

Determining subduction-zone fluid composition using a tourmaline mineral probe

V.J. van Hinsberg^{1*}, G. Franz², B.J. Wood³



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Abstract

Subduction zones are the sites where crustal materials are recycled into the mantle. In response to increasing pressures and temperatures during this process, hydrated minerals break down and release solute-bearing fluids and, above ~750 °C, form hydrous melts. Magmas generated by interaction of these melts and fluids with the mantle have a characteristic arc elemental signature. Here, a zoned refractory tourmaline grain, formed during Alpine subduction and uplift, was used to reconstruct the compositions of the fluids involved in element transfer. The reconstructed compositions confirm that slab-released fluids carry the arc-signature, and suggest that mineral–fluid element partitioning controls their compositions. However, these fluids are calculated to be dilute. To reconcile this with higher element-to-water ratios required for arc magmas, a two-stage arc-magma genesis model is favoured where fluids imprint their compositional signature progressively on a slab mélange that is subsequently transferred to, and interacts with the mantle to generate arc magmas.

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Introduction

The principal material fluxes from the surface into the deep Earth take place at subduction zones. Models of terrestrial element cycling hinge on accurate estimates of these fluxes and of the recycling of material by fluids and melts from the dehydrating slab in the “subduction factory” (Tatsumi, 2005). Estimates of element release from the slab, and hence constraints on the net flux through subduction zones, are derived from three main sources; (i) the compositional signatures of arc magmas (*e.g.*, Elliott *et al.*, 1997), which are Nb-Ta depleted and enriched in Li, B, Sr, Ba and Pb compared to mid-ocean ridge basalts (MORB);

(ii) experimentally-determined element partitioning between subduction-zone solids and liquids (*e.g.*, Keppler, 1996; Kessel *et al.*, 2005; Hermann *et al.*, 2006; Spandler *et al.*, 2007; Tsay *et al.* 2017); and (iii) element mass-balance on subducted rock lithologies (*e.g.*, Bebout *et al.*, 1999; Spandler *et al.*, 2003, 2004). Methods (i) and (iii) provide information on mass transfer from subducting lithologies into the region of melt generation, but no detail on element concentrations in fluids and melt, or total fluxes. Moreover, (iii) depends on the presence of accessory phases (see Klimm *et al.*, 2008; Hermann and Rubatto, 2009), as these phases can be the dominant repository of certain trace elements in the bulk rock. This fact makes the method critically dependent on preservation of these phases, as well as their representative sampling in bulk-rock studies. Method (ii) provides concentration information, and flux estimates when combined with models of release of volatiles (*e.g.*, Spandler *et al.*, 2003; Connolly, 2005), but only under model-dependent conditions of temperature, pressure, mineralogy and bulk composition. What is needed is a more direct record of subduction-zone fluid composition.

Here, well-preserved subduction-zone minerals (tourmaline, titanite and phengite) are used to quantitatively reconstruct the compositions of the fluids from which they grew by combining mineral compositions with mineral–fluid element partition coefficients (*cf.* Keppler, 1996). If D-values are known for the physico-chemical conditions of growth, absolute element concentrations in the fluid result. This approach avoids any assumption of the presence of accessory phases, but rather allows for their presence to be tested. Furthermore, minerals can simultaneously yield *P–T* conditions and age of growth that can be combined directly with reconstructed fluid compositions into a comprehensive and internally consistent database of the *P–T–X–t* evolution of a subduction zone.

Tourmaline as a Mineral Probe

A tourmaline grain from the Tauern Window Eclogite Zone (Austrian Alps) is the principal probe of fluid compositions in this study. The mineral tourmaline has exceptional *P–T* stability that covers subduction-zone conditions (Fig. S-1); its crystal-chemistry allows it to incorporate a diversity of (trace) elements; and it displays negligible volume-diffusional re-equilibration (*e.g.*, Henry and Dutrow, 1996; van Hinsberg *et al.*, 2011a,b). These features allow tourmaline to record its host environment composition throughout subduction and to preserve it for later interrogation. Tourmaline’s presence is dictated by the availability of boron, rather than by *P–T* conditions. At low grades, B dominantly resides in sheet silicates (Leeman and Sisson, 1996) and is released during prograde metamorphism in discontinuous reactions resulting in punctuated nucleation and growth, and in continuous reactions producing gradual growth. Owing to negligible diffusive re-equilibration, this growth is expressed as growth zones.

