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## RESEARCH ARTICLES

# Close packing and pressure-induced amorphization

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Recently a large number of crystalline compounds have been discovered to amorphize at high pressures. However, the molecular origin of this transformation is not understood. In this article, we show that this is a consequence of a competition between the close-packing and long range order—a principle well known in organic crystallography. We show that the tendency of these systems to acquire higher coordination under compression is sterically hindered at some pressure due to the strong nature of inter-molecular bonding of building blocks. This hindrance drives the system to sacrifice the translational order to achieve better packing. The application of principle is shown through the examples of  $\text{Ca(OH)}_2$ ,  $\text{SiO}_2$ , ice,  $\text{LiKSO}_4$ , etc.

FROM the analysis of the packings of organic molecules, Kitaigorodskii<sup>1</sup> found that 'if the shape of the molecules is such that the formation of a long-range order leads to a larger percentage of empty space than in the absence of such an order in a close-packing arrangement, then no

crystal is obtained'. We show in this article that this principle is also very apt for understanding the mechanism of pressure-induced amorphization of materials. Starting with the first report of amorphization of ice<sup>2</sup> in 1984, presently about 20 substances are known to undergo this crystal-amorphous (c→a) transition under pressure (see Table 1 of Sikka<sup>3</sup>). However, its driving mechanism is still not clearly understood. In our view, the following scenario represents the physical reality. Application of pressure promotes close packing but the shape of the basic building block in the crystal may not favour this. Further compression may result in steric hindrances and ultimately destabilize the parent crystal structure. Formation of a new crystal structure would require a change in the shape of the basic packing unit, e.g. coordination change or dissociation. This step will involve bond breaking/bond making and diffusion of some atoms that may be inhibited at the low temperatures of the high pressure experiments. The

system may then lower its free-energy by vitrification owing to the higher configurational entropy in the amorphous phase.

Before giving specific examples in support of the above picture, two general systematics, for the substances which have vitrified under pressure, may be noted. The first is that most of these substances (about 75%) contain tetrahedral molecules. Since it is not possible to get a close-packing with tetrahedra, these substances crystallize under ambient conditions in open structures. Ice  $I_h$  (ref. 4) and polymorphs of  $\text{SiO}_2$  (ref. 5) are classic examples of this. The second is that a thermodynamical explanation requires the existence of a three level free-energy diagram, with kinetic barriers, for pressure-induced  $c \rightarrow a$  transitions<sup>3</sup>. The parent crystalline phase (I) is first driven into a higher free-energy state. The free-energy of this crystalline state (I) can be lowered either by the formation of an energetically more favourable crystalline phase (II), or by amorphization. The phase II (in cases where data are available) is known to have a higher coordination of the basic building block (e.g. in ice VIII, the oxygens are 8 coordinated<sup>6</sup>; in the high pressure rutile phase of  $\text{SiO}_2$ , there are  $\text{SiO}_6$  octahedra<sup>7</sup>, etc.). The formation of these requires high temperatures (e.g.  $> 150$  K for ice<sup>8</sup> and  $\approx 1000^\circ\text{C}$  for  $\text{SiO}_2$  (ref. 9), etc.). Moreover, just before amorphization, the phase I is in a metastable state, in the stability region of phase II. Now we present some case studies.

### $\text{Ca}(\text{OH})_2$

In the structure of  $\text{Ca}(\text{OH})_2$ , the rod-like hydroxyl groups (again a shape which cannot be closely packed according to Kitaigorodskii<sup>1</sup>) surround the Ca atoms in octahedral coordination<sup>10</sup> (Figure 1). In the uncompressed crystal the O---O separation is  $3.33 \text{ \AA}$  and hydrogen atoms participate in a rare, extremely weak, bridge type of hydrogen bond. The van der Waals distance between the two non-bonded hydrogen atoms is  $2.2 \text{ \AA}$ . On application of pressure the oxygen atoms move towards the ideal close-packing positions<sup>11</sup>. The O-H-O bond becomes stronger and just before amorphization at 11 GPa, the H-H distance decreases to  $2 \text{ \AA}$  while O---O separation is  $\approx 3 \text{ \AA}$ . The reduction in H-H distance produces a strong repulsive contribution

