Appendix – Samples and Methods

This paper present full major and trace element abundance data and Sr and Nd isotope ratios of calc-alkaline and high-Nb basalts to dacites from the Sierra Chichinautzin Volcanic Field and from Popo. Straub et al. (2011) have already presented selected major and trace elements (SiO_2, MgO, Fe_2O_3, Ni, Sr, Nb, La, Gd, Y and Yb) and Nd isotope ratios from 11 samples also reported here (see Table 1). Additional high-Nb arc magmas (Texcal Flow and V. Chichinautzin) are reported by Straub et al. (2013). Samples are denoted for which the $^3He/^4He$ of olivine has been determined (Straub et al., 2011).

Sample freshness and preparation

The volcanic rock samples are typically fist-sized fragments from lava flows, dykes or bombs. Volcanic samples from monogenetic centers are always of impeccable origin with no, or negligible, traces of alteration. The loss on ignition (LOI) was measured on samples at Harvard and at WSU was always inconspicuous, and mostly around zero, which is consistent with the observed freshness of the samples. The exceptions are three samples from the oldest Popocatepetl series that have an estimated age of 200,000 to 600,000 yrs. While these samples are visually fresh, three of them have significantly lower sums of oxide (96.1-97.4%). Presumably, these samples are altered, despite they are otherwise inconspicuous in major and trace elements, and radiogenic isotopes.

The samples were crushed between steel plates. Rock chips of 4-8 mm size free from alteration were hand-picked under a binocular microscope, washed several times in triple-distilled water and methanol, and dried at 50ºC prior to powdering in an alumina mortar or an alumina shatter box. Sample powders were used for analyses of major and trace elements, and for the ratios of Sr-Nd isotopes.

Analytical methods

Major element analyses at Harvard University (Langmuir laboratory)

Major elements of rock powders were determined either by X-ray fluorescence analysis (XRF) at Washington State University (WSU Geoanalytical Laboratory) or by Directly-Coupled Plasma Spectroscopy (DCP) and Inductively-Coupled Plasma mass spectrometry (ICPMS; P only) at Harvard University; analyst: SM Straub). Methods as well as accuracy and precision are those reported by Straub et al. (2008; 2011; 2013).

XRF major element analyses followed the methods reported by Johnson et al. (1999). Measurements were carried out between 2007 and 2009 using a ThermoARL Advant'XP+ sequential X-ray fluorescence spectrometer. Sample powders were re-ground to a very fine powder which were weighted with pure dilithium tetraborate flux (Li_2B4O_7) (2:1 flux:rock), and fused at 1000°C. The bead was reground, refused, polished on diamond laps to provide a smooth flat analysis surface, and washed and rinsed in alcohol prior to analysis. Calibration is based on international rocks standardsPCC-1, BCR-1, BIR-1, DNC-1, W-2, AGV-1, GSP-1, G-2, and STM -1, using the values recommended by Govindaraju (1994). The precision of the XRF analyses, monitored by repeat analyses of two standard samples (BCR-P and GSP-1), is comparable to the Harvard DCP data, based on the data published by the WSU GeoAnalytical Laboratory (2009).

For DCP analyses approximately 0.15 g of powdered sample (or rock standard) was weighed into an alumina crucible and heated in a muffle furnace at 800º-900ºC for 30 min in order to drive off volatiles and oxidize the samples. The loss on ignition (LOI) was determined by re-weighting the crucibles after heating. Sample and standard powders (0.1000 ± 0.0001 g) were weighted with four times the amount of ultra-pure $LiBO_2$ flux into pre-ignited graphite crucibles and thoroughly stirred. The mixture was fused in a muffle furnace at 1050º-1100ºC for 10-15 min and completely dissolved into 50.0 mL of 1 N HNO_3. One milliliter this solution was added to 24.0 mL of a solution containing 3500 ppm Li and 10 ppm Ge (~1:6250 dilution). The solutions were used to obtain simultaneously elements Si, Al, Fe, Mg, Ca, Na, and Ti with a plasma emission spectrometer (Spectrametics, SMI III). Unknowns were analysed simultaneously with Harvard in-house standards MAR and LUM37, and USGS standards NBS688 and RGM1. Data were reduced by blank subtraction, external drift correction and standard calibration using the values of the Langmuir Laboratory at Harvard University for the standard values as of 2005 (Appendix Table 3). Calibrations were strongly linear ($R^2 \geq 0.999$) and sum of oxides were within 1% on average.

