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12. The Taylor number Ta is $4\Omega^2 d^4/\nu^2$, where Ω is the basic rotation rate, d is the thickness of the convecting region, and ν is the kinematic viscosity.
13. The Rayleigh number $R = (\alpha\beta\Delta T d^3)/\nu\kappa$ is a measure of the vigor of thermal convection; α is the thermal expansivity, β is $4\pi\bar{\rho}/3$, G is the gravitational constant, $\bar{\rho}$ is the density of the reference state, and ΔT is the temperature difference across the convecting fluid layer. The definitions of d and ν are in (12), and κ is the thermometric diffusivity.
14. An alias-free spectral transform method was used to compute the nonlinear terms. The time integration treats the nonlinear and Coriolis terms explicitly by an Adams-Bashforth scheme and the linear terms implicitly by a Crank-Nicolson scheme. Numerical stability is maintained by the Courant condition on the time step, and the adequacy of the spatial resolution is checked by calculations at different levels of resolution.
15. Additional calculations have been carried out at values of Ta and R smaller than the values used in the simulation reported here. None of these calculations yielded a banded structure in the longitudinally averaged zonal flow at the surface. The occurrence of banding in the surface zonal flow requires that the north-south convective columns have small diameters compared with the thickness of the convecting shell. This occurs only when both Ta and R are sufficiently large. The spatial resolution of the calculation (in spherical harmonic spectral space all harmonics of degree and order up to 144 were retained) allowed the successful simulation of the small-scale convective structures. The numerical solution reported here was calculated on a Cray YMP8/864 supercomputer at the San Diego Supercomputer Center. It required 256 megabytes of computer memory and 900 hours of CPU time. The solutions at lower values of Ta and R are in (15).
16. This research was supported by grants from the Institute of Geophysics and Planetary Physics at the Los Alamos National Laboratory and the National Aeronautics and Space Administration Ames Research Center.

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Water Sources for Subduction Zone Volcanism: New Experimental Constraints

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Despite its acknowledged importance, the role of water in the genesis of subduction zone volcanism is poorly understood. Amphibole dehydration in subducting oceanic crust at a single pressure is assumed to generate the water required for melting, but experimental constraints on the reaction are limited, and little attention has been paid to reactions involving other hydrous minerals. Experiments on an oceanic basalt at pressure-temperature conditions relevant to subducting slabs demonstrate that amphibole dehydration is spread over a depth interval of at least 20 kilometers. Reactions involving other hydrous minerals, including mica, epidote, chloritoid, and lawsonite, also release water over a wide depth interval, and in some subduction zones these phases may transport water to deep levels in the mantle.

Water plays an important role in subduction zones. It is incorporated in basaltic oceanic crust by hydrothermal alteration at mid-ocean ridges, and during subduction it is released in a series of mineral reactions that transform the hydrated basalt to eclogite. Some of this water moves upward and hydrates the mantle wedge overlying the slab. The consistent location of volcanic fronts 100 to 150 km above the slab (1, 2) has been interpreted to be a consequence of dehydration-melting involving amphibole in this hydrated mantle (2-4). The water may also allow the slab to melt directly if temperatures are high enough and will enhance mineral reactions at otherwise kinetically unfavorable low temperatures. Some water may be retained to great depth in high-pressure hydrous minerals and nominally anhydrous minerals.

Despite the obvious importance of hydrous minerals in subduction zones, the pressure-temperature conditions at which dehydration reactions occur in the slab are uncertain. Studies of the wet melting of natural basaltic rocks (5, 6) and peridotitic rocks (7, 8) have shown that amphibole is the most important hydrous phase at high pressures and temperatures in these compositions and indicate that it is stable to higher pressures in peridotitic mantle wedge than in subducted basaltic oceanic crust: ~30 kbar (7) versus ~27 kbar (5, 6). However, in these earlier studies amphibole stability was not investigated at temperatures below the wet solidus, which are particularly relevant for subduction zones, and only the final disappearance of the amphibole was documented so that the pressure-temperature interval over which amphibole dehydration occurs is uncertain. We therefore investigated the subsolidus stability of amphibole in a natural oceanic basalt, assumed to be typical of slab basalt.

