

Isotopic evidence for channeled fluid flow in low-grade metamorphosed Jurassic accretionary complex in the Northern Chichibu belt, western Shikoku, Japan

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ABSTRACT The low-grade metamorphosed Jurassic accretionary complex of the Northern Chichibu Belt, Hijikawa area, western Shikoku, is divided into two units, the Hijikawa and Kanogawa units, that are separated by an out-of-sequence thrust (OOST), the Ozu-Kawabegawa Fault. The Kanogawa unit south of the Ozu-Kawabegawa fault consists mainly of sandstone, shale, broken formation of alternating sandstone and shale, greenstone, chert, and pelitic melange, while the Hijikawa unit is characterized by a stack of subunits separated by small-scale thrusts. The subunits are mainly made up of basic, pelitic and psammitic semischists, schistose pelitic melange, and chert. Petrological and mineralogical constraints suggest peak metamorphic conditions of 204–247 °C at 1–3 kbar in the Kanogawa unit, and 228–289 °C at 3–5.6 kbar in the Hijikawa unit. Quartz and quartz-calcite veins are widely developed in the study area, especially in the Hijikawa unit. Regional variations in stable isotopic data show that the $\delta^{18}\text{O}_{\text{quartz}}$ and $\delta^{18}\text{O}_{\text{calcite}}$ values in veins tend to increase towards the Ozu-Kawabegawa Fault. The $\delta^{18}\text{O}_{\text{whole rock}}$ values are remarkably high in some subunits close to OOSTs within the Hijikawa unit. Oxygen isotopic compositions from vein quartz indicate that a higher $\delta^{18}\text{O}$ fluid migrated upward from depth along the Ozu-Kawabegawa Fault within the accretionary prism during prehnite-pumpellyite facies metamorphism. The fluid source is inferred to be pelitic rocks at higher temperatures and greater depths within the accretionary prism.

Key words: external fluid; low-grade metamorphosed Jurassic accretionary complex; Northern Chichibu belt; out-of-sequence thrust; stable isotopic alteration.

INTRODUCTION

Subduction is characterized by the cycling of fluids from the Earth's surface through the lithosphere to the lower mantle. Most of the fluids, trapped either within hydrous minerals or as pore water in the oceanic crust and superjacent sediments, are expelled within the top few tens of kilometres of the subduction zone. These escaping fluids permeate the wedge-shaped upper-plate accretionary prism at many sites within the subduction zone. Although the role of elevated pore fluid pressures in accretionary prisms has long been recognized (e.g. von Huene & Lee, 1982), recognition of the importance of spatially or temporally focused fluid flow, mud diapirs and water–rock interaction has occurred only recently (Langseth & Moore, 1990; Moore & Vrolijk, 1992; Sreaton *et al.*, 1995; Miller & Cartwright, 2000).

Out-of-sequence thrusts (OOSTs) are potentially the main pathways for up-dip fluid flow; however, it is not always clear that such up-dip fluid transport occurs in the OOSTs. Two hypotheses have been proposed concerning the hydrogeological environment along

OOSTs (MARGINS Office, 2003). Hypothesis 1 describes a deep connection with chemical dehydration reactions that effectively drive fluid pressure and fluid transmission. Breeding & Ague (2002) concluded that fluids from downgoing, subducted oceanic crust penetrated the overlying Otago Schist accretionary prism, New Zealand, resulting in the formation of a regional quartz vein network and massive time-integrated fluid fluxes of 10^4 – 10^5 m³ fluid m⁻² rock on the basis of regional mass balance analysis. In hypothesis 2, up-dip flow is limited and fluid pressures within the fault are set by local conditions. Recently, Lewis & Byrne (2003) argued that prism-scale fluid flow may be localized trenchward and arcward of an interwedge low-permeability zone, based on a field study of the Shimanto belt in Shikoku, south-west Japan. These results have implications for understanding the localization of OOSTs and the timing of fluid flow within such faults.

The transport of dissolved mass by fluid flow along faults from deep reaction zones has been observed in subduction zones around the world (e.g. Kastner *et al.*, 1991). Focused fluid flow along fault zones within accretionary prisms has been inferred from submersible

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observations of vent sites concentrated along thrust fault traces on the Cascadian margin (Moore *et al.*, 1990, 1991), from patterns of diagenetic deposits off coastal Oregon, USA (Carson *et al.*, 1991, 1994; Tobin *et al.*, 1993), and from chemical and thermal anomalies within fault zones in the toe of the Barbados Accretionary Complex as observed by the ODP (Moore, 1989; Fisher & Hounslow, 1990; Gieskes *et al.*, 1990; Vrolijk *et al.*, 1990; Kastner *et al.*, 1997). These fluids are unusual in that they are chloride-poor and may be sourced from mineral depletion in the deeper parts of the subduction zone (e.g. Gieskes *et al.*, 1990; Kastner *et al.*, 1991; Moore & Vrolijk, 1992; Silver *et al.*, 2000).

In the present study, the high-*P/T* and low-grade metamorphosed Jurassic accretionary complexes of the Hijikawa area in western Shikoku, Japan were investigated (Figs 1 & 2) using geology, metamorphic petrology and stable isotopes. The purpose of this study was to evaluate the extent to which the fluid, having infiltrated relatively permeable zones associated with an out-of-sequence thrust, isotopically altered the host rocks, and to determinate its source based on oxygen isotope analysis. An oxygen and carbon isotope study

was also undertaken of vein minerals and adjacent wallrocks to document the evolution of the isotopic composition of the fluid phase during deformation and its relationship with wallrock composition.

OUTLINE OF REGIONAL GEOLOGY

The Chichibu belt mainly comprises Permian to Early Cretaceous accretionary complexes and extends from the Kanto Mountains across Shikoku Island to the Okinawa Islands along a distance of ~1500 km (Isozaki, 1987; Yamakita, 1988; Hada & Kurimoto, 1990; Matsuoka & Yao, 1990) (Fig. 1). The Chichibu belt is divided into the Northern Chichibu, Kurosegawa and Southern Chichibu belts. The Mesozoic accretionary complex of the Northern Chichibu belt in the Ozu-Kanogawa area, western Shikoku, consists of low-grade metamorphosed or unmetamorphosed psammitic and pelitic rocks, chert, greenstones and limestone (Kashima, 1969) and is divided into five lithostratigraphic units, which in ascending order are the Ozu, Shirahigeyama, Kanogawa, Hijikawa and Mikabu greenstones units (Sakakibara *et al.*, 1998; Umeki & Sakakibara, 1998a) (Fig. 2). The Ozu unit is

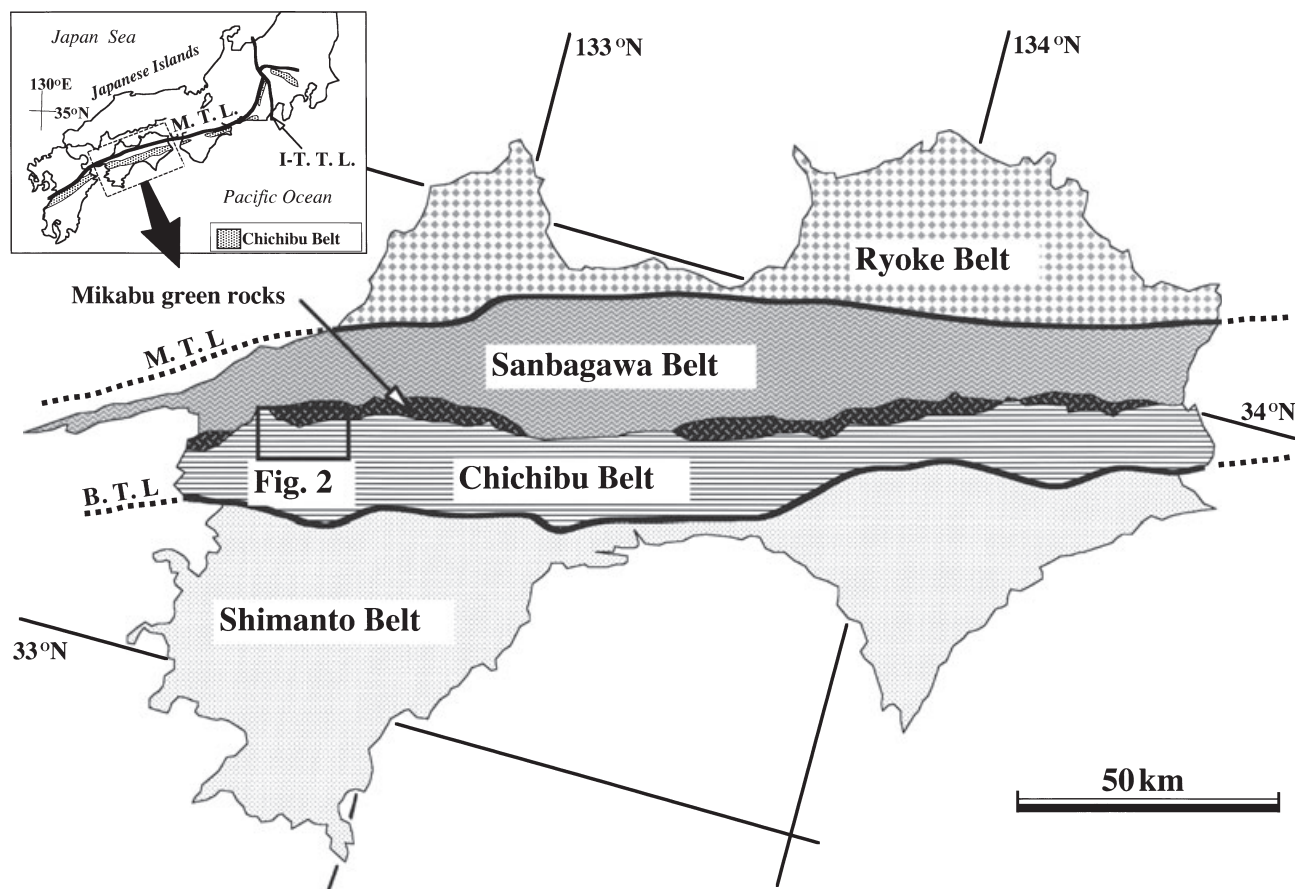


Fig. 1. Simplified geological map of Shikoku showing the location of Fig. 2. M.T.L., Median Tectonic Line; I-T.T.L., Itoigawa-Shizuoka Tectonic Line; B.T.L., Butsuzo Tectonic Line.

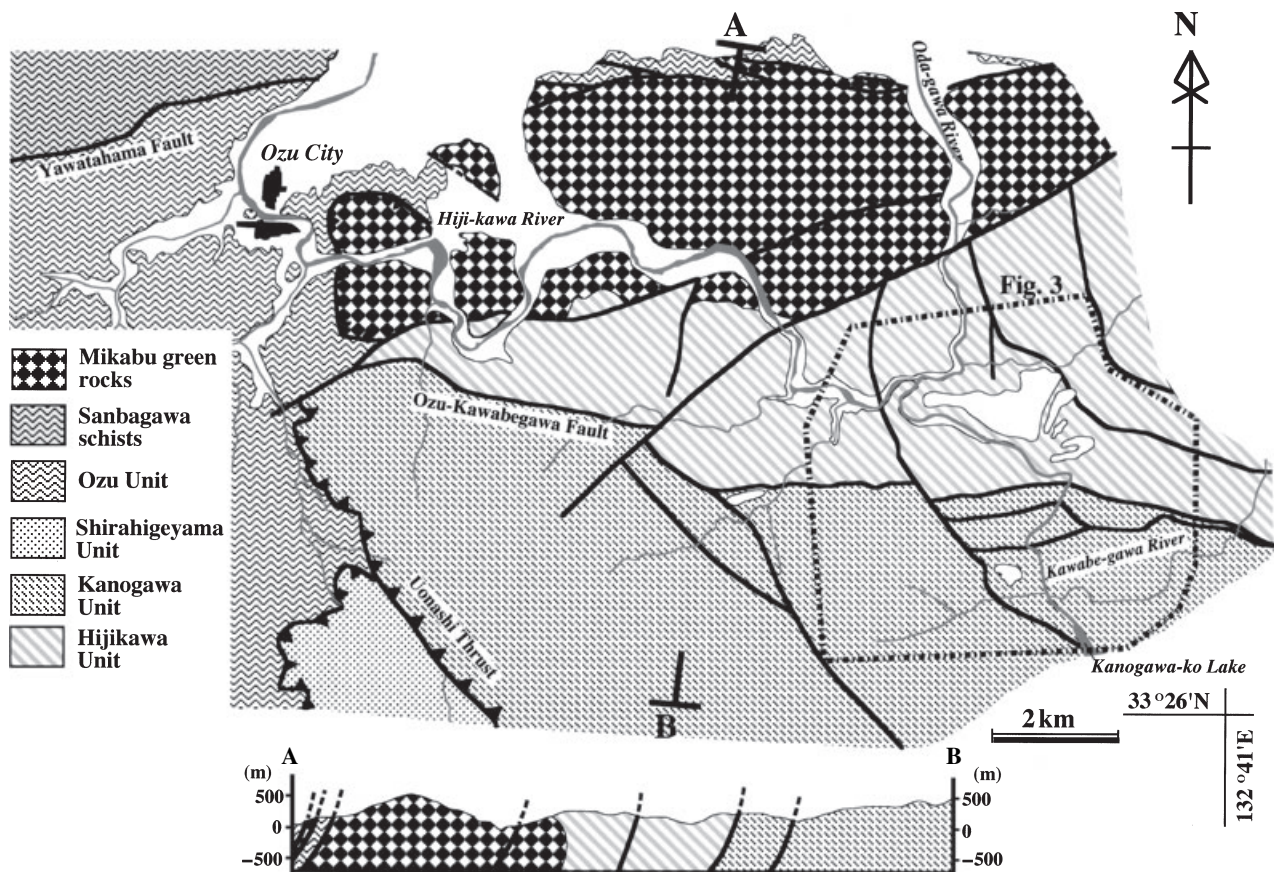


Fig. 2. Simplified geological map and schematic cross-section of Ozu-Kanogawa area, western Shikoku (simplified and modified from Sakakibara *et al.*, 1998). Location of Fig. 3 is also shown.

equivalent to a highly metamorphosed part of the Southern Chichibu belt, whereas the Shirahigeyama unit is the unmetamorphosed equivalent. The Kanogawa and Hijikawa units and the Mikabu greenstones are equivalent to the Northern Chichibu Belt and tectonically overlie the Ozu and Shirahigeyama units along the north-east-dipping Uonashi thrust (Fig. 2). The study area, centred on the Hijikawa area, is underlain chiefly by the Kanogawa and Hijikawa units of the Northern Chichibu belt along the Hijikawa River (Sakakibara *et al.*, 1998) (Figs 2 & 3).

