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18. Because the unit cell parameters were refined in the *Pbnm* space group, some uncertainties may have been introduced in the unit-cell volume of the high-temperature phase. However, because most of the major reflections exhibit a sharp increase in the corresponding *d*-spacings across 623 K, the apparent unit-cell volume represents a reasonable approximation to the real cell, with a multiplication factor because of change in number of formula units per cell. This approximation was further checked in an analysis where both phases were refined in pseudocubic cells. Although the estimated errors were a factor of 2 to 5 larger, a similar volume increase was observed. Volumetric thermal expansivities (that is, the slope of the data) were also similar to those shown in Fig. 1.
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Field-Based Evidence for Devolatilization in Subduction Zones: Implications for Arc Magmatism

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Metamorphic rocks on Santa Catalina Island, California, afford examination of fluid-related processes at depths of 15 to 45 kilometers in an Early Cretaceous subduction zone. A combination of field, stable isotope, and volatile content data for the Catalina Schist indicates kilometer-scale transport of large amounts of water-rich fluid with uniform oxygen and hydrogen isotope compositions. The fluids were liberated in devolatilizing, relatively low-temperature (400° to 600°C) parts of the subduction zone, primarily by chlorite-breakdown reactions. An evaluation of pertinent phase equilibria indicates that chlorite in mafic and sedimentary rocks and melange may stabilize a large volatile component to great depths (perhaps >100 kilometers), depending on the thermal structure of the subduction zone. This evidence for deep volatile subduction and large-scale flow of slab-derived, water-rich fluids lends credence to models that invoke fluid addition to sites of arc magma genesis.

SUBDUCTION TRANSFERS VOLATILE-rich, hydrothermally altered igneous rocks produced at mid-ocean ridges and sediments deposited on the sea-floor abyssal plain and in trenches to the upper mantle. At deep levels in subduction zones (>15 km), volatiles released by metamorphic devolatilization reactions play key roles in the geochemical evolution of the slab-mantle interface and in the overlying mantle wedge. Petrologic relations and trace element and isotopic systematics in arc volcanic rocks suggest that water-rich fluids flux partial melting in the source regions of arc magmatism [depths of 80 to 150 km (*1*)] and contribute slab-derived chemical components to such regions [radiogenic isotopic signatures of Pb, Sr, and Be, and trace elements (*2*)].

Direct field-based studies of the effects of fluid production and transport at depths >15 km have been lacking. Evaluations of the significance of fluid processes at great depths in subduction zones have been limited to the study of indirect products of subduction (arc volcanic rocks) and to theoretical models of thermal evolution and devolatilization (*3, 4*). Exposures of blueschists, eclogites, and other associated metamorphic rocks record relatively high-pressure, low-temperature conditions present in subduction zones at depths of 15 to 90 km (*4, 5*). They generally contain abundant veins and other evidence for fluid mobility and metasomatic interactions during metamorphism. These terranes allow direct assessments of volatile reservoirs in subducted rocks, of progressive volatile release during metamorphism, and of fluid transport mechanisms during subduction. In this report, I present stable isotope and field evidence, from blueschist and higher grade metamorphic rocks of the Catalina Schist (Santa Catalina Island, southern California). These data record the effects of progressive devolatilization and large-scale fluid transport at depths of 15 to 45 km in an Early Cretaceous subduction zone and, together with considerations of plausible subducted volatile reservoirs and rock pressure-temperature (*P-T*) histories, allow inference of the devolatilization history in deeper parts of subduction zones and its relevance to arc magmatism.

The Catalina Schist consists of three major metamorphic-tectonic units juxtaposed along low-angle faults (*6*). The structurally lowest, lawsonite-albite to blueschist facies unit is composed primarily of metasedimentary rocks, with lesser amounts of metamorphosed mafic and ultramafic rocks. This unit is structurally overlain by a unit that ranges in grade from glaucophanic greenschist to epidote amphibolite and consists primarily of metamorphosed mafic and sedimentary rocks. The structurally highest unit is amphibolite grade and contains metamafic and

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meta-ultramafic rock with only minor amounts of metasedimentary rocks. Zones of melange throughout the Catalina Schist represent mechanical mixing of sedimentary, mafic, and ultramafic rocks. The units were probably juxtaposed during initiation of subduction beneath the western margin of North America in the Early Cretaceous (*7*). Rock types similar to those in the Catalina Schist are found in many other noncollisional subduction-zone metamorphic terranes, particularly those along the western margin of North America (*8*) and on the sea floor (*9*).