Although amphibole is certainly the

principal hydrous phase in subducting oceanic crust, the need for data on other hydrous minerals (for example, chlorite, epidote, chloritoid, and pumpellyite) has been recognized (9). Dehydration of these phases in the slab at a greater depth than amphibole dehydration might produce the fluid involved in the petrogenesis of back-arc basin volcanics (10). Therefore, we also investigated the stability of other hydrous phases in basalt at temperatures close to the solidus and near the high-pressure limit of amphibole stability. In addition, to determine whether any hydrous minerals might remain stable within the basaltic part of the slab to much greater depth, we conducted two experiments at ~75 kbar and 1000°C using a basaltic composition and a basaltic composition. The basaltic composition was used to determine whether high concentrations of K and Ti affect the stability of hydrous minerals.

We performed most of the experiments at pressures of 20 to 30 kbar and temperatures of 650 to 725°C using piston-cylinder apparatus (11). These conditions were selected to span the expected range of pressure and temperature in subducting slabs after passing through blueschist- and eclogite-facies metamorphic zones (12). The starting composition (Table 1) was designed to approximate that of subducted oceanic crust. It consisted of mid-ocean ridge basalt (MORB) with seeds of garnet, omphacitic pyroxene, epidote, sodic amphibole, and phengitic mica to facilitate reaction at low temperatures (13). For the two experiments at 75 kbar we used a multianvil apparatus (14). The basaltic starting material contained MORB glass, sodic amphibole, lawsonite, quartz, and muscovite. The MORB was replaced by kaersutite amphibole in the basaltic composition (15).

Run products were examined under a petrographic microscope and with powder x-ray diffraction. We used Fourier transform infrared spectroscopy (FTIR) to identify hydrous phases and for quantifying modal variations. For standards we used hydroxyl-stretching frequencies obtained from natural samples, as well as published spectra of natural and synthetic samples (16). Compositions of some run products were determined by electron microprobe analysis (EMPA).

All run products (Table 1 and Fig. 1), including those produced at 75 kbar and 1000°C, contained garnet, clinopyroxene, and a silica polymorph, either quartz or coesite. Hydrous minerals were produced in all of the experiments at ≤30 kbar. Amphibole was the most abundant phase at 20 kbar, decreased in abundance to 25 kbar, and was absent at 30 kbar; mica and epidote were present in all of these exper-

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Table 1. Compositions of the starting material used in experiments at 20 to 30 kbar and of some representative minerals produced in the experi-

ments. Comp, component; Pyrox., pyroxene; Amph., amphibole; Chlor., chloritoid; and Start. mat., starting material.

Comp.	Start. mat.	Garnet 25 kbar 700°C	Garnet 30 kbar 670°C	Garnet 75 kbar 1000°C	Pyrox. 25 kbar 700°C	Pyrox. 30 kbar 670°C	Pyrox. 75 kbar 1000°C	Amph. 20 kbar 670°C	Amph. 20 kbar 700°C	Mica 30 kbar 670°C	Epidote 23 kbar 685°C	Chlor. 20 kbar 670°C
SiO ₂	49.20	38.36	38.44	40.65	54.06	55.30	56.45	49.18	46.80	51.32	37.77	26.16
TiO ₂	1.62	0.53	0.52	0.64	0.04	0.06	0.16	0.58	2.23	0.11	0.14	0.11
Al ₂ O ₃	14.11	21.53	21.05	21.89	7.42	6.68	12.23	13.73	11.41	24.89	24.94	40.16
FeO*	11.18	24.44	26.82	18.01	9.52	10.22	4.83	15.81	15.10	4.05	10.55	18.53
MnO	0.18	0.73	0.73	0.61	0.05	0.13	0.07	0.15	0.25	0.06	0.28	0.12
MgO	6.89	4.10	3.85	8.63	7.51	7.97	7.80	10.37	11.47	3.67	0.06	5.81
CaO	12.15	9.60	9.40	11.14	13.57	14.36	10.82	6.32	7.08	0.85	22.68	0.21
Na ₂ O	3.19	0.05	0.05	0.17	6.44	6.74	7.41	3.50	3.61	0.17	0.02	0.06
K ₂ O	0.35			0.02			0.06	0.22	0.27	9.50		0.02
Total	98.96	99.45	100.86	101.76	98.61	101.46	99.83	99.86	98.22	94.62	96.44	91.18

*All Fe as FeO.

iments; chloritoid crystallized at 23 kbar and 650°C, and 25 kbar and 650° to 700°C; and lawsonite crystallized at 30 kbar and 670°C.

