A re-interpretation of the Paricutin volcano petrogenesis: rapid fractionation with no crustal assimilation

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ABSTRACT

Paricutin volcano is the youngest and most studied monogenetic cinder cono in the Michoacán-Guanajuato volcanic field (Mexico), with an excellent historical record of its nine years (February 1943 to March 1952) of eruptive activity. The eruption produced lavas and tephras that range in composition from basalt to basaltic andesite. We have conducted new major and trace element and isotopic studies (whole rock Sr-Nd-Pb-Os) of the Paricutin lavas and tephras spanning the entire duration of the eruption, together with xenoliths found within the first erupted lavas and crustal samples representative of the Paricutin basement. This detailed study aimed to further constrain the potential roles of mantle source heterogeneity, subduction-related metasomatism, and crustal assimilation in the petrogenesis of Paricutin magmas. Although Paricutin has been traditionally considered as the classical example of fractional crystallization and crustal contamination, our multi-isotopic study has revealed that Paricutin compositional variations are inconsistent with crustal assimilation. Alternatively, we suggest that Paricutin geochemical evolution can be explained as the combination of variable degrees of fractional crystallization of magmas produced as result of pre-subduction mantle beneath the TMVB metasomatized by subduction components including sediment- and oceanic crust-derived fluids.

KEYWORDS (UP TO 6)

Parícutin, Monogenetic volcanism, Trans Mexican Volcanic Belt, Subduction zone, Mantle metasomatism.

HIGHLIGHTS (3 TO 5)

- Paricutin lavas and tephra samples show geochemical characteristics similar to subduction-related magmas.
- The geochemical variation with time is controlled by fractional crystallization.

- Multi-isotopic data show no important contribution of crustal assimilation in the formation of the volcano.
- The source heterogeneity is produced by a single "background" mantle metasomatized by two subduction components dominated by terrigenous sediment-derived fluid.

1. INTRODUCTION

Monogenetic eruptions are the most extensive type of volcanism on Earth and occur in all of the main tectonic settings (intraplate, extensional and subduction zones), providing information about the physical and chemical characteristics of the rising magma and the interaction with the external environment that influences its eruption style (e.g., Cañón-Tapia and Walker, 2004; Cañón-Tapia 2016). These volcanoes are the landforms produced by explosive and effusive temporally restricted eruptions triggered by the rise of compositionally distinct small magma batches, generating the smallest eruptions in terms of erupted magma volume (e.g., Chevrel et al., 2016; Larrea et al., 2017; Lorenzo-Merino et al., 2018). The duration of an individual eruption typically last from several days to years (Connor and Conway. 2000), but these centers normally appear grouped in volcanic clusters (hundreds to few thousands of years within a small area of few tens of km^2; e.g., Guilbaud et al., 2012; Reyes-Guzmán et al., 2018) and/or volcanic fields (millions of years in thousands of km^2; Gómez-Tuena et al. 2007b). This typical occurrence as grouped vents has been interpreted by Smith and Németh (2017) as the surface expression of a magmatic plumbing system that is spatially dispersed and episodic.

These monogenetic systems erupt basaltic magmas within a wide compositional range from strongly silica undersaturated to saturated and oversaturated (Smith and Németh, 2017). Strikingly, many monogenetic volcanoes are characterized by a systematic change in the chemical composition of the magma as the eruption progresses, often clearly correlated with the volcanostratigraphy (Brenna et al. 2010, 2011, 2012a; McGee et al. 2012; Németh et al. 2003; Rasoazanampanary et al.,

2016; Smith et al. 2008). These variations have been interpreted as the result of different degrees of fractionation/crystallization (Luhr and Carmichael, 1985), different degrees of crustal assimilation (e.g., McBirney et al., 1987; Cebriá et al., 2011) crystal-melt interactions (e.g., Smith et al., 2008), successive partial melting of distinct source components (e.g., Cook et al., 2005; Haase and Renno, 2008), and variations in melting and ascent dynamics (e.g., McGee et al., 2011; Reiners, 1998). But these variations are not solely noticeable within single stratigraphic sequences, but also, between individual centers in a contiguous volcanic field (e.g., Blondes et al., 2008; McGee et al., 2013; Strong and Wolff, 2003).

The Paricutin and Jorullo volcanoes are a good paired study case because both produced well documented historic eruptions where samples selected for geochemical analysis can be placed in stratigraphic context, they both exhibit a temporal compositional trend of increasing SiO_2 with time, representing possible endmembers in inferred extents of crustal interaction, with lesser or absent contamination of Jorullo lavas (e.g., Johnson et al., 2008; Luhr and Carmichael, 1985) and very extensive contamination of Paricutin lavas (e.g., Cebriá et al., 2011; McBirney et al., 1987; Luhr, 2001), and their close geographic proximity enables a comparison of potential variability of mantle and crustal processes in different volcanic centers in a relatively fixed tectonic/geologic setting. The detailed study of Jorullo volcanic products was carried out by Rasoazanampanary et al. (2016), whereas in this study we focus on Paricutin volcano.

Paricutin is one of the best studied monogenetic cones from the Michoacán-Guanajato volcanic field (MGVF), with an excellent historical record of the eruption (February 1943 - February 1952). We are revisiting the geochemistry of all products form Paricutin volcano, including lavas, tephras, xenoliths and the nearby basement rocks, to further evaluate the relative roles of crustal assimilation versus mantle source heterogeneity in the genesis of Paricutin magmas and their evolution. Our study involves for the first time the complete study of major and trace

96 elements, and Sr-Nd-Pb-Os isotopic determinations on whole-rock lavas, tephra, and crustal
97 xenoliths throughout the Paricutin eruptive history. The combination of these data allows to
98 uniquely constraint the relative roles of lower and upper crustal assimilation and the potential
99 addition of slab-derived components to the mantle wedge. Moreover, this study has important
100 implications regarding the establishment of magma reservoirs in mafic monogenetic volcanic
101 systems and the cause of temporal-compositional variations in the eruptive products.
102
103 **2. GEOLOGICAL BACKGROUND AND PREVIOUS STUDIES**
104 The Trans-Mexican Volcanic Belt (TMVB) is an active continental magmatic arc constituted
105 by nearly 8000 volcanic structures, and a few intrusive bodies, that extend from the Mexican Pacific
106 to the coast of the Gulf of Mexico along ~1000 km (Fig.1A-B; Demant, 1978). The quaternary
107 volcanism of the TMVB is related to the subduction of the Cocos Plate underneath the North
108 American Plate along the Middle America trench, at a rate of ~6 cm/year (DeMets et al., 1990; Fig.
109 1B). The crustal thickness along the front varies from ~30 km in western Mexico to 50 km in the
110 Sierra Chichináutzin Volcanic Field (Wallace and Carmichael, 1999). The TMVB follows an
111 overall E-W direction, forming an angle of ~16° with the trench (Fig. 1B), attributed to the near-
112 horizontal subduction and changing dip of the subducting plate (Pardo and Suárez, 1995). The
113 volcanism is diverse in composition, as both calc-alkaline and OIB-type magmas have erupted
114 across the belt, being the first type volumetrically dominant. The calc-alkaline magmas are derived
115 from partial melting of the subarc mantle modified by slab melts or slab dehydration (e.g., Blatter et
116 al., 2010; Cai et al., 2014; Petrone et al., 2003; Siebe et al., 2004; Straub et al., 2015). In contrast,
117 the origin of the OIB-type magmas is controversial as they have been interpreted as melts from an
118 unmodified subarc asthenospheric mantle (e.g. Luhr, 1997; Luhr et al., 2006; Siebe et al., 2004), an
119 enriched mantle source metasomatized by subduction fluid (Petrone et al., 2003), a pyroxenitic
120 mantle produced by subduction fluid/melt infiltration (Straub et al., 2008, 2015), or a deep mantle
121 plume (Marquez et al., 1999; Verma, 2000).

