High-pressure behavior and crystal-fluid interaction under extreme conditions in ==zeolite== paulingite [PAU-topology]

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High-pressure behavior and crystal-fluid interaction under extreme conditions in pauligite [PAU-topology]

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Abstract

The compressional behavior and the P-induced crystal-fluid interaction of a natural

paulingite-K have been explored on the basis of *in-situ* single-crystal and powder X-ray

diffraction, and *in-situ* single-crystal Raman spectroscopy with a diamond anvil cell and

a series of diverse pressure-transmitting fluids (*i.e.*, silicone-oil, methanol:ethanol = 4:1,

methanol:ethanol:water = 16:3:1). No evidence of any phase transition was observed

within the P-range investigated, independent on the used P-fluids. The compressional

behavior of paulingite is significantly different in response to the different nature of the

P-fluids. A drastically lower compressibility is observed when the zeolite is compressed

in methanol:ethanol or, even more noticeably, in methanol:ethanol:water mix. We

ascribe this phenomenon to the different crystal-fluid interaction at high pressure: 1)

silicone-oil is a "non-penetrating" P-medium, because of its polymeric nature, whereas

2) methanol-ethanol and water are "penetrating" P-fluids. The P-induced penetration

processes appear to be completely reversible on the basis of the X-ray diffraction data

alone. In contrast, the Raman spectra collected after the high-pressure experiments show, unambiguously, that a residual fraction of methanol and/or ethanol (and probably even extra H_2O) still resides in the zeolitic sub-nanocavities; such molecules are spontaneously released after a few days at atmospheric pressure. The actual compressibility of paulingite-K is that obtained by the compression experiment in silicone-oil, with an isothermal bulk modulus $K_0 = \beta_0^{-1} = 18.0(1.1)$ GPa

Keywords: Paulingite; high pressure; X-ray diffraction; compressibility; crystal-fluid interaction.

1. **Introduction**

Paulingite is a rare zeolite, found in vesicles in basalt flows, with ideal chemical formula: $(K,Na,Ca_{0.5},Ba_{0.5})_{10}(Al_{10}Si_{32}O_{84})\cdot nH_2O$ (with $n = 27\text{-}44$, $Z = 16$) [1,2]. In nature, K- and Ca-rich paulingite samples have been found [3,4]. The crystal structure of paulingite was solved and refined by Gordon et al. [5] in the space group *Im-3m*, and its tetrahedral framework was designated with the IZA-code "PAU" [6]. A structural re-investigation was carried out later by Bieniok et al. [7] and Lengauer et al. [8]. Paulingite is isotypic with the synthetic ECR-18 [9] and **[Ga-Si-O]**-PAU [10]. The tetrahedral framework topology of paulingite is one of the most complex among the zeolitic framework types. The description of Lengauer et al. [8] is probably the most comprehensive one. The PAU framework type (topological symmetry: *Im-3m*, with idealized $a = 34.838$ Å, [6]) is composed by the secondary building units 4 and 8, forming a connecting double 8-ring (D8R), which links alternatively the α-cage (truncated cuboctahedron) and the γ-cage (gmelinite-type cage). The principal channel systems in PAU framework are represented by two parallel (and independent) sets of a

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three-dimensional channel systems (8-membered ring channels) oriented along the principal axes and shifted ½, ½, ½ against each other. Along [111], a further channel system exists, made by α-cages and a modified form of the levyne-cages called π-cages [8], with a sequence: …π-π-α-π-π… . A view of the tetrahedral framework of paulingite is shown in Fig. 1. The framework density of paulingite is 15.9 T/1000 Å^3 [6]. The maximum diameter of a sphere that can virtually diffuse along a, b or c is 4.07 Å (according to [6]). In natural paulingites, the Si/Al-distribution of the tetrahedral framework was found highly disordered, and a series of extra-framework sites were located [7,8,11].

Lengauer et al. [8] and Bieniok [11] studied the dehydration and accompanying structural distortion of paulingite on temperature variations. To the best of our knowledge, no high-pressure experiments have so far been conducted on paulingite. The elastic properties of this zeolite and its stability field at high pressure are basically unknown. The long "free diameters" of the channel systems make this zeolite a good candidate to explore the P-induced penetration of external molecular species in response to hydrostatic compression, generating the so called "hyper-confinement regime": the behavior of a host-guest system in response to the combined effect of applied pressure, spatial confinement and morphological constraints at the sub-nanoscale [$e.g.$, 12-14]. In this light, the compressional behavior and the P-induced crystal-fluid interaction of a natural paulingite have been explored on the basis of in-$situ$ single-crystal and powder X-ray diffraction, and in-$situ$ single-crystal Raman spectroscopy with a diamond anvil cell and a series of different pressure-transmitting fluids.

