

## PROGRESS AND CHALLENGES USING $^{40}\text{Ar}/^{39}\text{Ar}$ GEOCHRONOLOGY IN COSTA RICA AND NICARAGUA

### PROGRESO Y RETOS DE LA GEOCRONOLOGÍA $^{40}\text{Ar}/^{39}\text{Ar}$ EN COSTA RICA Y NICARAGUA

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**Abstract:** To better estimate the extrusive flux of the Central American Arc, from 2002-2008, we obtained sixty one high precision  $^{40}\text{Ar}/^{39}\text{Ar}$  ages on geographically well-situated lavas and tephra from Costa Rica and Nicaragua. Here, we describe a number of observations encountered during this study using four examples that well document the precision, accuracy and general reliability of the  $^{40}\text{Ar}/^{39}\text{Ar}$  ages. First, low  $\text{K}_2\text{O}$  values, particularly in samples from Nicaragua, is a major limitation in or attempts to obtain reliable dates on samples under 1 My. Second, extensive weathering of samples due to the tropical climate of Central America has resulted in various levels of argon loss even when the hand sample appeared unaltered. Third, our field and geochronological data lead us to conclude that eruptive rates have not been constant over the past 15 to 20 My, but rather appears punctuated by gaps of up to several million years.

We attempted to address the temporal gaps in several ways. First, geochemical analyses were used to identify samples that may have erupted during time periods without known volcanism. For example, U/Th values in the active Central American arc are significantly higher than those obtained from the Miocene Coyoil Group except for four samples with intermediate values that were dated to determine if their ages were intermediate as well. However, all of these samples were found to be from a period with known volcanism. Second, we sought to locate the oldest sections of the active arc and the youngest sections of the Coyoil Group in order to better constrain the timing and duration of the apparent gap in volcanic productivity. This approach also failed to locate samples from periods without known volcanism. When these methods proved largely unsuccessful, our focus shifted to dating regions of minor volcanism between the active and Coyoil volcanic fronts as well as between Cosigüina and San Cristóbal, the longest stretch of the Central American Volcanic Front without active volcanism. This effort yielded ages on samples ranging from 1.1 to 3.6 Ma and, thus, substantially reduced the apparent volcanic gap in Nicaragua.

**Keywords:** Central American Volcanic Front, Geochronology,  $^{40}\text{Ar}/^{39}\text{Ar}$

**RESUMEN:** Con el principal objetivo de realizar mejores cálculos de la producción volcánica, en el Arco Volcánico de América Central, realizamos 61 dataciones  $^{40}\text{Ar}/^{39}\text{Ar}$  en tefras y lavas en localidades de frente volcánico de Costa Rica y Nicaragua por medio de varias campañas de campo y análisis de laboratorio (preparación de muestras, envío al reactor nuclear, espectroscopía de masas de las muestras radiactivas, al laboratorio de gases nobles del Departamento de Ciencias de la Tierra y Planetarias de la Universidad Rutgers) del 2002-2008. En este artículo presentamos diferentes observaciones que resultaron de este estudio donde se describe la precisión, exactitud y la confiabilidad de las edades  $^{40}\text{Ar}/^{39}\text{Ar}$ . El primer resultado muestra las limitaciones de esta técnica en muestras baja en  $\text{K}_2\text{O}$  con edades  $< 1$  Ma, especialmente en Nicaragua. El segundo resultado muestra los efectos de la pérdida de Ar por los procesos de meteorización típicos del trópico, inclusive afectando las muestras sanas a nivel críptico. El tercer resultado sugiere que las razones eruptivas del frente volcánico no han sido constantes durante los últimos 15-20 Ma, sino más bien representan ciclos eruptivos. Con el propósito de evaluar los hitos entre diferentes ciclos eruptivos, evaluamos los datos geoquímicos a lo largo del frente volcánico, en especial las relaciones U/Th, cuyos valores son inferiores (Grupo Coyol) en Nicaragua, comparados con el frente volcánico activo. Sin embargo, las muestras seleccionadas con base en geoquímica, resultaron ser de edades conocidas y no produjeron datos que llenan los hiatos entre ciclos de actividad volcánica. La siguiente estrategia que manejamos fue extender el muestreo en el Grupo Coyol, inmediatamente detrás del frente volcánico activo, sin embargo, esta estrategia no fue exitosa para encontrar muestras que llenaran los hiatos de actividad. No obstante, obtuvimos edades de 1.1-3,6 Ma entre los volcanes Cosiguina and San Cristóbal, los cuales limitan el hiato de actividad y mejoran nuestra percepción de los ciclos de actividad volcánica en América Central.