Evidence for fluid transport and associated mass transfer during metamorphism in the Catalina Schist includes veins, reaction zones between disparate lithologies, changes in bulk chemical composition, and changes in isotopic composition (*10–12*). The wide range of metamorphic grade represented by the Catalina Schist (inferred *T* range of 350° to 750°C at 5 to 11 kbars) makes these rocks particularly suitable for observing changes in volatile content with progressive metamorphism, inferring devolatilization histories, and estimating compositions and mass transport capabilities of the metamorphic fluids. The range in metamorphic grade also permits assessment of large-scale fluid exchange between different parts of a single evolving accretionary complex.

Measured $\delta^{18}O$ of quartz from veins, siliceous schists, and melange matrix in the Catalina Schist decreases with increasing metamorphic grade, from values near +17.4 per mil in the lawsonite-albite and blueschist facies rocks (petrologically inferred *T*, 400°C) to values near +14.4 per mil for the highest grade amphibolite facies rocks (inferred *T*, 650°C). On the basis of experimentally derived quartz-water isotope fractionations (Fig. 1A) and the quartz data, this trend in $\delta^{18}O$ is interpreted to reflect equilibration of the quartz in each unit at petrologically inferred peak metamorphic temperatures with waters of uniform $\delta^{18}O$ of +13 ± 1 per mil (see arrows and shaded region in Fig. 1A). Calculated water $\delta^{18}O$ values for other minerals in veins and melange matrix yield similar results [see figure 2 in (*11*)]. δD values of vein and melange matrix minerals show increases with increasing metamorphic grade that can be the result of equilibration at petrologically inferred temperatures with fluids of uniform δD (−15 ± 15 per mil; Fig. 1B).

Host rocks have equilibrated with the vein-forming fluids to varying degrees, as indicated by shifts from probable protolith (presubduction) oxygen isotopic compositions toward compositions in isotopic equilibrium with the fluids at petrologically inferred temperatures [see figure 2 in (*11*)].

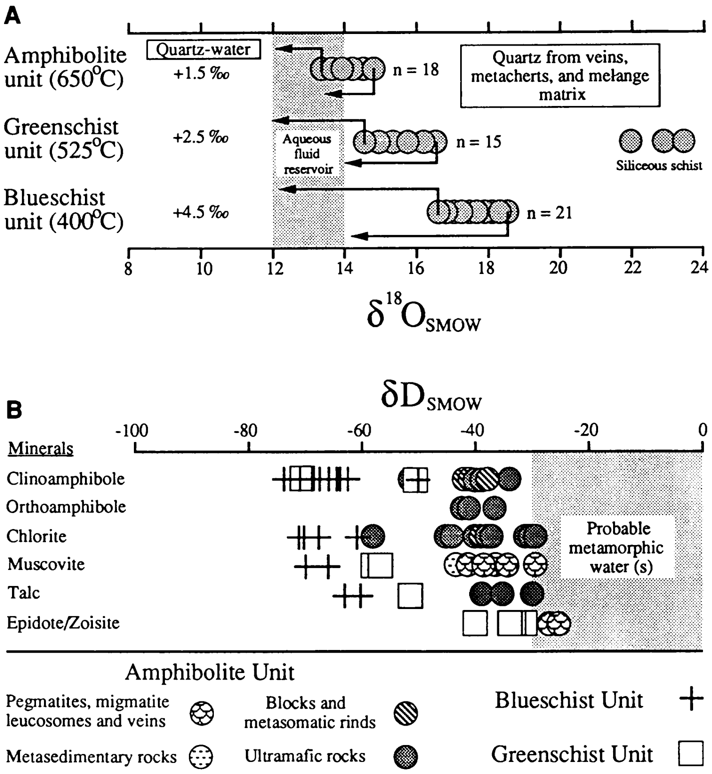

Fig. 1. Calculated fluid O and H isotopic compositions from data for the Catalina Schist; *n* = number of samples. Blueschist data include data for lawsonite-albite-facies rocks; greenschist data include data for glaucophanic greenschist- and epidote-amphibolite-facies rocks. (**A**) Quartz $\delta^{18}O$ data and inferred water $\delta^{18}O$ of +13 ± 1 per mil (shaded area). Arrows indicate experimentally derived quartz-water fractionations at each temperature. (**B**) Hydrogen isotope data and inferred range in δD of metamorphic fluids (shaded area).

