Slab-derived fluids and quartz-vein formation in an accretionary prism, Otago Schist, New Zealand

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ABSTRACT

Regional quartz-vein formation and the fluxes, flow paths, and sources of metamorphic fluids were investigated in the Mesozoic accretionary prism of New Zealand by using a new chemical mass-balance analysis of outcrops. Samples were collected at meter or submeter intervals along outcrop-length traverses and combined to obtain average chemical compositions of whole outcrops. Mass-balance analysis used Zr as an immobile reference frame and as a monitor of sedimentary sorting processes. SiO_2-Zr systematics produced by sedimentary processes differ greatly from those caused by metasomatic mass transfer of silica, allowing evaluation of vein-formation mechanisms. Relatively undeformed metasedimentary outcrops of low metamorphic grade (mostly prehnite-pumpellyite facies) are nearly unveined and characterized by sedimentary compositional trends. More deformed outcrops of higher metamorphic grade (mostly greenschist facies) contain 10–30 vol% quartz veins. These outcrops underwent mass addition of externally derived silica into quartz veins, accompanied by addition of Na and removal of K and W. Average silica additions suggest a time-integrated fluid flux of ~10^4 -10^5 $m^3_{(fluid)}/m^2_{(rock)}$ for fluids ascending through the prism. Dehydration of spilitized oceanic crust subducting beneath the prism is the most probable source for this large fluid flux and could also have caused the Na-K metasomatism. The W removed from deep levels of the prism may have been deposited in focused, retrograde Au-W-quartz veins at shallow levels by ascending fluids. Transfer of SiO_2 from subducting slabs into accretionary prisms is a plausible mechanism for long-term bulk silica enrichment of the continents beyond that possible by magmatic differentiation.

Keywords: fluid flow, quartz veins, accretionary prism, Otago Schist, New Zealand, Au-W mineralization.

INTRODUCTION

Quartz veins are mineralized fractures that are ubiquitous in metamorphic settings and can serve as valuable monitors of fluid flow. Veins may represent conduits for regionally migrating fluids (e.g., Ferry and Dipple, 1991; Ague, 1994), local (centimeter to meter scale) crack-fill diffusional processes (e.g., Yardley and Bottrell, 1992; Cox, 1993), or both (Ague, 1994, 1997). The evaluation of vein-formation mechanisms and the associated metasomatism has been a persistent problem in many orogens, but is vital for assessing the fluxes, flow paths, and chemical impact of fluids during metamorphism.

Accretionary prisms (or wedges) are primary agents of continental growth, yet the role of fluids during metamorphism and exhumation of a prism remains unclear. Fluid flow in prisms is driven mainly by expulsion of sediment pore waters during burial, diagenetic and prograde metamorphic devolitilization of metasedimentary rocks, and dehydration of subducting slabs. Modern settings allow analysis of fluid flow from the shallowest sediments of accretionary prisms, but existing petrologic and isotopic studies have yet to resolve metamorphic fluid fluxes and flow paths below the depths of compaction and pore-water expulsion. Significant regional fluid flow must occur in these crustal environments because most of the world's quartz vein–hosted gold deposits formed during greenschist facies metamorphism in accretionary terranes (Kerrich, 1999).

Our study of reactive fluid flow, centered on the Mesozoic accretionary prism of New Zealand, used mass-balance analysis to investigate the origin of quartz veins and assess regional fluid-flow paths through the prism. The field area is the classic Otago Schist metamorphic sequence comprising the Permian-Cretaceous Torlesse and Caples terranes. The monotonous, graywacke-mudstone turbidites were continuously deformed and metamorphosed during subduction (Mortimer, 2000). Regional deformational and metamorphic gradients were produced by burial and exhumation paths of rocks in the prism (e.g., Batt et al., 2001). Macroscopic deformation textures have traditionally been used to divide the metasedimentary rocks into four textural zones (Turnbull et al., 2001), corresponding to increasing deformational intensity and structural depth (Mortimer, 2000). Textural zones I and II comprise relatively undeformed and unveined rocks of low metamorphic grade (prehnite-pumpellyite to pumpellyite-actinolite facies; i.e., a proxy for protoliths) and zones III and IV include highly deformed and intensely veined rocks of higher metamorphic grade (mostly greenschist facies), containing to 30 vol% quartz veins.

