Dissolution processes of elements from subducting sediments into fluids: Evidence from the chemical composition of the Sanbagawa pelitic schists

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In order to evaluate the dissolution processes of elements from subducting sediments into fluids during early stages of metamorphism (up to oligoclase–biotite zone at about 30 km depth), the chemical composition of Sanbagawa pelitic schists, Sanbagawa Metamorphic Belt, Japan was studied. Samples from different metamorphic grades show similarities in their major element and Rb compositions, suggesting that the Sanbagawa schists experienced insignificant dissolution of these elements. Arsenic, N (as ammonium, NH$_4^+$) and Cs contents decrease with increasing metamorphic grade, demonstrating that their dissolution is enhanced under respective metamorphic stages (As: upper–garnet zone, NH$_4^+$: chlorite – oligoclase–biotite zone, Cs: garnet – albite–biotite zone). Dissolution mechanisms proposed are as follows. The NH$_4^+$ dissolution accompanies dehydration of the pelitic schists, which may produce fluids with a high potential to dissolve or oxidize NH$_4^+$. The thermal structure of the subducted slab is likely to influence the depth of the NH$_4^+$ dissolution. The Cs dissolution is caused mainly by fluid flow from underlying metamafic rocks and the amount of fluids possibly controls the degree of the Cs dissolution. Heterogeneous dissolution of Cs suggests that the fluid flow from the underlying metamafic rocks has a channelized structure. The mechanism of As dissolution is not clearly understood; however, it may be strongly related to graphitization of kerogens in the pelitic schists. Differences in Cs dissolution were observed between the Sanbagawa pelitic schists and other well-studied meta-sedimentary sequences, particularly the Catalina Schist, California and New Caledonia Schistes Lustrés. In the case of the Catalina Schists, Cs was dissolved into fluids more effectively than the Sanbagawa pelitic schists. In contrast, meta-sedimentary rocks of the Schistes Lustrés nappe did not experience any Cs dissolution, although rocks subducted deeper than their dehydration depth. One of the reasons for these differences may be variations in the amount of channelized structures among subduction zones.

Keywords: element mobility, subduction zones, pelitic schists, fluid flow, graphitization
Hydrothermal experiments were conducted to measure the chemical composition of fluids interacting with subducted decollement sediments. According to You et al. (1996), a hydrothermal system under low-\(T\), low-\(P\) (80 MPa, 25–350°C) showed that equilibrated aqueous fluids had high Pb/Ce, Cs/Rb and B/Nb. This suggests that interaction between subducted sediments and fluids at shallow depth plays an important role in element migration from the slab to the mantle wedge. In contrast, an insignificant amount of dissolved elements (LILE, Pb etc.) into fluids was determined by a hydrothermal experiment under higher-\(T\), higher-\(P\) conditions (2.2 GPa, 600–750°C; Spandler et al., 2007). This result clearly disagrees with that of You et al. (1996).

The element dissolution from subducting sediments into fluids has also been estimated by chemical analyses of exhumed meta-sedimentary rocks that experienced prograde metamorphism during subduction. In the case of the Catalina Schist, meta-sedimentary rocks exposed in California, Bebout et al. (1999) reported that samples which experienced prograde metamorphism under higher-\(T\) conditions (reaching up to epidote–blueschist/amphibolite or amphibolite facies) are depleted in N, B, Cs, As and Sb relative to the samples at lower-metamorphic grade (lawsonite–albite facies). This observation suggests that the dissolution of these elements from meta-sediments occurs in relatively warm subducting slabs during the early stage of prograde metamorphism. On the contrary, Spandler et al. (2003) examined samples of high-pressure, low-temperature metamorphic rocks from New Caledonia and concluded that significant amounts of trace elements are not liberated up to eclogite facies due to the decoupling of fluid release and trace element release in subducting slab. Thus, analyses of meta-sedimentary rocks can provide effective information for evaluation of the element dissolution from subducting sediments into fluids.

In this study, we analyzed the bulk chemical compo-
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sition of the Sanbagawa pelitic schists in order to identify (i) which elements were dissolved from the subducting sediments into fluids during metamorphism in the subduction zone and (ii) under which metamorphic stage the dissolution occurred. We further discuss the major factors controlling the element mobility into fluids and their variations among subduction zones.

GEOLoGICAL BACKGROUND AND SAMPLE DESCRIPTION

The Sanbagawa metamorphic belt extends from eastern Japan (Kanto) to western (Kyushu) over a distance of about 800 km and is derived from an Early Cretaceous accretionary complex (Isozaki and Itaya, 1990; Wallis, 1998). The Sanbagawa belt is divided into non-eclogitic unit and eclogitic domains (Takasu, 1989; Wallis and Aoya, 2000).