The north-dipping Ozu-Kawabegawa Fault separates the underthrust Kanogawa unit from the Hijikawa unit. It has been proposed that the Ozu-Kanogawa Fault is an out-of-sequence thrust within a Jurassic subduction zone; this claim has been made on the basis of: (i) structural and geological discontinuities, (ii) contrasting metamorphic conditions between both units, and (iii) the presence of a pelitic melange subzone with schistose fabrics in lower part of the Hijikawa unit, which is up to 1 km in thickness.

In the Kanogawa unit, both bedding and cleavage generally dip gently to the north-east, whereas schistosity in the Hijikawa unit dips steeply to the north-east (Fig. 3). The Kanogawa unit consists mainly of sandstone, shale, broken formation of alternating sand-

stone and shale, and pelitic melange including blocks and lenses of sandstone, greenstone, chert and limestone. The shales and sandstones preserve original sedimentary structures and lack veins, but a highly sheared phyllite zone with abundant veins occurs at the boundary between coherent sandstone and pelitic melange in the eastern part of the study area (Fig. 4). The Hijikawa unit can be subdivided into upper coherent semischist and lower schistose pelitic melange subunits (Fig. 3). The upper subunits consist mainly of basic semischist and chert, whereas the lower melange units mainly comprise pelitic semischist that includes lenses of chert and psammitic and basic semischist (Figs 3 & 5). The lower pelitic melange zone is characterized by a stack of subunits separated by small-scale thrusts (Fig. 5). The lower melange subunit is sheared by faulting and is well exposed north-east of the Hiji-kawa River (Figs 3, 5 & 6b). Veinlets are common in the Hijikawa unit.

On the basis of the above-mentioned geological descriptions, we consider the underlying Kanogawa unit to include mixed turbidite deposits that were transported down the continental slope, and oceanic fragments of chert and greenstones, whereas the over-riding upper subunit of the Hijikawa unit consists mainly of oceanic material. The lower subunit of the

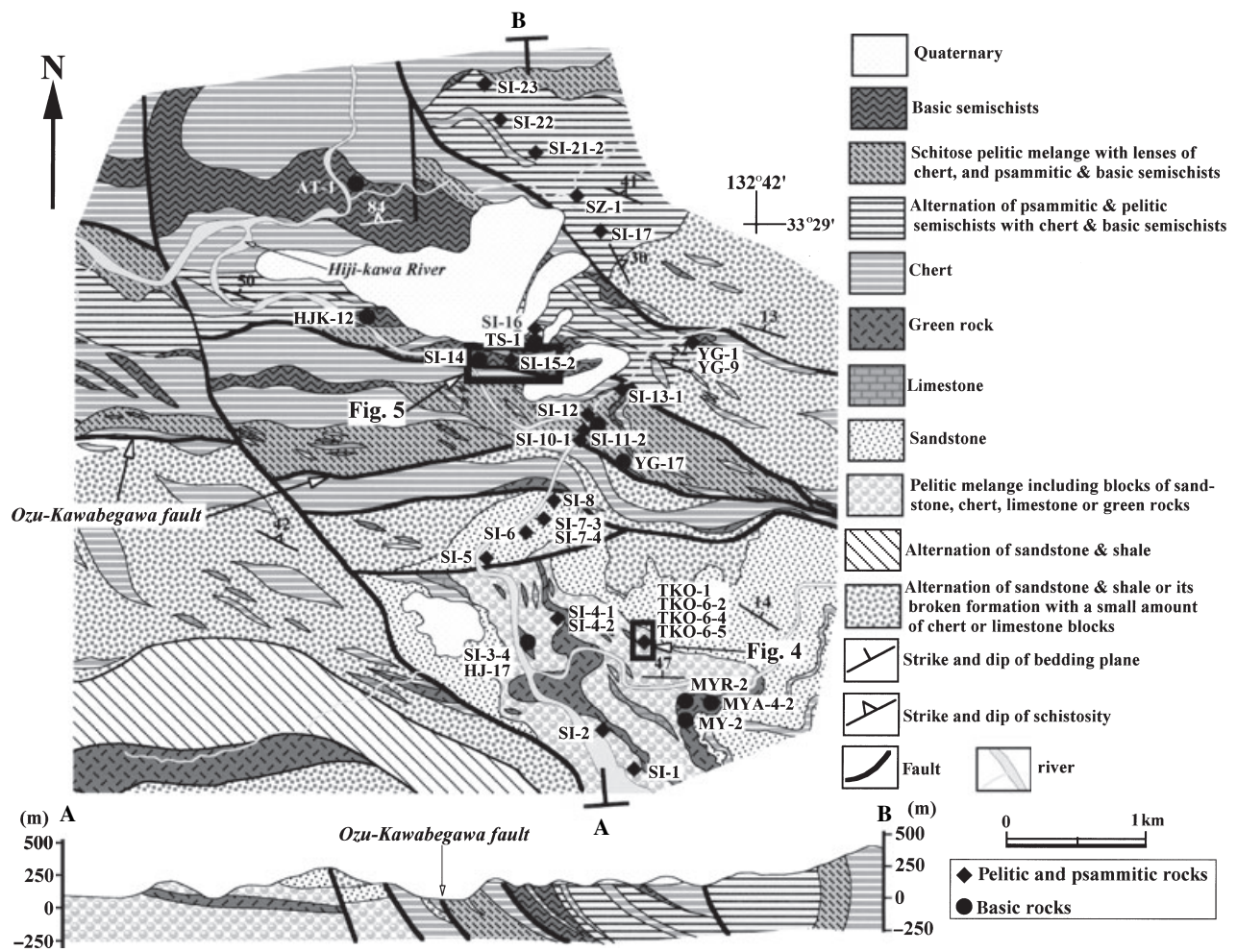


Fig. 3. Geological map of the study area and sample localities of pelitic, psammitic and basic rocks for stable isotope analyses.

Hijikawa unit is inferred to have been a tectonic mixing zone associated with movement along the out-of-sequence thrust.

METAMORPHIC CONDITIONS

Quantitative estimation of the conditions of low-grade metamorphism is generally difficult because of the common occurrence of incomplete equilibration between minerals at peak metamorphism. In this paper, the metamorphic peak conditions of the Kanogawa and Hijikawa units are estimated using chlorite composition and the mineral paragenesis of basic rocks.

Mineral paragenesis

Kanogawa unit

Pelitic and psammitic rocks in both units generally contain quartz + phengite + chlorite + carbonaceous materials $\pm$ albite $\pm$ calcite. Veins of quartz are rare and quartz-calcite ($\pm$ chlorite) veins are present only in highly sheared pelitic rocks (Fig. 4).

The primary igneous textures of metabasalts are well preserved in the Kanogawa unit. Primary phases include Cr-spinel, olivine, clinopyroxene, plagioclase and ilmenite. Relic clinopyroxene in metabasalts is commonly unaltered in both units. Igneous textures are preserved in basalts that have been completely albitized, while primary ilmenite is partly pseudomorphed by titanite. Basaltic glass has transformed to chlorite, titanite and hematite.

The Kanogawa metabasites are characterized by the key minerals prehnite, pumpellyite, epidote and chlorite (Sakakibara *et al.*, 1998; Umeki & Sakakibara, 1998a,b). Representative low-variance mineral assemblages are:

prehnite + pumpellyite + epidote + chlorite,
pumpellyite + epidote + chlorite + hematite.

Hijikawa unit

The Hijikawa metabasites are characterized by riebeckite, aegirine-augite, actinolite, green biotite, stilpnomelane, pumpellyite, chlorite, hematite and calcite

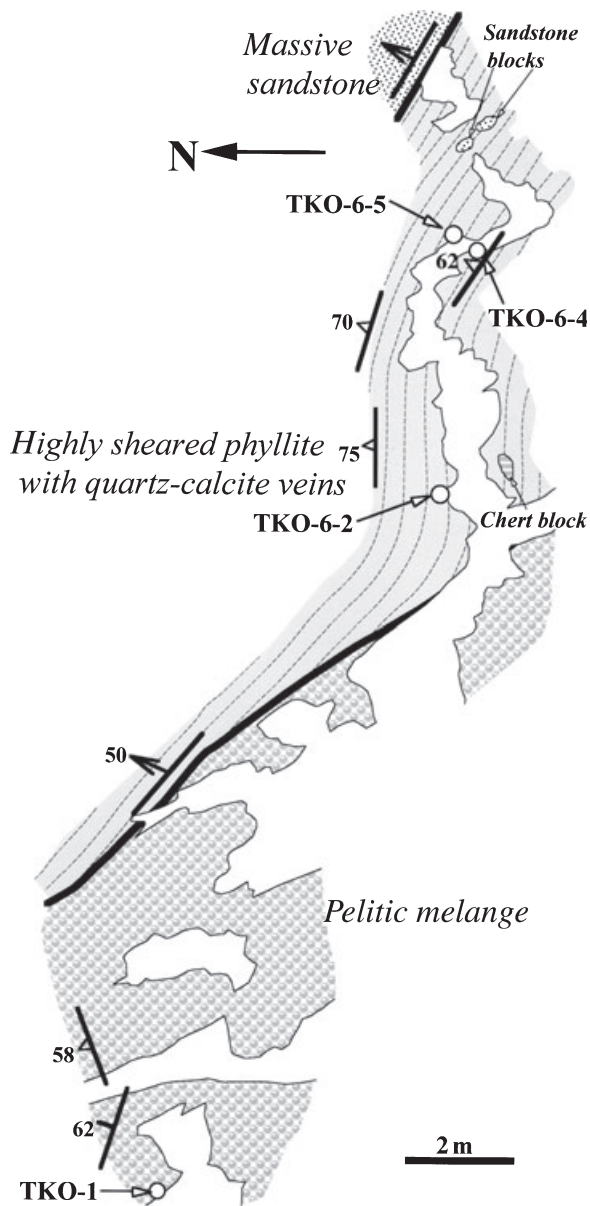


Fig. 4. A route map showing mode of occurrence of highly sheared phyllite with quartz-calcite veins in the Kanogawa unit. Sample localities of stable isotope analyses are also shown.

(Sakakibara *et al.*, 1998; Umeki & Sakakibara, 1998a,b). Albite is common, and aegirine or aegirine-augite ($X_{Jd} < 17$) have replaced primary igneous clinopyroxene along cracks or rims (Sakakibara *et al.*, 1998). Representative low-variance mineral assemblages are:

epidote + actinolite + pumpellyite + chlorite,
 epidote + actinolite + sodic pyroxene + chlorite,
 epidote + sodic pyroxene + pumpellyite + chlorite,
 green biotite + riebeckite + phengite + chlorite
 + calcite,

riebeckite + stilpnomelane + chlorite + calcite,
 riebeckite + phengite + chlorite + calcite,
 riebeckite + stilpnomelane + chlorite + calcite.

Pressure and temperature conditions

Accurate determination of the pressure and temperature conditions of low-grade metamorphic rocks is hindered by a lack of reliable geothermobarometers applicable to them. The pressure-temperature conditions of the Kanogawa and Hijikawa units were estimated by a combination of the more reliable geothermobarometers.

The Al^{IV} content in the tetrahedral site of chlorite increases with temperature (Cathelineau & Nieva, 1985). Cathelineau's (1988) empirical geothermometer relates Al occupancy of tetrahedral sites in chlorite to metamorphic temperature. Several attempts have been made to use the wide compositional variability of chlorite as an empirical geothermometer (Jowett, 1991; Zang & Fyfe, 1995; Xie *et al.*, 1997). On the other hand, its usefulness has been questioned, because of the possible contamination of electron microprobe analyses by the presence of submicrometre-scale intergrowths of other sheet silicates such as corrensite, smectite and berthierine (Shau *et al.*, 1990; Jiang *et al.*, 1994; Essene & Peacor, 1995; Schmidt *et al.*, 1999). However, the mixed layer problem is restricted to diagenetic environments (< 200 °C) (Xie *et al.*, 1997).

