

**The effect of pressure on open-framework silicates:
elastic behaviour and crystal-fluid interaction**

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42 **The effect of pressure on open-framework silicates:**
43 **elastic behaviour and crystal-fluid interaction**
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52
53 **Abstract**
54

55 The elastic behaviour and the structural evolution of microporous materials compressed
56 hydrostatically in a pressure-transmitting fluid are drastically affected by the potential crystal-fluid
57 interaction, with a penetration of new molecules through the zeolitic cavities in response to applied
58 pressure. In this manuscript, the principal mechanisms that govern the *P*-behaviour of zeolites with
59 and without crystal-fluid interaction are described, on the basis of previous experimental findings
60 and computational modelling studies.

61 When no crystal-fluid interaction occurs, the effects of pressure are mainly accommodated by
62 tilting of (quasi-rigid) tetrahedra around O atoms that behave as hinges. Tilting of tetrahedra is the
63 dominant mechanisms at low-mid *P*-regime, whereas distortion and compression of tetrahedra
64 represent the mechanisms which usually dominate the mid-high *P* regime. One of the most common
65 deformation mechanisms in zeolitic framework is the increase of channels ellipticity. The
66 deformation mechanisms are dictated by the topological configuration of the tetrahedral framework;
67 however, the compressibility of the cavities is controlled by the nature and bonding configuration of
68 the ionic and molecular content, resulting in different unit-cell volume compressibility in isotypic
69 structures.

70 The experimental results pertaining to compression in “penetrating” fluids, and thus with
71 crystal-fluid interaction, showed that not all the zeolites experience a *P*-induced intrusion of new
72 monoatomic species or molecules from the *P*-transmitting fluids. For example, zeolites with well-
73 stuffed channels at room conditions (*e.g.*, natural zeolites) tend to hinder the penetration of new
74 species through the zeolitic cavities. Several variables govern the sorption phenomena at high
75 pressure, among those: the “free diameters” of the framework cavities, the chemical nature and the
76 configuration of the extra-framework population, the partial pressure of the penetrating molecule in
77 the fluid (if mixed with other non-penetrating molecules), the rate of *P*-increase, the surface/volume
78 ratio of the crystallites under investigations, the temperature at which the experiment is conducted.

79 An overview of the intrusion phenomena of monoatomic species (*e.g.*, He, Ar, Kr), small
80 (*e.g.*, H₂O, CO₂) and complex molecules, along with the *P*-induced polymerization phenomena,
81 (*e.g.*, C₂H₂, C₂H₄, C₂H₆O, C₂H₆O₂, BNH₆, electrolytic MgCl₂·21H₂O solution) is provided, with a
82 discussion of potential technological and geological implications of these experimental findings.

83

84 **Keywords:** zeolites, porous materials, high pressure, compressibility, sorption phenomena, crystal-
85 fluid interaction

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88 Introduction

89 “Microporous materials” are a class of compounds characterized by open-structures with
90 cavities smaller than 20 Å in diameter. Cavities take the form of channels or cages. Materials with
91 pores larger than 20 Å are the so-called “mesoporous materials”. Zeolites are the most common (in
92 Nature) and most used (in industrial processes) microporous materials. The structure of natural and
93 synthetic zeolites is usually built up by a framework of SiO₄-AlO₄-PO₄-tetrahedra. The extra-
94 framework population consists of polar molecules (in particular H₂O) and monovalent or divalent
95 cations, which are commonly exchangeable. In hydrated zeolites, dehydration occurs at
96 temperatures lower than 400°C and is a usually reversible (and spontaneous) process. The
97 tetrahedral framework may be interrupted by (OH, F) groups, which occupy tetrahedral apexes that
98 are not shared with adjacent tetrahedra (Coombs et al. 1997). The general formula for common
99 Si/Al-zeolites is as follows: M⁺_xL⁺⁺_y [Al_(x+2y)Si_{1n-(x+2y)}O_{2n}]· *m*H₂O (where M⁺: monovalent cations;
100 L⁺⁺: divalent cations; usually *m* < *n*).

101 The microporous nature of zeolites governs the four main properties of this class of
102 materials: the selective (and spontaneous) cation-exchange capacity, the catalytic activity (mainly
103 promoted by Brønsted acid sites), the *T*-induced reversible hydration/dehydration processes and the
104 most-recently discovered *P*-induced sorption of molecules. These properties have made natural or
105 synthetic zeolites an object of attention for a long series of applications, spanning from soil
106 enhancement (*e.g.*, zeolites are used as slow release fertilizers, in areas where environmental issues
107 are of concern), environmental remediation, water treatment, animal feeding, biomedical and
108 veterinary applications (*e.g.*, drug delivery systems), cements and concretes production, gas
109 separation, catalysis in the petroleum industry (*e.g.*, almost all the world’s gasoline is produced
110 using zeolites) and nuclear-waste processing (*e.g.*, Komarneni 1985, Mumpton 1999, Kalló 2001,
111 Maxwell and Stork 2001, Ming and Allen 2001, Bish et al. 2003, Ackley et al. 2003, Colella 2011,
112 Gatta et al. 2016a). In this light, zeolites are nowadays considered as an important bulk commodity:

113 the world production of natural zeolites in 2016 was about 2.8 million of tons (price: 100-230 dollar
114 per ton) and the consumption of synthetic zeolites was approximately 1.6 million of tons (U.S.
115 Geological Survey 2017). World reserves of natural zeolites have never been estimated. However,
116 only in the U.S.A., resources are expected to approach 10 trillion tons for zeolite-rich deposits (U.S.
117 Geological Survey 2017).

118 The peculiar behavior of zeolites at non-ambient conditions, *e.g.* at high temperature (*HT*) or
119 at high pressure (*HP*), led to a large number of *in situ* experiments over the last 60 years. More
120 specifically, many experiments were devoted to the behavior of zeolites in response to applied
121 temperature: the mechanisms of *T*-induced dehydration, cation migration and rearrangement of
122 extra-framework populations have been investigated extensively, mainly by *in situ* single-crystal or
123 powder X-ray/neutron-diffraction (*e.g.*, Bish and Carey 2001; Pabalan and Bertetti 2001; Cruciani
124 2006 and references therein). *In situ* experiments on zeolites at high pressure have been done only
125 in the last 15-20 years, mainly for technical difficulties, allowing the description of: *i*) the
126 compressional behavior (and phase stability) in response to the applied pressure, along with the *P*-
127 induced deformation mechanisms at the atomic scale (*e.g.*, Gatta 2008, 2010a, 2010b and references
128 therein), *ii*) *P*-induced penetration of new molecules and its corresponding volume expansion (*e.g.*,
129 Lee et al. 2002a, 2002b), *iii*) *P*-induced variation of the ionic conductivity of zeolites (*e.g.*, Secco
130 and Huang 1999; Rutter et al. 2000), *iv*) and *P*-induced amorphization processes (*e.g.*, Gillet et al.
131 1996; Huang and Havenga 2001; Rutter et al. 2001; Greaves et al. 2003; Gulìn-Gonzàles and
132 Suffritti 2004; Goryainov 2005).

133 The *HP*-behavior of a zeolite compressed in a fluid is drastically dependent on the potential
134 crystal-fluid interaction. Gatta (2008, 2010a) and Gatta and Lee (2014) described the relation
135 between compressibility and microporosity, the framework flexibility (through deformation
136 mechanisms at the atomistic level), and the different role played by framework (*i.e.*, Si/Al-
137 ordering, different cross-linking of the “building block unit”) and extra-framework configuration
138 (*i.e.*, nature of cations and absorbed molecules, ionic valence, ionic radii, coordination number) on
139 the behavior of zeolites when no crystal-fluid interaction occurs. The aim of this work is a
140 comparative analysis, on the basis of previously published data, of the different behavior of zeolites
141 (natural or synthetic) when compressed in “penetrating” and in “non-penetrating” *P*-transmitting
142 fluids (*sensu* Gatta 2008). More specifically, the effects of crystal-fluid interaction on the elastic
143 behavior and on the structure rearrangement of zeolites will be described, along with their potential
144 geological and technological implications.

145

146

147 **Experimental methods**

148 The majority of the *in situ* high-pressure experiments on zeolites have been done by single-
149 crystal and powder X-ray diffraction, as well as IR/Raman spectroscopy, using the so-called
150 Merrill-Basset-type diamond-anvil cell (DAC) (Merrill and Bassett 1974; Miletich et al. 2000);
151 only a few experiments have been performed by *in situ* neutron powder diffraction, using the large-
152 volume Paris-Edinburgh press (*i.e.*, Besson et al. 1992; Colligan et al. 2005; Seryotkin et al. 2005).

153 HP-experiments with a DAC are usually conducted with the sample compressed
154 hydrostatically in a *P*-transmitting fluid. *P*-transmitting media can be stable in the liquid or solid
155 state at ambient conditions, or can be gaseous at ambient conditions and then liquefied at low-*T*
156 before the loading of the DAC, or loaded into the *P*-chamber at high-*P* by means of a gas-loading
157 device. The chemical nature and the behaviour of the *P*-transmitting fluid can play an important role
158 in the HP-experiments on zeolites (Gatta 2008, 2010a; Angel et al. 2007; Gatta and Lee 2014). *P*-
159 fluids can interact or not with the sample. Beside the potential crystal-fluid interaction, which will
160 be extensively described below, it is highly desirable to ensure that the stress applied to the sample
161 is homogeneous, *i.e.* without any differential stress or induced shear strain (Miletich et al. 2000;
162 Angel et al. 2007). A hydrostatic medium cannot support shear stresses, simply because it has no
163 shear strength. Non-hydrostatic stresses generate inhomogeneous strain in the crystal and, as a
164 consequence, (sample) diffraction peaks broadening with a reduction of the signal-to-noise ratio. In
165 addition, non-hydrostatic conditions can modify the compressional patterns of a given material
166 (deduced on the basis of the unit-cell parameters variation with *P*) and can also suppress or promote
167 phase transitions, including the promotion of *P*-induced amorphization phenomena (*e.g.*, Decker et
168 al. 1979; Kenichi 1999; Haines et al. 2001; Machon et al. 2003; Resel et al. 2004). Zeolites are
169 relatively soft materials, and the occurrence of deviatoric stress usually has a dramatic impact on
170 their behaviour at high pressure.

171 For experiments on zeolites at high pressure in a DAC, *P*-calibration has mainly been done
172 by the so-called ruby fluorescence method (*i.e.*, detecting the shift in the R₁ emission line of ruby
173 chips included in the compression chamber; *P*-uncertainty: ± 0.05 GPa, Mao et al. 1986). A further
174 method, especially used for single-crystal experiments, is based on the compressibility pattern of
175 quartz (*i.e.*, with quartz used as an internal standard in the compression chamber; *P*-uncertainty:
176 <0.01 GPa, Angel et al. 1997). For the few experiments by *in situ* neutron diffraction with the large-
177 volume press, lead as an internal standard (Colligan et al. 2005) or the calibration curve of the ILL
178 hydraulic-press load *vs.* *P* (Seryotkin et al. 2005) have been used.

179 The behaviour of a given material at high pressure is usually described on the basis of its
180 **compression** pattern (based on the evolution of the unit-cell parameters with *P*) and of its structural

181 rearrangements at the atomic scale (by structure refinements based on the intensity data collected at
182 high pressure). About zeolites, the compressional behaviour is usually well describable by *in situ*
183 powder or single-crystal experiments. On the other hand, whereas the quality of the HP single-
184 crystal data is usually good enough for structural refinements, the quality of powder data is often
185 not sufficient, and this **has** led to an intensive use of computational modelling techniques – for
186 example, **“rigid unit mode” (RUM) / geometric approaches**, classical force-field **methodologies**, *ab*
187 *initio* structural optimizations and molecular dynamics simulations – as a complementary tool to
188 unravel the structure evolution at the atom**istic** level, as described below. As a matter of fact, all the
189 experiments in a DAC provided intensities, of the Bragg peaks, usually affected by a series of
190 phenomena. Among those, the most critical are: the beam attenuation due to the absorption of the
191 DAC components, parasitic diffraction of the crystalline components of the DAC (especially
192 diamond anvils, their support plates and metal gasket), shadowing effects due to the DAC
193 components (especially gasket and DAC steel body) (*e.g.*, Miletich et al. 2005). For zeolites, which
194 are usually materials with constituents with poor X-ray diffraction properties, the adsorption
195 phenomena are likely the most impacting on the data quality. In addition, in powder experiments an
196 additional phenomenon usually occurs: the preferred orientation of crystallites, as common effect of
197 uniaxial loads.

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199

200 **Computational modeling**

201 The impressive evolution of High Performance Computing (HPC) resources in the last
202 decade, coupled with the concomitant development of theoretical chemistry, has fostered the
203 application of computational techniques to a broad category of problems in zeolite science (Van
204 Speybroeck et al. 2015). Theoretical tools are particularly precious in the study of events occurring
205 at extreme conditions – *e.g.* high-temperature or high-pressure – *i.e.* in cases where obtaining
206 experimental data at atomistic resolution or direct evidences of complex phenomena is often very
207 difficult. In this contribution, we will focus on high-pressure investigations, underlining how
208 modeling, in direct conjunction with experiment, can be used not only to aid structural
209 determinations when refinement of crystallographic data is problematic, but also as a powerful
210 predictive tool able to inspire the design and guide the fabrication of new zeolite materials through
211 the use of high pressure. Nowadays, the scope of computational approaches in exploring pressure
212 effects on open-framework silicates goes well beyond than that of providing the positions of the
213 atoms in the unit cell starting from no empirically based information (Woodley and Catlow 2008).
214 Nevertheless, structural elucidation performed “*in silico*” over the past two decades has fostered a

215 substantial advance of our understanding about how these materials respond to compression,
216 highlighting a key role of the guest species – molecules and cations - in guiding the deformation of
217 the zeolite framework as a consequence of the applied pressure.

218 Computational approaches used in zeolite modeling may be categorized into three broad
219 groups, based on the way in which the electronic structure and interatomic interactions of the
220 system are represented and calculated: *i*) “rigid unit mode” models and their extensions - namely,
221 template-based geometrical approaches; *ii*) classical force-field techniques – basically, Monte Carlo
222 (MC) and molecular dynamics (MD) approaches; *iii*) quantum mechanical methodologies (a.k.a.
223 “ab initio” or “first principles”).

224 The first category accounts solely for the strongest interactions in the system – covalent
225 bonding and steric exclusion – and is constituted by the “flexibility-centered” methods. As they are
226 based on simplified physical models, not only they are computationally fast and convenient, but
227 they can also help interpreting experimental data and/or theoretical results at higher levels of theory.
228 Application of these methods can provide valuable physical insight on the investigated phenomena,
229 which is especially important in the high-pressure studies of zeolites (*e.g.*, Sartbaeva et al. 2006,
230 2008; Wells et al. 2011). Specifically, the “rigid unit mode” (RUM) model (Giddy et al. 1993;
231 Hammonds et al. 1994, Dove et al 2000), treats the zeolite tetrahedra as fundamental, rigid,
232 interacting units and analyzes the flexibility of the structure in reciprocal space. Harmonic
233 constraints are applied to the vertices of the tetrahedra, in order to penalize the separation of two
234 adjacent units. RUMs, in which the polyhedra move as rigid bodies, without undergoing any
235 distortion of their internal geometry, appear at zero frequency and are particularly useful to identify
236 pressure-induced phase transitions. The template-based geometric analysis approach (Wells et al.
237 2002; Sartbaeva et al. 2006; Wells and Sartbaeva 2012, 2015), instead, works in the real-space and
238 considers both the atomic positions, and a set of geometrical templates reproducing the bonding
239 pattern of groups of atoms – tetrahedra, in the case of zeolites. It is a more flexible approach, in the
240 sense that there are still harmonic constraints - which connect atoms to the vertices of the
241 tetrahedral templates - but, unlike in RUM, tetrahedra are not forced by construction to match
242 exactly the input geometry. Rather, the templates and the atomic positions are iteratively relaxed in
243 order to minimize mutual mismatches and avoid overlap between non-bonded atoms. By using this
244 method, distortions from idealized geometry of the polyhedral templates can be readily visualized
245 and quantified. This approach, implemented in the GASP code and recently reviewed (Wells and
246 Sartbaeva 2012, 2015), has been successfully used for framework materials (Sartbaeva and Wells
247 2012). In particular, geometric simulations enabled to define an inherently geometrical feature of
248 the zeolite framework: the “flexibility window” (Sartbaeva et al. 2006, Wells et al 2015) – *i.e.* the

249 interval of unit-cell parameters in which the zeolite tetrahedral units can maintain their ideal shape.
250 This important concept and its usefulness in analyzing pressure-induced transformations will be
251 discussed in the following section, together with some applications to high-pressure studies of
252 zeolites.

253 Methods belonging to the second family are rooted in classical statistical mechanics and the
254 interatomic interactions are modeled by effective potentials (Sanders et al 1984; Demontis et al
255 1987, 1988, 1990; De Boer et al 1995). The parameters of the effective potentials are determined by
256 fitting large sets of either experimental or higher-level computational data (see e.g. Gabrieli et al.
257 2014, 2016). In the study of zeolite materials, the most popular methods are Monte Carlo (MC) and
258 Molecular Dynamics (MD) (Allen and Tildesley 1987; Demontis and Suffritti 1991; Frenkel and
259 Smit 1996). In the former one, the phase space of the system is sampled stochastically according to
260 a given statistical ensemble, and physical quantities – such as energies, bond distances, cell
261 parameters - are calculated by averaging over the sampled configurations. In MD, atoms are
262 represented as classical particles obeying the Newton equations of motion, thus generating a
263 trajectory; physical quantities are obtained by averaging over simulation time. Another widespread
264 approach is grand-canonical MC, which allows to simulate systems with a variable number of
265 particles. This technique was applied to the study of the pressure-induced H₂O intrusion in
266 hydrophobic silicalite-1 and LTA - as reported by Desbiens et al. (2005) and Coudert et al. (2009) –
267 and also to the screening of zeolite structures for two important industrial processes: the purification
268 of ethanol obtained from biomasses and isomerization of heavy alkanes in petroleum refining, both
269 performed under moderate pressure conditions (Bai et al. 2015).