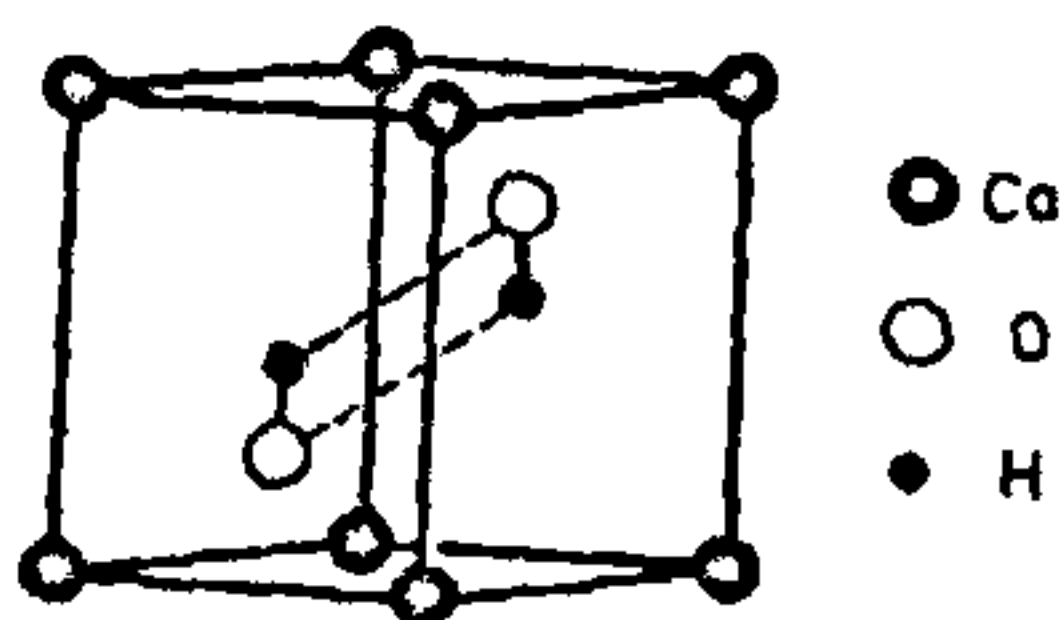


Figure 1. Unit cell of  $\text{Ca}(\text{OH})_2$ .

to the total energy. Using the bent hydrogen bond model of Chidambaram and Sikka<sup>12</sup> and including a repulsive interaction between the hydrogen atoms, it is seen that the gain in hydrogen bond energy ( $\approx -6.85 \text{ kJ/mole}$ ) is just offset by the repulsive energy of H-H atoms ( $6.81 \text{ kJ/mole}$ ) at 10.7 GPa. Thus, further compression will produce severe steric hindrance between the hydroxyl groups and would destabilize the crystal structure.

### Ice

The structure of ice  $I_h$  (Figure 2) has the oxygen frameworks consisting of two interpenetrating hexagonal close-packed (hcp) lattices of oxygen atoms<sup>4</sup>. The hydrogen bond here, between water molecules, is of a cooperative nature (i.e. O-H---O-H---O type). For such bonds a recent survey by Steiner and Senger<sup>13</sup> has shown that non-bonded hydrogens in O-H---O-H---O hydrogen bonds may approach each other to a well-defined minimal distance of  $\approx 2.05 \text{ \AA}$ . The H---H distance at ambient conditions is  $2.4 \text{ \AA}$ . From the known compressibility of ice ( $\approx 0.12 \text{ Mbar}^{-1}$ )<sup>14</sup>, we estimate that H---H distances ( $d_1$  and  $d_2$  in Figure 2) decrease to  $2.05 \text{ \AA}$  at 1 GPa. Again, we find that the amorphization of ice  $I_h$ , which takes place<sup>2</sup> at 1 GPa, coincides with the approach of limiting minimal distance.