Our results show that at temperatures below that of the water-saturated solidus, amphibole breaks down in a nearly isobaric reaction at 25 to 26 kbar. The slope (dP/dT) of the reaction is slightly positive from 675 to 700°C, but becomes slightly negative at higher temperatures. Our location of this reaction is in good agreement with the location determined from earlier work (5, 6). Amphibole made up about 50% by volume of the two experiments at 20 kbar. This content is similar to the maximum estimated by Hill and Boettcher (5). Although we did not conduct any experiments below 20 kbar, we assume that the amount of amphibole does not increase much below this pressure. Above 20 kbar the amount decreased, and at 25 kbar there was little remaining; thus, the main amphibole dehy-

dratation reaction begins at 20 kbar. At 700°C the reaction was completed at ~26 kbar. Only amphiboles synthesized in the two experiments at 20 kbar were large enough to obtain compositional analyses (Table 1) and were found to be close to barroisite: NaCaMg₃Al₂Si₇AlO₂₂(OH)₂ (17). Barroisitic amphiboles are common in rocks that have been metamorphosed at high pressure and high temperature (18).

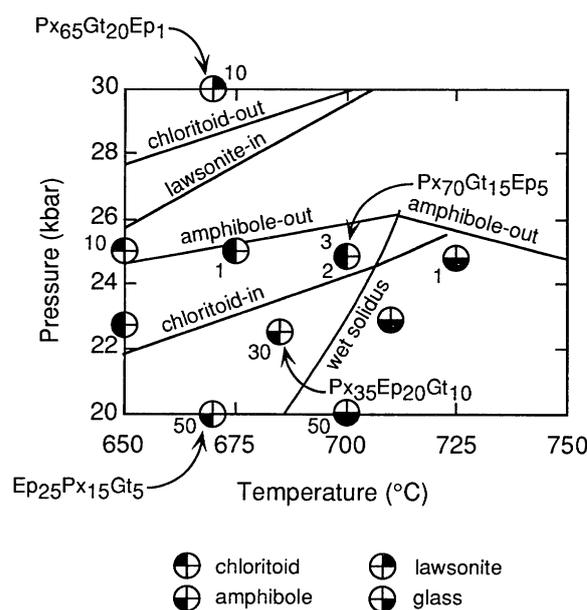
The mica synthesized in our experiments was phengite, of composition K(Mg_{0.3}Fe²⁺_{0.2}Al_{1.5})(Si_{3.5}Al_{0.5})O₁₀(OH)₂. Its abundance did not appear to change with pressure and temperature. Because of the low K content of the basaltic starting material, it cannot exceed 2% by weight. Mica was not produced from either bulk composition at 75 kbar and 1000°C, even though both experiments contained phengite seeds. All epidotes had an approximate composition of Ca₂(Al_{2.3}Fe³⁺_{0.7})Si₃O₁₂(OH). Epidote abundance decreased with

increasing pressure and was less than 1% by weight at 30 kbar. This pressure is likely to be close to its upper pressure stability limit. Epidote and mica have been found in earlier experimental studies on basalts (6), and they are common in high-pressure, high-temperature eclogite-facies metabasalts.

Chloritoid and lawsonite, which were both absent from the basaltic starting material used in the experiments at ≤30 kbar, were common phases in the run products. Their synthesis fields thus represent their minimum stability fields. Both were easily identified from powder FTIR by their characteristic hydroxyl-stretching frequencies. The intensity of the chloritoid band increased with increasing pressure and decreasing temperature above the chloritoid-in reaction, which lies between 650° and 685°C at 23 kbar and between 700° and 725°C at 25 kbar (Fig. 1). EMPA of chloritoid was successful in only one sample. The composition was close to (Mg_{0.8}Fe²⁺_{1.2})-(Al_{3.8}Fe³⁺_{0.2})Si₂O₁₀(OH)₄. Chloritoid was recently reported in experiments with a synthetic olivine basalt (19); the composition resulting from experiments at 24 kbar and 650°C is similar to that in our experiments. Also, magnesiochloritoid is found in natural high-pressure Mg-rich metapelites and metagabbros (20).