Application of the 'geothermometer' of Cathelineau (1988) yields metamorphic temperatures in the range of 204–247 °C for the Kanogawa unit and 228–289 °C for the Hijikawa unit (Table 1). The estimated temperatures are consistent with the recorded prehnite-pumpellyite facies (Cho *et al.*, 1986; Sakakibara, 1991) and pumpellyite-actinolite facies assemblages (Nakajima *et al.*, 1977; Aiba, 1982; Sakakibara, 1991).

Pressure conditions of the Hijikawa unit were estimated by the jadeite contents of sodic pyroxene. The jadeite content of sodic pyroxene which coexists with albite and quartz has been used as function of pressure at a given temperature (Essene & Fyfe, 1967; Brown & O'Neil, 1982; Maruyama & Liou, 1985; Sakakibara, 1991). Several experimental and calorimetric studies have been undertaken to derive a reasonable thermodynamic model for jadeitic pyroxene. Newton & Smith (1967), Popp & Gilbert (1972) and Liu & Bohlen (1995) showed experimentally that the jadeite-aegirine join was nearly ideal. Sodic pyroxene is known to change structure from $C2/c$ (augite, aegirine & jadeite) to $P2/n$ (omphacite) by the continuous order-disorder transformation (Carpenter, 1980). Holland (1990) showed that the jadeite activity at 600 °C in ordered omphacite derived by Landau theory is in good agreement with that reported previously for short-range ordered pyroxene and that the activity of jadeite in ternary jadeite-aegirine-diopside at 500 °C calculated for disordered $C2/c$ pyroxene is close to ideal. Based on the studies discussed above, jadeite activities

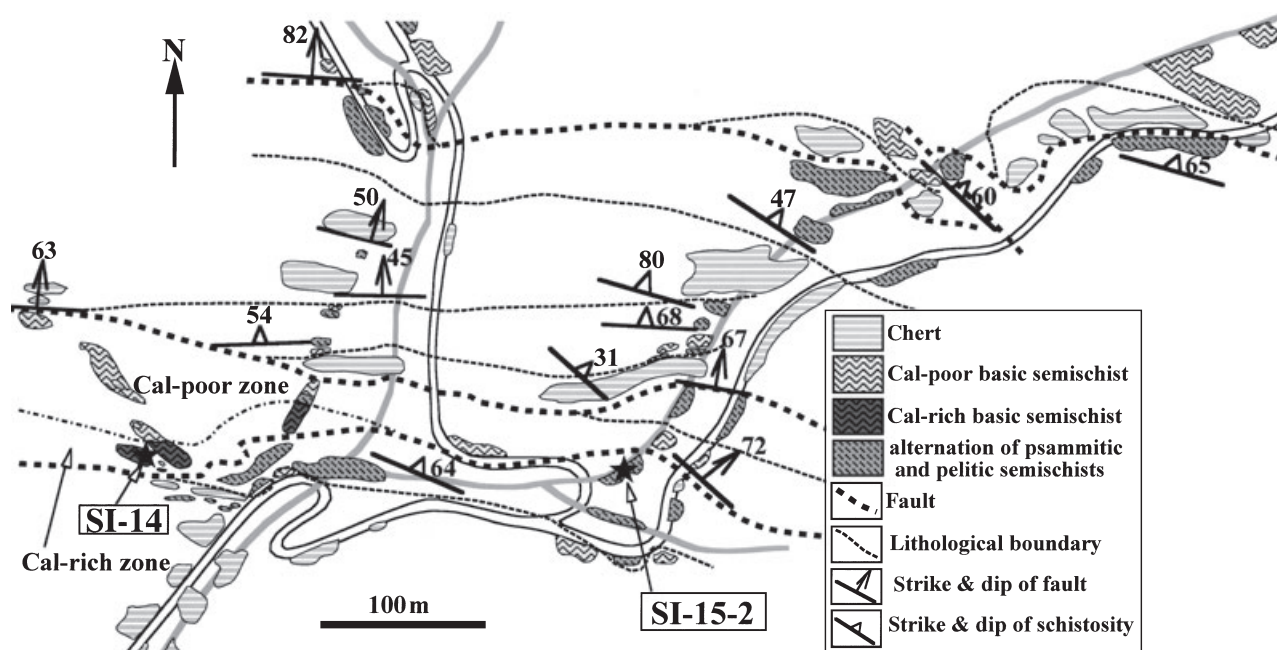


Fig. 5. Route map showing a stack of subunits separated by small scale thrusts in the Hijikawa unit. Sample localities for stable isotope analyses are also shown.

in jadeite-aegirine and jadeite-diopside solutions of disordered $C2/c$ pyroxene are equal to ideal and pseudo-ideal, respectively.

The sodic pyroxene of the Hijikawa metabasites are mainly jadeite-poor aegirine and aegirine-augite, the compositions of which range only in a domain around the aegirine-diopside join (Sakakibara *et al.*, 1997). However, the absence of quartz from the sodic pyroxene-bearing Hijikawa metabasites limits the usefulness of this geobarometer to constrain only the maximum pressure. The pressure condition can be calculated by using the equation after Essene & Fyfe (1967):

$$RT \ln X_{Jd} = \Delta V \cdot \Delta P$$

where ΔV is 19.68 cm^3 for the reaction albite = jadeite + quartz (Popp & Gilbert, 1972). The maximum pressure conditions are estimated to be 4.7 kbar at 230°C and 5.6 kbar at 290°C .

Recent studies (Frey *et al.*, 1991; Powell *et al.*, 1993; Banno, 1998; Robinson & Bevins, 1999; Banno *et al.*, 2000; Miyazaki & Okumura, 2002) showed that the facies boundary between the prehnite-pumpellyite and pumpellyite-actinolite facies has a positive slope in P - T space. Miyazaki & Okumura (2002) reviewed the available studies and showed that the facies boundary between the pumpellyite-actinolite and prehnite-pumpellyite facies is estimated to be 2.5 kbar at 220°C and 3.4 kbar at 300°C . Schematic petrogenetic grid calculated in the system NCMASH with average activities of the end-members (Frey *et al.*, 1991; Schiffman & Day, 1999)

shows that the region of prehnite + pumpellyite stability is restricted to a very small P - T field in the range of 2.1 kbar at 200°C and 3.2 kbar at 270°C . However, these stability fields of critical natural assemblages are oversimplified considerably by the absence of ferrous and ferric iron. Powell *et al.* (1993) used equilibria in the two univariant assemblages, prehnite + pumpellyite + epidote + chlorite + quartz and prehnite + actinolite + epidote + chlorite + quartz, and estimated pressure and temperature of the sample from Abitibi greenstones. From the intersection of these equilibria, they estimated 2.2 kbar at 250°C . Digel & Gordon (1995) also obtained reasonable P - T estimates of the invariant assemblage prehnite + pumpellyite + epidote + actinolite + chlorite on Flin Flon metabasites, Canada.

All recent studies point to the existence of wide stability fields for prehnite and pumpellyite from ~ 200 to 300°C and from perhaps ~ 1 to 3 kbar. In conclusion, peak metamorphism is assumed to have taken place at temperatures of 204 – 247°C and pressure of 1–3 kbar in the Kanogawa unit, and 228 – 289°C and 3–5.6 kbar in the Hijikawa unit, as determined by chlorite geothermometry, sodic pyroxene geobarometer and the schematic petrogenetic grid. The peak metamorphic temperature and pressure of the Hijikawa unit appear to be slightly higher than that of the Kanogawa unit. This implies that the final thrusting of the units into their present positions post-dated the timing of maximum temperatures (e.g. Ohmori *et al.*, 1997).

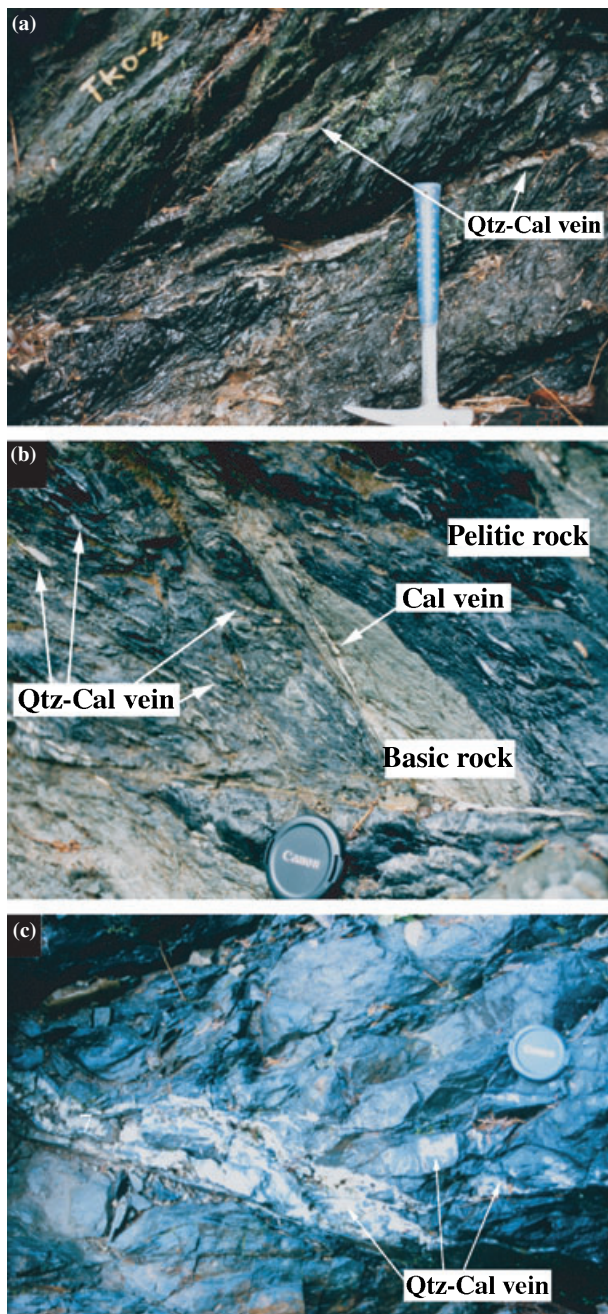


Fig. 6. Photographs of vein occurrences. (a) Highly sheared phyllite with quartz-calcite veins in the Kanogawa unit; (b) lenticular blocks of basic semischist in sheared pelitic semischist in the Hijikawa unit; (c) shear zone with quartz-calcite veins in the pelitic psammitic rocks in the Hijikawa unit.

VEINING IN THE CHICHIBU ACCRETIONARY COMPLEX

The abundance and volume of veins vary between units and between different host rocks. Veins ranging from 1 mm to 5 cm in width within pelitic rocks of both units are dominated by quartz or quartz + cal-

cite, locally with minor chlorite (Figs 6 & 7b–d). Veins within basic rocks invariably consist of calcite with minor chlorite (Figs 6 & 8). In the majority of cases, quartz in veins appears to be of single generation. Based on vein morphology and their relationship with folds and faults, most of the veins in the study area are inferred to have formed during deformation along the Ozu-Kawabegawa Fault, after the metamorphic peak.

Veining is generally developed in the Hijikawa unit rather than the Kanogawa unit. Veins locally comprise up to 10% of individual outcrops in the Hijikawa unit, but vein volumes of <0.1% are common in the Kanogawa unit. In the Kanogawa unit, veins are characteristically concentrated only within a highly sheared phyllite zone at the boundary between a thick sandstone bed and a pelitic melange that is rich in veinlets (Fig. 4).

Two styles of veining are recognized in the study area. First, extension veins formed during layer-parallel flexural-flow or flexural-slip folding. The veins generally lie at a high angle to bedding planes and occur in chert, sandstones and basaltic rocks. They are occasionally folded and truncated by slip along bedding planes during folding (Figs 7 & 8). Second, veins oriented parallel to thrusts and shear planes developed locally in pelitic and basic rocks at sites close to thrusts. In the Hijikawa unit, most of the highly sheared semischists of pelitic melange and fault breccia located near the Ozu-Kawabegawa Fault contain abundant quartz-calcite veins in pelitic rocks and calcite veins in basic rocks (Fig. 6). These thrust-parallel vein-rich zones extend up to 10 m above the fault surface.

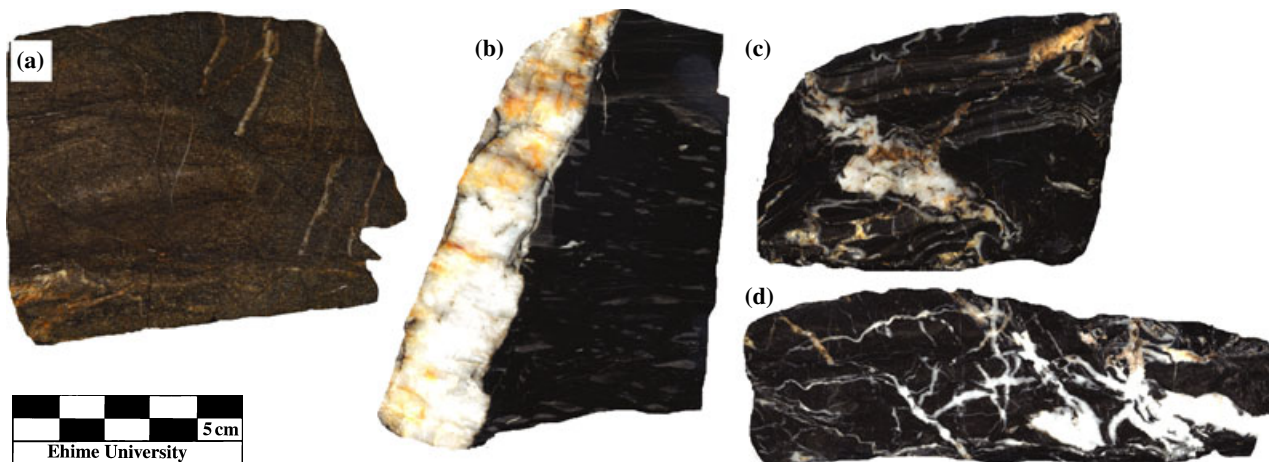
The sealed cracks are filled mostly not only with quartz but also with calcite (Fig. 9). Quartz-calcite-dominated veins commonly comprise idiomorphic prismatic quartz crystals that line the vein walls. Calcite is overgrown by larger crystals that fill the centre of the vein and are variably orientated. Calcite occasionally fills fractures in quartz veins, with fracture-parallel cavities or vugs common within such veins. The cavities were almost certainly occupied by calcite prior to weathering. In both units, synchronous growth of these two minerals can be commonly seen, but quartz might occasionally grow prior to calcite during formation of many veins.

