# Role of H<sub>2</sub>O in subduction-zone magmatism: New insights from melt inclusions in high-Mg basalts from central Mexico

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# ABSTRACT

Although there is a growing body of data on H<sub>2</sub>O in arc magmas, there is still considerable uncertainty about the relationship between H<sub>2</sub>O and various incompatible elements during enrichment of the mantle wedge by subduction processes. We report data for H<sub>2</sub>O, other volatiles (CO<sub>2</sub>, S, Cl), and trace elements in olivine-hosted melt inclusions from high-Mg basalts in central Mexico that exhibit varying degrees of subduction-related enrichment. Most melt inclusions were trapped at low pressure, but rare inclusions (Mg# 65-78, olivine hosts  $Fo_{85-90}$  trapped at upper to middle crustal pressures (1-6 kbar) contain high CO<sub>2</sub> (250–2120 ppm). The high-pressure inclusions indicate magmatic H<sub>2</sub>O contents from 1.3 to 5.2 wt%. Enrichment of H<sub>2</sub>O relative to Nb correlates positively with K/Nb, Ba/Nb, and La/Nb, indicating a clear link between H<sub>2</sub>O and trace element enrichment of the mantle wedge. Our results show that fluxing of the wedge with an H<sub>2</sub>O-rich component from the subducted slab is important in formation of magmas that are enriched in large ion lithophile (LILE) and light rare earth (LREE) elements relative to high field strength elements (HFSE). In contrast, magmas with low LILEs and LREEs relative to HFSEs have relatively low H<sub>2</sub>O, and must have formed largely by decompression melting of unmodified mantle. Our data for volcanoes <50 km apart show evidence of significant variability in the composition of H<sub>2</sub>O-rich subduction components that are added to the mantle wedge beneath central Mexico.

Keywords: basalt, magma, subduction zones, trace elements, volatiles, water.

# **INTRODUCTION**

Numerous lines of evidence indicate that water derived from subducted oceanic crust and sediment plays an important role in generating magmas in the mantle wedge above subduction zones. However, because volatiles are almost completely degassed from magmas during subaerial eruption, it is difficult to measure directly preeruption volatile concentrations. Thus, although the trace element characteristics of magmas associated with convergent plate margins are commonly ascribed to addition of a hydrous component (either fluid or silicate melt) from the slab to the wedge, there are still relatively few data sets that show a clear link between trace element enrichment and magmatic H<sub>2</sub>O contents.

It is well established, on the basis of melt inclusion and experimental data, that arc basaltic magmas can have relatively high  $H_2O$ (6–8 wt%; Sisson and Layne, 1993; Roggensack et al., 1997; Grove et al., 2002). However, some arc basaltic magmas are relatively dry and are inferred to be the result of decompression melting caused by upwelling in the mantle wedge (Sisson and Bronto, 1998). A problem exists in that some of these  $H_2O$ -poor arc magmas (e.g., Galunggung, Indonesia) have trace element characteristics such as high Ba/Nb that are generally attributed to enrichment of the mantle wedge by a hydrous component derived from the subducted slab (Pearce and Peate, 1995). Further complicating the issue, data for melt inclusions from island-arc tholeiites and boninites suggest that H<sub>2</sub>O and K<sub>2</sub>O are decoupled in the mantle source regions for arc magmas and that metasomatic hydrous fluids in subduction zones do not necessarily have high large ion lithophile element (LILE) contents (Sobolev and Chaussidon, 1996).

To address these puzzles, there is a need for data on H<sub>2</sub>O in primitive arc magmas with variable LILE/high field strength element (HFSE) and light rare earth element (LREE)/HFSE to quantify relations between H<sub>2</sub>O and trace element enrichment of the mantle wedge. Such relationships have been demonstrated for some arc and backarc magmas (Stolper and Newman, 1994; Newman et al., 2000; Grove et al., 2002). In this paper we report data for H<sub>2</sub>O and trace elements in melt inclusions from high-Mg basalts in central Mexico that exhibit varying degrees of subduction-related enrichment. The results show a clear relationship between H<sub>2</sub>O, LILEs, LREEs, and other incompatible elements during subductionrelated enrichment of the mantle wedge directly beneath arc-front volcanoes.