Lawsonite was synthesized only at 30 kbar and 670°C, but sluggish kinetics may have inhibited its growth at 25 kbar and 650°C (21). Our stability field for lawsonite is in good agreement with results from experiments up to 33 kbar on its own composition, in which lawsonite was stable up to 657°C at 25 kbar and 745°C at 33 kbar (22). No compositional analyses were obtained of our lawsonite, but the composition of most natural samples is close to CaAl₂Si₂O₇(OH)₂·H₂O. Lawsonite is a common constituent of high-pressure, low-temperature blueschist-facies metabasalt. Pseudomorphs after lawsonite are common in eclogite, and lawsonite is present locally (23).

Fig. 1. Results of experiments at 20 to 30 kbar. As well as the minerals represented by the symbols, all run products contained garnet (Gt), pyroxene (Px), and epidote (Ep). Their concentrations are given in percent by weight, estimated by mass balance from available electron microprobe analyses. All run products also contained 2 to 3% quartz or coesite, and about 2% mica. The approximate locations of reactions are shown. The small increase followed by decrease in amphibole abundance in the three higher temperature experiments at 25 kbar suggests that the amphibole-out reactions have the shallow slopes shown. No difference in results was observed between experiments with crystalline MORB and those with MORB glass. Experiments at 75 kbar are not shown but consist only of garnet, pyroxene, and coesite.



Three of the higher temperature samples contained a small amount of glass in interstices between crystals. The glass was quite distinct from the angular glass fragments of the starting material and thus represented formation of melt (Fig. 1). Our location of the wet basalt solidus is in agreement with earlier results (5, 6).

Our observations that amphibole dehydration is continuous from ~20 to 26 kbar (at 700°C) and that other hydrous phases are stable to higher pressures imply that water release from subducting slabs is complex and critically dependent on the rate that a specific slab heats up as it descends into the mantle. Recently Peacock (24) calculated that the top of subducted oceanic crust will reach a pressure of 20 kbar at temperatures from 150° to 1050°C, the actual temperature depending principally on the rate of shear heating in the subduction shear zone. The temperature range of our experiments is in the middle of this temperature range and includes reactions that will be important at both lower and higher temperatures. We calculated the amount of water that could be contained in the basaltic part of the slab as it subducts through four possible heating paths that cross our pressure-temperature window (Fig. 2). We assumed that the slab contains at least as much water at 20 kbar as the experimental sample at 670°C and 20 kbar. In the case where heating is rapid (high temperatures, path A), some water will be released below the wet solidus, and after crossing the solidus the continuing amphibole dehydration reaction will trigger partial melting in the slab. By about 750°C, all of the amphibole will have disappeared, leaving only a minor amount of epidote and mica. The melt produced will have a high H₂O content (~22% by weight) and a high SiO₂ content; it may rise through the slab and into the overlying mantle and crystallize, or continue its ascent. The top of a slab

following path B will release most of its original water below the solidus from 20 to 25 kbar (depths of about 70 to 90 km), largely as the result of amphibole breakdown; some of the water will presumably rise and hydrate the overlying mantle peridotite. Only a little amphibole remains as the path crosses the wet solidus, and therefore, if all the H₂O released in dehydration reactions has left the slab, the amount of water available for melting will depend on the stability limits of the other hydrous minerals present: chloritoid, epidote, and mica. In a slab following path C, all of the amphibole breaks down below 650°C in a continuous reaction to 25 kbar. At 25 kbar and 650°C, however, a significant amount of water is still contained in the slab within chloritoid, and the release of water at temperatures up to the solidus will therefore depend on its stability. Under this path, water may be released over a pressure interval of more than 10 kbar, that is from around 20 to 30 kbar; this water may rise and hydrate the overlying mantle wedge. Under path D, amphibole breaks down well below 650°C, but significant amounts of water remain in the slab incorporated in lawsonite, whose high-pressure stability has not been determined. The position of the wet basalt solidus above 35 kbar is also unknown. Thus the relative importance of lawsonite breakdown versus melting at greater depths is unclear, and lawsonite might dehydrate at a sufficient depth, and a low enough temperature, for the released water to be incorporated in a hydrous mineral, such as phase A (25), that is stable in cold mantle being dragged down with the slab. Its subsequent fate would then depend on the relations between the stability field of phase A and the pressure-temperature conditions of the down-dragged mantle. Our experiments demonstrate that all phases must dehydrate before 75 kbar and 1000°C. If subduction zone volcanism is