**Palabras Clave:** Frente Volcánico de América Central, Geocronología,  $^{40}\text{Ar}/^{39}\text{Ar}$

## INTRODUCTION

The development of  $^{40}\text{Ar}/^{39}\text{Ar}$  dating methods made it possible to obtain high precision ages from a wide variety of igneous material. Radiometric dates appear simple to interpret, but this accessibility often leads to misunderstandings about how these dates are obtained and even what geologic events in the rock's history the dates refer to. It is therefore important to be clear about what argon ages mean, how they are derived, and what affects their reliability.

The basis of the  $^{40}\text{Ar}/^{39}\text{Ar}$  dating technique is a modification of the  $^{40}\text{K}/^{40}\text{Ar}$  dating method based on the decay of  $^{40}\text{K}$  to  $^{40}\text{Ar}$  with a half-life of 1.26 Ga (Beckinsale and Gale, 1969). The  $^{40}\text{Ar}/^{39}\text{Ar}$  technique differs from the  $^{40}\text{K}/^{40}\text{Ar}$  method in that the K of a sample, is measured by conversion of  $^{39}\text{K}$  to  $^{39}\text{Ar}$  by neutron bombardment in nuclear reactor. Since the ratio of  $^{39}\text{K}$  to  $^{40}\text{K}$  is known, the derived  $^{39}\text{Ar}$  can be used as proxy for  $^{40}\text{K}$  measurement (Merrillhue and Turner, 1966). This technique has an advantage over conventional K-Ar dating, because both the radioactive parent  $^{39}\text{ArK}$  and the daughter  $^{40}\text{Ar}$  can be measured

by the same method, mass spectrometry, on the same sample split at the same time. This permits the measurement of smaller sample sizes (since splits are not needed for K and Ar measurement) and reduces measurement errors associated with weighing and homogeneity. Since these are now direct ratio measurements, not recombined yields per sample weight, samples can be incrementally heated, yielding series of relative increasing temperature ages that yield insight into the thermal history of the sample. Likewise these data can be plotted on isochron plots that give added information as to the initial argon concentration of the sample at the time of cooling.

The  $^{40}\text{Ar}/^{39}\text{Ar}$  technique can be applied to any K-bearing igneous rock or mineral phase that has not experienced extensive weathering or reheating since its formation. Within each rock,  $^{40}\text{K}$  is perpetually decaying, however  $^{40}\text{Ar}$  will not begin to accumulate until the material drops below its "blocking" temperature; the temperature below which crystal structure is strong enough to block the diffusion of argon.  $^{40}\text{Ar}$  is a relatively large atom and cannot escape the typical silicate mineral crystal lattice unless the sample is reheated or

physically abraded. Once the mineral has cooled beneath its blocking temperature, the “clock” begins and the daughter  $^{40}\text{Ar}$  accumulates. Blocking temperatures vary for different minerals, with amphibole  $\sim 500^\circ\text{C}$  (Hanson and Gast, 1967), biotite  $\sim 400^\circ\text{C}$ , and plagioclase  $\sim 200^\circ\text{C}$  (Berger and York, 1981). It is important to note that when we refer to a  $^{40}\text{Ar}/^{39}\text{Ar}$  “age”, we are referring to this moment in time and not necessarily the formation age. For example, plutonic rocks can remain above their blocking temperature for millions of years and metamorphic rocks can have their radiometric clocks reset by subsequent reheating, which means that the protolith of these rocks can form long before the radiometric clock begins (Berger and York, 1981). In contrast, extrusive volcanic rocks typically cool below their blocking temperature soon after the time of eruption and can yield true formation ages. All ages referred to in this paper are considered to be eruption ages.

While  $^{40}\text{Ar}/^{39}\text{Ar}$  dating is an extremely useful tool, it is not without its drawbacks, particularly in Central America and obtaining reliable dates is dependant on a number of factors, each of which can affect the reliability of the resulting age data.

## RADIOGENIC ARGON

Prior to the eruption of a lava or tephra, the magma is generally well above the blocking temperature of most K-bearing minerals, and normally is in equilibrium with the  $^{40}\text{Ar}/^{36}\text{Ar}$  ratio of the atmosphere (295.5, Steiger and Jager, 1977). All extrusive volcanic rocks therefore contain some  $^{40}\text{Ar}$  at the time of formation, but  $^{40}\text{Ar}$  of radiogenic origin (abbreviated  $^{40}\text{Ar}^*$ ) only begins to accumulate after they cool below their blocking temperature. A reliable date can be obtained if sufficient amounts of  $^{40}\text{Ar}^*$  accumulates to distinguish from  $^{40}\text{Ar}$  derived from equilibration with the atmosphere.

