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Stable hydrogen isotope compositions of tourmalines from the Sopron metamorphic complex: Metamorphic closure temperature and fluid composition

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RESEARCH ARTICLE



ABSTRACT

Stable hydrogen isotope compositions of metamorphic rocks and minerals can provide information on the origin of metamorphic fluids, which is especially important in systems that had experienced multiple metamorphic events. The Sopron orthogneiss-micaschist complex is a good target as it records signs of Variscan and Alpine metamorphic events as well as Variscan granitic magmatism. In this study tourmaline-bearing rocks (pegmatitic orthogneisses and kyanite-chlorite-muscovite schists) of the Sopron metamorphic complex were sampled and their tourmaline grains were analyzed for stable hydrogen isotope compositions ($\delta^2\text{H}$). The $\delta^2\text{H}$ values ($-23 \pm 1\%$, relative to V-SMOW) are in accordance with a fluid flux from devolatilization of subducted, seawater-containing rocks. Tourmaline-chlorite hydrogen isotope fractionations correspond to about 550 °C, indicating that $\delta^2\text{H}$ values formed close to peak metamorphic temperatures are preserved without retrograde isotope exchange during cooling.

KEYWORDS

tourmaline, chlorite, Sopron metamorphic complex, stable hydrogen isotope composition

INTRODUCTION

The pressure/temperature conditions of Alpine metamorphic phases that affected the metagranites, gneisses, and micaschists of the Sopron metamorphic complex (e.g., [Lelkes-Felváry et al., 1984](#); [Kisházy and Ivancsics, 1985](#)) have been determined using mineral assemblages, mineral chemistry data and stable isotope compositions (e.g., [Török, 1996](#); [Demény et al., 1997](#); [Török, 2003](#)). The peak metamorphic pressure and temperature were about 1.4–1.5 GPa and 550–600 °C, respectively ([Török, 2003](#)), which phase was associated with a flux of medium salinity fluids ([Török, 2001](#)). The metamorphic peak was followed by a flux of Mg-rich fluid ([Török, 2001](#)), causing Mg-metasomatism along shear zones that produced leucophyllites ([Demény et al., 1997](#)). Although the Mg-metasomatic event took place after the peak pressure condition, the temperature did not decrease significantly (from 550 to 600 °C, [Török, 2003](#), to $560 \pm 30^\circ\text{C}$, [Demény et al., 1997](#)). The sources of Mg-rich fluids have been inferred by Mg isotope analyses of leucophyllites by [Chen et al. \(2020\)](#), who assumed two major sources, devolatilization from subducted carbonate rocks and serpentinites.

The studies on mineral assemblages, metamorphic conditions, and fluid compositions were supplemented by discovering special, tourmaline-rich rocks in orthogneisses and kyanite-chlorite-muscovite-quartzites ([Spránitz et al., 2018](#)). Several tourmaline generations were distinguished on the basis of petrographic characteristics and mineral compositions:

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1) primary magmatic crystals in pegmatitic orthogneisses, 2) Fe-rich schorl related to prograde metamorphism and 3) Mg-rich tourmaline rims and crystals related to leucophyllite formation. Tourmaline contains hydrogen, whose diffusion stops below about 200–300 °C (Jibao and Yaquian, 1997); hence the hydrogen isotope composition is insensitive to low-temperature weathering, considering the general refractory nature of tourmaline. The aim of this study was to analyze the hydrogen isotope composition ($^2\text{H}/^1\text{H}$ ratio) of tourmalines of different generations to determine if primary magmatic compositions can be preserved and to obtain information on the metasomatic fluids that induced Mg-rich tourmaline formation.

