Supplementary Information

Molybdenum isotopes unmask slab dehydration and melting beneath the Mariana arc

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1. Supplementary Methods

Trace element analyses of the serpentinites were performed at Guizhou Tongwei Analytical Technology Co., Ltd. on a Thermal X series 2 equipped with a Cetac ASX-510 AutoSampler. Approximately 60 mg of each sample powder was dissolved in a Teflon bomb with a doubly distilled concentrated HF-HNO_3 (4:1) mixture. The dissolution was maintained in an oven at 185 °C for 3 days. The solutions were then evaporated, and the sample residues were re-dissolved with double distilled concentrated HNO_3 and evaporated again to convert the fluorides from the initial HF dissolution to nitrates. Then, the samples were dissolved in a final 3ml 2M HNO_3 stock solution. Finally, sample solutions were diluted with 2% HNO_3 to achieve a 4000 × dilution factor. An internal spike consisting of 12ppb ^{6}Li, 6ppb ^{61}Ni, Rh, In, and Re, and 4.5ppb ^{235}U was added to the sample solutions to monitor instrumental drift. USGS standard W-2a was used as a reference standard and crossed checked with BIR-1 and BHVO-2. Instrument drift mass biases were corrected with internal spikes and external monitors. The ICP-MS procedure for trace element analysis follows the protocol of Eggins et al.[1] with modifications as described in Kamber et al.[2] and Li et al.[3].

2. Supplementary Table

Supplementary Table 1 Input parameters for the geochemical modeling and calculated slab components for the Mariana arc lavas

Input parameters	DM1 (Depleted DMM)	DM2 (Enriched DMM)	MORB	AMOC	Sediments	Average eclogite and blueschist
Mo (μg/g)	0.014 [a]	0.024 [a]	0.46 [c]	0.37 [e]	2.49 [h]	0.17 [k]
Ce (μg/g)	0.421 [a]	0.726 [a]	14.86 [c]	11.40 [f]	34.30[i]	16.05 [k]
Nd (μg/g)	0.483 [a]	0.703 [a]	12.03 [c]	11.30 [f]	25.20 [i]	13.16 [k]
Hf (μg/g)	0.127 [a]	0.186 [a]	2.79 [c]	3.07 [f]	1.44 [i]	2.82 [k]
$\delta^{98/95}$Mo (‰)	-0.21 [b]	-0.21[b]	-0.21 [b]	0.36 [e]	-0.29 [h]	-0.51 [k]
^{143}Nd/^{144}Nd	0.513080 [d]	0.513025 [d]		0.513118 [g]	0.512310 [i]	
^{176}Hf/^{177}Hf	0.283220 [d]	0.283180 [d]		0.283164 [g]	0.282897 [j]	

Slab components	Shallow Fluid 700 ℃	Slab Melt 4 GPa	Deep Lithosphere Fluid	Slab Melt 6 GPa
Mo (μg/g)	2.46 [l]	1.17 [o]	5.07 [p]	1.06 [q]
Ce (μg/g)	1.69 [l]	50.08 [o]	1.87 [p]	53.92 [q]
Nd (μg/g)	0.71 [l]	18.26 [o]	0.68 [p]	30.21 [q]
Hf (μg/g)	0.05 [l]	1.24 [o]	0.05 [p]	1.14 [q]
$\delta^{98/95}$Mo (‰)	0.25 [m]	-0.40 [o]	0.06 [p]	-0.07 [q]
^{143}Nd/^{144}Nd	0.512958 [n]	0.512958 [n]		0.512958 [n]
^{176}Hf/^{177}Hf	0.283151 [n]	0.283151 [n]		0.283151 [n]

[a] The Ce-Nd-Hf of the depleted mantle are from Workman and Hart[4]. Mo is estimated according Ce/Mo = 30. DM: depleted mantle; DMM:

depleted mid-ocean ridge basalt (MORB) mantle.

[b] Depleted mantle from Bezard et al.[5].

[c] Average MORB from Gale et al.[6].

[d] Estimated according the “ambient mantle” for the Izu-Bonin-Mariana arc from Woodhead et al.[7].

