H₂O and CO₂ from Subduction Zone to Volcano

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Volatile Recycling & Magma Generation in Arcs

- accretionary wedge
- Forearc
- Back-arc
- oceanic crust
- Lithospheric mantle
- Asthenospheric mantle
- serpentinized "cold nose"
- Fluid migration
- Mantle wedge flow
- Partial melting

500 °C
1000 °C
Volatile Recycling & Magma Generation in Arcs

- Sediment
- Oceanic Crust
- Mantle

- Volcanic Arc
- Back-arc

- 500 °C
- 1000 °C

- Fluid migration
- Partial melting
- Syncretionary wedge
- Serpentinized "cold nose"
Volatile Recycling & Magma Generation in Arcs

Breeding et al. (2004)

Complex reaction zone at slab-wedge interface

Breeding et al. (2004)
Outline

• $\text{H}_2\text{O}$ and $\text{CO}_2$ inputs to arcs

• Age and temperature of oceanic crust

• Modeling of slab P-T paths and dehydration

• Complications and known unknowns

• Volatile contents of arc magmas – what controls $\text{H}_2\text{O}$?

• $\text{H}_2\text{O}/\text{Ce}$ & slab temperature variations

• Serpentinite, chlorite & fluid flux melting of the slab top

• $\text{CO}_2$ fluxes from arc volcanoes

• Why are arc magma $\text{CO}_2$ concentrations so poorly known?
H₂O & CO₂ in Sediment & Altered Oceanic Crust

**Figure 2** Estimates of the amount of H₂O in hydrates and CO₂ in carbonates in crustal columns being subducted. From Plank & Langmuir (1998) (squares) and Rea & Ruff (1996) (triangles). The shaded field represents altered MORB (Staudigel et al. 1996). Ophicarbonates after the data in Sciuto & Ottonello (1995) and Bonatti et al. (1974).
Variations in Thermal State of Subducted Lithosphere

Slab Thermal Parameter: $\Phi = V_c \times \text{Age} \times \sin \delta$

van Keken et al. (2011)
Geodynamic Modeling & the Effect of Slab Age

Old slab (130 Ma)

Young slab (10 Ma)

van Keken et al. (2011)
$H_2O$ Contents of Subducted Oceanic Crust

2.5 wt% $H_2O$

Typical slab depth beneath the volcanic front

0.07 wt% $H_2O$

Dehydration melting

$H_2O$-sat. melting

A: MORB

Hacker (2008)
Lithologies and H$_2$O Contents in Slabs during Subduction Dehydration

van Keken et al. (2011)
Temperatures from 2D Thermal Models

Boundary & Interface Conditions for Thermal Models

- Frictional heating applied to a prescribed depth
- Prescribed maximum depth of decoupling
- T & stress-dependent rheology
- Mantle wedge flow
- Full decoupling
- Inflow-outflow transition (not fixed)
- Mantle flows at subduction rate.

Comparison of Models

- Full coupling at 80 km depth
- Low viscosity channel limits deeper coupling

- Models with low-viscosity channels extending to depth predict cooler slab temperatures

Wada & Wang (2009)

Cooper et al. (2012)
Hebert et al. (2009)
Modeled Slab Top P-T Paths

Slab surface pressure-temperature conditions predicted (Syracuse et al. 2010)

Modern arcs

Sediment

Ocean crust

Grove et al. (2012)
Analog Experiments Simulating Mantle Wedge Flow

MacDougall et al. (2014)
Complications in Slab Geometry – Cascadia

The slab is very short

amount of subduction | > 2000 km
slab length | ~300 km

P-wave tomography (Darold & Humphreys, 2012)
• Oblique subduction
• Modest convergence rate
• Global endmember for hot slabs because of young oceanic crust

Abundant mafic cinder cones in the Lassen region
Key Conclusions About H$_2$O Fluxes Beneath Arcs

The top of the slab is sufficiently hot in all subduction zones that the upper crust, including sediments and volcanic rocks, is predicted to dehydrate significantly.

The degree and depth of dehydration in the deeper crust and uppermost mantle are highly diverse and depend strongly on composition (gabbro versus peridotite) and local pressure and temperature conditions.