2.   Materials and experimental methods

A sample of paulingite from vesicular olivine nephelinite of the Vinařická Hora Hill extinct volcano near Kladno (Czech Republic; GPS coordinates 50.1845°N, 14.0957°E) was used for our experiments. Quantitative electron microprobe analysis in wavelength dispersive mode (EPMA-WDS) was performed on polished single-crystals, optically free of defects, using a CAMECA SX-100 electron microprobe. The system was operated using a defocused electron beam ($\varnothing$ 5 μm), an accelerating voltage of 15 kV, a beam current of 7 nA measured by a Faraday cup and counting times of 10s on the peaks and 5s on the backgrounds. Natural crystals of diopside (for Si, Mg, Ca), jadeite (for Al, Na), rutile (for Ti), magnetite (for Fe), barite (for Ba), celestite (for Sr), and leucite (for K) were used as standards. $K\alpha$ spectral lines were used for quantification of all elements except Ba and Sr ($L\alpha$ lines). The results were corrected for matrix effects using a conventional routine in the CAMECA suite of programs. The chemical formula, obtained by averaging 30 point analyses, and calculated on the basis of 84 oxygen atoms, is the following:

$(Na_{0.37}K_{4.98}Mg_{0.04}Ca_{3.19}Sr_{0.03}Ba_{0.23})(Al_{11.14}Fe^{3+}_{0.05}Si_{30.54})O_{84}\cdot 22.2H_2O$ (Z=16)

($E\%$ = -8.49, R = 0.73, M/(M+D) = 0.60, Δ_{charge} = -0.10) [3,15].

Evidence of dehydration under the electron beam was observed, suggesting that the amount of H_2O molecules per formula unit (m.p.f.u.) might be underestimated. In fact, for some data points we obtained up to 27-28 H_2O m.p.f.u..

A single-crystal of paulingite (160 x 120 x 60 μm), free of defects under polarized microscope, was selected for the *in-situ* diffraction experiment with a diamond anvil cell (DAC). Diffraction data were first collected at ambient conditions with a Stoe StadiVari diffractometer with a 100-W air-cooled Incoatec Mo Iμs X-ray-source, a

high-brilliance 2D-focussing Quazar multilayer optics, and a Dectris Pilatus 300K pixel detector (with a 320-μm Si layer). Data were collected with 0.25° ω-scan step and 30 s of exposure time per frame. The diffraction pattern was indexed with a metrically cubic lattice with $a = 35.147(1)$ Å (Table 1). The reflection conditions were consistent with the space group Im-$3m$. The recorded intensities were integrated using X-AREA (Stoe & Cie GmbH, Germany), and corrected for Lorentz-polarization effects. After correction, the internal agreement factor for the m-$3m$ Laue class was $R_{int} = 0.0846$ (Table 1).

The same crystal was used for the high-pressure (HP) experiment, performed using an ETH-type diamond anvil cell (DAC). The DAC was equipped with two diamond anvils with culet face diameter of 600 μm and tungsten-carbide supports. Using the anvils, a stainless-steel foil of 250 μm thick was pre-indented to a thickness of about 130 μm, and a ~300 μm diameter hole was obtained by electro-spark erosion in the center of the pre-indentation to be used as a P-chamber. The experiment was conducted using a mixture of methanol:ethanol = 4:1 as hydrostatic P-transmitting medium [16], along with a few ruby spheres serving as P-calibrant [17,18]. Unit-cell parameters were measured between 0.0001 (crystal in the DAC with no pressure medium) and 3.3(1) GPa (Table 2). The complexity of paulingite structure, as related to the restricted reciprocal space coverage with the DAC, allowed only the unit-cell parameter measurement at high pressure, while the evaluation of Bragg intensities at the given wavelength does not match the particular requirements of resolution. However, the reflection conditions were consistent with the space group Im-$3m$ for all data points within the investigated P-range.

Two further *in-situ* HP synchrotron X-ray powder diffraction experiments were conducted at the 5A beamline at Pohang Accelerator Laboratory (PAL). An 18 keV

synchrotron X-ray beam of 200 μm in diameter was provided by a sagitally-focusing monochromator and mirrors, and each diffraction data were measured for 1 min on MAR345 imaging plate (Δd/d ~ 10^{-2}). The HP-experiments were performed using a Merrill-Bassett type DAC, equipped with two diamonds anvils (culet face diameter: 500 μm) and tungsten-carbide supports. A stainless-steel foil of 250 μm thick was pre-indented to a thickness of about 120 μm, and a ~200 μm diameter hole was made via electro-spark erosion as a sample chamber. The powdered sample of paulingite was loaded into the gasket hole along with a few ruby chips for the pressure measurements [17,18]. Two independent HP-experiments were performed respectively with: 1) methanol:ethanol:water (16:3:1) mixture (up to 5 GPa) and 2) silicone-oil (up to 2.5 GPa) added into the gasket hole as pressure-transmitting media [16]. At any pressure, the sample was equilibrated for about 15 minutes before the data collection. Unit-cell parameters were refined by Le Bail fitting using the FullProf package [19,20]. The whole diffraction pattern was fitted using the pseudo-Voigt profile function defined as $pV(2\theta) = \eta \times L(2\theta) + (1 - \eta) \times G(2\theta)$, where $L(2\theta)$ and $G(2\theta)$ are the Lorenzian and Gaussian components, respectively, and η is a refinable parameter. The background curve was manually pre-defined and subsequently refined with the equation: $B(2\theta) = a \times B_0(2\theta) \times [(1 + c) \times 2\theta + d] + b$, with $B(2\theta)$ corresponding to refined background at position 2θ and $B_0(2\theta)$ corresponding to pre-defined value of background at the same angular position, and a, b, c, d as refinable parameters. The quality of the HP-diffraction patterns and the complexity of the paulingite structure hindered any attempt of structural refinement by the Rietveld method [21]. The evolution of the unit-cell parameters with P for all three pressure-transmitting media (*i.e.*, methanol:ethanol = 4:1, methanol:ethanol:water = 16:3:1 and silicone-oil) is listed in Table 2 and shown in Fig. 2.