The DCP data were obtained between April and June 2005. Precision of the DCP analyses during that period had been monitored by repeat analyses of samples S1 (from V. Chichinautzin) and Popo5 (from Popocateptl). Standard deviation and RSD% listed in Appendix Table 3 are based on n=13 (S1) and n=16 (Popo 5) analyses from 6 different digests and runs between April and September 2005. Precision from these runs, reported as percentage of one standard deviation is ≤1% for SiO_2, Al_2O_3, Fe_2O_3 and Na_2O, and ≤1.5% for TiO_2, MnO, MgO and K_2O. A split of the same powders was analysed for P_2O_5 by ICP-MS methods (see below).

Consistency between Harvard and WSU analyses was tested by analyzing four basaltic to andesite samples by either method in either laboratory. At an origin of zero, all ten major elements have coefficients of correlation >0.999 at average slope close to 1.01±0.01. The data comparability was thus considered to be within the precision of the methods.

Trace element analyses

Abundances of elements were obtained from the same sample powders by ICP-MS methods, either at the Centro de Geociencias (CGEO), Juriquilla/Qro., Universidad Nacional Autónoma de México, Mexico, using a Thermo Series XII instrument (n=27 samples, analyst O. Perez and A. Gomez-Tuena), or at the Department of Earth and Planetary Sciences (Langmuir Laboratory) at Harvard University/Cambridge, USA using a Thermo Series X instrument (12 samples, analyst: SM Straub). The data at the CGEO were obtained in five runs between November 2006 and May 2009, while the data at Harvard were obtained between February and August 2005.

Sample preparation followed methods reported by Mori et al. (2007) (GCEO) and LaGatta (2003) (Harvard). An amount of 0.0500±0.0001 g of rock or standard powder was digested in a $HF:HNO_3$ mixture, and dissolved in HNO_3 prior to dilution by factors of 5000 (Harvard) and 2000 (CGEO). Samples were blank-corrected and corrected for instrumental drift by internal standards (10 ppb Ge; 5 ppb of In, Tm and Bi, and at Harvard also 5 ppb Rh). Data were normalized to abundances of either a highly enriched alkali basalt (sample PS-99-25 from the Palma Sola Massif, Gomez-Tuena et al., 2003), or K1919 (Harvard), that was repeatedly analysed during each run. In either laboratory, the same standard reference materials were used for calibration. These standards were Lamont in-house standard MAR (excluding W), and international standards JB-2 (Geological Survey of Japan), and BHVO-2 and BCR-2 (U.S. Geological Survey) (values are listed in Appendix Table 4). Calibrations were strongly linear, and R^2 ≥0.999 for most elements. Analyses were monitored by repeat analyses of the same samples ASC1_S and S1 (both from V. Chichinautzin) at Harvard and CGEO that were measured during each run. Average abundances and RSD% (based on 1 standard deviation) are based on up to 15 analyses from 8-10 different digests at Harvard and CGEO (Appendix Table 4). About half of ASC1_S analyses and one third of S1 analyses were obtained at CGEO. For all elements, the precision for ASC1_S and S1 is better than 2% (Appendix Table 4). The analytical data are presented in Table 1.

Radiogenic isotopes of Sr and Nd from bulk rock

Isotope ratios of Sr and Nd (n=29 samples) were analysed at the Institute for Earth Sciences (IES), Academia Sinica, Taipei, Taiwan (analysts SMS and GFZ). The data are presented in Table 1.