The accumulation of  $^{40}\text{Ar}^*$  is controlled by two main factors: The initial potassium content of the sample and the elapsed time since it dropped below the blocking temperature. A high potassium

sample can accumulate sufficient  $^{40}\text{Ar}^*$  to yield a reliable age in less time than a low potassium sample. A problem arises however, when trying to date young rocks with low potassium content, because there is very little  $^{40}\text{Ar}^*$  to measure.

While potassium contents of Central American arc basalts are comparable to basalts from other arcs (generally between 0.5 and 2 wt.%, Luff, 1982; Marsh, 1982; Smith et al., 1980; Wills, 1974), there is significant internal variability with central Costa Rican values almost doubling those in northwest Nicaragua (Figure 1, Carr et al., 2003). Northwest Costa Rican samples are also higher on average than those from Nicaragua, although there is significant overlap.

Volcanic material as young as a few thousand years has been successfully dated using  $^{40}\text{Ar}/^{39}\text{Ar}$  dating techniques (Renne et al., 1997; Lanphere et al., 1999), but those samples had potassium levels at least 10 times that of typical in Central America. It is likely the combination of young age and low potassium content that makes dating Nicaraguan volcanic front samples challenging. Thirty one Nicaraguan volcanic front samples have been dated at the Rutgers University Geochronology Lab and of those, only eight yielded reliable ages. Thirty five Costa Rican volcanic front samples have been dated at the Rutgers University Geochronology Lab and of those, thirty three yielded reliable ages, a significantly higher percentage than the Nicaraguan samples. Measuring  $\text{K}_2\text{O}$  contents and selecting only those samples with the highest levels can help solve this problem.

Weathering and hydrothermal alteration can also be problematic for argon geochronology of lavas, because both of these processes can cause the release of  $^{40}\text{Ar}^*$  that has been building up since the time of eruption or differential K and Ar loss during weathering. This is common in volcanic rocks, particularly in the tropical climate of Central America, and often affects only the phases that crystallized at the lowest temperatures as well as secondary phases, such as zeolites that are the result of low temperature alteration or metamorphism (Figure 2; Ching-Hua et al.,

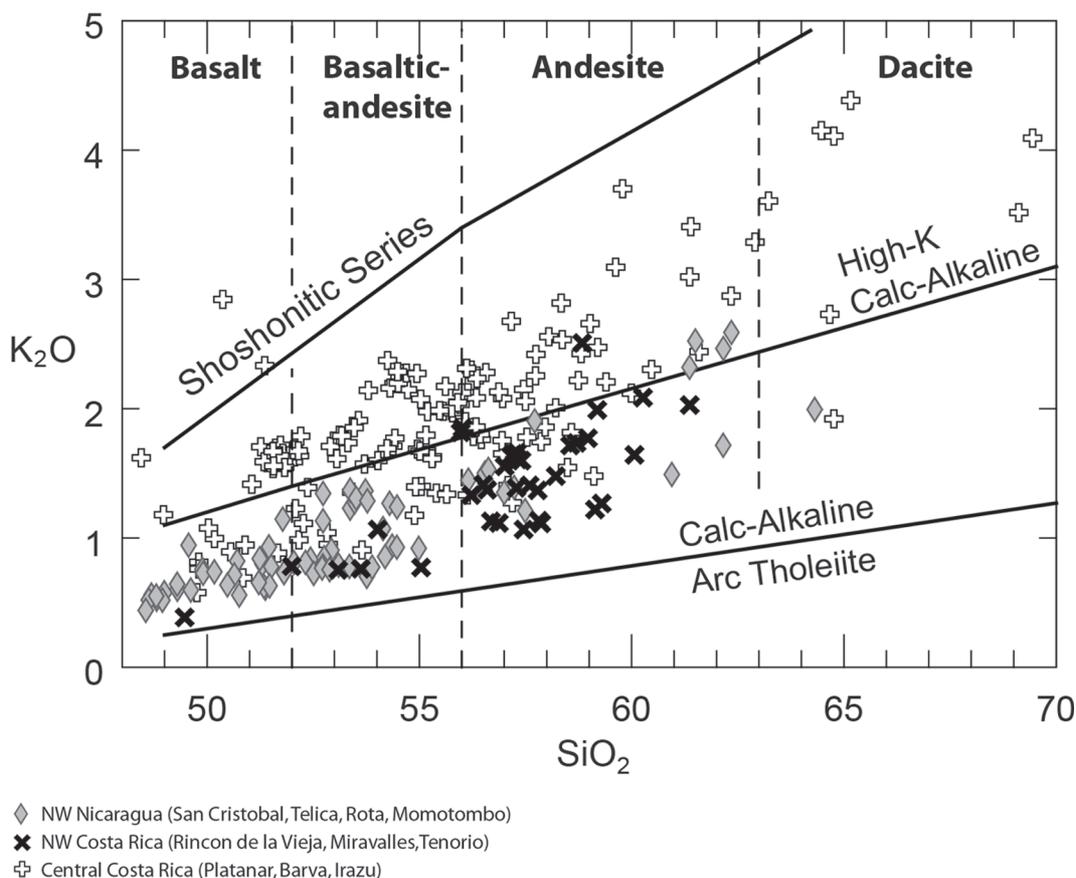


Fig 1: Geochemical classification diagram (Peccerillo and Taylor, 1976). Gray diamonds are Nicaragua, black Xs are northern Costa Rica, open crosses are central Costa Rica. Data from Carr et al. (2003)