[e] ODP Site 801 altered mafic oceanic crust (AMOC) super composite from Freymuth et al.[8].

[f] ODP Site 801 AMOC super composite from Kelley et al.[9].

[g] ODP Site 801 AMOC super composite from Chauvel et al.[10].

[h] Average Mariana sediment (ODP Sites 800, 801, 802) from Freymuth et al.[8].

[i] Average ODP Site 1149 sediment from Plank et al.[11].

[j] Bulk composition of ODP Site 1149 sediment from Chauvel et al.[10].

[k] Average composition of eclogite and blueschist from Chen et al.[12]. Samples SEC43-1 and SEC43-1 are not included.

[l] Trace element contents calculated for shallow slab fluid at 700 °C (90% AMOC + 10% Sediments; F=2%), applying batch dehydration model. Partition coefficients for Ce-Nd-Hf are from Kessel et al.[13] at 700 °C, 4 GPa. The Mo content is calculated according the uniform Ba/Mo=230 for the Pagan Northeastern Flank samples and the calculated Ba content for the fluid.

[m] Shallow fluid Mo isotope composition from Villalobos-Orchard et al.[14].

[n] Bulk mixing of 90% AMOC + 10% Sediments, constrained according the Hf-Nd isotope and Hf/Nd covariations of the Pagan samples.

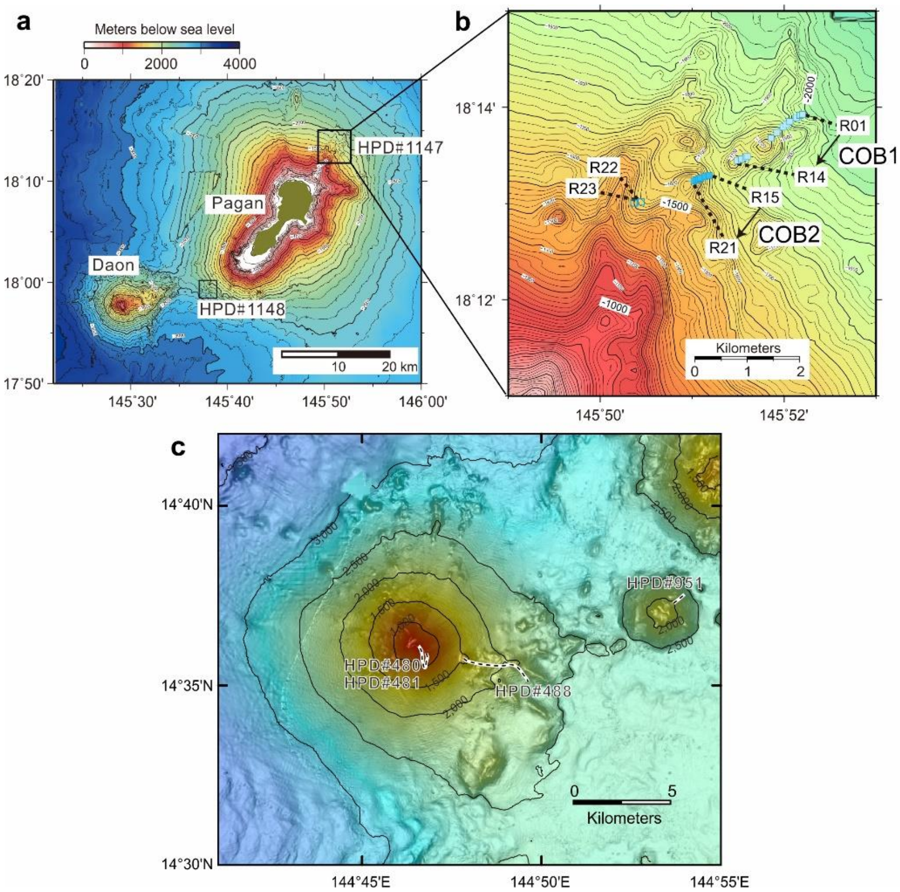
[o] Trace element contents calculated for model batch melting of the subducted slab (90% AMOC + 10% Sediments) at 900 °C with F=10%. Partition