The non-eclogite unit is composed largely of pelitic schists (meta-sedimentary rocks) and meta-mafic rocks and represents processes of underplating at depths of 15–30 km (Takasu, 1989). The pelitic schists in the non-eclogite unit belong to four metamorphic zones on the basis of their mineral assemblages: chlorite zone, garnet zone, albite–biotite zone and oligoclase–biotite zone in the order of increasing metamorphic grade (Banno et al., 1978; Enami, 1982). Peak P–T conditions range from 0.55 to 1.1 GPa and from 300 to 600°C, respectively (reviewed in Wallis et al., 2000), as estimated from Fe–Mg partitioning between chlorite and garnet (Banno and Sakai, 1989) and zonal structures of sodic pyroxene in equilibrium with albite and quartz (Enami et al., 1994).

We sampled pelitic schists along the Asemi River in central Shikoku (Fig. 1a), where lower to higher-grade metamorphic rocks are well exposed (Fig. 1b). In the sampling area the metamorphic grade increases from the chlorite to oligoclase–biotite zones from south to north. The metamorphic rocks along the Asemi River are mainly pelitic schists with minor amounts of psammitic and basic schists. Nine samples were collected in the chlorite zone, 8 samples in the garnet zone, 3 samples in the albite–biotite zone and 14 samples in the oligoclase–biotite zone (Fig. 1b).

An analytical methods

Rock samples were crushed and then milled down to 5 mm using an iron mill. Sieving was used to separate fine particles of less than 124 µm to prevent some contamination of iron. After washed in an ultrasonic bath with 18.2 MΩ water, these samples were dried at 70°C for 1 day, and powdered into less than 124 µm with an agate ball mill.

A similar procedure was used to prepare samples for separation of kerogens, although washing in the ultrasonic bath was eliminated, and the samples were powdered to a size of less than 500 µm with a stainless steel ball mill.

Major element composition was analyzed by X-ray fluorescence (Shimadzu SXF-1200). The glass beads were prepared by fusing mixtures of powder samples and Li2B4O7 in a weight ratio of 0.7:6:0. Sedimentary and
igneous rock reference samples issued by the Geological Survey of Japan (GSJ) were used for the calibration.

Trace element compositions (Rb, Cs and As) were analyzed by an inductively coupled plasma mass spectrometer (ICP-MS, Hewlett-Packard HP4500). About 30 mg of powder samples were digested using a mixture of HF and HClO₄, followed by evaporation on a hot plate. The digestion was repeated twice, and then only HClO₄ was added to the residue, followed by evaporation. After decomposition, the sample solutions dissolved in 2%-HNO₃ were centrifuged and the supernatant solutions were taken into a clean Teflon® beaker. The remnants were decomposed by mixture of HF and HClO₄ and then centrifuged in the same way. The supernatants were added to the Teflon® beaker. This treatment was repeated until almost no remnants were found. The supernatant solutions were dried up and dissolved in 2%-HNO₃. The standard solutions were prepared by diluting and mixing commercial 1000 ppm solutions (Kishida Chemicals, Chameleon Reagents for Atomic Absorption Analysis). The internal standard solution, 200 ppb In, was also used for analyses. In the case of As analysis, ⁴⁰Ar³⁵Cl interferes with ⁷⁵As. The corrected ⁷⁵As signal was estimated by using the following equation:

\[
{\text{As signal}} = \frac{m/z\ 75\ \text{signal} - 3.127 \left( \frac{m/z\ 77\ \text{signal}}{m/z\ 75\ \text{signal}} \right)}{0.815 \left( \frac{m/z\ 82\ \text{signal}}{m/z\ 75\ \text{signal}} \right)}
\]

This equation means that (i) ⁷⁷Se is estimated on the basis of natural abundance ratio of ⁷⁷Se/⁷⁵Se = 0.815; (ii) ⁴⁰Ar³⁵Cl is calculated by the subtraction of ⁷⁷Se from the total 77 signal; (iii) ⁴⁰Ar³⁵Cl is estimated on the basis of ⁴⁰Ar³⁵Cl/⁴⁰Ar³²Cl = 3.127 (natural abundance ratio of ³⁵Cl/³⁷Cl); and finally (iv) ⁷⁵As is calculated by subtraction of ⁴⁰Ar³⁵Cl from the total 75 signal.

We tested the reliability of the trace element (Rb, Cs and As) analyses, rock reference samples, JSl-1 and JSl-2, issued by GSJ were used for comparison. Each measured element is within the given content ±1σ (Table 1). Relative standard deviations (RSD) of the analytical errors are low enough for the following discussions.

