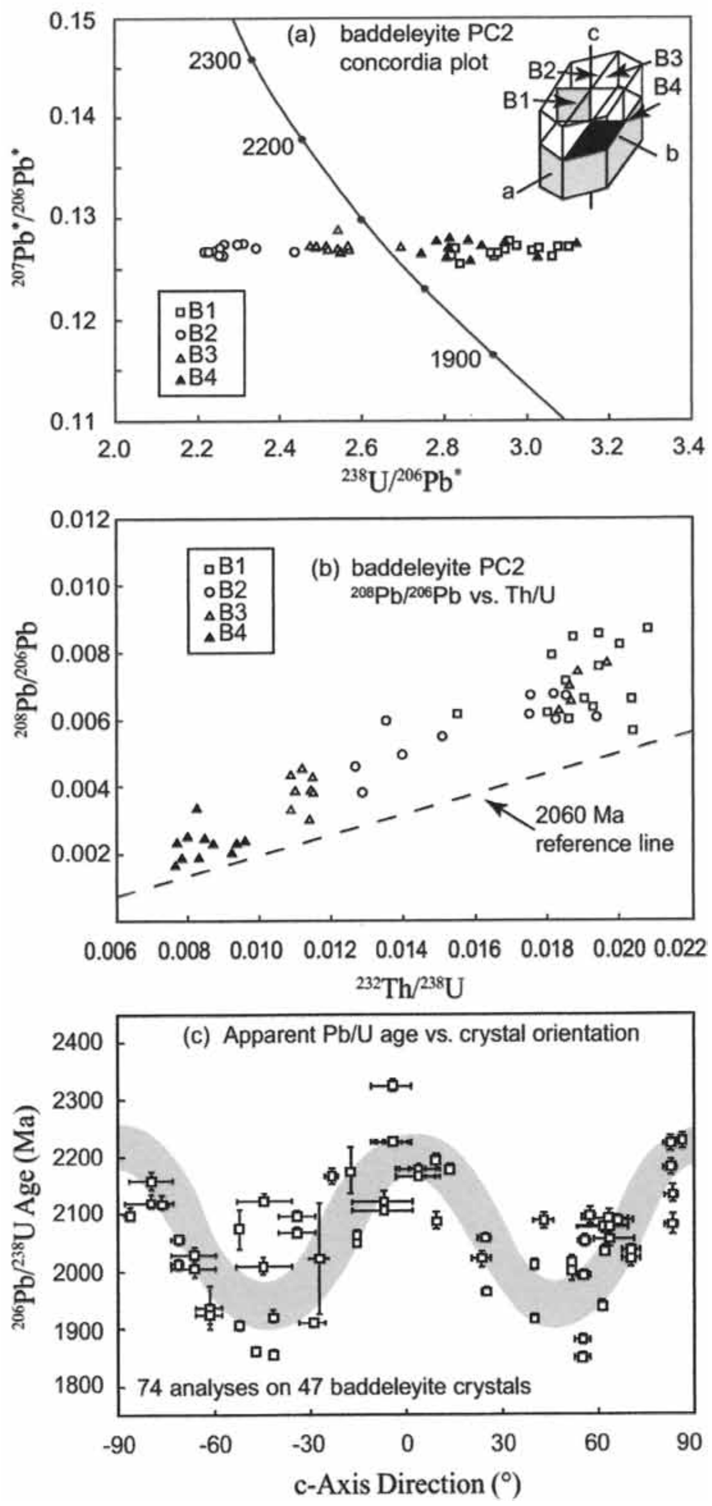

Figure 4. SHRIMP analytical results for baddeleyite, illustrating observed orientation effects [after Wingate and Compston, 2000]. (a) A U-Pb evolution (concordia) diagram showing apparent ages for four differently oriented surfaces (shown in the inset) of a single baddeleyite crystal (PC2 from the Phalaborwa carbonatite, South Africa). (b) Correlated variation in total $^{208}Pb/^{206}Pb$ with $^{232}Th/^{238}U$ for the same surfaces measured in (a). (c) Variation of apparent $^{206}Pb/^{238}U$ age with orientation for (100) surfaces of 47 oriented baddeleyite crystals.

salts remains elusive, because they have more radiogenic Pb in them than they should have if the Earth's age is 4.57 Ga (Dickin, 2005)! This problem has been called the "lead paradox" and still remains unsolved. What is clear is that Pb-Pb dating of these recent basalts produces anomalous old ages that represent the inheritance of the Pb isotopic compositions of the magmas' mantle sources.

The Pb isotopic compositions of volcanic rocks on the continents also form linear arrays that represent false Pb-Pb isochron ages. For example, Moorbath and Welke (1969) found that the wide variety of volcanic and plutonic rocks, both granitic and basaltic, on the Isle of Skye in northwest Scotland lay on a strong linear array on the $^{207}Pb/^{204}Pb$ vs. $^{206}Pb/^{204}Pb$ diagram with a Pb-Pb isochron age of ~3 Ga. They interpreted the linear array as a mixing line between radiogenic mantle-derived Pb and very unradiogenic Archean crustal Pb of the basement Lewisian Complex. By plotting $^{208}P/^{204}Pb$ vs. $^{206}Pb/^{204}Pb$ Thompson (1982) identified three Pb isotopic components in the Skye volcanic rocks. Those lavas were therefore interpreted as mantle-derived magmas that had suffered strong contamination in the granulite-facies lower crust during their ascent.