Another peculiarity of the TMVB among other volcanic arcs is the relative scarcity and irregular distribution of polygenetic volcanoes, which contrasts with the high abundance of monogenetic volcanoes (ca. 3000) (Demant, 1978; Tibaldi, 1992). The highest concentration of monogenetic volcanoes occurs in the Michoacán-Guanajuato Volcanic Field (MGVF), the western–central part of the TMVB where the arc reaches a maximum width of ~ 200 km (Hasenaka and Carmichael, 1985). The MGVF is the largest monogenetic field on Earth (Valentine and Connor, 2015), containing more than 1000 eruptive centers over a 40.000 km^2 area (Hasenaka, 1994) consisting mainly of scoria cones, lava domes, shield volcanoes and maars. The volcanism in this area started about 2.8 Ma and continues to present day, with the formation of the two only monogenetic volcanoes born in historical times: Jorullo (1759–1774) and Paricutin (1943–1952) (Fig. 1B-C).

Paricutin is located ~320 km west of Mexico City at latitude 19°29'35″N and longitude 102°15'05″W (Fig. 1B). Its eruption started in a cornfield on the 20th of February 1943 and ended 9 years later on the 4th of March 1952 (Luhr and Simkin, 1993). The eruption was of great interest to the geological community because of the opportunity to document the entire life cycle of a volcano for a better understanding of the origin, eruption dynamics, and evolution of monogenetic scoria cones. This led to a number of descriptive works (e.g., Fries, 1953; Foshag and González-Reyna, 1956; Scandone, 1979; Segerstrom, 1950; Wilcox, 1950; Williams, 1950) that were well summarized by Luh and Simkin (1993), followed by other works dealing with the physical and geomorphological evolution of the volcano and its products (Dóniz-Páez et al., 2013; Inbar et al., 1994; Pioli et al., 2008). Luhr and Simkin (1993) divided the development of the lava field into 23 eruptive phases by date of eruption, and from those original maps and the detailed description of the history of the eruption Larrea et al. (2017) created the Geological map of Paricutin, a unique sequence of illustrations that show in detail the lava field development of the volcano.

148

149 Petrographic and geochemical studies by Wilcox (1954), demonstrated a progressive change
150 in the bulk magma composition evolving from an olivine-bearing basaltic andesite with a SiO_2
151 content of ~55 wt. % to a pyroxene-bearing andesite with 60 wt. % SiO_2, explaining this variation
152 as a cause of fractional crystallization combined with up to 20 wt. % assimilation of basement
153 granitic rocks. Subsequent analysis of trace elements and Sr an O isotopic ratios by McBirney et al.
154 (1987) supported the interpretation of Wilcox (1954), strengthened Paricutin as the classic example
155 of assimilation - fractional crystallization in a subduction calc-alkaline suite. Moreover, they
156 defined a strong compositional shift in 1947, attributed to the increased importance of crustal
157 contamination. Luhr (2001) studied olivine-hosted melt inclusions in four tephra samples that span
158 the first two thirds of the 9-year eruption. He proposed an additional shift in magma composition in
159 July 1943, dividing the eruption in three stages, that were later accepted but slightly changed by
160 Erlund et al. (2010) based on their study of Paricutin tephras within a temporal framework, and
161 Rowe et al. (2011) based on lava compositions. Therefore, all these previous studies dealing with
162 the geochemical characteristics of lavas, tephras, and melt inclusions together with changes in the
163 eruptive style suggested three distinct eruptive stages (Fig. 2): Stage 1 (February-July 1943)
164 comprises the most mafic material, it is a compositionally distinct magma batch (K_2O <1 wt. %,
165 SiO_2 <56 wt.) and correlates with intense cineritic activity producing ~20% of the total volume;
166 Stage 2 (August 1943-1946) is characterized by K_2O >1 wt. %, limited major element variability
167 (e.g., SiO_2: 54.27 - 57.19 wt. %) and isotopic variation ($^{87}Sr/^{86}Sr$ ~0.7038), possibly representing a
168 different magma batch from Stage 1, accounting for ~ 50% of the volume; Stage 3 (1947-1952)
169 shows the most distinctive compositional change, characterized by a wide range in SiO_2 (56.7-61.58
170 wt. %) and $^{87}Sr/^{86}Sr$ (0.70398-0.70430), interpreted as a third magma batch affected by progressive
171 crustal assimilation (Fig. 2). Lastly, Cebriá et al. (2011) carried out a new sampling of lavas (1944-
172 1951), and their combined major, trace element and Sr-Nd isotopic modelling, reinforced the idea

of crustal assimilation (up to ~ 35-40% granite derived melts) coupled to fractional crystallization involved in the last stages of Paricutin evolution.

In this work, for the first time, we integrate all Paricutin products, including lavas, tephras, xenoliths and basement rocks, from a geochemical and stratigraphic point of view, to better understand the magmatic processes involved in the origin and evolution of Paricutin magmas.

3. SAMPLE COLLECTION AND ANALYTICAL METHODS

Fresh lava flows and tephra deposits were sampled in order to investigate the geochemical and isotopic variations throughout the eruption time. The samples comprise the 23 eruptive phases from late February 1943 to early February 1952 (Fig. 1; Luhr and Simkin, 1993), thus covering the entire time-span of the activity of the volcano. The eruptive phase of our collected lavas and literature samples was assigned based on eruption date and/or the geological map of the eruption (Larrea et al., 2017). Moreover, xenoliths and basement rocks were also studied in order to have representative samples of the potential contaminants interacting with Paricutin magmas.

Lava flows were collected in two main fieldwork campaigns: 2012 and 2015 (Fig.1C; Table 1 of the supplementary material). In 2012, lava flows were sampled all over the perimeter of the lava field. During the March and November 2015 fieldwork campaigns, the GIS based Paricutin volcano-stratigraphic map facilitated the identification of the 23 different eruptive phases in the field (see details in Larrea et al., 2017). Using this methodology, we sampled all the eruptive phases not sampled in 2012, and those samples from the covered eruptive phases (i.e., eruptive phases: 1, 2, 6, 11, and 16) were requested from the Smithsonian Museum of Natural History, in order to have at least one sample from each eruptive phase (UTM coordinates in Table 1 of the supplementary material). Unfortunately, samples from eruptive phases 2 and 11 were not available at the Smithsonian Museum.

Tephra deposits were also sampled to encompass the early explosive activity at Paricutin in February 1943. Five sites were excavated in areas located <1.5 km to the southwest of the main cone, chosen to capture the early explosive activity of the eruption (Fig. 1C; Table 1 of the supplementary material). In four of the trenches, the contact with the underlying soil was found, providing the complete section of the earliest tephra fall in proximal areas. The tephra deposits largely preserve their original stratigraphy and consist mostly of alternating layers of lapilli and fine ash. The late explosive activity of the volcano is represented by two bombs collected on the rim of the main cone (PAR-1533 and PAR-1534) and one bomb collected to the northwest of the cone (PAR-1532) (Fig. 1C; Table 1 of the supplementary material).

Moreover, three samples of the local basement rock, which are exposed at the edge of the Paricutin about 30 km to the southeast, according to McBirney et al. (1987), and fourteen xenoliths collected from lavas erupted in the first years of activity were also requested to Smithsonian Museum of Natural History for this study. Most xenoliths and all basement rocks were received as powders.

The petrographic study led to the selection of 32 lava flows, 29 tephra samples, 3 basement rocks and 11 xenoliths for whole rock chemical analyses (see results in Table 1 of the supplementary material). Samples were first cut into thin slabs, ground with silicon carbide sand paper to remove any metal traces from the rock saw, and cleaned meticulously with 18 MΩ H_2O in an ultrasonic bath. The samples were dried in an oven overnight at 100º C, then crushed in an alumina jaw-crusher and powdered in a high-purity alumina shatterbox. Major elements and a subset of trace elements (Ni, Cr, Sc, V, Ga, Cu, and Zn) were analyzed by X-ray fluorescence spectrometry (XRF), and all other trace elements were determined by inductively coupled plasma mass spectrometry (ICP-MS) at the Geoanalytical Laboratory at Washington State University.