1994). Under certain conditions, weathering and hydrothermal alteration can cause the release of all pre-eruption  $^{40}\text{Ar}^*$ , even in samples less than 100 ka. For example, on the southern flank of San Cristóbal, one smooth, lobe-shaped lava was found (12.7315°N/87.0540°W) to be so hydrothermally altered that it could be easily broken by hand. This sample was not collected, but is a reminder of how quickly alteration can occur. K is often lost from glass phases during weathering and hydration.

Another factor that can cause unreliable dates is incomplete degassing or trapping of pre-eruption  $^{40}\text{Ar}$ . When erupted lava is allowed to fully equilibrate with the atmosphere, the initial ratio of  $^{40}\text{Ar}$  to  $^{36}\text{Ar}$  will be 295.5. However, if pre-eruption  $^{40}\text{Ar}$  is not allowed to degass, the sample

is said to have “excess” argon. This can be seen in an isochron diagram of sample VE-071605-2 (Figure 2), which is described later in this paper.

## METHODS

Samples for  $^{40}\text{Ar}/^{39}\text{Ar}$  dating discussed here, were obtained from the cores of large boulders or lava blocks collected from the study areas. Samples were observed under binocular and petrographic microscopes and those that showed clear evidence of weathering or alteration were eliminated. For most samples, only the fine-grained matrix (composed mainly of microlitic plagioclase) was analyzed, because its lack of phenocrysts suggest that it was formed at the time of eruption.

