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Reply to comments on “Redistribution of trace elements during prograde metamorphism from lawsonite blueschist to eclogite facies: implications for deep subduction zone processes”

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We welcome the opportunity to reply to comments by Axel Liebscher regarding our manuscript (Spandler et al. 2003, Contrib Mineral Petrol 146:205–222). Before discussing the comments, we first wish to state that the phase identified as zoisite in the manuscript should have been labelled as epidote, due to the high ferric iron content. We wish to thank Axel Liebscher and Gerhard Franz for bringing this error to our attention. However, it should be noted that this error does not affect any of the conclusions of the paper, pertaining only to the correct application of epidote-group-mineral nomenclature.

The main focus of our paper is the distribution of trace elements among minerals during prograde subduction-zone metamorphism. We show that the breakdown of trace element-rich phases such as lawsonite and titanite does not lead to a significant change in the trace element content of rocks because the trace elements are redistributed into newly formed major and accessory phases. However, at the lawsonite blueschist to eclogite facies transition, there is significant dehydration and hence we postulated that there is a decoupling of fluid and trace element release from subducted rocks. In our argumentation, the bulk-rock geochemical data is only used to show that blueschist and eclogite facies samples are comparable in chemical composition. Liebscher claims our data does not support our conclusions for a decoupling of fluid and trace element release. He uses calculated fluid compositions based on differences in bulk-rock geochemistry to show that significant con-

centrations of trace elements may be liberated in fluids produced during the blueschist to eclogite facies transition. Below, we show that this procedure for calculating fluid compositions is fundamentally flawed and the fluid compositions calculated by Liebscher are meaningless. Furthermore, we will provide further evidence in support of our conclusion of the decoupling of fluid and trace element release in subducted slabs, including more appropriate estimated fluid compositions calculated on the basis of experimentally-derived fluid–mineral partitioning data.

The trace element composition of the fluids calculated by Liebscher most closely compare to highly-fractionated felsic alkaline melts rather than that expected of hydrous fluids produced during metamorphism under low temperature (T) conditions (note, the blueschist to eclogite transition is expected to occur at between 450 and 600°C and 1.5–2.0 GPa). For example, the pelite-derived fluid contains 4.1 wt% Ba, but no K whatsoever. Both the pelitic and mafic fluids contain between 10 and 20 wt% Ti and around 1.5 wt% P; elements that are considered to be highly insoluble in low- T hydrous fluids (e.g., Ayers and Watson 1991, 1993; Brenan et al. 1994). The Zr contents of the calculated fluids are also well above zircon saturation limits for a liquid of any temperature below 900°C (Watson and Harrison 1983). Clearly, the fluid compositions calculated by Liebscher do not resemble any feasible fluid that would be released by mineral dehydration reactions during blueschist to eclogite transition at low T .

It is clear that for the pelitic and subalkaline mafic samples the concentration of many trace elements is lower in the eclogite-facies rocks compared to their lower grade equivalents, as outlined by Liebscher. However, Liebscher has ignored the data we have presented for the alkaline mafic rocks, which taking Liebscher's approach, would have gained between 30 and 80% of almost all trace elements during metamorphism. This is clearly inconsistent with Liebscher's conclusions based on the pelitic and subalkaline mafic samples and

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shows that there are fundamental problems associated with calculating elemental gains and fluid compositions by directly comparing the composition of two rocks at different metamorphic grades.

Inherent in the calculations made by Liebscher is the assumption that the two rock pairs initially have exactly the same composition before transformation to eclogite-facies. In another publication (Spandler et al. 2004a), we have demonstrated that pre-subduction processes, such as magmatic differentiation, magmatic source variability, and seafloor alteration, have a much greater affect on bulk-rock geochemical variability than subduction zone metamorphism up to eclogite facies. In fact, there is strong geochemical and petrographic evidence that the high-*P* mafic rocks of New Caledonia underwent an episode of seafloor hydrothermal alteration prior to subduction (Spandler et al. 2004b). Therefore, it is unreasonable to assume that two rocks were identical in composition prior to subduction and that all geochemical differences that are now preserved in these rocks are due to eclogite-facies metamorphism. Without this assumption, Liebscher's claims of extensive elemental loss during metamorphism in the pelitic and mafic rocks are invalid.