The upper mantle dehydrates at intermediate depths in all but the coldest subduction zones.

On average, ~30% of the bound H$_2$O subducted globally in slabs reaches 240 km depth, carried principally ... in the gabbro and peridotite sections.

The predicted global flux of H$_2$O to the deep mantle is smaller than previous estimates but still amounts to about one ocean mass over the age of the Earth. At this rate, the overall mantle H$_2$O content increases by 0.037 wt % (370 ppm) over the age of the Earth.

Van Keken, Hacker, Syracuse, Abers (2014) JGR
How Do Fluids & Melts Move Through the Slab & Wedge?

Solid mantle flow deflects rising fluids & melts in the mantle wedge

Compaction pressure gradients cause updip flow within the slab

Wilson et al. (2014)  
Cagnioncle et al. (2007)
Downdragging of forearc mantle supplies fluid through multistage process

Hydration of olivine forms a low-viscosity channel

Hattori & Guillot (2004)

Hebert et al. (2009)
Diapiric Rise of Sediments or Melange from the Slab Top

Figure 5 | Summary of conditions for sediment diapir formation in global subduction zones. a, Diapir initiation temperature versus sediment layer thickness\(^{30}\), and b, diapir initiation depth versus subarc slab depth (as compiled in ref. 8) calculated for 17 slab-top geotherms\(^{8}\). Subducting sediment layer thicknesses are corrected for compaction to a density of 2,800 kg m\(^{-3}\). Numbers (in order of increasing slab thermal parameter) correspond to subduction zones: 1—Cascadia, 2—Nankai, 3—Mexico, 4—Colombia-Ecuador, 5—SC Chile, 6—Kyushu, 7—N. Sumatra, 8—Alaska, 9—N. Chile, 10—N. Costa Rica, 11—Aleutians, 12—N. Hikurangi, 13—Mariana, 14—Tonga-Kermadec, 15—Kamchatka, 16—Izu, and 17—NE Japan.
Magmatic Volatile Contents – The View from Above

Modified from Richards (2011)
Data & Methods

- Melt inclusions trapped in olivine phenocrysts provide a record of volatiles & trace elements.
- Published data for 100 volcanoes from 18 subduction zone segments.

Cooper et al. (2012) G-Cubed
Ruscitto et al. (2012) G-Cubed
Plank et al. (2013) EPSL
Compositional Variations in Arc Melt Inclusions

Global arc database of melt inclusions from Ruscitto et al. (2012)
Volatile Contents of Primitive Arc Magmas

Each data point represents a single volcano based on melt inclusion data.
All compositions have been corrected to equilibrium with Fo$_{90}$ olivine.

$H_2O$ release in A from van Keken et al. (2011)
Comparison of Volatile Contents & Slab Thermal Parameter

Ruscitto et al. (2012)
Subduction Recycling of Seawater Chlorine

Ruscitto et al. (2012)
• Arcs With Hotter Slabs Have Lower $H_2O$ Outfluxes
• Consistent with prediction that hot slabs strongly dehydrate beneath the forearc

Ruscitto et al. (2012)
H$_2$O Contents of Arc Magmas

Global Average: 3.9 ± 0.45 wt% H$_2$O

Modified from Plank et al. (2013)
Flux Melting in Subduction Zones

- $\text{H}_2\text{O}$-rich magmas form as fluids or hydrous melts percolate upward through the inverted thermal gradient in the mantle wedge.

Grove et al. (2006)
Interpretation 1: Feedback between mantle H$_2$O & degree of melting limits melt H$_2$O

Plank et al. (2013); Kelley et al. (2010)
**H$_2$O and Trace Elements in Cascades Melt Inclusions**

- Correlation of volatiles and LILEs indicates variable addition of a hydrous subduction component.

- Mixing calculations show that the subduction component accounts for 70-98% of the H$_2$O dissolved in Lassen region mafic magmas.