STABLE ISOTOPE ANALYSES

General isotope systematics

A total of 42 samples were collected from 32 localities in the study area (Figs 3–5). Approximately 1–3 mm³ powder samples of veins and whole rock were extracted using a dentist drill. Calcite-rich basic rocks were treated with acetic acid (60.05% CH₃COOH) to remove calcite.

Sample no.	Hijikawa unit					Kawabegawa unit				
	TS-1	TB-2-1		052009		HJ-11	YG-19	051606	053008	
SiO ₂	32.1	28.9	29.0	29.6	27.2	29.0	28.8	30.3	29.2	30.3
TiO ₂	0.1	0.0	0.3	0.1	0.0	0.1	0.3	0.1	0.0	0.1
Al ₂ O ₃	16.9	17.6	17.3	16.3	17.7	15.8	16.1	15.6	14.3	15.6
FeO	13.9	17.5	19.0	18.2	29.2	28.0	29.3	21.3	28.6	21.3
MnO	0.2	0.2	0.2	0.2	0.5	0.5	0.3	0.3	0.1	0.3
MgO	25.7	23.4	22.6	23.2	12.8	13.0	13.6	18.0	13.6	18.0
CaO	0.2	0.1	0.1	0.0	0.0	0.3	0.4	0.4	0.8	0.4
Na ₂ O	0.0	0.3	0.1	0.0	0.0	0.2	0.3	0.0	0.1	0.0
K ₂ O	0.3	0.0	0.0	0.4	0.0	0.2	0.1	0.1	0.0	0.1
Total	89.4	88.0	88.6	88.0	87.5	87.1	89.2	86.1	86.5	86.1
Si	6.20	5.82	5.85	5.99	5.88	6.25	6.08	6.34	6.35	6.34
Al ^{IV}	1.80	2.18	2.15	2.01	2.12	1.75	1.92	1.66	1.65	1.66
ΣZ	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00
Al ^{VI}	2.05	2.00	1.95	1.89	2.38	2.26	2.09	2.19	2.02	2.19
Ti	0.02	0.00	0.04	0.02	0.00	0.02	0.04	0.01	0.00	0.01
Fe ²⁺	2.25	2.94	3.20	3.07	5.26	5.05	5.17	3.74	5.20	3.74
Mn	0.03	0.04	0.04	0.03	0.09	0.10	0.05	0.05	0.02	0.05
Mg	7.42	7.03	6.79	6.98	4.13	4.17	4.27	5.63	4.39	5.63
Ca	0.05	0.01	0.02	0.01	0.01	0.06	0.09	0.09	0.18	0.09
Na	0.00	0.12	0.02	0.00	0.01	0.07	0.12	0.02	0.02	0.02
K	0.08	0.01	0.01	0.10	0.01	0.06	0.03	0.02	0.00	0.02
ΣW,X,Y	11.90	12.15	12.07	12.10	11.88	11.79	11.86	11.75	11.84	11.75
Total	19.90	20.15	20.07	20.10	19.88	19.79	19.86	19.75	19.84	19.75
X _{Fe}	0.233	0.295	0.320	0.305	0.560	0.548	0.548	0.399	0.542	0.399
Tc (°C)*	228	289	284	262	280	220	247	205	204	205

Table 1. Representative chemical compositions of chlorites.**Fig. 7.** Photographs of polished samples of pelitic and psammitic rocks for isotope analyses. (a) Sandstone with quartz veins from the Kanogawa unit (SI-7–3); (b) quartz vein in schistose pebbly shale from the Hijikawa unit (SI-15–2); (c) pelitic semischist with deformed quartz vein from the Hijikawa unit (SI-13–1); (d) quartz-calcite veins in pelitic semischist from the Hijikawa unit (SI-12).

Stable isotope ratios were measured at Monash University, Australia, using a Finnigan MAT 252 mass spectrometer. Oxygen isotope ratios of quartz in veins and whole-rock samples were analysed following the procedure of Clayton & Mayeda (1963), but using ClF₃ as the oxidizing reagent. CO₂ was extracted from calcite by the reaction of mixed carbonate-silicate powders with H₃PO₄ in sealed vessels for 12–18 h at 25 °C (McCrea, 1950). Calculated $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values are expressed relative to V-SMOW and V-PDB, respectively. NBS28 analysed at the same time as samples from this study yielded $\delta^{18}\text{O} = 9.64 \pm 0.24\text{‰}$ ($n = 13$), while the long-term average $\delta^{18}\text{O}$ value of NBS28 measured at Monash University is

$9.58 \pm 0.12\text{‰}$. The internal calcite standard ISACC yielded $\delta^{13}\text{C} = -6.32 \pm 0.08\text{‰}$ and $\delta^{18}\text{O} = 12.60 \pm 0.11\text{‰}$ ($n = 27$). This standard was calibrated using IAEA-CO-1, and its long-term average $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values are $-6.37 \pm 0.06\text{‰}$ and $12.68 \pm 0.13\text{‰}$, respectively. Whole-rock and mineral $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values for vein minerals from the Kanogawa and Hijikawa units are presented in Tables 2 and 3.

Whole-rock isotopic compositions

Whole-rock $\delta^{18}\text{O}$ values for pelitic, psammitic and basic rocks in the Kanogawa unit are 12.4–15.6‰ (mean 14.0‰), 12.7–15.6‰ (mean 14.3‰) and

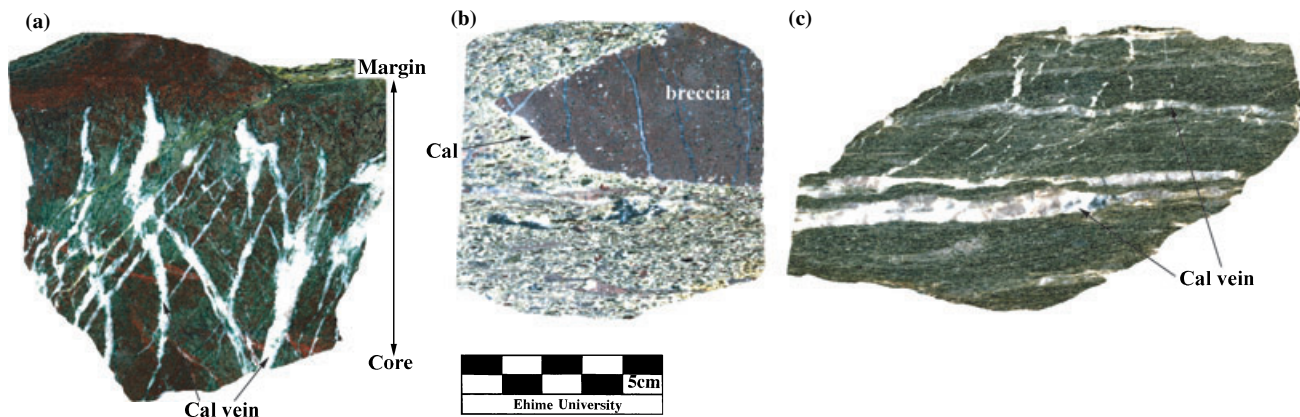


Fig. 8. Photographs of polished samples of basic rocks for isotope analyses. (a) Pillow basalt with calcite veins from the Kanogawa unit (SI-3-4); (b) basaltic hyaloclastite including breccia from the Hijikawa unit (TS-1-1); (c) sheared basic semischists with calcite veins from the Hijikawa unit (SI-11-2).

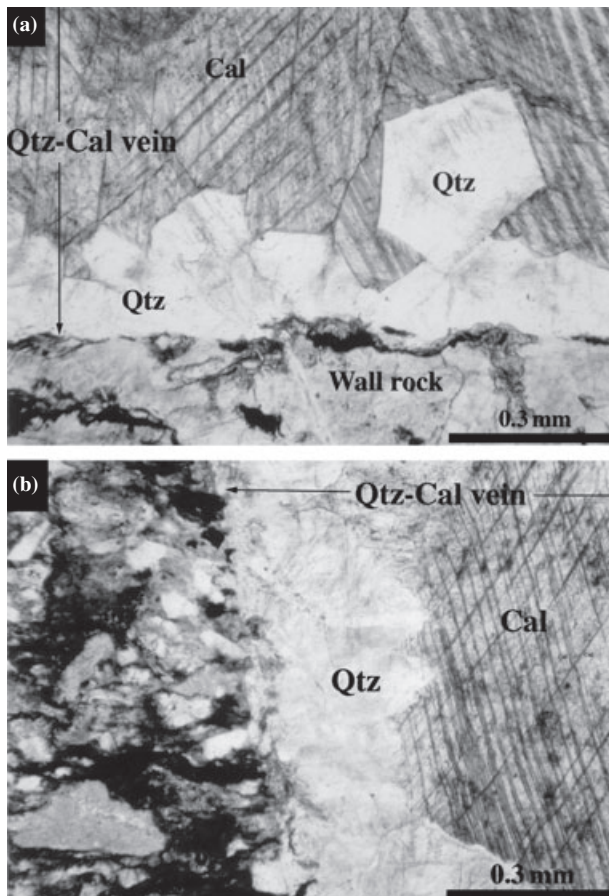


Fig. 9. Photomicrographs of quartz-calcite veins. (a) Shale from the Kanogawa unit (TKO-6-2); (b) pelitic semischist from the Hijikawa unit (YG-1).

11.2–12.6‰ (mean 12.1‰), respectively (Tables 2 & 3; Figs 10 & 11). Whole-rock $\delta^{18}\text{O}$ values for pelitic, psammitic and basic rocks in the Hijikawa unit are 14.8–18.1‰ (mean 16.6‰), 15.9–18.4 (mean 17.1) and

12.7–18.2‰ (mean 15.0‰), respectively (Tables 2 & 3; Figs 10 & 11). Rocks of the Hijikawa unit thus have distinctly higher $\delta^{18}\text{O}$ values than those of the Kanogawa unit. The $\delta^{18}\text{O}$ values for the Hijikawa basic schists vary widely and are lower than $\delta^{18}\text{O}$ values for the Hijikawa metabasites (sample nos SI-11-2 & AT-1), which are similar to those of the Kanogawa metabasites.

Vein isotopic compositions

In this study, quartz and calcite in veins were studied as an indicator of fluid composition. Vein minerals grew from the metamorphic fluid, and stable isotope values are unlikely to have been affected by subsequent resetting because mineral growth was below the blocking temperature for oxygen diffusion (i.e. below $\sim 300^\circ\text{C}$; Cole & Ohmoto, 1986). The oxygen isotope composition of the vein minerals is thus likely to reflect the composition of the fluid that was present at the time of vein formation. The composition of the fluid itself is influenced by both equilibrium and kinetic factors, for example, the rate of infiltration of fluid into the system relative to the rate of oxygen equilibrium with solid phases, the dissolution and precipitation of solid phases, and diffusion within solid phases. Buffering of the fluid composition by the rock requires extensive fluid–mineral interaction by either solution/redeposition or surface exchange coupled with diffusion in the solid phases.

Kanogawa unit

The $\delta^{18}\text{O}$ values for quartz veins from the Kanogawa shales and sandstones are 18.4–19.8‰ (mean 19.0‰), with $\Delta^{18}\text{O}$ (vein-wallrock) values of 1.0–2.2‰ (Table 2; Fig. 10). Within the highly sheared phyllite zone (Figs 4 & 6), $\delta^{18}\text{O}$ values for calcite and quartz in calcite-quartz veins are 15.9 and 16.9–18.1‰, respectively (sample nos TKO-6-2 & TKO-6-4 in Table 2).

Table 2. Oxygen and carbon isotope analyses (‰) of pelitic and psammitic rocks.

