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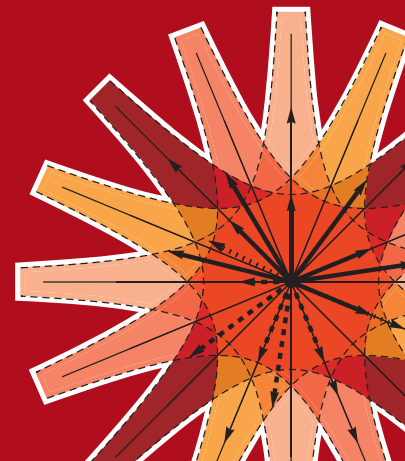# Flexibility windows and phase transitions of ordered and disordered ANA framework zeolites

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Abstract – The analcime-like feldspathoids are a group of microporous minerals with the **ANA** framework topology. Analcime proper has predominantly Na as its channel cation content, while leucite contains predominantly K, pollucite contains Cs and wairakite contains Ca. Under compression, all these minerals display structural displacive phase transitions to low-symmetry forms at relatively low pressures (0.5–3.2 GPa). We show, using geometric simulation, that these phase transitions are controlled by the "flexibility window" of the **ANA** framework, defined as the range of framework densities over which the tetrahedral units of the framework can in principle be made geometrically ideal. We discuss experimental compression data for these minerals and its relationship to the theoretical flexibility of the **ANA** framework, the influence of cation content, and framework ordering.

Introduction. – Many minerals have structures that can be described as a "framework" of linked polyhedra, with non-framework ions and molecules occupying spaces surrounded by the framework. Examples include the AMO_3 perovskites, viewed as a framework of corner-sharing MO_6 octahedra with interstitial A ions, and the dense framework silicates such as quartz, with their framework of corner-sharing SiO_4 tetrahedra. The zeolites [1] —a broad group of framework minerals whose corner-sharing tetrahedral aluminosilicate frameworks contain cages, pores and channels large enough to contain not only ions but also H_2O and other small molecules— are of particular interest in chemical industries [2,3] as molecular sieves, shape-selective catalysts and ion-exchange materials.

The polyhedra making up a crystalline framework are not usually geometrically ideal. Small distortions from perfect regularity are visible in crystal structures, due to electrostatic and steric interactions between framework and extra-framework atoms/ions. The question naturally arises whether, absent such interactions, it is in principle possible to make the framework polyhedra perfectly regular, for a given set of unit-cell parameters and a given framework topology. This question of *perfectibility* can be answered using geometric simulation —a simulation method adapted for framework structures, in which the ideal bonding geometry of a polyhedral unit is represented by a template to which framework atoms are tethered by harmonic constraints [4]. The method of geometric simulation has been successfully applied in a number of studies on zeolites and other framework mineral structures [4–10].

It has recently been observed that known zeolite frameworks are typically perfectible over a wide range of densities [11]. This range is termed the "flexibility window". Under ambient conditions zeolite structures tend towards the low-density edge of their flexibility window. Although the flexibility window is an essentially geometric phenomenon, it has a physical significance [12]. If a structure lies within its flexibility window, so that its polyhedra can in principle be made perfectly regular, then

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small distortions of the polyhedra are variations about a minimum; their energy cost should therefore be second-order in the size of the distortion. If on the other hand the structure lies outside its flexibility window, its polyhedra are intrinsically strained before other interactions are taken into account. The energy cost of further distortions should therefore be larger and first-order in the size of the distortion. There is thus an energetic incentive for structures to remain within their flexibility window. Given the known tendency of zeolite structures to respond to pressure through displacive mechanisms based on cooperative rotations of the framework polyhedra [13,14], we expect to find connections between the pressure behaviour of zeolites, particularly pressure-induced phase transitions, and the limits of the flexibility window.