### $\text{SiO}_2$ , $\text{GeO}_2$ and $\text{AlPO}_4$ - $\alpha$ quartz type

For these covalent substances, it is known that the onset of amorphization coincides with the bending of T-O-T (T for Si, Ge, Al, P) angles to near  $125^\circ$  and severe distortion of  $\text{TO}_4$  tetrahedra as oxygen approaches a close-packing configuration<sup>15-17</sup>. Following Thatchari and Tiller<sup>18</sup>, we can infer that the value  $125^\circ$  has a steric origin. They have shown that the distribution of T-O-T angles in silica is determined by the minimum intertetrahedral separation. When the latter is stipulated to be  $2.9 \text{ \AA}$  (about twice the van der Waals radius of oxygen) the distribution of T-O-T angle has a

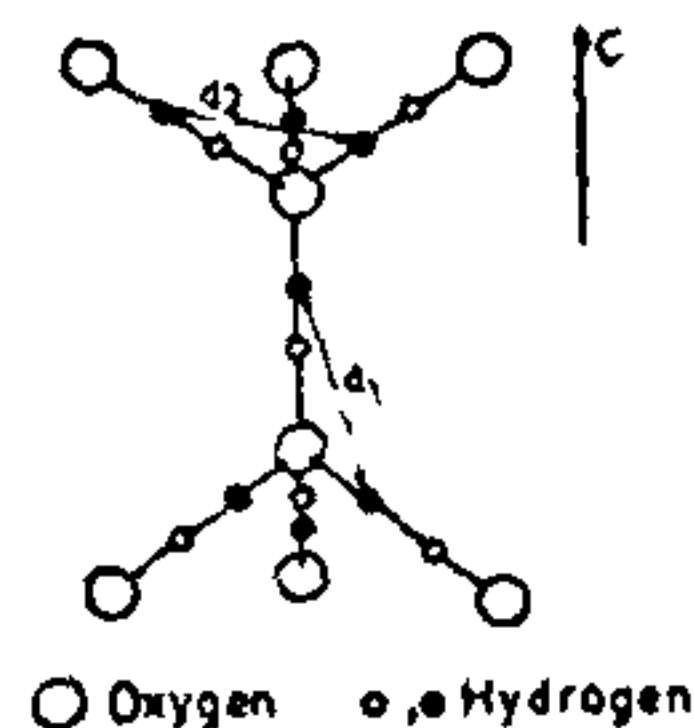


Figure 2. Cooperative hydrogen bond in ice  $I_h$ , based on the half-hydrogen model (open and filled circles). Note that either open or filled circles are occupied at a given time.



maximum around  $145^\circ$  with lower and upper cutoffs of  $120^\circ$  and  $180^\circ$  respectively, in excellent agreement with experimental data on silica glass. Single-crystal X-ray diffraction results<sup>15</sup> on  $\text{SiO}_2$  quartz reveal that at 12.5 GPa, when the Si–O–Si angle is  $124.2^\circ$ , the inter-tetrahedral oxygen separations are 2.934 Å and 2.719 Å. The distortion of  $\text{SiO}_4$  tetrahedra seems to permit a value lower than the van der Waals limit but is still within the 10% variation from the values used by Ramachandran and his co-workers<sup>19</sup> for formation of accepted structures in conformational analysis of biological structures.