Sample no.	Rock type	$\delta^{18}\text{O}$ (WR)	$\delta^{18}\text{O}$ (Qtz vein)	$\delta^{18}\text{O}$ (Cal vein)	$\delta^{13}\text{C}$ (Cal vein)	$\Delta^{18}\text{O}$ (Qtz–Cal)	Characteristic remarks
Tinu awagonaK							
SI-1	P	14.0					Shale with original sedimentary structure
SI-2	P	14.0					Pebbly mudstone including sandstone breccia
TKO-1-1	P	13.1					Shale with original sedimentary structure
TKO-1-2	S	12.7					Sandstone with original sedimentary structure
TKO-6-2	P	13.8	18.1	15.9	–4.8	2.2	Highly sheared pelitic rock with Qtz–Cal veins (up to 3 cm width)
TKO-6-4	P	12.4	16.9	15.9	–4.7	1.0	Highly sheared pelitic rock with Qtz–Cal veins (up to 2.5 cm width)
TKO-6-5	P	13.9					Highly sheared pelitic rock without veins
SI-4-1	P	13.6	18.4				Shale
SI-4-2-1	P	14.3					Shale with original sedimentary structure
SI-4-2-2	S	15.6					Sandstone with original sedimentary structure
SI-5	S	14.5					Sandstone
SI-6	P	15.6					Shale
SI-7-3	S		19.8				Sandstone
SI-7-4	P	12.8	18.9				Pebbly mudstone
SI-8	P	15.2					Pebbly mudstone
Tinu awakijiH							
SI-10-1	P	16.3					Pelitic semischist with Qtz veins (up to 1 mm width)
SI-11-2	P			20.9	0.1		Pelitic semischist with Cal veins (up to 1 cm width)
SI-12-1	P	16.3	20.5	18.7	–5.2	1.8	Pelitic semischist with Cal veins (up to 1 cm width)
SI-12-2	S		19.0	19.2	–4.7	0.2	Psammitic semischists with veins (up to 2 mm width) including Qtz and Cal
SI-13-1A	P	14.8	20.5	17.3	–6.9	3.2	Pelitic semischist with original sedimentary structure including deformed veins (about 2 cm width)
SI-13-1B	S	18.4					Psammitic semischist
SI-15-2	P	17.9	20.8				Pelitic semischists with a straight Qtz–Cal vein (about 2 cm width)
YG-1	S	15.9	20.0	17.8	–4.2	2.2	Psammitic semischist with Qtz–Cal veins (up to 1.5 cm width)
YG-9	P	15.8	19.6	18.2	–0.7	1.4	Pelitic semischist with Qtz–Cal veins (up to 2 cm width)
SI-16	S	17.1					Psammitic semischist without veins
SI-17	P	16.2					Pelitic semischist without veins
SZ-1	P	18.1					Pebbly mudstone
SI-21-2	P	16.8	18.7				Pelitic semischists containing straight Qtz veins (0.6–1.0 cm width)
SI-22	P	15.2					Pelitic semischists characterized by axial-plane cleavages
SI-23	P	17.2					Pebbly mudstone

Table 3. Oxygen and carbon isotope analyses (‰) of basic rocks.

No.	$\delta^{18}\text{O}$ (whole rock)	$\delta^{18}\text{O}$ (Cal in matrix)	$\delta^{13}\text{C}$ (Cal in matrix)	$\delta^{18}\text{O}$ (Cal vein)	$\delta^{13}\text{C}$ (Cal vein)	Characteristic remarks
UK						
MY-2	12.5			15.8	–7.7	Basalt including Cal veins
MYR-1	12.6			16.3	–0.5	Basalt including Cal veins
MYA-4-2	11.9					Basalt
SI-3-4	11.2			15.3	0.3	Pillow basalt characterized by the abundance in Cal vein
HJ-17	12.5			16.9	2.0	Pillow basalt characterized by the abundance in Cal vein
UH						
YG-17	12.0			20.1	2.6	Basalt including Cal veins
				19.8	–2.4	
SI-11-2	12.7	19.0	0.6	19.2	1.1	Basaltic hyaloclastite characterized by the abundance in Cal vein
SI-14	18.2			20.2	4.1	Cal-rich basaltic hyaloclastite veins (up to 1 cm width)
				19.9	2.8	
TS-1-1	16.3			19.2	4.0	Basaltic breccia in hyaloclastite
				19.9	4.6	
TS-1-2	15.8					Matrix of Cal-rich basaltic hyaloclastite
HJK-12	15.2	13.4	–9.9	18.0	0.7	Matrix of Cal-rich basaltic hyaloclastite
AT-1	12.7			19.1	2.7	Basalt including Cal veins

KU, Kanogawa unit; HU, Hijikawa unit.

The $\delta^{18}\text{O}$ values for quartz from these veins are higher than those for calcite from calcite-quartz dominated veins. The $\Delta^{18}\text{O}$ (quartz–calcite) values of the veins vary from 1.0 to 2.2 (Table 2).

The $\delta^{18}\text{O}$ values for calcite veins from the Kanogawa metabasalts are 15.3–20.1‰ (Table 3), which are higher than those for the host rocks. Within individual samples of Kanogawa metabasalt, the difference in $\delta^{18}\text{O}$ values between the vein and wallrock, $\Delta^{18}\text{O}$ (vein–

wallrock), varies widely from 3.3 to 8.1‰ (Fig. 11). The $\delta^{13}\text{C}$ values for calcite in the veins are also highly variable, from –7.7 to 2.6‰ (Table 3).

Hijikawa unit

The $\delta^{18}\text{O}$ values for quartz in veins from the Hijikawa pelitic and psammitic schists are 18.7–20.8‰ (mean 19.9‰), with $\Delta^{18}\text{O}$ (vein–wallrock) values of 1.9–5.7‰.

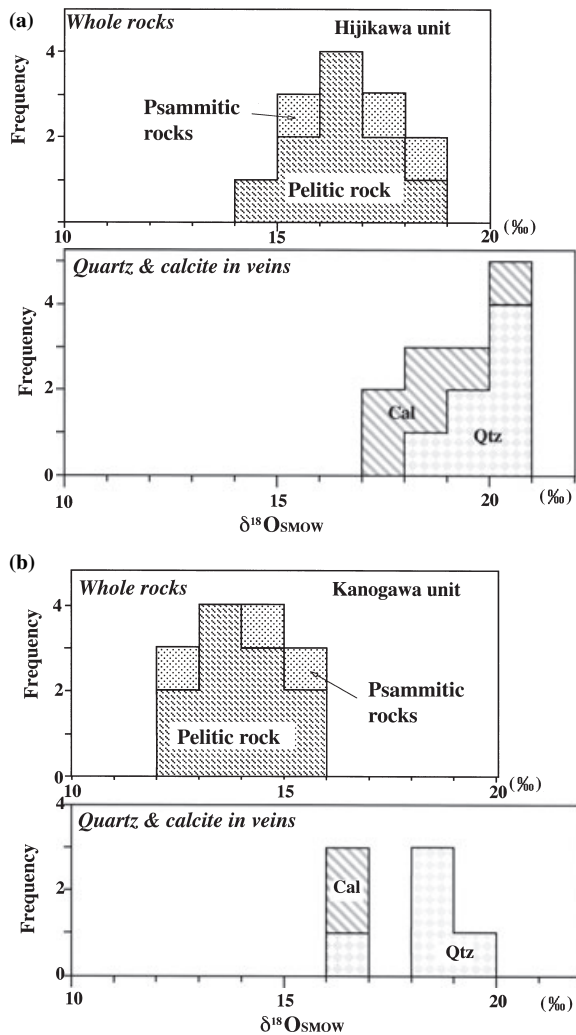


Fig. 10. Oxygen isotope compositions of whole rocks and veins of basic, pelitic and psammitic rocks. (a) Whole rocks and calcite veins of basic rocks in the Hijikawa unit; (b) whole rocks of pelitic and psammitic rocks and quartz-calcite veins of pelitic rocks in the Kanogawa unit.

The $\delta^{18}\text{O}$ values for calcite in veins from the Hijikawa pelitic and psammitic schists are 17.3–20.9‰ (mean 19.9‰), with $\Delta^{18}\text{O}$ (vein-wallrock) values of 1.9–2.5‰ (Table 2). The $\delta^{18}\text{O}$ values for calcite and quartz in calcite-quartz veins are 17.3–19.2‰ and 19.0–20.5‰, respectively (Table 2). The $\delta^{18}\text{O}$ values of quartz from these veins are higher than those of calcite from calcite-quartz-dominated veins. The $\Delta^{18}\text{O}$ (quartz-calcite in veins) values are –0.2 to 3.2 (Table 2).

The $\delta^{18}\text{O}$ values for calcite in veins from the Hijikawa metabasites are 18.0–20.2‰ (mean 19.2‰) (Table 3), which are higher than those of their host rocks. Although the $\delta^{18}\text{O}$ values for calcite in these veins are approximately constant, $\Delta^{18}\text{O}$ (vein-wallrock) values vary greatly from 2.0 to 6.5‰ (Fig. 11). In contrast to the oxygen isotopes, $\delta^{13}\text{C}$ values for calcite in the veins are highly variable, from –9.9 to 4.6‰ (Table 3).

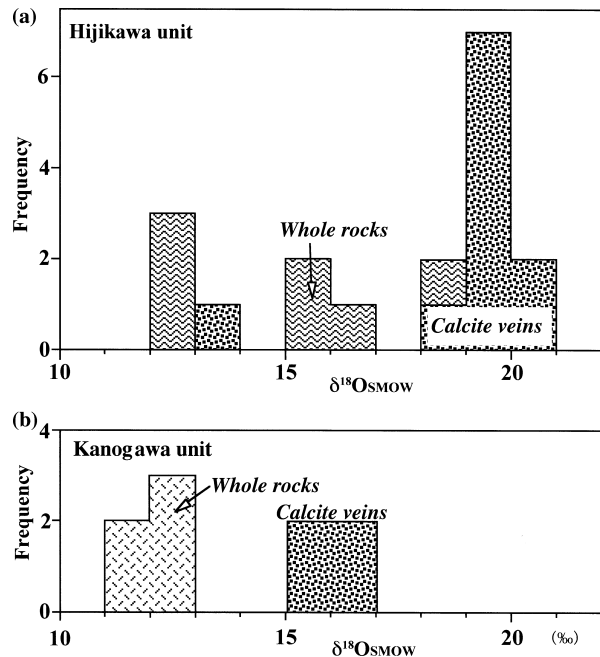


Fig. 11. Oxygen isotope compositions of whole rocks and calcite veins of basic rocks.

Calcite-quartz $\delta^{18}\text{O}$ fractionation in veins

The $\delta^{18}\text{O}_{\text{Qtz}}$ values for coexisting calcite and quartz from the same vein enable the degree of isotopic equilibrium between the phases to be assessed (Jenkin *et al.*, 1991, 1994). Quartz segregations within quartz-calcite veins in pelitic and psammitic rocks have consistently higher $\delta^{18}\text{O}$ values than calcite in the same veins (Table 2). The $\Delta^{18}\text{O}_{(\text{Qtz-Cal})}$ values in all samples except no. SI-12-2 vary from –0.2 to 3.2‰, corresponding to apparent isotopic temperatures of 70–343 °C on the basis of data from Chiba *et al.* (1989) (Fig. 12). The sample SI-12-2 has negative $\Delta^{18}\text{O}_{(\text{Qtz-Cal})}$ values that cannot represent equilibrium at any temperature. The variations in $\Delta^{18}\text{O}_{(\text{Qtz-Cal})}$ values presented in Fig. 12 reflect isotopic disequilibrium due to changes in fluid characteristics during the growth of vein minerals. Two end-member possibilities exist for explaining this isotopic disequilibrium: changes in the $\delta^{18}\text{O}$ values of fluid and changes in the temperature of fluid that equilibrated with vein minerals. As mentioned above, although textural evidence indicates that these two phases were deposited in the same fissure veins, quartz generally grew prior to calcite.

Regional variations in stable isotopic compositions

Regional variations in whole-rock stable isotopic data and vein minerals from the Hijikawa area are presented in Fig. 13. The most striking aspect of the data is the contrast between $\delta^{18}\text{O}_{\text{vein minerals}}$ values and these for whole-rock samples from nearby wallrock. The $\delta^{18}\text{O}_{\text{quartz}}$ and $\delta^{18}\text{O}_{\text{calcite}}$ values for pelitic and basic

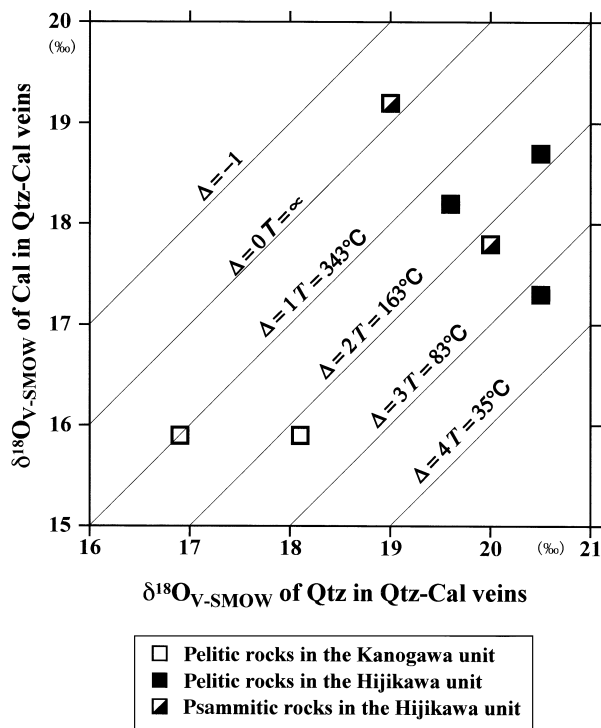


Fig. 12. $\delta^{18}\text{O}_{\text{cal}}$ vs. $\delta^{18}\text{O}_{\text{qtz}}$ for vein from the Hijikawa and Kanogawa units. Temperatures corresponding to $\Delta^{18}\text{O}_{\text{qtz-cal}}$ are calculated using the fractionation factor of Chiba *et al.* (1989).

rocks in both units tend to increase toward the schistose pelitic melange zone that overlies the Ozu-Kawabegawa Fault (Fig. 13). The $\delta^{18}\text{O}_{\text{whole rock}}$ values

for metabasites, and pelitic and psammitic rocks in the highly sheared pelitic melange zone within the Hijikawa unit are extremely high and show a spike of high values.