Organic element compositions (C, H and N) were determined by a EuroVector® CHNS-O Elemental Analyzer. About 20 mg of powder samples were wrapped in tin capsules. We used L-cystine (C₆H₁₂N₂O₄S₂) or 2,5-Bis(5-tert-butyl-2-benzoxazolyl) thiophene (hereafter BBOT; C₂₆H₂₆N₂O₂S) for the standard samples.

For the gravimetric determinations of H₂O (–) and loss on ignition (LOI), quartz tubes containing about 300 mg of powder samples were heated at 110°C for 2–3 hours and at 900°C for 1–2 hours, respectively.

The C, H, N and O contents in separated kerogens were determined as follows. Powder samples of about 100 g were decomposed by repeated treatment with HCl and HF. Between repeated acid treatments, the solutions were removed and the remnants were washed with distilled water twice. The remnants were treated by bromoform flotation in order to remove heavy minerals such as pyrite and zircon. Then low molecular weight organic compounds were also removed by Soxhlet extraction with chloroform for 3 days. We regarded the remnants obtained by these procedures as “kerogens”.

The organic elements (C, H, N and O) of the kerogens were analyzed with a EuroVector® CHNS-O Elemental Analyzer. About 1 mg of kerogen was wrapped in a tin or silver capsule for the analysis of C, H, N or O, respec-

<table>
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<th>JSl-2</th>
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<td>RSD (%)</td>
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</tr>
<tr>
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<td>1.09</td>
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<tr>
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</tr>
<tr>
<td>Cs</td>
<td>7.6</td>
<td>1.31</td>
</tr>
</tbody>
</table>

Table 1. (a) Analytical results of rock reference samples, JSl-1 and -2, issued by the Geological Survey of Japan (GSJ). Average values and RSD of each analyzed element are listed. Number means the number of repeated analyses. (b) Preferred contents and standard deviation cited from http://riodb02.ibase.aist.go.jp/geostand/welcomej.html
Table 2. Major and trace element compositions of the Sanbagawa pelitic schists

| Zone         | No. 1 | No. 2 | No. 3 | No. 4 | No. 5 | No. 6 | No. 7 | No. 8 | No. 9 | No. 10 | No. 11 | No. 12 | No. 13 | No. 14 | No. 15 | No. 16 | No. 17 |
|--------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| Garnet Zone  |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |
| **SiO**₂ (wt%) | 64.80 | 70.40 | 61.27 | 71.81 | 56.33 | 60.68 | 68.55 | 67.65 | 56.33 | 66.19 | 68.95 | 75.16 | 71.64 | 71.64 | 72.37 | 69.25 | 56.23 | 64.05 |
| CaO          | 3.17  | 3.70  | 3.46  | 3.26  | 3.69  | 3.57  | 3.42  | 3.51  | 3.27  | 3.51  | 3.70  | 3.70  | 3.70  | 3.70  | 3.70  | 3.70  | 3.70  | 3.70  |
| MgO          | 1.54  | 1.72  | 1.86  | 1.79  | 1.86  | 1.78  | 1.77  | 1.80  | 1.77  | 1.80  | 1.78  | 1.78  | 1.78  | 1.78  | 1.78  | 1.78  | 1.78  | 1.78  |
| MnO          | 0.09  | 0.07  | 0.09  | 0.07  | 0.09  | 0.09  | 0.09  | 0.09  | 0.09  | 0.09  | 0.09  | 0.09  | 0.09  | 0.09  | 0.09  | 0.09  | 0.09  | 0.09  |
| TiO₂         | 0.17  | 0.12  | 0.10  | 0.12  | 0.16  | 0.14  | 0.12  | 0.14  | 0.12  | 0.14  | 0.12  | 0.14  | 0.12  | 0.14  | 0.12  | 0.14  | 0.12  | 0.14  |
| P₂O₅         | 0.90  | 0.88  | 0.88  | 0.88  | 0.88  | 0.88  | 0.88  | 0.88  | 0.88  | 0.88  | 0.88  | 0.88  | 0.88  | 0.88  | 0.88  | 0.88  | 0.88  | 0.88  |
| **H₂O**       | 5.67  | 5.67  | 5.67  | 5.67  | 5.67  | 5.67  | 5.67  | 5.67  | 5.67  | 5.67  | 5.67  | 5.67  | 5.67  | 5.67  | 5.67  | 5.67  | 5.67  | 5.67  |
| **Total (1)** | 100.28| 99.93 | 98.05 | 99.46 | 98.79 | 98.99 | 99.48 | 98.60 | 101.10| 98.61| 99.04| 98.45| 98.48| 98.94| 98.92| 98.01| 97.53|       |
| LOI           | 4.15  | 4.23  | 4.19  | 4.86  | 4.85  | 4.84  | 4.84  | 4.84  | 4.84  | 4.84  | 4.84  | 4.84  | 4.84  | 4.84  | 4.84  | 4.84  | 4.84  | 4.84  |
| **Total (2)** | 95.13 | 94.72 | 94.16 | 94.60 | 94.34 | 94.16 | 94.16 | 94.16 | 94.16 | 94.16 | 94.16 | 94.16 | 94.16 | 94.16 | 94.16 | 94.16 | 94.16 | 94.16 |
| Bb            | 132.59| 50.75 | 54.75 | 127.86| 97.16 | 100.12| 91.00 | 127.86| 97.16 | 100.12| 91.00 | 100.12| 91.00 | 100.12| 91.00 | 100.12| 91.00 | 100.12|
| Cs             | 9.16  | 2.81  | 2.83  | 3.87  | 7.74  | 7.74  | 7.74  | 7.74  | 7.74  | 7.74  | 7.74  | 7.74  | 7.74  | 7.74  | 7.74  | 7.74  | 7.74  | 7.74  |
| H₂O(−)        | 0.53  | 0.24  | 0.41  | 0.24  | 0.47  | 0.47  | 0.47  | 0.47  | 0.47  | 0.47  | 0.47  | 0.47  | 0.47  | 0.47  | 0.47  | 0.47  | 0.47  | 0.47  |
| **Note:** Fe²⁺ denotes total iron Fe₂O₃ and LOI does loss on ignition. Total (1) means the total contents of major elements, H₂O(−) and H₂O(−). Total (2) means the total mass of major elements and LOI. "n.d." means not detected because of under detection limit.
Standard was BBOT or acetanilide (C₈H₉NO) for the analysis of C, H, N or O, respectively. The degree of graphitization was also determined with an X-ray diffractometer (Rigaku-Denki, MultiFlex) using indices of apparent d₀₀₂ and peak width.