SAMPLING TECHNIQUE

Our goal was to measure bulk compositions of whole outcrops as a function of the deformational (and metamorphic) gradient in the prism to evaluate whether silica and other components were mobile at the outcrop scale. An unprecedented, outcrop-scale traverse-sampling technique was developed to average chemical and grain-size variability in metasedimentary rocks, while integrating all vein material and metasomatic features. More than 600 samples, totaling 2 metric tons, were collected from 21 outcrops over a combined traverse distance of nearly 1 km, a length scale sufficient to characterize regional variations, making this the only sampling effort of its type and magnitude ever undertaken in a metamorphic terrane.

From each outcrop, 3–5 kg samples were collected at set intervals along a measuring tape oriented at a high angle to lithologic layering or foliation[1]. The typical outcrop traverse was 50 m long and consisted of 26 samples. The Macraes Flat Au-W deposit had to be sampled differently; at this site, 16 specimens were randomly selected from the mine dumps. Veins are commonly surrounded by a zone of altered rock (i.e., selvage; Cox, 1993; Ague, 1994), so larger samples (to 16 kg) were taken from highly veined outcrops to include vein, altered selvage, and host rock. From each sample, a representative slab was cut (see footnote 1), cleaned, and pulverized. For a given traverse, 2 g of each pulverized sample were mixed to form an outcrop composite that was then chemically analyzed (see footnote 1). Because rock density varies little (2.72–2.82 g/cm^3; see footnote 1), mass composites are nearly equivalent to volume composites.

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[1] GSA Data Repository item 2002053, Data tables and graphical and detailed text descriptions of sampling technique and statistical analysis, is available from Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301-9140, editing@geosociety.org, or at www.geosociety.org/pubs/ft2002.htm.

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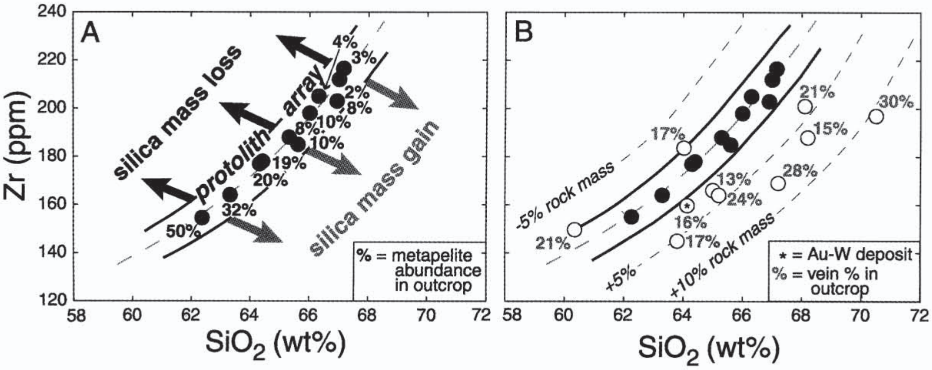

Figure 1. Zr vs. SiO_2 plots for outcrops. Symbol size indicates analytical variability in replicate composites. A: Low-grade textural zone outcrops (closed circles) plot within elongate, positively sloped protolith array. Note decreasing SiO_2 and Zr with increasing metapelite abundance (black %). Metasomatic silica addition or removal trajectories at high angles to protolith array. Array drawn with width ±2% mass change. B: Most high-grade textural zone outcrops (open circles) plot outside array and underwent metasomatic mass additions to 11% by quartz precipitation in veins. Low-grade textural zone outcrops within array contain <3 vol% quartz veins.

OUTCROP CHEMISTRY

MgO, Fe_2O_3, TiO_2, and Al_2O_3 are inversely correlated with SiO_2 in the outcrops, as observed in other metasedimentary terranes (e.g., Moss et al., 1995). The correlations can be attributed either to sedimentary processes that segregated Mg, Fe, Ti, and Al into fine-grained, clay-rich, sediment fractions or to metasomatic SiO_2 mobilization that resulted in relative dilution or enrichment of immobile elements (Ague, 1994, 1997; Moss et al., 1995; Roser and Korsch, 1999). Evaluation of these two processes requires a mineral, like zircon (the primary repository of Zr in sediments), that behaves very differently during sedimentary sorting than during interactions with metamorphic fluids. Zircon tends to be sorted into the coarse, quartz-rich sediment fraction because of its high density and resistance to weathering (Moss et al., 1995; Ague, 1997), yet zircons have been shown to be nearly insoluble in common metamorphic fluids (thus Zr remains immobile) (Ayers and Watson, 1991; Ague, 1994).