SAMPLES

Tourmaline-bearing samples were collected following the excellent description of Spránitz et al. (2018); hence the reader is referred to their Fig. 1 and Table 1. Tourmaline grains were separated for hydrogen isotope analyses from three occurrences: Bükkfatorrás Ditch (sample T1), Seprőkötő Hill (sample T5), and Récényi Road quarry (sample T6) (see Table 1 in Spránitz et al., 2018). Optical microscopic pictures of the samples are shown in Fig. 1. The tourmaline of sample T1 was collected from tourmaline-rich orthogneiss at the Bükkfatorrás Ditch location. The images of T1 tourmalines show the typical magmatic textures presented by Spránitz et al. (2018) and Fehér (2022). Based on their chemical composition data, the core is of schorlitic (Spránitz et al., 2018) composition, or would fall into the schorl-foitit transition (Fehér, 2022). The cores are surrounded by blue rims that have Fe-rich chemical composition (Spránitz et al., 2018), still in the schorl-foitit transition, but with higher Fe content (Fehér, 2022). The kyanite–chlorite–muscovite quartzites (samples T5 and T6 from the Seprőkötő Hill and

the Récényi Road quarry locations, respectively) mainly contain the magmatic tourmaline core with larger amounts of Fe-rich overgrowths (Fig. 1) and colorless tourmaline rims. The magmatic core and the Fe-rich, blue tourmaline are of schorl-dravite composition, while the Mg-rich rim is almost pure dravite (Spránitz et al., 2018). The Mg-rich variety is determined as dravite-magnesiofoitite by Fehér (2022). Separation of different tourmaline generations was not possible due to the amount needed for stable isotope analyses, but the differences in tourmaline chemistry are represented by the two main rock types studied. The orthogneiss-hosted tourmaline is dominated by the earliest generation, the magmatic tourmaline core (sample T1, Fig. 1), whereas the kyanite-chlorite-muscovite quartzites contain mainly the Fe-rich tourmaline generation with smaller amount of the earliest schorlitic one and the Mg-rich dravite, which latter was not detected in the orthogneiss.

Table 1. H₂O contents (wt%) and stable hydrogen isotope compositions (in ‰ relative to V-SMOW) for tourmalines (T1, T5, T6) and tourmaline-free batches of the sample samples (T1-N, T5-N, T6-N). The OH-minerals analyzed in the tourmaline-free samples are also indicated. Std.: standard deviation; *n*: number of measurements

		$\delta^2\text{H}$	std.	H ₂ O	std.	<i>n</i>
T1	orthogneiss	−23.2	0.8	3.1	0.04	6
T5	ky-chl-mu quartzite	−23.9	0.6	2.9	0.04	6
T6	ky-chl-mu quartzite	−22.7	1.3	2.9	0.05	6
T1-N muscovite	orthogneiss	−43.6	1.1	0.6	0.01	6
T5-N chlorite	ky-chl-mu quartzite	−39.6	0.9	3.8	0.05	6
T6-N chlorite	ky-chl-mu quartzite	−38.7	1.3	3.6	0.17	10

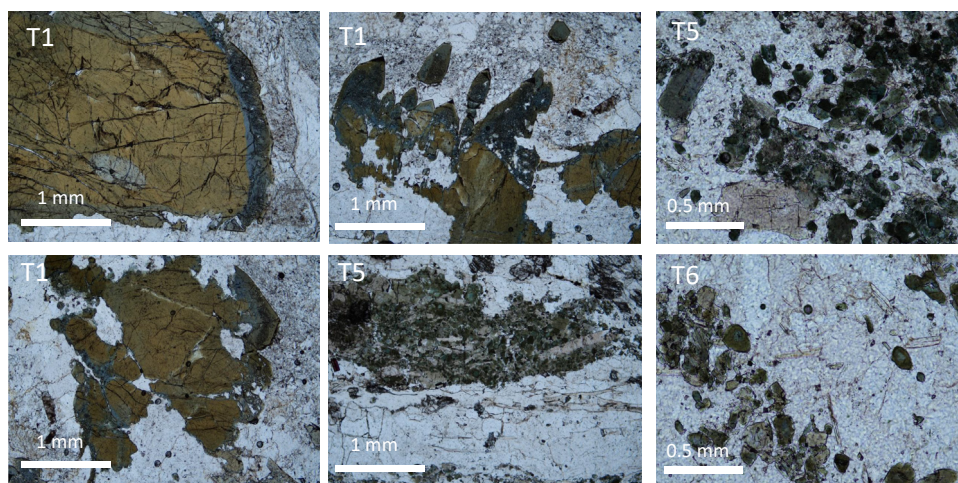


Fig. 1. Optical microscopic pictures of tourmaline-bearing samples (crossed Nicols). T1: brown schorlitic cores with blue Fe-rich rims in the orthogneiss of Bükkfatorrás Ditch. T5 and T6: tourmalines (dominated by brown magmatic cores and blue, Fe-rich rims with schorl composition) of the kyanite-chlorite-muscovite quartzites of Seprőkötő Hill (sample T5), and Récényi Road quarry (sample T6) (see Table 1 in Spránitz et al., 2018)