**RESULTS AND DISCUSSION**

Analytical results are presented in Table 2. In the following discussion, re-calculated compositions on a volatile free basis and elemental ratios are used to eliminate the contribution of volatile components such as H₂O.

All analyzed Sanbagawa samples of any metamorphic grade show little variations in their conservative element (Si, Ti, Al, K and Rb) composition. Major element and Rb compositions correspond to those of their source material, i.e., marine sediments (Fig. 3). This result suggests that these elements did not undergo significant dissolution into fluids during prograde metamorphism.

Figures 3a and 3b show clear negative correlations between SiO₂, Al₂O₃ and TiO₂, all data points overlapping irrespective of the sample metamorphic grade. Such
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a characteristic is common to marine sediments along Japan Arc such as the Japan Trench and the Nankai Trough. This relationship is attributed to clastic detritus being diluted by the contribution of biogenic silica (Sugisaki, 1981). Ti and Al neither precipitating nor being dissolved during weathering and sedimentation (Sugisaki and Yamamoto, 1984). The SiO$_2$ contents of all Sanbagawa samples are comparable to those of marine sediments and show no systematic change with increasing metamorphic grade. For these reasons, SiO$_2$, TiO$_2$ and Al$_2$O$_3$ compositions of all samples are interpreted to be mostly inherited from their source marine sediments.

As shown in Figs. 3c and 3d, there are weak negative correlations of K$_2$O and Rb with SiO$_2$ for marine sediments ($\gamma = -0.78$ and -0.69, respectively). Significantly, most of the Sanbagawa samples show K, Si and Rb compositions overlapping those of marine sediments along Japan Arc. According to Plank and Langmuir (1998), K in clastic detritus is diluted by biogenic silica. However, a weak negative correlation is found for marine sediments in the SiO$_2$–K$_2$O diagram, whereas scattered nature is shown by the Sanbagawa samples. This suggests that components other than clastic detritus and biogenic silica are contributing to the Sanbagawa samples. Different degrees of diagenetic K and Rb uptake by clay minerals and variations in detrital clay mineralogy (e.g., illite vs. kaolinite) are considered as an additional cause of K and Rb variations.

The Rb/K$_2$O ratios in all metamorphic grades of the Sanbagawa samples fall within the range recorded for marine sediments apart from two outliers (Fig. 4). This correlation suggests that K$_2$O and Rb abundances of the Sanbagawa samples are modified by the diagenetic uptake perhaps controlled by clay mineralogy (K, Rb-rich illite vs. -poor kaolinite).

We conclude that all metamorphic grades of the Sanbagawa samples experienced insignificant dissolution of Si, Ti, Al, K and Rb during prograde metamorphism in bulk, although local re-distribution of K and Rb is feasible.