In berylite,  $\text{AlPO}_4$ , which is isostructural with quartz, a plot of O---O separation as a function of pressure is shown in Figure 3 (ref. 17). In spite of the fact that it contains tetrahedra of different sizes ( $\text{Al}-\text{O}=1.73$  Å and  $\text{P}-\text{O}=1.52$  Å), it is borne out of molecular dynamical calculations that the limit for the O---O distance is 2.8 Å at 30 GPa, just where the amorphization begins to be indicated in the calculations<sup>17</sup>. Free energy ( $G=E-TS$ ) calculations of the phases I, II and amorphous state for the three level system show that  $E$ , the internal energy part for the amorphous phase, is very close to that of the crystalline phase I. Therefore, it is the entropy contribution which makes it more stable.

### $\text{LiKSO}_4$

It is an ionic compound belonging to a structural family with the general formula  $\text{A}'\text{A}''\text{B}\text{X}_4$  ( $\text{A}', \text{A}''=\text{Li}^+, \text{Na}^+, \text{NH}_4^+$ , etc.,  $\text{B}\text{X}_4=\text{SO}_4^{2-}, \text{SeO}_4^{2-}$ , etc.). These compounds form frameworks of six-membered rings of vertex connected  $\text{BX}_4$  and  $\text{A}'\text{X}_4$  tetrahedra. In these, the orientational and rotational degrees of freedom of the tetrahedra lead to different phases (e.g.  $\text{LiKSO}_4$  shows a large number of crystal-crystal phase transitions under temperature<sup>20</sup> and pressure<sup>21</sup>). An ideal packing diagram is shown in Figure 4. The  $\text{A}'$  and  $\text{B}$  atoms occupy hexagonal close packed lattices and  $\text{A}''$  ion is stuffed between the rings. Under compression,

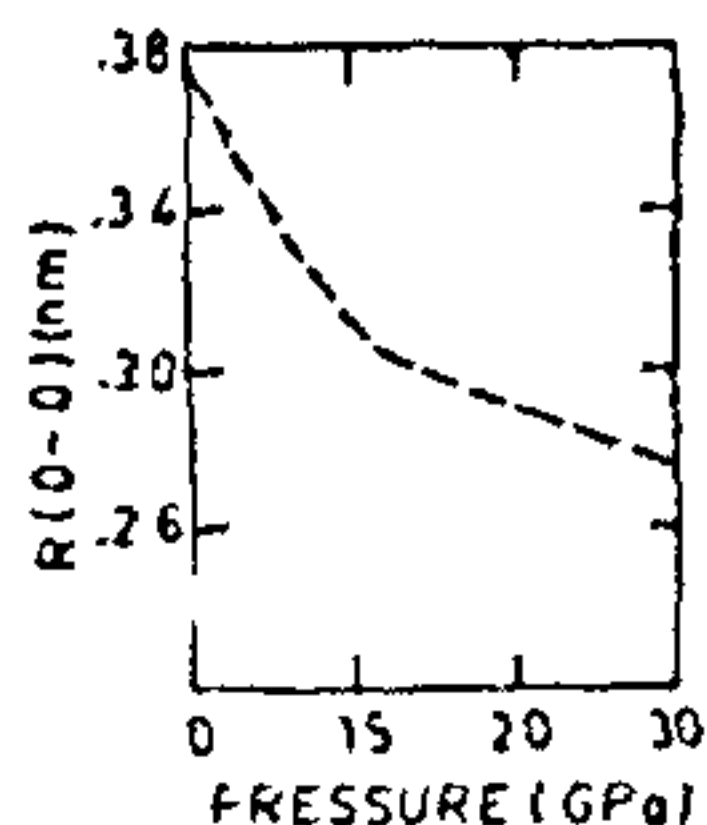


Figure 3. O---O separation as a function of pressure in  $\text{AlPO}_4$  (from the results of molecular dynamical calculations (ref. 17))