Tourmaline-free parts of the samples were also hand-picked and analyzed for hydrogen isotope compositions and water contents. The mineralogical compositions of tourmaline-free rock samples were analyzed by X-Ray diffraction (XRD) in order to determine the contribution of chlorite and muscovite to the hydrogen content. Samples T5-N and 6-N contained only chlorite, whereas sample T1-N contained only muscovite as OH-mineral.

METHODS

Petrographic analysis was conducted on polished thin ($\sim 30\ \mu\text{m}$) sections using a Nikon Eclipse E600 POL optical microscope. The XRD measurements were conducted using a Rigaku Miniflex600 powder diffractometer on powdered samples. In order to determine the hydrogen isotope compositions, tourmaline grains and tourmaline-free pieces were separated by hand picking from coarsely crushed samples under a stereomicroscope; the samples were powdered in an agate mortar and wrapped in Ag foil capsules. The capsules were placed into a heatable carousel (Uni-prepTM, Eurovector SpA, Milan, Italy), heated to $110\ ^\circ\text{C}$ while pumped for an hour using a Cole Palmer[®] Air Cadet[®] diaphragm pump and a liquid nitrogen trap, flushed with He, and dropped into the high-temperature conversion unit (TC/EA) in a continuous flux of He carrier gas. The reaction tube was packed with glassy carbon and heated to $1,430\ ^\circ\text{C}$. The TC/EA unit was attached to a Thermo Finnigan delta V mass spectrometer which was used to determine $^2\text{H}/^1\text{H}$ ratios in the H_2 gas. The hydrogen contents were calculated on the basis of size of the mass 2 signal peak and the sample weights. The hydrogen isotope compositions were expressed in the δ -notation ($\delta^2\text{H} = (R_1/R_2 - 1) \cdot 1000$, where R_1 and R_2 are the $^2\text{H}/^1\text{H}$ ratios in the sample and the standard, respectively) in permil (‰) relative to V-SMOW. The H isotope compositions of laboratory standards (IAEA CH-7 polyethylene foil and NBS-22 oil) that were used for calibration yielded an average reproducibility of $< \pm 2\%$. The accuracy of isotope compositions was checked using in-house test samples that had been measured in other laboratories. A $\delta^2\text{H}$ value of $-30.1 \pm 1.6\%$ ($n = 6$) was obtained for an in-house test amphibole sample (TOB-A1) that had been analyzed before at the University of Lausanne ($\delta^2\text{H} = -29\%$; Demény et al., 2005) and at the Université Claude Bernard Lyon 1 ($\delta^2\text{H} = -28.6 \pm 6.0\%$, $n = 5$; Fouré et al., 2017). Another test sample, phlogopite 97/24 yielded a $\delta^2\text{H}$ value of $-90.1 \pm 1.2\%$, close to the reported value of -92% (analyzed at the University of Lausanne; Demény et al., 2004).

RESULTS AND DISCUSSIONS

Independent of the rock type (sample T1: tourmaline-rich orthogneiss; samples T5 and T6: kyanite–chlorite–muscovite quartzite with tourmaline veins), the tourmalines yielded

very similar $\delta^2\text{H}$ values between -23.9 and -22.7% and water contents around $3.0\ \text{wt}\%$ (Table 1). The tourmaline-free bulk rock separates' $\delta^2\text{H}$ and $\text{H}_2\text{O}\%$ values are identical (with the analytical precision) for samples T5-N and T6-N. Sample T1-N yielded lower $\delta^2\text{H}$ value ($-43.6 \pm 1.1\%$), but with a very low H_2O content ($0.6\ \text{wt}\%$).