270 While MD can follow the time evolution of a system up to nanosecond scales, with MC it is
271 possible to sample configurations not easily encountered along a standard trajectory. Nonetheless,
272 both of them allow to simulate systems of larger size compared to quantum-mechanical
273 calculations. They are normally applied to zeolites with large unit cells and to dynamic processes
274 such as adsorption, intrusion, and diffusion of extraframework species (e.g., Smit et al. 2008;
275 Combariza et al. 2013, Balestra et al. 2015, Gutiérrez-Sevillano et al. 2016; Viani et al. 2016).
276 Although a few examples of first-principles MD applications are available - such as the site-to-site
277 H₂O diffusion in a partially dehydrated zeolite (Ceriani et al. 2004a) – classical MD still remains
278 the method of choice for these kind of problems. To deal with temperature-induced or pressure-
279 induced structural changes, special techniques are available – for example, constant-pressure
280 molecular dynamics (MD) (Andersen 1980) or the Parrinello-Rahman approach (Parrinello and
281 Rahman 1980; Parrinello and Rahman 1981), where the cell parameters are considered as additional
282 dynamical variables, so that the simulation box is allowed to deform. However, very often the

283 system must cross a significant energy barrier; in those cases, the phase transition becomes very
284 unlikely in the accessible simulation time. To overcome this problem, free-energy minimisation
285 techniques were devised (Gale 1997); they were applied, e.g., to the monoclinic-to-orthorhombic
286 phase transition in MFI zeolite at high temperature (Grau-Crespo et al. 2002). In another powerful
287 approach, named metadynamics (Laio and Parrinello 2002; Martonak et al. 2003), penalty functions
288 prevent the simulation from visiting again previously sampled configurations. Some examples of
289 application to zeolites are the temperature-induced reconstructive phase transition from anhydrous
290 Li-ABW to eucryptite (Ceriani et al. 2004b), and the simulation of pressure-induced amorphization
291 in β -eucryptite at 3 GPa (Narayanan et al. 2013). In the latter case, simulations revealed that the
292 amorphization mechanism, at the atomistic level, consisted in the tilting and distortion of tetrahedra
293 centered at Al/Si sites, accompanied by changes in the Al coordination and disordering of Li
294 cations.

295 In the third category of computational approaches, the electronic structure of the system is
296 described quantum-mechanically ("from first principles") either *via* quantum chemistry methods –
297 *i.e.*, by solving the time independent Schrödinger equation for the electronic wavefunction– or
298 through Density Functional Theory (DFT) approaches, where the energy as an unique functional of
299 the electronic density. Since the exact form of the functional is unknown, approximated expressions
300 are adopted (Parr and Yang 1989). In the simplest one, the local density approximation (LDA), the
301 exchange correlation energy functional is calculated using the expression of a homogeneous gas of
302 free electrons. To model zeolites, more accurate functional forms are used, which include
303 dependency from the gradient of the density and are known as Generalized Gradient (GGA)
304 approximations (*e.g.*, Perdew 1986; Becke 1988; Lee et al. 1988; Perdew et al. 1996; Wu 2006;
305 Perdew et al. 2008). Hybrid functionals, which combine DFT with Hartree-Fock exchange (*e.g.*,
306 Becke 1993; Adamo and Barone 1999) can also be adopted; they are more accurate but more
307 demanding than pure-DFT functionals. Also, an approximate treatment of dispersion effects -
308 particularly crucial for modeling *e.g.* the sorption of hydrocarbons in zeolites - may be introduced
309 through the use of long-range corrections (*e.g.*, Grimme 2006; Tkachenko and Scheffler 2009;
310 Grimme 2011).

311 Several functionals have been proposed over the years, and new ones are continuously
312 developed. In this rapidly evolving scenario, benchmarking plays a crucial role to ensure that the
313 choice of functional would be appropriate for the system under investigation. Benchmarking studies
314 are generally designed to identify a functional (or a group of functionals) able to model a given set
315 of physical quantities – *e.g.* cell parameters, bond distances and angles, vibrational and elastic
316 properties – for a series of zeolite types by achieving a reasonable compromise between accuracy

317 and cost. In this respect, dispersion-corrected GGA functionals perform particularly well, as it
318 emerges from a series of recent benchmarks. Such detailed benchmark studies were performed both
319 on hybrid functionals (Görtl and Hafner 2012; Görtl et al. 2012; Coudert 2013; Román-Román and
320 Zicovich-Wilson 2015) and on GGA functionals using extensive databases of experimental data on
321 aluminosilicate (Fischer 2015; Fischer et al. 2015; Bryukhanov et al. 2017) and neutral framework
322 zeolites (Fischer 2016, 2017).

323 First principles methodologies can properly describe the breaking and forming of chemical
324 bonds occurring, *e.g.*, in chemical reactions, or in reconstructive phase transitions, but imply a high
325 computational overhead. Fortunately, the crystalline lattice of zeolites can be modeled by using
326 either periodic-DFT (*e.g.*, Ballone et al. 2002; Otero Arèan et al. 2008; Marx and Hutter 2009) or
327 periodic ab initio methods (Pisani 1996, 1999; Dovesi et al. 2005; Larin et al. 2005; Demichelis et
328 al. 2010), where a simulation box - characterized by a given atomic content, corresponding *e.g.* to
329 the crystallographic unit cell of the studied material - is replicated in the three dimensions forming
330 an infinite lattice. Tensorial schemes for ab initio calculations of elastic properties (bulk modulus,
331 shear modulus, Poisson ratio, etc.) at high pressure have been also implemented (*e.g.*, Erba et al.
332 2017) and tested on garnets and other minerals (Erba et al. 2014a, 2014b).

333 While standard (static) quantum chemical methods can accurately describe a limited number
334 of atoms, classical approaches are more appropriate for an extended zeolite system. These
335 methodologies can be combined giving rise to hybrid quantum mechanics/molecular mechanics
336 (QM/MM) (see *e.g.* Bludský et al. 2005; Morpurgo 2015); hybrid ab initio/DFT variants have also
337 been proposed (see *e.g.* Tuma and Sauer 2004, 2006; Piccini et al. 2016). Other approaches aimed
338 at bridging the gap between first-principles and classical descriptions are based on the partitioning
339 of the total electron density among individual subsystems (Wesolowski and Warshel 1993;
340 Tabacchi et al. 2005; Maertzke et al. 2009; De Silva and Wesolowski 2012), which maintains an
341 accuracy level suitable for modeling *e.g.* dye-zeolite hybrid composites (Zhou et al. 2013). There
342 are, however, situations where both a quantum-mechanical treatment of the electronic structure and
343 a description of thermal effects via the atomic motion are needed. These requirements can be
344 satisfied by the first principles molecular dynamics (FPMD) approach, originally proposed by Car
345 and Parrinello (Car and Parrinello 1985; Remler and Madden 1990; Marx and Hutter 2009).

346 FPMD enables to study the time evolution of a system with first-principles accuracy,
347 because the forces on the atoms at each MD time step are obtained using a quantum mechanical
348 description of the electrons. More commonly, the electronic structure is treated with DFT (Marx
349 and Hutter 2009), even though wavefunction-based variants of this technique exist as well. The Car-
350 Parrinello scheme for FPMD defines a fictitious dynamical system in which the potential energy

351 surface depends on both the nuclear and the electronic degrees of freedom (Car and Parrinello
352 1985). The electronic wavefunction coefficients are propagated in time as classical degrees of
353 freedom, and their dynamics generates at each time step the correct adiabatic electronic
354 configuration corresponding to the new ionic positions. Hence, if at the beginning of the simulation
355 the electronic orbitals correspond to the ground state, they will follow the motion of nuclei
356 adiabatically, and remain in that state as the nuclear configuration evolves in time. However, the
357 dynamical parameters (fictitious electronic mass and time step) have to be chosen so that the
358 transfer of energy between ions and electrons is kept very small during the simulation (Remler and
359 Madden 1990). This condition is easily satisfied in systems with a large energy gap, such as
360 zeolites.

361 FPMD has been implemented using different types of basis sets (Lippert et al. 1999;
362 VandeVondele et al. 2005; Marx and Hutter 2009), namely plane waves (PW), projector augmented
363 waves (PAW), and localized functions (VandeVondele et al. 2005). Periodic boundary conditions
364 are generally adopted in all cases. In applications to zeolites, this implies the capability of
365 describing the full crystal from first principles, thus properly reproducing the flexibility properties
366 of the framework – which are especially important in governing the response of zeolites to an
367 applied pressure. Whereas the direct simulation of a pressure-induced phase transition would
368 require variable cell parameters, in many other cases it is convenient to hold the cell parameters
369 fixed at the values experimentally determined at such pressure conditions (where available),
370 which are known to be very accurate. Importantly, no constraints – either symmetry restraints or
371 “frozen” nuclear positions - are normally imposed to the atoms in the simulation cell, which are
372 thus left free to move according to their own potential energy surface determined by the interatomic
373 interactions.

374 FPMD simulations, due to their high computational cost, are limited to elapsed times of the
375 order of tens of ps, which are too short to observe activated events such as *e.g.* chemical reactions,
376 or reconstructive phase transitions. Such processes can be considered rare events on the FPMD time
377 scale. To address these problems, rare-event sampling techniques have been developed, such as the
378 above mentioned metadynamics (Laio and Parrinello 2002; Barducci et al. 2011). In the case of
379 zeolites, the FPMD extension of metadynamics (Iannuzzi et al. 2003) has been mainly applied to
380 study activated processes occurring at high temperature, *e.g.* the methanol-to-olefin process
381 catalyzed by H-SAPO-34 (De Wispelaere et al. 2015), and the fabrication of zeolite hybrid
382 functional materials (Calzaferri et al. 2003; Cao et al. 2016) through the intrusion of dye molecules
383 inside the one-dimensional channels of zeolite L (Tabacchi et al. 2016). Other popular statistical
384 sampling methods are the so-called “bluemoon” ensemble (Carter et al. 1988), the “transition path

385 sampling" (Dellago et al. 1999) or the "nudged elastic band" (Jónsson et al. 1998; Sheppard et al.
386 2012). In all cases, a basic knowledge of the behavior of the system at equilibrium conditions -
387 which may generally be obtained via exploratory simulations – is **needed**. Considering the rapid
388 and continuous increase in computing power, it may be foreseen that these methods will become
389 useful tools in the prediction of the high-pressure behavior of zeolite materials.

391 **High-pressure behavior without any crystal-fluid interaction**

392 In order to describe the HP-behavior of a zeolite without any interference of the P -fluid, the
393 sample (polycrystalline or single crystal) is compressed in a “non-penetrating” P -transmitting
394 medium (*sensu* Gatta 2008): a fluid made by molecules which cannot penetrate through the
395 structure cavities in response to the applied pressure. Usually, the mix methanol:ethanol = 4:1,
396 glycerol, isopropanol, perfluorether, fluorinert, or various grades of silicone-oils are used as
397 nominally non-penetrating P -transmitting fluids (Angel et al. 2007; Gatta 2008; Klotz et al. 2009).

398 Simulation or structure refinements showed that open-framework materials accommodate
399 the volume compression mainly by *tilting*, *distortion* and *contraction* of the primary building units:
400 the tetrahedra. *Tilting* of tetrahedra occurs around the bridging oxygen atoms that act as “hinges”; as
401 a consequence, this mechanism does not generate distortion of the tetrahedra, but changes the inter-
402 tetrahedral T-O-T angles with P . *Distortion* of tetrahedra is reflected by changes in the intra-
403 tetrahedral O-T-O angles, preserving the average T-O bond length. *Contraction* of tetrahedra is
404 expressed by compression of the T-O bond distances. Tilting, distortion and contraction of
405 tetrahedra act simultaneously at any pressure. However, tilting is an energetically less-costly
406 mechanism if compared to distortion or contraction, and this corroborates the experimental
407 evidence that tilting is the dominant mechanism at low- P regime, whereas distortion and then
408 contraction become dominant at higher pressure, when tilting cannot accommodate the effect of
409 pressure efficiently any further (Gatta 2010a; Gatta and Lee 2014). In other words, there is a
410 hierarchy of the deformation mechanisms (Gatta 2010a), and this is independent on the nature of the
411 cations in tetrahedral coordination (*e.g.*, Si, Al, P, Be, B,...). As a matter of fact, at least up to 3-5
412 GPa, tetrahedra behave as “rigid-units” at least to a first approximation: *e.g.*, the estimated fictive
413 bulk modulus (defined as $K_{P_0, T_0} = -V_0(\partial P/\partial V)_{P_0, T_0} = 1/\beta_{P_0, T_0}$, where β_{P_0, T_0} is the volume
414 compressibility coefficient at ambient conditions) of SiO_4 is 580(24) GPa (Zhang et al. 1998).
415 Significantly, the rigid-unit behavior is fully supported by available atomistic data obtained from
416 FPMD simulations, and may also hold at above the 5 GPa threshold. For example, the Si and Al
417 tetrahedral units of the zeolite gismondine undergo volume contractions of only 0.05% and 0.08%
418 respectively at 7.6 GPa (Betti et al. 2007). **Moreover, the above mentioned hierarchy of deformation**

419 mechanisms is further corroborated by recent lattice-dynamics calculations on a low-silica zeolite
420 with LTA framework (Gulin-Gonzàles et al. 2016).

421 Tilting of tetrahedra can be observed in all the *HP*-experiments on zeolites, whose structure
422 refinements or simulations are available. A common effect of tilting is the deformation of the
423 secondary building units (SBU) of the zeolitic frameworks, which are represented by “open forms”
424 (*e.g.*, 4-, 5-, 6-, 8-, 10- or 12-membered rings of tetrahedra) or “3D closed forms” (*e.g.*, double 6-
425 membered rings, T_5O_{10} units of the “fibrous zeolites group”, $T_{10}O_{20}$ units of the “heulandite group”;
426 Baerlocher et al. 2007). Usually, tilting of tetrahedra produces a continuous rearrangement of the
427 structure, reflected by a monotonic unit-cell volume compression. It is common, for example, to
428 observe that the ellipticity of the zeolitic channels tends to increase monotonically with *P*, *via* tilting
429 of the tetrahedra that confine the channels, without any “inversion” (Gatta and Lee 2006); an
430 “inversion” in ellipticity at high-*P* usually leads to a phase transition. More complex is the
431 description of the response, at the atomic scale, of zeolites with secondary building units made by
432 3D closed forms, which behave as “rigid block-units” at a first approximation: at high pressure,
433 their structures respond first by rotation of the SBUs, followed by SBUs compression (but keeping
434 the tetrahedra undeformed), and finally by deformation or compression of the tetrahedra
435 themselves. The first two mechanisms are substantially based on tilting, and are very efficient to
436 accommodate the effect of pressure at low-medium *P*-regime. Two examples in this respect are
437 those of the “fibrous zeolites group” (NAT, THO, and EDI framework type; SBU: T_5O_{10} or 4=1
438 unit; Baerlocher et al. 2007) and of the “heulandite group” (HEU framework type; SBU: $T_{10}O_{20}$ or
439 4-4=1 unit; Baerlocher et al. 2007). All fibrous zeolites studied at high-*P* (*i.e.*, natrolite, scolecite,
440 thomsonite, edingtonite) show a similar deformation mechanism in response to applied pressure:
441 cooperative rotation (anti-rotation) of the SBU about the axis of the SBU-chains, which in turn
442 gives rise to the compression of the 8-membered rings channels (parallel to the SBU chain axis),
443 with an increase of their ellipticity (Gatta 2005; Gatta and Wells 2004; Gatta et al. 2016b). In
444 fibrous zeolites, the estimated fictive bulk modulus of the SBU is approximately twice those of the
445 zeolites (*i.e.*, ~115 GPa for the SBU *vs.* ~43 GPa for natrolite, ~55 GPa for scolecite, ~49 GPa for
446 thomsonite and ~59 for edingtonite) (Gatta 2005). The identical framework topology of natrolite
447 and scolecite (*i.e.*, NAT, Baerlocher et al. 2007) allowed also to speculate about the role played by
448 the extra-framework population on the compressional behavior of isotopic materials: the framework
449 topology control the main deformation mechanisms (in this case: cooperative anti-rotation of the
450 SBU by tilting of tetrahedra), but the channel population (*i.e.*, ionic radius of cations, valence, and
451 their bonding configuration) controls the compressibility of the cavities, with a resulting different
452 compressibility of unit-cell volume. In addition, fibrous zeolites provide further experimental

453 evidence: ordering of the Si/Al in the tetrahedral sites does not influence structure compressibility,
454 which is virtually identical in orthorhombic (fully ordered Si/Al distribution) and tetragonal (highly
455 disordered Si/Al distribution) edingtonite (Gatta et al. 2004a, 2004b).

456 In heulandite, the corrugation (and thus the shortening) of the zig-zag chains of SBUs,
457 parallel to [102], is the main deformation mechanism in response to applied pressure, which acts
458 basically by tilting of tetrahedra. Also in this case, the estimated fictive bulk modulus of the SBU
459 (*i.e.*, ~63 GPa) is approx. twice that of the zeolite (*i.e.*, ~28 GPa) (Comodi et al. 2001, Gatta et al.
460 2003). In general, the experimental findings on zeolites with closed-form SBUs show that the
461 compressibility of the structure is the combined effect of soft channels and relatively stiff 3D SBUs
462 compression.

463 Important quantitative insight on the tilting deformation mechanism may be obtained by
464 investigating how the T–O–T angles evolve as a function of increasing pressure even in structures
465 with “open” SBU. Interestingly, such angles were identified to be responsible of the pressure-
466 induced framework modification up to 8–10 GPa on the basis of integrated experimental-
467 computational data collected for a series of zeolites – bikitaite (BIK framework type, Ferro et al.
468 2002; Fois et al. 2002a; Baerlocher et al. 2007), yugawaralite (YUG framework type, Fois et al.
469 2005a,2005b; Baerlocher et al. 2007), and gismondine (GIS framework type, Betti et al. 2007;
470 Baerlocher et al. 2007). For example, in gismondine, the average value of the T–O–T angle
471 decreases significantly (from 142.8° to 137.8°) in passing to room pressure to 7.4 GPa (Betti et al.
472 2007). As a general trend, the decrease of the average T–O–T angle correlates with both applied
473 pressure and volume contraction: namely, the higher the compression, the higher the variation of the
474 angle. This analysis, therefore, brings further support to the intuitive argument that the framework
475 responds to compression by modifying its most flexible element, that is, the junction between
476 tetrahedral units.