DISCUSSION

Quartz and calcite within veins are usually in isotopic disequilibrium because the temperature and/or isotopic composition of vein-forming fluids changes during the course of vein formation. In contrast, interdigitation of quartz and calcite fibres, and similar curvature and orientation of fibres in fibrous quartz-calcite veins indicate that both minerals precipitated contemporaneously from the same vein-forming fluids (Durney, 1972; Durney & Ramsay, 1973).

Quartz and calcite that precipitated in isotopic equilibrium should provide meaningful information on the temperature of vein formation if isotopic exchange did not occur subsequent to vein growth. At low metamorphic grades, diffusion rates are too slow for significant isotopic exchange to occur. For quartz-calcite veins within low- to medium-grade tectonites, retrograde exchange by solid-state diffusion is insignificant unless cooling rates were extremely slow or effective grain sizes for diffusion were less than several tens of microns.

Fluid sources

An important area of uncertainty concerning the origin of vein minerals in accretionary prisms is whether they formed from relatively large volumes of external fluid

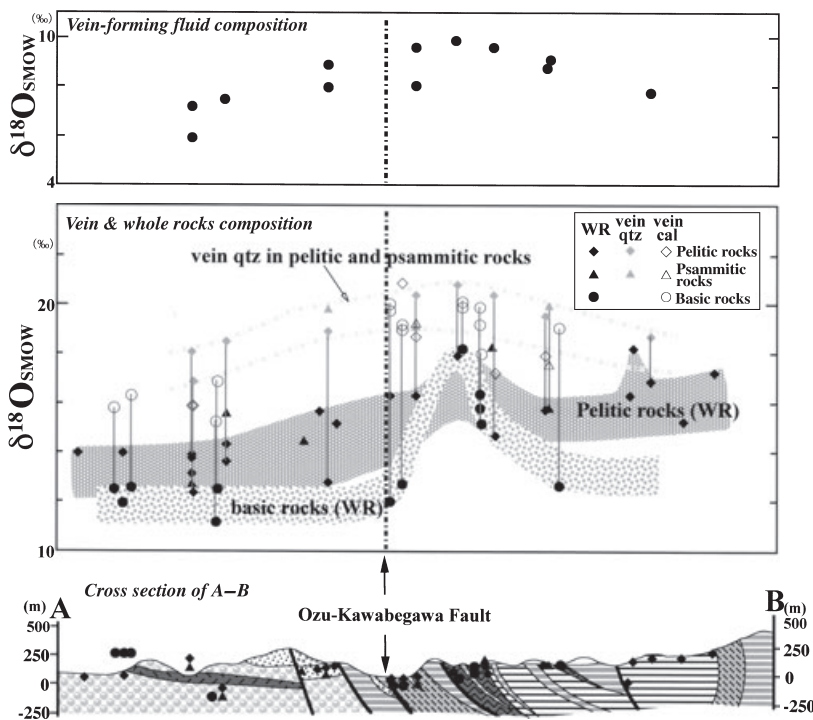


Fig. 13. Compositional variations of oxygen isotope compositions on the line of cross-section a-b in Fig. 3. Tie line show a pair of vein mineral and whole rock in sample. WR, whole rock.

or from localized fluids that were in equilibrium with host wallrock (Vrolijk *et al.*, 1988; Fisher & Brantley, 1992). Moreover, the composition of fluid is influenced by both equilibrium and kinetic factors: the rate of fluid infiltration into the system relative to the rate of oxygen equilibrium with solid phases, the dissolution and precipitation of solid phases, and diffusion within solid phases. Buffering of the fluid composition by the host rock requires extensive fluid–mineral interaction by either solution/redeposition or surface exchange that is coupled with diffusion in the solid phases (Slater *et al.*, 1994).

Fluids that interact with rocks within accretionary prisms can be released by devolatilization reactions at depth during low-grade or high-*P/T* metamorphism. Dehydration of phyllosilicates in clastic sedimentary rocks and hydrothermally altered basalts most likely contributes to the fluid budget within subduction zones. Carbon dioxide within fluids can be generated from both the breakdown of organic matter and devolatilization reactions within underthrust limestone (Moore & Vrolijk, 1992). If fluids are reducing at these levels, methane will be the predominant carbon species, as based on C–O–H equilibrium (Holloway, 1984). Although some CO₂-rich fluid inclusions occur within accretionary prisms (Myers, 1987; Sisson, 1989), water-rich and methane-rich fluid inclusions are more common (Vrolijk *et al.*, 1988).

Sadofsky & Bebout (2001) discussed the expected isotopic trends for veins produced by two end-member models (fluids sourced from seawater and fluids derived from host rocks) of fluid–rock interaction within subduction zones. Host rock isotopic compositions were assumed to be sedimentary organic C ($\delta^{13}\text{C} = -25\text{‰}$; Sadofsky, 2001) and the oxygen isotope composition of clastic quartz in the host rock ($\delta^{18}\text{O} = 19\text{‰}$; Magaritz & Taylor, 1976; Bebout, 1991). The authors concluded that some of the higher $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values for veins can be explained by up-dip (down-*T*) flow of fluid that equilibrated with rocks at higher temperatures and greater depth in the accretionary prism (Sadofsky & Bebout, 2001); however, at sub-greenschist facies conditions, quartz detritus in sediments is a refractory phase for oxygen isotope exchange (Cole & Ohmoto, 1986). Slater *et al.* (1994) concluded that the composition of pore and vein fluids are buffered by the phyllosilicate component of the host sediment, which was in disequilibrium with quartz detritus at temperatures of 200–310 °C.

The stable isotopic data described above provide some important constraints on the origin of vein-forming fluids in the present study area. These data display a positive correlation between the composition of vein quartz and calcite and that of the immediately adjacent whole rock (Figs 14 & 15). This correlation can be explained if it is accepted that fluid–phyllosilicate interactions have a significant effect on the overall fluid composition (Moore & Vrolijk, 1992).

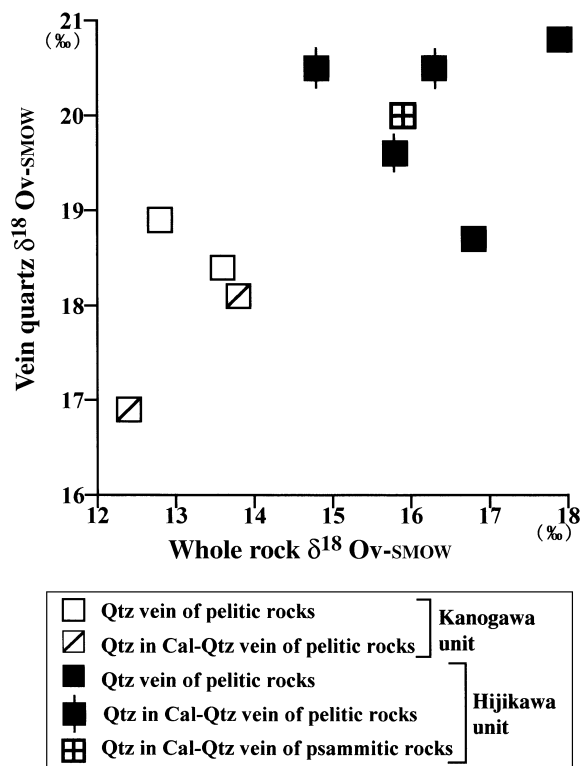


Fig. 14. $\delta^{18}\text{O}_{\text{V-SMOW}}$ of whole rock vs. $\delta^{18}\text{O}_{\text{V-SMOW}}$ of vein quartz.

The $\delta^{13}\text{C}$ values for vein calcite are higher in the metabasites than in pelitic and psammitic rocks (Fig. 16). This may reflect the reduced impact of organic C in the mafic rocks (e.g. Sadofsky & Bebout, 2001).

For appropriate metamorphic temperatures immediately following tectonic juxtaposition between the Hijikawa and Kanogawa units (240 °C), the oxygen isotope composition of the fluid from which vein-quartz grew can be estimated from the quartz–water fractionation data of Sharp & Kirschner (1994) (Fig. 13):

$$1000\ln\alpha_{(\text{quartz-H}_2\text{O})} = -2.9 + 3.65 \times 10^6 \times T^{-2}$$

Calculated fluid oxygen isotope compositions increase steadily from south to north to the schistose melange zone north of the Ozu-Kawabegawa Fault (Fig. 13). The higher $\delta^{18}\text{O}$ values for whole-rock samples and veins along the Ozu-Kawabegawa Fault are inferred to reflect the up-dip flow of fluid derived from pelitic rocks at higher temperatures and greater depths within the accretionary prism.

Isotopic alteration of the Kanogawa and Hijikawa metabasites prior to and synchronous with subduction

Stable isotopes of ophiolitic rocks and metabasites from accretionary complexes are commonly used as monitors of fluid flow within subduction zones (e.g.

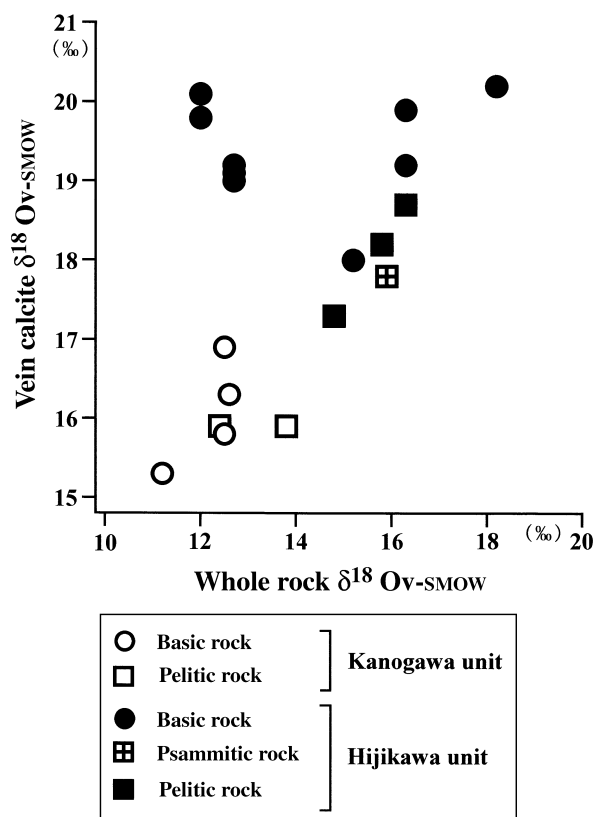


Fig. 15. $\delta^{18}\text{O}_{\text{V-SMOW}}$ of whole rock vs. $\delta^{18}\text{O}_{\text{V-SMOW}}$ of vein calcite from basic rocks.

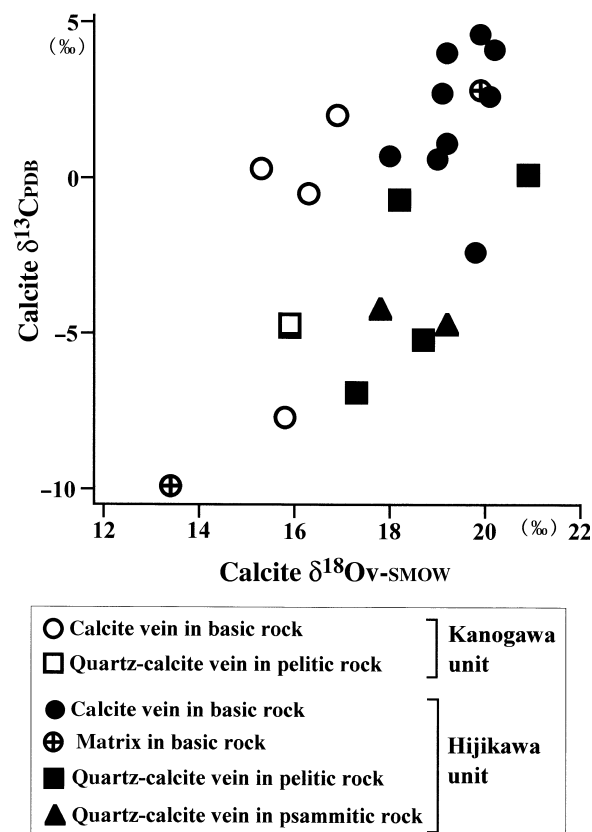


Fig. 16. $\delta^{18}\text{O}_{\text{V-SMOW}}$ of calcite vs. $\delta^{13}\text{C}_{\text{PDB}}$ of calcite from basic rocks.

