

The geogenic impact on groundwater composition in the Netherlands

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The quality of groundwater is vital for both its natural function and anthropogenic use. Surprisingly, the geogenic control on groundwater composition has received little attention while the petrological composition of the rock matrix forms a major factor on groundwater composition. We have systematically investigated the geogenic control on both major groundwater composition and a series of trace elements at a national scale for the Netherlands. Several thousands of existing groundwater analyses were classified on geological formation. Additionally, the samples were grouped into 26 unique geographical regions. Regional statistics were created for all solutes of interest. An interpretation was established in terms of salinity, pH and carbonate status, redox status and nutrients. Interesting regional differences are noted within both the Pleistocene part of the Netherlands where phreatic aquifers are dominant, and the Holocene part where a reactive layer of clay and peat lies at the surface. This holds both for the major groundwater composition as well as for trace elements. These differences can partly be related to the sedimentary origin of the deposits, where marine deposits are more reactive than fluvial deposits. Upon result, the buffering capacity of marine deposits is larger but the natural contamination with arsenic, nutrients and salinity, too. This buffering capacity is monitored by an additional field and laboratory campaign, which establishes regional statistics on reaction capacities of sediment.

The crystal chemistry of (As,Sb,Bi)-bearing dumortierite

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Dumortierite [c. (Al, \square)Al₆(BO₃)Si₃O₁₃(O,OH)₂] and holtite [c. (Ta, \square ,Al)Al₆(BO₃)(Si,Sb,As)₃O₁₂(O,OH, \square)₃], are isostructural minerals found in a few granitic pegmatites. Dumortierite may contain several wt.% of Sb₂O₃, As₂O₃, Ta₂O₅, thereby blurring compositional distinctions between the two, although generally As > Sb in dumortierite. For this study we investigated the effect of minor amounts of Sb and As on the crystal structures of dumortierite samples D21 (Rats quarry, Hartmannsdorf, Saxony), D31 (Tonagh Island, Enderby Land, Antarctica) and D27 (Uval'dy Lake, Il'men Mountains, southern Urals, Chelyavinskaya Oblast', Russia). Average electron microprobe compositions for sample D21 show 2.32 wt.% As₂O₃ (0.14 atoms per formula unit) and 0.57 wt.% Sb₂O₃ (0.02 Sb apfu); for D31, 2.85 wt.% As₂O₃ (0.18 apfu) and 1.03 wt.% Sb₂O₃ (0.04 apfu); and for D27, 1.69 wt.% As₂O₃ (0.10 apfu) and 0.68 wt.% Sb₂O₃ (0.03 apfu). Analyses of samples D21 and D27 show no appreciable Ta, whereas sample D31 contains on average 1.62 wt.% Ta₂O₅ (0.04 apfu). Sample D27 also contains Bi (1.07 wt.% Bi₂O₃, 0.03 apfu).

Crystal structure refinements of single-crystal X-ray diffraction data converged to R1 values 1.92, 1.62, and 3.04% for samples D21, D31, and D27 respectively (all D27 crystals investigated were twinned in the normal fashion for dumortierite, with three twin individuals related by 120° rotation about a threefold twin axis parallel to a). For all three samples the results suggest that the As and Sb atoms are at the Sb1 and Sb2 sites, as is the case for holtite. However in the dumortierite samples the atomic displacement parameters (ADPs) associated with the atoms at these sites are unusually large, with U_{eq} Sb1 values of 0.03 Å², 0.02 Å², and 0.09 Å², and U_{eq} Sb2 values of 0.02 Å², 0.03 Å², and 0.06 Å², for samples D21, D31, and D27, respectively (for holtite these values are generally less than or equal to 0.01 Å²). Atomic displacement parameters for the coordinating oxygen atoms are no larger than in holtite and dumortierite with no As or Sb.

The reason for the large ADPs remains under investigation but may be a function of the small amounts of As and Sb at these sites, or perhaps indicates the presence of both trivalent and pentavalent As and Sb (and perhaps Bi, or Bi³⁺ and Bi⁵⁺) at the Sb1 and Sb2 positions.