Walowski et al. (2015)
Comparison of Melt Inclusions & Experimental $\text{H}_2\text{O}$ Estimates

Interpretation 2: Arc magmas start with higher $\text{H}_2\text{O}$ than is recorded in melt inclusions

Modified from Grove et al. (2012)
How Hot is the Slab Top? – $\text{H}_2\text{O}/\text{Ce}$ Slab Geothermometer

- Geochemical data for arc magmas can be used to infer slab top temperatures
- Requires allanite and/or monazite to be present in metasediment & metabasalt

Plank et al. (2009); Cooper et al. (2012)
Cascades
Mexico
Costa Rica
Guatemala
Aleutians
Nic.
Marianas
Kamchatka
L. Ant.
Ton.

\( \text{H}_2\text{O}/\text{Ce-slab fluid} \)

Decreasing Average

Temp. (°C)

730 (solidus)

\( T_{4GPa} \) (°C)

Cooper et al. (2012)
Comparison of Temperatures from $\text{H}_2\text{O}/\text{Ce}$ & Geodynamic Models

- Relatively good agreement between geodynamic models & $\text{H}_2\text{O}/\text{Ce}$ temperatures
- Suggests mainly vertical rise of slab components

Cooper et al. (2012)
Relationship of $\text{H}_2\text{O}/\text{Ce}$ to Other Slab Tracers

Ruscitto et al. (2012)
Slab components become more solute-rich (more melt-like) with increasing slab temperature.
Hot Temperatures Can Cause Melting of the Slab Top Beneath Arcs

Walowski et al. (2015); solidi from Poli & Schmidt (1998), Hermann & Spandler (2008)
Modeling of $\text{H}_2\text{O}$ Released from the Downgoing Slab

- Model results for the southern Cascades using localized hydration and 2 km of hydrated upper mantle

- Modeling uses methods of Wada et al. (2012) & assumes localized hydration & vertical fluid migration
Shear Velocity Model for the Southern Cascades

Liu et al. (2012)
Because slab surface temperatures are at or above the MORB + H₂O solidus, the upper oceanic crust is likely flux-melted by fluids rising from the slab interior.
Reevaluating carbon fluxes in subduction zones, what goes down, mostly comes up

Peter B. Kelemen\textsuperscript{a,1} and Craig E. Manning\textsuperscript{b,1}

values in Mt C per year

values in parentheses are from Dasgupta & Hirschmann, EPSL 2010

"36?" comes from Dasgupta & Hirschmann
Dasgupta RIMG 2013 suggested a value of
5 Mt C/yr for subduction of altered peridotite
(-) indicates that Dasgupta & Hirschmann did not estimate a value

Fig. 5. Major fluxes of carbon estimated in this paper, with values from Dasgupta and Hirschmann (1) for comparison.
Volcanic Gases

- Measure SO\(_2\) flux by remote sensing
- Collect & analyze fumarole gases
- Use fumarole gas ratios (e.g., CO\(_2\)/SO\(_2\)) to calculate fluxes of other components

Modified from Fischer et al. (2002)
Fluxes of Volatiles from Subduction-related Magmatism

Assuming 2–4 km\(^3\)/yr magma flux
Kelemen & Manning (2015)
Wallace (2005)
Minimum for arc magmas based on global CO$_2$ flux

Magma flux = 8 km$^3$/yr
Minimum for arc magmas based on global CO$_2$ flux

Magma flux = 2–4 km$^3$/yr

Wallace (2005)
Effect of low CO₂ solubility on degassing

Basalt (49 wt.% SiO₂)

DEGASSING TRENDS
1200°C

Closed-system with 2% exsolved vapor

Closed
Open System

PPM CO₂ dissolved in melt

Wt.% H₂O dissolved in melt

Problem 1: Low CO\textsubscript{2} Solubility at Crustal Pressures

- When basaltic magma reaches the magma chamber beneath the summit of Kilauea, most of the original dissolved CO\textsubscript{2} has already been degassed.
Problem 2: Formation of Shrinkage Bubbles

Mauna Loa melt inclusion

Wallace et al. (2015)

Experimental reheating data

- 1.5 kbar
- 1 kbar
- 500 bars
- 100 bars

\( \text{CO}_2 \) (ppm)

\( \text{H}_2\text{O} \) (wt.%)
Post-Entrapment Modification of Melt Inclusions

Pre-eruption cooling

Inclusion entrapment

Crystal

Melt inclusion

Crystallization along melt – crystal interface

Vapor bubble

Diffusive exchange

Eruptive cooling

Modified from Wallace (2005)