477 A few representative examples can be considered in order to highlight that tilting can act as
478 the main deformation effect even when the saturation of one mechanism is achieved at low- P . Gatta
479 et al. (2005) and Gatta and Wells (2006) reported, by experiments and computational modelling,
480 that the framework of levyne (LEV framework type, Baerlocher et al. 2007) reacts, under
481 compression, by tilting of tetrahedra following two distinct deformation mechanisms: the first
482 dominant at $P < 1$ GPa, through the cooperative rotation of tetrahedra belonging to the double 6-
483 membered rings; the second at $P > 1$ GPa, through compression of the 4-membered ring (“joint-
484 unit”) between the aforementioned 6-membered rings, as the double 6-membered rings have already
485 reached a limit configuration at $P \sim 1$ GPa. These two mechanisms can explain the anomalous
486 elastic behavior of levyne, with an increase of the c -axis length between 0-1 GPa followed by a

487 monotonic compression at $P > 1$ GPa. Up to 5 GPa, structure refinements and simulations show no
488 distortion or compression of the tetrahedra, at a significant level, in lewyne structure.

489 More recently, Comboni et al. (2017) reported the HP-behavior of phillipsite (PHI
490 framework type, Baerlocher et al. 2007) up to 9.4 GPa by an *in situ* single-crystal diffraction
491 experiment. Despite a hydrous P -transmitting fluid was used (*i.e.*, methanol:ethanol:water =
492 16:3:1), no clear evidence of P -induced penetration of extra molecules through the zeolitic cavities
493 was observed within the P -range investigated. However, two different compressional regimes
494 occur. Between 0.0001 and 2.0 GPa, phillipsite behaves as an unusually stiff porous material: the
495 refined bulk modulus is $K_{P0,T0} = 89(8)$ GPa. Between 2.0 and 9.4 GPa, the material turns to be
496 drastically softer and its bulk modulus decreases to $K_{P0,T0} = 18.8(7)$ GPa. The structure refinements
497 proved that, at $P > 2$ GPa, a P -induced change in the configuration of the H₂O molecules, coupled
498 with a change of the tilting mechanisms of the framework tetrahedra, gives rise to a completely
499 different compressional behavior. Accordingly, the evolution of the monoclinic β angle with
500 pressure shows two distinct trends in the two compressional regimes: with a negative slope between
501 0.0001-2.0 GPa, and a positive slope between 2.0-9.4 GPa. The tilting of the tetrahedra, in response
502 to the hydrostatic compression, causes the deformation of the 8-membered ring of tetrahedra which
503 confine the [010] channel and, in turn, the inversion of β vs. P trend. In this specific case, the
504 saturation of a tilting mechanism and the role played by the extra-framework population concur to a
505 change of the compressional behavior, without any P -induced phase transition.

506 Levyne and phillipsite are two representative examples of zeolites which do not undergo any
507 P -induced phase transition, despite they experience a change of deformation mechanisms, reflected
508 by a change of the unit-cell volume compressional pattern. The list can be extended for example to
509 gobbinsite (GIS framework type, Baerlocher et al. 2007) (Gatta et al. 2010, 2012; Gatta and Lotti
510 2011), cancrinite (CAN framework type, Baerlocher et al. 2007) (Lotti et al. 2012) or nepheline (a
511 feldspathoid, Gatta and Angel 2007). On the other hand, some zeolites with high “framework
512 density” (FD, defined as the number of T atoms in a volume of 1000 Å³, Baerlocher et al. 2007) or
513 hydrophobic zeolites (*i.e.*, zeolites nominally without any extra-framework population) tend to react
514 to applied pressure with phase transitions, which are usually displacive in character, and the high-
515 pressure polymorphs can have distorted tetrahedra. A representative example, in this respect, is that
516 of zeolites of the analcime-group (*i.e.*, analcime, leucite, wairakite and pollucite; ANA framework
517 type, Baerlocher et al. 2007): all these zeolites experience a first-order phase transition from the
518 high-symmetry low- P polymorph (cubic analcime and pollucite, tetragonal leucite and monoclinic
519 wairakite) to a triclinic high- P polymorph, at relatively low- P (~ 1 GPa for analcime, ~ 2.4 GPa for
520 leucite, ~ 2.5 GPa for wairakite, ~ 0.7 GPa for pollucite; Gatta et al. 2006, 2008, 2009a; Ori et al.

521 2008a). The phase transitions are fully reversible upon decompression. For analcime, in particular,
522 structure refinements (based on single-crystal intensity data) revealed that the main deformation
523 mechanisms of the HP-polymorph act through deformation of the 4- and 6-membered rings of
524 tetrahedra by tilting of the polyhedra, along with their significant distortion. A spectacular HP-
525 behavior with two *P*-induced phase transitions in all-silica ferrierite (FER framework type,
526 Baerlocher et al. 2007) was recently reported by Lotti et al. (2015a), by *in situ* single crystal and
527 powder X-ray diffraction experiments, using penetrating and non-penetrating fluids. Using silicone
528 oil, as a polymeric non-penetrating *P*-fluid, the experimental data show a remarkable flexibility of
529 the ferrierite framework at high pressure with two displacive phase transitions, following the path
530 *Pmnn*-to-*P12₁/n1*-to-*P2₁/n11*, the first at ~0.7 GPa and the second at ~1.24 GPa (Fig. 1). The
531 transitions are fully reversible. As reported by Lotti et al. (2015a), the two monoclinic space groups
532 do not share a group-subgroup relationship: the multistage phase transition requires an intermediate
533 structure with *P*-1 symmetry, as common subgroup of both *P12₁/n1* and *P2₁/n11*. The three
534 polymorphs share a virtually identical bulk compressibility, but with a different anisotropic
535 compressional pattern. Also in this case, the structure evolution in response to applied pressure is
536 mainly governed by tilting, and the phase transitions are the effect of deformation mechanisms
537 saturation, followed by the promotion of new ones in a structure configuration which is
538 energetically more favourable.

539 Phase transitions can drive to “new materials” which are industrially important: a new
540 zeolite ITQ-50 was obtained by compressing a synthetic all-silica zeolite ITQ-29 in a DAC with a
541 non-penetrating *P*-transmitting fluid (Jordà et al. 2013). As from the crystallographic data, it was
542 possible to obtain only the cell parameters of the new material and the structure was obtained with
543 the aid of classical force field calculation. Remarkably, the pressure-synthesized microporous
544 material showed better performances than the precursor zeolite in the propene/propane separation -
545 an important industrial process.

546 Besides the modification induced to the framework, it is useful to highlight how of the
547 organization of the extraframework species is modified by compression. For example, the natural
548 zeolite bikitaite hosts in its one-dimensional channels hydrogen bonded chains of H₂O molecules,
549 which at room conditions display a behaviour typical of a solid phase of water at low
550 dimensionality – hence the name “one-dimensional ice” – (Fois et al.1999;2001b) and an
551 impressive resistance towards dehydration despite being not hydrogen-bonded to the framework
552 (Ceriani et al. 2004a). Indeed, upon compression, the one-dimensional ice structure persisted up to
553 5 GPa, but new hydrogen bonds were formed between the H₂O chains and the framework oxygen
554 atoms (Ferro et al. 2002). Even more intriguingly, a similar behaviour was found when bikitaite was

555 compressed in penetrating (water-containing) medium up to 4 GPa: the H₂O chains were preserved
556 up to the highest pressure with no intercalation of additional H₂O molecules (Seryotkin 2016),
557 highlighting thus the exceptional stability of this confined H₂O nanostructure. Actually, also the
558 synthetic zeolite Li-ABW hosts in its monodimensional channels the same peculiar H₂O wires (Fois
559 et al 2001a;2001b): in this case, however, the supramolecular H₂O architecture is easily disrupted
560 when moderate pressures are applied (Fois et al. 2008a). Theoretical calculations revealed that the
561 reason why these two similar systems display such a different response to compression is the
562 electric polarization of the zeolite framework, which is considerably higher in bikitaite compared to
563 Li-ABW, thus providing a greater electrostatic stabilization to the H₂O chain (Fois et al.
564 2001a,2008a). Porous materials with monodimensional channel systems can host other interesting
565 examples of confined H₂O nanostructures - such as the H₂O-triple helix in VPI-5 aluminophosphate
566 (Fois et al. 2002), or the pressure-induced H₂O nanotube in zeolite LTL (Lee et al. 2007). The
567 interest in the behaviour of one-dimensional channel materials – at both standard and high-*P*
568 conditions - stems from the possibility of filling them, upon H₂O evacuation, with guest species of
569 suitable size, for example drugs (Delle Piane et al. 2014) or luminescent molecules, giving rise to
570 low-dimensionality systems endowed by technologically appealing properties (see, e.g. Calzaferri et
571 al. 2003; Fois et al. 2005c; Manzano et al. 2013; Gigli et al. 2014; Cucinotta et al. 2014, Calzaferri
572 2017; Gartzia-Rivero et al. 2017).

573 The key question is: why some zeolites experience *P*-induced phase transitions (with no
574 crystal-fluid interaction) and others not? And, in addition, which are the limit conditions above
575 which an open-framework structure undergoes a phase transition? Is it possible to predict a
576 transition pressure? The state of the art of the knowledge does not allow to provide an unambiguous
577 answer to these questions. However, the experimental findings about *P*-induced phase transitions in
578 zeolites (with no crystal-fluid interaction) appear to be well predictable by the “flexibility window”
579 theory. The “flexibility window” (Sartbaeva et al. 2006) is a pervasive property of zeolitic
580 frameworks, and it defines a range of densities over which the corner-sharing TO₄ units, making up
581 the framework, can in principle be made perfectly tetrahedral (*i.e.*, a range of densities over which
582 the tetrahedra retain their holosymmetric shape). This window is limited at high density by contacts
583 between oxygen atoms on neighbouring TO₄ units, and at low density by extension of the intra-
584 tetrahedral T-O bonds (though not, in general, by linear T-O-T angles). Gatta et al. (2009b) reported
585 that the ANA cubic framework, for example, displays a narrow flexibility window: the framework
586 could be compressed by only 3% in volume before oxygen atoms came into contact. The geometric
587 simulations on the ANA framework (using a tetrahedral geometry appropriate to the Si:Al ratio of
588 natural cubic analcime) (Sartbaeva et al. 2006, 2008; Wells et al. 2011), with the experimental cubic

589 unit-cell parameters measured at high pressure (Gatta et al. 2006), showed that the structures are
590 perfectible over the whole observed range of cubic analcime, from ambient conditions up to around
591 1 GPa. The theoretical upper and lower limits of the flexibility window in cubic analcime were
592 obtained by simulations using the unit-cell parameters outside the range observed in the experiment.
593 The low-density edge of the window was found to be near the density observed for the analcime
594 structure at ambient conditions (*i.e.*, the ambient structure is close to maximal extension), whereas
595 the high-density edge of the window on compression lies near the last observed cubic structure
596 before the transition. Overall, the *P*-induced phase transition in analcime, observed at about 1 GPa,
597 is well predictable on the basis of the flexibility window of this structure.

598

599 **High-pressure behavior with crystal-fluid interaction**

600 “Penetrating” *P*-transmitting media are a class of fluid which contain molecules able to
601 penetrate, through selective sorption, into the zeolitic cavities in response to applied pressure. This
602 phenomenon implies a drastic effect on the compressional pattern and on the *P*-induced
603 deformation mechanisms at the atomic level. Elemental gaseous media at ambient conditions (*e.g.*
604 helium, nitrogen, neon, argon, xenon, krypton) and small molecules (*e.g.*, H₂O, CO₂) are potentially
605 penetrating media. Even some larger molecules, usually used as *P*-transmitting media (*e.g.*
606 methanol, ethanol, ethylene, ethylene glycol, acetylene) could be considered as potentially
607 penetrating media. Penetrability of external molecules (or atoms) at high pressure is governed by
608 several variables, among those the most important are: the “free diameters” of the framework
609 cavities, the chemical nature and the configuration of the extra-framework population, the partial
610 pressure of the penetrating molecule in the fluid (if mixed with other non-penetrating molecules,
611 *e.g.* *P*(H₂O) in a mixture of alcohols–H₂O), the temperature at which the experiment is conducted.
612 A given molecule can, therefore, act as a penetrating medium for some zeolites and as a non-
613 penetrating medium for other zeolites.

614 The effects of the *P*-induced penetration depend on the nature of the penetrating atoms or
615 molecules through the zeolitic cavities, and, for a comparative analysis, it is convenient to
616 distinguish among monoatomic species, small molecules and larger molecules.

617

618 - *P*-induced penetration of monoatomic species

619

620 Lee et al. (2010) showed that, when compressed in liquid Ar, natural natrolite (of ideal
621 composition Na₁₆Al₁₆Si₂₄O₈₀·16H₂O, NAT framework type, Baerlocher et al. 2007) can incorporate
622 a significant amount of Ar under moderate pressure- and temperature-conditions (*i.e.*, 60 °C for 10
623 h). The *P*-induced penetration of Ar gives rise to a spectacular *P*-induced expansion of the unit-cell

624 volume (*i.e.*, ~6.5% larger unit-cell volume than the starting zeolite) at $P \sim 3.0\text{-}3.5$ GPa, with a new
625 Ar-bearing form of natrolite described as $\text{Na}_{16}\text{Al}_{16}\text{Si}_{24}\text{O}_{80} \cdot 16\text{H}_2\text{O} \cdot 6\text{Ar}$. The expansion of the unit-
626 cell volume is governed by the expansion of the 8-membered ring channels along [001], where the
627 extra-framework population lies. The structure refinement of $\text{Na}_{16}\text{Al}_{16}\text{Si}_{24}\text{O}_{80} \cdot 16\text{H}_2\text{O} \cdot 6\text{Ar}$ showed
628 that Na^+ remains 6-coordinated, with the Ar-Na distances ranging between 2.90-3.22 Å and the Ar-
629 O distances at ~3.24 Å. In other words, Ar interacts *via* short-range van der Waals forces. Natrolite
630 served as an efficient host system for further experiments with monoatomic penetrating species: Xe
631 and Kr. Seoung et al. (2014) reported how Ag-natrolite, ideally $\text{Ag}_{16}\text{Al}_{16}\text{Si}_{24}\text{O}_{80} \cdot 16\text{H}_2\text{O}$, adsorbs
632 xenon into its 8-membered ring channels at 1.7 GPa and 250 °C, while Ag^+ is reduced to metallic
633 Ag^0 and possibly oxidized to Ag^{2+} . The sorption of Xe gives rise to an expansion by 3.2 % of the
634 unit-cell volume, with a weak interaction of Xe and Ag (*i.e.*, Ag-Xe ~3.1 Å). Surprisingly, the
635 sorption of xenon is irreversible after pressure release, and requires heat to desorb. Using liquid Kr
636 as *P*-transmitting fluid, Ag-natrolite adsorbs Kr at 2.1 GPa and after annealing at 250 °C, with a
637 partial reduction of Ag^+ to metallic Ag^0 . The penetration phenomenon leads to a moderate unit-cell
638 volume expansion (only ~1.2%), and appears to be fully reversible under decompression.

639 In zeolites with larger cavities than those in natrolite, the *P*-induced penetration of
640 monoatomic species does not imply a unit-cell volume expansion, but rather a different
641 compressional behavior if compared to that obtained in a non-penetrating fluid. For example, Niwa
642 et al. (2013) reported how the synthetic zeolite Linde-type A (LTA framework type, Baerlocher et
643 al. 2007) compressed in liquid He and Ar shows different compressional patterns, which are, in
644 turn, different if compared to those reported for compression in liquid water (penetrating) or in
645 silicone oil (non-penetrating polymeric fluid). Structure refinements were not performed, leaving
646 open questions about the mechanisms at the atomic scale. However, the evolution of unit-cell
647 volume *vs.* *P* is sufficient to prove that the *P*-induced penetration of He, Ar and H₂O occurs, with a
648 reduction of the compressibility, if compared to that with a non-penetrating fluid, by 50%, 15% and
649 700%, respectively. The sorption of extra H₂O molecules affects dramatically the compressibility of
650 Linde-type A. The reduction of compressibility reflects the “pillar effect” that the new intruded
651 molecules generate, making the zeolitic cavities less compressible (not collapsible).

652

653 - *P*-induced penetration of small molecules

654 Experiments devoted to the *P*-induced penetration of small molecules are probably the most
655 common. The *P*-induced penetration phenomenon was firstly discovered using water, or hydrous
656 mixtures, by Hazen (1983) and Hazen and Finger (1984), on the basis of the significantly different
657 compressional pattern of a synthetic zeolite (*i.e.*, Linde Na-A; LTA framework type, Baerlocher et

658 al. 2007) in different fluids. Lee et al. (2002a, 2002b) reported the very first structure refinements
659 proving the *P*-induced sorption of extra-H₂O molecules, from the *P*-transmitting fluid through the
660 zeolitic cavities (the so called *P*-induced “superhydration”), in a natrolite and its synthetic
661 counterpart K₁₆Ga₁₆Si₂₄O₈₀·12H₂O. Natrolite, ideally Na₁₆Al₁₆Si₂₄O₈₀·16H₂O (NAT framework
662 type, Baerlocher et al. 2007), transforms to Na₁₆Al₁₆Si₂₄O₈₀·32H₂O at ~1.2 GPa (via the
663 intermediate ordered-paranatrolite phase with 24 H₂O molecules per formula unit, stable between
664 0.9 and 1.2 GPa, Lee et al. 2005), doubling the number of molecules p.f.u. of H₂O with a
665 consequent unit-cell volume expansion by ~2.5%, if compared to natrolite stable at ambient *P*. The
666 extra H₂O molecules intruded in the 8-membered ring channel are bonded to Na, which increases its
667 coordination number. The *P*-induced superhydration effect is completely reversible in natrolite but
668 not in its synthetic counterpart K₁₆Ga₁₆Si₂₄O₈₀·12H₂O, suggesting that the chemical nature of extra-
669 framework (and likely framework) population plays an important role in governing the penetration
670 reversibility. The *P*-induced penetration of H₂O in natrolite was described with different
671 experimental methods (Colligan et al. 2005; Seryotkin et al. 2005), and it was observed in almost all
672 the fibrous zeolites with spectacular volume expansion (e.g., natrolite, scolecite and thomsonite, e.g.
673 Lee et al. 2002a, 2002b, 2005; Colligan et al. 2005; Gatta 2005; Likhacheva et al. 2006, 2007;
674 Seoung et al. 2013, 2015; Seryotkin et al. 2017), with the exception of edingtonite (EDI framework
675 type, Baerlocher et al. 2007) (Gatta et al. 2004a, 2004b): the large Ba-polyhedron fills very
676 efficiently the 8-membered ring channel along [001], which is in an already expanded configuration
677 if compared to the other fibrous zeolites, hindering further penetration of H₂O molecules.