Bebout, 1991; Getty & Selverstone, 1994; Barnicoat & Bowtell, 1995; Barnicoat & Cartwright, 1995, 1997; Miller & Cartwright, 2000). Fresh oceanic basaltic rocks such as mid-oceanic ridge basalt (MORB), and ocean island basalt (OIB) generally have uniform $\delta^{18}\text{O}$ values (MORB: 5.2–6.4‰, OIB: 4.6–7.5‰). During seafloor weathering and hydrothermal alteration, primary glass transforms to the hydrated alteration product palagonite (e.g. Staudigel & Hart, 1983) such that the basaltic sequence becomes enriched in ^{18}O (e.g. 7.9–16‰ in the Troodos ophiolite, Heaton & Sheppard, 1977; 4.1–10.1‰ in altered oceanic basalts, Stakes & O'Neil, 1982; 7.9–10.7‰ in the Josephine Ophiolite, Harper *et al.*, 1988). In contrast, deeper parts of the oceanic crust become depleted in ^{18}O by 1–3‰ at temperatures in excess of about 300 °C (Hoefs, 1987). Muehlenbachs & Clayton (1976) and Gregory & Taylor (1981) concluded that ^{18}O enrichment is balanced by ^{18}O depletion, which acts as a buffer for the oxygen isotope composition of ocean water. The extent to which the $\delta^{18}\text{O}$ values of oceanic crust are changed depends on the duration and temperature of isotopic exchange with seawater.

Petrological evidence indicates that the Kanogawa and Hijikawa metabasalts originated from MORB or OIB (Umeki & Sakakibara, 1998b). As mentioned

above, $\delta^{18}\text{O}$ values for Kanogawa greenstones are nearly constant (11.9–12.6‰), but those for Hijikawa metabasites vary widely (12.7–18.2‰). The lower $\delta^{18}\text{O}$ values (11.9–12.7‰) for metabasites in both units probably reflect seafloor weathering and hydrothermal alteration. In addition, metabasites with higher $\delta^{18}\text{O}$ values (15.2–18.2‰) are restricted to the highly sheared pelitic melange zone that overlies the Ozu-Kawabegawa Fault. Hence, it is inferred that metabasites in the Kanogawa and Hijikawa units with low $\delta^{18}\text{O}$ values were strongly modified by the focused flow, along the Ozu-Kawabegawa Fault, of an external fluid with high $\delta^{18}\text{O}$ values.

Fluid flow and isotopic alteration along the out-of-sequence thrust

Accretionary prisms are dynamic environments. Fluid flow is affected by tectonic change, which also influences the structural development of the accretionary prism (Fisher & Hounslow, 1990). Veins that formed during sequential opening and precipitation events have previously been observed in cores recovered from depths of several hundred metres in the Barbados prism (Vrolijk & Sheppard, 1991) and in rocks buried to depths of more than 10 km

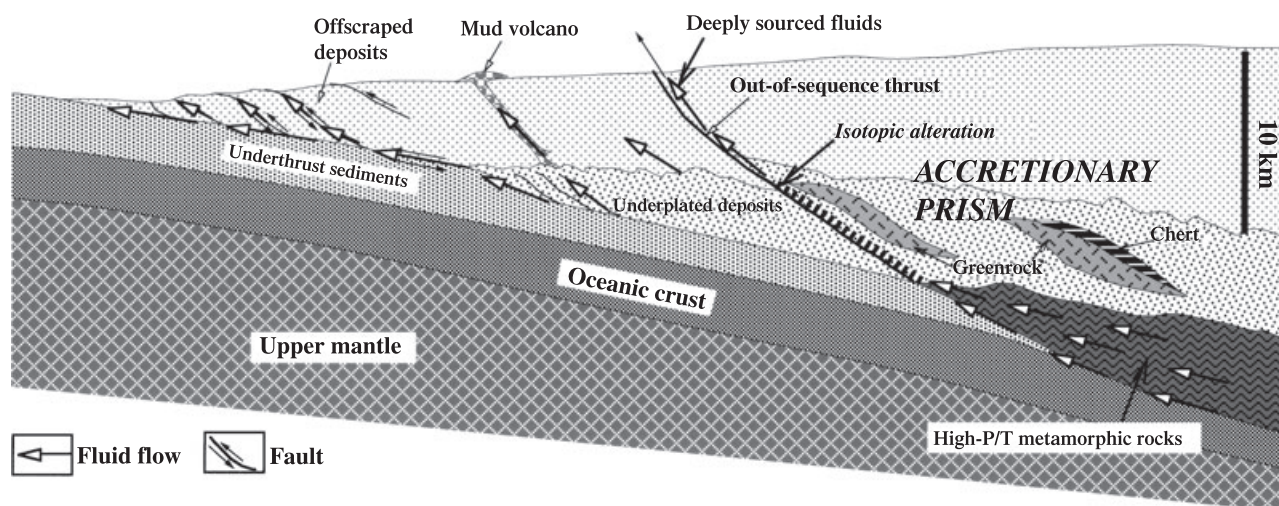


Fig. 17. Schematic cross section of an accretionary prism showing major tectonic elements and features controlling fluid emplacement and expulsion (modified from fig. 1 of Moore & Vrolijk, 1992).

(Vrolijk, 1987; Fisher & Bryne, 1990), suggesting transience in fluid flow over these depths. In some accretionary complexes, fluids migrate rapidly to the surface from depths in excess of 2 km (Sample, 1996). Focused fluid flow out of accretionary prisms occurs along fault zones (Fig. 17). Focused fluid flow is typically three to four orders of magnitude faster than distributed flow (Moore & Vrolijk, 1992). During the geological evolution of accretionary prisms, distributed flow through pore spaces decreases as a result of consolidation and cementation, whereas flow along fracture systems becomes dominant over time. Observations from both modern and ancient prisms suggest episodic fluid flow that is probably coupled to episodic fault displacement and ultimately to the earthquake cycle (Moore & Vrolijk, 1992).

Results of the present study indicate that vein formation largely results from the extensive infiltration of externally buffered fluids with high $\delta^{18}\text{O}$ values from greater depths within the accretionary prism; however, once the fluids have migrated upward along the out-of-sequence thrust, they are then controlled by local processes. Within the highly sheared zone proximal to the out-of-sequence thrust, the rocks are isotopically altered by fluid–rock interactions due to the infiltration of large volumes of high- $\delta^{18}\text{O}$ fluids along zones of high permeability.

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REFERENCES

- Aiba, T., 1982. Sanbagawa metamorphism of the Nakatsu-Nanokawa district in the northern Chichibu belt of the middle east of Shikoku. *Journal Geological Society of Japan*, **88**, 875–885 (in Japanese with English abstract).
- Banno, S., 1998. Pumpellyite-actinolite facies of the Sanbagawa metamorphism. *Journal of Metamorphic Geology*, **16**, 117–128.
- Banno, S., Toriumi, M., Obata, M. & Nishiyama, T., 2000. *Dynamics of Petrogenesis*. University of Tokyo Press, Tokyo.
- Barnicoat, A. C. & Bowtell, S. A., 1995. Seafloor hydrothermal alteration in metabasites from high-pressure ophiolites of the Zermatt-Aosta area of the western Alps. *Museo Regionale di Scienze Naturali di Torino, Bollentino*, **13**, 191–220.
- Barnicoat, A. C. & Cartwright, I., 1995. Focussed fluid flow during subduction: oxygen isotope data from high-pressure ophiolites of the western Alps. *Earth and Planetary Science Letters*, **132**, 53–61.
- Barnicoat, A. C. & Cartwright, I., 1997. The gabbro-eclogite transformation: an oxygen isotope and petrographic study of west Alpine ophiolites. *Journal of Metamorphic Geology*, **15**, 93–104.
- Bebout, G. E., 1991. Field-based evidence for devolatilisation in subduction-zones: implications for arc magmatism. *Science*, **251**, 413–416.
- Breeding, C. M. & Ague, J. J., 2002. Slab-derived fluids and quartz-vein formation in an accretionary prism, Otago Schist, New Zealand. *Geology*, **30**, 499–502.
- Brown, E. H. & O'Neil, J. R., 1982. Oxygen isotope geothermometry and stability of lawsonite and pumpellyite in the Shuksan Suite, North Cascades, Washington. *Contributions to Mineralogy and Petrology*, **80**, 240–244.
- Carpenter, M. A., 1980. Mechanism of exsolution in sodic pyroxenes. *Contributions to Mineralogy and Petrology*, **71**, 289–300.
- Carson, B., Holmes, K., Umstadd, K., Strasser, J. C. & Johnson, H. P., 1991. Fluid expulsion from the Cascadia accretionary prism: evidence from porosity distribution, direct measurements, and GLORIA imagery. *Philosophical Transactions of the Royal Society of London, Series A*, **335**, 331–340.
- Carson, B., Seke, E., Paskevich, V. & Holmes, M. L., 1994. Fluid expulsion sites on the Cascadia accretionary prism: mapping diagenetic deposits with processed GLORIA imagery. *Journal of Geophysical Research*, **99**, 11959–11969.

- Cathelineau, M., 1988. Cation site occupancy in chlorites and illites as a function of temperature. *Clay Minerals*, **23**, 471–485.
- Cathelineau, M. & Nieva, D., 1985. A chlorite solid solution geothermometer. The Los Azufres (Mexico) geothermal system. *Contributions to Mineralogy and Petrology*, **91**, 235–244.
- Chiba, H., Chako, T., Clayton, R. N. & Goldsmith, J. R., 1989. Oxygen isotope fractionations involving diopside, forsterite, magnetite and calcite: application to geothermometry. *Geochimica et Cosmochimica Acta*, **53**, 2985–2995.
- Cho, M., Liou, J. G. & Maruyama, S., 1986. Transition from the zeolite to prehnite-pumpellyite facies in the Karmutsen metabasite, Vancouver Island, British Columbia. *Journal of Petrology*, **27**, 467–494.
- Clayton, R. N. & Mayeda, T. K., 1963. The use of bromine pentafluoride in the extraction of oxygen from oxides and silicates for isotopic analysis. *Geochimica et Cosmochimica Acta*, **27**, 43–52.
- Cole, D. R. & Ohmoto, H., 1986. Kinetics of isotopic exchange at elevated temperatures and pressures. *Reviews in Mineralogy*, **16**, 41–90.
- Digel, S. G. & Gordon, T. M., 1995. Phase relations in metabasites and pressure-temperature relations in prehnite-pumpellyite to greenschist facies transition, Flin Flon, Manitoba, Canada. 67–80. In: *Low-grade Metamorphism of Mafic Rocks, Special Paper No. 296* (eds Schiffman, P. & Day, H. W.), Geological Society of America, Boulder, CO.
- Durney, D. W., 1972. Solution-transfer, an important geological deformation mechanism. *Nature*, **235**, 315–317.
- Durney, D. W. & Ramsay, J. G., 1973. Incremental strains measured by syntectonic crystal growth. In: *Gravity and Tectonics* (eds de Jong, K. A. & Scholten, R.), pp. 67–96. Wiley, New York.
- Essene, E. J. & Fyfe, W. S., 1967. Omphacite in Californian metamorphic rocks. *Contributions to Mineralogy and Petrology*, **15**, 1–23.
- Essene, E. J. & Peacor, D. R., 1995. Clay mineral thermometry – a critical perspective. *Clays and Clay Minerals*, **43**, 540–553.
- Fisher, D. & Brantley, S. L., 1992. Models of quartz overgrowth and vein formation: deformation and episodic fluid flow in an ancient subduction zone. *Journal of Geophysical Research*, **97**, 20043–20061.
- Fisher, D. & Bryne, T., 1990. The character and distribution of mineralized fractures in the Kodiak Formation, Alaska: implications for fluid flow in an underthrust sequence. *Journal of Geophysical Research*, **95**, 9069–9080.
- Fisher, A. T. & Hounsflow, M. W., 1990. Transient fluid flow through the toe of the Barbados accretionary complex: constraints from Ocean Drilling Program Leg 110 heat flow studies and simple models. *Journal of Geophysical Research*, **95**, 8845–8858.
- Frey, M., de Capitani, D. & Liou, J. G., 1991. A new petrogenetic grid for low-grade metabasites. *Journal of Metamorphic Geology*, **9**, 497–509.
- Getty, S. R. & Selverstone, J., 1994. Stable isotopic and trace element evidence for restricted fluid migration in 2GPa eclogites. *Journal of Metamorphic Geology*, **12**, 747–760.
- Gieskes, J. M., Vrolijk, P. & Blanc, G., 1990. Hydrogeochemistry of the northern Barbados Accretionary Complex Transect: Ocean Drilling Program Leg 110. *Journal of Geophysical Research*, **95**, 8809–8818.
- Gregory, R. T. & Taylor, H. P., 1981. An oxygen isotope profile in a section of Cretaceous oceanic crust, Samail ophiolite, Oman: evidence for $\delta^{18}\text{O}$ buffering of oceans by deep (> 5 km) seawater-hydrothermal circulation at mid-ocean ridges. *Journal of Geophysical Research*, **86**, 2737–2755.
- Hada, S. & Kurimoto, C., 1990. Northern Chichibu Terrane. In: *Pre-Cretaceous Terranes of Japan* (eds Ichikawa, K., Mizutani, S., Hara, I., Hada, S. & Yao, A.), pp. 165–183. Publication of IGCP Project No. 224, Osaka.
- Harper, G. D., Bowman, J. R. & Kuhns, R. J., 1988. A field, chemical and stable isotope study of subseafloor metamorphism of the Josephine Ophiolite, California-Oregon. *Journal of Geophysical Research*, **93**, 4625–4656.
- Heaton, T. H. E. & Sheppard, S. M. F., 1977. *Hydrogen and Oxygen Isotope Evidence for Seawater-Hydrothermal Alteration and Ore Deposition, Troodos Complex, Cyprus, Special Publication 7*. Geological Society, London, pp. 42–57.
- Hoefs, J., 1987. *Stable Isotope Geochemistry*. Springer-Verlag, New York.
- Holland, T. J. B., 1990. Activities of components in omphacitic solid solutions. *Contributions to Mineralogy and Petrology*, **105**, 446–453.
- Holloway, J. R., 1984. Graphite-CH₄-H₂O-CO₂ equilibria at low-grade metamorphic conditions. *Geology*, **12**, 455–458.
- von Huene, R. & Lee, H., 1982. The possible significance of pore fluid pressure and subduction zones, Studies of Continental Margin Geology. *American Association of Petroleum Geologists Bulletin Memoirs*, **34**, 781–791.
- Isizaki, Y., 1987. End-Permian convergent zone along the northern margin of Kurosegawa Landmass and its products in central Shikoku, southwest Japan. *Journal of Geoscience of Osaka City University*, **30**, 51–131.
- Jenkin, G. R. T., Linklater, C. & Fallick, A. E., 1991. Modeling of mineral $\delta^{18}\text{O}$ values in an igneous aureole: closed-system model predicts apparent open-system $\delta^{18}\text{O}$ values. *Geology*, **19**, 1185–1188.
- Jenkin, G. R. T., Craw, D. & Fallick, A. E., 1994. Stable isotopic and fluid inclusion evidence for meteoric fluid penetration into an active mountain belt; Alpine Schist, New Zealand. *Journal of Metamorphic Geology*, **12**, 429–444.
- Jiang, W. W., Peacor, D. R. & Buseck, P. R., 1994. Chlorite geothermometry? – Contamination and apparent octahedral vacancies. *Clays and Clay Mineralogy*, **42**, 593–605.
- Jowett, E. C., 1991. Fitting iron and magnesium into the hydrothermal chlorite geothermometer. GAC/MAC/SEG Joint Annual Meeting (Toronto) Program with Abstracts, **16**, A62.
- Kashima, N., 1969. Stratigraphical studies of the Chichibu Belt in western Shikoku. *Memoirs of the Faculty of Science, Kyushu University, Series D: Geology*, **19**, 387–436.
- Kastner, M., Elderfield, H. & Martin, J. B., 1991. Fluids in convergent margins: What do we know about their composition, origin, role in diagenesis and importance for oceanic chemical fluxes. *Philosophical Transactions of the Royal Society of London, Series A*, **335**, 275–288.
- Kastner, Z., Zheng, Y., Laier, T., Jenkins, W. & Ito, T., 1997. Geochemistry of fluids and flow regime in the decollement zone at the northern Barbados Ridge. Proceedings of the Ocean Drilling Program, Scientific Results, **156**, 311–319.
- Langseth, M. G. & Moore, J. C., 1990. Introduction to special section on the role of fluids in sediment accretion, deformation, diagenesis, and metamorphism in subduction zones. *Journal of Geophysical Research*, **95**, 8737–8741.
- Lewis, J. C. & Byrne, T. B., 2003. History of metamorphic fluids along outcrop-scale faults in a Paleogene accretionary prism, SW Japan: implications for prism-scale hydrology. *Geochimica Geophysica Geosystems*, **119**, 9007, doi:10.1029/2002GC000359.
- Liu, J. & Bohlen, R., 1995. Mixing properties and stability of jadeite-acmite pyroxene in the presence of albite and quartz. *Contributions to Mineralogy and Petrology*, **119**, 433–440.
- Magaritz, M. & Taylor, H., 1976. Oxygen, hydrogen and carbon isotope studies of the Franciscan formation, Coast Ranges, California. *Geochimica Cosmochimica Acta*, **40**, 215–234.
- MARGINS Office, 2003. *NSF MARGINS Program-Science Plans 2004*. <http://www.nsf-margins.org/Publications/SciencePlans/MAREINSSciencePlans.html>.
- Maruyama, S. & Liou, J. G., 1985. The stability of Ca-Na pyroxene in low-grade metabasite of high-pressure intermediate facies series. *American Mineralogist*, **70**, 16–29.
- Matsuoka, A. & Yao, A., 1990. Southern Chichibu Terrane. In: *Pre-Cretaceous Terranes of Japan* (eds Ichikawa, K., Mizutani,