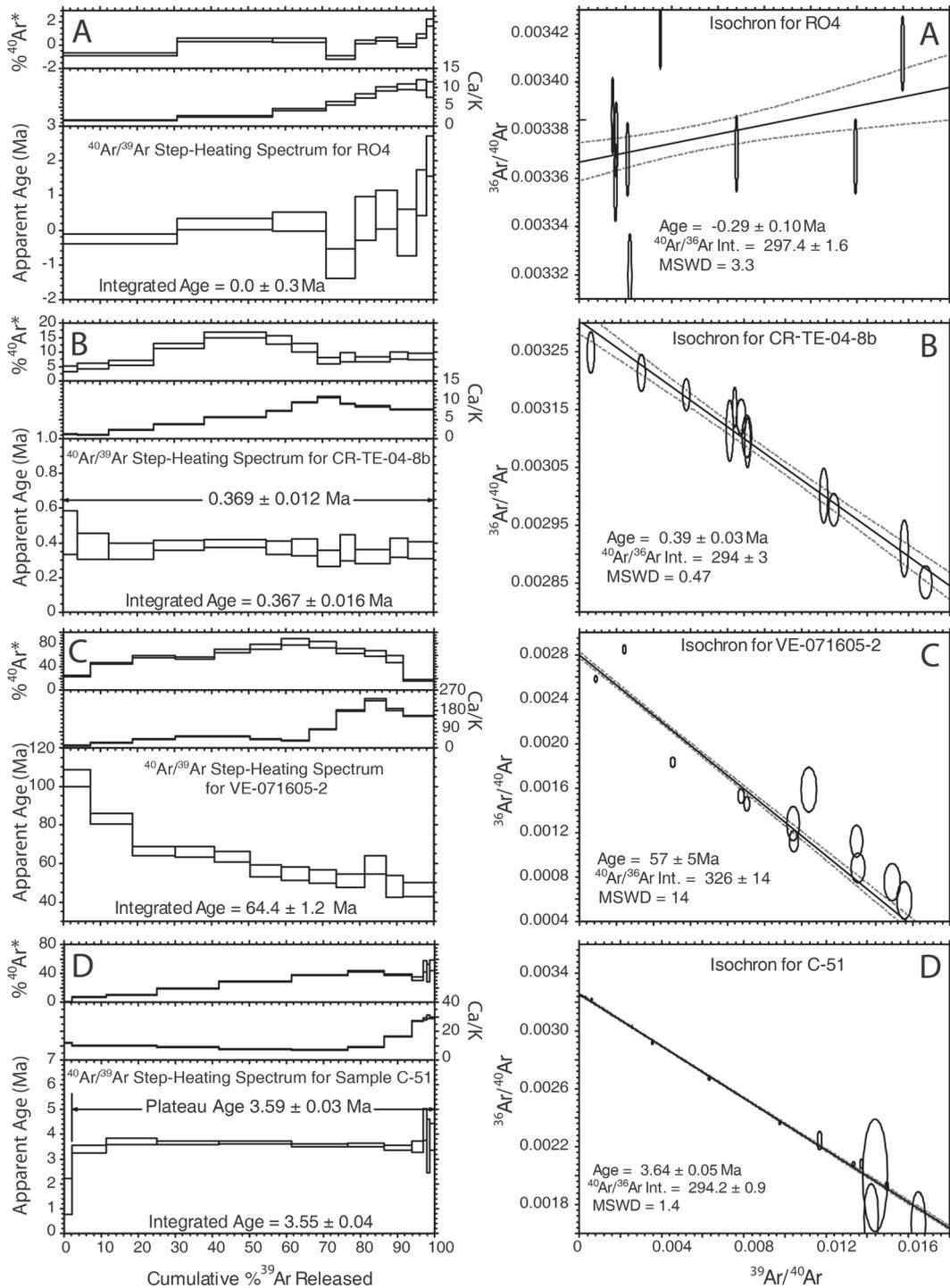


Fig. 2: Step-heating spectra and Isochron plots for A) RO-4 from Rota in Nicaragua B) CR-04-TE-8b from Tenorio in Costa Rica C) VE-071605-2 from Isla Venado off the Nicoya Peninsula in Costa Rica D) C-51 from between Cosigüina and San Cristóbal in Nicaragua

Phenocrysts were removed through a combination of hand picking and magnetic separation. A biotite mineral separate was analyzed for sample C-06-NIC-2, a biotite rich tephra. Samples were prepared and analyzed following methods outlined in Carr et al. (2007) and therefore it will not be described in detail here.

It is worth noting that all ages are based on either matrix or mineral separates as opposed to whole rock analysis. The main difference is that with the whole rock method, the entire sample is analyzed and may include radiogenic argon from weathered phases, pre eruption phenocrysts, or xenolithic contamination. By analyzing only the fine-grained matrix, we minimize these factors and limit the possibility of obtaining anomalously old ages. Even with this precaution, it can be difficult to eliminate pre-eruption phases entirely, particularly if they are small and of the same minerals that make up the matrix. Low temperature alteration can also be difficult to completely eliminate during sample preparation.

For these reasons, samples were incrementally heated with up to 15 increasing temperature steps and the released gases measured each time. Each temperature step is based on an increase in laser power wattage (typically between 2 and 32 watts) and those power limits have been empirically determined to vary the temperature of the sample between 500°C and 1150°C. This method yielded the incremental heating release spectra diagrams seen throughout this paper as opposed to total fusion ages, which are generated by releasing trapped argon with a single high temperature step. Total fusion analysis includes the radiogenic argon component of the entire sample in a single measurement and can mask internal variability and evidence of weathering and xenolithic contamination. Release spectra diagrams plot the apparent age of each individual temperature step, which may or may not be the same throughout the sample. Ideally, apparent ages from consecutive temperature steps representing at least 50% of the total  $^{39}\text{Ar}$  would form an age plateau at the 95% confidence level. Typically, the plateau age (if there is one) is reported along with the integrated age, which is simply the weighted average of each individual temperature step and is essentially the same as a total fusion age.

The incremental-heating method is also beneficial because multiple steps can be plotted on an inverse isochron diagram (examples in Figure 2). In this type of diagram,  $^{36}\text{Ar}/^{40}\text{Ar}$  is plotted against  $^{39}\text{Ar}/^{40}\text{Ar}$ . In an ideal sample, the individual temperature steps plot along a single line, such that the slope provides the age and the y-intercept provides the initial  $^{36}\text{Ar}/^{40}\text{Ar}$  value.

## CASE STUDIES

The first sample case study is RO-4 (Figure 2A), a lava collected from Rota Volcano in Nicaragua (Figure 5, Carr et al., 2007). RO-4's extremely low radiogenic argon yields (-1.1 to 1.9%) is typical of Nicaraguan active front lavas. Negative values simply reflect the fact that the error exceeds the amount of the measured gas. This can be clearly seen in the first temperature step, which accounts for approximately 30% of the total released  $^{39}\text{Ar}$ , yet the apparent age is below 0. The low  $^{40}\text{Ar}^*$  yield is most likely due to its relatively young age (the present Nicaraguan front is no more than 350 ka, Carr et al., 2007) rather than its potassium content, which at 1.22 wt.% (Carr et al., 2003), is one of the highest in Nicaragua. Although evidence of weathering was not detected in hand sample or thin section, due to the sample's location in a tropical climate and proximity to active volcanism (and therefore sources of hydrothermal activity), low-temperature alteration cannot be entirely ruled out. In addition, the apparent age seems to increase in the last 5 temperature steps, which could suggest that radiogenic argon was released only at the lower temperature phases. This sample is considered not to have yielded a reliable date and is included here only to illustrate the difficulty in evaluating the age of a sample when the radiogenic argon yield is low.