coefficients for Ce-Nd-Hf are from Kessel et al.[13] at 900 °C, 4 GPa. Partition coefficients for Mo are from Adam and Green[15] and Chen et al.[12], considering a 2 wt.% rutile in the source and a ratio between clinopyroxene and garnet of 70:30. Mo isotopes calculated according Mo isotope equilibrium fractionation factor of $\Delta^{98/95}Mo_{melt-rutile}$ = 0.5‰ at 900°C between the melt and the residual rutile. The Mo isotope fractionation factor is calculated according the experimental result of $\Delta^{98/95}Mo_{melt-rutile}$ = 0.33 ± 0.06‰ at 1175°C between the melt and the residual rutile[12].

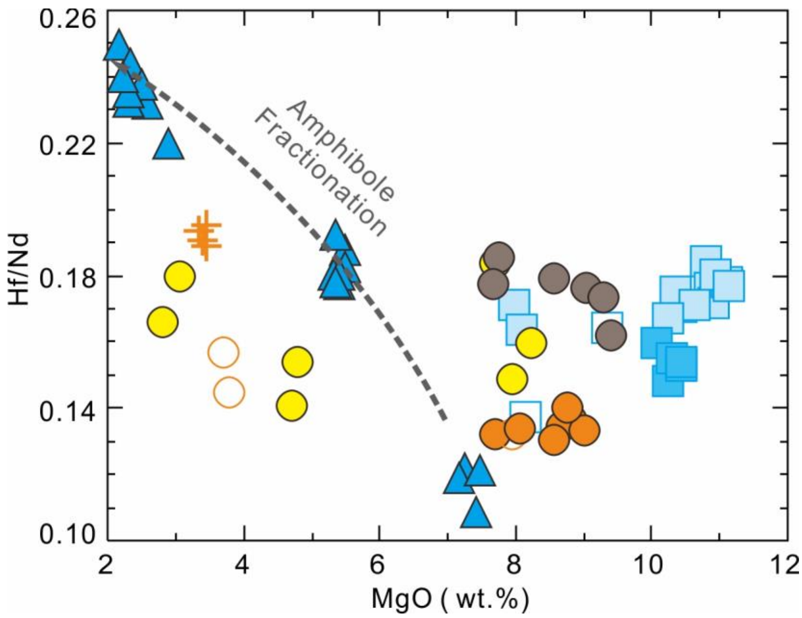
[p] Trace element contents calculated for fluid from the deep slab lithosphere at 700 °C, applying batch dehydration model and F=2%. The deep lithosphere fluid is assumed to equilibrate with an eclogite source that has experienced 2% fluid percolation and Mo loss at shallow depth. Partition coefficients for Ce-Nd-Hf are from Kessel et al.[13] at 700 °C, 4 GPa. Partition coefficient for Mo calculated after Bali et al.[16] at 700 °C, 2.61 GPa, oxygen fugacity of FMQ+ 4 and NaCl content of 5 wt.%, considering a 2 wt.% rutile in the source and a ratio between clinopyroxene and garnet of 70:30. Mo isotopes calculated according Mo isotope equilibrium fractionation factor of $\Delta^{98/95}Mo_{fluid-rutile}$ = 0.73‰ at 700°C between the fluid and the residual rutile. The Mo isotope fractionation factor is calculated according the experimental result of $\Delta^{98/95}Mo_{melt-rutile}$ = 0.33 ± 0.06‰ at 1175°C between the melt and the residual rutile[12].

[q] Trace element contents calculated for model batch melting of deep fluid fluxed slab (2% Deep fluid+98% slab) at 900 °C with F=10%. The slab is assumed to have experienced early melting at 4 GPa (900 °C; F=10%). Partition coefficients for Ce-Nd-Hf from Kessel et al.[13] at 900 °C, 6 GPa. Partition coefficient for Mo from Adam and Green[15] and Chen et al.[12], considering a 2 wt.% rutile in the source and a ratio between clinopyroxene and garnet of 70:30. Mo isotopes calculated according Mo isotope equilibrium fractionation factor of $\Delta^{98/95}Mo_{melt-rutile}$ = 0.5‰ at 900°C between the melt and the residual rutile. The Mo isotope fractionation factor is calculated according the experimental result of $\Delta^{98/95}Mo_{melt-rutile}$ = 0.33 ± 0.06‰ at 1175°C between the melt and the residual rutile[12].

