

Development of Computer Generated Structural Models : Teaching Aids in Soil Mineralogy

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Abstract : *Computer programs and graphics provide new generation tools for constructing structural models of minerals. These models can be rotated, providing views of different surfaces and angles, and can be subjected to 'virtual' reactions. Thereby, conceptualisation of mineral structures and understanding their reactivity or formation are greatly simplified.*

In this paper, we have presented development of 3D structures of minerals based on mathematical computation of the atomic positions in the crystal. This was used as input into the program RasMol or Moldraw to enable viewing and molecular rotation. Structures for oxides like goethite, hematite, gibbsite and boehmite were derived and their reactions with phosphate visualised. Subsequently, structures of olivine, epidote, tourmaline, enstatite, tremolite and kaolinite, representing the major classes of silicate minerals, were developed and their weathering simulated. Neoformation of layer silicates was also picturised.

The method presented here can be extended to any clay mineral and their weathered products as also neoformation routes under any given situation.

Crystallographic concepts of mineralogy are crucial for a clear understanding of various complex reactions that occur in the soil environment. Weathering and soil formation are two such processes whose comprehension can be greatly simplified by a good knowledge of crystal structures. Thus, crystal structure models help students to conceptualise the relative stabilities of minerals, grasp why olivine is unstable and mica or microcline are more stable or how degree of silica cross-linking affects mineral stability, comprehend the silica tetrahedral sheet, aluminium octahedral sheet, interlayer spaces, tetrahedral holes, differences between 2:1, 1:1, and 2:2 minerals, etc.

Many students cannot easily grasp 2D projections or pictures of models in books. Such lack of clear concepts of crystal structures, have been a drawback to this subject. However, there is no need to despair any more. Numerous modern tools for molecular modelling and visualisation have opened up new vistas for teaching and research on soil minerals. Many such tools are available free and can be downloaded from the internet, e.g., *RasMol*, *Xmol*, *Spartan*, *Moldraw*, *Unichem*, etc. To build and visualise crystals using the software, one needs the crystal coordinates for all atoms in terms of the lattice parameters. Some such lattice coordinates are available from various internet sources as described above

and from institutional websites. When such 'molecule building' information is not available, they can be computed and used for generating crystal structures.

In this paper, we show how crystal structures can be built up using basic geometrical and crystallographic concepts. Lattice coordinates for silica in various oxygen shared structures, silicates belonging to different groups, iron and aluminium oxides, and weathered residues have been derived. These can be downloaded (www.rcais.org.in/silicate) and viewed in *RasMol*.

Methods

The program *RasMol*, a freeware molecule viewer from the University of Massachusetts, runs on PCs and can be downloaded free from www.umass.edu/microbio/rasmol/. Any structure is viewed by opening the respective xyz file from File → Open. Molecules can be rotated by pressing the left mouse and moving it.

Two examples are provided to show how the xyz coordinates of a structure can be derived. In the first, a simple structure of a silica tetrahedron is derived and in the second, a complex structure of tourmaline is derived.

(i) *Deriving coordinates for a silica tetrahedron* : Fig. 1a is a 2D projection of a tetrahedron; O_A , O_B and O_C are oxygen atoms at positions A, B and C on the basal plane. O_D is the oxygen atom at the tip of the tetrahedron (point D) and point X is the projection of point D on to the plane containing ΔABC . The lengths AB, BC and CA represent the O-O distance which is taken as 2.6 Å (Grim, 1968). The x,y,z coordinates of O_B are assigned as 0, 0, 0. The x-coordinate of O_C is 2.6 and its y- and z-coordinates are 0. Therefore, $O_B = (0, 0, 0)$ and $O_C = (2.6, 0, 0)$.

Since ABC is an equilateral triangle, the line AP which passes through its center bisects BC. Therefore, $AP = 1.3$ Å and the x-coordinate of O_A is 1.3. In the ΔABP , $\angle B = 60^\circ$

$$\therefore AP = \sqrt{(AB^2 - BP^2)} = 2.252. \text{ The z-coordinate of } O_A \text{ is 0, hence } O_A = (1.3, 2.252, 0).$$

The x- and y-coordinates of O_D are given by the coordinates of the projected point X. The distances to A, B, C form the point X are such that $AX = BX = CX$. Hence, BX bisects $\angle B$. $\therefore \angle XBP = 30^\circ$. $\tan \angle XBP = XP/BP$, i.e., $\tan 30^\circ = XP/1.3$.