Further experiments on paulingite were performed by *in-situ* Raman spectroscopy using different *P*-transmitting fluids. Room and high-pressure (*P*-range 0.0001- 6 GPa, in compression and decompression) Raman spectra were collected using an Olympus BX41 microscope attached to a HORIBA Jobin Yvon LabRam 800HR confocal Raman spectrometer, equipped with a charge-coupled detector (CCD). The sample was excited with the 532 nm laser. The laser beam was focused on the sample on a spot with nearly 2 μm of diameter (objective 50x). Using an 1800 grooves mm^{-1} holographic grating, the spectra were collected in backscattered geometry in the spectral ranges 60 – 1200 cm^{-1}, with 210 s counting time and 2 accumulations, and 1400 – 4000 cm^{-1}, with 60 s counting time and 2 accumulations. Two different experiments were performed: the first using the mix methanol:ethanol = 4:1 and the second using the mix methanol:ethanol:water = 16:3:1 as *P*-transmitting fluids. The pressure was adjusted and controlled by means of the ruby fluorescence method [17,18]. The position of the fluorescence and Raman bands was measured using a Gauss-Lorentzian de-convolution procedure with the PeakFitv4.12 software, with a precision of 0.2 cm^{-1}. Peak positions are reported in Table 3.

3. Results

3.1 Structure refinement at room conditions

The structure refinement of paulingite based on the intensity data collected at ambient conditions was performed using the SHELXL-97 software [22], starting from the structure model of Lengauer et al [8]. Neutral scattering factors for O, Si, Na, K, Ca, and Ba have been used. A preliminary test based on the Sheldrick's $|E^2-1|$ criterion and on the statistics of distribution of the normalized structure factors ("*E* statistics"), along

with the reflections conditions, suggested the space group *Im*-3*m* as highly likely. The secondary isotropic extinction effect was corrected according to Larson's formalism [23], as implemented in the SHELXL-97 package [22]. The first cycles of the structure refinement were conducted with the framework sites only. The tetrahedral sites were modeled with the scattering curve of Si alone. The extra-framework population was located on the basis of the maxima of the difference-Fourier maps of the electron density. The last cycles of refinement were conducted with all the Si sites (*i.e.,* Si1 – Si8) and some of the extra-framework cationic site (*i.e.*, K(1), Ca(1) and K(2A)) modeled anisotropically, and all the other atomic sites modeled as isotropic. The refinement converged to a final $R_1 = 0.0730$ for 2460 unique reflections with $F_o > 4\sigma(F_o)$ and 191 refined parameters, with no significant correlations between refined parameters. The highest/lowest residuals in the difference-Fourier maps were +1.1 and -0.8 $e^-/Å^3$, respectively. Details on the structure refinements are in Table 1. Refined atomic occupancies, coordinates and isotropic/equivalent atomic displacement parameters are in Table 4. Relevant interatomic distances are listed in Table 5.

3.2 In-situ high-pressure X-ray diffraction experiments

The evolution of the unit-cell volume (normalized to the room-*P* values) as a function of pressure with the crystal compressed in methanol:ethanol = 4:1 mix, methanol:ethanol:water = 16:3:1 mix and silicone-oil are shown in Fig. 2. There is no evidence of a phase transition within the *P*-range investigated, even not when using different types of *P*-transmitting fluids. The compressional behavior of the cubic paulingite host structure is significantly different in response to the different nature of the *P*-fluids. The highest compressibility is observed for squeezing the crystal embedded in silicone-oil, while compression in methanol:ethanol and

methanol:ethanol:water mixtures is significantly smaller. The polymeric nature of silicone-oil suggests that this fluid is a "non-penetrating fluid" [12,13] through the zeolitic sub-nanocavities in response to the applied pressure. In this light, the actual compressibility of paulingite is that observed in silicone-oil (*i.e.*, with no crystal-fluid interaction at high pressure). The isothermal Birch-Murnaghan equation of state, truncated to the second-order in energy [24], was used to fit the experimental *P-V* data within the *P*-range investigated (*i.e.* 0.0001-2.5(1) GPa), giving the following isothermal bulk modulus: $K_0 = \beta_0^{-1} = V_0(\partial P/\partial V) = 18.0(1.1)$ GPa ($\beta_0 = 0.055(3)$ GPa^{-1}), with $V_0 = 43793(184)$ Å^3.