678 The role of the cations in natrolite under superhydration conditions was recently explored
679 theoretically by investigating the *P*-induced behaviour of Na-, Rb-, and Cs-natrolite (Kremleva et
680 al. 2013) and of the K-substituted counterpart (Kremleva et al. 2014). With calculations based on
681 density functional theory (DFT), these studies were able to reproduce approximately the critical
682 pressure values at which the corresponding transformations were found to occur in experiments,
683 providing therefore valuable insight on their microscopic details. Based on the modelling results,
684 these authors also predicted the possible formation, at high pressure conditions, of two isomers of
685 superhydrated K-NAT, with either positive or negative chain rotation angles (Kremleva et al. 2014).

686 An additional *P*-induced expansion phenomenon was observed in laumontite, ideally
687 Ca₄Al₈Si₁₆O₄₈·*n*H₂O with *n*≤18 (LAU framework type, Baerlocher et al. 2007). Using a partially
688 dry sample with 12H₂O m.p.f.u., Lee et al. (2004) showed, using a hydrous *P*-transmitting fluid and
689 a powder sample, that laumontite experiences a phase transition at *P* = 0.2(1) GPa, with a
690 spectacular unit-cell volume increase of ~2.6%. The structure refinements proved that the expansion
691 reflects the transition to a fully hydrated form (with 18H₂O m.p.f.u.), by selective sorption of extra

692 H₂O, which leads to the expansion of the 8-membered ring channels along [001]. Significantly, *P*-
693 induced hydration in laumontite was first investigated by a computer modeling study performed
694 with a classical force field by White et al. (2004). Such a study predicted the occurrence of full
695 hydration at moderate pressures, which was then confirmed by the experiments, evidencing that,
696 when pressure is applied, the structural stability of the laumontite-type framework increases
697 because of the fully occupied H₂O network.

698 Fibrous zeolites and (partially dehydrated) laumontite represent rare examples of *P*-induced
699 insertion of H₂O molecules with spectacular expansion of the unit-cell volume. Usually, the
700 penetration of extra H₂O molecules from the *P*-fluid is not accompanied by unit-cell volume
701 expansion, as shown *e.g.* for: the synthetic Linde-type A (ideally Na₁₂Al₁₂Si₁₂O₄₈ · 26 H₂O, LTA
702 framework type; Hazen 1983, Hazen and Finger 1984, Arletti et al. 2003, Likhacheva et al. 2009,
703 Niwa et al. 2013); synthetic Li-, (Na,Cs)- and Cd-RHO zeolites [(Li,Na,Cs)₁₂(Al₁₂Si₃₆O₉₆)·44H₂O,
704 RHO framework type; Lee et al. 2001]; synthetic all-silica zeolite Y (FAU framework type,
705 Colligan et al. 2004); gismondine (ideally Ca₄Al₈Si₈O₃₂·16H₂O, GIS framework type; Ori et al.
706 2008b) and its synthetic K-gallosilicate counterpart (K-GaSi-GIS, Lee et al. 2008); boggsite (ideally
707 Ca₈Na₃Al₁₉Si₇₇O₁₉₂·70H₂O, BOG framework type; Arletti et al. 2010); synthetic Na-ZSM-5 (*i.e.*
708 (Na_{4.58}K_{0.02})(Ca_{0.18}Mg_{0.03}Ba_{0.01}Fe_{0.05}Sr_{0.01})(Al_{4.48}Si_{91.35})O₁₉₂·28.39H₂O, MFI framework type, Arletti
709 et al. 2011) and H-ZSM-5 (*i.e.*, (H_{6.8}Na_{1.1})(Al_{7.9} Si_{89.8})O₁₉₂·36H₂O, MFI framework type, Quartieri
710 et al. 2011); all-silica ferrierite (FER framework type; Lotti et al. 2015a); paulingite (ideally
711 (K,Na,Ca_{0.5},Ba_{0.5})₁₀(Al₁₀Si₃₂O₈₄)·*n*H₂O, with *n* = 27–44, PAU framework type; Gatta et al. 2015);
712 synthetic AlPO₄-5 (AFI-framework type; Lotti et al. 2016).

713 The experiment of Colligan et al. (2004), on a purely siliceous zeolite Y (FAU framework
714 type, Baerlocher et al. 2007), deserves a particular attention. Colligan et al. (2004) compressed a
715 synthetic all-silica zeolite Y (FAU framework type) in silicone oil and in methanol:ethanol:water
716 =16:3:1 mix using a DAC, and described its *HP*-behavior on the basis of *in situ* synchrotron X-ray
717 powder diffraction data, with Rietveld structure refinements and computational modelling. This was
718 probably the first experiment in which a neutral and hydrophobic zeolitic framework was used in
719 order to describe *P*-induced penetration phenomena, giving the opportunity to examine the effect of
720 pressure on a porous silicate without interferences due to extra-framework charge-balancing cations
721 and their interactions with framework oxygen atoms. Compressed in the mixture of alcohols-water,
722 this zeolite shows a drastically lower compressibility than that observed in (non-penetrating)
723 silicone oil. In addition, in alcohols-water mix, two distinct compressional patterns occurred, with a
724 changeover at 4 GPa. The Rietveld structure refinements proved that new extra-framework sites
725 occur at high pressure, modelled as partially or fully occupied by oxygen atoms of H₂O molecules.

726 The sum of the extra-framework site occupancies increases with pressure, and the pore filling
727 saturation is achieved at about 4.0 GPa. This last experimental finding allowed the authors to
728 explain the change of the compressional behavior of this zeolite compressed in
729 methanol:ethanol:water =16:3:1 mix: *i*) *P*-induced intrusion of H₂O molecules is the principal
730 process that occurs between 0.0001 and 4 GPa, leading to a drastically lower compressibility if
731 compared to that observed in silicone oil; *ii*) when the filling of the pores is completed, at *P* > 4
732 GPa a new compressional pattern, with higher compressibility, is observed and the effect of
733 hydrostatic compression is predominantly accommodated by framework deformation (mainly *via*
734 tetrahedral tilting). Unfortunately, no structure refinements were performed in decompression,
735 leaving open questions about the reversibility of the intrusion process. With this experiment,
736 Colligan et al. (2004) showed how polar molecules (*i.e.*, H₂O molecules) can be intruded in a
737 neutral framework in response to applied pressure.

738 Some experiments have been performed using liquid CO₂ as penetrating *P*-transmitting
739 fluid. Natrolite (Na₁₆Al₁₆Si₂₄O₈₀·16.0H₂O), for example, transforms to
740 Na₁₆Al₁₆Si₂₄O₈₀·16H₂O·8CO₂ at 1.5 GPa (Lee et al. 2011). The penetration of extra CO₂ molecules
741 through the 8-membered ring channels, running along [001], leads to an expansion of the channels
742 and, in turn, to a spectacular unit-cell volume increase by ~6.8%. The CO₂-bearing natrolite stable
743 at high pressure contains ~12 wt% of CO₂, and its symmetry decreases from orthorhombic (Sp. Gr.
744 *Fdd2*) to monoclinic (Sp. Gr. *Cc*). The intruded CO₂ molecules give rises to a rearrangement of the
745 extra-framework population, with a migration of the H₂O molecules toward one side of the channel.
746 CO₂ molecules interact with both Na and H₂O, and lie in a plane almost perpendicular to the
747 channel direction. The structure refinements after decompression showed that
748 Na₁₆Al₁₆Si₂₄O₈₀·16H₂O·8CO₂ is meta-stable after *P*-release (even after an equilibration time of 1
749 h).

750 Haines et al. (2010) showed that the *P*-induced intrusion of extra molecules of CO₂ in
751 silicalite (MFI framework type) hinders its *P*-induced amorphization (at least up to 20-23 GPa),
752 whereas in a non-penetrating fluid this zeolite showed effects of amorphization at 4-5 GPa.

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754

755 - *P*-induced penetration of complex molecules and polymerization phenomena

756 Santoro et al. (2013) reported the first evidence of *P*-induced photo-polymerized ethylene in
757 the channels of silicalite (MFI framework type, Baerlocher et al. 2007), using single crystal and
758 powder of SiO₂-silicalite compressed in supercritical fluid C₂H₄. The penetration of C₂H₄ molecules
759 occurs at 0.5–1.5 GPa, and the polymerization is promoted under ultraviolet (351–364 nm)

760 irradiation. Experimental evidence, based on optical spectroscopy and X-ray diffraction, confirmed
761 that the structure of C₂H₄-bearing silicalite, recovered at ambient pressure, contains single
762 polyethylene chains confined by the zeolitic channels. The C₂H₄-bearing silicalite shows a
763 significant increase of its bulk modulus and density if compared to the parental silicalite, in
764 response to the *P*-induced pore-filling effect.

765 On the same zeolite, a further experiment was reported by Scelta et al. (2014) devoted to the
766 *P*-induced polymerization of acetylene molecules (to poly-acetylene chains) through the zeolitic
767 cavities. The authors used a multi-methodological approach, based on *in situ* and *ex situ*
768 measurements (by IR spectroscopy, Raman spectroscopy and X-ray diffraction), in order to describe
769 how with a DAC and using only high pressure (~4 GPa; no temperature or ultraviolet irradiation) it
770 is possible to promote the penetration and re-organization (*via* polymerization) of C₂H₂ molecules
771 through the zeolite channels.

772 Silicalite was also selected as the zeolitic host for a further experiment aimed to investigate
773 the *P*-induced polymerization in all-silica zeolites: Santoro et al. (2015) reported the *P*-induced
774 synthesis of all-transoid polycarbonyl [-(C=O)-]_{*n*} in a zeolite, starting from mixtures of (solid) CO
775 and powder or single crystal of silicalite, compressed in a DAC. Using a multi-methodological
776 approach (based on IR, Raman, single-crystal X-ray diffraction, and *ab initio* computational
777 methods for calculating the vibrational spectrum of polymerised CO), the authors reported how
778 compressing the zeolite in solid CO, evidence of CO penetration through the zeolitic cavities with a
779 re-organization in a polymeric configuration were found. The experimental findings indicated that
780 the average interaction between confined polymerised CO and the host silicalite is of the van der
781 Waals type, and the resulting IR spectra are compatible with the all-transoid polycarbonyl
782 [-(C=O)-]_{*n*} chains predicted by DFT studies. The *ex situ* measurements proved that the *P*-induced
783 penetration and polymerization of CO is an irreversible process. To the best of our knowledge, this
784 is one of the very rare examples in which the *P*-induced penetration of external molecules occurs in
785 a solid host compressed in a solid medium.

786 The same group of researchers (Santoro et al. 2016) extended their experiments on a
787 different zeolite with a mono-dimensional system of channels: the all-silica ZSM-22 (TON
788 framework type, Baerlocher et al. 2007). Polycrystalline ZSM-22 compressed (up to 5-10 GPa) in
789 (liquid) acetylene and (liquid) CO, loaded cryogenically in a DAC, experiences similar phenomena
790 as those previously described for silicalite: the intrusion and the subsequent irreversible
791 polymerization of C₂H₂ (to poly-acetylene) and CO (to polycarbonyl [-(C=O)-]_{*n*}).

792 Arletti et al. (2015) investigated the behavior of a synthetic high-silica mordenite (MOR
793 framework type, Baerlocher et al. 2007) compressed in a non-penetrating fluid (*i.e.*, silicone oil)

794 and a series of potentially penetrating fluids: the mix methanol:ethanol:water = 16:3:1,
795 water:ethanol = 3:1, and ethylene glycol, by *in situ* (e.g., synchrotron X-ray powder diffraction,
796 Raman spectroscopy) and *ex situ* measurements (e.g., synchrotron X-ray powder diffraction, IR
797 spectroscopy). The experimental findings showed that: *i*) the elastic behaviour with a non-
798 penetrating fluid is consistent with that previously reported (with *P*-induced phase transition from a
799 *C*-centered to a primitive space group at ~1 GPa, Lotti et al. 2015b), *ii*) the *P*-induced intrusion of
800 guest molecules, from the *P*-fluids through the cavities of this zeolite, occurs for all the (nominally)
801 penetrating fluids and at low pressure. For example, evidence of the ethylene glycol penetration was
802 reported already at 0.1 GPa, and this phenomenon appears to be only partially reversible upon
803 decompression. Whereas methanol or ethanol cannot be intruded at high pressure in Na-mordenite
804 (*i.e.*, Na₆Al_{6.02}Si_{42.02}O₉₆ · 19H₂O), as reported by Gatta and Lee (2006) and Lotti et al. (2015b), the
805 absence of the extra-framework population promotes the penetration of these molecules through the
806 empty channels of high-silica mordenite in response to applied pressure.

807 More recently, Richard et al. (2016) used a combination of *in situ* Raman spectroscopy and
808 X-ray diffraction to investigate the *P*-induced insertion of BNH₆ (ammonia borane, solid at ambient
809 conditions) in the cavities of the hydrophobic silicalite-1F (MFI framework type, Baerlocher et al.
810 2007). A single crystal of silicalite was compressed in a powder of BNH₆, using a DAC. The
811 experimental findings showed how BNH₆ molecules penetrate through the cavities of the silicalite-
812 1F structure at very low-*P* (~0.1 GPa), and the insertion leads to the appearance of new Raman
813 modes. Raman spectra collected at high-*P* showed how orientational disorder of the –BH₃ and
814 –NH₃ groups, pertaining to the intruded molecules, occur within the *P*-range investigated, if
815 compared to the bulk ammonia borane used as *P*-transmitting medium. *In situ* X-ray powder
816 diffraction experiments showed that the compressibility of the BNH₆-bearing silicalite-1F is three
817 times lower than that of the parental silicalite-1F (with empty cavities), in response to the *P*-induced
818 pore-filling effect.

819 Very recently, Arletti et al. (2017) showed how the hydrophobic all-silica ferrierite (FER
820 framework type, Baerlocher et al. 2007) compressed in the ethanol:water = 1:3 mixture experiences
821 a transition between 0.8 and 1.3 GPa from the orthorhombic (Sp. Gr. *Pmnn*) to monoclinic
822 symmetry (Sp. Gr. *P2₁/n*), coupled with a penetration of the *P*-fluid molecules. The X-ray powder
823 diffraction data and modelling (using a dispersion-corrected density functional approximation)
824 showed that the (H₂O,ethanol)-bearing ferrierite, stable at high pressure, is able to separate the
825 ethanol–water mixture into ethanol dimer wires and H₂O tetramer squares (Fig. 2). The specific
826 zeolite type – ferrierite - is pivotal for achieving the H₂O-ethanol organization in such a peculiar
827 two-dimensional arrangement. Ferrierite has two parallel channel systems of different diameter – 6-

828 and 10-membered rings - which are perfectly tailored to host, respectively, H₂O tetramers and
829 ethanol dimers. Surprisingly, the confined supramolecular organization remains stable even upon
830 complete pressure release, which is a key requirement in view of potential technological
831 applications. Indeed, the intrusion of pure H₂O in all-silica FER was observed by Cailliez et al.
832 (2008) at considerable lower pressures (below 0.30 GPa) using a porosimeter: such an experiment
833 achieved complete filling of the zeolite framework, but H₂O was reversibly extruded upon pressure
834 release (Cailliez et al. 2008). Notably, powder X-ray diffraction data indicated intrusion of H₂O
835 molecules at comparable pressure values (0.2 GPa) when ferrierite was compressed in a DAC with
836 a methanol:ethanol:H₂O = 16:3:1 mixture – in this case, the maximum pressure reached was 1.5
837 GPa, and H₂O was retained also at room conditions (Arletti et al. 2014). This suggests that
838 pressures higher than 0.3 GPa are instrumental for the irreversible encapsulation of H₂O and ethanol
839 molecules in ferrierite, ensuring thus the stability of the supramolecular architecture of dimers and
840 tetramers at room conditions (Arletti et al. 2017).

841 Previous experiments on the same zeolites were performed by Lotti et al. (2015a) on single
842 crystal and polycrystalline samples, using silicone oil (as a polymeric non-penetrating *P*-fluid) and
843 methanol:ethanol:H₂O = 16:3:1 mixture, ethylene glycol and 2methyl-2propen-1ol (as potentially
844 penetrating fluids). The experiments with the potentially penetrating media enhanced the occurrence
845 of *P*-induced intrusion of fluid molecules, with different phase-transition paths and compressibility
846 patterns. However, the disordered distribution of the maxima in the calculated residual electron
847 density map, obtained by single-crystal X-ray structure refinements, did not allow to define a
848 unique scenario of the configuration of the intruded molecules (Lotti et al. 2015a). The starting
849 orthorhombic polymorph was always restored upon decompression with all the used *P*-fluids. The
850 authors highlighted the different *HP* behaviour observed for single crystal and powder sample using
851 the same *P*-fluid, along with the different *P*-induced phase-transition paths in response to different
852 process kinetics (Lotti et al. 2015a).

853 The aforementioned experiments on all-silica silicalite (MFI framework type), ZSM-22
854 (TON framework type), mordenite (MOR framework type) and ferrierite (FER framework type)
855 were all devoted to describe the *P*-induced penetration of molecular guest systems in a zeolitic host.
856 Recently, Arletti et al. (2016) reported the behaviour of an all-silica ferrierite compressed in an
857 electrolytic MgCl₂·21H₂O solution. The *P*-induced intrusion was found to occur at very low *P*
858 (about 0.19 GPa); the phenomenon is reversible (as proved by the X-ray diffraction before and after
859 the *P*-induced intrusion experiment) and it is affected by a moderate hysteresis. The Rietveld
860 refinement, based on the synchrotron diffraction data collected at *P*~0.28 GPa (above the intrusion
861 pressure), showed that both ions and H₂O molecules of the aqueous solution (used as *P*-transmitting

862 fluid) were intruded in the cavities, with an ordered distribution: *i*) the Mg^{2+} site lies at the center of
863 the FER cage and it is coordinated by four H_2O molecules (with partial site occupancy) in a square
864 planar configuration, *ii*) the Cl^- site is located in the 10-membered ring channels parallel to [001],
865 coordinated by two H_2O molecules. Mg^{2+} and Cl^- are partially solvated. The idealized composition
866 of the electrolyte guest solution in the zeolitic cavities is: $\text{MgCl}_2 \cdot 10\text{H}_2\text{O}$. At $P \sim 0.68$ GPa, a phase
867 transition from orthorhombic (Sp. Gr. $Pmnn$) to monoclinic (Sp. Gr. $P2_1/n$) symmetry was also
868 observed.