Chemical changes in the Sanbagawa pelitic schists during prograde metamorphism

In order to identify chemical changes in the Sanbagawa pelitic schists during prograde metamorphism, selected elements have been plotted against horizontal distance from the northernmost sample (Fig. 5). Arsenic dissolution As shown in Fig. 5a, most chlorite zone samples and some garnet zone samples have relatively high As contents (6–10 ppm), while other samples in the higher metamorphic grade have As contents below the detection limit: less than 0.1 ppm. In addition, the garnet zone samples with higher As contents (Nos. 10 and 11) occur up until upper garnet zone close to the iso-grade between the chlorite and garnet zones (Figs. 1b and 5a). It is highly probable that As dissolution was enhanced significantly during upper–garnet zone metamorphism ($P \sim 0.75$ GPa, $T \sim 450^\circ$C).

Some marine sediments show lower As contents, which can be caused by (i) higher contribution of biogenic silica with low As content and (ii) lower contribution of Fe–Mn oxyhydroxides with high As concentration (Maher, 1984). Such marine sediments with lower As contents may be the source for two chlorite zone samples with low As contents (Nos. 2 and 4: 2.35 and 2.66 ppm, respectively). These samples are characterized by (i) higher SiO$_2$ contents (>70 wt%) and (ii) lower Fe$_2$O$_3$ and MnO contents (<3.2 wt% and <0.07 wt%, respectively) relative to other chlorite zone samples (Table 2). The former probably means higher contribution of biogenic silica, and the latter suggests lower contribution of Fe–Mn oxyhydroxides.

Graphitization of kerogens The H/C, O/C and N/C ratios of kerogens extracted from the Sanbagawa samples de-
crease dramatically near the iso-grad between the chlorite and garnet zones and remain close to zero from the upper–garnet through the oligoclase–biotite zones (Table 3; Fig. 5b). Apparent d002 and peak width (FWHM) also show a similar decrease and reach the value of ordered graphite (d002 = 3.33–3.36). Hence, it is suggested that the graphitization proceeded with release of CH4, CO2 and/or H2O during prograde metamorphism from the upper–chlorite to lower–garnet zones. Arsenic contents sharply decrease at the same point where the process of graphitization is complete (Fig. 5a).

NH4+ dissolution As shown in Fig. 5c, N contents of the Sanbagawa samples decrease successively from the chlorite to the oligoclase–biotite zones, except for three low N samples from the chlorite zone. As stated earlier, two samples (Nos. 2 and 4) among these three show higher SiO2 content and may be diluted with the biogenic component. Bebout and Fogel (1992) compared N/K2O ratios among the Catalina meta-sedimentary rocks in order to examine NH4+ dissolution from subducting sediments into fluids, supposing that most of nitrogen exists as NH4+ substituting for K+ (Stevenson, 1962; Honma and Itihara, 1981). Nitrogen is also likely to be contained in organic matters. However, in the case of the Sanbagawa samples, the nitrogen content of kerogens is estimated to be low relative to that of bulk rock (Table 4), which indicates that most of nitrogen exists as NH4+.

A decrease in N/K2O ratios with increasing metamorphic grade (Fig. 6a) clearly suggests NH4+ (N) dissolution from the Sanbagawa samples is likely to have occurred successively during prograde metamorphism from the chlorite to oligoclase–biotite zones. In particular, it was probably enhanced during prograde metamorphism from the chlorite to garnet zones (P ~ 0.7 GPa, T ~ 400 °C) and from the albite–biotite to oligoclase–biotite zones (P ~ 0.9 GPa, T ~ 550 °C), according to significant differences in N/K2O ratios between the chlorite and garnet zone samples and the albite–biotite to oligoclase–biotite zone samples, respectively. The N/K2O ratios are not constant among the samples in the same metamorphic grade. This may be due to (i) inconstant N/K2O ratios of marine sediments, (ii) local redistribution of K in diagenetic process, and (iii) variable degree of the NH4+ dissolution among the samples. Regarding (i), Müller (1977) reported that NH4+/K2O ratios of marine sediments are dependent on their sedimentological or stratigraphical unit. Rests are deduced from the observations of the Sanbagawa samples.