$\therefore XP = 0.751$. This is the y-coordinate of X (O_D). To compute the z-coordinate of O_D , we must first compute the length of BX. Here, $\cos \angle XBP = BP/BX$, i.e., $\cos 30^\circ = 1.3/BX$. $\therefore BX = 1.501$. Now we consider the ΔBXD (Fig. 1b). Here, $\angle BXD = 90^\circ$ and BD is the O-O distance, i.e., 2.6 Å. $\therefore DX = \sqrt{(BD^2 - BP^2)} = \sqrt{(2.6^2 - 1.501^2)} = 2.123$. The coordinates of O_D are thus, (1.3, 0.751, 2.123).

We now need to derive the coordinates of the Si atom which is at a point S on the line DX. Since the tetrahedral angle is $109^\circ 28'$, in the ΔBSD (Fig. 1) we

have $\angle \text{BSD} = 109^0 28'$. $\therefore \angle \text{BSX} = 180^0 - 109.467^0 = 70.533^0$. $\tan \angle \text{BSX} = \text{BX/SX}$, i.e., $\tan 70.533^0 = 1.501/\text{SX.} = 0.531$. Hence, the coordinates of Si = (1.3, 0.751, 0.531). The coordinates are then written in Notepad in the following format:

```
5
Tetrahedron
Si 1.3 0.751 0.532
O 0.0 0.000 0.000
O 1.3 2.252 0.000
O 2.6 0.000 0.000
O 1.3 0.751 2.123
```

The first line (5) describes the number of atoms and the second line is a descriptive one. The first column of the subsequent lines give atom names; the second, third and fourth columns give coordinates of the atoms (as derived here). Equal spacings must be maintained between columns. The file is then saved with the extension .xyz (name.xyz). This file is opened in *RasMol* to produce a tetrahedral model as shown in Fig. 2a.

By an extension of the same process, the structures of an octahedron (Fig. 2b) and silica units in nesosilicates (no O atom shared between the tetrahedrons), sorosilicates (one O atom shared), inosilicates (2 O atoms shared), cyclosilicates (2.5 O atom shared), phyllosilicates (3 O atoms shared) and tectosilicates (4 O atoms shared) are derived. Models are shown in Fig. F1a-f (on-line supplementary figures, can be downloaded from www.rcais.org.in/silicate). Structures of the oxides, viz., hematite, goethite, gibbsite and boehmite have also been derived in this way (Fig F2a-d; on-line models).

(ii) *Deriving coordinates for olivine (idealised structure)* : In the structure, isolated silica tetrahedral are linked by magnesium/iron octahedra. Oxygens form a close packed sheet along the 100 plane and the tips of the silica tetrahedra point above or below this plane in alternate rows (Fig. 3). Here, we illustrate a method of deriving coordinates based on crystallographic data. The cell dimensions (Deer *et al.*, 1975) as shown in the Fig. 3 are $a = 4.822 \text{ \AA}$ (perpendicular to plane of paper), $b = 10.488$ and $c = 6.09$ (along the x and y axis of the box). We start by assigning coordinates 0, 0, 0 to the position M_1 . Then M_2 has x coordinates at $\frac{1}{2}$ the b direction, i.e., at $10.488/2 = 5.244$. Its y coordinate is 0 and z coordinate at $\frac{1}{2}$ distance along the a direction, i.e., at $4.822/2 = 2.411$. The coordinates of M_3 are 10.488, 0, 0. The x and y coordinates of M_4 are $\frac{1}{4}$ of the b and c dimensions and are, therefore, at 2.622, 1.5225, 0. The coordinates for other Mg atoms can be similarly derived.

To derive the positions of oxygens, first we derive the O-O distance in this crystal. Here, the distance O_1 to O_2 is $\frac{1}{2}$ of c dimension, i.e., 3.045 \AA . \therefore In the $\Delta O_2 O_1 M_1$ formed by the projections of these atoms on the plane of the paper (Fig. 4a), $O_2 O_1 = 3.045$, $\angle O_1 O_2 M_1 = 30^0$ since the line $M_1 O_2$ bisects the $\angle O_3 O_2 O_1$. $\therefore \angle O_1 M_1 O_2 = 60^0$ and $\tan 60^0 = O_2 O_1 / O_1 M_1$, i.e., $O_1 M_1 = 1.758$. Next, we need to derive the vertical separation between the O atoms in the octahedron. The 6