Relatively unveined, low-grade textural zone outcrops define a tightly grouped data array having positive Zr correlation with SiO_2 (Fig. 1A). Psammite-rich outcrops occupy the high-SiO_2, high-Zr end, and pelite-rich outcrops occupy the low-SiO_2, low-Zr end. We conclude that variations in outcrop compositions within the array are due to sedimentary depositional processes that produced differing proportions of psammite and pelite from one outcrop to the next. The unique advantage of combining our sampling strategy with the SiO_2 versus Zr plot is that trends of metasomatic mass transfer of silica have negatively sloped trajectories at high angles to the protolith array (Fig. 1A), providing an unambiguous indication of outcrop-scale mass transfer.

Most (80%) of the bulk compositions from high-grade textural zone outcrops plot outside the array and indicate mass addition (Fig. 1B). Vein measurements indicate that all high-grade textural zone outcrops contain abundant quartz veins (Figs. 1B and 2A). Although some vein silica is local, outcrop mass gains of as much as 11% from mass-balance analysis (Ague and van Haren, 1996) indicate that a significant part of the silica was introduced from an external source. The remainder (20%) of the high-grade textural zone outcrops plot within or very near the array. Those outcrops are inferred to contain veins of locally derived silica and may represent minor, localized zones of <2% mass loss. SiO_2-Zr distributions for low- and high-grade textural zone groups are statistically different at the 95% confidence level (two-dimensional Kolmogorov-Smirnov [K-S] test; Press et al., 1992).

Three generations of quartz veins are present in some high-grade textural zone outcrops (Fig. 2A). For example, millimeter-wide, foliation-parallel quartz veins with metamorphic stilpnomelane are cut by two generations of centimeter-wide quartz veins containing albite, actinolite, and clinozoisite that are texturally associated with the destruction of K-rich sheet silicates (Fig. 2, B and C), strongly suggesting the mass transfer of alkali metals. Chemical differences between the Torlesse and Caples terranes have been documented (Roser and Korsch, 1999); however, outcrop bulk-chemical data suggest that high-grade textural zone outcrops underwent systematic addition of Na and, in some cases, Ca and removal of K during vein formation (Fig. 3, A and B), consistent with petrographic observations (Fig. 2, B and C). W was also removed from high-grade textural zone outcrops (Fig. 3C), and Rb and Ba (not shown) behave similarly to K. Reported W concentrations (W*) were measured from aqua regia leach fractions, which attack grain boundaries, common sulfides, and Fe-oxides, and are regarded as proxies for the W most easily mobilized by common metamorphic fluids. Most low- and high-grade textural zone groups are statistically different at the 95% confidence level (Fig. 3). The general absence of metamorphic quartz veins and metasomatic textures in low-grade textural zone rocks suggests little interaction with the deeper quartz vein-forming fluids.

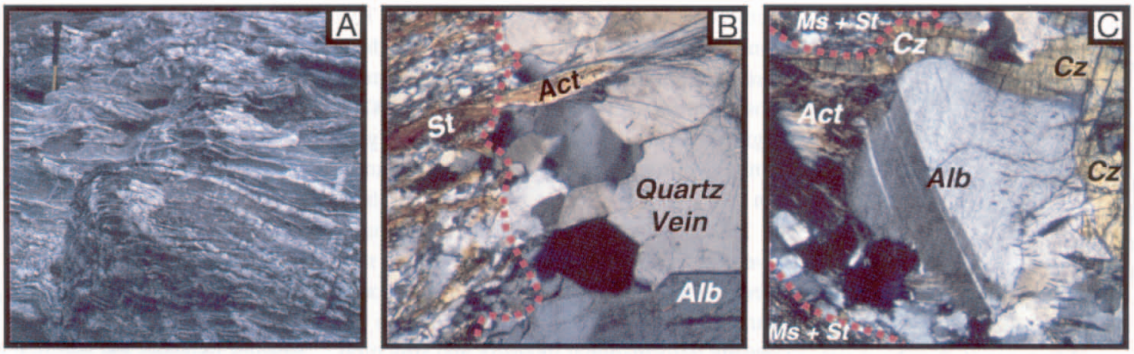

Figure 2. A: Photograph of textural zone III outcrop (near Beaumont) with ~30 vol% veins that has undergone total outcrop mass increase of 11% by silica addition. Hammer handle is 30 cm. B and C: Photomicrographs of veins from outcrop. Stilpnomelane (St) and muscovite (Ms) in wall rock were destroyed as albite (Alb), actinolite (Act), and clinozoisite (Cz) formed in peak-metamorphic veins. Dotted red lines mark vein margins. Fields of view are 1.4 mm (B) and 2.2 mm (C) wide.