# GEOLOGIC SETTING, SAMPLE DESCRIPTION, AND ANALYTICAL METHODS

The Quaternary Chichináutzin volcanic field in central Mexico, directly south of Mexico City, is part of the subduction-related Trans-Mexican volcanic belt. The Chichináutzin volcanic field contains numerous cinder cones and shield volcanoes as well as larger stratovolcanoes such as the active Popocatépetl. Crustal thickness may be as great as 50 km (Wallace and Carmichael, 1999), and the top of the subducted slab probably is no more than ~100 km beneath this region (Pardo and Suárez, 1995). Thus the mantle wedge is probably  $\leq$ 50 km thick, greatly reducing the distance that slab-derived components must travel before reaching the melting region.

We present data for volatiles, and major and trace elements in melt inclusions from five cinder cones in this region from which high-Mg (8–10 wt% MgO) lavas have erupted (Table 1). These cones were chosen to span a wide range of LILE/HFSE and LREE/HFSE ratios (Fig. 1), which vary from ocean island basalt (OIB)–like compositions (Xitle) to strongly LILE-enriched arc-like compositions<sup>1</sup>. All olivine-hosted melt inclusions were collected from ash and scoria, and are naturally glassy because of rapid quenching during deposition.

# H<sub>2</sub>O AND OTHER VOLATILES IN MELT INCLUSIONS

Most melt inclusions have relatively low H<sub>2</sub>O and S, and CO<sub>2</sub> below detection (Fig. 2). Such low values indicate that most inclusions formed at low pressures (<500 bar) from magmas that had already undergone significant shallow-level degassing. Rare melt inclusions (Mg# 65-78 [Mg# = 100 Mg/(Mg +  $Fe^{2+}$ ], olivine hosts  $Fo_{85-90}$ ) trapped at upper to middle crustal pressures (1-6 kbar) contain high CO<sub>2</sub> (250-2120 ppm). Because CO<sub>2</sub> solubility in basaltic melts is low, decompression during magma ascent causes exsolution and loss of CO<sub>2</sub> but does not strongly deplete the residual melt of H<sub>2</sub>O until most CO<sub>2</sub> is degassed (Dixon et al., 1995; Newman et al., 2000). Therefore, the high-pressure melt in-

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<sup>&</sup>lt;sup>1</sup>GSA Data Repository item 2003021, Table DR1, trace element abundances, is available from Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301-9140, editing@geosociety.org, or at www.geosociety.org/pubs/ft2003.htm.

TABLE 1. MAJOR, TRACE, AND VOLATILE ELEMENT CONCENTRATIONS IN HIGH-CO<sub>2</sub> MELT INCLUSIONS

Volcano Inclusion	Jumiltepec J1-8	Las Tetillas Te-6	Tuxtepec Tux-15	Tepetlapa Tp-3	Tepetlapa Tp-6	Xitle X2-4
SiO <sub>2</sub>	52.4	50.4	45.4	51.8	52.0	51.7
TiO <sub>2</sub>	0.94	1.05	1.14	1.73	1.76	1.87
Al <sub>2</sub> Õ <sub>3</sub>	15.7	16.8	14.1	17.1	16.6	16.5
FeOT	6.72	6.15	7.21	5.74	5.81	7.34
MnO	0.07	0.09	0.10	0.10	0.09	0.11
MgO	7.65	6.54	9.35	5.86	6.19	6.21
CaO	7.94	8.64	10.78	8.55	8.75	8.06
Na <sub>2</sub> O	3.23	3.77	3.18	4.08	4.03	3.89
K₂Õ	1.24	0.84	1.70	1.13	0.96	1.28
$P_2O_5$	0.24	0.20	0.54	0.45	0.40	0.73
S	0.152	0.116	0.597	0.171	0.181	0.094
CI	0.196	0.080	0.190	0.107	0.104	0.072
H <sub>2</sub> O	3.0 (0.2)	3.6 (0.4)	5.2 (0.5)	3.2 (0.2)	3.2 (0.4)	1.3 (0.1)
CÔ <sub>2</sub>	250 (40)	960 (120)	2120 (180)	1800 (120)	1430 (180)	370 (50)
Total	99.5	98.2	99.5	100.0	100.1	99.1
Mg#	74	73	78	70	71	65
Olivine (Fo%)	88.2	87.8	89.6	87.5	87.5	85.0
%PEC	4	5	7	2	6	3
Rb	12	8	21	12	10	12
Sr	655	353	1236	687	652	561
Υ	19	19	31	29	27	34
Zr	128	122	181	249	235	302
Nb	4	3	4	18	16	29
Ba	444	169	1453	353	305	368
Th	1.1	1.1	4.8	1.8	2.2	0.9
U	0.5	0.2	0.8	0.4	0.4	0.4
La	21	10	59	22	24	27
Ce	46	25	143	52	59	61
Nd	27	16	84	27	31	34
Sm	4.6	3.3	15.8	5.3	6.0	6.5
Eu	3.0	1.2	4.2	2.8	3.2	2.8
Dy	3.5	3.7	7.0	4.4	5.0	6.2
Er	1.8	2.1	3.0	2.2	2.5	3.0
Yb	1.6	1.8	2.6	2.1	2.0	2.7