The "analcime group" of minerals with the **ANA** framework topology includes the aluminosilicates analcime (or analcite) [15], leucite [16], wairakite [17–19] and pollucite [20]. These are compositional end members distinguished by the interstitial ions typically found in the structural channels. Analcime is the Na end member (ideally $Na_{16}Al_{16}Si_{32}O_{96} \cdot 16H_2O$); it is commonly defined as a feldspathoid, though the Commission of the International Mineralogical Association includes analcime in the zeolite group [21]. Leucite contains K ($K_{16}Al_{16}Si_{32}O_{96}$), wairakite contains Ca ($Ca_8Al_{16}Si_{32}O_{96} \cdot 16H_2O$) and pollucite contains Cs ($Cs_{12}Na_4Al_{16}Si_{32}O_{96} \cdot 12H_2O$). Leucite is the only nominally anhydrous member of the "analcime group" [22]. Hsianghualite ($Li_{16}Ca_{24}Be_{24}Si_{24}O_{96}F_{16}$) also has **ANA** framework topology, but is not a zeolitic aluminosilicate framework and we do not consider it further. The aluminosilicate end members have broadly similar behaviour under pressure, transforming displacively at relatively low pressures ($<$ 1–3 GPa) from a high-symmetry ambient form to a very low-symmetry compressed form.

We have previously found [12] that the phase transition in cubic analcime occurs when the structure is compressed sufficiently that the cubic framework can no longer remain within its flexibility window. In a further study [23] we demonstrated that the same is true of tetragonal leucite. We also considered the behaviour of wairakite; however, geometric simulations of wairakite with a simplified uniform tetrahedral bond length (representing full Al/Si disorder in the framework) did not match experimental data, as the simulations found that the framework was not perfectible within part of its cubic range. We tentatively attributed the discrepancy to Si/Al order in the wairakite framework, as experimentally observed [17–19].

We now make use of geometrical simulation combined with experimental data on the compression behaviour of analcime, leucite, wairakite and pollucite, and of an Al/Si ordered structure for wairakite, to connect the flexibility windows and pressure-induced phase transitions of all the end members of the analcime group.

Experimental data. – The high-P behaviour under hydrostatic conditions of analcime, leucite and pollucite has been investigated by *in situ* X-ray single-crystal diffraction with a diamond anvil cell up to $\sim$ 7–8 GPa [15,16,20] and that of wairakite by *in situ* synchrotron powder diffraction up to $\sim$ 7.8 GPa [19]. The structure refinement of analcime, leucite and pollucite at room conditions proved a disordered Si/Al-distribution in the tetrahedral framework. In contrast, the structure refinements of wairakite suggested a highly ordered Si/Al-distribution; for our simulation, we used the structure model of wairakite from [18]. All the four members of the **ANA** group experience a phase transition from high-symmetry to low-symmetry polymorph under pressure: 1) analcime, between 0.91(5) and 1.08(5) GPa from $Ia\bar{3}d$ to $P\bar{1}$ symmetry; 2) pollucite, between 0.54(4) and 0.79(3) GPa from $Ia\bar{3}d$ to $P\bar{1}$ symmetry; 3) leucite, between 2.19(4) and 2.77(1) GPa from $I4_1/a$ to $P\bar{1}$ symmetry; 4) wairakite, between 2.5(1) and 3.2(1) GPa from $I2/a$ to $P\bar{1}$ symmetry. For analcime and leucite, the P-induced phase transition is unambiguously a first-order transition; in contrast, for pollucite and wairakite the order of the transition cannot be unambiguously defined. The structural refinement of the low-P and high-P polymorphs of analcime showed that the P-induced phase transition at $\sim$ 1 GPa is displacive in character [15]. Structure refinements of the high-P polymorphs of pollucite, leucite and wairakite are not available. On the basis of the structural homology among the **ANA** members, we can expect the same displacive character of the P-induced transition in pollucite, leucite, and wairakite.

Simulation methods. – The method of geometric simulation has been described in detail in the literature [4, 7,8,11]. Briefly, the input to the simulation is a cell or supercell of a framework structure, with all framework atoms represented and without symmetry constraints on atomic positions (that is, with $P1$ symmetry), and a set of polyhedral specifications describing the shape and size of bonded units (*e.g.* a SiO_4 tetrahedron with bond length 1.61 Å). Hard-sphere steric radii are also given; as is conventional for zeolite studies [1] we assign a radius of 1.35 Å to framework oxygen atoms, whose collision typically limits the flexibility window at high densities. Each bonded unit identified in the framework is assigned an appropriately shaped polyhedral template; harmonic constraints penalise displacements of the atoms from the vertices of the templates. In a geometric relaxation, the positions of all atoms and the positions and orientations of all templates are relaxed together so as to determine whether it is possible to bring all atoms within a small tolerance (0.001 Å) of ideal polyhedral geometry.

