Hydrous microporous minerals comprise a versatile group of crystal structures including e.g. zeolites, or more generally polyhedral framework structures, tobermorite-group minerals (CSH) and many more. In general, these compounds have technological applications in their anhydrous state (e.g. catalysis, ad- and absorption), thus understanding their dehydration behavior with special emphasis on structural modification is an important issue towards application. We systematically studied the dehydration of zeolite-like minerals using single-crystal X-ray methods at step-wise increased temperature under dry conditions. It has recently been shown that such dehydration experiments must be carried out under controlled humidity conditions (Bish and Wang, 2010). Under very dry conditions dehydration proceeds at lower temperature but the activation energy necessary for structural transformation is reduced thus the framework remains preserved. In contrast, under humid conditions dehydration occurs at higher temperature possibly leading to rupture of intra-framework bonds due to increased activation energy. Most commonly bond rupture causes structural amorphization.

Under humid conditions scolecite, CaAl$_2$Si$_3$O$_{10}$$\cdot$$3$H$_2$O ($V$ = 2289 Å$^3$), dehydrates at 175°C to metascolecite (2 H$_2$O, $V$ = 2240 Å$^3$), which becomes X-ray amorphous at 300°C. Under dry nitrogen conditions metascolecite (2H$_2$O, $V$ = 2234 Å$^3$) is formed at 150°C, which further dehydrates at 215°C to a strongly compressed phase with 1 H$_2$O ($V$ = 1989 Å$^3$) and subsequently at 225°C to an anhydrous phase with scolecite framework ($V$ = 1850 Å$^3$), which becomes X-ray amorphous at 275°C. Thus under dry conditions the framework structure withstands a volume reduction of 20% (Cametti et al., 2015).
Two different dehydration routes were also observed for gismondine \( \text{Ca(AlSiO}_4\cdot18\text{H}_2\text{O}, V = 1044 \text{ Å}^3 \) \) (Wadoski-Romeijn and Armbruster, 2013): (1) above 75°C phase B \((12 \text{H}_2\text{O}, V/2 = 993 \text{ Å}^3)\) and above 150°C phase C \((8 \text{H}_2\text{O}, V/2 = 868 \text{ Å}^3)\), between 200 and 440°C the structurally unknown phase D \( (2-4 \text{H}_2\text{O}) \) is observed. (2) at 75°C phase LT-\(I2/a\) \((16 \text{H}_2\text{O}, V = 1000 \text{ Å}^3)\), at 150°C phase HT-\(I2/a\) \((4 \text{H}_2\text{O}, V = 827 \text{ Å}^3)\). Above 250°C the latter phase transforms topotactically via selected rupture and reconnection of intra-framework bonds to a Ca feldspar structure \((V = 671 \text{ Å}^3)\). Thus the volume is reduced by 36% without losing crystallinity. It may be supposed that the second mechanism is preferred under dry conditions.

A unique case is observed (Pakhomova et al., 2013) for the dehydration of amicite \( \text{K}_4\text{Na}_4(\text{Al}_8\text{Si}_8\text{O}_{32})\cdot11\text{H}_2\text{O} \) \((V = 1053 \text{ Å}^3)\), which has the same framework topology as gismondine. Upon dehydration at 75°C amicite was found to partly dehydrate into two separate but coherently intergrown phases, both of space group \(I2/a\), one K-rich \(\sim\text{K}_8(\text{Al}_8\text{Si}_8\text{O}_{32})\cdot4\text{H}_2\text{O} \) \(V = 957 \text{ Å}^3\) and the other Na-rich \(\sim\text{Na}_8(\text{Al}_8\text{Si}_8\text{O}_{32})\cdot2\text{H}_2\text{O} \) \(V = 828.2(3) \text{ Å}^3\). Upon further heating above 75°C the Na- and K- phases loose remaining \(\text{H}_2\text{O}\) with only minor influence on the framework structure and become anhydrous at 175°C and 375°C, respectively. The two anhydrous phases persist up to 425 °C. Most interestingly, upon rehydration under
ambient conditions the lamellar intergrowth of $K_8(Al_8Si_8O_{32})$ and $Na_8(Al_8Si_8O_{32})$ homogenizes to one phase $K_4Na_4(Al_8Si_8O_{32})·11H_2O$.

Two microporous modifications of $Ca(VO)(Si_4O_{10})·4H_2O$ composition, cavansite ($V = 1289$ Å$^3$) and pentagonite ($V = 1310$ Å$^3$) were stepwise dehydrated (Danisi et al., 2012, 2013). For cavansite dehydration occurred at 75°C (3 H$_2$O, 1283 Å$^3$), at 175° ($V = 2$ H$_2$O, 1207 Å$^3$), and at 350°C (1 H$_2$O, $V = 1156$ Å$^3$), and amorphization at 400°C. For pentagonite H$_2$O is released at 100°C (3 H$_2$O, $V = 1287$ Å$^3$), at 175°C (1 H$_2$O, $V = 1069$ Å$^3$). At 225°C an anhydrous phase with pentagonite framework topology formed ($V = 1036$ Å$^3$) stable up to 600°C. The volume reduction between 25°C and 225°C amounts to 21%. The higher stability of pentagonite is due to increased flexibility of the framework, allowing Ca to obtain 5-fold coordination by bonding to both sites of the channel walls. In contrast, the cavansite framework appears rather stiff and after removal of the last H$_2$O molecule the structure collapses as Ca is not privileged to attract an additional bonding partner at the channel walls.