Liebscher also claims that the similarity between the rock pairs is a function of our sample selection criteria. As stated above, the main objective of the paper was to examine trace element distribution among minerals of rocks of subducting oceanic crust at different metamorphic grades. Therefore, it was imperative that rocks of generally comparable composition were used for this study. For more comprehensive study of bulk-rock geochemistry of high-grade mafic rocks from New Caledonia, we refer the reader to Spandler et al. (2004a). In this paper, we also show that mafic rocks do not lose significant amounts of trace elements during metamorphism up to eclogite facies. Several other recent publications also support this conclusion (Chalot-Prat et al. 2003; Straub and Layne 2003; Volkova et al. 2004). In Fig. 1, we present trace element data for a range of pelitic rocks of varying metamorphic grade. All of the samples are from northern New Caledonia and are understood to originally comprise part of the same sedimentary sequence. The pelitic samples have not been significantly affected by retrogression and were analysed by the same methods outlined in Spandler et al. (2003). As can be seen in Fig. 1, there is some variation in the trace element composition of the pelitic rocks, but there is no systematic loss (or gain) of trace elements (including the fluid-mobile elements) associated with prograde metamorphism. We suggest that the trace element variations are not due to metamorphism, but are largely inherent variations in the composition of the original sedimentary rocks.

Liebscher states that the trace element composition of the fluid is controlled by mineral-fluid partitioning. On this point we agree completely. In our paper, we did not attempt to calculate fluid compositions as there is very little fluid-mineral partitioning data for the conditions relevant to the blueschist to eclogite-facies transition.

Nonetheless, here we have calculated estimates of the maximum concentration of several key trace elements in the fluid using data from experimental studies of mineral solubilities and fluid-mineral partitioning. These experimental studies were conducted at slightly higher temperatures (600–700°C) than what is relevant for the blueschist to eclogite-facies transition. For elements that are hosted by phengite (Cs, Rb, Ba) and garnet (Y, Lu, Yb), we used mineral-fluid partition coefficients of Green and Adam (2003) (Note, we use the same garnet-fluid partition coefficient of Lu for Yb). Ti and P concentrations were calculated using the rutile and apatite solubility data of Ayers and Watson (1991, 1993). Fluid Nb and Zr contents were calculated using rutile-fluid partitioning data from Brenan et al. (1994). The Zr data is also consistent with other published Zr fluid-mineral partition coefficients (e.g. Rubatto and Hermann 2003).

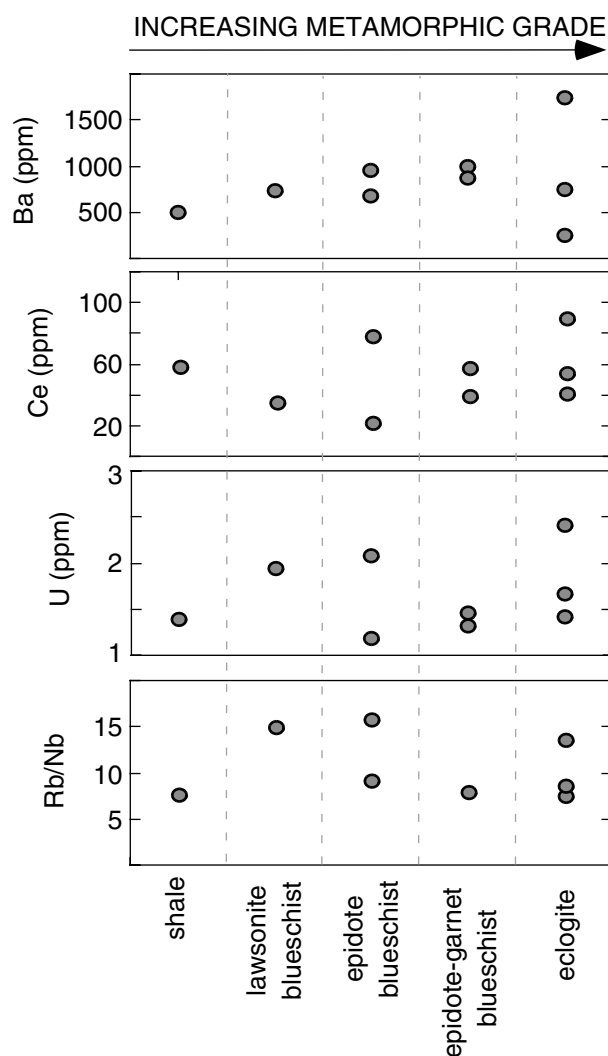


Fig. 1 Selected trace element concentrations and Rb/Nb ratio of pelitic rocks of varying metamorphic grade from northern New Caledonia. Note, there are no systematic geochemical trends associated with prograde metamorphism from shale up to eclogite facies

There are no published experimental data for LREE partitioning between epidote and fluid. Instead, we use extrapolated allanite-melt partitioning data from Hermann (2002) to calculate fluid Ce contents for the allanite-bearing samples. As melt-fluid partitioning tends to be $\gg 1$ (Green 1994) and most of the partitioning and solubility data used is appropriate for higher T conditions ($> 600^\circ\text{C}$), we regard the calculated trace element concentrations as maximum values.