1. Department of Earth and Planetary Sciences, McGill University, Montreal, Quebec, Canada

* Corresponding author (email: V.J.vanHinsberg@gmx.net)

2. Department of Applied Geosciences, Technical University Berlin, Berlin, Germany

3. Department of Earth Sciences, University of Oxford, United Kingdom



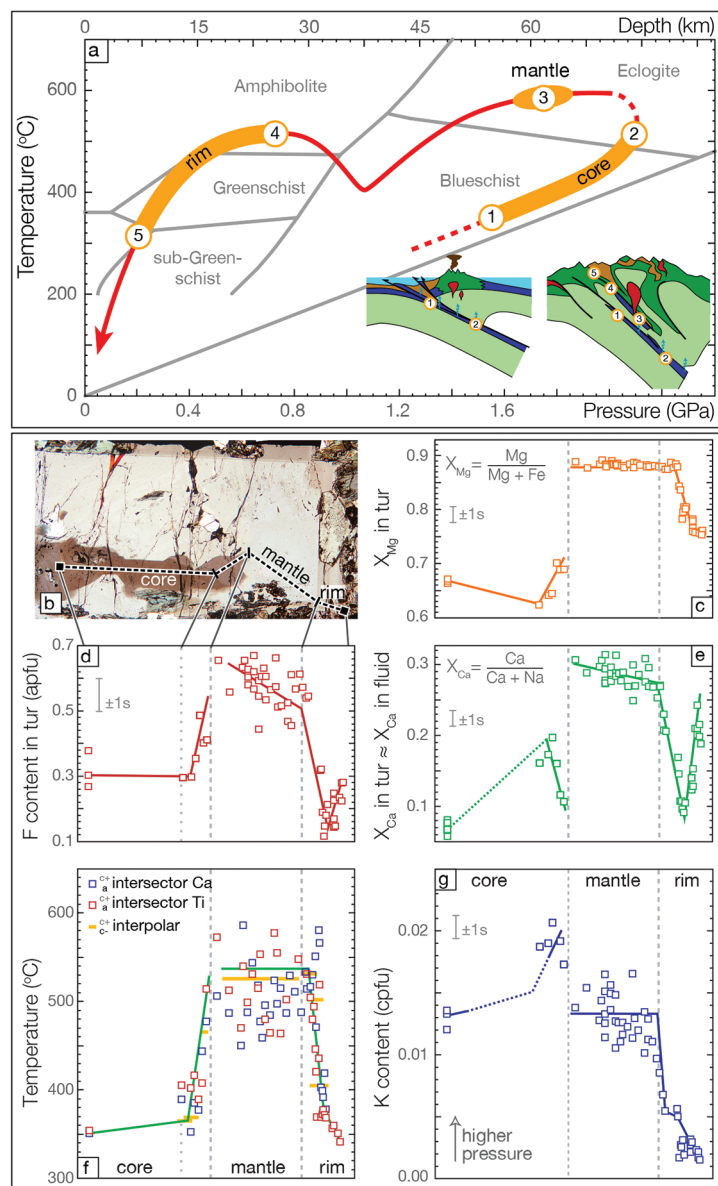


Figure 1 Reading the Tauern tourmaline record. (a) Tauern Eclogite Zone P - T path (Zimmermann *et al.*, 1994) with conditions recorded by tourmaline growth zones shown. Inset cartoons locate these in a schematic subduction-zone cross-section. (b) PPL image of the tourmaline

transect. (c) X_{Mg} sharply defines the tourmaline growth zones. (d) F-content in tourmaline, >0.5 apfu F in the outer core and mantle. (e) X_{Ca} of tourmaline, which tracks the X_{Ca} in the coexisting fluid (von Goerne *et al.*, 2011). (f) Temperature transect across the tourmaline grain calculated from inter-sector and inter-polar thermometry. (g) Tourmaline K-content, which acts as a qualitative barometer. Uncertainties shown are the typical 1 σ analytical precision.