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870

871 **Discussion and conclusions**

872 If we consider the behaviour of zeolites when compressed in penetrating and non-
873 penetrating P -fluids, the first general consideration we can make is that the P -induced intrusion of
874 new molecules through the zeolitic cavities has a drastic impact of the elastic behaviour and on the
875 structure evolution of a given zeolite. The experimental findings pertaining to compression in non-
876 penetrating fluids showed that:

877 1) The flexibility observed in this class of open-framework materials, in response to applied P
878 or T , is based mainly on tilting of (quasi-rigid) tetrahedra around O atoms that behave as
879 hinges. Tilting of tetrahedra is the dominant mechanisms at low-mid P -regime, whereas
880 distortion and compression of tetrahedra represent the mechanisms which usually dominate
881 the mid-high P -regime. One of the most common deformation mechanisms in zeolitic
882 framework, able to accommodate the effect of pressure, is the increase, though without
883 inversion, of channels ellipticity. As we can learn from the experiments on isotypic zeolites,
884 the deformation mechanisms are dictated by the topological configuration of the tetrahedral
885 framework and are not influenced by the Si/Al/P-distribution or by the extra-framework
886 population. However, the compressibility of the cavities is controlled by the nature and
887 bonding configuration of ionic and molecular content, resulting in different unit-cell volume
888 compressibility in isotypic structures.

889 2) The range of compressibility of zeolites is significantly large, with bulk moduli $\sim 10 < K_{P0,T0}$
890 $< \sim 90$ GPa. The microporosity does not necessarily imply high compressibility, as several
891 zeolites are stiffer than non-zeolitic rock-forming minerals (*e.g.*, quartz, feldspars,
892 feldspathoids, scapolites, micas; Gatta and Lee 2014). In general, zeolites with stuffed
893 channels (*i.e.*, with an extra-framework population) are stiffer than zeolites with empty
894 channels. If the microporosity is represented by the framework density, then the
895 compressibility of zeolites is not directly related to microporosity.

896

897 The experimental findings pertaining to compression in penetrating fluids, and thus with crystal-
898 fluid interaction, showed that not all the zeolites experience a P -induced intrusion of new
899 monoatomic species or molecules from the P -transmitting fluids. For example, zeolites with well-
900 stuffed channels at ambient conditions (*e.g.*, natural zeolites) tend to hinder the penetration of new
901 species through the channels. There must be several variables that govern the sorption phenomena
902 at high pressure beyond the “free diameters” of the framework cavities, among those: the chemical
903 nature and the configuration of the extra-framework population, the partial pressure of the
904 penetrating molecule in the fluid (if mixed with other non-penetrating molecules, *e.g.* $P(\text{H}_2\text{O})$ in a
905 mixture of alcohols– H_2O), likely the rate of the P -increase, the surface/volume ratio of the
906 crystallites under investigations, the temperature at which the experiment is conducted. As shown
907 by Lotti et al. (2015a), the rate of the P -increase and the surface/volume ratio of the crystallites can
908 play an important role in governing the crystal-fluid interaction, through P -induced penetration
909 phenomena, and deserve further investigations.

910 The re-organization of the intruded molecules in zeolitic hosts, promoted by applied
911 pressure and by other variables (*e.g.*, ultraviolet irradiation, moderate temperature), is one of the
912 most fascinating discovery in material science over the last decade, with potential technological and
913 geological implications. The aforementioned experiments of Santoro et al. (2013, 2015, 2016),
914 Scelta et al. (2014), Richard et al. (2016), Arletti et al. (2015, 2017) indicate new routes for creating
915 hybrid host-guest composite materials, where an inorganic framework drives the formation of
916 organic polymer with low dimensionality, acting as a stable host for it. The new hybrid inorganic-
917 host/organic-guest materials display completely different physicochemical properties if compared to
918 the parental zeolites, in which the interesting properties imparted by pressure would be retained also
919 at standard conditions, and could be exploited in applications. In this fascinating perspective, a
920 crucial question to be addressed is whether moderate pressures, *e.g.* below 1 GPa, might be
921 sufficient to induce “technologically appealing” irreversible processes, such as the supramolecular
922 organization of simple species in complex patterns, or the formation of one-dimensional polymer
923 chains. Avoiding the use of extreme pressures would be highly desirable for practical applications;
924 for this reason, future investigations along this route should be aimed not only to obtain new
925 composites, but also to determine, or predict, the pressure value at which the transformation would
926 become quantitative and irreversible. Whether supramolecular organization of the included species
927 appears at a certain pressure onset, or if it gradually evolves with increasing pressure, is just one of
928 the questions to be addressed in order to gather molecular-level knowledge, and hence control, of
929 these processes. A further issue to be investigated is the influence of the composition of the P -

930 transmitting media on the intrusion, organization, and transformation processes inside the
931 framework. Additionally, unravelling the molecular details of the pressure-driven penetration of
932 guest species inside the zeolite pores would be a highly challenging task, which would involve a
933 thorough study of the external surfaces of the zeolite material (Hendriks et al. 2017) under non-
934 standard conditions. In this respect, modelling could play a crucial role: the behaviour of surfaces
935 and interfaces under high-temperature conditions has already enabled to capture new phenomena
936 that were not directly accessible to experimental observation (Ceriani 2004a; Fois 2000, Fois
937 2010b; Tabacchi 2015b) – for example, that the opening of zeolite pores may be enlarged by
938 concerted rotations of the tetrahedral units induced by the intrusion of bulky molecules (Tabacchi
939 2016). With this premises, we envisage that a combined experimental and modelling endeavour to
940 explore the interfaces of open-framework materials at high-pressure conditions might reveal the
941 occurrence of new, unexpected processes of key relevance for future advances in zeolite science
942 and technology.

943 The confinement of molecular species inside zeolite channels at normal pressure is already a
944 successful strategy to build supramolecular architectures: materials with innovative properties have
945 been fabricated by constraining molecules in an ordered arrangement within these nanosized spaces.
946 The encapsulation of dyes into the monodimensional system of channels of zeolite L has led to
947 functional composites suitable for a variety of applications – from solar energy technology to
948 nanomedicine (Popovic et al. 2007; Calzaferri 2012; Fois et al. 2012; Cucinotta et al. 2014; Insuwan
949 et al. 2016; Gartzia-Rivero et al. 2017). Host–guest assemblies working as light-harvesting antenna
950 systems are promising materials for the field of molecule-based devices (Calzaferri et al. 2003; Fois
951 et al. 2010a; Martinez-Martinez et al. 2014). These systems usually consist of chromophores hosted
952 in the one-dimensional pores of zeolite L. Like in the antenna systems of natural photosynthetic
953 organisms, upon photon absorption, a confined dye molecule can transfer its excitation energy to a
954 neighboring dye molecule, and the energy transfer continues up to the end of the supramolecular
955 chain, where energy could be collected (Calzaferri et al. 2003). To interface the artificial antenna
956 with other components in a working device, the zeolite termination should be functionalized with
957 suitable molecules named “stopcocks” (Maas et al. 2002), which can also be used to avoid leaking
958 of dye molecules from zeolite channels (Calzaferri 2012; Tabacchi et al. 2015a; Cao et al. 2016;
959 Gartzia-Rivero et al. 2017). Based on this principle, highly versatile composites to be used as tailor-
960 made devices for multiple applications have been created, but their behaviour under non-standard
961 conditions is still to be explored. The study of high-pressure effects on dye-zeolite hybrids would be
962 indispensable for future progress of this technology from fundamental bases. Moreover, by
963 exploiting high pressure, the intrusion of different kinds of dyes might be obtained, with the

964 possibility of organizing these molecules in a complex pattern determined by the topology of the
965 framework and by the related intermolecular interactions, which could ultimately lead to hybrid
966 composites with new, unexpected opto-electronic properties.

967 High-pressure effects might probably be exploited to improve catalytic processes of
968 relevance for industrial and sustainable applications. These processes may either involve zeolites
969 with strong Lewis acid sites – such, *e.g.*, the titanium silicalite TS1 catalyst (Taramasso et al. 1983)
970 adopted in olefin epoxidation processes (Bellussi et al. 1992) – or, more commonly, moderately
971 hydrophilic synthetic zeolites (*i.e.*, with high Si/Al ratio) having protons as extraframework
972 cations (see *e.g.*, Fois et al. 2008b). These Brønsted acid sites may activate the intruded molecules.
973 These zeolites are used, for example, in the production of biofuels, as catalysts for cracking and
974 isomerization reactions. Thanks to its framework topology, exhibiting relatively small cavities,
975 hydrophilic ferrierite shows an impressive transition state selectivity for such reactions (see *e.g.*,
976 Martinez et al. 2011). However, just because of the small pore diameters, the reaction normally
977 takes place only on the external surface of the zeolite, at its pore opening (Wiedemann et al. 2016).
978 As a consequence of this “pore-mouth catalysis”, only a small proportion of the catalytic sites
979 is actually exploited. Reasonably, moderate pressures could favour the intrusion of the reactant
980 molecules inside the zeolite pores, thus enhancing the performances of the industrial process.
981 Concerning Lewis-acid catalysts, as the olefin epoxidation cycle involves the direct participation of
982 the zeolite framework as active oxygen mediator (Spanò et al. 2006), it can be argued that the use of
983 pressure may help to lower the associated free energy barrier, with beneficial effects on catalysis.
984 Besides improving catalytic processes, high-pressure effects might be also effectively exploited to
985 create new zeolite structures starting from a common, economically convenient parent material.
986 Importantly, the new phases might display better performances than the starting material, as
987 demonstrated by Jordà et al. (2013).

988 In this broad scenario, modelling studies play a key role. Simulations have become an
989 extremely versatile tool for addressing the complex behaviour of zeolites at high-pressure
990 conditions, and for connecting the experimentally measured response of the system to its features at
991 the atomistic-detail level. Nowadays, the scope of computational investigations is no longer limited
992 to the interpretation of experimental results: they should aim at opening new routes in the various
993 aspects of zeolite technology. Integrated theoretical-experimental approaches would be instrumental
994 in this perspective: they are currently widely adopted and are going to gain further momentum from
995 the growing increase of computing power and the continuous development of faster numerical
996 algorithms.

997 Concerning the geological implications of the experimental findings on the *P*-induced
998 crystal-fluid interaction in zeolites, it is not difficult to consider the potential role played by zeolites
999 (especially Ca-bearing zeolites, like laumontite) found as among the main mineralogical
1000 components of the oceanic basalts and their transformation products, as we know by the ODP -
1001 ocean drilling project (*e.g.*, Alt et al. 1986; Sevigny et al. 1992; Yasukawa et al. 2014;
1002 <http://iodp.americangeosciences.org/vufind/>). For example, these zeolites may act as potential
1003 carrier of H₂O or CO₂ (or even H₂S, CH₄, Ar, Xe, or Kr), sorbed under the combined effect of
1004 pressure and temperature during genetic and post-genetic conditions, which can be later released
1005 when the oceanic crust is subducted. In addition, whereas it is well known the utilization of
1006 synthetic zeolites in petrochemistry (*e.g.*, Vermeiren and Gilson 2009 and references therein), the
1007 role played by natural zeolites on generation, migration and accumulation of hydrocarbons
1008 (processes that occur at moderate *P/T* conditions) is still unknown. Some zeolite-like minerals, for
1009 example melanophlogite (a polymorph of SiO₂ with an open-framework structure, also called
1010 *chlatrasil*; Tribaudino et al. 2008, 2010; Gatta et al. 2014), contain CH₄, CO₂ or N₂ in their
1011 structural cavities. Natural methane clathrates - solids condensed at moderate pressure in which a
1012 large amount of methane is trapped within a framework of H₂O - share with zeolites the framework
1013 topologies and the host-guest structures. The experimental findings pertaining to the *HP*-behaviour
1014 of zeolites can be potentially extended to clathrates. For example, methane clathrates are stable at a
1015 higher temperature than liquefied natural gas (*i.e.*, 110-250 K), and this promotes some interest in
1016 converting natural gas into clathrates instead of using the conventional liquefaction technology for
1017 transportation. The production of methane clathrates from natural gas requires less energy and a
1018 smaller refrigeration plant if compared to liquefied natural gas. Can the application of moderate
1019 pressure improve the methane clathrates condensation with a more efficient insertion of CH₄ in the
1020 H₂O framework?

1021

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References

- Ackley MW, Rege SU, Saxena H (2003) Application of natural zeolites in the purification and separation of gases. *Micropor Mesopor Mater* 61:25-42.
- Allen M, Tildesley D (1987) *Computer Simulation of Liquids*, Clarendon Press, Oxford.
- Alt JC, Honnorez J, Laverne C, Emmermann R (1986) Hydrothermal alteration of a 1 km section through the upper oceanic crust, Deep Sea Drilling Project Hole 504B: Mineralogy, chemistry and evolution of seawater-basalt interactions. *J Geophys Res* 91:10309–10335.
- Angel RJ, Allan DR, Miletich R, Finger LW (1997) The use of quartz as an internal pressure standard in high-pressure crystallography. *J Appl Crystallogr* 30:461-466.
- Angel RJ, Bujak M, Zhao J, Gatta GD, Jacobsen SJ (2007) Effective hydrostatic limits of pressure media for high-pressure crystallographic studies. *J Appl Crystallogr* 40:26-32.
- Arletti R, Ferro O, Quartieri S, Sani A, Tabacchi G, Vezzalini G (2003) Structural deformation mechanisms of zeolites under pressure. *Am Mineral* 88:1416-1422.
- Arletti R, Quartieri S, Vezzalini G (2010) Elastic behavior of zeolite boggsite in silicone oil and aqueous medium: A case of high-pressure-induced over-hydration. *Am Mineral* 95:1247–1256.
- Arletti R, Vezzalini G, Morsli A, Di Renzo F, Dmitriev V, Quartieri S (2011) Elastic behavior of MFI-type zeolites: 1- Compressibility of Na-ZSM-5 in penetrating and non-penetrating media. *Micropor Mesopor Mater* 142:696-707.
- Arletti R, Vezzalini G, Quartieri S, Di Renzo F, Dmitriev V (2014) Pressure-induced water intrusion in FER-type zeolites and the influence of extraframework species on structural deformations. *Micropor Mesopor Mater* 191:27-37.
- Arletti R, Leardini L, Vezzalini G, Quartieri S, Gigli L, Santoro M, Haines J, Rouquette J, Konczewicz L (2015) Pressure-induced penetration of guest molecules in high-silica zeolites, the case of mordenite. *Phys Chem Chem Phys* 17:24262-24274.
- Arletti R, Ronchi L, Quartieri S, Vezzalini G, Ryzhikov A, Nouali H, Daou TJ, Patarin J (2016) Intrusion-extrusion experiments of MgCl₂ aqueous solution in pure silica ferrierite: Evidence of the nature of intruded liquid by in situ high pressure synchrotron X-ray powder diffraction. *Micropor Mesopor Mater* 235: 253-260.
- Arletti R, Fois E, Gigli L, Vezzalini G, Quartieri S, Tabacchi G (2017) Irreversible Conversion of a Water-Ethanol Solution into an Organized Two-Dimensional Network of Alternating Supramolecular Units in a Hydrophobic Zeolite under Pressure. *Angew Chem Int Ed* 56: 2105–2109.

- 1065 Baerlocher C, McCusker LB, Olson DH (2007) Atlas of zeolite framework types (sixth edition), 84
1066 p., Elsevier, Amsterdam.
- 1067 Bai P, Jeon MY, Ren L, Knight C, Deem MW, Tsapatsis M, Siepmann, JI (2015) Discovery of
1068 optimal zeolites for challenging separations and chemical transformations using predictive
1069 materials modeling. *Nat Commun* 6:5912
- 1070 Balestra SRG, Hamad S, Ruiz-Salvador AR, Domínguez-García V, Merkling PJ, Dubbeldam D,
1071 Calero S (2015) Understanding Nanopore Window Distortions in the Reversible Molecular
1072 Valve Zeolite RHO. *Chem Mater* 27:5657-5667.
- 1073 Ballone P, Quartieri S, Sani A, Vezzalini G (2002) High-pressure deformation mechanism in
1074 scolecite: a combined computational-experimental study. *Am Mineral* 87:1194–1206.
- 1075 Barducci A, Bonomi M, Parrinello M (2011) Metadynamics. *WIREs Comput Mol Sci* 1:826–843.
- 1076 Becke AD (1988) Density-functional exchange-energy approximation with correct asymptotic
1077 behavior. *Phys Rev A* 38:3098-3100.
- 1078 Becke AD (1993) Density-functional thermochemistry. III. The role of exact exchange. *J Chem*
1079 *Phys* 98:5648–5652.
- 1080 Bellussi G, Carati A, Clerici MG, Maddinelli G, Millini R (1992) Reactions of titanium silicalite
1081 with protic molecules and hydrogen peroxide, *J Catal* 133:220-230.
- 1082 Betti C, Fois E, Mazzucato E, Medici C, Quartieri S, Tabacchi G, Vezzalini G, Dmitriev V (2007)
1083 Gismondine under HP: Deformation mechanism and re-organization of the extra-framework
1084 species. *Microporous Mesoporous Mater* 103:190-209.
- 1085 Besson JM, Nelmes RJ, Hamel G, Loveday JS, Weill G, Hull S (1992) Neutron powder diffraction
1086 above 10 GPa. *Physica B* 180:907–910.
- 1087 Bish DL, Carey JW (2001) Thermal Behavior of Natural Zeolites. *Rev Mineral Geochem* 45:403–
1088 452.
- 1089 Bish DL, Vaniman DT, Chipera SJ, Carey JW (2003) The distribution of zeolites and their effects
1090 on the performance of a nuclear waste repository at Yucca Mountain, Nevada, U.S.A.. *Am*
1091 *Mineral* 88:1889-1902.
- 1092 Bludský O, Silhan M, Nachtigall P, Bucko T, Benco, L, Hafner J (2005) Theoretical investigation
1093 of CO interaction with copper sites in zeolites: Periodic DFT and hybrid quantum
1094 mechanical/interatomic potential function study. *J Phys Chem B* 109:9631-9638.
- 1095 Bryukhanov IA, Rybakov AA, Larin AV, Trubnikov DN, Vercauteren DP (2017) The role of water
1096 in the elastic properties of aluminosilicate zeolites: DFT investigation. *J Mol Model* 23: 68.

