# Ultra high-pressure tourmalines

ANDREAS ERTL AND EKKEHART TILLMANNS

Institut für Mineralogie und Kristallographie, Geozentrum,
Universität Wien, Althanstrasse 14, 1090 Wien, Austria
(andreas.ertl@a1.net, ekkehart.tillmanns@univie.ac.at)

The temperature and pressure stability of tourmaline is very large. It ranges from diagenetic/epigenetic to high-grade metamorphic and magmatic conditions. In this investigation tourmalines from metamorphic rocks occurring in three ultra high-pressure (UHP) localities were structurally and chemically characterized in order to generate accurate structural formulae and to test for any systematic response related to varying temperatures and pressures. Dravite from the Parigi, Dora Maira, Western Alps, Italy locality (~3.7 GPa, 800°C) has the formula ${}^{X}(\mathrm{Na}_{0.9}\mathrm{Ca}_{0.1})$ ${}^{Y}(\mathrm{Mg}_{1.8}\mathrm{Al}_{1.0}\mathrm{Fe}^{2+}{}_{0.1}\square_{0.1})$ ${}^{Z}(\mathrm{Al}_{5.1}\mathrm{Mg}_{0.9})$ $(\mathrm{BO}_3)_3$ ${}^{T}\mathrm{Si}_6\mathrm{O}_{18}$ ${}^{V}(\mathrm{OH})_3$ ${}^{W}[(\mathrm{OH})_{0.7}\mathrm{F}_{0.3}]$, with cell dimensions of $a = 15.935(1)$, $c = 7.201(1)$ Å. Dravite from the Lago di Cignana, Western Alps, Italy locality (~2.7-2.9 GPa, 600-630°C) has a formula of ${}^{X}(\mathrm{Na}_{0.8}\mathrm{Ca}_{0.1}\square_{0.1})$ ${}^{Y}(\mathrm{Mg}_{1.6}\mathrm{Al}_{0.8}\mathrm{Fe}^{2+}{}_{0.5}\mathrm{Mn}^{2+}{}_{0.1})$ ${}^{Z}(\mathrm{Al}_5\mathrm{Mg})$ $(\mathrm{BO}_3)_3$ ${}^{T}\mathrm{Si}_6\mathrm{O}_{18}$ ${}^{V}(\mathrm{OH})_3$ ${}^{W}[(\mathrm{OH})_{0.7}\mathrm{F}_{0.4}]$ with cell dimensions of $a = 15.945(1)$, $c = 7.210(1)$ Å. ”Oxy-schorl” from the Saxony Ore Mountains, Germany locality (>2.9 GPa, 870°C) has the formula ${}^{X}(\mathrm{Na}_{0.9}\square_{0.1})$ ${}^{Y}(\mathrm{Al}_{1.6}\mathrm{Fe}^{2+}{}_{1.2}\mathrm{Ti}^{4+}{}_{0.1})$ ${}^{Z}(\mathrm{Al}_5\mathrm{Mg})$ $(\mathrm{BO}_3)_3$ ${}^{T}\mathrm{Si}_6\mathrm{O}_{18}$ ${}^{V}(\mathrm{OH})_3$ ${}^{W}[\mathrm{O}_{0.8}\mathrm{F}_{0.1}(\mathrm{OH})_{0.1}]$ with cell dimensions of $a = 15.929(1)$, $c = 7.183(1)$ Å. There is no structural evidence for significant substitution of Si by Al or B in the UHP tourmalines (<T-O> distances ~1.620 Å), even in tourmaline from the highest temperature sample from the Saxony Ore Mountains. This contrasts with tourmalines formed at high grade, but lower pressure conditions having significant amounts of ${}^{[4]}\mathrm{Al}$. For this limited data set there is a very good positive correlation between the sum of ${}^{[6]}\mathrm{Al}$ in the UHP tourmalines and the determined temperature conditions of tourmaline formation of the different localities. Furthermore there is a highly negative correlation between the <Y-O> distances of the UHP tourmalines and the temperature conditions of tourmaline formation. Hence, an Al-Mg disorder between the Y and the Z site seems to be dependent on the temperature during crystallization. Because of the very limited localities with the occurrence of UHP tourmalines more extensive detailed studies are not currently possible. Consequently, to further elucidate the relations between metamorphic conditions and the crystal chemistry of tourmalines, efforts will be concentrated on diagenetic to high-grade metamorphic tourmalines from petrologic well characterized environments.

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# Development of a hyphenated technique (HG-ICP-MS/HG-MC-ICP-MS) for isotopic study of germanium species

R. ESCOUBE[1]*, V.N. EPOV[1], S. BERAIL[1], E. TESSIER[1],
D. AMOUROUX[1], V. PERROT[1], O.J. ROUXEL[2]
AND O.F.X. DONARD[1]

[1]LCABIE, U. Pau et Pays de l'Adour, CNRS UMR 5254,
Hélioparc 64053 Pau, France
(*correspondence: r.escoube@etud.univ-pau.fr)
[2]Marine Chemistry & Geochemistry, Woods Hole
Oceanographic Institution, Woods Hole, MA02543, USA

Germanium (Ge) is a trace metalloid which has a strong chemical similarity to silicon (Si). In the oceans, inorganic Germanium ($\mathrm{Ge}_i$) exhibits nutrient-like properties and is closely correlated with silica concentrations in the water column. Germanium is one of the rare elements which presents organic forms (Methyl and Dimethyl) characterized as unreactive in natural environment. Their behaviours have been deduced by their constant concentration over the water column and into the different oceans. But their sources, sinks and interaction with $\mathrm{Ge}_i$ cycle remain unknow.

In previous studies, Rouxel *et al.* [2] and Siebert *et al.* [3] developed a new technique of hydride generation to introduce Ge into the MC-ICP-MS. Rouxel and collaborators [4, 5] preconcentrate the inorganic germanium in aqueous samples by Mg precipitates and then analyzed by hydride generation.

In our study, we adapted the method of online hydride generation coupled to a MC-ICP-MS [2, 3] to measure of mono-elemental specie standards (MMGe and DMGe Alfa Aesar JMC). We have studied and optimized the operational conditions to volatilize the germanium species and assess any related fractionation. An online hydride gas injection (Cetac, HGX-200) of the different species is bracketed by traditional spray chamber introduction to measure the hydride volatilisation effects of reaction time, pH of the reaction (acidity of the sample, concentration of the reagent), matrix effects (addition of Iron, L-cysteine) on the precision and accuracy of the isotope ratio. This work on individual fractionation of germanium species will be later followed by an online hyphenated system on natural samples.

[1] Froelich & Andrea (1981) *Science* **213**, 205-207. [2] Rouxel *et al.* (2006) *GCA* **70** (13) 3387-3400. [3] Siebert *et al.* (2006) *GCA* **70** (15) 3986-3995.[4] Escoube *et al.* (2008) *EGU2008-A-12035*. [5] Rouxel *et al.* (2008) *GCA* **72** (12) A809