Hydrogen isotope compositions reflecting the Mg-metasomatic metamorphic phase

As the tourmalines formed in three generations, and as hydrogen is very mobile, it is a straightforward question what hydrogen isotope ratios represent compared to the compositions of less mobile elements. As Büttner and Kasemann (2007) pointed out, trace element contents and boron isotopic compositions remained intact in undeformed tourmaline grains, and only plastic deformation could facilitate diffusion of trace elements and boron at the metamorphic temperature of $550\text{--}600\ ^\circ\text{C}$. Compared to other elements, hydrogen can diffuse in tourmaline until a closure temperature of about $200\text{--}300\ ^\circ\text{C}$ (Jibao and Yaquian, 1997). The diffusion coefficient for hydrogen in tourmaline is about 10^{-14} to $10^{-13}\ \text{m}^2\ \text{s}^{-1}$ in the temperature range of $550\text{--}600\ ^\circ\text{C}$ (Jibao and Yaquian, 1997). This diffusion coefficient range means that at this temperature tourmaline grains of $0.1\text{--}5\ \text{mm}$ sizes can exchange hydrogen isotopes with a fluid in days to weeks, i.e., instantaneously in geologic time scales. This implies that the hydrogen isotope composition of tourmaline records the composition of the last metamorphic fluid flux. The elevated Mg content of the latest tourmaline generation suggests that the hydrogen isotope composition of tourmalines would belong to the metamorphic fluid that caused Mg metasomatism in the gneiss series.

The different tourmaline generations yielded very close $\delta^2\text{H}$ values (Table 1), indicating that the earliest, magmatic tourmaline grains underwent complete hydrogen isotope exchange with the metamorphic fluids. The average $\delta^2\text{H}$ value of all of the tourmaline analyses ($-23 \pm 1\%$, $n = 18$) was used to infer the fluid composition using the tourmaline-water hydrogen isotope fractionation equation of Kotzer et al. (1993) and a metamorphic temperature of $550\ ^\circ\text{C}$. The calculated $\delta^2\text{H}_{\text{water}}$ value is $-11.4 \pm 0.6\%$, which is close to the composition of $\sim 0\%$ inferred from chlorite values by Demény et al. (1997). The similar ^2H -enrichment indicates that the Mg-tourmaline formation was also related to the leucophyllite-forming metasomatic fluids. On the basis of seawater-like hydrogen isotope composition and associated Mg-enrichment, Demény et al. (1997) suggested that the fluids were emanated from subducted serpentinites that had experienced interaction with seawater. Additionally, Chen et al. (2020) suggested two fluid types involved in the Mg-metasomatic phase, a low- $\delta^{26}\text{Mg}$ fluid from carbonate-rich rocks and a high- $\delta^{26}\text{Mg}$ fluid released by devolatilizing serpentinites. The slightly lower $\delta^2\text{H}$ value of tourmaline-related water compared to the chlorite-related one may be related to the variations in the contribution of these fluid types.



Metamorphic temperature inferred from hydrogen isotope fractionations

As the closure temperatures of hydrogen diffusion are above 200–300 °C for tourmalines and muscovites (Jibao and Yaquian, 1997), and no metamorphic influence affected the rocks after the Mg-metasomatism, the hydrogen isotope data may record closure temperatures. Stable hydrogen isotope fractionations expressed as $1000 \cdot \ln \alpha$ values ($\alpha = (1000 + \delta^2\text{H}_{\text{tourmaline}})/(1000 + \delta^2\text{H}_x)$) were calculated for tourmaline-muscovite and tourmaline-chlorite pairs, using tourmaline-H₂O (Kotzer et al., 1993), muscovite-H₂O (Suzuoki and Epstein, 1976), and chlorite-H₂O (Graham et al., 1987) hydrogen isotope fractionation equations. The tourmaline-free samples T5-N and T6-N contain only chlorite as OH-mineral (anhydrous silicates would not contribute to the hydrogen isotope analyses). The $1000 \cdot \ln \alpha$ values calculated for the tourmaline and the chlorite fractions (T5 – T5-N; T6 – T6-N) are 16.1 and 16.4, respectively. The T1 – T1-N pair yielded a slightly higher value of 21.1. However, the tourmaline-free fraction of T1-N contained only a very small amount of muscovite (yielding 0.6 wt% H₂O) without chlorite suggesting that relict magmatic muscovite may have provided the hydrogen content. The $\delta^2\text{H}$ value ($-43.6 \pm 1.1\text{‰}$) is close to the value of -46‰ determined for the >0.5 mm muscovite fraction in gneisses of the same system that could represent relict magmatic muscovite (Demény et al., 1997). As the two minerals would record different fluid influences, the measured tourmaline-muscovite hydrogen isotope fractionation is meaningless in this case.