The Tauern tourmaline grain occurs in a meta-sedimentary retrogressed eclogite that preserves relics of a garnet–omphacite–phengite–titanite eclogite paragenesis, overprinted by an amphibolite-facies amphibole–plagioclase–epidote–carbonate paragenesis (Fig. S-2a). Peak conditions for this unit have been estimated at 630 °C and 2.5 GPa (*e.g.*, Selverstone *et al.*, 1992; Hoschek, 2007). There is no evidence for partial melting and tourmaline is interpreted to have formed from aqueous fluid throughout its growth history. Tourmaline is a minor accessory phase in these rocks, and is therefore unable to exert control on element concentrations in the fluid. Rather, it acts as a passive recorder of its environment.

Detailed petrographic examination reveals a zoned brown core, a blue-green mantle, and a strongly zoned outer rim (see the Supplementary Information for more details). Hourglass sector-zoning is present (Fig. S-2b), indicating that growth compositions have been preserved (van Hinsberg *et al.*, 2006). Inter-sector thermometry (van Hinsberg and Schumacher, 2007), combined with qualitative K-barometry and inclusion mineralogy suggests growth of the tourmaline core during prograde subduction and its associated progressive internal B-release, formation of the mantle zone following detachment from the subducting slab from external fluids that were released in deeper slab devolatilisation, and rim growth during retrogression that records the orogenic uplift of the Eclogite Zone (Fig. 1a). This single tourmaline grain thus chronicles the subduction to uplift history, and can provide information on the associated fluids at multiple stages along this path.

Tourmaline Composition and Fluid Reconstruction

Compositions of individual tourmaline growth zones and mineral inclusions were determined by EMP (major elements) and LA-ICP-MS (trace elements). Tourmaline compositions are dominated by the dravite end-member with lesser schorl, uvite and foitite, have variable X_{Ca} and X_{Mg} , and high F contents in core and mantle (Fig. 1, Table S-1). Tourmaline and mineral inclusion compositions constrain growth to be from an acidic aqueous solution with Na concentrations from 0.45 to 0.75 mol L⁻¹, variable X_{Ca} and an F-content between 2 and 1400 ppmm (Supplementary Information). Trace element concentrations in tourmaline are low, from tens of ppmm for the LILE to ppbm for the HFSE (Table S-3).

Tourmaline–fluid trace element partition coefficients, required to convert tourmaline compositions to those of their formation fluids, have not been determined experimentally and were therefore estimated (see Supplementary



Information for details and discussion). As a result, absolute concentrations in the fluid calculated from tourmaline are interpreted to have an associated uncertainty of an order of magnitude. However, element ratios, patterns and the overall elemental signature are robust. A further confirmation of reconstructed fluid compositions is the good agreement between the fluid composition reconstructed from the tourmaline mantle, and the same fluid reconstructed from phengite and titanite inclusions within this growth zone (Tables S-2, S-3).

Controls on Fluid Composition

The high-*P* Tauern subduction-zone fluids, reconstructed from tourmaline, phengite and titanite, are dilute aqueous solutions with $<0.75 \text{ mol L}^{-1} \text{ Na}$ and total trace element concentrations $<500 \text{ ppm}$ (Fig. 2a). Titanium concentrations suggest saturation in rutile when experimental solubilities (Manning *et al.*, 2008; Rapp *et al.*, 2010; Tsay *et al.*, 2017) are extrapolated to Tauern conditions, consistent with the presence of rutile inclusions in tourmaline's core and mantle. In contrast, fluid REE concentrations are at a median level of only tens of ppbm (Fig. 2a), which is at least 2 orders of magnitude below that required for saturation in the common REE-minerals (Tropper *et al.*, 2011). This level is consistent with REE concentrations in eclogite-fluid experiments with allanitic zoisite (Tsay *et al.*, 2017), where mineral–fluid partitioning, rather than mineral solubility would control REE concentrations.