225 Details of the analytical procedures and detection limits are available on the Geoanalytical
226 Laboratory website (http://environment.wsu.edu/facilities/geolab/). Measurements of geochemical
227 reference standards were carried out in order to guarantee the quality and accuracy of the analyses.
228 Major element data from these samples were published in Larrea et al (2017).
229
230 All selected samples were analyzed for Sr, Nd and Pb isotopes, however, just 11 lavas, 3
231 tephras, 5 xenoliths and 3 basement rocks were selected for Os determinations spanning the
232 geochemical variability of Paricutin products (see results in Table 1 of the supplementary material).
233 Sample preparation and Sr, Nd, Os and a subset of Pb isotopic measurements were performed at
234 Miami University (Ohio, USA). For Sr, Nd and Pb analyses, approximately 200 mg of powdered
235 samples were dissolved in concentrated HF–HNO_3 and separations of Pb, Sr, and Nd from a given
236 sample aliquot were performed by ion exchange chromatography following standard procedures
237 described in Snyder et al. (2005). The isotopic compositions of Sr, Nd and a subset of Pb were
238 measured by thermal ionization mass spectrometry (TIMS) using a Thermo-Finnigan Triton. Sr and
239 Nd isotope ratios were corrected for fractionation using $^{86}Sr/^{88}Sr = 0.1194$ and $^{144}Nd/^{146}Nd =$
240 0.7219. External precision based on long-term two standard deviation (2 SD) reproducibility of the
241 NBS 987 and La Jolla reference materials gave ±0.00002 and ±0.000007 for $^{87}Sr/^{88}Sr$ and
242 $^{143}Nd/^{144}Nd$, respectively. Lead isotope ratios were corrected for fractionation by 0.1% per amu,
243 based on measured ratios in the NBS 981 Pb standard compared to the accepted values of Todt et al.
244 (1996). The TIMS 2 SD external reproducibility of the NBS 981 standard reference material on
245 $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$, and $^{208}Pb/^{204}Pb$ are ±0.016, ±0.02, and ±0.068, respectively. Additionally,
246 high-precision Pb isotopic measurements were obtained for 17 lava flows, 10 tephras, 11 xenoliths,
247 and 3 basements rocks on separate sample dissolutions (Table 1 of the supplementary material).
248 These measurements were performed on a Nu Plasma multicollector inductively coupled plasma
249 mass spectrometer (MC-ICP-MS) at the Department of Terrestrial and Magnetism (DTM), Carnegie
250 Institution of Washington, using the Tl-spike method to correct for instrumental mass bias based on

measured $^{205}Tl/^{203}Tl$ ratios. Measured $^{204}Hg/^{202}Hg$ was used to correct for the isobaric interference of ^{204}Hg on ^{204}Pb. The 2 SD external reproducibility of the NBS 981 standard reference material during the analytical campaign was ±0.003 for $^{206}Pb/^{204}Pb$, ±0.002 for $^{207}Pb/^{204}Pb$, and ±0.005 for $^{208}Pb/^{204}Pb$.

Eleven lava flows, 3 tephras, 5 xenoliths, and 3 basement rocks were selected for Os isotopes (Table 1 of the supplementary material). Os chemistry and mass spectrometry were performed at Miami University. Approximately 1 g of sample was used for Os measurements. Samples were digested in reverse aqua regia (2:1 ratio of concentrated HNO_3: HCl) in a sealed Carius tube, following the methods described by Shirey and Walker (1995). The extraction of Os was done using an HBr macro-distillation technique (Yu, 2011) based on the method of Nägler and Frei (1997). Os was further purified by a micro-distillation step (Roy-Barman, 1993; Roy-Barman and Allegre, 1995) prior to isotopic analyses. Osmium isotopic compositions were analyzed by negative thermal ionization mass spectrometry (NTIMS) as OsO_3^-. Osmium isotope ratios were corrected for oxygen using the oxygen isotopic abundances of Nier (1950) and for mass fractionation using $^{192}Os/^{188}Os=3.0826$. The external reproducibility (2 SD) for $^{187}Os/^{188}Os$ measurements based on the long-term reproducibility of a NIST Os solution standard is ±0.0007, although some of our samples present slightly higher in-run errors (see Table 1 of the supplementary material).

4. RESULTS

4.1 PETROGRAPHY

The petrography and mineralogy of Paricutin lavas, have been described in detail by Bannister et al. (1998) and Wilcox (1954). Paricutin lavas are porphyritic with <8 % volume of phenocrysts. Olivine is the dominant phenocryst in all samples erupted prior to 1947. After 1947, the lavas are characterized by decreasing olivine and increasing orthopyroxene phenocryst contents. Plagioclase phenocryst are absent in all the lavas. Chromite microphenocrysts are present as

277 inclusions in most olivine and orthopyroxene phenocrysts in all the lavas. The groundmass is made
278 up of glass and olivine, plagioclase, orthopyroxene and minor amounts of clinopyroxene and spinel
279 microcrysts.
280
281 Tephra deposits sampled in this study were described in detail in Pioli et al. (2008) and
282 Erlund et al. (2010); these deposits are characterized by fine stratification that comprises millimeter
283 to decimeter-thick lapilli and ash layers. The xenoliths and basement rocks were described by
284 McBirney et al. (1987) as fragments of siliceous rocks (granite, granodiorite and quart monzonite)
285 with diverse degrees of alteration and/or fusion.
286
287 **4.2 WHOLE ROCK CHEMISTRY**
288 Whole rock major element, trace element and isotopic analyses of the studied samples are
289 available in Table 1 of the supplementary material.
290
291 **4.2.1 Major and trace elements**
292 The composition of sampled lava flows and tephra deposits ranges from basaltic andesite to
293 andesite following the TAS classification by Le Bas et al. (1986; not shown) with SiO_2 contents
294 between 52.98 and 60.48 wt. % and MgO ranging from 3.53 to 7.51 wt. %., in agreement with
295 previously published data from Paricutin (Cebriá et al., 2011; Erlund et al., 2010; McBirney et al.,
296 1987; Luhr, 2001; Rowe et al. 2011 and Wilcox, 1954). As already described by McBirney et al.
297 (1985), Luhr (2001) and Rowe et al. (2011), Paricutin eruptive products became richer in SiO_2 and
298 K_2O as the eruption progressed (Fig. 2), but the drastic compositional change after 1947 described
299 by these authors, is no longer observable in the samples in this study. Even, tephra samples do not
300 encompass the full compositional range of the eruption (we just have samples from the beginning
301 and end of the eruption), they fall within the range of the lavas, showing a strictly monotonic
302 variation in SiO_2 or MgO content with stratigraphic height (Fig. 2-3).

303

304 Bivariate plots of selected major elements versus SiO_2 (wt. %) are presented in Fig. 3. The
305 samples produce a continuous trend in these variation diagrams, although there is a clear change in
306 the slope at SiO_2 contents of ~56 wt. % for most oxides. Major elements including MgO, CaO and
307 FeO decrease with increasing SiO_2, whereas Na_2O and K_2O increase with increasing SiO_2. Al_2O_3
308 seems to decrease with increasing SiO_2, but do not show a well-defined trend. In contrast, TiO_2 and
309 P_2O_5 show variable behavior: the samples with $SiO_2 < 56$ wt. % show positive correlation with
310 SiO_2, whereas the samples with $SiO_2 > 56$ wt. % show a negative correlation with SiO_2. As already
311 noticed by Bannister et al (1998), Paricutin samples are characterized by low Ni (180-43 ppm) and
312 Cr (244-70 ppm) contents.
313

314 Whole rock trace element abundances also correlate with SiO_2 (Fig. 4). As observed for
315 major elements, there is also a clear change in the slope at SiO_2 contents of ~56 wt. % for most trace
316 elements. Incompatible elements such as La and Ba, show positive correlations with increasing
317 SiO_2, whereas compatible trace elements such as Ni and Cr and Sc show negative correlations with
318 increasing SiO_2. All Paricutin samples have high Th/Nb and low Ce/Pb and Nb/U relative to MORB
319 and OIB (Th/Nb~0.05; Ce/Pb>25; Nb/U>47; Sun and McDonough (1989) and Workman and Hart
320 (2005), respectively; Fig. 4f-h). Paricutin samples show a clear correlation between Th/Nb, Ce/Pb,
321 Nb/U and SiO_2, with a slight increase in Th/Nb and decrease in Ce/Pb and Nb/U with increasing
322 SiO_2, towards bulk continental crust compositions (Rudnick and Gao, 2003), for those samples with
323 $SiO_2 > 56$ wt. %.
324