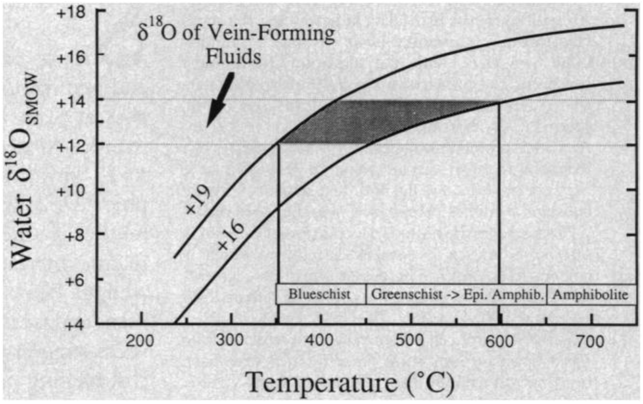

Fig. 2. Plot of water $\delta^{18}O$ versus temperature. Curves are calculated for water in equilibrium with quartz with $\delta^{18}O$ of +16 and +19 per mil.

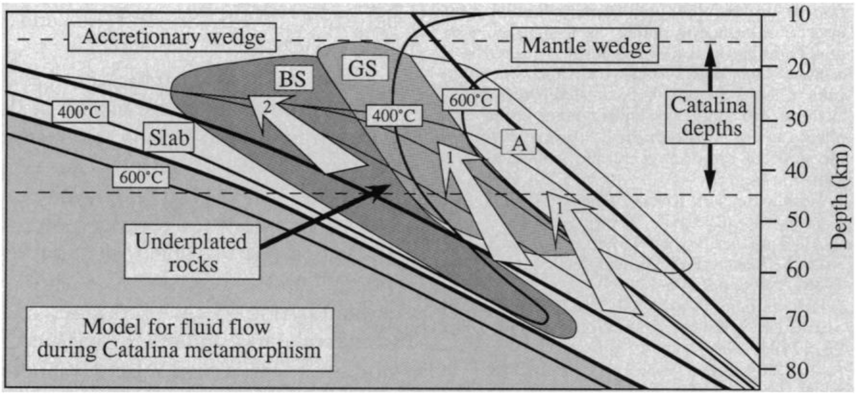

Fig. 3. Model for structural setting, thermal environment, and fluid flow during metamorphism of the Catalina Schist. Shaded areas labeled BS, GS, and A denote schematic stability fields for the blueschist, greenschist, and amphibolite facies, respectively, at the slab-mantle interface. Arrows represent plausible fluid flow paths from 400° to 600°C regions, where maximum water loss occurred, into cooler and warmer parts of the subduction zone.

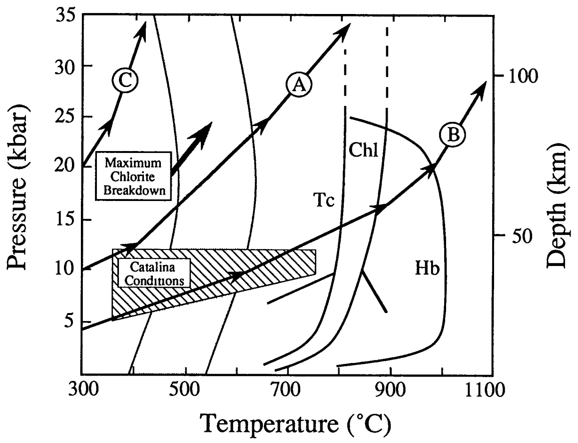

Fig. 4. A *P*-*T* diagram showing the approximate 400° to 600°C interval of maximum chlorite and chloritoid breakdown in mafic and sedimentary rocks (shaded region) and calculated *P*-*T* paths for subducted rocks at the top of the slab [from (*4*)]. Paths A and C were calculated for subduction of oceanic crust ~50 million years old; path B was calculated for crust ~10 million years old. Sources of chlorite and chloritoid breakdown reactions are given in (*21*). Curves labeled Tc and Chl are breakdown curves for talc and 14A-clinochlore in more ultramafic bulk compositions such as melange matrix (*28*). The area with the diagonal pattern indicates inferred *P*-*T* conditions for the Catalina Schist [from (*6, 10*)].