For isotope analyses, ~100-200 mg of unleached sample powder was digested in a 3:1 HF + HNO$_3$ solution. Sr was first separated using Eichrom Sr Spec resin. Fe was then removed by cation exchange resin AG50x8 (100-200 mesh), prior to separation for Nd using Eichrom Tru-Spec resin followed by an Alpha-hydroxyisobutyric acid (Alpha-HIBA) separation chemistry. Sr and Nd isotope ratios were acquired by thermal ionization mass spectrometry (TIMS). Sr isotope ratios were acquired on a Finnigan® MAT 262 thermal ionization mass spectrometer in the static mode. The measured $^{87}Sr/^{86}Sr$ ratios were corrected for mass-fractionation by normalizing to $^{86}Sr/^{88}Sr$ 0.1194. Multiple analyses of NBS 987 give an external reproducibility for $^{87}Sr/^{86}Sr$ =0.710238 ±19 (27 ppm, 2σ, n=27) for measurements in fall 2007and early winter 2008, and $^{87}Sr/^{86}Sr$ = 0.710257 ±16 (23 ppm, 2σ, n=5) for measurements performed in the winter 2009/10. Samples were adjusted to $^{87}Sr/^{86}Sr$ = 0.710240 for NBS 987. Nd isotope ratios were measured in Nd metal form with a Thermo Triton thermal ionization mass spectrometer in the static mode. $^{143}Nd/^{144}Nd$ ratios were corrected for mass fractionation by normalizing to $^{146}Nd/^{144}Nd$ of 0.72190. Multiple analyses of the JMC standard give an external reproducibility for $^{143}Nd/^{144}Nd$ of 0.511812±9 (18 ppm, 2s; n=32) for measurements from in fall 2007and early winter 2008, and $^{143}Nd/^{144}Nd$ of 0.511818±8 (16 ppm, 2s; n=4) for measurements between in the winter 2009/10. The data were adjusted to the accepted JMC average (0.511833), considered to be equal to the $^{143}Nd/^{144}Nd$ = 0.511860 for the La Jolla standard (van de Flierdt et al., 2004).

Apppendix B: Calculating ^{3}He/^{4}He *vs* SiO$_2$ mixing curves in Fig. 1c

In order to obtain mixing trajectories between mantle melts and crustal material, the He abundances in these components must be known. While this is not straightforward, some simple assumption can be made (e.g. Straub et al., 2013). We assume He in the subarc mantle is similar to the He=1.5 * 10^{-5} cm^3 STP/g in MORB source (Allegre et al., 1986/1987; Sarda and Graham, 1990). This a maximum, as OIB-type mantle sources are considered to have less He [OIB sources He=1.1 * 10^{-10} cm^3 STP/g (Moreira and Sarda, 2000)]. Thus, a 5% mantle melt has He = 3.0 * 10^{-4} cm^3 STP/g, if He was perfectly incompatible during melting (Appendix Table 5). The crustal ^{4}He abundances can be estimated from U= 0.633 ppm and Th= 3.06 ppm, which is the average of upper and lower crustal xenoliths from within, or close to, the MVB (Ruiz et al., 1988b; Roberts

and Ruiz, 1989; Schaaf et al., 1994; Lawlor et al., 1999; Gomez-Tuena et al., 2003; Martinez-Serrano et al., 2004; Ortega-Gutiérrez et al., 2011). Because of the continuous He loss from crust, we calculated the abundance of radiogenic ^{4}He= 8.86 cm^3 STP/g produced *per year* for a crustal volume of 0.02 km^3 which approximates the average of a typical eruptive volumes produced by the monogenetic volcanoes (e.g. Siebe et al., 2004). Mixing curves are shown in Fig. 1c, assuming the 'old Texcal Flow', a high-Nb basalt with the highest ^{3}He/^{4}He = 8 R$_a$ olivine and most mantle melt-like characteristics as best proxy to a melt from subduction unmodified mantle (=, from Straub et al., 2011; 2013).

Because He in the crustal material is four orders of magnitude higher than He in mantle melts, the mixing curve (curve a) clearly misses the data if only trace amount of the crust were assimilated. The crust is so enriched that even if 99.99% of this crustal He had been driven off by some process (e.g. heating by intruding magma), the mixing curve would still miss the data. (curve b). The MVB data can be only matched (stippled curve c), if the crustal component had much less He than the mantle melt (~6% of mantle He) which is not borne out by any known data (Ballentine and Burnard, 2002).

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