The data collected at room conditions after decompression proved that the compressional behavior of paulingite in all the three aforementioned *P*-fluids was completely reversible (*i.e.*, the differences of the unit-cell volumes measured before and after the H*P*-experiments were within 3σ).

3.3 *In-situ high-pressure Raman experiments*

The Raman spectrum of paulingite collected at ambient conditions between 200 – 3600 cm^{-1} is shown in Fig. 3. The Raman active modes between 400 – 600 cm^{-1} (*i.e.*, $\nu 1$, $\nu 2$, $\nu 3$ and $\nu 4$, Table 3) can be tentatively assigned to the motion of oxygen atoms in the plane bisecting the T-O-T bond [*i.e.*, δ(T-O-T) bending], and are very intensive. The mode at about 774 cm^{-1} (*i.e.*, $\nu 5$, Table 3) can be ascribed to the T-O-T symmetric stretching (*i.e.*, ν_s(T-O-T)) and those between 900 – 1200 cm^{-1} (*i.e.*, $\nu 6$, $\nu 7$ and $\nu 8$, Table 3) to the T-O-T anti-symmetric stretching (*i.e.*, ν_{as}(T-O-T)). The weak mode with frequency at about 1640 cm^{-1} (*i.e.*, $\nu 9$, Table 3) and those between 3200 – 3700 cm^{-1}

(*i.e.*, ν12-14, Table 3) are due to the O-H bending or O-H stretching of the H₂O molecules, respectively [25-29].

The evolution of the Raman spectra of paulingite crystals compressed in methanol:ethanol and methanol:ethanol:water mix, respectively, do not show any clear evidence of a phase transition within the *P*-range investigated (Fig. 4), such as band splitting or drastic deviations from observed linear $\partial\nu/\partial P$ trendlines. This observation applied to all series of spectra, independent on having been acquired on compression or decompression. However, all the spectra collected at high pressure are affected by the Raman active bands of the *P*-fluids, in particular by the C-C and C-O stretching modes (900 – 1150 cm⁻¹), and by C-H symmetric and anti-symmetric stretching modes (2750 – 3100 cm⁻¹) [30]. The evolution of the wave numbers with *P* of the three most intensive bands ascribable to paulingite between 400 – 600 cm⁻¹ (*i.e.*, ν1, ν2, and ν3, Table 3) with *P*, with the two different *P*-fluids, is show in Fig. 5. A subtle change of the slope is observed at about 3.5 GPa with both the *P*-fluids, in compression and decompression, but it cannot be related to any detectable symmetry-related change of the X-Ray diffraction patterns at *P* > 3.5 GPa.

Figure 6 shows the Raman spectra of paulingite at 1 bar in air after decompression and being recovered from the pressure cell. For the experiment with methanol:ethanol mix as *P*-fluid, the spectra were recorded 2 days and 4 days after being under atmospheric conditions. For the experiment with methanol:ethanol:water mix, the spectra were collected 1 hour, 1 day and 4 days later. Surprisingly, the most intensive Raman bands ascribable to methanol (or ethanol) (*i.e.*, C-H symmetric and anti-symmetric stretching modes, 2750 – 3100 cm⁻¹) were observed even 2 days after the DAC opening. Only after 4 days the Raman spectrum of paulingite did not show any significant evidence of those.

4.   Discussion

The chemical composition of the sample from Vinařická Hora used in this study shows that this zeolite sample is a "paulingite-K", according to the classification of Coombs et al. [1]. Passaglia et al. [2] reported the EPMA-WDS data of two chemically different paulingites from Vinařická Hora, showing that Ba-rich "paulingite-Ca" and "paulingite-K" occur, though associated with different minerals.

The single-crystal structure refinement of the natural paulingite used in this study confirms the general structure model previously reported. As expected, the extra-framework population obtained in this study and that of the Ba-rich paulingite-Ca of Lengauer et al. [8] show some differences. In particular, in our refinement we located (Table 4): 1) one independent site populated by K and Ba (*i.e.*, K(1)) coordinated to 6 oxygen sites (belonging to the framework) and 4 H_2O molecules; 2) a further K-rich site with high positional disorder and therefore modeled as two sub-sites: K(2A) and K(2B) (with partial site occupancy and only 0.68(4)Å apart) coordinated to 2 H_2O molecules and 7-8 oxygen sites; 3) an additional K-site (*i.e.*, K(3)) with very low site occupancy and coordinated to 6 H_2O molecules; 4) a further K-site (*i.e.*, K(4)) with very low site occupancy and coordinated to 8 oxygen atoms (*i.e.*, bridging O sites of the 8-memberered ring channels running along the principal axes); 5) one Ca-site coordinated to 8 H_2O molecules (*i.e.*, Ca(1)), 6) an additional Ca-site (*i.e.*, Ca(2)), with partial site occupancy and coordinated to 3 oxygen sites and 4 H_2O molecules; 5) a further cationic site (modeled with the scattering curve of Ca) (*i.e.*, Ca(3)) with a very low site occupancy and virtually coordinated by 5 H_2O molecules, lying in the 8-membered ring channels. The population of the cationic sites was modeled on the basis of the site electron density and on the coordination environment. The bonding schemes of the sites