In the absence of a reliable plateau, how should this data be interpreted? The isochron yields a negative age and an atmospheric initial  $^{40}\text{Ar}/^{36}\text{Ar}$ , so we can conclude that there is simply too little radiogenic argon to obtain a reliable age. In the absence of clear evidence of chemical or physical alteration, we can simply conclude that

the sample is of very recent age, or more precisely, that the sample's age is indistinguishable from 0.

The next sample case study is CR-TE-04-8b (Figure 2B), a lava collected from Tenorio Volcano along the Costa Rican volcanic front (Figure 5, Carr et al., 2007). All temperature steps form a  $0.369 \pm 0.012$  Ma plateau at the 95% confidence level and the  $^{40}\text{Ar}^*$  yields range from 4 to 16%. The isochron age agrees with the plateau age within the margin of error at  $0.39 \pm 0.03$  Ma and the initial  $^{40}\text{Ar}/^{36}\text{Ar}$  ratio is within the range of atmospheric values at  $294 \pm 3$ . In addition, the mean squared weighted deviation (MSWD) of the individual steps is only 0.47, which means that the errors fully account for the scatter about the isochron line. The large plateau and the high  $^{40}\text{Ar}^*$  yield (relative to Nicaraguan volcanic front samples) is consistent with the majority of other Costa Rican samples. For all of these reasons, this is considered to be an excellent example of a reliable age in contrast to the previous sample RO-4.

The third case study is a pillow basalt from Isla Venado off Costa Rica's Nicoya Peninsula (VE-07165-2; Figure 2C). This sample is overlain by a unit of reworked volcanoclastic sediments that was dated using biostratigraphy to 100 m.y.. This sample had an initial  $^{40}\text{Ar}/^{36}\text{Ar}$  ratio of  $326 \pm 14$ , higher than atmospheric ratios and evidence of excess argon and is likely due to its submarine eruption, which prevented complete degassing and equilibration with the atmosphere. The release spectra (Figure 2C) show the individual temperature steps falling from 105 Ma to 45 Ma throughout the analysis. Not only does this sample lack a plateau, but the isochron is also problematic with a mean squared weighted deviation of 14, well above the variation accounted for by the errors. One could attempt to refit the isochron with a different line by including only the high temperature steps that appear to be approaching a plateau. This approach would increase the age and the initial  $^{40}\text{Ar}/^{36}\text{Ar}$  ratio, but we believe that would be over interpreting very low-quality data. Although a reliable age cannot be obtained from this sample, the high initial  $^{40}\text{Ar}/^{36}\text{Ar}$  ratio suggests that it the age is probably much younger than the

>100 Ma estimate based on field data. This may simply mean that the contact between the pillow basalts and the overlying unit is a thrust fault and not depositional, however further fieldwork is needed to make this determination. Given the glassy nature of pillow basalts, the spectra may also reflect K-loss during hydrothermal alteration. It may also be that the formation is a pillow dike and not a lava flow.

The last sample case study is C-51 (Figure 2D), a lava collected from a low lying area between the volcanic front volcanoes of Cosigüina and San Cristóbal in northwest Nicaragua. This sample has a plateau age of  $3.59 \pm 0.03$  in agreement with an isochron age of  $3.54 \pm 0.05$ . These ages were first reported in Carr et al. (2007) and are included here as an example of how low degrees of weathering or alteration can affect the release spectra of a sample. Although, the plateau includes 98% of the total released  $^{39}\text{Ar}$ , the first temperature step is not included and is almost 2 Ma younger than the rest of the plateau. This is common even in samples with robust ages and is evidence of low-temperature alteration, which releases radiogenic argon trapped in low-temperature phases within the lava.

## VOLCANIC HISTORY

Previous geochronological work in Nicaragua (Ehrenborg, 1996; Elming et al., 2001; Plank et al., 2002, Carr et al., 2007, Saginor et al., 2011) suggest that the NW/SE trending Coyoil Arc migrated steadily toward the southwest until ~7 Ma when volcanic production abruptly ceased. The Coyoil volcanic front lasted from 25 Ma to 7 Ma (Plank et al., 2002) and consists of extensive lavas and ignimbrites throughout the Nicaraguan Highlands. Volcanism wouldn't resume until 3.6 Ma and then only between Cosigüina and San Cristóbal (Carr et al., 2007, Saginor et al., 2011). Several attempts were made aimed at filling in this missing period in the volcanic record.

