Zeolite Structures

# Pressure-Induced Hydration Effects in the Zeolite Laumontite**

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The hydration level of minerals is an important indicator of the conditions prevailing during their formation and during any subsequent geological transformation. The precise water content of mineral zeolites, often highly sensitive to pressure and temperature due to their microporous structure, is particularly key in estimating rock porosity. The presence of the mineral zeolite laumontite near petroleum deposits, for example, can significantly reduce rock permeability, which may limit the production potential of the reservoir.[1] However, since laumontite readily partially dehydrates at ambient conditions[1,2] the exact composition during formation and subsequent diagenesis remains a key question. Neuhoff and Bird[1] postulated that laumontite ($Ca_4Si_{16}Al_{18}O_{48}\cdot 18\,H_2O$) actually forms as "leonhardite" ($Ca_4Si_{16}Al_{18}O_{48}\cdot 14\,H_2O$)[3] and only becomes fully hydrated at elevated pressures. Lee et al.[4–6] recently showed that another natural zeolite, natrolite, undergoes pressure-induced overhydration. As a consequence, it is imperative that we can determine the structure of such zeolites at nonambient conditions if we are to understand, not only their geochemistry, but also to assess the impact of extreme conditions on their suitability as, for example, nuclear-waste-containment and barrier materials. Here, we show using computational methods that laumontite can transform from the low-water "leonhardite" composition to the fully hydrated structure under the influence of pressure.

Laumontite ($LAU\cdot 18\,H_2O$; Figure 1) is one of the more common natural zeolites. The structure comprises channels bounded by eight tetrahedral units, parallel to the *c* axis, that contain $Ca^{2+}$ ions coordinated to the framework and water (labeled[2] W2 and W8), together with an additional hydrogen-bonded water network (W1 and W5). At ambient conditions the water molecules labeled W1 are readily lost (reversibly) to give $Ca_4Si_{16}Al_{18}O_{48}\cdot 14\,H_2O$ ($LAU\cdot 14\,H_2O$). Indeed, typical samples of laumontite have $\approx 16\,H_2O$ molecules per unit cell and the fully hydrated material can only be obtained by prolonged immersion in water.[2,7,8] Furthermore, laumontite often occurs with a composition of $Ca_4Si_{16}$-

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[**] The EPSRC is acknowledged for funding of this work.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

DOI: 10.1002/ange.200352364

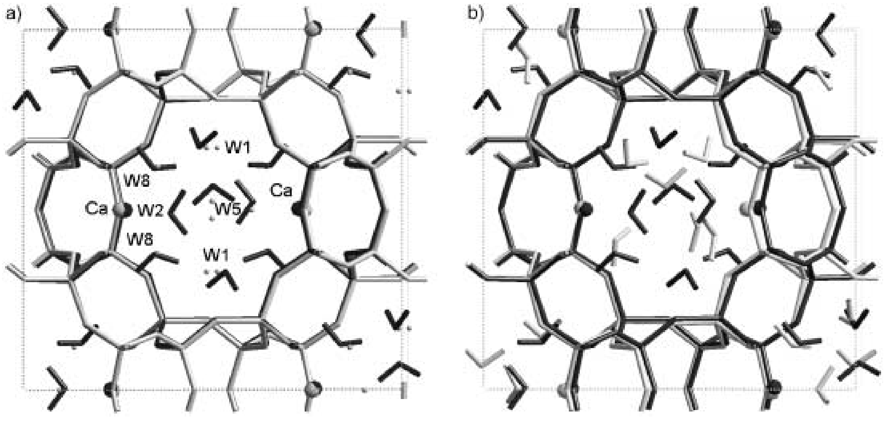

***Figure 1.*** a) Comparison of calculated LAU·18 $H_2O$ (black) with the experimental structure (gray) of Fridriksson et al.[8] Note that all possible partially occupied experimental water sites (O only) are shown. For example, only one of the adjacent W1 sites can be occupied, as is the case for the W5 site; b) comparison of the calculated LAU·14 $H_2O$ structure (gray) obtained by dehydration of the calculated LAU·18 $H_2O$ structure (black). Note the loss of the W1 water molecules and the increase in disorder (also see Supporting Information).