K(1), K(2A), K(2B), Ca(1), and Ca(2)) are well defined. We expect that the bonding environments of the poorly occupied K(3), K(4) and Ca(3) sites are more complex than those here described. Likely, we missed further H_2O sites with very low site occupancy and bonded to K(3), K(4) and Ca(3) sites. K(3), K(4) and Ca(3), along with W(11), W(12) and W(13), populate the 8-membered ring channels oriented along the principal axes and shifted ½, ½, ½ against each other. An inspection of the difference-Fourier maps of the electron density showed a significant degree of disorder in the distribution of the extra-framework population along these channels. In this light, the position of K(3), K(4) and Ca(3), along with those of W(11), W(12) and W(13), should be considered as tentative. We cannot exclude that their electron density maxima could be also due to truncation effect of the Fourier-series.

The chemical formula deduced on the basis of the structure refinement is

$(K_{4.2}Ca_{2.0}Ba_{0.3})_{\Sigma 6.5}T_{24}O_{84} \cdot 20H_2O$, showing a deficit of the cationic and molecular population if compared to the EPMA-WDS data [*i.e.*, with

$(Na_{0.37}K_{4.98}Mg_{0.04}Ca_{3.19}Sr_{0.03}Ba_{0.23})_{\Sigma 8.74}$ and $22.2H_2O$]. This comparative analysis corroborates the suspect that additional H_2O sites and cationic sites, with very low site occupancies, are missed in the structure model here presented.

A drastically lower compressibility is observed when the zeolite is compressed in methanol:ethanol or, even more markedly, in methanol:ethanol:water mix if compared to the compressional pattern in silicone-oil. We can ascribe this phenomenon to the different crystal-fluid interaction at high pressure: 1) silicone-oil is a "non-penetrating" *P*-medium, because of its polymeric nature, whereas 2) methanol-ethanol and water are potentially "penetrating" *P*-fluids [12-14]. The kinetic diameters of H_2O, methanol and ethanol, and the maximum diameter of a sphere that can diffuse through the paulingite

cavities (*i.e.*, 4.07 Å), suggest that at least H_2O and methanol are potentially penetrating molecules. However, we cannot exclude that at high pressure even ethanol behaves as penetrating molecule. When molecules belonging to the *P*-fluid penetrate through the zeolitic cavities in response to the applied pressure, they act as extra-filler of the channels (or cages), making the zeolite less compressible because the cavities are more efficiently stuffed. Among the potentially penetrating molecules used in our experiments, H_2O is the smallest one in kinetic diameter and thus the most penetrating one. This can explain the lower compressibility of paulingite when compressed in methanol:ethanol:water mix if compared to the compression in methanol:ethanol mix.

Previous experiments on *P*-induced penetration of external H_2O molecules showed that this unusual phenomenon can give rise to: 1) new extra-framework sites, with significant change of the configuration of the extra-framework population (*e.g.*, in fibrous zeolites or in laumontite, [31,32]) or 2) increasing the occupancy factors of sites partly occupied at room *P* without new sites [*e.g.*, 33]. The first case usually produces a *P*-induced expansion of the unit-cell volume, with a discontinuity in the evolution of *V vs. P*. In the second case, the evolution of *V vs. P* follows a continuous trend. In paulingite, the scenario is more complex: the penetration process involves H_2O and also methanol (and ethanol). Despite the compressional patterns appear to be continuous in methanol:ethanol and methanol:ethanol:water mix, we are forced to consider that new extra-framework sites occur at high pressure, populated by methanol (or ethanol) atoms. The extra H_2O molecules likely increase the occupancy factors of H_2O-sites partially occupied at room *P*, but we cannot exclude the occurrence of new H_2O sites at high pressure. The lack of the structure refinements at high pressure does not allow any speculation about the amount of *P*-fluids molecules penetrated in response to the applied pressure, neither their location into the structure voids. The X-ray diffraction

data confirm that the penetration of methanol, ethanol and H_2O does not change the long-range order of the structure, thus the lattice properties are kept preserved within the P-range investigated, and the zeolite does not reveal a mechanically-induced structural collapse as commonly manifested by pressure–induced amorphization.