First, U/Th values in Nicaraguan volcanics experienced a significant increase between the Miocene and present arc (Figure 3, Plank et al., 2002), however there were three samples thought

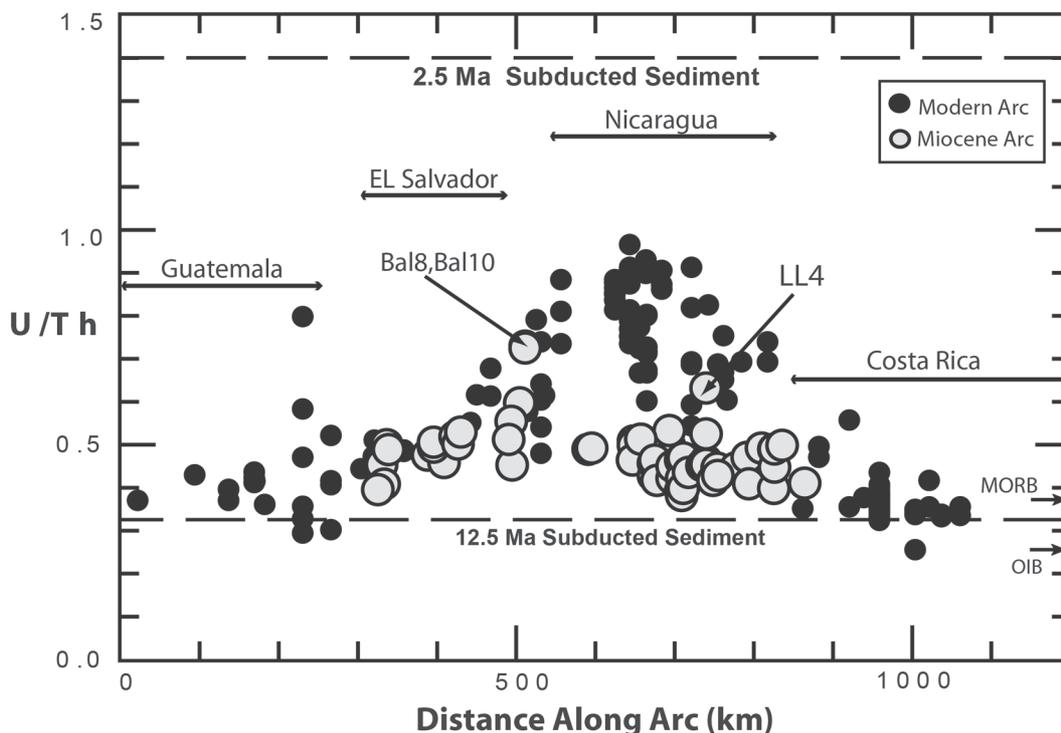


Fig. 3: Along arc variation in U/Th with country section labeled. Black circles are the modern arc and gray circles are Miocene (Condie, 2005; Carr et al., 2003). 3 samples selected for dating are labeled (Carr et al. 2007; Saginor et al., 2011)

to be Miocene that had U/Th values between those typical for the Miocene and active arcs. These samples were selected for dating, because their intermediate U/Th values raised the possibility that their ages were intermediate as well. Sample LL-4 is from the Las Lajas volcano just east of the Nicaraguan depression and samples Bal-8 and Bal-10 are from the Balsamo Formation in El Salvador. LL-4 was found to be 9.5 Ma, which places it firmly within the Coyal Group (Carr et al., 2007). Samples Bal-8 and Bal-10 were found to be older than the active volcanic front and yielded ages of 1.3 and 1.1 Ma, respectively.

Second, an attempt was made to constrain both the timing and duration of this apparent hiatus in Nicaraguan volcanism by refining estimates for the youngest material within the Coyal Group as well as the oldest sections of the active arc. For the latter task, satellite images ([\[ssc.nasa.gov/mrsid/\]\(https://zulu.ssc.nasa.gov/mrsid/\)\) and topographic maps were used to identify areas within the active arc where the morphology suggested the oldest material could be found.](https://zulu.</a></p>
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$^{40}\text{Ar}/^{39}\text{Ar}$  ages obtained using this method were reported in Carr et al. (2007), with a maximum age of 330 ka. Plank et al. (2002) suggested that Miocene volcanism in Nicaragua ceased  $\sim 7$  Ma after the Coyal volcanic front migrated towards the southwest for at least 5 m.y. In an effort to locate Coyal volcanics younger than 7 Ma, fieldwork was focused between the active arc and the westernmost Coyal lavas (Figure 4, Carr et al., 2007).