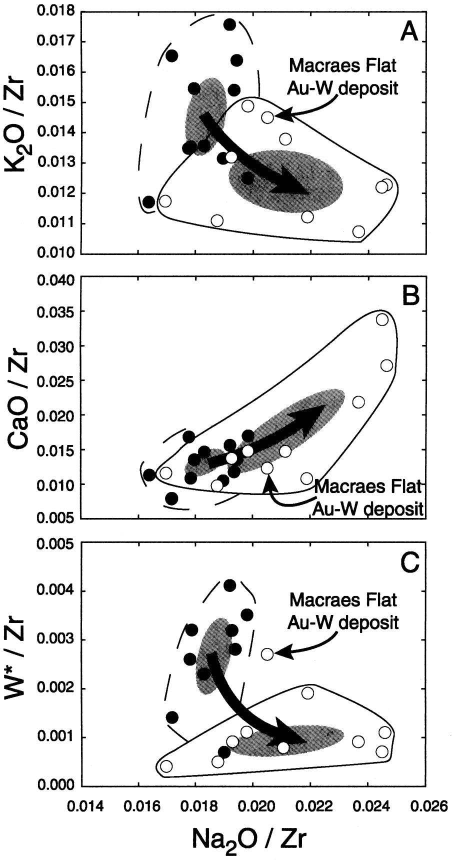

Figure 3. Alkali and trace element plots, normalized to Zr. A–C: Bulk addition of Na (and limited Ca) and removal of K and W occurred during metasomatism of high-grade textural zone outcrops (open circles), relative to low-grade textural zone outcrops (closed circles). W* concentrations are aqua regia leach fractions and are interpreted as proxies for most easily mobilized W that was likely involved in ore-metal transport and deposition. Arrows indicate direction of chemical shifts during alteration. Gray ellipses indicate 95% confidence regions for mean ratios calculated for low- and high-grade textural zone outcrops by using bootstrap methods (Ague and van Haren, 1996). Univariant Student's *t*-tests indicate Na_2O/Zr, K_2O/Zr, and W*/Zr ratios for low- and high-grade groups differ at 96.3%, 98.9%, and 98.9% confidence levels, respectively. K-S tests (Press et al., 1992) indicate Na_2O/Zr vs. K_2O/Zr and Na_2O/Zr vs. W*/Zr groupings differ at 97.7% and 99.9% levels, respectively. CaO/Zr groupings are not different at 95% level, but significant Ca addition likely occurred in some outcrops (shown in plot B). Silica addition to veins decreases concentrations of Zr and all ratioed elements equally and cannot produce shifts from protolith array (Ague and van Haren, 1996). Normalization to Zr also greatly reduces effects of sedimentary variability and sorting seen in Figure 1A (Ague, 1994; Ague and van Haren, 1996). Macraes Flat data are excluded from statistical analysis due to effects of Au-W mineralization. W* data are unavailable for two outcrops.

FLUID FLUX THROUGH THE PRISM

Regional-scale fluid flow in a direction of decreasing temperature (down-*T* flow) will tend to precipitate quartz, whereas fluids flowing in a direction of increasing *T* (up-*T* flow) will tend to dissolve it (Ferry and Dipple, 1991; Ague, 1994; Manning, 1994). Here we estimate the time-integrated fluid flux needed to precipitate the observed externally derived silica as quartz veins in the prism by assuming a down-*T*, upward-directed flow system.

