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Correlation between Fe^{3+} content and δ^{18}O in hydrothermal tourmaline

I.A. Baksheev (1), V.I. Ustinov (2)

Geology Dept. Lomonosov Moscow State University, Moscow, Russia (baksheev@geol.msu.ru / Fax: +7 095-9328889), (2) Vernadsky Institute of Geochemistry and Analytical Chemistry RAS, Moscow, Russia.

Middle temperature (300-400^{o}C) hydrothermal propylitic type alteration and related quartz veins often comprise tourmaline of the shorl-dravite series. For instance tourmaline occurs in the Berezovskoe and the Zolotaya Gora Au deposits located in the Central and the South Urals, respectively, in the Shabrovskoe talc deposit located in the Central Urals.

Propylitic tourmaline from above deposits is characterized by a linear positive correlation between $Fe_{tot}/(Fe_{tot}+Mg)$ (0.11-0.29) and $\delta^{18}O_{tour}$ ‰ (+5.0 - +13.1) (r=0.89). This correlation is caused by an enrichment of mineralizing fluids in ^{18}O as the $Fe_{tot}/(Fe_{tot}+Mg)$ ratio increases. It could be explained by so called “salt effect” that is a great increasing Fe content in fluids during tourmaline crystallization. This is related clearly to geological environment. Propylitic tourmaline with the low $Fe_{tot}/(Fe_{tot}+Mg)$ ratio crystallized in quartz vein hosted in the talc-carbonate altered rock, whereas that with the high ratio crystallized in quartz veins hosted in altered gabbroic. However, there are no experiments on the “salt effect” for the Fe saturated solutions. This provides a discussion on the assumption.

Observed correlation $Fe_{tot}/(Fe_{tot}+Mg)$ vs. $\delta^{18}O_{tour}$ ‰ is suggested to be explained by variability of the CO_2/H_2O ratio in mineralizing fluids. This ratio changes as CO_2 increases. It is illustrated by simple equation:

$$\delta^{18}\mathbf{O}_{tour} = \delta^{18}\mathbf{O}_{CO2} + \Delta^{18}_{tour-CO2} + \boldsymbol{b}[(\delta^{18}\mathbf{O}_{H2O} - \delta^{18}\mathbf{O}_{CO2}) - (\Delta^{18}_{tour-CO2} - \Delta^{18}_{tour-H2O})],$$

where $\Delta^{18}_{tour-CO2}$ and $\Delta^{18}_{tour-H2O}$ – fractionation factors in the tourmaline-

$CO_2(H_2O)$ system, b – the CO_2/H_2O ratio in fluid.

Addition of CO_2 with the constant oxygen isotopic composition to fluid determines the $\delta^{18}O_{tour}$ value as a linear function of b. If initial fluid is CO_2-bearing then the $\delta^{18}O_{CO2}$ è b corrections are necessary.

Good enough interpretation is interrupted by one point fallen out from the $\delta^{18}O$ – $Fe_{tour}/(Fe_{tour}+Mg)$ linear plot. This fact can be explained only by a local change of $\delta^{18}O_{H2O}$. However a reason of the $\delta^{18}O_{H2O}$ decreasing is difficulty believed all the more so in the same geological environment. This causes additional study of tourmalines.

The Fe^{3+} content in tourmaline ranges from 0.03 to 0.47. Correlation factors between $Fe^{3+}$and $\delta^{18}O_{tour}$ and $Fe^{3+}$and $\delta^{18}O_{H2O}$ are 0.90 and 0.95, respectively. In addition there is a good correlation between isotopic composition of the propylitic tourmalines and CO_2 concentration in fluid. Taking into account that the F^{3+}/Fe_{tot} ratio in tourmaline, ranging from 0.120-0.603, reflects oxidizing environment during crystallization, the mineralizing fluids could be considered to contain air O_2 ($\delta^{18}O \approx 23.0\%_{¸}$) as oxidation agent, initial CO_2 and CO. CO and O_2 interacted to form isotopic heavy CO_2. In turn this led to increasing of the $\delta^{18}O$ value of tourmaline in result of isotopic exchange.

Well known Uralian Emerald Mines (EM) are related to the phlogopite alteration, that is higher temperature (360-490^{o}C) than propylitic. The $Fe_{tot}/(Fe_{tot}+Mg)$ value of the EM tourmaline (0.20-0.30) is close to that of the propylitic tourmaline. The Fe^{3+}/Fe_{tot} ratio however is less and ranges from 0.054 to 0.139 indicating a reduced environment during crystallization. Fe^{3+} content ranges from 0.04 to 0.07. Oxygen isotopic composition of these tourmalines ranging from +8.1 to +10.6$\%_{¸}$ is close to that of the propylitic ones. In contrast to propylitic tourmaline there is a weak negative correlation between $Fe_{tot}/(Fe_{tot}+Mg)$ and $\delta^{18}O_{tour}$ $\%_{¸}$ (r= -0.72) and between Fe^{3+} and $\delta^{18}O_{tour}$ $\%_{¸}$ (r= -0.65). A strong negative correlation is between Fe^{3+}/Fe_{tot} and $\delta^{18}O_{H2O}$ $\%_{¸}$ (r= -0.95) and between Fe^{3+}/Fe_{tot} and $\delta^{18}O_{H2O}$ $\%_{¸}$ (r= -0.98). Presently we can not adequately explain such relations in tourmaline from the EM and would be very appreciated for advices from international scientific community.