The calculated trace element contents for fluid in equilibrium with samples 803, 1101, and 1008 are between one and five orders of magnitude lower than the fluid compositions calculated by Liebscher (Fig. 2). All calculated fluids have less than 3 ppm Ti, less than 0.2 ppm of Nb and Zr, and less than 0.1 ppm of Yb and Lu. The fluid in equilibrium with the mafic sample 803 has around 0.7 ppm P and 0.2 ppm Y. The pelitic-sourced fluid has 1 ppm Cs, 1.5 ppm Rb, 5 ppm Ba, 0.43 ppm Ce, 0.5 ppm P, and 1.6 ppm Y. The fluid in equilibrium with sample 1101 has 0.5 ppm Cs, 3 ppm Rb, 20 ppm Ba, 0.43 ppm Ce, 3.6 ppm P, and 0.3 ppm Y.

Based on the LOI and calculated water contents in Table 1 of our paper, we assume that 1 and 3 wt% H_2O is lost from the pelitic and mafic rocks respectively during eclogite-facies metamorphism. Using our calculated fluid compositions, we have calculated the percentage loss of elements from the host rock during metamorphism (Fig. 3). For almost all of the elements and rocks the element loss is less than 0.1%. Even Cs, which is regarded to be highly compatible in the fluid phase, is only depleted by 0.67% from the pelitic rock and 1.7% from the alkaline mafic rock. All of the losses are within the analytical detection limits for bulk-rock trace element analysis and therefore are impossible to quantify using geochemical differences between low and high-grade metamorphic rocks. These calculations, to-

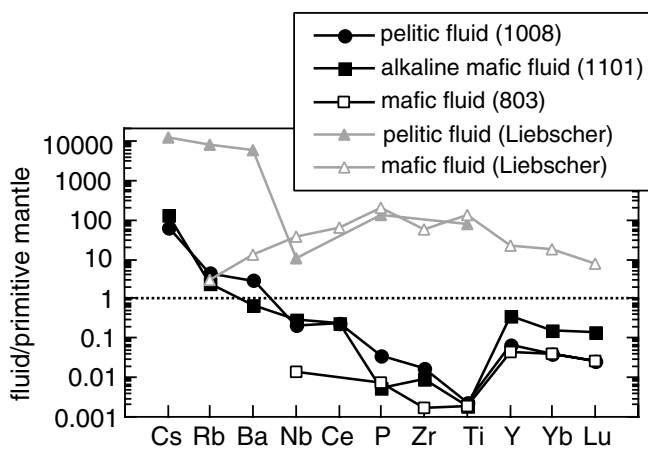


Fig. 2 Primitive mantle normalised compositions of fluids calculated using mineral–fluid partitioning data (see text), and fluids calculated by Liebscher. Apart from Cs, the trace element content of fluids produced at the blueschist to eclogite facies transition is too low to cause significant mantle metasomatism. Normalising values are taken from Sun and McDonough (1989)

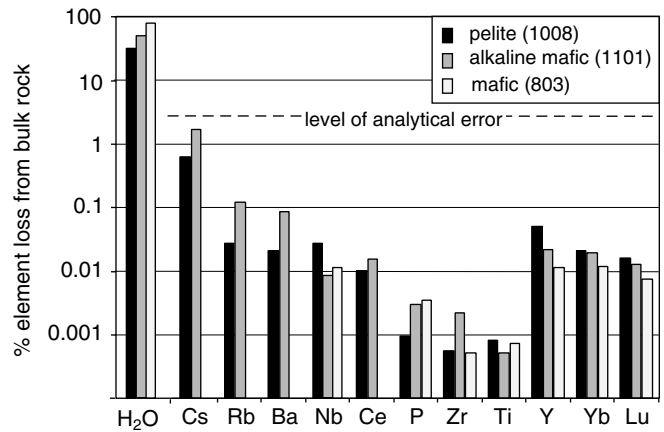


Fig. 3 Percentage loss of elements (in log scale) from alkaline mafic sample 1101, pelitic sample 1008, and mafic sample 803 after extraction of the calculated fluid compositions. Note, large amounts of H_2O are lost from the rocks, but all other element losses are within the range of analytical errors and hence could not be resolved by bulk rock chemical analysis

gether with the additional data presented above and in Spandler et al. (2004a), reaffirm our major conclusion that subducted rocks do not undergo significant geochemical modification during metamorphism up to eclogite facies. We reiterate that trace elements are almost completely redistributed into newly formed major and accessory minerals, indicating that there is a decoupling of fluid and trace element release in subducted slabs.