Cesium dissolution A slight decrease in Cs contents is observed with increasing metamorphic grade, though Cs
concentration of the Sanbagawa samples is variable in each metamorphic grade (Fig. 5d). As shown in Fig. 6b, some samples from higher metamorphic grades— the albite–biotite and oligoclase–biotite zones— have lower Cs/Rb ratios than low grade metamorphic samples. These results show possible dissolution of Cs into fluids was probably enhanced during prograde metamorphism from the garnet to albite–biotite zones (Peacock, 1993; Hacker, 2008). In this context, meta-mafic rocks could release fluids during prograde metamorphism from the garnet to albite–biotite zones, if source mafic rocks contained H2O content larger than 2.3 wt% due to hydrothermal alteration before subduction. On the contrary, meta-ultramafic rocks cannot have produced fluids due to antigorite breakdown at 600°C during prograde metamorphism of the overlying metasedimentary rocks from the chlorite to albite–biotite zones (peak T: up to 600°C). That’s because conduction of heat downward from mantle wedge into the top of slab results in warmer P-T path for the top of slab compared to the base (Peacock, 1990; Hacker, 2008).

Meta-mafic rocks decrease their maximum H2O content from 3.4 wt% to 2.3 wt% from greenschist to epidote–amphibolite facies, i.e., from garnet to olivoclase–biotite zones (Peacock, 1993; Hacker, 2008). In this context, meta-mafic rocks could release fluids during prograde metamorphism from the garnet to albite–biotite zones, if source mafic rocks contained H2O content larger than 2.3 wt% due to hydrothermal alteration before subduction. On the contrary, meta-ultramafic rocks cannot have produced fluids due to antigorite breakdown at 600°C during prograde metamorphism of the overlying metasedimentary rocks from the chlorite to albite–biotite zones (peak T: up to 600°C). That’s because conduction of heat downward from mantle wedge into the top of slab results in warmer P-T path for the top of slab compared to the base (Peacock, 1990; Hacker, 2008).

Mechanisms of the element dissolution
Possible sources of free fluid during prograde metamorphism: The major discussion is about the sources of free fluids dissolving As, Cs, and NH4+. The candidates for the fluid source are meta-sedimentary rocks, meta-mafic rocks and meta-ultramafic rocks that may flush over metasedimentary rocks (e.g., Bebout et al., 2007).

Meta-sedimentary rocks themselves might have released fluids successively during prograde metamorphism from the chlorite to albite–biotite zones, because breakdown of chlorite (2Chlorite + 4Qtz = 3Garnet + 8H2O) continued from the chlorite to garnet zones and reaction of chlorite with phengite (Chlorite + 2phengite = muscovite + biotite + Qtz + 4H2O) continued from the garnet to albite–biotite zones (Sakai et al., 1985; Inui and Toriumi, 2002; Hacker, 2008).

Note: “n.d.” of X-ray diffraction data (FWHM and Apparent d002) means not detected because of unclear graphite peaks in X-ray diffraction analysis.
“n.d.” of other data means not detected because of under detection limit.

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Table 4. Estimated ratios of nitrogen in kerogens against bulk amounts of nitrogen of the Sanbagawa pelitic schists. On the supposition that all carbon in the schists is derived from kerogens, the ratios are calculated as below:

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<th>Sample No.</th>
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<th>Bulk rock</th>
<th>Estimated ratio (%)</th>
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<tr>
<td></td>
<td></td>
<td>C (wt%)</td>
<td>N (wt%)</td>
<td>C (ppm)</td>
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<td>1</td>
<td>Chlorite Zone</td>
<td>72.5</td>
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<td>Albite–biotite Zone</td>
<td>83.2</td>
<td>n.d.</td>
<td>1,100</td>
</tr>
<tr>
<td>20</td>
<td></td>
<td>92.4</td>
<td>n.d.</td>
<td>2,800</td>
</tr>
<tr>
<td>21</td>
<td>Oligoclase–biotite Zone</td>
<td>75.6</td>
<td>n.d.</td>
<td>5,000</td>
</tr>
<tr>
<td>22</td>
<td></td>
<td>82.7</td>
<td>n.d.</td>
<td>2,600</td>
</tr>
<tr>
<td>24</td>
<td></td>
<td>88.0</td>
<td>n.d.</td>
<td>2,500</td>
</tr>
<tr>
<td>28</td>
<td></td>
<td>87.9</td>
<td>n.d.</td>
<td>5,400</td>
</tr>
</tbody>
</table>

Note: "n.d." means not detected because of under detection limit.

Fig. 6. Relationship diagrams of (a) N-K$_2$O and (b) Cs-Rb. Sample symbols are the same as those in Fig. 5. Non-biogenic marine sediments from world-wide ocean (Ben Ohman et al., 1989) and GLOSS (global subducted sediment) by Plank and Langmuir (1998) are also plotted by small open squares and gray large circle, respectively.
Sanbagawa samples. Interestingly, the As dissolution was enhanced along with completion of graphitization during prograde metamorphism in both of the samples (Bebout et al., 1999). Also, previous studies pointed out that ordered graphite in metamorphic rocks is attained at 400–500°C with little pressure dependence (Landis, 1971; Wang, 1989). From the above overview, we suggest that As dissolution from meta-sedimentary rocks may possibly be associated with graphitization of kerogens, although the mechanism is not clear in detail.