325 Paricutin lavas and tephras show an enrichment in light rare earth elements (LREE) but
326 depletion in heavy rare earth elements (HREE) relative to normal mid-oceanic basalts (N-MORB).
327 In addition, on a N-MORB-normalized (Sun and McDonough, 1989) multi-element diagram (Fig.
328 6), the samples exhibit typical arc trace element patterns with enrichments of fluid-mobile large ion

329 lithophile elements (LILE) such as Rb, Ba, K, Pb, and Sr, and depletions in high-field strength
330 elements (HFSE) such as Nb and Ta. However, the samples exhibit little to no anomaly in Hf
331 concentration (Hf/Hf* ~0.91 - 1.06, where Hf/Hf* = $Hf_N/[Nd_N+Sm_N)/2]$; Wade et al., 2005), as also
332 observed in Jorullo volcano (Rasoazanampanary et al., 2016).
333
334 Paricutin xenoliths and basement rocks are the most evolved products which is in accordance
335 to the mineralogic and petrologic observations by McBirney et al. (1987). They present SiO_2
336 contents from 63.25 to 76.87 wt. % and the lowest MgO contents (0.05 – 2.49 wt. %). They do
337 present variable contents in most oxides (e.g., Na_2O, Al_2O_3, K_2O, P_2O_5), apart from decreasing
338 MgO, Ti_2O, CaO and FeO with increasing SiO_2 content (Appendix 1 - Fig. 1). Whole rock trace
339 element abundances of xenolith and basement rocks are also quite variable, but they show negative
340 correlations with increasing SiO_2 (Appendix 1 - Fig. 2); they also display closer values to the bulk
341 continental crust compositions for Th/Nb, Ce/Pb and Nb/U trace element ratios (Rudnick and Gao,
342 2003). On a N-MORB-normalized (Sun and McDonough, 1989) multi-element diagram (Appendix
343 1 - Fig. 3), the samples share some features with the lava flows and tephras, including the positive
344 K and Pb anomalies, and the Nb-Ta, La-Ce, P and Ti depletions. The most pronounced differences
345 are the positive U and Th anomalies and the varied Rb-Ba and Sr contents.
346
347 **4.2.2 Isotopic data**
348 The Sr-Nd-Pb-Os isotope data obtained for lavas, tephras, xenoliths and basement rocks are
349 plotted in Figure 6 and 7. Paricutin lavas and tephras display significant ranges in $^{87}Sr/^{86}Sr$,
350 $^{143}Nd/^{144}Nd$, and Pb isotopes but exhibit a relatively limited range in $^{187}Os/^{188}Os$ (Fig. 6). $^{87}Sr/^{86}Sr$
351 ranges from 0.70380 to 0.70415, $^{143}Nd/^{144}Nd$ from 0.512845 to 0.512733. Moreover, all samples
352 define a positive trend in Pb-Pb isotope systems ($^{206}Pb/^{204}Pb$ from 18.608 to 18.713; $^{207}Pb/^{204}Pb$
353 from 15.559 to 15.624; $^{208}Pb/^{204}Pb$ from 38.28 to 38.56). Xenoliths and basement rocks show more
354 radiogenic Sr and Pb, and less radiogenic Nd values than lavas and tephras from Paricutin. The

$^{87}Sr/^{86}Sr$ isotopic composition ranges from 0.70429 to 0.70853, $^{143}Nd/^{144}Nd$ from 0.512570 to 0.512782, $^{206}Pb/^{204}Pb$ from 18.675 to 19.525, $^{207}Pb/^{204}Pb$ from 15.594 to 15.648 and $^{208}Pb/^{204}Pb$ from 38.50 to 39.01 (Fig. 7). Overall as the eruption progressed with time, lava and tephra samples display more radiogenic $^{87}Sr/^{86}Sr$, $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$, and less radiogenic $^{143}Nd/^{144}Nd$, approximately trending towards the compositions of the xenoliths and local granitic basement, but opposite to the Mexican lower crustal xenoliths (Fig. 7).

The samples analyzed for Os isotopes include 11 lavas, 3 tephras, 5 xenoliths and 3 basement rocks, that span the geochemical variability of Paricutin products (Table 1 of the supplementary material). Lava and tephra $^{187}Os/^{188}Os$ ratios range from 0.12582 to 0.15553 over a range in Os concentrations from 2 to 37 ppt (Fig. 6). Xenolith and basement rocks exhibit large variations in $^{187}Os/^{188}Os$, ranging from 0.12811 to 1.41408 with a range in Os concentrations from 0.5 to 27 ppt. All samples except PAR-1215 and PAR-1213 and one xenolith (W-47-11) are characterized by more radiogenic $^{187}Os/^{188}Os$ than the primitive upper mantle values (~ 0.1296; Meisel et al., 1996).

These new Sr, Nd, Pb and Os isotopic compositions are similar to those determined in previous studies for Paricutin volcano (e.g., Cebriá et al. 2011; McBirney et al. 1987; Reid, 1979), and fall within the isotopic trend of the High-MgO Jorullo samples (Fig. 6) and within the range of the TMVB (Luhr et al., 2006; Gómez Tuena et al. 2007) (Fig. 7). They are compositionally intermediate between local subducting terrigenous and pelagic sediments from DSDP Site 487, and the subducting altered oceanic crust (AOC) and East Pacific Rise (EPR) basalts (Fig. 7).

5. DISCCUSION

5.1 Crustal assimilation vs. fractional crystallization

Previous petrological, geochemical and isotopic studies have proposed that crustal contamination is an important process involved in the petrogenesis of Paricutin magmas (e.g., Cebriá et al., 2011; Erlund et al., 2010; Luhr, 2001; McBirney et al., 1987; Rowe et al., 2011; Wilcox, 1954), reinforcing the idea of Paricutin as the classic example of assimilation coupled with fractional crystallization in a subduction calc-alkaline suite. However, some aspects of the temporal-compositional changes and the observed isotopic variations of our new data could potentially be indicative of crustal assimilation by mantle melts, whereas others are more prone to a mantle affected by subduction-related metasomatism. Accordingly, both hypotheses are explored below.

The potential effect of crustal assimilation can be assessed by the relationship of isotopic signatures and highly incompatible trace element ratios with indices of fractionation, as geochemical compositions resulting from crustal contamination will imprint enriched trace element and isotopic signatures on the magmas. In Paricutin, it is clear the existence of a negative correlation of $^{87}Sr/^{86}Sr$ and $^{143}Nd/^{144}Nd$, the very low Ce/Pb and Nb/U ratios relative to MORB and OIB, the suprachondritic $^{187}Os/^{188}Os$ ratios, and the correlation between Sr-Nd-Pb isotopic systems with indices of differentiation such as SiO_2 or MgO (see Figs. 3, 4 and 6). All these behaviors are expected if progressive assimilation fractional crystallization (AFC) played a role in the evolution of Paricutin magmas. However, these characteristics can be also explained by alternative processes (see discussion below). For example, the low Ce/Pb and Nb/U ratios requires crustal involvement in the petrogenesis of the magmas, whether by shallow level contamination or by crustal recycling into the mantle. In addition, although McBirney et al. (1987) and Cebriá et al. (2011) modelled the AFC process involving the assimilation of a hypothetical crustal contaminant (up to 40% of granite-derived melts), which composition is quite far from the basement and/or the xenolith rocks analyzed in this study, the Paricutin samples do not trend towards these local granitic rocks in Sr and Nd isotope space as observed in Figure 7.