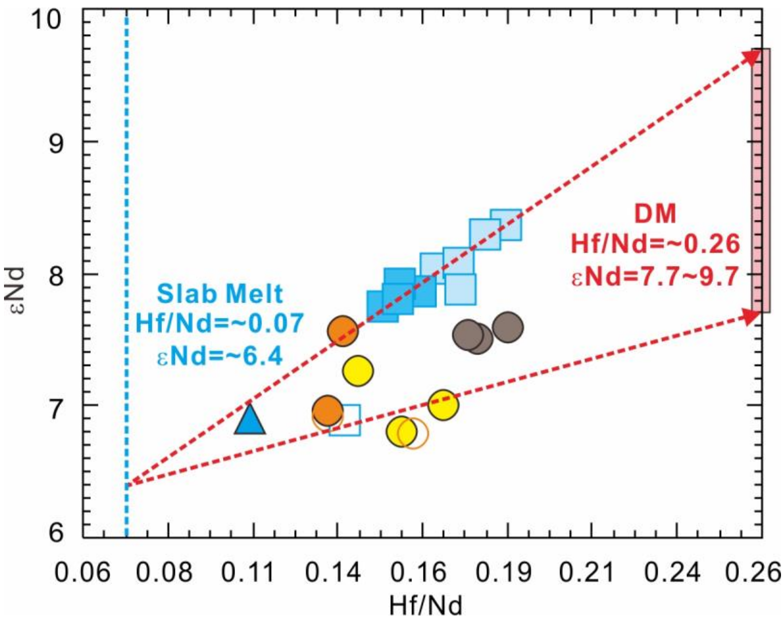
3. Supplementary Figures



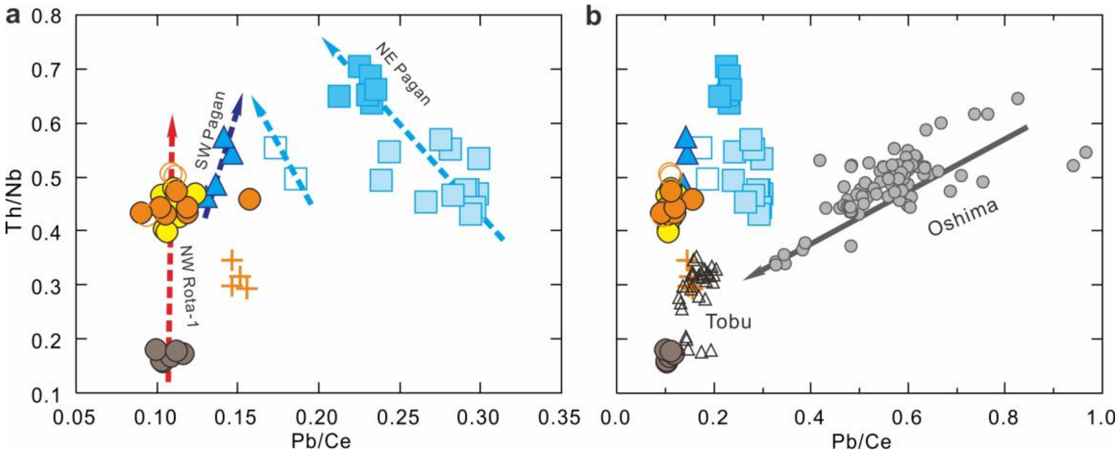
Supplementary Fig. 1 Volcanoes of this study from the Mariana Bathymetric Compilation with sampling locations. a Pagan and Daon volcanoes from the Mariana Bathymetric Compilation showing the locations of ROV Hyper-Dolphin dives during cruise NT10-12[17]: the Northeastern Flank of Pagan (HPD1147) and the Southern Flank of Pagan (HPD1148). **b** Bathymetry of Pagan's northeastern slopes showing HPD1147 dive tracks[17]. During this dive, two distinct types of primitive clinopyroxene-olivine basalt (COB1 and COB2) lavas were collected only 500m apart. **c** NW Rota-1 volcano showing the sampling tracks of ROV Hyper-Dolphin[18]: the Summit (HPD 480 and 481), Eastern Flank (HPD 488), and East Knoll (HPD 951). COB: clinopyroxene-olivine basalt; POB: plagioclase-olivine basalt.