Mechanism of the NH₄⁺ dissolution As mentioned above, NH₄⁺ dissolution from the Sanbagawa samples is likely to have occurred successively during prograde metamorphism from the chlorite to oligoclase–biotite zones. At these metamorphic stages, meta-sedimentary rocks could release fluids successively. It is, therefore, probable to consider that fluids responsible for NH₄⁺ dissolution was supplied from meta-sedimentary rocks themselves.

In the present Sanbagawa samples the major potassium-bearing mineral is phengitic muscovite, and both of NH₄⁺ and Rb⁺ are likely to exist in XII sites. There is a subtle difference of ionic radii between Rb⁺ (1.72 Å from Shannon, 1976) and NH₄⁺ (1.67 to 1.72 Å from Knop et al., 1979), suggesting that Rb and NH₄⁺ should dissolve from muscovite into fluids in nearly the same proportions. However, the Sanbagawa samples experienced only NH₄⁺ dissolution but not Rb dissolution. This indicates that the NH₄⁺ dissolution was caused by fluids with a high potential to dissolve NH₄⁺ preferentially; for example, fluids containing high concentration of metal elements that form a stable complex with NH₄⁺.

Another possible explanation of the preferential NH₄⁺ dissolution in the Sanbagawa samples is oxidation of NH₄⁺ to soluble NO₂⁻ or NO₃⁻. According to Mottl et al. (2004), sulfate contents of brines from top of Mariana forearc seamounts increase with increasing distance from the trench axis, reaching a concentration nearly twice that in seawater at Conical Seamount at 90 km distance from the trench axis. This observation suggests that the dehydrated fluid from shallow subduction zone, comparable depth range to the Sanbagawa samples, may have an oxidative character. If so, such the fluid can oxidize NH₄⁺ to soluble oxide forms.

Mechanism of the Cs dissolution As mentioned before, the Cs dissolution from the Sanbagawa samples into fluids was probably enhanced during prograde metamorphism from the garnet to albite–biotite zones (P ~ 0.8 GPa, T ~ 500°C).

At the metamorphic condition from the garnet to albite–biotite zones, maximum H₂O content of meta-mafic rocks decreases from 3.4 w% to 2.3 wt% and excess H₂O in meta-mafic rocks was released. External fluids from meta-mafic rocks to the meta-sedimentary rocks are the another candidate for the source of fluids dissolving Cs. As shown in Figs. 5d and 6b, various degree of the Cs dissolution is observed in the same metamorphic grade. External flow of fluids rising from subducting slab to mantle wedge is recognized as “channelized flow” (Miller et al., 2003; Zack and John, 2007; John et al., 2004, 2008). Some models suggest that the channelized flow, gathering fluid-filled micro-cracks, has enough high pressure for opening fractures allowing the flow to rise up inside slab with low permeability due to high-pressure (Davies, 1999; Miller et al., 2003). The characteristics of the channelized flow can explain various degrees of the Cs dissolution (Figs. 5d and 6b). Zack and John (2007) pointed out that the channelized flow is heterogeneous and yields closed system behavior in some parts of slabs. This probably resulted in heterogeneous degrees of the Cs dissolution.

Moreover, possible factors that may control element mobility in subduction zones have been identified. There are thermal history of the slab (Bebout et al., 1999), and open or closed behaviors of the fluids in the slab (John et al., 2004, 2008). Studies of meta-sedimentary rocks formed in various subduction zones are necessary to investigate the details of the element dissolution processes. However, we could not discuss these factors in detail because of lack of enough data.

Comparison with other meta-sedimentary rocks

We will examine whether the suggested dissolution mechanisms in this study can be applicable to other meta-sedimentary rocks. We refer to other studies comparable to the present in which meta-sedimentary rocks are analyzed to elucidate the element mobility: the Catalina schists in California (e.g., Bebout and Fogel, 1992; Bebout et al., 1999) and Schists Lustrès nappe in western Alps, Europe (Busigny et al., 2003). The former show a variety of temperature condition, while the latter show relatively low temperature condition in their P-T path during subduction. Therefore it is possible to make sure whether the difference of depths where both meta-mafic rocks and meta-sedimentary rocks release fluids, i.e., thermal characteristics of the slab can control the dissolution of Cs and NH₄⁺ from meta-sedimentary rocks into fluids.