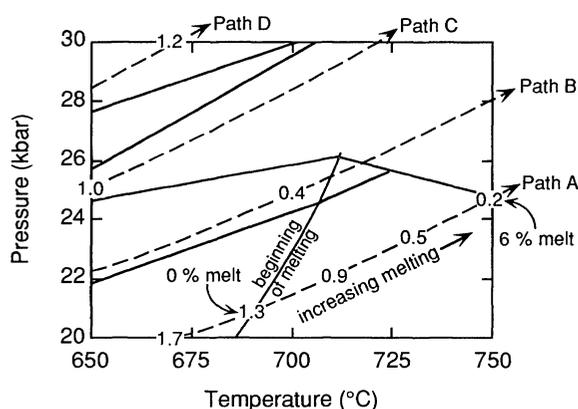
caused by melting of hydrated peridotitic mantle wedge, in which amphibole is stable to ~30 kbar, most of the water released from the slab in these four paths will be available to produce amphibole in the wedge and to allow melting to occur.

Temperatures typically decrease toward the slab interior at any depth. Therefore, low-temperature hydrous phases such as chloritoid and lawsonite may be stable in the interior of the slab even if they are unstable at its top. The history of water release will therefore depend on the pressure-temperature conditions of the entire hydrated region of the slab. It may be that in cold subduction zones no water at all is released until these low-temperature hydrous minerals dehydrate. Depending on the depth at which this occurs, the water may either produce amphibole in the mantle wedge or ascend to a region of the mantle that is at a temperature above its wet solidus. The resulting melt could produce volcanoes that fall in the observed depth to the subducted slab of 124 ± 38 km if slab dehydration occurs at this same depth. The latter scenario would obviate the need for the escalator transport mechanism (4) to explain the geometry of subduction zone volcanism.

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Fig. 2. Summary of experimental results showing mineral reactions from Fig. 1, H₂O contents of four of our subsolidus experiments, and estimated H₂O contents of basaltic slab at three supersolidus temperatures. Dashed lines represent four schematic pressure-temperature-time paths of subducted slab which pass through these points. Paths are based on paths for the top of the oceanic crust of Peacock (24). H₂O contents (in percent by weight) for the experiments were calculated from mineral compositions in Table 1, for ideal H₂O contents (amphibole = 2.1, mica = 4.5, epidote = 1.9, chloritoid = 7.5, lawsonite = 11.5); we estimated the high-temperature H₂O contents by assuming that amphibole abundance decreased continuously from 50 to 0%, and epidote abundance from 25 to 5%, between 670 and 750°C. The amount of melt increases from 0% at the wet solidus to 6% at 750°C.



- ≥ 2.8 log units above the Ni-NiO buffer. Although the fO_2 in subduction zones is likely to be higher than 1 log unit below the Ni-NiO buffer [B. J. Wood, L. T. Bryndzia, K. E. Johnson, *Science* **248**, 337 (1990)], our measured fO_2 is probably unrealistically high. However, because our modal assemblages and mineral compositions are similar to those obtained in experiments on a synthetic olivine basalt, buffered to Ni-NiO (19), we suggest that the difference in fO_2 has little effect on phase relations.
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Pliocene Paleoclimate and East Antarctic Ice-Sheet History from Surficial Ash Deposits

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The preservation, age, and stratigraphic relation of an in situ ashfall layer with an underlying desert pavement in Arena Valley, southern Victoria Land, indicate that a cold-desert climate has persisted in Arena Valley during the past 4.3 million years. These data indicate that the present East Antarctic Ice Sheet has endured for this time and that average temperatures during the Pliocene in Arena Valley were no greater than 3°C above present values. One implication is that the collapse of the East Antarctic Ice Sheet due to greenhouse warming is unlikely, even if global atmospheric temperatures rise to levels last experienced during mid-Pliocene times.