Quartz-rich rocks interpreted to be metamorphosed cherts had initial $\delta^{18}O$ values between +25 and +35 per mil (*13*), but most presently have values identical to those of the vein quartz (Fig. 1A) (*13*). The $\delta^{18}O$ values of many mafic rocks (metamorphosed basaltic and gabbroic rocks) are shifted from probable protolith compositions; expected protolith values are +5 to +9 per mil (*14*), whereas measured values range from +10 to +15 per mil. The $\delta^{18}O$ values of amphibolite-grade melange matrix are shifted from values expected for simple mechanical mixing (probably between +5 and +8 per mil) to higher values [$>$ +8 per mil (*12*)] that reflect equilibration with the infiltrating fluids. Some higher grade, particularly amphibolite grade, metasedimentary and metamafic rocks away from veins and melange zones have $\delta^{18}O$ values indicating failure to equilibrate with the fluids [high-$\delta^{18}O$ metasedimentary rocks and low-$\delta^{18}O$ metamafic rocks (*11*)]. Isotopic homogenization of host rocks is particularly evident near veins and in melange zones (*10, 12*); this, together with vein abundance [up to 50% by volume in some exposures (*11*)], suggests that the fluid flow was primarily localized along fractures and shear zones.

Calculated O isotope compositions for the fluids indicate that the fluids originated through devolatilization reactions in relatively low-*T*, sediment-rich parts of the subduction zone. Equilibration of water-rich fluid with metasedimentary rocks similar to those of the Catalina Schist (quartz $\delta^{18}O$ of +16 to +19 per mil in all units) in the temperature range of ~350° to 600°C (between curves in the shaded region, Fig. 2) could produce the inferred +13 ± 1 per mil range in fluid $\delta^{18}O$ values (within dotted lines, Fig. 2). This inference of a relatively low-*T* fluid source is consistent with expected volatile loss during inferred devolatilization reactions and trends in volatile content in the Catalina Schist with increasing metamorphic grade. For both mafic and sedimentary rocks, most of the water loss is expected to occur during chlorite breakdown reactions (chlorite contains approximately 12% water by weight), generally over the *T* interval of 400° to 600°C. Accordingly, the water content in mafic and sedimentary rocks of the Catalina Schist decreases progressively with decreases in chlorite modal abundances corresponding to metamorphism over this *T* interval (*15, 16*).

Petrologic and geochemical evidence, including the O and H isotope systematics, vein mineralogy, fluid inclusion data, and evidence for partial melting of mafic rocks (*17*), suggests that the fluids were water-rich but contained other C-O-H-S-N species. Calculations of C-O-H fluid compositions in equilibrium with graphite in low-*T* metasedimentary rocks (400°C, 10 kbars) indicate that water-rich fluids (mole fraction of H_2O > 0.98) could have resulted from devolatilization of such rocks (*10*). Trends in N concentration and isotopic composition and C isotope compositions of metasedimentary rocks with increasing metamorphic grade indicate that the fluids contained minor amounts of N_2 and CH_4 (*10, 12*); some fluid inclusions contain CH_4 (*17*). The presence of sulfide minerals in veins indicates S mobility in the fluids, probably as H_2S (*10*).

The units of the Catalina Schist represent progressive underplating of sedimentary, mafic, and ultramafic rocks during early stages of subduction (Fig. 3) (*6*). Such a setting accounts for the relatively high inferred temperatures (400° and 600°C isotherms on Fig. 3) (*18*). The O isotope data indicate that some up-*T* fluid flow occurred during metamorphism (arrows labeled 1 on Fig. 3). Most of the fluid flow was probably down-*T*, however, parallel to the thrust surface (arrow 2 in Fig. 3); precipitation of the abundant quartz veins in the lower grade units is best explained by down-*T* flow (*11, 19*). The inferred O isotope compositions of the fluids are probably the result of equilibration with metasedimentary rocks similar to those of the Catalina Schist at temperatures similar to those inferred for the lower grade units (400° to 600°C). This suggests a fluid source in devolatilizing, relatively low-*T* parts of the subduction zone. However, the fluids need not have been derived from the low-grade units as exposed and are likely to have been derived from greater depths (see inferred "Catalina depths" and fluid flow arrows in Fig. 3) (*20*). If so, fluids would have risen along flow paths that are dominantly parallel to the subduction thrust.