The measured tourmaline-chlorite hydrogen isotope fractionation data are plotted in Fig. 2 along with the tourmaline-muscovite and tourmaline-chlorite fractionation

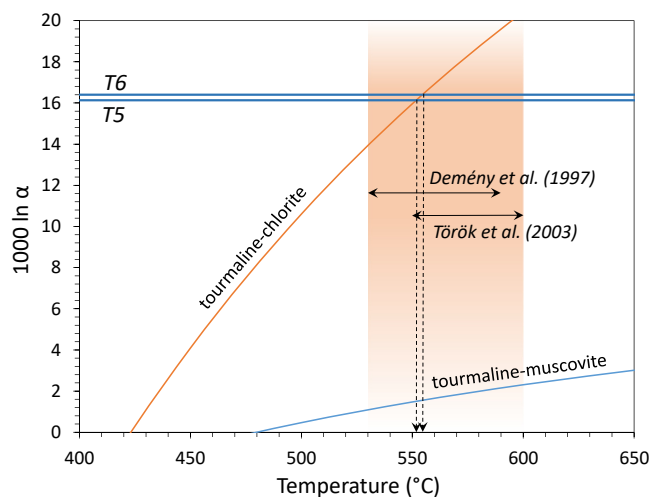


Fig. 2. Stable hydrogen isotope fractionations relative to temperature. Tourmaline-muscovite and tourmaline-chlorite fractionations were calculated using the equations of Suzuoki and Epstein (1976), Graham et al. (1987), and Kotzer et al. (1993). Shaded bar marks the common temperature range of Demény et al. (1997) and Török et al. (2003). Measured tourmaline-rock values for the samples T5 and T6 are also plotted as horizontal lines. Dashed lines indicate the temperatures that correspond to the measured fractionations

curves and presumed metamorphic temperatures. The T5 and T6 data plot well within the published temperature range of 530–600 °C (Demény et al., 1997; Török, 2003), corresponding to 550–560 °C. The data indicate that the measured tourmaline-rock hydrogen isotope fractionation records the metamorphic temperature. This observation also implies that the rock must have cooled quickly after the metasomatic event. Fig. 6 of Jibao and Yaquian (1997) shows changes of the diffusion coefficient with cooling rate and grain size. At an infinitely low cooling rate (close to 0 °C/Ma), the closure temperatures are about 180 °C (0.1 mm grains) to about 320 °C (10 mm grains), while the closure temperatures rise to ~380 °C (0.1 mm grains) and ~760 °C (10 mm grains) at a rate of 5 °C/Ma. The large, cm-sized tourmaline grains of sample T1 (orthogneiss) show severe internal cracking that helps fluid infiltration and reduces the effective grain size for isotope exchange to about 0.1 mm (see Fig. 1). As there is no $\delta^2\text{H}$ difference between the orthogneiss-hosted and the quartzite-hosted tourmalines, the isotope exchange within the fluid-chlorite-muscovite-tourmaline system must have stopped at about 550 °C upon cooling. For grain sizes around 0.1–1 mm (see Fig. 6 of Jibao and Yaquian, 1997), this can happen only at cooling rates of >5 °C/Ma, i.e., the rock system cooled rapidly after the Alpine metamorphic and Mg metasomatic events.

CONCLUSIONS

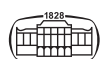
Tourmaline grains of the Sopron metamorphic complex were separated from the occurrences described by Spráňitz et al. (2018) and their stable hydrogen isotope compositions were determined. The $\delta^2\text{H}$ values record the composition of the last metamorphic fluid flux related to Mg-metasomatism. The $\delta^2\text{H}$ values ($-23 \pm 1\text{‰}$) and their agreement with leucophyllite compositions (Demény et al., 1997) indicate that this fluid was the same that induced leucophyllite formation. Tourmaline-chlorite hydrogen isotope fractionations correspond to about 550 °C in good agreement with earlier leucophyllite formation temperature estimations (550–600 °C; Demény et al., 1997; Török, 2003), suggesting a short metasomatic event and a sudden cooling.

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