406

407 Os isotopes are one of the most sensitive isotopic tracers of crustal assimilation, due to the
408 order of magnitude difference between the Os isotope signatures of crustal versus mantle-derived
409 rocks (e.g., Widom and Shirey, 1996). Previous studies of relatively mafic lavas from the TMVB
410 have suggested that lower crustal assimilation may play a role in their petrogenesis, based on a
411 correlation of $^{187}Os/^{188}Os$ with MgO and Ni (Chesley et al., 2002; Lassiter and Luhr, 2001). Rather,
412 the Paricutin samples have relatively low and constant $^{187}Os/^{188}Os$ compared to other MGVF
413 samples (Fig. 6e and 6f), and the weak positive correlation of $^{187}Os/^{188}Os$ with $^{206}Pb/^{204}Pb$ (Fig. 7e)
414 is opposite that expected for assimilation of lower crust, and potentially just consistent only with
415 involvement of upper crust components. A simple mixing model to show the effects of crustal
416 assimilation in Os isotopes starting from the Paricutin most primitive magma, shows that the
417 assimilation of up to 40% of basement rocks as interpreted by Cebriá et al. (2011) and McBiney et
418 al. (1987) would generate higher radiogenic $^{187}Os/^{188}Os$ ratios than those observed in Paricutin
419 samples (Fig. 8a; see details in figure caption). Additionally, Os isotopes do correlate with trace
420 trace element abundances or ratios (e.g., Ce/Pb and Sr/Nd) being diagnostic of slab input.
421

422 The lava samples in this study do not exhibit a correlation between $^{187}Os/^{188}Os$ and MgO,
423 Os or Ni (Fig. 6f, 8a and 8b5); however, the samples PAR-1212 and PAR-1205, show 0.15553 and
424 0.15511 $^{187}Os/^{188}Os$ ratios respectively, that could point to a minor crustal contamination imprint.
425 AFC modeling using Paricutin mean basement rock composition as assimilant and Paricutin most
426 mafic composition as staring point, shows that the Os isotopic composition of these two samples
427 can be reproduced with <20% of AFC with a very low rate of assimilated/crystalized melt (r= 0.2;
428 Fig. 8b). This means that no crustal assimilation or very minor is involved in the petrogenesis of
429 Paricutin magmas. Therefore, given the apparent conflicts with the involvement of major crustal
430 assimilation in the petrogenesis of Paricutin magmas, alternative explanations are considered below.
431

Major and trace element trends of Paricutin lavas and tephra samples are generally compatible with a fractional crystallization process not involving crustal assimilation. Marked decreases in MgO, FeO, CaO, Ni, Cr and Sc with increasing SiO_2 (Figs. 4 and 5) are consistent with fractionation of olivine, orthopyroxene and clinopyroxene as the eruption progressed (Figs. 4 and 5). In addition, the change from increasing to decreasing TiO_2 at SiO_2 ~56%, indicates that Fe-Ti oxides became part of the fractionating mineral assemblage at that point (Cebriá et al. 2011). The lack of a clear decrease in Al_2O_3 or Sr with increasing SiO2 (Fig. 3), and the lack of negative Eu anomalies (Fig. 5), suggest that plagioclase was not a major phase in the fractionating mineral assemblage. This statement is in accordance with our petrographic observations, and it was previously noted by Wilcox (1954) and McBirney et al. (1987), being also frequent in other volcanoes of the MGVF (e.g., Blatter and Carmichael, 1998; Lange and Carmichael, 1990). The increase in highly incompatible element abundances such as La, Ba, Nb, Zr, Rb with increasing SiO_2 is also consistent with closed system fractional crystallization of one or more similar parental magmas.

METLS modeling can further constrain the fractional crystallization process operating in the Paricutin in terms of pressure, temperature, fO_2 and fractionating mineral assemblages. The major element model was carried out using the rhyolite-MELTS v.1.2.0. algorithm (Ghiorso and Gualda, 2015; Gualda et al., 2012) which better characterizes melts containing dissolved H_2O. Sample PAR-1537 is considered to represent the naturally occurring major element composition closest to a primary magma (7.47 wt. % MgO and 180 ppm Ni) and is used as the starting composition for the model. One polybaric and three isobaric fractional crystallization models have been calculated at different initial pressures (as indicated for each model in Fig. 9), with cooling steps of 5 ºC, 2.5wt. % water content and oxygen fugacity fixed relative to the QFM+1 (quartz-fayalite-magnetite) buffer. The water content was chosen in accordance to the range of total water contents in Paricutin glass/melt inclusions (1.8-4.2 wt.%; Erlund et al. 2010; Luhr, 2001) that

458 brackets the estimate by Eggler (1972) of 2.2 ± 0.5 wt.% based on phase-equilibrium experiments.
459 The oxygen fugacity buffer was selected based on the comparison carried out by Bannister et al.
460 (1998) among the different log fO_2formulations (Kilinc et al., 1983; O'Neill and Wall 1987; Wood,
461 1991). As observed in Fig. 9, the major element compositions of Paricutin lavas and tephras are best
462 modeled by a polybaric fractionation process starting at 300 MPa (ΔP= 45; $\Delta T/\Delta P$=9), at which
463 conditions the liquidus temperature is 1176°C. The residual melt compositions obtained from this
464 polybaric fractional crystallization model closely reproduce the compositions of Paricutin magmas,
465 with the following fractionated phases: olivine, spinel, orthopyroxene, clinopyroxene, feldspars, and
466 minor Fe-Ti oxides. The different rhyolite-MELTS models shown in Fig. 9 demonstrate that a
467 change in the initial conditions of the model (e.g., P and T) cannot account for the slightly distinct
468 Na_2O and K_2O contents of Paricutin samples; these anomalous values might be explained by the
469 lack of feldspars within the fractionating mineral assemblage in Paricutin, which are included in the
470 rhyolite-MELTS models. Accordingly, the evolution of Paricutin lavas and tephras seems to be
471 primarily controlled by fractional crystallization of cogenetic parental magmas, and we consider the
472 chemical and isotopic variations more likely to be a result of mantle source heterogeneity, for which
473 we explore the petrogenetic implications below.
474
475 **5.2 Mantle Source Heterogeneity and rapid fractional crystallization: the new hypothesis to**
476 **explain Paricutin's evolution**
477 The impact of slab components on arc magmas and their significance for arc petrogenesis
478 and subduction cycling are on the cutting edge of arc research (e.g., Gómez-Tuena et al., 2014;
479 Hacker et al., 2011; Plank, 2004; Straub et al., 2015; Tatsumi and Kogiso, 2003), being also
480 intensely debated in the TMVB, where much recent progress has been made. As noted by Straub et
481 al. (2015), several studies suggest that andesites and dacites evolve from primary basaltic mantle
482 melt by interaction with the thick continental basement (i.e., fractional crystallization coupled with
483 crustal assimilation; e.g., Agustín-Flores et al., 2011; Marquez et al., 1999; Verma, 1999), whereas

other authors more recently have proposed that the entire range of central TMVB magmas (basaltic to dacitic and even rhyolitic in composition) are near-primary melts from a subduction-modified mantle that pass through the crustal basement nearly unaffected (Gómez-Tuena et al., 2007a, 2008; Rasoazanampanary et al., 2016; Siebe et al., 2004; Straub et al., 2008, 2013;)

Paricutin lavas and tephra define a clear trend in $^{87}Sr/^{86}Sr$ vs. $^{143}Nd/^{144}Nd$ and $^{206}Pb/^{204}Pb$ space and $^{206}Pb/^{204}Pb$ vs. $^{207}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$ (Fig. 6). These observed trends indicate that at least two components are involved in Paricutin magma petrogenesis. The defined Sr-Nd-Pb isotope range of the lavas and tephra samples are more limited than that of the crustal xenoliths and basement samples, and they are well bracketed by slab components such as the altered oceanic crust (AOC) and trench sediment components (Fig. 7). Moreover, the trace element characteristics of Paricutin samples, including LILE enrichments and HFSE depletions (Fig. 5), strongly suggest the involvement of subduction-related hydrous fluid in their petrogenesis. We therefore explore below whether Paricutin magmas could be originated by addition of subduction components to a homogeneous Mexican pre-subduction mantle wedge.