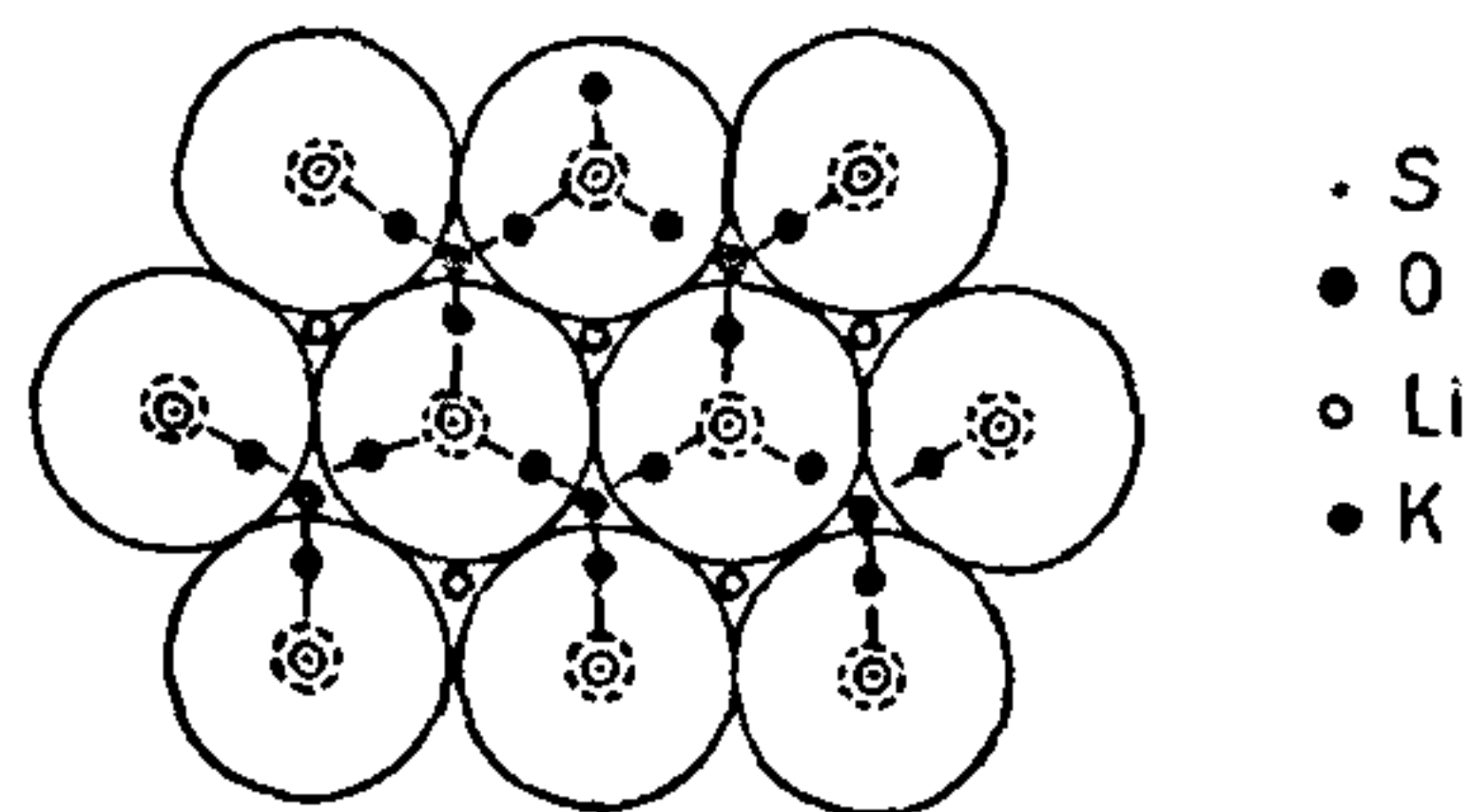


Figure 4. Ideal packing diagram of  $\text{LiKSO}_4$  as projected on the basal plane showing the close packing of  $\text{SO}_4$  tetrahedra. Centred small dots represent S, full circles O. The  $\circ$  and  $\bullet$ , shown in the interstices, represent Li and K while open dotted and full circles (around S) are O and Li as projected on the basal plane. The K atoms are  $\approx 1.7$  Å out of plane at normal pressure.