Flux calculations were made for representative high-grade textural zone conditions of 350–450 °C and 6–8 kbar (Mortimer, 2000). Fluid inclusions indicate that peak-metamorphic fluids were nearly pure H_2O (Smith and Yardley, 1999). A lithostatic pressure gradient of −0.28 bar/m and a geothermal gradient of −0.015 °C/m (Mortimer, 2000, and references therein) were combined with the solubility expression of Manning (1994) to obtain the average local-equilibrium silica-solubility gradient, $\partial C_{SiO_2}/\partial z = -0.009\,74$ mol/(m^3·m) (*z* vertical; C_{SiO_2} = concentration of dissolved SiO_2 in fluid). These parameters and the method of Ferry and Dipple (1991) yield the time-integrated flux of 4.5×10^6 $m^3_{(fluid)}/m^2_{(rock)}$ needed to precipitate quartz veins by regionally flowing fluids. The local fluid-rock equilibrium assumption is not critical for the flux calculations because concentration gradients governed by reaction kinetics in quasi–steady-state flow systems approach local-equilibrium gradients (Ague, 1998). To obtain an order-of-magnitude estimate of the flux necessary for the observed external silica deposition, it is adequate to multiply 4.5×10^6 m^3/m^2 by the average fractional mass increase undergone by high-grade textural zone rocks (0.038 ± 0.026, 2σ; this value includes all high-grade textural zone outcrops and is statistically >0 at the 98.97% confidence level). Thus, a time-integrated flux range of 54 000–288 000 m^3/m^2 (2σ) is estimated for quartz-vein formation in high-grade textural zone rocks. Thermal models of subduction zones (Barr and Dahlen, 1989) suggest that about half of an accretionary wedge is under high-grade textural zone conditions; thus we multiply the high-grade textural zone flux by 0.5 and obtain a flux range for the entire prism of 27 000–144 000 m^3/m^2. With equal fractions of high- and low-grade textural zone rocks in the wedge, we calculate the average chemical composition of the New Zealand prism as (wt% unless noted) SiO_2, 65.4; Al_2O_3, 15.3; CaO, 2.62; MgO, 1.81; Na_2O, 3.53; K_2O, 2.45; Fe_2O_3 (total Fe), 4.75; MnO, 0.08; TiO_2, 0.64; P_2O_5, 0.15; loss on ignition, 2.46; Rb, 92 ppm; Sr, 300 ppm; Zr, 181 ppm; and Ba, 569 ppm.

DISCUSSION

Convective fluid flow through a prism requires bulk-silica dissolution along up-*T* flow paths and corresponding silica precipitation along down-*T* flow paths. The absence of widespread silica loss suggests that regional metamorphic convective flow was unlikely and that fluids flowed primarily upward through the prism (Peacock, 1990). Local convective cells may have been superimposed on the dominantly upward-directed regional flow system, resulting in minor, isolated SiO_2 losses, with little effect on the regional silica budget.

Pore waters are expelled at shallow depths during burial, so the most significant deep metamorphic fluid sources are dehydrating metasedimentary rocks and the subducting slab. Metasedimentary rocks are unlikely sources because the maximum closed-system fluid flux for dehydration of a metasedimentary pile equivalent to the entire thickness of the prism (~25 km) is ~1.4×10^3 m^3/m^2, more than an order of magnitude too small to produce the observed SiO_2 additions. This calculation used 2 wt% H_2O loss during dehydration, no H_2O input from the downgoing slab, and densities (ρ) of $\rho_{(H_2O)}$ = 1000 kg/m^3 and $\rho_{(rock)}$ = 2800 kg/m^3 (see footnote 1). We conclude that the New Zealand prism must have undergone fluid infiltration from the subducting slab.

The Dun Mountain ophiolite and scattered metabasites are remnants of the oceanic crust that subducted beneath the prism (Coombs et al., 1976). The remnants consist largely of spilitized basalt (i.e., the Na-rich, K-poor, quartz-saturated alteration product of seawater and basalt interaction at mid-ocean ridges). Thermal models indicate that geothermal gradients in accretionary wedges are not inverted (Barr and Dahlen, 1989); therefore, spilite-equilibrated, silica-saturated fluids rising from the altered, subducting slab must have followed down-*T* flow paths and precipitated quartz into fractures.

For the subducting slab to be a viable fluid source, it must be capable of generating the flux necessary for the observed silica addition. Models suggest time-integrated fluid fluxes from dehydrating slabs in the range 10^4–10^5 m^3/m^2 (Peacock, 1990) for the ~10^8 yr subduction duration in New Zealand (Mortimer, 2000, and references therein). These fluxes may be even larger, with significant updip, slab-parallel, fluid-flow contributions from depth (Peacock, 1990). Regardless, the model flux range correlates remarkably well with our flux range of ~10^4–10^5 m^3/m^2 and indicates that the slab is the only source capable of supplying enough fluid for the external silica deposition.