*Note*: Major elements (wt%) by electron microprobe.  $H_2O$  (wt%) and  $CO_2$  (ppm) by Fourier transform infrared (FTIR) spectroscopy using band assignments and compositionally dependent absorption coefficients from Dixon et al. (1995) and Dixon and Pan (1995) as described in Cervantes (1999).  $CO_2$  (1515 and 1430 cm<sup>-1</sup>) and molecular  $H_2O$  (1630 cm<sup>-1</sup>) absorbances were measured after subtraction of a reference spectrum for decarbonated basaltic glass. 1 $\sigma$  uncertainties in parentheses are mostly due to uncertainties in thickness of sectioned inclusions. Accuracy of the absorption coefficients is about ±20%. Trace elements (in ppm) were measured by Cameca IMS-3f ion microprobe at Wood's Hole Oceanographic Institution. Analytical procedures and uncertainties were described in Shimizu (1998). All data have been modified from analyzed values to account for postentrapment crystallization (% PEC) of the olivine host (Sobolev and Chaussidon, 1996). Mg# is calculated using Fa<sup>3+</sup>/Fe<sup>2+</sup> ratios from whole rock samples (Wallace and Carmichael, 1999). No postentrapment diffusive loss of Fe from the inclusions has occurred (Danyushevsky et al., 2000).

clusions suggest primary  $H_2O$  contents of 1.3– 5.2 wt% (Fig. 2). Because some loss of  $H_2O$ could have occurred, these should be regarded as minima. It is difficult to assess how representative these  $H_2O$  values are for each volcano because of the scarcity of high-pressure inclusions, but two inclusions from Tepetlapa have identical  $H_2O$ , suggesting some degree of reproducibility (Table 1). The range of primary  $H_2O$  contents is similar to estimates for mafic magmas in other parts of the Trans-Mexican volcanic belt inferred from phase equilibria, plagioclase compositions, and melt inclusions (Luhr, 2001; Carmichael, 2002).

Dissolved S concentrations in the highpressure melt inclusions vary from typical values for basaltic magmas ( $\sim$ 1000 ppm) to as high as 6000 ppm. Cl contents (700–1900 ppm) are relatively high, but within the range of basaltic melt inclusions from other arc volcanoes (e.g., Roggensack et al., 1997).

# H<sub>2</sub>O AND TRACE ELEMENT ENRICHMENT OF THE MANTLE WEDGE

Our results show that enrichment of the mantle wedge in  $H_2O$  is correlated with enrichment in LILEs and LREEs relative to HFSE (Fig. 3). Hydrous enrichment appears to have been superimposed on a mantle wedge that was already heterogeneous in composition, because the highly variable Nb and Ta contents (Fig. 1) are unlikely to be caused by fluid enrichment processes (Pearce and Peate, 1995). Variable depletion of the mantle wedge is probably caused by earlier partial melting events (Wallace and Carmichael, 1999).