This approach extended the geographic distribution of the Coyal Group  $\sim 10$  km into the Nicaraguan Depression, although did not extend its temporal range. Two samples were found in this area with ages of 1.13 and 1.48, which places

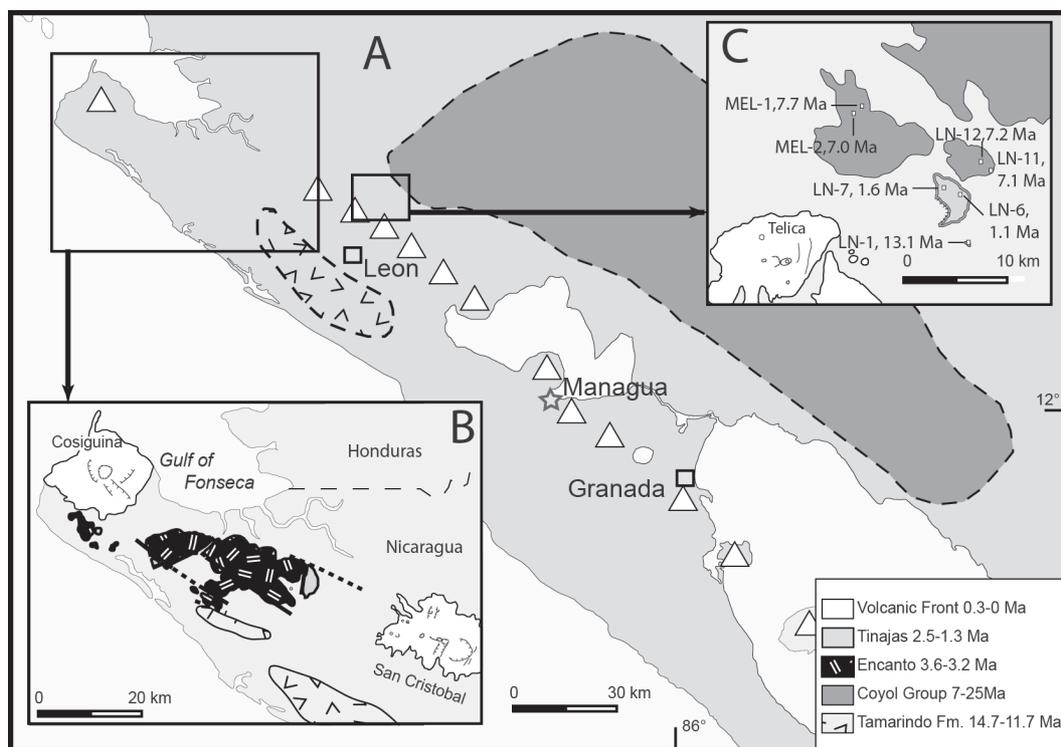


Fig. 4: Map of northwest Nicaragua and two primary study areas

them in the Tinajas unit as defined in Saginor et al. (Saginor et al., 2011).

We also collected samples between Cosiguina and San Cristóbal, the longest stretch of the volcanic front without an active volcano. This effort revealed two previously unknown volcanic units: The Tinajas (2.5-1.3 Ma) and the Encanto (3.6-3.2 Ma). Both of these are described in Saginor et al. (2011). These two units also decreased the duration of the temporal gap in Nicaragua, leaving only 3.4 Ma (7 to 3.6 Ma) without known volcanism.

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#### CONCLUSIONS

Samples from the Nicaraguan volcanic front are generally lower in  $\text{K}_2\text{O}$  than samples from the Costa Rican front. In addition, the front may be slightly younger in Nicaragua than Costa Rica. These two factors make obtaining reliable Nicaraguan  $^{40}\text{Ar}/^{49}\text{Ar}$  ages difficult because it leads to lower  $^{40}\text{Ar}^*$  yields.

The volcanic history in Nicaragua is incomplete and several attempts have been made to locate samples that fill in these temporal gaps. First, samples with U/Th values between the Miocene and active volcanic fronts were analyzed to see if their ages were intermediate as well. Second, satellite imagery was used to direct fieldwork toward the most weathered sections of the active Nicaraguan volcanoes and to a topographic low just behind the active front. Third, volcanic material was collected between Cosiguina and San

Cristóbal, the longest stretch of the volcanic front without an active volcano. These efforts decreased the duration of the temporal gap in Nicaragua to about 3.4 Ma, which lasted from 7 to 3.6 Ma. It is also important that detailed geologic maps of northwest Nicaragua be developed to fully understand the volcanic history of the region.

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