$Al_{18}O_{48}$·14 $H_2O$, commonly referred to as "leonhardite",[3] particularly in mineral deposits that are geothermal in nature (i.e., near the earth's surface). However, the water content of laumontite in deeper deposits cannot be determined accurately, due to the facile loss of water at ambient conditions. Here, we have constructed models for LAU·18 $H_2O$ and LAU·14 $H_2O$ phases and performed energy minimization calculations to simulate the dehydration behavior and then determine the relative stability and structure of these phases to the application of external pressure.

Computer modeling of zeolitic materials has enjoyed considerable success over the past couple of decades, driven in no small degree by their application as catalysts. Consequently, most studies have focused on acidic, high-silica (uncommon in natural zeolites) materials in their dehydrated state. Furthermore, modeling of hydrated systems is notoriously difficult, often failing to accurately reproduce experimental observations.[9] However, we believe that we have made significant progress in this field recently, demonstrating that we are both able to reproduce experimental structures and also to provide thermochemical mechanisms for cation and framework compositions.[10,11] The simulations are based on the classical Born model of solids with interatomic potentials describing the forces between the atoms. Energy minimizations were performed with the GULP program,[12] by using the potential parameters described by Jackson and Catlow[13] and de Leeuw et al.,[14,15] with minor modifications by Lewis et al.[11] We have already successfully modeled a number of hydrated calcium-bearing zeolites[10,11] using these parameters and methods.

Optimized models of the unit cell of fully hydrated laumontite (LAU·18 $H_2O$) were constructed that compared very favorably (Figure 1) with the latest crystallographic study by Fridriksson et al.[8] A number of alternative models have also been optimized that give a similar quality of fit and differ only by the relative orientations of the hydrogen-bonded water molecule in the center of the channel. The largest deviation from experiment is ≈2%, mainly due to the Ca–$OH_2$ bond lengths being underestimated by ≈5%.

A stepwise dehydration[11] of the structure was performed, similar in some respects to that used by Ferey and co-workers[16,17] to simulate the removal of templates from zeolites by calcination. Each unique water molecule is removed in turn, with each of the structures obtained being then optimized, before removing a further water molecule from the lowest-energy structure; a procedure repeated until all the water is removed (Figure 2). At the "leonhardite" (LAU·14 $H_2O$) composition, only water from the W1 site had been lost, with the W5 water molecules being the next to be lost: the same as found experimentally,[2,8] which confirms the accuracy of the potentials in modeling the energetics of the system. The calculated average enthalpy of dehydration of the first four water molecules (75 kJ $mol^{-1}$) is significantly lower than that of the remaining water molecules (102 kJ $mol^{-1}$), corroborating the experimental observation[2,7,8] of facile dehydration at ambient conditions, particularly to give a composition with ≈16 $H_2O$. The total dehydration enthalpy of LAU·18 $H_2O$ and LAU·14 $H_2O$ is calculated to be 96 and 102 kJ $mol^{-1}$ per water molecule, respectively, which compares remarkably well with experimental values of 80 and 84 kJ $mol^{-1}$.[18] The changes in unit-cell dimensions (Figure 2; see also the Supporting Information) are also in excellent agreement with those measured during in situ diffraction studies of dehydration,[2] with major changes noted when the water content reduces to 14 $H_2O$