3000 5 kbar Vapor-saturation isobars 2000 CO<sub>2</sub> (ppm) 3 kbar 1000 Closed-system 1 kbar degassing Degassed inclusions 2 з 5 6 n 4

H<sub>2</sub>O (wt%)

Figure 1. Trace elements in whole-rock samples of high-Mg basalt and basaltic andesite from Chichináutzin volcanic field (for data tabulation, see text footnote 1). Concentrations of  $H_2O$  (in wt%) in highpressure melt inclusions from each sample are indicated (see Fig. 2).





Figure 3. Correlations between  $H_2O$ , K, and La in melt inclusions from Chichináutzin volcanic field. Data for Mariana Trough glasses are shown as small open circles (Stolper and Newman, 1994). Value for normal mid-ocean-ridge basalt (NMORB) is shown as open square.

Therefore, the patterns shown in Figure 1 likely reflect a variably depleted wedge overprinted by enrichment with an  $H_2O$ -rich component from the slab. Enrichment of  $H_2O$  relative to Nb correlates positively with K/Nb, Ba/Nb, and La/Nb (Fig. 3), and with other volatiles, S/Nb, Cl/Nb, and CO<sub>2</sub>/Nb.

Our results demonstrate that fluxing of the mantle wedge with an H<sub>2</sub>O-rich component derived from the subducted slab is important in formation of magmas with high LILE/ HFSE and LREE/HFSE. In contrast, the Xitle sample shows little enrichment of LILEs or LREEs compared to HFSEs and has the lowest H<sub>2</sub>O of any of the high-pressure inclusions (Fig. 1), indicating a mantle source that has been little affected by a component from the slab (Fig. 4). This finding suggests that melting may have been caused largely by decompression (e.g., Sisson and Bronto, 1998). Tepetlapa is distinct from the other H2O-rich magmas because it comes from a region of the mantle wedge that is less depleted in HFSEs than the source for magmas erupted at Tux-

tepec, Las Tetillas, and Jumiltepec (Fig. 1). However, the Tepetlapa sample has elevated H<sub>2</sub>O/Y, H<sub>2</sub>O/Nb, and Ba/Nb relative to Xitle (Figs. 3 and 4), showing that its mantle source has been enriched by a hydrous component from the slab. Although our interpretation distinguishes flux and decompression melting, it is likely that decompression melting is important in the formation of all Chichináutzin magmas, but the extent of melting is higher for regions of the wedge that have been fluxed by water from the slab (Grove et al., 2002). Only in the case of Xitle-which represents a common type of basalt in the Trans-Mexican volcanic belt and appears to come from a mantle source that has not been enriched in H<sub>2</sub>O—is melting likely to be caused mainly by decompression.

A multistage mantle enrichment and melting model was proposed for volcanic rocks in the western Trans-Mexican volcanic belt to account for decoupling of Ba-Sr-K, which reside in mantle amphibole and/or phlogopite, and B-Cs-U, which have shorter residence times in the mantle due to their low partition coefficients for mantle assemblages (Hochstaedter et al., 1996). However, this model does not seem applicable to the Chichináutzin lavas because U shows strong positive correlation with the LILEs and LREEs (Fig. 1). Lack of decoupling between U and LILEs further supports our model that fluid-fluxed melting, rather than metasomatic formation of amphibole or phlogopite followed by later melting (e.g., Pearce and Peate, 1995), plays an important role in the mantle wedge beneath central Mexico.

An alternative to our model for Xitle is that the high-Nb Xitle basalt comes from a region of the wedge that was enriched by silicate melts from the subducted slab rather than a hydrous fluid. Silicate melts are not expected to be depleted in HFSEs, so these melts could metasomatize the mantle wedge such that subsequent partial melting of the wedge would produce HFSE-enriched lavas (Defant and Kepezhinskas, 2001). This process could occur in the Trans-Mexican volcanic belt because the subducted slab at the trench is relatively young, and therefore hot, making it more likely to melt beneath the wedge (Peacock, 1996). However, Xitle has H<sub>2</sub>O/Nb similar to ratios for normal mid-ocean-ridge basalt (NMORB), enriched MORB, and some OIB (Fig. 4), which seems inconsistent with slab-melt metasomatism of the wedge. We also note that complete miscibility between silicate melts and hydrous fluids at high pressures (Bureau and Keppler, 1999) may ultimately obscure a clear distinction between solute-rich fluids and volatile-rich silicate melts.