Fluid compositions reconstructed from well-preserved high-*P* minerals from the Dora Maira, Syros and New Caledonia palaeo-subduction zones using a similar methodology overlap with those reconstructed for the Tauern Eclogite Zone (Fig. 2a). Absolute concentrations vary by 2–3 orders of magnitude, but elemental patterns are consistent, and similarly suggest rutile-saturated, but REE-phase-undersaturated conditions. Hence, Ti concentrations will be controlled by solubility and are therefore independent of bulk-rock composition and mineral paragenesis until the saturating phase is exhausted (see Klimm *et al.*, 2008). However, for elements controlled by partitioning, such as the REE, differences in slab bulk-rock composition will impart differences in absolute element content of slab-derived fluids. Elemental patterns will persist, assuming no changes in major mineral paragenesis, as is indeed observed (Fig. 2a). Hence, arc magmas will share a characteristic element signature, but absolute concentrations can vary, even on a local scale, depending on the composition and mineralogy of the material that enters the trench.

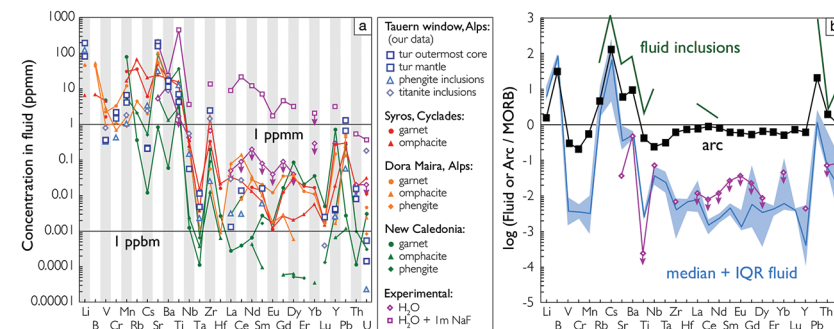


Figure 2 (a) Element concentrations in fluids reconstructed from the Tauern tourmaline outer core and mantle and its mineral inclusions (blue symbols), and eclogite minerals from other subduction-zone terrains show a consistent pattern. **(b)** MORB-normalised concentrations for average arc magma parallel those of subduction-zone fluids supporting a genetic link. See the Supplementary Information for data sources and calculation method. Uncertainties are given as the Interquartile Range (IQR) and maximum estimates marked with an arrow.

Arc Volcanic Compositional Signature

To evaluate the resulting fluid compositions, these are compared in a typical arc-magma plot of Ba/Th vs. La/Sm (Fig. 3). La/Sm is controlled by residual garnet in the slab and high values signify a meta-sedimentary input (*e.g.*, Elliott *et al.*, 1997), whereas Ba/Th indicates fluid involvement, given the contrasting fluid mobility of Ba and Th (*e.g.*, Keppler, 1996; Elliott *et al.*, 1997). Tourmaline-reconstructed fluids show the high Ba/Th at low La/Sm signature expected for subduction-zone fluids. This is moreover most distinct for the outermost core and mantle zones, which are interpreted to record the fluid released in slab devolatilisation and that which flushes the subduction channel, respectively. The latter is modified en-route to enrich fluid-compatible Ba over incompatible Th, consistent with models for subduction-zone fluids (Manning, 2004). Fluids reconstructed from phengite and titanite inclusions in the mantle zone are within error of those derived from tourmaline. Ba/Th values are lowest for the orogenic uplift part of the history, and suggest that a high Ba/Th ratio is characteristic for slab-derived fluids.

Normalised to MORB, the element patterns of the reconstructed fluids, as well as those of fluid inclusions in subduction-zone rocks (*e.g.*, Scambelluri *et al.*, 2001) parallel that of average primitive arc magma; elevated in large-ion lithophile elements while depleted in V, Cr, and Ti (Fig. 2b). This shows that addition of these slab-derived fluids could confer the arc-characteristic element signature, as was concluded for Ba/Th .