Primitive arc magmas generally contain between 2 and 6 wt% H_2O , and may contain very high concentration of slab-derived elements such as LILE, U, Th and LREE. Therefore, a one-stage process of fluxing the mantle source regions with the low trace-element composition fluids calculated here cannot produce arc magmas. We suggest that the high trace-element flux needed to produce arc magmas requires complex slab processes such as fluid fluxing through relatively high- T sections of the slab (e.g. slab-mantle wedge interface), to cause hydrous melting of pelitic and mafic rocks or high element solubilities in the fluids.

References

- Ayers JC, Watson EB (1991) Solubility of apatite, monazite, zircon, and rutile in supercritical aqueous fluids with implications for subduction zone geochemistry. *Phil Trans R Soc Lond* 335:365–375
- Ayers JC, Watson EB (1993) Rutile solubility and mobility in supercritical aqueous fluids. *Contrib Mineral Petrol* 114:321–330
- Brenan JM, Shaw HF, Phinney DL, Ryerson FJ (1994) Rutile-aqueous fluid partitioning of Nb, Ta, Hf, Zr, U, and Th: implications for high field strength element depletions in island-arc basalts. *Earth Planet Sci Lett* 128:327–339
- Chalot-Prat F, Ganne J, Lombard A (2003) No significant element transfer from the oceanic plate to the mantle wedge during subduction and exhumation of the Tethys lithosphere (Western Alps). *Lithos* 69:69–103

- Green TH (1994) Experimental studies of trace element partitioning applicable to igneous petrogenesis-Sedona 16 years later. *Chem Geol* 117:1–36
- Green TH, Adam J (2003) Experimentally-determined trace element characteristics of aqueous fluid from partially dehydrated mafic oceanic crust at 3.0 GPa, 650–700°C. *Eur J Mineral* 15:815–830
- Hermann J (2002) Allanite: thorium and light rare earth element carrier in subducted crust. *Chem Geol* 192:289–306
- Rubatto D, Hermann J (2003) Zircon formation during fluid circulation in eclogites (Monviso, Western Alps): implications for Zr and Hf budgets in subduction zones. *Geochim Cosmochim Acta* 67:2173–2187
- Spandler CJ, Hermann J, Arculus RJ, Mavrogenes JA (2003) Redistribution of trace elements during prograde metamorphism from lawsonite blueschist to eclogite facies; implications for deep subduction-zone processes. *Contrib Mineral Petrol* 146:205–222
- Spandler CJ, Hermann J, Arculus RJ, Mavrogenes JA (2004a) Geochemical heterogeneity and element mobility in deeply subducted oceanic crust; insights from high-pressure mafic rocks from New Caledonia. *Chem Geol* 206:21–42
- Spandler CJ, Hermann J, Rubatto D (2004b) Exsolution of thortveitite, yttrialite and xenotime during low temperature recrystallization of zircon from New Caledonia, and their significance for trace element incorporation in zircon. *Am Mineral* (in press)
- Straub SM, Layne GD (2003) Decoupling of fluids and fluid-mobile elements during shallow subduction: evidence from halogen-rich andesite melt inclusions from the Izu arc volcanic front. *Geochem Geophys Geosyst* 4: Art No. 9003
- Sun SS, McDonough WF (1989) Chemical and isotopic systematics of oceanic basalts; implications for mantle composition and processes. In: Saunders AD, Norry MJ (eds) *Magmatism in the ocean basins*. *Geol Soc Lond Spec Publ* 42:313–345
- Volkova NI, Frenkel AE, Budanov VI, Lepezin GG (2004) Geochemical signatures for eclogite protolith from the Maksyutov Complex, South Urals. *J Asian Earth Sci* (in press)
- Watson EB, Harrison TM (1983) Zircon saturation revisited, temperature and composition effects in a variety of crustal magma types. *Earth Planet Sci Lett* 64:295–304