Geometric simulations are carried out using the program GASP, originally developed by SAW [4]. In this study we make use of a recent improvement to the code, the implementation of the limited-memory BFGS algorithm [24] by Dr. Kapko as reported in [25], which
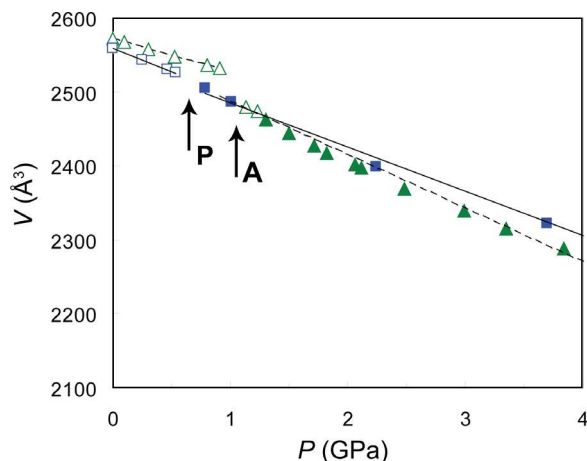
Fig. 1: (Colour on-line) P-V data for analcime (triangles) and pollucite (squares) annotated with results of geometric simulation. Points are labelled with open symbols if the framework is found to be perfectible and with closed symbols if the framework is intrinsically distorted. For both, the ambient/low-P structure is perfectible, while the high-P structure is generally not. Locations of the phase transitions of analcime (A) and pollucite (P) are indicated by arrows.

Fig. 2: (Colour on-line) P-V data for wairakite (diamonds) and leucite (circles) annotated with results of geometric simulation. Points are labelled with open symbols if the framework is found to be perfectible and with closed symbols if the framework is intrinsically distorted. For both, the ambient/low-P structure is perfectible, while the high-P structure is not. Locations of the phase transitions of wairakite (W) and leucite (L) are indicated by arrows.

greatly accelerates geometric relaxation compared to the previous steepest-descent minimiser.

Analcime, leucite and pollucite frameworks are modelled using an averaged T–O bond length of 1.65 Å, representing an appropriate weighted average of the Si–O and Al–O bond lengths [12,23] for a fully disordered framework. We have previously found that this disordered model does not match the experimental data for wairakite. Highly ordered Si/Al-distribution in wairakite structure have been reported [18,26]; accordingly, we model wairakite framework using distinct Si and Al sites, for which bond lengths of 1.61 Å for Si–O and 1.75 Å for Al–O, respectively, are used.

For each P-V point where unit-cell parameters are available for a structure, we impose the given parameters on a model of the framework and use geometric relaxation to determine the perfectibility of the structure. We also determine the theoretical limits of the flexibility window for the cubic framework of pollucite by looping over a range of densities.

Results. – In fig. 1 we summarise the results of geometric simulation at experimental P-V data points for analcime and pollucite, while in fig. 2 we consider non-cubic forms: leucite and wairakite. Analcime and pollucite are cubic ($Ia\bar{3}d$) under ambient conditions, leucite is tetragonal ($I4_1/a$) and wairakite is monoclinic ($I2/a$). All structures transform under pressure to very low-symmetry ($P\bar{1}$) triclinic forms.

Points are labelled with open symbols if the framework is found to be perfectible (that is, it lies within the flexibility window) and with closed symbols if the framework is intrinsically distorted. It is clear that the behaviour of all four aluminosilicate end members follows the same
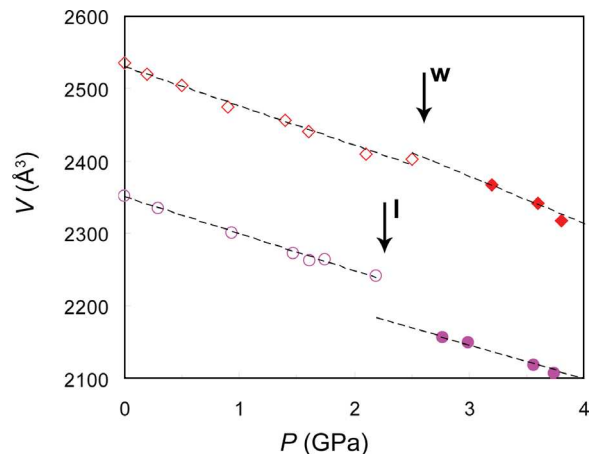
pattern; the ambient/low-P structure is perfectible while the compressed structure is generally not. We note that in analcime some data points for the compressed structure are also perfectible.