Our model involves silica-saturated, Na-rich, K-poor fluids moving up from the spilitized slab, precipitating quartz into vein sets in deep levels of the prism (Fig. 4). A slow

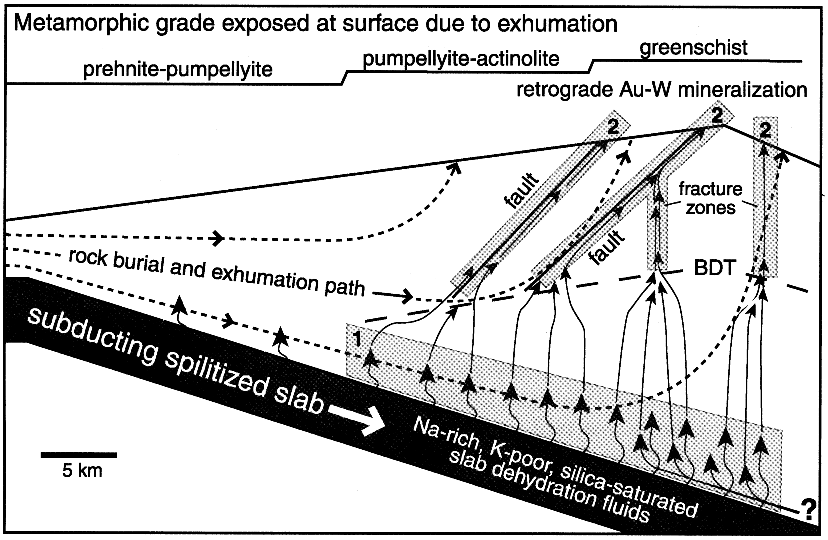

Figure 4. Model two-tier flow system. Subducting spilite dehydrates, releasing Na-rich, K-poor, silica-saturated fluids into wedge. Deeper fluids may be channelized updip and mix with fluids from slab. Quartz-vein formation, Na addition, and K and W removal occurred in zone 1. Fluids likely channelized into fault zones near brittle-ductile transition (BDT). At shallow depths, retrograde metasomatism and Au-W mineralization occurred in fracture-controlled conduits (zone 2).

exhumation rate (~0.2 km/m.y.; Adams et al., 1985) suggests that rocks had long residence times within the prism, allowing prolonged metasomatism and vein formation at depth. We envision that spilite-equilibrated fluids were out of equilibrium with high-grade textural zone metasedimentary rocks above the slab, driving reactions that added Na and, in some cases, Ca to the wall rocks and removed K to the fluid (Fig. 3, A and B). The reaction front propagated to shallower depths until fluids equilibrated with metasedimentary rocks. We predict that the equilibrated fluids became focused into conduits, likely near the brittle-ductile transition (Craw and Norris, 1991), and quartz precipitation was restricted to narrow vein sets in faults or fracture zones and accompanied, at least in part, by down-*T*, retrograde fluid and wall-rock reactions (Fig. 4).

The shallow regions of our flow model have implications for ore deposition. Au-W lodes in the Otago Schist formed in the upper 10 km of the prism as meter-wide quartz veins, often near fault zones, in retrograde high-grade textural zone rocks (Craw and Norris, 1991). Incorporating average ore-forming conditions of 250–300 °C and 1.5–2 kbar (Craw and Norris, 1991) into the previously described flux expression suggests that if deep prograde metamorphic fluids and the shallow retrograde metamorphic flow system were connected, then mineralized quartz veins should occupy ~0.4% of the prism. This result is consistent with the observed rarity of Au-W-quartz veins in the Otago Schist (Craw and Norris, 1991). We suggest that the shallow, localized ore veins were sinks for the W removed from high-grade textural zone rocks at depth (Figs. 3C and 4), providing a link between deep and shallow fluids. The link is further strengthened by similar fluid inclusions from both peak-metamorphic and ore veins (Smith and Yardley, 1999).

Our results strongly suggest that a large fraction of the fluid released during dehydration of a downgoing slab, at least to depths of 25–30 km, migrates upward into the overlying crust and contributes to quartz-vein formation in accretionary prisms. It has been suggested that the continental crust could not have achieved its current high bulk-silica content simply through magmatic differentiation (McLennan and Taylor, 1996). If so, regional fluid-flow processes in accretionary environments, such as those described for the New Zealand prism, may have played important roles in the long-term silica enrichment of the continents.

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