Faure (1986, p. 327) thus offers an important word of caution—"not all linear arrays on the Pb-Pb isochron diagram are isochrons." Linear correlations of Pb isotopic ratios for volcanic rocks can also result from mixing of leads of different isotopic compositions in varying proportions. The pitfalls of distinguishing mixing lines from isochrons affects the interpretation of Pb isotopes in young volcanic rocks. Thus, if young volcanic rocks yield false Pb-Pb isochrons that are mixing lines then Pb-Pb isochrons obtained from older volcanic rocks may likewise be due to mixing. Even if the original colinearity of Pb isotope ratios on mixing lines may be modified by subsequent decay of U and Th, which ultimately scatters the ratios off the line, the original initial colinearity due to mixing remains significant. The present-day U-Th-Pb isotopic ratios therefore do not represent the ages of the volcanic rocks and may result in false Pb-Pb isochrons.

Discussion

From this brief survey of the problems with the four principal radioisotope methods for age-dating of volcanic rocks, namely, K-Ar, Ar-Ar, Rb-Sr, and U-Th-Pb, several observations can be made.

First, many of the conventional sources used here to document the problems with these age-dating methods are several decades old, so why are there not more recent literature sources? The answer is straightforward. Since documentation of the problems with each of these methods early in the history of their use, the scientific community is today more careful in admitting these problems, so there appear to be fewer papers documenting them. Instead they tend to only use those radioisotope dating methods that they remain confident work well. Otherwise, to continue admitting these problems would undermine their narrative that the Earth's 4.57 Ga history has been successfully unraveled from the strata pages of the rock record, each dated as successively millions of years between them. Even geologists generally have not been exposed to these "trade secrets" of geochronology so they, like the general public, believe the millions of years are established fact.

Yet these problems persist, as the more recent textbooks continue to document them. For example, Faure (1986) extensively documented and discussed these problems of inheritance, open-system behavior, contamination, and mixing in the second edition of his textbook. Then Faure and Mensing (2005) simply repeated the same extensive documentation with few new updated examples, except for more documentation of mantle and crustal isotopic domains, inheritance from them, and mixing between them, as reported by Snelling (2005). Similarly, Dickin (2005, pp. 136–173) in the second edition of his textbook also repeats all the same examples documenting these problems as in the first edition, as do Rollinson and Pease (2021, pp. 178–218) in the second edition of Rollinson (1993, pp. 215–265). These textbook examples document that nothing has changed in the decades since these problems were first admitted, and that it is still valid to use the older documentation of examples that adequately, cogently, and comprehensively describe these problems, as done here.

Second, even in the conventional (uniformitarian) literature there is extensive documentation of the multiple problems with these methods. These problems stem from the assumptions on which those methods are based. The initial conditions are unknown and are assumed for ancient volcanic rocks, yet present volcanic rocks frequently record inheritance of their isotopic compositions from their sources, both upper mantle and lower crustal sources. Then contamination frequently occurs due to open-system behavior. During magma ascent, mixing can occur with wall-rocks, and then after extrusion and crystallization, parent and/or daughter isotopes may be lost from volcanic rocks or their constituent mineral crystals via diffusion, leaching by fluids, or even weathering. And finally, constant decay rates are assumed at today's measured rates, but even those are not yet precisely determined. Furthermore, as Snelling (2014, 2016) discovered, the K and Rb decay rates are calibrated against the ^{238}U decay rate, which has been determined, but not precisely (Snelling, 2017a). There is still uncertainty over the ^{235}U decay rate, so that also affects the desired accuracy of Pb-Pb dates.

In any case, none of these assumptions are even provable, because the past is beyond reach of present direct scientific investigation. No geochronologists were present when the volcanic rocks formed to measure their initial isotopic compositions or those of their constituent minerals. And no geochronologists were present in the subsequent years to check for any open-system behavior and to measure the decay rates. Yet if geochronologists were being consistent in applying their uniformitarian reasoning, they would admit that since these radioisotope systems have the well-documented problems of inheritance, open-system behavior, contamination, and mixing in the present, then such behavior must have happened in the past, thus rendering these methods and the ages for volcanic rocks derived by using them as unreliable, at best.

Third, the conventional geology community trumpets the apparent agreement between the ages for many volcanic rock units derived by these radioisotope methods and their presumed ages based on their relative stratigraphic and/or biostratigraphic positions in the rock record as proving these age-dating methods work. And often there is such agreement, especially where zircon U-Pb ages for volcanic units have been used to date bracketed sedimentary strata. Furthermore, the recognized ages for most volcanic units are those that have been deemed acceptable, and yet they usually do correspond to the correct numerical and stratigraphic order.