Bubble expansion but little to no additional olivine crystallization or diffusion of CO₂ into the bubble

Wallace et al. (2015)

% CO₂ lost

Vol% bubble

0 1 2 3 4 5 6

0 20 40 60 80 100

200 300 400 500 600 bars

Modified from Wallace (2005)
How Much \( \text{CO}_2 \) is Lost? – Raman Results on Bubble \( \text{CO}_2 \) Densities

Aster et al. (in prep.)
How Much CO$_2$ is Lost? – Modeling Crystallization & Cooling Contraction

$$\Delta T = \text{Temperature difference between trapping & eruption}$$

- Eruptive expansion down to glass transition temperature
- Pre-eruptive vol.\% = 0.0101 \times \Delta T

Aster et al. (in prep.)
Comparison of CO$_2$ Restoration Methods

Aster et al. (in prep.)
Comparison of Corrected vs. Measured Melt Inclusion Values

Walowski et al. (in prep.)
higher than that of Hilton et al. (85) and other recent reviews because of improving data quality and data density. The source of CO$_2$ in arc volcano emissions can be ambiguous. Where CO$_2$ contents correlate with $^3$He, it is inferred that most of the CO$_2$ is introduced from the mantle into the base of arc crust. Where CO$_2$ and $^3$He are correlated, and $^3$He/CO$_2$ ratios are lower than in other tectonic settings, and/or where $\delta^{13}$C reflects input of nonmantle carbon, this is ascribed to recycling of carbon from subducting sediment and altered oceanic crust. However, arc volcanoes—particularly in continental arcs—may also emit CO$_2$ added to magmas during metamorphism of carbon-bearing lithologies within the crust (31). CO$_2$ contents in melt inclusions in phenocrysts in arc lavas can be used to place lower bounds on CO$_2$ in parental magmas passing from the mantle into arc crust, as reviewed by Wallace (7). However, because the extent of prior degassing of CO$_2$ from decompressing melts currently cannot be determined with confidence, melt inclusion data have little utility in estimating an upper bound for magmatic input of CO$_2$ into arc lithosphere (e.g., ref. 86). Wallace (7) and Blundy et al. (86) arrive at similar estimates for CO$_2$ contents in primitive magmas passing from the mantle into arc crust. However, the estimate of Wallace was derived using inferred arc magma fluxes together with the volcanic CO$_2$ flux estimated by Hilton et al. (85), so these values are not independent. The estimate of Blundy et al. is based on the assumption that observed andesites are produced by 80% crystal fractionation from parental basalts, which could be too high; for example, using a value of 40% crystal fractionation would increase the estimated magmatic CO$_2$ flux by a factor of 2 compared with that of Hilton et al.

Additional studies of $^3$He/CO$_2$ are warranted to separate subduction zone versus arc crust contributions to CO$_2$ in arc volcanoes. Meanwhile, available results seem to indicate that most CO$_2$ emerging from arc volcanoes is derived from recycling of subducted CO$_2$. Estimates of CO$_2$ in parental magmas, before crystal fractionation, need to be refined.

Diffuse Outgassing of Carbon at Forearcs and Arcs: 4–12 Mt C/y or More

Diffuse outgassing of subducted carbon as CO$_2$, methane, and other hydrocarbons could be an important part of the global carbon budget (5, 63, 87). However, even the most up-to-date reviews reflect measurements on a large range of scales that make it difficult to extract global estimates. We focus here on diffuse outgassing of CO$_2$ in arcs (forearc, arc, backarc). Evidence for such output is abundant. Haggerty and coworkers (ref. 88 and SI Text) first documented carbonate chimneys and authigenic carbonate deposited by fluids from subducting sediment and oceanic crust at and near seamounts in the Mariana and Bonin forearcs. Fryer and coworkers subsequently found...
Summary Questions

• How much hydration & carbonation of oceanic upper mantle occurs during bend faulting at the outer rise?

• What happens to H$_2$O & CO$_2$ stored in the forearc wedge?

• How do fluids & melts migrate through the slab & wedge?

• How do variations in mantle temperature modulate subduction inputs?

• How much CO$_2$ is really in arc magmas?