- S., Hara, I., Hada, S. & Yao, A.), pp. 203–216. Publication of IGCP Project No.224, Osaka.
- McCrea, J. M., 1950. On the isotope chemistry of carbonates and a paleotemperature scale. *Journal of Chemical Physics*, **18**, 849–857.
- Miller, J. A. & Cartwright, I., 2000. Distinguishing between seafloor alteration and fluid flow during subduction using stable isotope geochemistry: examples from Tethyan ophiolites in the Western Alps. *Journal Metamorphic Geology*, **18**, 467–482.
- Miyazaki, K. & Okumura, K., 2002. Thermal modelling in shallow subduction: an application to low P/T metamorphism of the Cretaceous Shimanto accretionary complex, Japan. *Journal Metamorphic Geology*, **20**, 441–452.
- Moore, J. C., 1989. Tectonics and hydrogeology of accretionary prisms: role of decollement zone. *Journal of Structural Geology*, **11**, 95–106.
- Moore, J. C. & Vrolijk, P., 1992. Fluids in accretionary prisms. *Reviews of Geophysics*, **30**, 113–135.
- Moore, J. C., Orange, D. & Kulm, L. V. D., 1990. Inter-relationship of fluid venting and structural evolution: Alvin observations from the frontal accretionary prism, Oregon. *Journal of Geophysical Research*, **95**, 8795–8808.
- Moore, J. C., Brown, K. M., Horath, F., Cochrane, G., MacKay, M. & Moore, G., 1991. Plumbing accretionary prisms: effects of permeability variations. *Philosophical Transactions of the Royal Society of London, Series A*, **335**, 275–288.
- Muehlenbachs, K. & Clayton, R. N., 1976. Oxygen isotope studies of fresh and weathered submarine basalts. *Canadian Journal of Earth Science*, **9**, 172–184.
- Myers, G., 1987. Fluid Expulsion during the Understanding of the Kodiak Formation: A Fluid Inclusion Study. MS thesis, University of California, Santa Cruz, CA, pp. 41.
- Nakajima, T., Banno, S. & Suzuki, T., 1977. Reactions leading to the disappearance of pumpellyite in low-grade metamorphic rocks of the Sanbagawa metamorphic belt in central Shikoku, Japan. *Journal of Petrology*, **18**, 263–284.
- Newton, R. C. & Smith, J. V., 1967. Investigations concerning the breakdown of albite in the earth. *Journal of Geology*, **75**, 268–286.
- Ohmori, K., Taira, A., Tokuyama, H., Sakaguchi, A., Okamura, M. & Aihara, A., 1997. Paleothermal structure of the Shimanto accretionary prism, Shikoku, Japan: role of an out-of-sequence thrust. *Geology*, **25**, 327–330.
- Popp, R. K. & Gilbert, M. C., 1972. Stability of acmite-jadeite pyroxenes at low pressure. *American Mineralogist*, **57**, 1210–1231.
- Powell, W. G., Carmichael, D. M. & Hodgson, C. J., 1993. Thermobarometry in a subgreenschist to greenschist transition in metabasites of the Abitibi greenstone belt, Superior Province, Canada. *Journal of Metamorphic Geology*, **11**, 165–178.
- Robinson, D. & Bevins, R. E., 1999. Patterns of regional low-grade metamorphism in metabasites. In: *Low-grade Metamorphism* (eds Frey, M. & Robinson, D.), pp. 143–168. Blackwell Science Ltd., Oxford.
- Sadofsky, S., 2001. *Behavior and cycling of volatile elements in the crust and mantle: evidence from field-based studies of nitrogen-isotope geochemistry and high-P/T low-grade metamorphism*. PhD Thesis, Lehigh University, Bethlehem, Pennsylvania.
- Sadofsky, S. & Bebout, G. E., 2001. Paleohydrogeology at 5- to 50-kilometer depths of accretionary prisms: The Franciscan Complex, California. *Geophysical Research Letters*, **28**, 2309–2312.
- Sakakibara, M., 1991. Metamorphic petrology of the Northern Tokoro Metabasites, Eastern Hokkaido, Japan. *Journal of Petrology*, **32**, 333–364.
- Sakakibara, M., Ofuka, H., Kimura, G. *et al.*, 1997. Metamorphic evolution of the Susunai metabasites in southern Sakhalin, Russian Republic. *Journal of Metamorphic Geology*, **15**, 565–580.
- Sakakibara, M., Oyama, Y., Umeki, M., Sakakihara, H., Shono, H. & Goto, S., 1998. Geotectonic division and regional metamorphism of Northern Chichibu Belt in western Shikoku, Japan. *The Journal of the Geological Society of Japan*, **104**, 604–622 (in Japanese with English abstract).
- Sample, J. C., 1996. Isotopic evidence from authigenic carbonates for rapid upward fluid flow in accretionary wedges. *Geology*, **24**, 897–900.
- Schiffman, P. & Day, H. W., 1999. *Low-Grade Metamorphism of Mafic Rocks, Special Paper No. 296*. Geological Society of America, Boulder, CO, pp. 187.
- Schmidt, D., Livi, K. J. T. & Frey, M., 1999. Reaction progress in chloritic material: an electron microbeam study of the Taveyanne greywacke, Switzerland. *Journal of Metamorphic Geology*, **17**, 229–241.
- Screaton, E. J., Carson, B. & Lennon, G. P., 1995. Hydrogeologic properties of a thrust fault within the Oregon Accretionary Prism. *Journal of Geophysical Research*, **100**, 20025–20035.
- Sharp, Z. D. & Kirschner, D. L., 1994. Quartz-calcite oxygen isotope thermometry: a calibration based on natural isotopic variations. *Geochimica et Cosmochimica Acta*, **58**, 4491–4501.
- Shau, Y. H., Peacor, D. R. & Essene, E. J., 1990. Corrensite and mixed-layer chlorite/corrensite in metabasalt from northern Taiwan: TEM/AEM, EMPA, SRD, and optical studies. *Contributions to Mineralogy and Petrology*, **105**, 123–142.
- Silver, E., Kastner, M., Fisher, A., Morris, J., McIntosh, K. & Saffer, D., 2000. Fluid flow paths in the Middle America Trench and Costa Rica margin. *Geology*, **28**, 679–682.
- Sisson, V. B., 1989. Petrologic and age constraints on the origin of a low-pressure/high-temperature metamorphic complex, southern Alaska. *Journal of Geophysical Research*, **94**, 4392–4410.
- Slater, D. J., Yardley, B. W. D., Spiro, B. & Kniper, J., 1994. Incipient metamorphism and deformation in the Variscides of SW Dyfed, Wales: first steps towards isotopic equilibrium. *Journal of Metamorphic Geology*, **12**, 237–248.
- Stakes, D. S. & O'Neil, J. R., 1982. Mineralogy and stable isotope geochemistry of hydrothermally altered oceanic rocks. *Earth and Planetary Science Letters*, **57**, 285–304.
- Staudigel, H. & Hart, S. R., 1983. Alteration of basaltic glass: mechanisms and significance for the oceanic crust-sea water budget. *Geochimica Cosmochimica Acta*, **47**, 337–350.
- Tobin, H. J., Moore, J. C., MacKay, M. E., Orange, D. L. & Kulm, L. V. D., 1993. Fluid flow along a strike-slip fault at the toe of the Oregon accretionary prism: implications for the geometry of frontal accretion. *Geological Society of America Bulletin*, **105**, 569–582.
- Umeki, M. & Sakakibara, M., 1998a. Geology and petrologic study of basic rocks of Northern Chichibu Belt in the Hijikawa district, western Shikoku, Japan. *The Journal of the Geological Society of Japan*, **104**, 590–603 (in Japanese with English abstract).
- Umeki, M. & Sakakibara, M., 1998b. Biotite-bearing basic semischists from the northern Chichibu belt in the Hijikawa district, western Shikoku, Japan. *Japanese Association of Mineralogy, Petrology and Economic Geology*, **69**, 390–402 (in Japanese with English abstract).
- Vrolijk, P., 1987. Tectonically-driven fluid flow in the Kodiak accretionary complex, Alaska. *Geology*, **15**, 466–469.
- Vrolijk, P. & Sheppard, S. M. F., 1991. Syntectonic carbonate veins from the Barbados accretionary prism (ODP Leg 110) – record of paleohydrology. *Sedimentology*, **38**, 671–690.
- Vrolijk, P., Myers, G. & Moore, J. C., 1988. Warm fluid migration along tectonic melanges in the Kodiak accretionary complex, Alaska. *Journal of Geophysical Research*, **93**, 10313–10324.
- Vrolijk, P., Chambers, S., Gieskes, J. & O'Neil, J., 1990. Stable isotopic ratios of interstitial fluids from the northern Barbados accretionary prism. *Proceeding of Ocean Drilling Program, Science Results*, **110**, Part 2, 189–205.
- Xie, X., Byerly, G. R. & Ferrell, R. E., 1997. Ilb trioctahedral chlorite from the Barberton greenstone belt: crystal structure

- and rock composition constraints with implications to geothermometry. *Contributions to Mineralogy and Petrology*, **126**, 275–291.
- Yamakita, S., 1988. Jurassic-Earliest Cretaceous allochthonous complexes related to gravitational slidings in the Chichibu Terrane of eastern and central Shikoku, Southwest Japan. *Journal of Faculty of Science, University of Tokyo, Section II*, **21**, 467–514.
- Zang, W. & Fyfe, W. S., 1995. Chloritization of the hydrothermally altered bedrocks at the Igarapé Bahia gold deposit, Carajás, Brazil. *Mineralium Deposita*, **30**, 30–38.

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