The pre-subduction mantle beneath the TMVB (without subduction influence) is interpreted to be similar to the mantle source of the mafic alkaline volcanism that occurs behind the arc in the Northern Mexican Extensional Province (named NMEP-type mantle by Luhr et al., 2006; Fig. 8). According to Straub et al. (2015), this pre-subduction mantle is highly depleted through serial melting processes that are triggered by the continuous hydrous flux from slab since the arc became active in the Pliocene. Therefore, as the best representative of this pre-subduction mantle wedge we have selected the isotopic composition of the “Old Texcal Flow”, which is a monogenetic basalt flow that has been interpreted as a magma with the least slab influence in central Mexico (Straub et al., 2013), but with a depleted mantle (DMM) trace element composition as suggested by many previous studies (e.g. Ferrari et al., 2001; Petrone et al., 2003; Petrone and Ferrari, 2008; Orozoco et

al., 2007; Johnson et al., 2009; see Table 2 of the supplementary material). The subduction components dredged from the DSDP site 487 on the incoming Cocos Plate 487 are assumed to represent the materials being subducted beneath the TMVB (e.g., Cai et al., 2014; Gómez-Tuena et al., 2003; Gómez-Tuena et al., 2007). These include ~105 m of primarily terrigenous sediments, overlying ~70 m of late Miocene to Pliocene pelagic sediments, which in turn overlies basaltic oceanic crust (Verma, 2000). The composition of the subducted AOC was recalculated by Straub et al. (2015) based on its age of ~5-6 million years older than the oceanic crust at the current trench based on the convergence rate of 47 km/Ma and the arc-trench gap of 360 km (e.g., Manea and Manea, 2011) (see Table 2 of the supplementary material). The two types of sediment were analyzed for major and trace element abundances and Sr-Nd-Pb isotopes by Verma (2000), LaGatta (2003) and Cai et al. (2014). The mean composition of these sediments used in the models presented below are summarized in Table 2 of the supplementary material.

Paricutin samples generally have higher $^{87}Sr/^{86}Sr$ and lower $^{143}Nd/^{144}Nd$ than the NMEP (Fig. 8c), suggesting that Paricutin magmas could potentially be produced by addition of just one subduction components to the mantle wedge; however, in order to reproduce the $^{87}Sr/^{86}Sr$ - $^{206}Pb/^{204}Pb$ isotopic trend defined by Paricutin samples (Fig. 8d) it is needed the existence of two subduction components as also proposed for the petrogenesis of Jorullo magmas (Rasoazanampanary et al., 2016). In other words, we need the input of one subduction component (SC1) characterized by higher $^{87}Sr/^{86}Sr$, and lower $^{143}Nd/^{144}Nd$ and $^{206}Pb/^{204}Pb$ into the mantle wedge, and the subsequent addition of a second subduction component (SC2) with higher $^{87}Sr/^{86}Sr$ and $^{206}Pb/^{204}Pb$, and lower $^{143}Nd/^{144}Nd$ into the already metasomatized mantle (Fig. 8e and 8f). Because the AOC is rather unradiogenic in $^{87}Sr/^{86}Sr$ and highly radiogenic in $^{143}Nd/^{144}Nd$, a high proportion of sediment relative to AOC is required to produce subduction components sufficiently high in $^{87}Sr/^{86}Sr$ and low in $^{143}Nd/^{144}Nd$ to generate the isotopic signatures of Paricutin samples (Fig. 8c). However, terrigenous and pelagic sediments have similar $^{87}Sr/^{86}Sr$ and $^{143}Nd/^{144}Nd$, but

536 very distinct $^{206}Pb/^{204}Pb$ (Fig. 8d), and therefore, Pb isotope signatures will be strongly controlled by
537 the type of sediment involved.
538
539 In order to investigate the amount and relative importance of the subducted materials that
540 might contribute to the source of the Paricutin magmas, we have conducted modeling of trace
541 element and isotope data (Fig. 8c-d). In the modeling we have estimated the compositions of
542 possible components that could be released from the subducting Cocos plate (described above),
543 considering the experimentally determined mobilities for trace elements during subduction
544 dehydration. The trace element composition of oceanic crust-derived fluid was calculated by using
545 the mobility data of Kessel et al. (2005) at 800-900 °C and 4 GPa, and for sediment-derived fluid
546 we have used the D values at 700°C from Johnson and Plank (1999). The total extraction of hydrous
547 fluid during dehydration was assumed to be 1.5 wt.% in both oceanic crust and sediment. All
548 parameters used in the model present in Fig. 8 c-f are given in Table 2 of the supplementary
549 material. In order to reproduce the Paricutin sample trend in the Sr-Nd-Pb isotope space, we need
550 mixing between the mantle wedge and fluid derived from a first subducting slab (SC1) composed of
551 ~70% sediment (85:15 terrigenous to pelagic) and ~30% AOC to produce a metasomatized mantle
552 (~4% subduction component) that can be subsequently metasomatized (<5%) by a second slab
553 (SC2) composed of ~99% sediment (95:5 terrigenous to pelagic) and ~1% AOC (see Fig. 8e and
554 8f). Moreover, the proposed model for Paricutin magmas originated by background mantle
555 metasomatized by subduction components would be in accordance to the unradiogenic Os
556 signatures presented by most Paricutin samples, because Os is not significantly lost from the slab
557 during dehydration (Becker, 2000).
558 In addition, it is noticeable in Fig. 8c and 8d that slightly variations in the composition of
559 the subduction components SC1 and SC2 could explain the existing isotopic variability in the Sr-
560 Nd-Pb isotopic space of the those TMVB magmas not affected by crustal assimilation.
561

562 **5.3 How this model correlates with previous studies on Paricutin volcano?**

563 As summarized in section 2, all previous studies of Paricutin volcano dealing with the
564 geochemical variation of Paricutin products with time (i.e., Cebriá et al., 2011; Erlund et al., 2010;
565 Luhr, 2001; McBirney et al., 1987; Rowe et al., 2011; Wilcox, 1954) proposed assimilation together
566 with fractional crystallization as the main magmatic processes controlling the evolution of the
567 magmas. These authors indicated the presence of a strong compositional shift after 1947, attributed
568 to the increased importance of crustal contamination, that has been proved in this work as inexistent
569 thanks to a detailed sampling of the lavas and tephras in a well constrained temporal framework that
570 prevented biased sampling (Fig. 2). In addition, we have merged all the previous analyzed data with
571 our own results, and we have proposed an alternative model to explain the same geochemical trend
572 in major and trace elements, and isotopes.
573
574 Luhr (2001) studied olivine-hosted glass inclusions in four tephra samples from May 1943
575 to March 1948 and proposed an additional shift in magma composition in July 1943, dividing the
576 eruption in three stages. The analysis of the melt inclusions by Fourier transform infrared
577 spectroscopy (FTIR) allowed the estimation of the total water content from 1.8 to 4 wt. %, and the
578 calculation of pressures of entrapment from 1 to 2.45 kbar that correlate to depths from 1.3 to 9.6
579 km. These calculated water contents and pressures are in accordance to the parameters we used in
580 our rhyolite-MELTS model. Erlund et al. (2010) studied the complete tephra record for the eruption
581 placed in a temporal framework by comparing both bulk tephra and olivine phenocryst
582 compositions to dated samples of lava and tephra, and proposed syn-eruptive assimilation of wall
583 rock in a shallow complex of dikes. Afterwards, Rowe et al. (2011) studied major and trace element
584 compositions of olivine- and orthopyroxene-hosted melt inclusions, and they tried to integrate those
585 data with new trace element analyses of the erupted lavas and data for entrained xenoliths and
586 xenolith glasses to provide a more comprehensive evaluation of the evolution of Paricutin volcano.
587 They found that melt inclusion compositions are bimodal with an undegassed, low-Si population

