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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 $P2/a$ with a = 19.068 (8), b = 4.745 (2), c = 10.289 (3) Å, β = 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 $^{[4]}$(Be, 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 $(Ca,REE)_8(Th,U,Y,REE)_4(Ti,Fe^{3+},Al)_2(O,F,OH_x)_4(Be,Li)_{4-x}Si_8B_8O_{44}$, where electroneutrality is assured by the appropriate mixing of heterovalent substituents at the M sites.