The patterns observed by X-ray diffraction in compression and decompression, with the mentioned penetrating P-fluids, show no clear evidence of partial reversibility of the P-induced penetration phenomena, within the limits of experimental accuracy. The P-induced penetration processes appear to be completely reversible on the basis of the X-ray diffraction data alone. The Raman spectra collected at room conditions after the high-pressure experiments show, unambiguously, that a residual fraction of methanol (and/or ethanol and probably even extra H_2O) still resides into the zeolitic sub-nanocavities; these extra-molecules are spontaneously released into the atmosphere after a few days. Overall, these experimental findings suggest that the amount of residual extra molecules incorporated into the cavities is not significant at the X-ray scale, but it is significant in Raman spectroscopy. This lead to consider that the P-induced crystal-fluid interaction phenomena are better described when complementary X-ray diffraction and spectroscopic techniques are used.

The actual compressibility of paulingite-K is that obtained by the compression experiment in silicone-oil, with an isothermal bulk modulus $K_0 = \beta_0^{-1} = 18.0(1.1)$ GPa. Paulingite appears to be one of the softest zeolite ever found [14].

5. Acknowledgements

6. References

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Table 1. Details pertaining to the data collection protocol, unit-cell parameter and structure refinement of paulingite at ambient conditions.

P (GPa)	0.0001
T (K)	293
Radiation	Mo$K\alpha$
Space group	$Im\text{-}3m$
a (Å)	35.147(1)
Scan type	ω-scan
Step scan (°)	0.25
Exposure time per frame (s)	30
Maximum 2θ (°)	70.40
	$-44 \leq h \leq +54$
	$-54 \leq k \leq +51$
	$-7 \leq l \leq +54$
Measured reflections	31781
Unique reflections	7959
Unique reflections with $F_0 > 4\sigma(F_0)$	2460
R_{int}	0.0846
Number of l.s. parameters	191
$R_1, F_0 > 4\sigma(F_0)$	0.0730
wR^2	0.1295
GooF	1.076
Residuals (e^-/ Å^3)	+ 1.09 / -0.84

Note: $R_{int} = \Sigma|F^2_{obs} - (\text{mean})|/\Sigma[F^2_{obs}]$; $R_1 = \Sigma||F_{obs}| - |F_{calc}||/\Sigma|F_{obs}|$;
$wR_2 = \{\Sigma[w(F^2_{obs} - F^2_{calc})^2]/\Sigma[w(F^2_{obs})^2]\}^{0.5}$,
$w = 1/[\sigma^2(F^2_{obs}) + (0.01 \cdot P)^2]$, $P = [\text{Max}(F^2_{obs},0) + 2 \cdot F^2_{calc}]/3$

Table 2. Unit-cell volumes (normalized to the room-P values) of paulingite *vs.* P, compressed in different P-transmitting fluids.

Silicone-oil		Methanol:ethanol = 4:1		Methanol:ethanol:water = 16:3:1	
P (GPa)	*V/V*$_0$	*P* (GPa)	*V/V*$_0$	*P* (GPa)	*V/V*$_0$
0.0001	1.0000(8)	0.0001	1.0000(5)	0.0001	1.0000(4)
0.69(8)	0.9710(8)	0.16(8)	0.9991(4)	0.56(8)	0.9950(4)
1.01(8)	0.9595(12)	0.38(8)	0.9963(4)	1.02(8)	0.9921(4)
1.56(8)	0.9296(13)	0.49(8)	0.9909(4)	1.56(8)	0.9863(4)
2.11(8)	0.9098(11)	0.89(8)	0.9862(4)	2.11(8)	0.9793(5)
2.53(8)	0.8985(16)	1.18(8)	0.9811(4)	2.53(8)	0.9706(5)
		1.56(8)	0.9674(4)	3.12(8)	0.9667(6)
		1.95(8)	0.9592(4)	4.10(8)	0.9489(7)
		2.23(8)	0.9528(4)	5.12(8)	0.9328(10)
		1.42(8)	0.9638(4)		
		1.73(8)	0.9594(4)		
		2.31(8)	0.9373(5)		
		2.81(8)	0.9205(4)		
		3.33(8)	0.9024(6)		

Table 3. Wave numbers of selected Raman bands of paulingite at room conditions.

Bands	Wave numbers (cm^{-1})
ν_1	422.4
ν_2	473.9
ν_3	495.9
ν_4	557.2
ν_5	774.1
ν_6	937.1
ν_7	993.3
ν_8	1109.8
ν_9	1639.8
ν_{10}	2329.5
ν_{11}	2945.4
ν_{12}	3264.7
ν_{13}	3433.1
ν_{14}	3553.4

Table 4. Fractional site coordinates, site occupancy factors (*s.o.f.*) and displacement parameters (Å^2) based of the structure refinement of paulingite at room conditions.