Comparison with earlier results [23] indicates that Si/Al ordering in the wairakite structure widens its flexibility window; in a disordered model of the wairakite cell, all points above $P = 0.9\,\text{GPa}$ are not perfectible. This is consistent with the recent observation [25] that ordering can make structures relaxable for which a pure-silica model form is intrinsically strained.

It is conventional, when discussing zeolite structures, to use "framework density", defined as the number of tetrahedral units per $1000\,\text{Å}^3$. The analcime group are among the densest of zeolites; under ambient conditions, framework densities are $18.64\,\text{T/Å}^3$ for cubic analcime and $18.76\,\text{T/Å}^3$ for cubic pollucite, $18.93\,\text{T/Å}^3$ for monoclinic wairakite, and $20.38\,\text{T/Å}^3$ for tetragonal leucite.

This survey of experimental data points implicitly provides information on the limits of the flexibility window of the low-P structure. We expect the limit to lie between the last observed density of the low-P structure, where it is still perfectible, and the first observed density of the high-P structure. For the cubic structures (analcite and pollucite) we can easily compare these experimental limits on the flexibility window with the theoretical limit, obtained by uniformly scaling the cubic unit-cell to cover a range of densities around the ambient value.

To parallel the calculations previously carried out on analcime [12] we perform simulations of the cubic framework of pollucite, starting at the observed ambient framework density ($18.76\,\text{T/Å}^3$) and progressively compressing or expanding the simulation cell. On compression we find

the edge of the flexibility window at a framework density of around $19.17 \, \text{T}/\text{Å}^3$. Pollucite is observed in its cubic form at a framework density of $19.01 \, \text{T}/\text{Å}^3$ at a pressure of $0.54 \, \text{GPa}$ and, after the phase transition, is observed in its triclinic form at a framework density of $19.16 \, \text{T}/\text{Å}^3$ at a pressure of $0.79 \, \text{GPa}$. The transition from cubic to triclinic in pollucite thus occurs just at the edge of the flexibility window for the cubic framework of pollucite; the match is surprisingly close given the extreme simplicity of our simulation model.

Simulation of expansion (which is, of course, not experimentally observed) finds an upper limit of the flexibility window at a framework density of $18.58 \, \text{T}/\text{Å}^3$. Both analcime and pollucite thus lie towards the less dense edge of the flexibility window, consistent with the behaviour of other zeolite frameworks [11].

Discussion. – We have considered experimental data and simulation results for all four end members of the analcime group of aluminosilicate zeolites. We can now confirm our conjecture [12,23] that the pressure-induced phase transitions of aluminosilicates in the analcime group are controlled by the flexibility window of the framework. Our geometric simulations concern only the framework and do not include the ions and water molecules lying in the channels. There is a very wide variation in the ionic content of the end members of the group, and leucite is anhydrous while the other members are hydrated. We nonetheless find common behaviour for all four end-member minerals, with the ambient/low-P structure being perfectible while the high-P form is intrinsically distorted.

This suggests that the phase transitions of these minerals are effectively controlled by the self-interactions of the framework; the effect of the ionic content on the transition is indirect rather than direct. That is, the ionic content presumably influences the ambient crystal structure (cubic, tetragonal or monoclinic), which in turn affects the flexibility window; we have seen that tetragonal leucite is relaxable at densities far beyond the flexibility window of the cubic analcime or pollucite framework. However, the ionic content does not maintain an analcime structure in its high-symmetry form if the framework is not perfectible. This is in contrast to a recent result on goosecreekite [25] which appears to be stabilised in a non-perfectible form by ion/framework interactions; goosecreekite contains divalent cations, as does wairakite.

The inclusion of ordering in wairakite makes certain structures perfectible which, in a fully disordered simulation using a single uniform tetrahedral size, would be intrinsically distorted. It may at first seem counterintuitive that the inclusion of ordering should make the geometric relaxation easier. In effect, however, we are introducing additional degrees of freedom to the system by allowing different polyhedral sizes, while not introducing additional distance constraints.

We may speculate that the unusually high density of the analcime group is connected to the dominance of the framework in the pressure-induced phase transition. The influence of the flexibility window of less dense zeolites on their pressure-induced phase transitions will be an interesting avenue of research.

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