However, what is not often mentioned is that the ages assigned to many volcanic units have only been determined using one of these four radioisotope dating methods. Rarely has more than one of these methods been used on the same volcanic rock unit. Yet when two methods have been utilized in the conventional literature, there is often disagreement which is never explained because the unacceptable date is merely rejected as being due to open-system behavior or contamination, just as Austin and Snelling (1998) found.

So, what might we expect if samples from rock units were age-dated by multiple radioisotope methods? Vardiman et al. (2005) reported on an extensive research effort in which it was demonstrated that several sampled rock units yielded different ages when the same samples were subjected to three or more of the radioisotope dating methods (Austin, 2005; Snelling, 2005). It was found that there was a systematic pattern in the resultant ages, the K-Ar isochron age always being the youngest, the Rb-Sr isochron being next youngest, and either the Pb-Pb or Sm-Nd isochron ages being the oldest. As there were also other lines of evidence that a lot of radioactive decay must have occurred in a recent short catastrophic event (fission tracks, radiohalos, helium diffusion from zircons, ^{14}C), Vardiman et al. (2005) concluded that radioisotope decay rates must have been accelerated by up to six orders of magnitude compared to today's slow decay rates during the global Genesis Flood cataclysm. They found that the systematic pattern in the ages obtained by the different methods on the same samples could be explained according to the atomic weights of the parent isotopes and the mode of decay. ^{40}K being the lightest atomic weight and a β-decayer, its decay rate was accelerated much less compared to the heavier α-decaying ^{238}U isotope.

Therefore, the apparent agreement between the radioisotope ages of volcanic rocks and their presumed ages based on their relative stratigraphic and/or biostratigraphic positions in the rock record, plus the observation the radioisotope ages of the volcanic rocks usually match their stratigraphic order, can be readily explained. In a volcanic rock erupted in the first month of the year-long Flood cataclysm, for example, after crystallization the parent radioisotopes would have experienced eleven months' worth of accelerated decay. By comparison, in volcanic rock units erupted in the sixth and eleventh months of that cataclysmic event, and thus progressively laid down higher in the stratigraphic record, the parent radioisotopes would only have experienced six months' and one month's worth of accelerated decay respectively. So these three volcanic rock units today would have progressively younger millions-of-years radioisotope ages in the correct sequence from bottom to top of the stratigraphic record. But their true ages would be six orders of magnitude younger!

Thus, the radioisotope contents of volcanic rocks do not provide their absolute ages, because they are obtained by calculations based on unproven assumptions. However, their radioisotope contents can fingerprint the sources of the magmas. And their calculated ages may indicate when the lavas were erupted during the Earth's history relative to the level at which they are found in the rock record, as well as being a chemical property that enables correlation between volcanic rock layers of identical calculated "accelerated decay" ages in different regions or on different continents.

Summary and Conclusions

The K-Ar, Ar-Ar, Rb-Sr, and U-Th-Pb radioisotope methods used by geochronologists to age-date volcanic rocks are fraught with anomalies which are well-documented in the conventional literature. These anomalies are due to the unproven assumptions on which these methods are based that are erroneously regarded as reliable. However, if the present is any guide to the past, then the experimentally-determined inheritance by recently-erupted volcanic rocks of daughter isotopes from their mantle and crustal sources that invalidate their radioisotope ages should also indicate the radioisotope ages obtained on ancient volcanic rocks cannot be trusted either. Similarly, open-system behavior after recently-erupted lavas crystallize, such as excess ^{40}Ar*, or diffusion loss of ^{40}Ar*, diffusion loss of Pb, fluid movements of K, Rb, Sr, U, Th, and Pb, and contamination with and mixing of wall-rock isotopes during magma ascent, should also indicate the radioisotope ages obtained on ancient volcanic rocks cannot be trusted either.

Yet, there is often agreement between the ages of volcanic rock units obtained by these radioisotope methods and their presumed ages based on their relative stratigraphic and/or biostratigraphic positions in the rock record, plus the radioisotope ages of the volcanic rocks usually match their stratigraphic order. However, most volcanic rock units are only age-dated by one radioisotope method and the radioisotope ages obtained may be rejected if they do not match the expected stratigraphic or biostratigraphic ages.

Instead, when volcanic rocks are age-dated by multiple radioisotope methods they often yield wildly different, but systematic, old ages according to the parent radioisotopes. These anomalous ages can be reconciled by postulated accelerated radioisotope decay in a recent catastrophic event, such as the global Genesis Flood cataclysm; the systematic old ages being due to the different atomic weights and modes of decay of the parent radioisotopes. This then explains why the accepted conventional ages match the depositional order in the stratigraphic record.

Taking all these considerations together, the absolute millions-of-years ages for volcanic rocks claimed in the conventional literature using these radioisotope age-dating methods are simply unreliable. However, where there is often agreement between these claimed ages for volcanic rocks and their stratigraphic positions and presumed biostratigraphic ages in the rock record, these highly-inflated radioisotope ages are reconciled by the accelerated decay of the parent radioisotopes during the recent global Genesis Flood cataclysm. Although this working model has some challenges, such as a plausible mechanism, dispersal of heat, and other Earth and space consequences, ongoing research to resolve such challenges continues to validate it as a plausible reconciliation.

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