

Carbothermal mobilisation of HFSE minerals

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Sanidinites are magmatic cumulates with trachytic to phonolitic composition. The sanidinites from Laacher See volcano, Eifel, Germany, are famous for their abundant crystallization of high field strength element (HFSE) minerals with individual idiomorphic crystals. Remarkable is the occurrence of two late magmatic generations of zircon (Fig. 1). Type I zircon is rich in REE and Th. It exposes an oscillatory zoning and is always strongly affected by resorption. It is mantled by a REE and Th depleted, type II zircon, but with abundant inclusions of thorite and pyrochlore as well as calcite, and fluid inclusions.

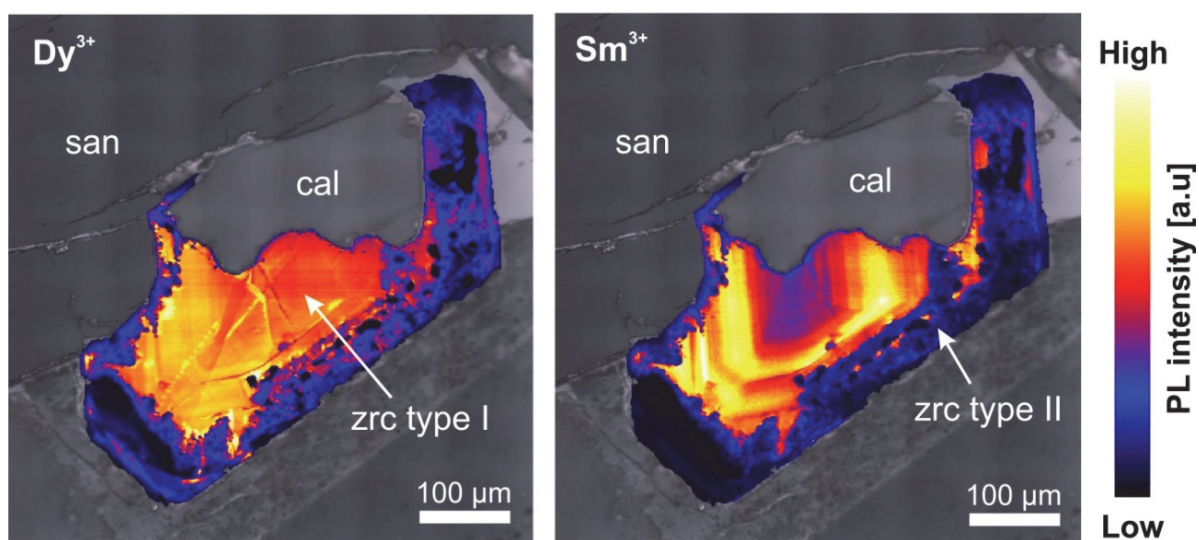


Fig. 1. Laser-induced photoluminescence maps overlay microscopic images of a strongly resorbed zircon (type I) within a miarolitic cavity of a nosean-bearing, calcite-rich sanidinite from Laacher See volcano, Eifel, Germany. The intensity of Dy^{3+} and Sm^{3+} emissions is colour-coded. It indicates high REE concentrations within the zircon core (type I). The type I zircon shows clear oscillatory zoning and strong resorption features. The euhedral overgrowth-rim of type II zircon is depleted in REE and rich in inclusions

The geochemical investigation of the sanidinites reveals a high content of volatiles in these rocks, up to 5 wt% SO_3 and 0.5wt % Cl. There is a positive correlation of Zr and REE with Na_2O , SO_3 , Cl, and LOI (CO_2).

Our investigations point to following crystallization sequence: Sanidine crystallized first, forming a framework of interlocking crystal laths with miarolitic cavities. Afterwards, different mineral assemblages crystallized within the miarolitic cavities. According to the composition and mineral assemblages within the cavities, two groups of sanidinites can be distinguished: (1) Häüyne sanidinites (HS) contain clear blue häüyne, plagioclase, clinopyroxene and biotite, as well as accessory apatite, magnetite and titanite. HFSE are mainly incorporated in titanite with concentrations up to 3.3 wt% ZrO_2 and 4

wt% Nb₂O₅, and apatite. Zircon was only rarely observed. (2) Nosean sanidinites (NS) contain high proportions of nosean and calcite and minor to accessory contents of clinopyroxene, biotite and apatite. A special feature is the occurrence of often euhedral HFSE minerals, including zircon (ZrSiO₄), baddeleyite (ZrO₂), thorite (ThSiO₄) and pyrochlore (Ca₂Nb₂O₇).

Detailed mineralogical and microchemical investigations give evidence for a further subdivision of the crystallization sequence within the cavities of the nosean sanidinites: Two different generations of nosean can be distinguished: N-I Nosean is characterized by abundant concentrically arranged silicate melt inclusions and high amount of CO₂ vapour inclusions, indicating crystallization from a residual, CO₂ vapour saturated melt. In contrast, N-II nosean is characterized by a mostly euhedral grain shape and the absence of melt- and fluid inclusions. Its occurrence together with calcite, pyrochlore, thorite and baddeleyite suggests its crystallization from a CO₂-rich (co-magmatic) fluid (vapour). The microchemistry of nosean indicates the presence of SO₃ and Cl in the fluid. The change from a silicate melt dominated condition to fluid dominated environment is evidence by etching and resorption structures, as well as carbonate filled fluid veins, observed only within sanidine and N-I nosean. Further indications for the formation of the mineral assemblage out of a gaseous phase are beside the high volatile content in the whole rock composition, the porous structure of the nosean sanidinites with abundant "empty" miarolitic cavities and abundant CO₂ vapour inclusions in the minerals. The euhedral grain shape of most crystals within the cavities, and the jagged grain boundaries of calcite are typical for the growth from a fluid.

These trends correlate with the changed growth features of zircon. The oscillatory zoned type I zircons (see Fig. 1), with typically high contents of Th and REE (up to 2.2 wt% REE₂O₃), indicate a late magmatic growth from a highly evolved melt. The strong resorption textures of type I zircon point to changed crystallization conditions thereafter. The newly grown type II zircon is characterized by low REE and Th concentrations and abundant inclusions of thorite, pyrochlore and fluids (CO₂) and minor calcite. These zircons occur not only as rims around type I zircon (see Fig. 1), but also as individual euhedral crystals within the miarolitic cavities. They also appear along grain boundaries or as fillings of etching holes within the sanidine laths. Notably, type II zircon appears always in conjunction with calcite.

Our results indicate a late stage co-magmatic, carbothermal formation of the calcite bearing nosean sanidinites. This process can explain the relative enrichment of HFSE minerals, carbonates and volatiles in nosean sanidinites. It leads to the formation of two different generations of nosean and zircon. According to our observations, we conclude that after the crystallization of type I zircon from a melt enriched in REE, it was partly dissolved and transported by a CO₂-rich fluid/vapour and re-precipitated as REE-poor type II zircon together with pyrochlore, forming individual euhedral crystals within the miarolitic cavities. The occurrence of baddeleyite in some samples is an indicator for changed crystallization conditions, marked by a fluid with lower Si activity.

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