Site	s.o.f.	x	y	z	Uiso/Ueq
Si(1)	Si, 1	0.31386(4)	0.25	0.18614(4)	0.0124(4)
Si(2)	Si, 1	0.40210(4)	0.25	0.09790(4)	0.0132(4)
Si(3)	Si, 1	0.31323(4)	0.24992(4)	0.09794(4)	0.0127(3)
Si(4)	Si, 1	0.45581(4)	0.10726(4)	0.04437(4)	0.0156(3)
Si(5)	Si, 1	0.40186(4)	0.17827(4)	0.04441(4)	0.0138(3)
Si(6)	Si, 1	0.31264(4)	0.17832(4)	0.04478(4)	0.0126(2)
Si(7)	Si, 1	0.25940(4)	0.10748(4)	0.04447(4)	0.0121(2)
Si(8)	Si, 1	0.17098(4)	0.10761(4)	0.04402(4)	0.0130(3)
O(1)	O, 1	0.16288(16)	0.09301(17)	0	0.025(1)
O(2)	O, 1	0.26830(16)	0.09624(16)	0	0.024(1)
O(3)	O, 1	0.30313(16)	0.18845(17)	0	0.026(1)
O(4)	O, 1	0.40882(18)	0.19009(19)	0	0.033(1)
O(5)	O, 1	0.44802(18)	0.09506(18)	0	0.032(1)
O(6)	O, 1	0.5	0.12147(18)	0.05091(18)	0.031(1)
O(7)	O, 1	0.16055(17)	0.07166(11)	0.07166(11)	0.026(1)
O(8)	O, 1	0.26807(18)	0.06980(12)	0.06980(12)	0.028(1)
O(9)	O, 1	0.14367(12)	0.14367(12)	0.05435(16)	0.027(1)
O(10)	O, 1	0.28540(12)	0.28540(12)	0.19583(17)	0.028(1)
O(11)	O, 1	0.28741(14)	0.28741(14)	0.08865(18)	0.031(1)
O(12)	O, 1	0.44599(19)	0.06980(13)	0.06980(13)	0.034(2)
O(13)	O, 1	0.21522(12)	0.12154(11)	0.05002(11)	0.0238(9)
O(14)	O, 1	0.28773(12)	0.14129(13)	0.05889(11)	0.0287(9)
O(15)	O, 1	0.35719(12)	0.16711(12)	0.05255(12)	0.030(1)
O(16)	O, 1	0.42774(13)	0.14210(14)	0.05662(13)	0.035(1)
O(17)	O, 1	0.29999(12)	0.21641(13)	0.06855(12)	0.029(1)
O(18)	O, 1	0.41533(13)	0.21377(13)	0.07081(13)	0.032(1)
O(19)	O, 1	0.35781(12)	0.26204(12)	0.09051(12)	0.0280(9)
O(20)	O, 1	0.30750(11)	0.23539(11)	0.14187(11)	0.0217(8)
K(1)	K, 0.807(5); Ba, 0.193(5)	0.25596(5)	0.25596(5)	0	0.0431(8)
Ca(1)	Ca, 0.97(1)	0.17895(6)	0.17895(6)	0.17895(6)	0.035(1)
K(2A)	K, 0.86(2)	0.35586(19)	0.10251(12)	0.10251(12)	0.052(2)
K(2B)	K, 0.10(2)	0.3401(12)	0.1104(6)	0.1104(6)	0.033(8)
Ca(2)	Ca, 0.135(1)	0.4595(5)	0.1182(5)	0.1824(5)	0.086(5)
Ca(3)	Ca, 0.26(1)	0.1799(8)	0	0	0.086(1)*
K(3)	K, 0.24	0	0	0	0.086(1)*
K(4)	K, 0.05(1)	0.465(5)	0	0	0.086(1)*
W(1)	O, 1	0.2083(2)	0.2083(2)	0.0534(3)	0.086(1)*
W(2)	O, 1	0.2184(3)	0.2184(3)	0.2184(3)	0.086(1)*
W(3)	O, 1	0.3008(3)	0.1497(2)	0.1497(2)	0.086(1)*
W(4)	O, 1	0.1397(3)	0.1397(3)	0.1397(3)	0.086(1)*
W(5)	O, 1	0.4117(3)	0.1475(2)	0.1475(2)	0.086(1)*
W(6)	O, 0.63(2)	0.2761(5)	0.3376(5)	0	0.086(1)*
W(7)	O, 0.52(2)	0.1407(4)	0.1407(4)	0.2222(6)	0.086(1)*
W(8)	O, 0.67(2)	0.2158(3)	0.2158(3)	0.1324(4)	0.086(1)*
W(9)	O, 0.44(2)	0.2891(7)	0.4182(7)	0	0.086(1)*
W(10)	O, 0.34(3)	0.5	0.1368(9)	0.1368(9)	0.086(1)*
W(11)	O, 0.39(3)	0.2544(15)	0	0	0.086(1)*
W(12)	O, 0.43(2)	0.1266(6)	-0.0267(5)	0.0267(5)	0.086(1)*
W(13)	O, 0.11(3)	0.087(6)	0	0	0.086(1)*

Notes: The *s.o.f.* of the K(4) was fixed in the last cycles of refinement. Si(1-8), K(1), Ca(1) and K(2A) refined anisotropically. * *U*iso restrained to one group value.