- 1097 Cailliez F, Trzpit M, Soulard M, Demachy I, Boutin A, Patarin J, Fuchs AH (2008)
1098 Thermodynamics of water intrusion in nanoporous hydrophobic solids. *Phys Chem Chem Phys*
1099 10:4817-4826.
- 1100 Calzaferri G, Huber S, Maas H, Minkowski C (2003) Host–guest antenna materials. *Angew Chem*
1101 *Int Ed* 42:3732-3758.
- 1102 Calzaferri G (2012) Nanochannels: Hosts for the Supramolecular Organization of Molecules and
1103 Complexes. *Langmuir* 28: 6216–6231.
- 1104 Calzaferri G (2017) Entropy in multiple equilibria, theory and applications. *Phys Chem Chem Phys*
1105 19:10611-10621.
- 1106 Cao P, Khorev O, Devaux A, Sägger L, Kunzmann A, Ecker A, Häner R, Brühwiler D, Calzaferri
1107 G, Belser P (2016) Supramolecular organization of dye molecules in zeolite L channels:
1108 synthesis, properties, and composite materials. *Chem Eur J* 22: 4046–4060.
- 1109 Car R, Parrinello M (1985) Unified approach for molecular dynamics and density-functional theory.
1110 *Phys Rev Lett* 55: 2471-2474.
- 1111 Carter EA, Ciccotti G, Hynes JT, Kapral R (1989) Constrained reaction coordinate dynamics for the
1112 simulation of rare events. *Chem Phys Lett* 156:472-477.
- 1113 Ceriani C, Fois E, Gamba A, Tabacchi G, Ferro O, Quartieri S, Vezzalini G (2004a) Dehydration
1114 dynamics of bikitaite: Part II. Ab initio molecular dynamics study. *Am Mineral* 89:102-109.
- 1115 Ceriani C, Laio A, Fois E, Gamba A, Martoňák R, Parrinello M (2004b) Molecular dynamics
1116 simulation of reconstructive phase transitions on an anhydrous zeolite. *Phys Rev B* 70:113403.
- 1117 Colella C (2011) A critical reconsideration of biomedical and veterinary applications of natural
1118 zeolites. *Clay Miner* 46:295-309.
- 1119 Colligan M, Forster PM, Cheetham AK, Lee Y, Vogt T, Hriljac JA (2004) Synchrotron X-ray
1120 Powder Diffraction and Computational Investigation of Purely Siliceous Zeolite Y under
1121 Pressure. *J Am Chem Soc* 126:12015-12022.
- 1122 Colligan M, Lee Y, Vogt T, Celestian AJ, Parise JB, Marshall WG, Hriljac JA (2005) High
1123 Pressure Neutron Powder Diffraction Study of Superhydrated Natrolite. *J Phys Chem B*
1124 109:18223-18225.
- 1125 Combariza AF, Gomez DA, Sastre G (2013) Simulating the properties of small pore silica zeolites
1126 using interatomic potentials. *Chem Soc Rev* 42:114–127.
- 1127 Comboni D, Gatta GD, Lotti P, Merlini M, Liermann H-P (2017) On the *P*-induced behavior of the
1128 zeolite phillipsite: an in situ single-crystal synchrotron X-ray diffraction study. *Phys Chem*
1129 *Minerals* 44:1-20.

- 1130 Comodi P, Gatta GD, Zanazzi PF (2001) High-pressure structural behavior of heulandite. *Eur J*
1131 *Mineral* 13:497-505.
- 1132 Coombs DS, Alberti A, Armbruster T, Artioli G, Colella C, Galli E, Grice JD, Liebau F, Mandarino
1133 JA, Minato H, Nickel EH, Passaglia E, Peacor DR, Quartieri S, Rinaldi R, Ross M, Sheppard
1134 RA, Tillmanns E, Vezzalini G (1997) Recommended nomenclature for zeolite minerals: report
1135 of the Subcommittee on Zeolites of International Mineralogical Association, Commission on
1136 new minerals and minerals names. *Can Mineral* 35:1571-1606.
- 1137 Coudert FX, Cailliez F, Vuilleumier R, Fuchs AH, Boutin A (2009) Water nanodroplets confined in
1138 zeolite pores. *Faraday Discuss* 141:377-398.
- 1139 Coudert FX (2013) Systematic investigation of the mechanical properties of pure silica zeolites:
1140 stiffness, anisotropy, and negative linear compressibility. *Phys Chem Chem Phys* 15:16012-
1141 16018.
- 1142 Cruciani G (2006) Zeolites upon heating: Factors governing their thermal stability and structural
1143 changes. *J Phys Chem Solids* 67:1973-1994.
- 1144 Cucinotta F, Guenet A, Bizzarri C, Mróz W, Botta C, Milián-Medina B, Gierschner J, De Cola, L
1145 (2014) Energy Transfer at the Zeolite L Boundaries: Towards Photo- and Electroresponsive
1146 Materials. *ChemPlusChem* 79:45-57.
- 1147 De Boer K, Jansen, APJ, Van Santen, RA (1995) Structure-stability relationships for all-silica
1148 structures. *Phys Rev B* 52:12579-12590.
- 1149 De Silva P, Wesolowski TA (2012) Exact non-additive kinetic potentials in realistic chemical
1150 systems. *J Chem Phys* 137:094110.
- 1151 De Wispelaere K, Ensing B, Ghysels A, Meijer EJ, Van Speybroeck V (2015) Complex Reaction
1152 Environments and Competing Reaction Mechanisms in Zeolite Catalysis: Insights from
1153 Advanced Molecular Dynamics. *Chem Eur J* 21:9385–9396.
- 1154 Decker DL, Petersen S, Debray D, Lambert M (1979) Pressure-induced ferroelastic phase transition
1155 in $\text{Pb}_3(\text{PO}_4)_2$: A neutron-diffraction study. *Phys Rev B* 19:3552–3555.
- 1156 Dellago C, Bolhuis PG, Chandler D (1998) Efficient transition path sampling: Application to
1157 Lennard-Jones cluster rearrangements. *J Chem Phys* 108:9236-9245.
- 1158 Demichelis R, Civalleri B, Ferrabone M, Dovesi R (2010) On the performance of eleven DFT
1159 functionals in the description of the vibrational properties of aluminosilicates. *Int J Quantum*
1160 *Chem* 110:406–415.
- 1161 Demontis P, Suffritti GB, Quartieri S, Fois ES, Gamba A (1987) Molecular dynamics studies on
1162 zeolites. II: A simple model for silicates applied to anhydrous natrolite. *Zeolites* 7:122-127.

- 1163 Demontis P, Suffritti GB, Quartieri S, Fois ES, Gamba A (1988). Molecular dynamics studies on
1164 zeolites. 3. Dehydrated zeolite A. *J Phys Chem* 92(4):867-871.
- 1165 Demontis P, Suffritti GB, Quartieri S, Fois ES, Gamba A (1990). Molecular dynamics studies on
1166 zeolites. 4. Diffusion of methane in silicalite. *J Phys Chem* 94(10):4329-4334.
- 1167 Desbiens N, Demachy I, Fuchs AH, Kirsch-Rodeschini H, Soulard M, Patarin J (2005) Water
1168 Condensation in Hydrophobic Nanopores. *Angew Chem Int Ed* 44: 5310–5313.
- 1169 Dove MT, Trachenko KO, Tucker MG, Keen DA (2000) Rigid Unit Modes in framework
1170 structures: theory, experiment and applications. *Rev Mineral Geochem* 39:1–33
- 1171 Dovesi R, Orlando R, Civalleri B, Roetti C, Saunders VR, Zicovich-Wilson CM (2005) CRYSTAL:
1172 a computational tool for the ab initio study of the electronic properties of crystals. *Z Kristallogr*
1173 220:571–573.
- 1174 Erba A, Mahmoud A, Orlando R, Dovesi R (2014a) Elastic properties of six silicate garnet end
1175 members from accurate ab initio simulations. *Phys Chem Minerals* 41:151–160.
- 1176 Erba A, Mahmoud A, Orlando R, Dovesi R (2014b) Erratum to: elastic properties of six silicate
1177 garnet end-members from accurate ab initio simulations. *Phys Chem Minerals* 41:161–162.
- 1178 Erba A Caglioti D, Zicovich-Wilson CM, Dovesi R (2017) Nuclear-relaxed elastic and piezoelectric
1179 constants of materials: Computational aspects of two quantum-mechanical approaches. *J*
1180 *Comput Chem* 38: 257–264.
- 1181 Ferro O, Quartieri S, Vezzalini G, Fois E, Gamba A, Tabacchi G. (2002). High-pressure behavior of
1182 bikitaite: An integrated theoretical and experimental approach. *Am Mineral* 87:1415-1425.
- 1183 Fischer M, Delgado MR, Areán CO, Duran CO (2015) CO adsorption complexes in zeolites: how
1184 does the inclusion of dispersion interactions affect predictions made from DFT calculations?
1185 The case of Na-CHA. *Theor Chem Acc* 134:91
- 1186 Fischer M (2015) Structure and bonding of water molecules in zeolite hosts: benchmarking plane-
1187 wave DFT against crystal structure data. *Z Kristallogr* 230:325–336.
- 1188 Fischer M, Evers FO, Formalik F, Olejniczak A (2016) Benchmarking DFT-GGA calculations for
1189 the structure optimisation of neutral-framework zeotypes. *Theor Chem Acc* 135: 257.
- 1190 Fischer M, Angel R (2017) Accurate structures and energetics of neutral-framework zeotypes from
1191 dispersion-corrected DFT calculations. *J Chem Phys* 146: 174111.
- 1192 Fois E, Tabacchi G, Quartieri S, Vezzalini G (1999). Dipolar host/guest interactions and
1193 geometrical confinement at the basis of the stability of one-dimensional ice in zeolite bikitaite. *J*
1194 *Chem Phys* 111: 355-359.
- 1195 Fois E, Gamba A, Tabacchi G (2000). First-principles simulation of the intracage oxidation of
1196 nitrite to nitrate sodalite. *Chem Phys Lett* 329:1-6.

1197 Fois E, Gamba A, Tabacchi G, Quartieri S, Vezzalini G (2001a) Water molecules in single file:
1198 first-principles studies of one-dimensional water chains in zeolites. *J Phys Chem B* 105:3012-
1199 3016.

1200 Fois E, Gamba A, Tabacchi G, Quartieri S, Vezzalini G (2001b) On the collective properties of
1201 water molecules in one-dimensional zeolitic channels. *Phys Chem Chem Phys* 3: 4158-4163.

1202 Fois E, Gamba A, Tabacchi G, Ferro O, Quartieri S, Vezzalini G (2002a) A theoretical investigation
1203 on pressure-induced changes in the vibrational spectrum of zeolite bikitaite. *Stud Surf Sci Catal*
1204 142:1877-1884.

1205 Fois E, Gamba A, Tilocca A (2002b) Structure and Dynamics of the Flexible Triple Helix of Water
1206 inside VPI-5 Molecular Sieves. *J Phys Chem B* 106:4806–4812.

1207 Fois E, Gamba A, Tabacchi G, Arletti R, Quartieri S, Vezzalini G (2005) The “template” effect of
1208 the extra-framework content on zeolite compression: The case of yugawaralite. *Am Mineral*
1209 90:28-35.

1210 Fois E, Gamba A, Tabacchi G, Quartieri S, Arletti R, Vezzalini G (2005) High-pressure behaviour
1211 of yugawaralite at different water content: an ab initio study. *Stud Surf Sci Catal*, 155:271-280.

1212 Fois E, Gamba A, Medici C, Tabacchi G (2005). Intermolecular Electronic Excitation Transfer in a
1213 Confined Space: A First-Principles Study. *ChemPhysChem* 6:1917-1922.

1214 Fois E, Gamba A, Medici C, Tabacchi G, Quartieri S, Mazzucato E, Arletti R, Vezzalini G,
1215 Dmitriev V (2008a) High pressure deformation mechanism of Li-ABW: Synchrotron XRPD
1216 study and ab initio molecular dynamics simulations. *Microporous Mesopor Mater* 115: 267-280.

1217 Fois E, Gamba A, Tabacchi G, Trudu F (2008b) First principles studies on boron sites. *Stud Surf*
1218 *Sci Catal* 174:751-754.

1219 Fois E, Tabacchi G, Calzaferri G (2010a) Interactions, Behavior and Stability of Fluorenone inside
1220 Zeolite Nanochannels. *J Phys Chem C* 114, 10572-10579.

1221 Fois E, Tabacchi G, Barreca D, Gasparotto A, Tondello G (2010b) “Hot” Surface Activation of
1222 Molecular Complexes: Insight from Modeling Studies. *Angew Chem Int Ed* 49:1944-1948.

1223 Fois E, Tabacchi G, Calzaferri G (2012) Orientation and Order of Xanthene Dyes in the One-
1224 Dimensional Channels of Zeolite L: Bridging the Gap between Experimental Data and
1225 Molecular Behavior. *J Phys Chem C* 116:16784-16799.

1226 Frenkel D, Smit B (2001) *Understanding Molecular Simulation*. Academic Press, San Diego, USA.

1227 Gabrieli A, Sant M, Demontis P, Suffritti GB (2014) Fast and efficient optimization of Molecular
1228 Dynamics force fields for microporous materials: Bonded interactions via force matching.
1229 *Microporous Mesoporous Mater* 197:339–347.

- 1230 Gabrieli A, Sant M, Demontis P, Suffritti GB (2016) A Combined Energy-Force Fitting Procedure
1231 to Develop DFT-Based Force Fields. *J Phys Chem C* 120:26309–26319.
- 1232 Gale JD (1997) GULP: A computer program for the symmetry-adapted simulation of solids. *J*
1233 *Chem Soc Faraday Trans* 93:629-637.
- 1234 Gartzia-Rivero L, Bañuelos J, López-Arbeloa I (2017) Photoactive Nanomaterials Inspired by
1235 Nature: LTL Zeolite Doped with Laser Dyes as Artificial Light Harvesting Systems. *Materials*
1236 10:495.
- 1237 Gatta GD (2005) A comparative study of fibrous zeolites under pressure. *Eur J Mineral* 17:411-422.
- 1238 Gatta GD (2008) Does porous mean soft? On the elastic behaviour and structural evolution of
1239 zeolites under pressure. *Z Kristallogr* 223:160–170.
- 1240 Gatta GD (2010a) Extreme deformation mechanisms in open-framework silicates at high-pressure:
1241 Evidence of anomalous inter-tetrahedral angles. *Micropor Mesopor Mater* 128:78–84.
- 1242 Gatta GD (2010b) Microporous materials at high pressure: Are they really soft? In E. Boldyreva
1243 and P. Dera, Eds., *High-Pressure Crystallography: From Fundamental Phenomena to*
1244 *Technological Applications. NATO Science for Peace and Security – Series B (Physics and*
1245 *Biophysics)*, 481-491. Springer Science, ISBN 978-90-481-9257-1.
- 1246 Gatta GD, Wells SA (2004) Rigid unit modes at high pressure: an explorative study of a fibrous
1247 zeolite-like framework with EDI topology. *Phys Chem Minerals* 31:465-474.
- 1248 Gatta GD, Lee Y (2006) On the elastic behaviour of zeolite mordenite: a synchrotron powder
1249 diffraction study. *Phys Chem Minerals* 32:726 – 732.
- 1250 Gatta GD, Wells SA (2006) Structural evolution of zeolite levyne under hydrostatic and non-
1251 hydrostatic pressure: geometric modelling . *Phys Chem Minerals* 33:243-255.
- 1252 Gatta GD, Angel RJ (2007) Elastic behavior and pressure-induced structural evolution of nepheline:
1253 implications for the nature of the modulated superstructure. *Am Mineral* 92:1446-1455.
- 1254 Gatta GD, Lotti P (2011) On the low-temperature behavior of the zeolite gobbinsite: A single-
1255 crystal X-ray diffraction study. *Micropor Mesopor Mater* 143:467–476.
- 1256 Gatta GD, Lee Y (2014) Zeolites at high pressure: A review. *Mineral Mag* 78:267-291.
- 1257 Gatta GD, Boffa Ballaran T, Comodi P, Zanazzi PF (2004a) Isothermal equation of state and
1258 compressional behaviour of tetragonal edingtonite. *Am Mineral* 89:633-639.
- 1259 Gatta GD, Boffa Ballaran T, Comodi P, Zanazzi PF (2004b) Comparative compressibility and
1260 equation of state of orthorhombic and tetragonal edingtonite. *Phys Chem Minerals* 31:288-298.
- 1261 Gatta GD, Comodi P, Zanazzi PF (2003) New insights on high-pressure behaviour of microporous
1262 materials from X-ray single-crystal data. *Micropor Mesopor Mater* 61:105-115.