one degree of freedom allowed is the rotation of  $\text{BX}_4$  groups by  $60^\circ$ . This happens for every third  $\text{SO}_4^{2-}$  group in  $\text{LiKSO}_4$  at 2 GPa (ref. 17). Further compression produces a drastic reduction in  $c/a$  ratio from 1.68 to 1.4, with the result that the intertetrahedral oxygens come closer and the K–O bonds also shorten. Just prior to the amorphization, the latter are almost covalently bonded ( $\text{K}-\text{O} \approx 2.6$  Å, equal to the sum of Pauling single bond radii). Naturally, the increase of pressure beyond this point destabilizes the crystal structure.

The above examples clearly prove the proposition set forth in the introduction that the pressure-induced amorphization takes place to achieve close-packing. When the basic packing unit cannot tolerate further steric constraints, the amorphization sets in due to frustration resulting from the unfavourable kinetics to achieve a better coordination in the crystalline form. This fact seems to be independent of the type of bonding in the constituent units.

#### Note added in proof:

Recently  $\text{C}_{60}$  fullerite has been shown to transform to amorphous carbon near 20 GPa (Snoke *et al. Phys. Rev.*, 1992, **B45**, 14419 and *Phys. Rev. Lett.*, 1992, **69**, 466). The reason for this transformation is again the steric hindrance produced by short intramolecular van der Waals contacts. The shortest non-bonded C–C bond length of 3.12 Å at ambient reduces to 2.75 Å at the point of this phase transition ( $V/V_0 \approx 0.68$ ) which is very close to the intralayer distance at which graphite undergoes a phase transition (Zhao and Spain *Phys. Rev.*, 1989, **B40**, 993) and is also less than Ramachandran's limit of 2.9 Å. In fact, we find that the total (non-bonded) energy becomes fully repulsive at this point.

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# Fluid processes in the Earth's lower crust: evidence from microscale isotopic zonation in graphite crystals

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Coarse graphite crystals in a felsic pegmatite dyke at Mannantala, and adjacent to cordierite-rich patches within metapelites at Chittikara in the Kerala Khondalite Belt illustrate crystallization of graphite from CO<sub>2</sub>-rich fluids at temperatures around 700°C. A microscale sampling technique reveals remarkable carbon isotopic zonation within the domain of individual graphite crystals, with lighter cores ( $\delta^{13}\text{C} = -12.5\text{‰}$ ) mantled by heavier rims ( $-10.6\text{‰}$ ). The zonation patterns are correlated with equilibrium isotopic fractionation from CO<sub>2</sub>-rich fluids which infiltrated through structural pathways,

or which were transferred through magmatic conduits. The core compositions of the graphite crystals indicate  $\delta^{13}\text{C}$  values of  $-5$  to  $-6\text{‰}$  for the fluid from which they started crystallizing. This range is identical to the composition of CO<sub>2</sub> trapped within inclusions in the associated minerals, and comparable with CO<sub>2</sub> derived from carbon reservoirs in the subcontinental lithosphere. These results, when coupled with the geodynamics of fluid transfer mechanism in the lower crust, have important bearing on the genesis of gemstone and rare metal mineralization associated with veins and pegmatites.

MAGMATIC, metamorphic and metallogenic processes are often controlled by fluid movements and fluid-rock interaction processes in the earth's deep crust and in the crust-mantle interface. Stable isotopes of carbon, oxygen, hydrogen, nitrogen and sulphur provide important tracers of such fluid processes. Carbon, largely a trace

constituent within the earth, occurs in various forms such as, carbonate minerals, CO<sub>2</sub> trapped as inclusions within minerals, and graphite. Graphite is commonly associated with a variety of supracrustal rocks metamorphosed under a range of pressure-temperature (P-T) conditions, where it is mostly a product of the conversion of organic matter present in ancient sediments<sup>1</sup>. Graphite has also been recorded from ultramafic nodules

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