Table 5. Relevant interatomic distances based on the structure refinement of paulingite at room conditions.

Si(1) - O(10) x 2	1.632(2)		K(1) - W(6) x 2	2.957(17)
Si(1) - O(20) x 2	1.654(4)		K(1) - W(1) x 2	3.022(10)
<Si(1) – O>	1.643		K(1) - O(3) x 2	2.895(7)
			K(1) - O(17) x 4	3.183(4)
Si(2) - O(18) x 2	1.657(5)			
Si(2) - O(19) x 2	1.634(4)		Ca(1) - W(4)	2.388(18)
<Si(2) – O>	1.646		Ca(1) - W(2)	2.404(18)
			Ca(1) - W(7) x 3	2.434(19)
Si(3) - O(11)	1.633(2)		Ca(1) - W(8) x 3	2.455(16)
Si(3) - O(17)	1.634(5)			
Si(3) - O(19)	1.645(5)		K(2A) - K(2B)	0.68(4)
Si(3) - O(20)	1.639(4)		K(2A) - O(15) x 2	2.871(6)
<Si(3) – O>	1.638		K(2A) - W(5)	2.977(11)
			K(2A) - W(3)	3.041(13)
Si(4) - O(5)	1.640(3)		K(2A) - O(14) x 2	3.153(7)
Si(4) - O(6)	1.648(3)		K(2A) - O(16) x 2	3.305(7)
Si(4) - O(12)	1.628(2)			
Si(4) - O(16)	1.630(5)		K(2B) - W(3)	2.39(4)
<Si(4) – O>	1.637		K(2B) - O(14) x 2	2.80(4)
			K(2B) - O(15) x 2	2.91(3)
Si(5) - O(4)	1.634(2)		K(2B) - W(5)	3.12(3)
Si(5) - O(15)	1.643(5)		K(2B) - O(8)	3.24(3)
Si(5) - O(16)	1.621(5)			
Si(5) - O(18)	1.625(5)		Ca(2) - W(9)	2.16(3)
<Si(5) – O>	1.631		Ca(2) - W(10)	2.24(3)
			Ca(2) - W(5)	2.32(3)
Si(6) - O(3)	1.648(2)		Ca(2) - O(18)	2.53(2)
Si(6) - O(14)	1.645(5)		Ca(2) - W(6)	2.56(3)
Si(6) - O(15)	1.638(5)		Ca(2) - O(19)	2.76(2)
Si(6) - O(17)	1.639(5)		Ca(2) - O(16)	2.82(2)
<Si(6) – O>	1.643			
			Ca(3) - W(11)	2.62(7)
Si(7) - O(2)	1.642(2)		Ca(3) - W(12) x 4	2.30(4)
Si(7) - O(8)	1.625(2)			
Si(7) - O(13)	1.641(4)		K(3) – W(13) x 6	3.06(21)
Si(7) - O(14)	1.631(5)			
<Si(7) – O>	1.635		K(4) – O(5) x 4	3.39(3)
			K(4) – O(12) x 4	3.53(3)
Si(8) - O(1)	1.655(3)			
Si(8) - O(7)	1.635(2)			
Si(8) - O(9)	1.631(2)			
Si(8) - O(13)	1.644(4)			
<Si(8) – O>	1.641			

Figure 1. (*Top*) Skeletal and polyhedral representation of the PAU framework type. (*Bottom*) 8-membered ring channel parallel to <100> viewed perpendicular to the channel axis. Skeletal scheme from: http://www.iza-structure.org/databases/.

Figure 2. Evolution of the unit-cell volumes (normalized to the room-P values) with P of paulingite in three different P-transmitting fluids. The error bars are smaller than the symbols size.

Figure 3. Single-crystal Raman spectrum of paulingite collected at room conditions in the region 200 - 3600 cm^{-1}. The list with the frequencies of the main Raman bands is given in Table 3.

Figure 4. Raman spectra of paulingite, in the regions 200 – 1200 cm^{-1} and 1400 – 4000 cm^{-1}, collected at high pressure in methanol:ethanol = 4:1 mix.

Figure 5. Evolution of the Raman active bands assigned to δ(T-O-T) bending (*i.e.*, ν1, ν2, and ν3, Table 3) with P of paulingite compressed in methanol:ethanol = 4:1 (*left side*) and methanol:ethanol:water = 16:3:1 (*right side*) mix. Data collected in compression (solid symbols) and decompression (open symbols).

Figure 6. Raman spectra of paulingite collected at room conditions after the high-P experiments. The encircled modes are ascribable to molecules of methanol or ethanol incorporated into the zeolite cavities (*i.e.*, C-H symmetric and anti-symmetric stretching modes, 2750 – 3100 cm^{-1}).