Inferred devolatilization reaction histories predict that substantial water release in subducted mafic and sedimentary rocks occurs, in general, in the *P*-*T* interval over which chlorite breaks down (*21, 22*). Most devolatilization reactions are relatively insensitive to *P*; thus, chlorite breakdown probably occurs over a similar 400° to 600°C *T* interval for a wide range of *P*. Much of the loss of water-soluble species (large-ion lithophile elements, B, N_2, and so forth) may occur over this breakdown interval. The depth at which this fluid release occurs is largely dependent on the thermal structure of the subduction zone. For early stages of subduction (Fig. 4, rock *P*-*T*-time path A) and for cases where young, hot oceanic crust is subducted (path B), rocks experience relatively high-temperature *P*-*T*-time paths. Rocks encounter the 400° to 600°C interval of chlorite or chloritoid breakdown at relatively shallow levels, as recorded by the Catalina Schist (Figs. 3 and 4). Relatively cool *P*-*T*-time paths taken by rocks during later stages of subduction (*4*) could result in water loss at much greater depths (path C corresponds to subduction of ~500 km of oceanic crust), perhaps to more than 100 km. Most numerical models suggest that, in mature subduction zones, subsolidus 400° to 600°C conditions along the slab-mantle interface may extend to depths equal to or greater than those inferred for sites of arc magma genesis (80 to 150 km) (*4, 18, 23*).

Mechanical mixing and fluid-rock interaction in the melange of the amphibolite unit gave rise to chlorite- and talc-rich assemblages [some nearly monomineralic (*24*)]. In more ultramafic bulk compositions, breakdown of chlorite and talc occurs at higher temperatures (see Tc and Chl curves in Fig. 4), compared with the 400° to 600°C interval of maximum chlorite breakdown in mafic and sedimentary bulk compositions (shaded area in Fig. 4). The development of such mixing zones could thus result in the stabilization of extremely volatile-rich assemblages to great depths (>>100 km), where they could release large amounts of water-rich fluid.

The evidence presented here for devolatilization and large-scale fluid transport, together with evidence for mass transfer in the fluids (*11*), lends credence to models invoking fluid-mediated additions to arc magma source regions (*2*). If deep volatile subduction occurs in chlorite-bearing mafic and sedimentary rocks and melange, previous studies may underestimate the slab volatile component subducted to depths of arc magma source regions (*1*). The results from the Catalina Schist indicate that, despite the highly heterogeneous nature of the rock package subducted, devolatilization and fluid-rock interactions at depths of 15 to 45 km produced a fluid composition homogenized with respect to stable isotope systematics. Such homogenization is compatible with the findings of Morris *et al.* (*25*) and with their interpretation that the slab-derived component is homogeneous in B-Be systematics. Fluids like those that affected the Catalina Schist could contribute significantly to mantle wedge budgets for C, H, S, N, F, and Cl (*26*). Known variations in the nature of the subducted lithologic package (*8, 9, 27*) and variations in geometric and mechanical factors affecting thermal evolution of subduction zones (*23*) point to the necessity of considering geochemical evolution at convergent margins on a system-by-system basis. It may ultimately be possible to correlate devolatilization histories inferred from lithologic and geophysical data with the petrology and geochemistry of arc-volcanic rocks for single subduction systems.

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12. O and H isotope analyses of mineral separate and whole-rock samples are referenced relative to SMOW (standard mean ocean water), using the δ convention. The δ value expresses the difference in absolute isotopic ratios between a sample and a standard, defined as follows:

$$\delta_x = \left[\frac{R_x - R_{std}}{R_{std}}\right] 10^3$$

where $R_x = (D/H)_x$, $(^{18}O/^{16}O)_x$. R_x = ratio for sample; R_{std} = ratio for standard.

Stable isotope compositions of fluid species were calculated from mineral data with the use of various experimental fractionation data compiled in J. R. O'Neil, *Mineral. Soc. Am. Rev. Mineral.* **16**, 1 (1986). Many of the O and H isotope data for the amphibolite unit are from M. D. Barton *et al.*, *Eos* **68**, 1525 (1987). Systematics for N are discussed in G. E. Bebout and M. L. Fogel, *Carnegie Inst. Washington Yearb.* **1989–90**, 19 (1990).