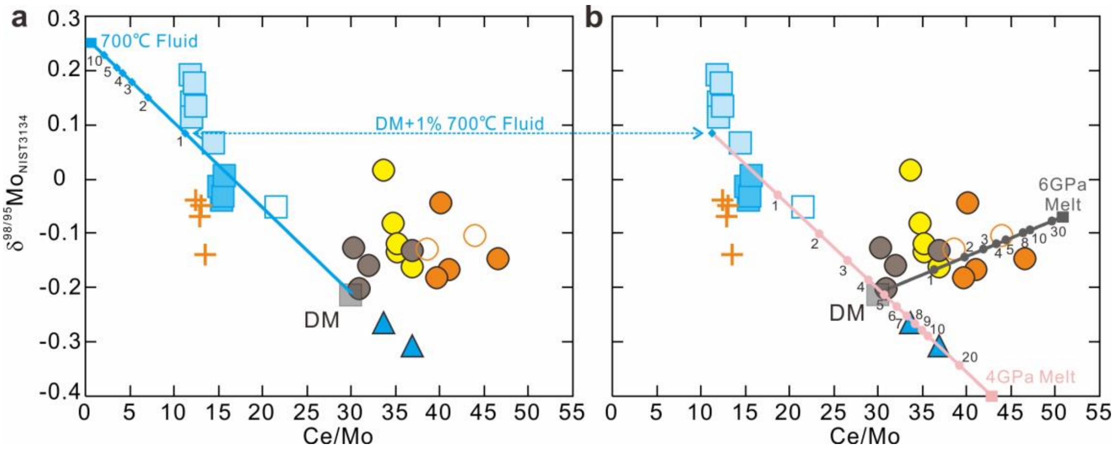
Supplementary Fig. 2 Hf/Nd versus MgO diagram for Pagan and NW Rota-1 samples.



Supplementary Fig. 3 εNd versus Hf/Nd diagram used to estimate the εNd and Hf/Nd of the slab melt and ambient mantle. The slab melt is estimated to have εNd of ~ 6.4 and Hf/Nd of 0.07. Then the slab surface is constrained to be composed of altered mafic oceanic crust and sediments with a ratio of 9:1. The ambient mantle is estimated to have εNd between 7.7 and 9.7. DM: depleted mantle.



Supplementary Fig. 4 Th/Nb versus Pb/Ce diagrams for Pagan and NW Rota-1 samples unaffected by amphibole fractional crystallization. Izu-Oshima and Izu-Tobu samples[19] are also plotted for comparison in diagram **b**. The variation of the Izu-Oshima (volcanic front) samples is explained by addition of Izu-Tobu (backarc) magma to the Izu-Oshima plumbing system. This model is difficult to explain the geochemistry of Pagan samples. Note the high Pb/Ce and high Th/Nb characteristics indicate the slab fluid for the Oshima volcano may be supercritical. It is different with that for the Pagan volcano.



Supplementary Fig. 5 $\delta^{98/95}$Mo versus Ce/Mo diagrams for Pagan and NW Rota-1 samples unaffected by amphibole fractional crystallization, showing slab dehydration/melting process. The depleted mantle (DM), 700 °C slab fluid, 4 GPa slab melt and 6 GPa slab melt compositions are listed in the Supplementary Table 1. The numbers on the mixing curves between different compositions represent the mass percentage of the slab fluid/melt. Blue line in **a** is the mixing trend between DM and the 700℃ slab fluid. Pink line in **b** is the mixing trend between the partially serpentinized mantle (DM + 1% 700 °C fluid) and the 4 GPa slab melt. Gray line in **b** is the mixing trend between the DM and the 6 GPa slab melt.

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