The Catalina meta-sedimentary rocks Bebout et al. (1999, 2007) suggested that Cs dissolution from the Catalina meta-sedimentary rocks was enhanced during the higher-T prograde metamorphism (up to epidote–blueschist/amphibolite or amphibolite facies), while the dissolution was not enhanced during the lower-T one (lawsonite–albite – lawsonite–blueschist facies). Comparing Cs/Rb ratios among the samples. According to Peacock (1993), maximum H₂O contents of meta-mafic rocks decrease during the higher-T prograde metamorphism (greenschist – epidote–blueschist/amphibolite or amphibolite facies), while it doesn’t decrease during...
lower-\( T \) one (lawsonite–albite – lawsonite–blueschist facies). Therefore, the Cs dissolution from the higher-\( T \) Catalina samples is considered to have been caused by dehydration of the underlying meta-mafic rocks along higher-\( T \) \( P-T \) path. This view is consistent with Bebout et al. (2007) and Zack et al. (2001), who suggested external fluid flow is required for the Cs dissolution from the Catalina samples. Significantly, the degree of the Cs dissolution is different between the Catalina and Sanbagawa samples; ~75% Cs was dissolved from the former (Bebout et al., 1999), while ~40% Cs from the latter. One of the reason for such a difference is thought to be variation in propagation of the channelized flow such as a difference in initial \( H_2O \) content of mafic rocks.

The \( NH_4^+ \) dissolution from the Catalina meta-sedimentary rocks was associated with successive dehydration of the meta-sedimentary rocks with increasing metamorphic grade (Bebout and Fogel, 1992). On the other hand, Rb dissolution from the Catalina samples is not confirmed (Bebout et al., 1999). These results are similar to the Sanbagawa samples. Therefore it is possible that the \( NH_4^+ \) dissolution from the Catalina samples was caused by fluid release from the meta-sedimentary rocks alone. Furthermore, Bebout (1997) indicated that \( N \) isotopic compositions in the Catalina samples are controlled by local scale of fluids-rock interactions. This result may mean that \( NH_4^+ \) was dissolved into local fluids derived from the Catalina meta-sedimentary rocks themselves. 

\textit{Schist Lustrès nappe} Busigny et al. (2003) analyzed meta-sedimentary rocks of the Schist Lustrès nappe, which experienced low-\( T \) \( P-T \) path reaching up to UHP (ultra-high-pressure) facies (peak \( P \): 2.9 GPa, peak \( T \): 630°C) in cool subduction zone. They demonstrated that insignificant amount of Cs was dissolved from the samples during prograde metamorphism up to UHP facies because Cs/Rb ratios of all samples are comparable to unmetamorphosed sedimentary protoliths. Significantly, Busigny et al. (2003) also pointed out that the samples behaved as a closed system on the basis of the isotopic ratios of C and O in calcite. This implies undeveloped fluids in the Schist Lustrès nappe samples in contrast to the Sanbagawa and Catalina (additional external fluid perhaps from meta-mafic unit). Such a closed element behavior was possibly caused by (i) insufficient element dissolution from meta-mafic rocks due to low-\( T \) path and/or (ii) impermeable fluid behavior in the Schist Lustrès nappe unit under high pressure, and (iii) less external fluid supplied to the meta-sediment body.

\textbf{CONCLUSIONS}

We discussed element dissolution from the Sanbagawa schists into fluids during prograde metamorphism from the chlorite to oligoclase–biotite zones by means of their chemical compositions.

(i) Insignificant dissolution of major elements (Si, Ti, Al and K) and Rb occurred.

(ii) Dramatic As dissolution occurred during the upper–garnet zone metamorphism (\( P \): about 0.8 GPa, \( T \): about 450°C). It accompanied formation of ordered graphite.

(iii) \( NH_4^+ \) dissolution was enhanced successively during prograde metamorphism from the chlorite to oligoclase–biotite zones. This dissolution was caused by dehydration of the pelitic schists, which produced fluids with a high potential to dissolve or oxide \( NH_4^+ \).

(iv) Cs dissolution was enhanced during prograde metamorphism from the garnet to albite–biotite zones. The degree of Cs dissolution, however, is heterogeneous in the same metamorphic grade. This dissolution may be attributed to effective fluid transfer by the channelized flow from the underlying meta-mafic rocks, although other factors such as chemical composition of fluids must also be discussed.

In this study, we elucidated the element dissolution processes from subducting sediments into fluids at shallow depths (up to oligoclase–biotite zone) and the factors controlling the element mobility. This study also indicates that chemical changes in meta-sedimentary rocks with increasing metamorphic grade are an effective way for examination of element dissolution processes in subduction zones.

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\textbf{REFERENCES}