- 1263 Gatta GD, Comodi P, Zanazzi PF, Boffa Ballaran T (2005) Anomalous elastic behavior and high-
1264 pressure structural evolution of zeolite levynite. *Am Mineral* 90:645-652.
- 1265 Gatta GD, Nestola F, Boffa Ballaran T (2006) Elastic behavior, phase transition and pressure
1266 induced structural evolution of analcime. *Am Mineral* 91:568-578.
- 1267 Gatta GD, Rotiroti N, Boffa Ballaran T, Pavese A (2008) Leucite at high-pressure: elastic
1268 behaviour, phase stability and petrological implications. *Am Mineral* 93:1588-1596.
- 1269 Gatta GD, Rotiroti N, Boffa Ballaran T, Sanchez-Valle C, Pavese A (2009a) Elastic behavior and
1270 phase-stability of pollucite, a potential host for nuclear waste. *Am Mineral* 94:1137-1143.
- 1271 Gatta GD, Sartbaeva A, Wells AS (2009b) Compression behaviour and flexibility window of the
1272 analcime-like feldspathoids: experimental and theoretical findings. *Eur J Mineral* 21:571-580.
- 1273 Gatta GD, Birch DW, Rotiroti N (2010) Reinvestigation of the crystal structure of the zeolite
1274 gobbinsite: A single-crystal X-ray diffraction study. *Am Mineral* 95:481-486.
- 1275 Gatta GD, Lotti P, Nestola F, Pasqual D (2012) On the high-pressure behavior of gobbinsite, the
1276 natural counterpart of the synthetic zeolite Na-P2. *Micropor Mesopor Mater* 163:259-269.
- 1277 Gatta GD, Bersani D, Lottici PP, Tribaudino M (2014) High-pressure Raman study of CH₄ in
1278 melanophlogite (type I clathrate). *Mineral Mag* 78:1661-1669.
- 1279 Gatta GD, Scheidl KS, Pippinger T, Skála R, Lee Y, Miletich R (2015) High-pressure behavior and
1280 crystal-fluid interaction under extreme conditions in paulingite [PAU-topology]. *Micropor*
1281 *Mesopor Mater* 206:34-41.
- 1282 Gatta GD, Brundu A, Cappelletti P, Cerri G, de' Gennaro B, Farina M, Fumagalli P, Guaschino L,
1283 Lotti P, Mercurio M (2016a) New insights on pressure, temperature, and chemical stability of
1284 CsAlSi₅O₁₂, a potential host for nuclear waste. *Phys Chem Minerals* 43:639-647.
- 1285 Gatta GD, Tabacchi G, Fois E, Lee Y (2016b) Behaviour at high pressure of
1286 Rb₇NaGa₈Si₁₂O₄₀·3H₂O (a zeolite with EDI topology): a combined experimental-computational
1287 study. *Phys Chem Minerals* 43:209-216.
- 1288 Giddy AP, Dove MT, Pawley GS, Heine V (1993) The determination of rigid unit modes as
1289 potential soft modes for displacive phase transitions in framework crystal structures. *Acta*
1290 *Crystallogr. A* 4:697-703.
- 1291 Gigli L, Arletti R, Tabacchi G, Fois E, Vitillo JG, Martra G, Agostini G, Quartieri S, Vezzalini G
1292 (2014) Close-Packed Dye Molecules in Zeolite Channels Self-Assemble into Supramolecular
1293 Nanoladders. *J Phys Chem C* 118 15372-15743.
- 1294 Delle Piane M, Corno M, Pedone A, Dovesi R, Ugliengo, P (2014) Large-Scale B3LYP
1295 Simulations of Ibuprofen Adsorbed in MCM-41 Mesoporous Silica as Drug Delivery System. *J*
1296 *Phys Chem C* 119: 26737-26749.

1297 Gillet P, Malézieux JM, Itié JP (1996) Phase changes and amorphization of zeolites at high
1298 pressure: The case of scolecite and mesolite. *Am Mineral* 81:651-657.

1299 Göttl F, Hafner J (2012) Structure and properties of metal-exchanged zeolites studied using
1300 gradient-corrected and hybrid functionals. I. Structure and energetics. *J Chem Phys* 136:064501.

1301 Göttl F, Grüneis A, Bučko T, Hafner J (2012) Van der Waals interactions between hydrocarbon
1302 molecules and zeolites: periodic calculations at different levels of theory, from density
1303 functional theory to the random phase approximation and Møller–Plesset perturbation theory. *J*
1304 *Chem Phys* 137:114111.

1305 Goryainov SV (2005) Pressure-induced amorphization of $\text{Na}_2\text{Al}_2\text{Si}_3\text{O}_{10}\cdot 2\text{H}_2\text{O}$ and KAlSi_2O_6
1306 zeolites. *Phys Status Solidi* 202:R25-R27.

1307 Grau-Crespo R, Acuay E, Ruiz-Salvador, AR (2002) A free energy minimisation study of the
1308 monoclinic–orthorhombic transition in MFI zeolite. *Chem Commun* 2544-2545.

1309 Greaves GN, Meneau F, Sapelkin A, Colyer LM, Gwynn IA, Wade S, Sankar G (2003) The
1310 rheology of collapsing zeolites amorphized by temperature and pressure. *Nature Mat* 2:622-629.

1311 Grimme S (2006) Semiempirical GGA-type density functional constructed with a long-range
1312 dispersion correction. *J Comput Chem* 27:1787–1799.

1313 Grimme S (2011) Density functional theory with London dispersion corrections. *Wiley Interdiscip*
1314 *Rev Comput Mol Sci* 1:211–228.

1315 Gulín-González J, Suffritti GB (2004) Amorphization of calcined LTA zeolites at high pressure: a
1316 computational study. *Microporous Mesoporous Mater* 69:127–134.

1317 Gulín-González J, Pupo CT, Conyedo EN, Ruiz-Puentes A, Demontis P, Suffritti, GB (2016). A
1318 lattice dynamics study of ZK-4 microporous material under different temperature and pressure
1319 conditions. *Micropor Mesopor Mater* 226:191-200.

1320 Gutiérrez-Sevillano JJ, Calero S, Hamad S, Grau-Crespo R, Rey F, Valencia S, Palomino M,
1321 Balestra SRG, Ruiz-Salvador AR (2016) Critical Role of Dynamic Flexibility in Ge-Containing
1322 Zeolites: Impact on Diffusion. *Chem Eur J* 22:10036-10043.

1323 Haines J, Léger JM, Gorelli F, Hanfland M (2001) Crystalline post-quartz phase in silica at high
1324 pressure. *Phys Rev Lett* 87:15503.

1325 Haines J, Cambon O, Levelut C, Santoro M, Gorelli F, Garbarino G (2010) Deactivation of
1326 Pressure-induced amorphization in silicalite SiO_2 by insertion of guest species. *J Am Chem Soc*
1327 132: 8860–8861.

1328 Hammonds KD, Dove MT, Giddy AP, Heine V (1994) Crush: a Fortran program for the analysis of
1329 the rigid-unit mode spectrum of a framework structure. *Am Mineral* 79:1207–1209

- 1330 Hazen RM (1983) Zeolite molecular sieve 4A: anomalous compressibility and volume
1331 discontinuities at high pressure. *Science* 219:1065-1067.
- 1332 Hazen RM, Finger LW (1984) Compressibility of zeolite 4A is dependent on the molecular size of
1333 the hydrostatic pressure medium. *J Appl Phys* 56:1838-1840.
- 1334 Hendriks FC, Schmidt JE, Rombouts JA, Lammertsma K, Bruijninx PC, Weckhuysen BM (2017).
1335 Probing Zeolite Crystal Architecture and Structural Imperfections using Differently Sized
1336 Fluorescent Organic Probe Molecules. *Chem Eur J* 23: 6305–6314.
- 1337 Huang Y, Havenga EA (2001) Why do zeolites with LTA structure undergo reversible
1338 amorphization under pressure? *Chem Phys Letter* 345:65-71.
- 1339 Iannuzzi M, Laio A, Parrinello M (2003). Efficient exploration of reactive potential energy
1340 surfaces using Car-Parrinello molecular dynamics. *Phys Rev Lett* 90:238302.
- 1341 Insuwan W, Rangriwatananon K, Meeprasert J, Namuangruk S, Surakhot Y, Kungwan N,
1342 Junguttiwong S (2016). Combined experimental and theoretical investigation on Fluorescence
1343 Resonance Energy Transfer of dye loaded on LTL zeolite. *Microp Mesop Mater* 241:372-382.
- 1344 Jónsson H, Mills G, Jacobsen KW (1998) Nudged Elastic Band Method for Finding Minimum
1345 Energy Paths of Transitions. In: *Classical and Quantum Dynamics in Condensed Phase*
1346 *Simulations*, Eds. Berne BJ, Ciccotti G, Coker DF, World Scientific, Singapore, pp. 51–66.
- 1347 Jordá JL, Rey F, Sastre G, Valencia S, Palomino M, Corma A, Segura A, Errandonea D, Lacomba
1348 R, Manjón FJ, Gomis Ó, Kleppe AK, Jephcoat AP, Amboage M, Rodríguez-Velamazán JA
1349 (2013) Synthesis of a Novel Zeolite through a Pressure-Induced Reconstructive Phase Transition
1350 Process. *Angew Chem Int Ed* 52: 10458–10462.
- 1351 Kalló D (2001) Applications of natural zeolites in water and wastewater treatment. *Rev Mineral*
1352 *Geochem* 45:519-550.
- 1353 Kenichi T (1999) Absence of the *c/a* anomaly in Zn under high pressure with a helium-pressure
1354 medium. *Phys Rev B* 60:6171–6174.
- 1355 Klotz S, Chervin J-C, Munsch P, Le Marchand G (2009) Hydrostatic limits of 11 pressure
1356 transmitting media. *J Phys D: Appl Phys* 42:075413.
- 1357 Komarneni S (1985) Phillipsite in Cs decontamination and immobilization. *Clays Clay Min* 33:145-
1358 151.
- 1359 Kremleva A, Vogt T, Rösch N (2013) Monovalent cation-exchanged natrolites and their behavior
1360 under pressure. A computational study. *J Phys Chem C* 117:19020-19030.
- 1361 Kremleva A, Vogt T, Rösch N (2014) Potassium-Exchanged Natrolite Under Pressure.
1362 Computational Study vs Experiment. *J Phys Chem C* 118: 22030-22039.

- 1363 Laio A, Parrinello M (2002) Escaping free-energy minima. Proc Natl Acad Sci USA 99:12562-
1364 12566.
- 1365 Larin AV, Trubnikov DN, Vercauteren DP (2005) Improvement of X-ray diffraction geometries of
1366 water physisorbed in zeolites on the basis of periodic Hartree-Fock calculations. Int J Quantum
1367 Chem 102:971–979.
- 1368 Lee C, Yang W, Parr RG (1988) Development of the Colle-Salvetti correlation-energy formula into
1369 a functional of the electron density. Phys Rev B 37:785–789.
- 1370 Lee Y, Hriljac JA, Vogt T, Parise JB, Edmondson M, Anderson P, Corbin D, Nagai T (2001) Phase
1371 Transition of Zeolite RHO at High-Pressure. J Am Chem Soc 123:8418-8419.
- 1372 Lee Y, Vogt T, Hriljac JA, Parise JB, Artioli G (2002a) Pressure-Induced Volume Expansion of
1373 Zeolites in the Natrolite Family. J Am Chem Soc 124:5466-5475.
- 1374 Lee Y, Vogt T, Hriljac JA, Parise JB, Hanson JC, Kim SJ (2002b) Non-framework cation migration
1375 and irreversible pressure-induced hydration in a zeolite. Nature 420:485-489.
- 1376 Lee Y, Hriljac JA, Vogt T (2004) Pressure-induced migration of zeolitic water in laumontite. Phys
1377 Chem Minerals 31:421-428.
- 1378 Lee Y, Hriljac JA, Parise JB, Vogt T (2005) Pressure-induced stabilization of ordered paranatrolite:
1379 a solution to the paranatrolite controversy. Am Mineral 90:252-257.
- 1380 Lee Y, Kao CC, Kim SJ, Lee HH, Lee DR, Shin, TJ, Choi JY (2007) Water Nanostructures
1381 Confined inside the Quasi-One-Dimensional Channels of LTL Zeolite. Chem Mater 19:6252-
1382 6257.
- 1383 Lee Y, Kim SJ, Kao CC, Vogt, T (2008) Pressure-Induced Hydration and Order-Disorder
1384 Transition in a Synthetic Potassium Gallosilicate Zeolite with Gismondine Topology. J Am
1385 Chem Soc 130:2842-2850.
- 1386 Lee Y, Hriljac JA, Vogt T (2010) Pressure-Induced Argon Insertion into an Auxetic Small Pore
1387 Zeolite. J Phys Chem C 114:6922–6927.
- 1388 Lee Y, Liu D, Seoung D, Liu Z, Kao CC, Vogt T (2011) Pressure- and Heat-Induced Insertion of
1389 CO₂ into an Auxetic Small-Pore Zeolite. J Am Chem Soc 133:1674–1677.
- 1390 Likhacheva AY, Seryotkin YV, Manakov AY, Goryainov SV, Ancharov AI, Sheromov MA (2006)
1391 Anomalous compression of scolecite and thomsonite in aqueous medium to 2 GPa. High Pres
1392 Res 26:449–453.
- 1393 Likhacheva AY, Seryotkin YV, Manakov AY, Goryainov SV, Ancharov AI, Sheromov MA (2007)
1394 Pressure-induced over-hydration of thomsonite: a synchrotron powder diffraction study. Am
1395 Mineral 92:1610–1615.

- 1396 Likhacheva AY, Malyshev ME, Manakov AY, Goryainov SV, Ancharov AI (2009) Non-
1397 hydrostatic compression of zeolite NaA in water medium: connection to anomalous
1398 conductivity. *Z Kristallogr* 224:137–143.
- 1399 Lippert G, Hutter J, Parrinello M (1997) A hybrid Gaussian and plane wave density functional
1400 scheme. *Mol Phys* 92:477-488
- 1401 Lotti P, Gatta GD, Rotiroti N, Cámara F (2012) High-pressure study of a natural cancrinite. *Am*
1402 *Mineral* 97:872–882.
- 1403 Lotti P, Arletti R, Gatta GD, Quartieri S, Vezzalini G, Merlini M, Dmitriev V, Hanfland M (2015a)
1404 Compressibility and crystal-fluid interactions in all-silica ferrierite at high pressure. *Micropor*
1405 *Mesopor Mater* 218:42 – 54.
- 1406 Lotti P, Gatta GD, Merlini M, Liermann H-P (2015b) High-pressure behavior of synthetic
1407 mordenite-Na: an in situ single-crystal synchrotron X-ray diffraction study. *Z Kristallogr*
1408 230:201–211.
- 1409 Lotti P, Gatta GD, Comboni D, Merlini M, Pastero L, Hanfland M (2016) AlPO₄-5 zeolite at high
1410 pressure: Crystal-fluid interaction and elastic behavior. *Micropor Mesopor Mat* 228:158-167.
- 1411 Maas H, Calzaferri G (2002) Trapping Energy from and Injecting Energy into Dye–Zeolite
1412 Nanoantennae. *Angew Chem Int Ed* 41:2284–2288.
- 1413 Maerzke KA, McGrath MJ, Kuo, IFW, Tabacchi G, Siepmann JI, Mundy, CJ (2009) Vapor–liquid
1414 phase equilibria of water modelled by a Kim–Gordon potential. *Chem Phys Lett* 479: 60-64.
- 1415 Machon D, Dmitriev VP, Bouvier P, Timonin PN, Shirokov VB, Weber H-P (2003)
1416 Pseudoamorphization of Cs₂HgBr₄. *Phys Rev B* 68:144104.
- 1417 Manzano H, Gartzia-Rivero L, Bañuelos J, López-Arbeloa I (2013) Ultraviolet–Visible Dual
1418 Absorption by Single BODIPY Dye Confined in LTL Zeolite Nanochannels. *J Phys Chem C*
1419 117: 13331-13336.
- 1420 Mao HK, Xu J, Bell PM (1986) Calibration of the ruby pressure gauge to 800 kbar under quasi-
1421 hydrostatic conditions. *J Geophys Res* 91:4673-4676.
- 1422 Martínez C, Corma A (2011). Inorganic molecular sieves: Preparation, modification and industrial
1423 application in catalytic processes. *Coord Chem Rev* 255:1558-1580.
- 1424 Martínez-Martínez V, García R, Gómez-Hortigüela L, Sola Llano R, Pérez-Pariente J, López-
1425 Arbeloa I (2014) Highly Luminescent and Optically Switchable Hybrid Material by One-Pot
1426 Encapsulation of Dyes into MgAPO-11 Unidirectional Nanopores. *ACS Photonics* 1: 205-211.
- 1427 Martoňák R, Laio A, Parrinello M (2003) Predicting crystal structures: The Parrinello–Rahman
1428 method revisited. *Phys Rev Lett* 90:75503.

1429 Marx D, Hutter J (2009) *Ab initio* molecular dynamics: basic theory and advanced methods.
1430 Cambridge University Press.

1431 Maxwell IE, Stork WHJ (2001) Hydrocarbon processing with zeolites. *Stud Surf Sc Catal* 137:
1432 747–819.

1433 Merrill L, Bassett WA (1974) Miniature diamond anvil pressure cell for single-crystal X-ray
1434 diffraction studies. *Rev Sc Instr* 45:290-294.

1435 Miletich R, Allan DR, Kuhs WF (2000) High-pressure single-crystal techniques. *Rev Mineral*
1436 *Geochem* 41:445–519.

1437 Miletich R, Hejny C, Krauss G, Ullrich A (2005) Diffraction techniques: Shedding light on
1438 structural changes at extreme conditions. In R. Miletich, Ed, *Mineral behaviour at extreme*
1439 *conditions*. European Mineralogical Union Notes in Mineralogy, Volume 7, pp. 281-338.

1440 Ming DW, Allen ER (2001) Use of natural zeolites in agronomy, horticulture, and environmental
1441 soil remediation. *Rev Mineral Geochem* 45:619-654. Morpurgo S (2015) A DFT study on Cu(I)
1442 coordination in Cu-ZSM-5: Effects of the functional choice and tuning of the ONIOM approach.
1443 *J Comput Chem* 36:660–669.

1444 Mumpton FA (1999) La roca magica: Uses of natural zeolites in agriculture and industry. *Proc Natl*
1445 *Acad Sci USA* 96:3463–3470.

1446 Narayanan B, Reimanis IE, Ciobanu, CV (2013). Atomic-scale mechanism for pressure-induced
1447 amorphization of β -eucryptite. *J Appl Phys*, 114:083520.

1448 Niwa K, Tanaka T, Hasegawa M, Okada T, Yagi T, Kikegawa T (2013) Pressure-induced noble gas
1449 insertion into Linde-type A zeolite and its incompressible behaviors at high pressure. *Micropor*
1450 *Mesopor Mater* 182:191–197.

1451 Ori S, Quartieri S, Vezzalini G, Dmitriev V (2008a) Pressure-induced structural deformation and
1452 elastic behavior of wairakite. *Am Mineral* 93:53-62.

1453 Ori S, Quartieri S, Vezzalini G, Dmitriev V (2008b) Pressure-induced over-hydration and water
1454 ordering in gismondine: A synchrotron powder diffraction study. *Am Mineral* 93:1393–1403.