588 similar in composition to the whole-rock samples and a degassed, high-Si population recording late-
589 stage degassing and crystallization of the magma. Melt inclusions and phenocrysts in crustally
590 contaminated magmas should record a progression from a primitive uncontaminated magma toward
591 a contaminated more evolved magma. However, Rowe et al. (2011) noted that this progressive
592 contamination or mixing of magmas is not recorded in melt inclusions hosted in both olivine and/or
593 orthopyroxene at Paricutin. In order to explain this situation, they suggested that contamination in
594 the Paricutin magmatic system is decoupled from crystallization, or at least from the crystallization
595 recorded by melt inclusions in the lavas. One mechanism they proposed to explain this apparent
596 decoupling is that the thermal conditions required for inclusion entrapment were not favorable to
597 coupled crustal assimilation and fractional crystallization, and therefore, Rowe et al. (2011)
598 proposed that melt inclusions in short-lived, small-volume magmatic systems might provide a
599 biased sampling of magma chamber processes and melt evolution. In contrast, they also indicated
600 that if the melt inclusion compositions record a representative sampling of magma chamber
601 processes, none of the previous models for magma chamber development and melt evolution at
602 Paricutin would be appropriate; in accordance, we have explored an alternative model that is in
603 accordance to the melt inclusion results they all obtained.
604
605 The calculation of the volume of lava emitted by Paricutin volcano was carried out by
606 Larrea et al. (2017). Notable characteristics of the Paricutin eruption include an erratic variation in
607 effusion rate with an overall increase in the effective viscosity of the magma, and a variation in the
608 importance of effusive relative to explosive activity throughout the nine years of eruption,
609 accompanied by the progressive change in the bulk magma composition that has been studied in
610 this work. Larrea et al. (2017) indicated that magma pre-eruptive volatile content and the degassing
611 mechanism were the key factors controlling the explosive activity at Paricutin volcano. The
612 termination of the eruption was not exclusively related to high effective viscosity, but rather was a
613 combination of limited supply of magma and progressive volatile loss, consistent with the overall

614 decrease in effusion rate in the last eruptive phases favoring stalling, cooling, crystallization and an
615 increase in density of the residual magma, which ultimately became uneruptible. However, in June
616 2006, a seismic swarm was recorded 15 km from the summit of cone. More than 700 earthquakes
617 with magnitude (M_L) exceeding 2.4 were located, being related to a dike emplacement event
618 (Gardine et al. 2011), indicating that magmatic activity in the area is still ongoing.
619
620 **5.4 Magma generation, evolution and eruption, comparison with Jorullo volcano**
621 Paricutin has been traditionally considered a classical example of magma differentiation by
622 progressive crustal assimilation and fractional crystallization. However, our major and trace
623 element and multi-isotopic study of the Paricutin volcanic products (lava and tephra) indicates that
624 the temporal-compositional variation identified within the 9-year monogenetic eruption can be
625 attributed to changes in the mantle source over time together with fractional crystallization as the
626 main processes controlling the evolution of the magmas.
627
628 Based on our mixing models, we suggest that Paricutin magmas are derived from melting of
629 a metasomatized mantle source produced by a multi-step subduction modification of an NMEP-type
630 mantle wedge, as illustrated in Fig 8. The NMEP-type magma was advected by corner flow into the
631 sub-arc environment and subsequently infiltrated by a H_2O-rich component (SC1) derived through
632 dehydration of the subducting Cocos plate (terrigenous sediment > pelagic sediment >AOC), which
633 produced a metasomatized mantle. Influx of a second subduction component (SC2), composed of
634 mostly terrigenous sediment-derived fluid was next added to the metasomatized source (< 5%) to
635 produce the source of the Paricutin magmas. As pointed by Rasoazanampanary et al. (2016) in
636 Jorullo volcano, the difference in the relative proportions of the sediment types in SC1 versus SC2
637 might be due to the heterogeneity in the sediment pile and/or to incomplete homogenization of a
638 heterogeneous sediment-derived fluid, or due to the existence of a horst and graben structure in the
639 subducting plate, that could lead to variability in sediment proportions according to Patino et al.

(2000). The pressure of melt extraction has been calculated using the silica-activity barometer of Putirka (2008) and the mantle potential temperatures of Putirka et al. (2007). The calculations indicate that Paricutin magmas were extracted at pressures of ~1.3-1.6 GPa corresponding to depths of 50-60 km (Table 4 of the supplementary material).

Paricutin whole-rock major elements compositions progressively evolve from basaltic andesite to andesite, forming a liquid line of descent that might be indicative of crystal fractionation as a key process during the differentiation of the magmas. Fractional crystallization processes have been modelled using rhyolite-MELTS to explain the major element variation presented by Paricutin samples. A polybaric fractional crystallization process starting at 300 MPa, with 2.5 wt. % H_2O, oxygen fugacity fixed relative to the QFM+1 buffer and olivine, spinel, orthopyroxene and clinopyroxene as the fractionating mineral assemblage, better fits the liquid line of descent formed by Paricutin samples. In addition, no petrological evidence for crustal assimilation has been found (no xenocrysts are present), and all Paricutin eruptive products have low phenocryst contents (< 10 volume %); the present mineral phases change with time and host composition: early basaltic andesite has phenocrysts of olivine, and orthopyroxene and clinopyroxene appear as the silica content of the whole-rock increases. Therefore, the observed Paricutin geochemical variation with time might be explained by melts that rose from depth and underwent rapid fractionation without losing the total connection with the mantle source area. Regardless, the data obtained in this study suggest that limited to no crustal assimilation was involved in the differentiation of Paricutin magmas despite the presence of crustal xenoliths in some lavas as described by McBirney et al. (1987). As future work, we have started a detailed petrological study of the deposits to estimate the magma residence times and processes that lead to the chemically zoned eruption.

As pointed by McGee et al. (2013) and McGee et al. (2015) high-resolution sampling in monogenetic volcanoes and volcanic fields has the potential to reveal fine-scale heterogeneity of the

mantle, because physical parameters such as eruptive volume and eruption style are inherently controlled by the melting of a heterogeneous mantle, which causes melts to behave independently despite their close spatial and temporal association due to their distinct segregation and ascent mechanisms. Together, this detailed study of Paricutin comprises the first comprehensive documentation of the temporal-volumetric-chemical evolution of the complete Paricutin eruptive cycle, providing a new insight into the origin of the chemical variation observed in this monogenetic eruption. Our results suggest that the mantle is heterogeneous on a small spatial scale beneath the volcano, and that two distinct slab-derived fluid fluxes interacted with the mantle wedge to produce the Paricutin metasomatized mantle source. This process of magma genesis and evolution controlled by mantle source heterogeneity together with fractional crystallization has been also proposed as the driving mechanism in the evolution of other monogenetic volcanoes in the MGVF and elsewhere. For example, the study of the neighbor historic Jorullo volcano by Rasoazanampanary et al. (2016) revealed that two distinct magma batches with similar initial major and trace element compositions, evolved separately within a complex magmatic plumbing system that led to sequentially more evolved magmas erupted with time from a progressively less metasomatized source. Therefore, the detailed study of the two well-constrained eruption sequences of Paricutin and Jorullo allowed to reinterpret the processes involved in the geochemical changes with the progression of the eruptions, no longer representing possible endmembers in inferred extents of crustal interaction as previously suggested by other authors. This study has demonstrated the importance of combining the study of major and trace elements together with isotopes, not just including the traditional Sr-Nd-Pb systems, but also Os isotopes as a good tracer of crustal contamination. Accordingly, this study opens the possibility to revisit other volcanic systems that have been traditionally linked to crustal contamination to fully re-evaluate the causes of their geochemical and isotopic variability through time contributing to a better understating of the spatio-temporal variability in the sources of the magmatism within the TMVB.