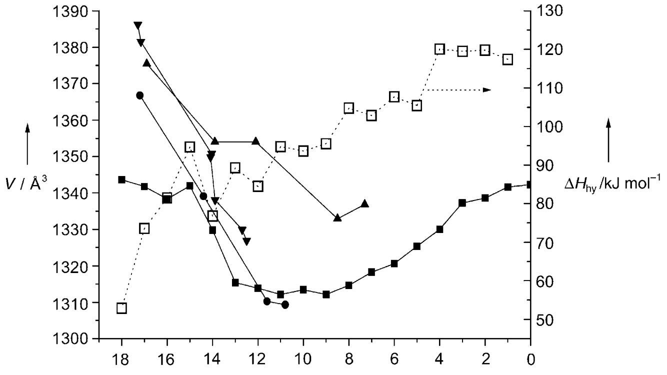

***Figure 2.*** Calculated dehydration profile of laumontite: Dehydration enthalpies, $\delta H_{hy}$ (-----, □, right axis), for each of the water molecules (each is relative to vapor-phase water) and calculated (■) unit-cell volumes, V, compared with the experimental values of Stahl et al.[2] (▲), Armbruster and Kohler[7] (●), and Fridriksson et al.[8] (▼), on the left axis. Experimentally, water is lost at four distinct temperatures. Full dehydration is not possible experimentally without transformation to wairakite (note that our model would not allow such a structural transformation). Stahl et al.[2] report that eight $H_2O$ molecules remain up to 600 °C, which corresponds to the increase to higher dehydration energies at such a composition observed in our calculations.

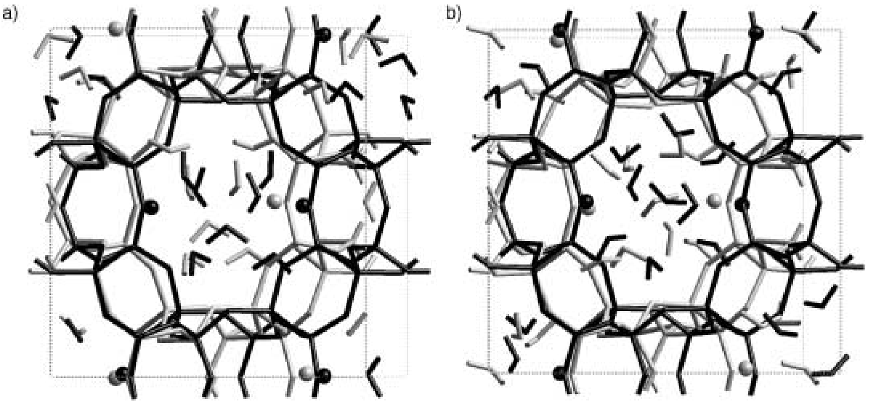

*Figure 4.* Phase transformations at high pressure: a) LAU·14 $H_2O$ at 3.5 GPa (gray) compared to 2.5 GPa (black); b) LAU·18 $H_2O$ at 5.5 GPa (gray) compared to 0.01 GPa (black). Also see Supporting Information.

molecules per unit cell. We find that the $\beta$ angle in the cell increases initially before decreasing and there is a rapid decrease in $b$ and $c$ when the hydrogen-bonded water molecules are removed, whilst $a$ decreases more gradually (Supporting Information, Figure 1).

Structurally, the same trends in water-site occupation are observed as in experiments, that is, W1 water molecules being lost first followed by W5. In addition, after the W1 water molecule is lost, disorder is introduced at the W8 site, which concurs with the smearing of electron density at this site that was found by Fridriksson et al.[8] Similarly, it was found that below a composition of LAU·12 $H_2O$, (corresponding to the loss of all the original hydrogen-bonded water molecules) the remaining water is further disordered with often little distinction between the W2 and W8 sites. Such disorder is a consequence of the remaining water having to satisfy both the coordination sphere of $Ca^{2+}$ and maintain the structural integrity of the pore. This provides an explanation of why, experimentally, the structure undergoes a phase transformation to wairakite when the water content drops to $\approx 8\,H_2O$.[2]

Both the LAU·18 $H_2O$ and LAU·14 $H_2O$ structures were then subjected to optimization at pressures of 0–15 GPa (Figure 3). LAU·14 $H_2O$ undergoes volume contraction, which becomes more severe as the pressure increases (between 2–3 GPa) and then undergoes a dramatic phase transformation at 3.5 GPa (Figure 4a). In contrast, the rate of change of cell volume with pressure for the fully hydrated structure (LAU·18 $H_2O$) does not increase significantly until it also undergoes a phase transition at $\approx 5.5$ GPa (Figure 4b). However, the perturbation to the water structure is much more severe in LAU·18 $H_2O$ when it undergoes this phase transformation (compared to that calculated for LAU·14 $H_2O$); evidence that at such pressures a complete structural rearrangement may occur. We note that wairakite is found in deeper deposits than laumontite[19] and that a phase transformation to wairakite occurs on the thermal dehydration of laumontite.

