

Crystal structure of non-metamict Th-rich hellandite-(Ce) from Latium (Italy) and crystal chemistry of the hellandite-group minerals

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ABSTRACT

The crystal structure of a Th-U-rich, Y-poor hellandite-(Ce) occurring in a volcanic ejectum from Capranica (Vico volcanic complex, Latium, Italy) was refined to an R index of 1.5% for 2226 observed reflections [$I > 3 \sigma(I)$]. Hellandite from Capranica is monoclinic $P2_1/a$ with $a = 19.068$ (8), $b = 4.745$ (2), $c = 10.289$ (3) Å, $\beta = 111.18$ (3)°. The extra-framework (distorted) tetrahedral cavity, usually occupied by H in hellandite, is partially (35–40%) occupied by Be and/or Li. When this is the case, the $[B_4Si_4O_{22}]$ tetrahedral chains of hellandite are locally cross-linked to form a sheet, which is built up by the same types of rings as in semenovite but in a different arrangement. The structure refinement and the electron- and ion-microprobe analyses provide constraints on hellandite-group crystal chemistry. The presence of $^{14}(\text{Be}, \text{Li})$ at the Be site is coupled with the substitution of F and/or O for OH at the O5 site; the amount of extra-framework cations thus constrains the OH content in the general formula. X-ray data exclude the presence of other OH sites in the structure, in agreement with direct H determination by ion probe (1.02 H apfu + 0.98 F apfu = 2.0 apfu of monovalent anions at O5 vs. 4.5–8 apfu proposed previously). The complete chemical analysis also eliminates the need for a vacancy at the REE sites. The general formula of hellandite-group minerals is thus $(\text{Ca}, \text{REE})_8(\text{Th}, \text{U}, \text{Y}, \text{REE})_4(\text{Ti}, \text{Fe}^{3+}, \text{Al})_2(\text{O}, \text{F}, \text{OH}_x)_4(\text{Be}, \text{Li})_{4-x}\text{Si}_8\text{B}_8\text{O}_{44}$, where electroneutrality is assured by the appropriate mixing of heterovalent substituents at the M sites.