1455 Otero Areán C, Nachtigallova D, Nachtigall P, Garrone E, Delgado MR (2007) Thermodynamics of
1456 reversible gas adsorption on alkali-metal exchanged zeolites—the interplay of infrared
1457 spectroscopy and theoretical calculations. *Phys Chem Chem Phys* 9:1421-1437. Pabalan RT,
1458 Bertetti FP (2001) Cation-Exchange Properties of Natural Zeolites. *Rev Mineral Geochem*
1459 45:453–518.

1460 Parrinello M, Rahman A (1980) Crystal Structure and Pair Potentials: A Molecular-Dynamics
1461 Study. *Phys Rev Lett* 45:1196-1199.

- 1462 Parrinello M, Rahman A (1981) Polymorphic transitions in single crystals: A new molecular
1463 dynamics method. *J Appl Phys* 52:7182-7185.
- 1464 Perdew JP (1986) Density-functional approximation for the correlation energy of the
1465 inhomogeneous electron gas. *Phys Rev B* 33:8822-8824.
- 1466 Perdew JP, Burke K, Ernzerhof M (1996) Generalized gradient approximation made simple. *Phys*
1467 *Rev Lett* 77:3865–3868.
- 1468 Perdew J, Ruzsinszky A, Csonka G, Vydrov O, Scuseria G, Constantin L, Zhou X, Burke K (2008)
1469 Restoring the density-gradient expansion for exchange in solids and surfaces. *Phys Rev Lett*
1470 100:136406.
- 1471 Piccini GM, Alessio M, Sauer J (2016) Ab Initio Calculation of Rate Constants for Molecule–
1472 Surface Reactions with Chemical Accuracy. *Angew Chem Int Ed* 55:5235:5237.
- 1473 Pisani C (1996) Quantum mechanical ab initio calculation of the properties of crystalline materials,
1474 *Lecture Notes in Chemistry*, Vol. 67, Springer-Verlag, Heidelberg.
- 1475 Pisani C (1999), Software for the quantum-mechanical simulation of the properties of crystalline
1476 materials: state of the art and prospects *J Mol Struct (Theochem)* 463:125-137.
- 1477 Popovic Z, Otter M, Calzaferri G, De Cola L (2007) Self-assembling living systems with functional
1478 nanomaterials. *Angew Chem Int Ed* 46: 6188-6191.
- 1479 Quartieri S, Montagna G, Arletti R, Vezzalini G (2011) Elastic behavior of MFI-type zeolites:
1480 Compressibility of H-ZSM-5 in penetrating and non-penetrating media. *J Solid State Chem*
1481 184:1505-1516.
- 1482 Remler D, Madden P (1990) Molecular dynamics without effective potentials via the Car-Parrinello
1483 approach. *Mol Phys* 70:921-966.
- 1484 Resel R, Oehzelt M, Shimizu K, Nakayama A, Takemura K (2004) On the phase-transition in
1485 anthracene induced by high pressure. *Solid State Commun* 129:103–106.
- 1486 Richard J, León Cid S, Rouquette J, van der Lee A, Bernard S, Haines J (2016) Pressure-Induced
1487 Insertion of Ammonia Borane in the Siliceous Zeolite, Silicalite-1F. *J Phys Chem C*
1488 120:9334–9340.
- 1489 Román-Román EI, Zicovich-Wilson CM (2015) The role of long-range van der Waals forces in the
1490 relative stability of SiO₂-zeolites. *Chem Phys Lett* 619:109-114.
- 1491 Rutter MD, Secco RA, Huang Y (2000) Ionic conduction in hydrated zeolite Li-, Na- and K-A at
1492 high pressures. *Chem Phys Letter* 331:189-195.
- 1493 Rutter MD, Uchida T, Secco RA, Huang Y, Wang Y (2001) Investigation of pressure-induced
1494 amorphization in hydrated zeolite Li-A and Na-A using synchrotron X-ray diffraction. *J Phys*
1495 *Chem Solids* 62:599-606.

1496 Sanders MJ, Leslie M, Catlow CRA (1984) Interatomic potentials for SiO₂. *J Chem Soc Chem*
1497 *Commun* 1271–1273.

1498 Santoro M, Gorelli FA, Bini R, Haines J, van der Lee A (2013) High-pressure synthesis of a
1499 polyethylene/zeolite nano-composite material. *Nat Commun* 4:1557.

1500 Santoro M, Dziubek K, Scelta D, Ceppatelli M, Gorelli FA, Bini R, Thibaud J-M, Di Renzo F,
1501 Cambon O, Rouquette J, Hermet P, van der Lee A, Haines J (2015) High Pressure Synthesis of
1502 All-Transoid Polycarbonyl $[-(C=O)-]_n$ in a Zeolite. *Chem Mater* 27:6486–6489.

1503 Santoro M, Scelta D, Dziubek K, Ceppatelli M, Gorelli FA, Bini R, Garbarino G, Thibaud J-M, Di
1504 Renzo F, Cambon O, Hermet P, Rouquette J, van der Lee A, Haines J (2016) Synthesis of 1D
1505 Polymer/Zeolite Nanocomposites under High Pressure. *Chem Mater* 28:4065–4071.

1506 Sartbaeva A, Wells SA, Treacy MMJ, Thorpe MF (2006) The flexibility window in zeolites. *Nature*
1507 *Mat* 5:962–965.

1508 Sartbaeva A, Gatta GD, Wells SA (2008) Flexibility window controls pressure-induced phase
1509 transition in analcime. *Europhys Let* 83:26002.

1510 Sartbaeva A, Wells SA (2012) Framework flexibility and rational design of new zeolites for
1511 catalysis. *Appl Petrochem Res* 2:69-72.

1512 Scelta D, Ceppatelli M, Santoro M, Bini R, Gorelli FA, Perucchi A, Mezouar M, van der Lee A,
1513 Haines J (2014) High Pressure Polymerization in a Confined Space: Conjugated Chain/Zeolite
1514 Nanocomposites. *Chem Mater* 26:2249–2255.

1515 Secco RA, Huang Y (1999) Pressure-Induced Disorder in Hydrated Na-A Zeolite. *J Phys Chem*
1516 *Solids* 60:999-1002.

1517 Seoung D, Lee Y, Kao CC, Vogt T, Lee Y (2013) Super-Hydrated Zeolites: Pressure-Induced
1518 Hydration in Natrolites. *Chem Eur J* 33:11100

1519 Seoung D, Lee Y, Cynn H, Park C, Choi KY, Blom DA, Evans WJ, Kao CC, Vogt T, Lee Y (2014)
1520 Irreversible Xenon Insertion into a Small Pore Zeolite at Moderate Pressures and Temperatures.
1521 *Nature Chem* 6:835-839.

1522 Seoung D, Lee Y, Kao CC, Vogt T, Lee Y (2015) Two-step pressure-induced superhydration in
1523 small pore natrolite with divalent extra-framework cations. *Chem Mat* 27:3874-3880.

1524 Seryotkin YV, Bakakin VV, Fursenko BA, Belitsky IA, Joswig W, Radaelli PG (2005) Structural
1525 evolution of natrolite during over-hydration: a high-pressure neutron diffraction study. *Eur J*
1526 *Mineral* 17:305-313.

1527 Seryotkin YV (2016) Evolution of the bikitaite structure at high pressure: A single-crystal X-ray
1528 diffraction study. *Micropor Mesopor Mater* 226: 415-423.

- 1529 Seryotkin YV, Bakakin VV, Likhacheva AY, Dementiev SN, Rashchenko SV (2017) Structural
1530 behavior of Ti-exchanged natrolite at high pressure depending on the composition of pressure-
1531 transmitting medium. *Phys Chem Minerals* (*in press*, doi:10.1007/s00269-017-0887-0).
- 1532 Sevigny JH, Whitechurch H, Storey M, Salters VJM (1992) Zeolite-facies metamorphism of central
1533 Kerguelen Plateau basalts. *Proc Ocean Drilling Program, Scientific Results* 120:63-69.
- 1534 Sheppard D, Xiao P, Chemelewski W, Johnson DD, Henkelman G (2012) A generalized solid-state
1535 nudged elastic band method. *J Chem Phys* 136:074103.
- 1536 Smit B, Maesen TL (2008) Molecular simulations of zeolites: adsorption, diffusion, and shape
1537 selectivity. *Chem Rev* 108:4125-4184.
- 1538 Spano E, Tabacchi G, Gamba A, Fois E (2006). On the Role of Ti (IV) as a Lewis Acid in the
1539 Chemistry of Titanium Zeolites: Formation, Structure, Reactivity, and Aging of Ti-Peroxo
1540 Oxidizing Intermediates. *A First Principles Study. J Phys Chem B*, 110:21651-21661.
- 1541 Tabacchi G, Hutter J, Mundy, CJ (2005) A density-functional approach to polarizable models: A
1542 Kim-Gordon response density interaction potential for molecular simulations. *J Chem Phys* 123:
1543 074108.
- 1544 Tabacchi G, Fois E, Calzaferri G (2015a) Structure of Nanochannel Entrances in Stopcock-
1545 Functionalized Zeolite L Composites. *Angew Chem Int Ed* 54: 11112–11116.
- 1546 Tabacchi G, Fois E, Barreca D, Carraro G, Gasparotto A, Maccato C (2015b) Modeling the first
1547 activation stages of the Fe(hfa)₂TMEDA CVD precursor on a heated growth surface. In:
1548 Advanced Processing and Manufacturing Technologies for Nanostructured and Multifunctional
1549 Materials II: A Collection of Papers Presented at the 39th International Conference on Advanced
1550 Ceramics and Composites (pp. 83-90). John Wiley & Sons, Inc., Hoboken, NJ, USA.
- 1551 Tabacchi G, Calzaferri G, Fois E (2016) One-dimensional self-assembly of perylene-diimide dyes
1552 by unidirectional transit of zeolite channel openings. *Chem Commun* 52:11195-11198.
- 1553 Taramasso M, Perego G, Notari B (1983) U.S. Patent 441051.
- 1554 Tkatchenko A, Scheffler M (2009) Accurate molecular Van Der Waals interactions from ground-
1555 state electron density and free-atom reference data. *Phys Rev Lett* 102:073005.
- 1556 Tribaudino M, Artoni A, Mavris C, Bersani D, Lottici PP, Belletti D (2008) Single-crystal X-ray
1557 and Raman investigation on melanophlogite from Varano Marchesi (Parma, Italy). *Am Mineral*
1558 93:88-94.
- 1559 Tribaudino M, Gatta GD, Lee Y (2010) A high-pressure cubic-to-tetragonal phase-transition in
1560 melanophlogite, a SiO₂ clathrate phase. *Micropor Mesopor Mater* 129:267–273.
- 1561 Tuma C, Sauer J (2004) A hybrid MP2/planewave-DFT scheme for large chemical systems: proton
1562 jumps in zeolites. *Chem Phys Lett* 387:388-394.

1563 Tuma C, Sauer J (2006) Treating dispersion effects in extended systems by hybrid MP2:DFT
1564 calculations - protonation of isobutene in zeolite ferrierite. *Phys Chem Chem Phys* 8:3955-3965.

1565 U.S. Geological Survey (2017) Mineral commodity summaries 2016. U.S. Geological Survey,
1566 Reston, Virginia, 202 p.

1567 VandeVondele J, Krack M, Mohamed F, Parrinello M, Chassaing T, Hutter J (2005) Quickstep:
1568 Fast and accurate density functional calculations using a mixed Gaussian and plane waves
1569 approach. *Comp Phys Commun* 167:103–12.

1570 Vermeiren W, Gilson JP (2009) Impact of zeolites on the petroleum and petrochemical industry
1571 *Top Catal* 52:1131-1161.

1572 Viani L, Minoia A, Cornil J, Beljonne D, Egelhaaf HJ, Gierschner J (2016). Resonant Energy
1573 Transport in Dye-Filled Monolithic Crystals of Zeolite L: Modeling of Inhomogeneity. *J Phys*
1574 *Chem C* 120:27192-27199.

1575 Wells SA, Dove MT, Tucker MG (2002) Real-space rigid-unit-mode analysis of dynamic disorder
1576 in quartz, cristobalite and amorphous silica. *J Phys Condens Matter* 14:4567-4584.

1577 Wells SA, Sartbaeva A, Gatta GD (2011) Flexibility windows and phase transitions of ordered and
1578 disordered ANA framework zeolites. *Europhys Let* 94:56001.

1579 Wells SA, Sartbaeva A (2012) Template-Based Geometric Simulation of Flexible Frameworks.
1580 *Materials* 5:415-431.

1581 Wells SA, Sartbaeva A (2015) GASP: software for geometric simulations of flexibility in
1582 polyhedral and molecular framework structures. *Mol Simul* 41:1409-1421.

1583 Wells SA, Leung KM, Edwards PP, Sartbaeva (2015) A Flexibility windows in faujasite with
1584 explicit water and methanol extra-framework content. *Dalton Trans* 44:5978-5984.

1585 Wesolowski TA, Warshel A (1993). Frozen density functional approach for ab initio calculations of
1586 solvated molecules. *J Phys Chem* 97: 8050-8053.

1587 White CLIM, Ruiz-Salvador AR, Lewis DW (2004) Pressure-induced hydration effects in the
1588 zeolite laumontite. *Angew Chem Int Ed* 54:469-472.

1589 Wiedemann SC, Ristanović Z, Whiting GT, Reddy Marthala VR, Kärger J, Weitkamp J, Wels B,
1590 Bruijninx PCA, Weckhuysen BM (2016). Large Ferrierite Crystals as Models for Catalyst
1591 Deactivation during Skeletal Isomerisation of Oleic Acid: Evidence for Pore Mouth Catalysis.
1592 *Chem Eur J* 22:199-210.

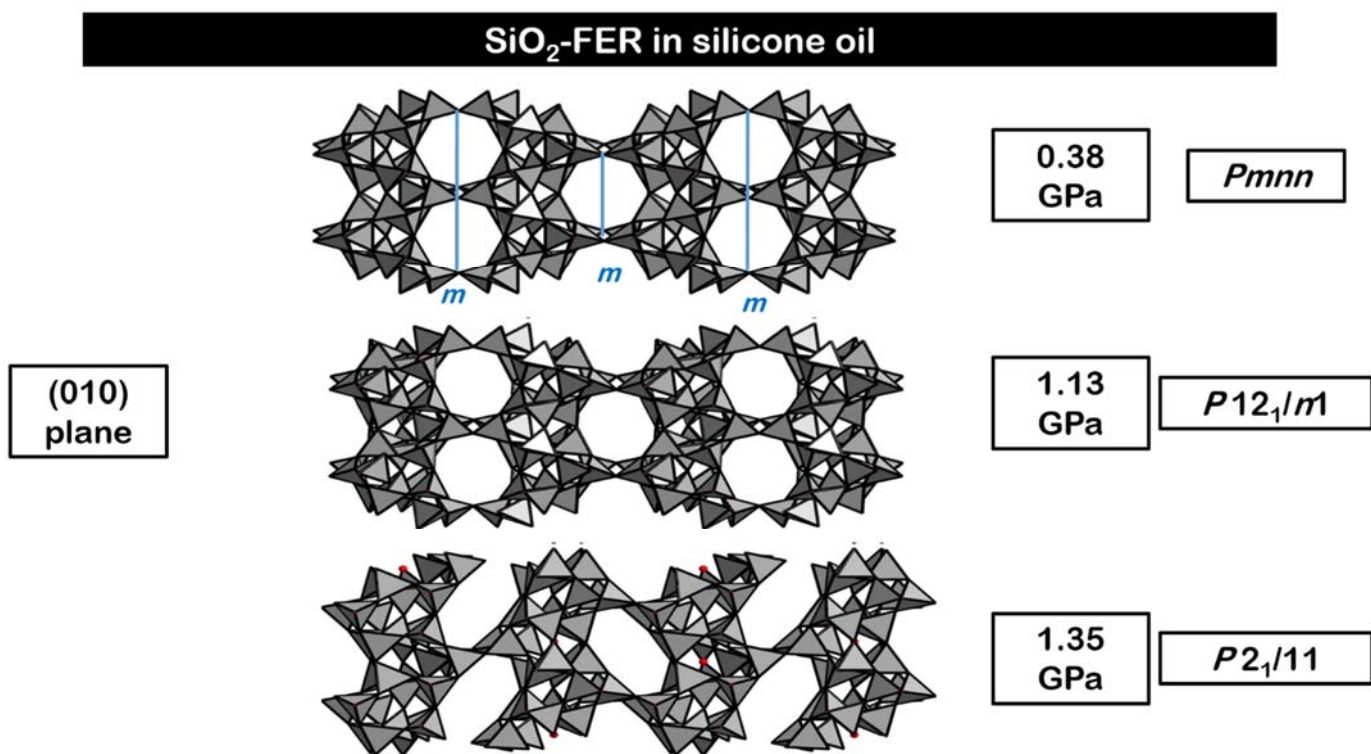
1593 Woodley SM, Catlow R (2008) Crystal structure prediction from first principles. *Nat Mat* 7:937-
1594 946.

1595 Wu Z, Cohen R (2006) More accurate generalized gradient approximation for solids. *Phys Rev B*
1596 73:235116.

- 1597 Yasukawa K, Liu H, Fujinaga K, Machida S, Haraguchi S, Ishii T, Nakamura K, Kato Y (2014)
1598 Geochemistry and mineralogy of REY-rich mud in the eastern Indian Ocean. *J Asian Earth Sc*
1599 93:25–36.
- 1600 Zhang L, Ahsbahs H, Kutoglu A (1998) Hydrostatic compression and crystal structure of pyrope to
1601 33 GPa. *Phys Chem Minerals* 25:301-307.
- 1602 Zhou X, Wesolowski TA, Tabacchi G, Fois E, Calzaferri G, Devaux A (2013) First-principles
1603 simulation of the absorption bands of fluorenone in zeolite L. *Phys Chem Chem Phys* 15:159-
1604 167.
- 1605

1606 Figure 1. Structure evolution of the all-silica ferrierite compressed in a non-penetrating fluid (see
1607 text for further details).

1608



1609 Figure 2. Surpramolecular organization of the H₂O and ethanol molecules inside the two-
1610 dimensional channel system of hydrophobic all-silica ferrierite. The guest molecules are in ball-
1611 and-stick representation. Hydrogen bonds are shown as dashed lines. Atom colors: H = white; C =
1612 cyan; O(ethanol) = red; O(H₂O) = blue. The structure is projected in the *ab* plane.
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