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1004

1005 **FIGURE CAPTIONS**

1006 **Fig. 1. a)** General geotectonic map of Mexico with the location of the Mexican provinces (solid
1007 black lines) and the Trans-Mexican Volcanic Belt (TMVB; gray polygon), Mexico City and
1008 Paricutin volcano (red triangle). **b)** Simplified regional tectonic map of the TMVB with volcanism
1009 from 0 to 6 Ma shown in gray (modified from Pasquarè et al., 1991) and the location of the historic
1010 Paricutin and Jorullo eruptions. The Michoacán–Guanajuato Volcanic Field (MGVF; Hasenaka &
1011 Carmichael, 1985), EPR: East Pacific Rise. The black contours are the depth to the subducted slab
1012 in kilometers (from Pardo and Suárez, 1995). **c)** Aerial photograph of the Paricutin volcano
1013 including the sample locations from this study: lavas (circle) and tephras (square); see
1014 supplementary material Table 1 for sample location coordinates. This map was created using
1015 ArcGIS® software by Esri. ArcGIS® and ArcMap™.
1016

1017 **Fig. 2.** Temporal-compositional variations in Paricutin magmas. Variation in SiO_2, K_2O, $^{87}Sr/^{86}Sr$,
1018 $^{143}Nd/^{144}Nd$ and $^{206}Pb/^{204}Pb$ content of the lavas and tephras throughout the eruption. The three

eruptive phases described by Luhr (2001) and Erlund et al. (2010) are shown based on the geochemical limits defined by Rowe et al. (2011). Circles represent lava samples and squares tephra samples; big white symbols are samples analyzed in this study and gray small symbols are literature data from Cebriá et al. (2011), Erlund et al. (2010), McBirney et al. (1987), Luhr (2001), Reid (1979), Rowe et al. (2011), Wilcox (1954). These color and symbol designations are used for all following figures.

Fig. 3. Whole rock major element vs. SiO_2 (wt.%) for the Paricutin lavas and tephras analyzed in this study. Samples from literature (gray dots) same as in Fig. 2.

Fig. 4. Trace element abundances and trace elements ratios vs. SiO_2 (wt.%) for the Paricutin lavas and tephras analyzed in this study. Samples from literature (gray dots) same as in Fig. 2. Bulk continental crust values shown from Rudnick and Gao (2003).

Fig. 5. N-MORB-normalized (Sun and McDonough, 1989) multi-element diagrams for Paricutin lavas and tephras.

Fig. 6. Isotope variation diagrams for Paricutin lavas and tephras. Jorullo volcano High-MgO (purple diamonds) and Low-MgO (blue diamonds) samples from Rasoazanampanary et al. (2016) are shown for comparison. Samples from literature (gray dots) from Cebriá et al. (2011), McBirney et al. (1987) and Reid (1979). Purple arrow and gray arrow show the geochemical trend described by basement rocks (B.R.) and xenoliths (Xen.), respectively.

Fig. 7. Isotope variation diagrams for Paricutin lavas and tephras samples and literature data for the TMVB (gray dots; Gómez-Tuena et al. (2007) and Luhr et al. (2006)) for comparison. Potential contaminants of Paricutin magmas are shown for comparison: Paricutin basement granitoid (purple

star; this study), Paricutin xenoliths (black star; this study), La Huacana granitoid (blue star; Rasoazanampanary et al., 2016), Acapulco granodiorite (green star; Straub et al. 2015) and lower crust xenoliths (green triangle; Lawlor et al. (1999) and Schaaf et al. (1994)). Also shown are: terrigenous sediment (orange cross) and pelagic sediment (yellow cross) from LaGatta (2003), and the average altered oceanic crust (blue cross) from Verma (2000), and data from the East Pacific Rise (EPR; red field) from "ready-to-use datasets" at PetDB (http://www.earthchem.org/petdb). Purple arrow and gray arrow show the geochemical trend described by basement rocks (B.R.) and xenoliths (Xen.), respectively.

Fig. 8. a) $^{187}Os/^{188}Os$ vs. Os for Paricutin samples and Jorullo samples for comparison (Rasoazanampanary et al., 2016); the red solid curve represents the mixing between the most mafic Paricutin sample (starting point) and the Paricutin basement rocks, to show the geochemical effect of crustal assimilation by the most mafic Paricutin magmas; tick marks show the relative proportions of the mixing components. Model parameters are provided in Table 2 of the supplementary material. **b)** $^{187}Os/^{188}Os$ vs. Ni for Paricutin and Jorullo samples; the red dashed curve represents an assimilation fractional crystallization model (AFC) between the most mafic Paricutin sample (starting point) and the Paricutin basement composition. Tick marks represent percentage increments of assimilation plus fractional crystallization at a ratio of assimilation/crystallization (r value) of 0.2. Primitive upper mantle (PUM; Meisel et al., 1996). Model parameters are provided in Table 3 of the supplementary material. **c)** $^{87}Sr/^{86}Sr$ vs. $^{143}Nd/^{144}Nd$ and **d)** $^{87}Sr/^{86}Sr$ vs. $^{206}Pb/^{204}Pb$ showing mixing between the mantle wedge (Old Texcal Flow from Straub et al., 2015) and potential subduction components with variable mixtures of altered oceanic crust (AOC; Cenozoic MORB from Straub et al., 2015) and pelagic and terrigenous sediment derived fluids (LaGatta, 2003). The black dashed curves in the diagrams indicate mixing between sediment-derived fluid (with 100% of terrigenous and 100% pelagic sediment) and AOC-derived fluids, which comprise the most extreme possible subduction components that could be added to the

mantle wedge source. Tick marks show the relative proportions of the mixing components. See detailed explanation of the red mixing solid curves in e) and f). **e)** $^{87}Sr/^{86}Sr$ vs. $^{143}Nd/^{144}Nd$ and **f)** $^{87}Sr/^{86}Sr$ vs. $^{206}Pb/^{204}Pb$ isotopic models to account for the compositional variation at Paricutin, involving a mantle wedge and two slab components SC1 and SC2. The triangles represent the two different slab components, SC1 and SC2, that best reproduce Paricutin isotopic variability. The red curves represent a mixing model of the mantle wedge plus 4% subduction fluid SC1 derived from 70% sediment (85:15 terrigenous:pelagic) and 30% AOC, and a subsequent addition of up to 5% of subduction fluid SC2 derived from 99% sediment (95:5 terrigenous:pelagic) and 1% AOC. For all the above, model parameters are provided in Table 2 of the supplementary material, and tick marks show the relative proportions of the mixing components.

Fig. 9. Major element concentrations versus MgO (wt. %) for the Paricutin studied lavas and tephras. Curves represent the evolution paths of residual melts modeled using Rhyolite-MELTS (Gualda et al. 2012; Ghiorso and Gualda, 2015). Polybaric (Polyb.) and isobaric (Isob.) fractional crystallization models were carried out at different initial pressures (as indicated for each model), with cooling steps of 5 °C, initial water content of 2.5%, oxygen fugacity fixed relative to the QFM+1 buffer, and using PAR-1537 (this study) as the initial composition.

APPENDIX

APPENDIX-1 Fig. 1. Whole rock major element vs. SiO_2 (wt.%) for the Paricutin lavas and tephras, xenoliths and basement rocks analyzed in this study. Gray small symbols are literature data from Cebriá et al. (2011), Erlund et al. (2010), McBirney et al. (1987), Luhr (2001), Reid (1979), Rowe et al. (2011), Wilcox (1954).

APPENDIX-1 Fig. 2. Trace element abundances and trace elements ratios vs. SiO_2 (wt.%) for the Paricutin lavas and tephras, xenoliths and basement rocks analyzed in this study. Samples from

literature (gray dots) same as in Appendix-1 Fig. 1. Bulk continental crust values shown from Rudnick and Gao (2003).

APPENDIX-1 Fig. 3. N-MORB-normalized (Sun and McDonough, 1989) multi-element diagrams for the Paricutin lavas and tephras (gray polygon), xenoliths and basement rocks analyzed in this study.

SUPPLEMENTARY MATERIAL

Table 1. Major element (wt.%), trace element (ppm; Os ppb) and isotope composition of the studied lavas, tephras, xenoliths and basement rocks from Paricutin volcano.

Table 2. Source components and parameters used for the isotope mixing models.

Table 3. Parameters used for the assimilation fractional crystallization (AFC) model.