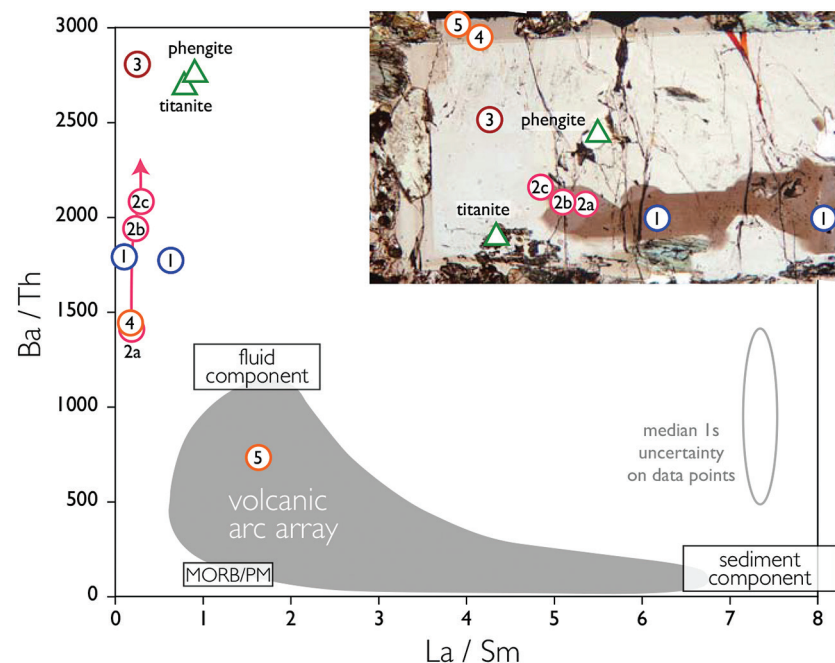


Figure 3 Fluid compositions reconstructed from tourmaline (circles) and its mineral inclusions (triangles), show a consistent, high Ba/Th at low La/Sm signature. Addition of this fluid to the arc-magmatism source region can explain the trend to elevated Ba/Th compared to mid-ocean ridge basalt (MORB) and primitive mantle (PM).

Material Transfer from the Slab to Mantle

A fluid to primitive mantle ratio of 10:3 is required to produce the observed range of Ba/Th in arc magmas. Such high fluid-to-rock ratios are incompatible with the common conceptual model of arc magmatism where mantle is metasomatised by fluids, and subsequently partially molten, to initiate magmatism. Even when fully hydrated, the mantle cannot accommodate more than ~10 wt. % H_2O . Moreover, arc-magmas are incompatible with the compositional dilution that high fluid-rock ratios impart. MORB-normalised fluid compositions (Fig. 2b) are also incompatible with a model of simple fluid addition to the mantle, with reconstructed concentrations of Sr and Ba, for example, unable to lead to the observed enrichment in arc magmas. This suggests a decoupling of water and its solutes during arc magma genesis.

Rather than batch fluid transfer to the mantle, we envision channelling of fluids along the slab interface mélangé at high fluid-to-rock ratios. The arc-signature is indeed observed in palaeo-subduction mélanges (Marschall and Schumacher, 2012), and the compositional range therein is in agreement with a progressive, and locally variable imprint of this signature by fluids flushing the mélangé. Diapirism of this mélangé into the mantle can subsequently transfer the compositional signature to the source region of arc magmas (cf. Marschall and Schumacher, 2012 and references therein).

Conclusions

Reconstruction of subduction-zone fluid compositions from eclogite minerals is a powerful method that allows absolute element concentrations in these fluids to be constrained when partition coefficients for the relevant P - T - X conditions are known. Tourmaline-reconstructed subduction-zone fluid compositions show that fluid-induced selective element release from the subducting slab can imprint the compositional signature characteristic of arc magmas. The compositions of these fluids appear controlled by mineral-fluid partitioning, except for Ti, and subduction-zone fluids are therefore expected to have variable compositions, but share a common elemental signature. Conversion of these fluid compositions into a net element flux in subduction zones is still imprecise, not least because our data indicate that a simple batch model of element transfer from slab to mantle and crust is untenable. Fluids instead likely migrate along the slab interface and progressively redistribute elements as recorded in refractory minerals.

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Additional Information

Supplementary Information accompanies this letter at www.geochemicalperspectivesletters.org/article1719

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