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16. In the blueschist/lawsonite-albite unit, metamafic rocks contain 5 to 8% water by weight; metasedimentary rocks contain 3 to 6% water (*15*). Highest grade, amphibolite-grade metasedimentary and metamafic rocks contain only 0.5 to 1.5% water in relatively water-poor phases such as micas and hornblende.
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19. Over a wide range of *P*, quartz solubility in water increases with increasing *T* [J. V. Walther and H. C. Helgeson, *Am. J. Sci.* **277**, 1315 (1977)]; fluids flowing up-*T* would thus be expected to leach rather than precipitate quartz. Down-*T* flow could result in the precipitation of quartz [see (*11*)].
20. Fluids that infiltrated high-grade units are likely to have been produced at greater depths than those recorded by exposures of the Catalina Schist (see Fig. 3). Low-grade units record similar to lower pressures than high-grade units (*6, 10*), suggesting that transfer of fluid from low-grade to high-grade units as exposed is unlikely. Fluids are expected to rise as a result of buoyancy [see *4*)].
21. See, for example, W. S. Fyfe *et al.*, *Fluids in the Earth's Crust* (Elsevier, Amsterdam, 1978). P. O. Koons and A. B. Thompson [(*Chem. Geol.* **50**, 3 (1985)], W. Schreyer [*Mineral. Mag.* **52**, 1 (1988)], and F. S. Spear and J. T. Cheney [*Contrib. Mineral. Petrol.* **101**, 149 (1989)] more specifically consider phase equilibria involving chlorite and chloritoid (contains ~5 to 7% water) at high *P*. Chloritoid is not likely to be as important a phase because its stability is restricted to rocks more aluminous and more Fe-rich than most typical subduction-related sedimentary rocks. High-*P* phase equilibria for mafic rocks are discussed by J. G. Liou, S. Maruyama, and M. Cho [in *Low-Temperature Metamorphism*, M. Frey, Ed. (Blackie, London, 1987), pp. 59–113], M. J. Apted and J. G. Liou [*Am. J. Sci.* **283**, 328 (1983)], and (*18*). Mafic equilibria at 400° to 600°C for a wide *P* range are dominated by continuous reactions involving chlorite breakdown and stabilization of more aluminous hornblende.
22. This discussion considers plausible devolatilization histories of mafic and sedimentary rocks and differs from others that primarily consider the effects of devolatilizing ultramafic rocks in subduction zones [for example, S. E. Kesson and A. E. Ringwood, *Chem. Geol.* **78**, 83 (1989)]. Uncertainty remains regarding the degree to which deep, ultramafic parts of the ocean lithosphere are hydrated on the sea floor (*14, 15*) or in shallow parts of subduction zones. Hydrated, serpentine-bearing ultramafic rocks (up to ~14% water by weight) are expected to undergo maximum dehydration over a similar 400° to 600°C interval [see (*3*)].
23. See M. N Taksoz and A. T. Hsui, *Tectonophysics* **50**, 177 (1978); S. Honda and S. Uyeda, in *Arc Volcanism: Physics and Tectonics,* D. Shimozuru and I. Yokoyama, Eds. (Terra Scientific, Tokyo, 1983), pp. 117–140; I. S. Sacks and H. Sato, paper presented at the V. M. Goldschmidt Conference, 2 to 4 May 1990, Hunt Valley, Baltimore (Geochemical Society, University Park, PA, 1990), p. 78.
24. S. S. Sorensen, *J. Metamorph. Geol.* **6**, 405 (1988); G. E. Bebout and M. D. Barton, *Eos* **68**, 1524 (1987).
25. J. D. Morris, W. P. Leeman, F. Tera, *Nature* **344**, 31 (1990). Analyses of the B concentration for metasedimentary rocks of the Catalina Schist show a decrease from up to 100 ppm in lowest grade rocks to <10 ppm in the highest grade rocks [G. E. Bebout, J. G. Ryan, W. P. Leeman, *Eos* **71**, 1663 (1990)], consistent with progressive B release to fluids during devolatilization. This finding is consistent with the findings of A. E. Moran, V. B. Sisson, and W. P. Leeman [paper presented at the V. M. Goldschmidt Conference, 2 to 4 May 1990, Hunt Valley, Baltimore (Geochemical Society, University Park, PA, 1990), p. 66]. These results indicate that B loss, accompanying water loss in subducted sedimentary rocks, may occur to great depths in subduction zones, conceivably to depths sufficient for substantial B addition to arc magma source regions.
26. G. E. Bebout and M. D. Barton, *Abstr. 28th Int. Geol. Conf.* (1989), pp. 1–108; G. E. Bebout and M. D. Barton, *Eos* **70**, 1376 (1989).
27. D. E. Karig and R. W. Kay, *Philos. Trans. R. Soc. London Ser. A* **301**, 223 (1978); M. Cloos and R. S. Shreve, *Pure Appl. Geophys.* **128**, 501 (1988).
28. Sources for the breakdown of talc, chlorite, and hornblende are J. V. Chernosky, Jr., *et al.* [*Am. Mineral* **70**, 223 (1985)], D. M. Jenkins and J. V. Chernosky, [*ibid.* **71**, 924 (1986)], and D. M. Jenkins [*Contrib. Mineral. Petrol.* **83**, 375 (1983)].

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