We estimate the compositions of hydrous components added to the mantle wedge from





Figure 4. Comparison of melt inclusions from Chichináutzin volcanic field, glasses from Mariana Trough, and average values for mid-ocean-ridge basalt (MORB) and ocean island basalt (Kilauea). (E—enriched, N—normal.) Nb/Y varies as function of source composition but should not be affected by addition of fluid components from slab to wedge (Pearce and Peate, 1995). H<sub>2</sub>O/Y shows extent of enrichment of source with H<sub>2</sub>O-rich component derived from slab.

Figure 5. Trace element concentrations for H<sub>2</sub>O-rich components that must be added to depleted mantle wedge to account for compositions of Tuxtepec and Las Tetillas. Shown for comparison are values for Mariana Trough (Stolper and Newman, 1994) and range of values estimated for Mount Shasta region of Cascades (Grove et al., 2002). Ta in melt inclusions was calculated from ion probe Nb data using average whole-rock Nb/Ta ratio (=17) for all samples.

the subducted slab using mass-balance models (Stolper and Newman, 1994; Grove et al., 2002). Relations between H<sub>2</sub>O and incompatible elements suggest that an H<sub>2</sub>O-rich component of constant composition cannot account for the range of magma compositions. The major element range of components is: H<sub>2</sub>O (48–50 wt%), Na<sub>2</sub>O (23–36 wt%), K<sub>2</sub>O (10–15 wt%), S (1.5–6.0 wt%), TiO<sub>2</sub> (3–4 wt%), P<sub>2</sub>O<sub>5</sub> (2–5 wt%), and Cl (1.0–1.6 wt%). Other elements (e.g., SiO<sub>2</sub>) are likely to be present in the H<sub>2</sub>O-rich components (Bureau and Keppler, 1999), but are difficult to model geochemically.

Trace element abundances in one of the modeled end members (Las Tetillas component) are similar to values estimated for the Marianas and Cascades (Fig. 5). In contrast, the Tuxtepec H<sub>2</sub>O-rich component has much higher concentrations of most incompatible elements. All volcanoes we studied are <50 km apart, demonstrating that hydrous subduction components can be quite variable on a small scale. This may be due to the relatively thin ( $\leq$ 50 km) mantle wedge, so that there is little distance for slab-derived components to reequilibrate during migration in the mantle.

The compositional effects of recycled subducted sediment can be distinguished using ratios such as K/Na, Ba/Na, and Th/Na in arc lavas (Plank and Langmuir, 1993). Values of these ratios in the Tuxtepec and Las Tetillas H<sub>2</sub>O-rich components span nearly the entire global range documented for arc basalts. The Tuxtepec component, with relatively high values of these ratios, is similar to sediment that is currently being subducted beneath Mexico (Deep Sea Drilling Project Site 487; Plank and Langmuir, 1998). In contrast, the Las Tetillas component closely resembles the basaltic slab-related end member (Plank and Langmuir, 1993). If the Tuxtepec component, with its high S, Cl, and CO<sub>2</sub>, represents subducted sediment, then our results suggest that sediment subduction plays an important role in recycling these volatiles through arc volcanoes.

#### CONCLUSIONS

High-Mg basaltic magmas in central Mexico have varying degrees of subduction-related enrichment that are correlated with magmatic  $H_2O$  contents. Our results demonstrate that fluxing of the wedge with an  $H_2O$ -rich component from the slab is important in formation of magmas that are enriched in LILEs and LREEs relative to HFSEs. In contrast, magmas with low LILEs and LREEs relative to HFSEs also have relatively low  $H_2O$ , and therefore must have formed primarily by decompression melting rather than by fluxing with  $H_2O$ .

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