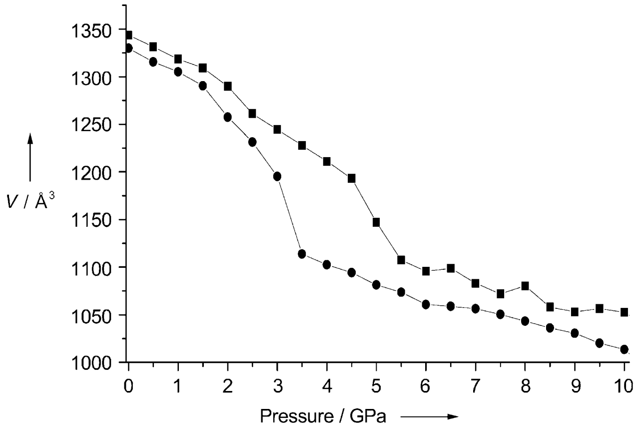

*Figure 3.* Calculated unit-cell volume $V$ as a function of pressure: LAU·18 $H_2O$ (■) and LAU·14 $H_2O$ (●) undergo a phase transformation between 4–5.5 GPa and 3–3.5 GPa, respectively.

A convergence in the enthalpies of the two systems (LAU·18 $H_2O$ compared with LAU·14 $H_2O$ + 4 $H_2O$) is observed; although the exact crossover point is dependant on the phase of water we choose. However, since these calculations do not include entropic contributions, we would not wish to rely solely on an energetic argument of stability. Nevertheless, it is quite clear that structurally, LAU·14 $H_2O$ begins to collapse at $\approx 1.5$–2.0 GPa and becomes increasingly unstable above 3.5 GPa. In contrast, LAU·18 $H_2O$ remains stable to higher pressures. Indeed (assuming that the uptake of water is not kinetically controlled), it may be expected that LAU·14 $H_2O$ would transform to LAU·18 $H_2O$ once the cell volumes become comparable ($\approx 1.5$–2 GPa). Experimentally, the overhydration of the zeolite natrolite occurs at $\approx 1.2$ GPa,[5] whilst in a separate study on the natrolite family[20] we calculated that the overhydrated phase was not favored up to a pressure of $\approx 4$ GPa. Thus, given such a discrepancy between experiment and calculation (which is relatively small, in this context[20]) we expect "leonhardite" to be fully transformed to laumontite below 1 GPa, and may transform at significantly lower pressures. Such pressures correspond to depths of up to $\approx 10$ km, where laumontite is typically found.

We note that the methods used here make many simplifications (e.g., by being a static representation at 0 K), but their suitability is clear, not only from the reproduction of experimental observations (structure and dehydration behavior), but also from their general applicability, robustness, and low computational cost. Furthermore, we are able to simulate our materials at conditions inaccessible to experimentation, such as the "leonhardite" composition at high pressures. Other (more costly) methods provide further detail of the mechanisms, for example, librations of the water molecules[21] but the methods used here are clearly appropriate for the modeling of phase changes.

Our simulations clearly show that when pressure is applied, the structural stability of the laumontite framework is enhanced by the presence of a fully occupied water network. Conversely, since the W1 water molecule is only loosely bound, we do not consider it necessary for the water network to be fully occupied during the formation of the laumontite structure. Indeed, a number of other calcium zeolites form with little or no water that is not directly coordinated to the calcium ions. Our results, therefore, support the postulate of Neuhoff and Bird[1] that laumontite formation at the earth's surface results in a material with the "leonhardite" (LAU·14 $H_2O$) composition and that subsequent application of pressure, as a result of burial, leads to diagenesis to the fully hydrated phase (LAU·18 $H_2O$). Thus, fully hydrated laumontite can be considered to be a pressure-induced overhydrated phase of the "as-formed" material. Since we predict that the transformation to the LAU·18 $H_2O$ structure will occur at (or below) pressures of $\approx 1$ GPa, we suggest that laumontite should be treated as being fully hydrated when considering its impact on rock porosity and petrology. Work is underway to determine if there is scope for any higher levels of hydration, analogous to the overhydration of natrolite.[4]

Received: July 14, 2003 [Z52364]

**Keywords:** computer chemistry · geochemistry · high-pressure chemistry · phase transitions · zeolites

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