Two divergent hypotheses have been developed with regard to Pliocene paleoclimate and East Antarctic Ice Sheet dynamics. The first hypothesis, based on the ecology of warm-water marine diatoms and *Nothofagus* (Southern Beech) wood within Sirius Group glacial deposits in the Transantarctic Mountains, postulates that East Antarctic ice-sheet deglaciation occurred about 3.0 million years ago (Ma) (1-8).

This hypothesis relies on two fundamental assumptions. The first is that reworked marine diatoms within the Sirius Group originated in ocean basins in the interior of East Antarctica and were subsequently transported into the forested Transantarctic Mountains by an expanded East Antarctic ice sheet. The second is that the biostratigraphy of sub-Antarctic deep-sea cores applies to far southern regions of interior Antarctica and hence can be used to apply confining ages to the Sirius Group. The latter assumption has apparently been confirmed by independent dating of volcanic ash in association with marine diatoms in the CIROS-2 core, southern Victoria Land (1). In sharp contrast, the second hypothesis postulates that the East Antarctic Ice

Sheet has been relatively stable under persistent cold-desert conditions since around 14 Ma (9). This hypothesis is based on interpretation of the marine-oxygen isotope record, which shows little change at about 3.0 Ma. To evaluate these contradictory hypotheses, we examined Pliocene surficial sediments in Arena Valley, southern Victoria Land, for physical evidence of either warmer-than-present climates, including traces of meltwater (for example, rills, stream channels, mudflows, or levees), or persistent cold-desert conditions similar to the present climate (in which desert pavement, ultraxerous soil, and sand wedges are common).

The Dry Valleys region of southern Victoria Land features about 4000 km² of predominantly ice-free, mountainous desert between the McMurdo Sound sector of the Ross Sea and the East Antarctic polar plateau (Fig. 1). Arena Valley, which lies at an average elevation of 1400 m in the Quartermain Mountains along the western margin of the Dry Valleys region, extends for 70 km² and is predominantly ice-free. A cold-based peripheral lobe of the upper Taylor Glacier extends 0.5 km into lower Arena Valley (10). Mean annual temperatures in Arena Valley are about -30°C , and precipitation is less than 45 mm of water equivalent (11). Under such climatic conditions ablation of Taylor Glacier at the valley mouth is entirely by sublimation (10). Glacial drifts, hummocky moraines,

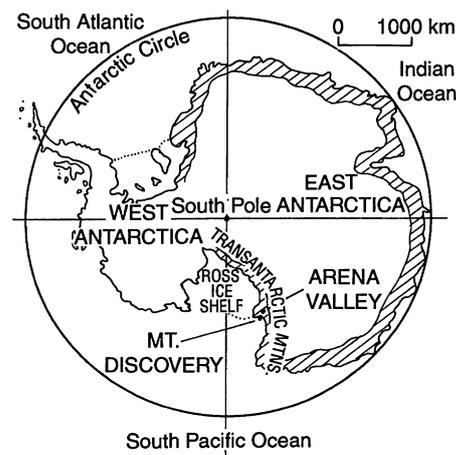


Fig. 1. Location map of Arena Valley, southern Victoria Land, Antarctica. Hatch marks represent the areal extent of surface-melting ablation zones in East Antarctica that we calculate would occur with a 22°C rise in atmospheric temperature over Antarctica. We suggest that Pliocene deglaciation of the East Antarctic Ice Sheet from elevated atmospheric temperatures would require a rise of the 0° isotherm to at least an elevation of 1600 m, or about 200 m elevation above the Arena Valley Ash deposit. Outside Antarctica, sediments that lie at or near the 0°C isotherm show a dynamic surficial stratigraphy.

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