oxygens surrounding M_1 form a hexagon (Fig. 4b). $\therefore \angle ABC = 120^\circ$. M_1 is at the center of the hexagon, therefore, $M_1B = M_1C = BC = 1.758$. The points O_1 , O_4 and the projection of O_4 on the plane containing O_1 form a triangle (Fig. 4c) where the distance O_4-P gives the vertical separation between the two layers of oxygens. Since $O_1-O_4 = 3.045$ and $P-O_1 = 1.758$, $\therefore O_4P = \sqrt{(3.045^2 - 1.758^2)} = 2.486$. Since oxygens are equally above and below the plane containing M_1 , the z coordinates of the atom O_4 is $2.486/2 = 1.243$ and that of O_1 is -1.243 (z axis considered negative above the plane of paper and positive below it). The coordinates of O_1 are, therefore, $1.758, 0, -1.243$. O_2 differs from O_1 only in its y coordinate, which is the O-O distance, viz., 3.045 . The x coordinate of O_4 is $\frac{1}{2}$ of the distance M_1-O_1 since the triangle formed by the projections of M_1 , O_1 and O_4 is equilateral and the perpendicular from O_1 to M_1-O_1 bisects it. O_3 has x coordinate equal and opposite to O_4 , y coordinate $\frac{1}{2}$ of O_2 and z coordinate equal to O_2 . Coordinates for other O surrounding M_1 are similarly derived.

Next, we need to derive the position of Si which is within the tetrahedron formed by O_1 , O_2 , O_3 and O_4 (Fig. 4a-b); Si is located at S on the line O_4-P (Fig. 4c) and forms an angle 190.467° at O_4-S-O_1 . $\therefore \angle PSO_1 = 180^\circ - 109.467^\circ = 70.533^\circ$. The distance $P-O_1$ is equal to the x direction distance of O_1 , i.e., $P-O_1 = 1.758$. In the ΔPSO_1 , $\tan 70.533 = 1.758/SP$. $\therefore SP = 0.6214$. The z coordinate of Si is 0.6214 below that of O_1 , i.e., at $-1.243 + 0.6214 = -0.6306$.

The next section of the crystal, R (Fig. 3), has Mg atoms which are displaced by $\frac{1}{2}b$ (along the x coordinate) and $\frac{1}{2}a$ (along the z coordinate). $O_{7, 8, 9}$ are below M_2 and $O_{10, 11, 12}$ are above it by the distance 1.243 . Thus, O_8 has x coordinates equal to $10.488/2 + 1.758$ (x coordinate O_2), y coordinate the same as O_2 and z coordinate 1.243 below M_2 , i.e., $1.243 + 4.822/2 = 3.654$. Thus $O_{7, 8, 9}$ have z = 3.654 and $O_{10, 11, 12}$ have z = $4.822/2 - 1.243 = 1.168$.

At a distance 4.822 below M_1 (not shown), there is an equivalent set of Mg and O for the units Q and S. These atoms have the same x and y coordinates as the surface atoms but have z values 4.822 more than these. Thus M_{1b} has coordinates $0, 0, 4.822$ and O_{1b} has coordinates $1.758, 0, 3.654$ ($4.822 - 1.243$). Coordinates of all atoms in the unit crystal (Fig. 3) can be obtained by similarly considering the displacements along the x, y or z directions. The resulting set of coordinates is then saved as a file in notepad with extension xyz.

Using similar methodologies, silica framework structures in 0, 1, 2, 2.5, 3 and 4 fold coordinations were drawn. Structural models of the oxide minerals, viz., hematite, goethite, gibbsite and boehmite were also derived. Among the silicates, the model of one mineral belonging to each class was developed. This may be noted that the structural units are not necessarily that of a single cell. Most single cells have far too many atoms and are complex and difficult to view. Therefore, only sections of cells are shown having the basic bonding units that are typical of the crystal.

Results and Discussion

The structures in *RasMol* or in *Moldraw* : Connectivities of atoms in *RasMol* may be sometimes incorrect. To view correct connectivities, the *case.mol*

files may be viewed in *Moldraw*. In RasMol, the models are rotated by holding down the left mouse while moving it and in *Moldraw* rotation is done by holding down the right mouse. Models F3a-b (on-line supplementary material; www.rcais.org.in/silicate) show a silica tetrahedron and an aluminium octahedron. It is essential for students to understand these structures before advancing to more complex structures. In particular, students should rotate the models to understand why the tetrahedron is projected as a triangle and the octahedron is projected as a hexagon or a square. Model F1a-f (on-line material) show silica units in various silicates. These may also be rotated to understand their projected representations.

The model of gibbsite (F2a) is the simplest structure of a real mineral that the students should grasp next. From this model, typical 2D representations as seen in books, can be understood. Structural differences between gibbsite and boehmite as well as hematite and goethite can be seen from the models (F2a-d; on-line material) and may be useful for research students working with sesquioxides.

Model F4a (on-line material) shows how silica tetrahedra are linked by Mg/Fe octahedra in the olivine structure. Linking between Al octahedral, Ca in 8-fold coordination and one-oxygen shared silica units in the epidote structure, can be understood from Model F5a. Similarly, the product formed after the first stage of weathering of epidote involving removal of Ca^{2+} ions, can be seen in the model (F5b). Enstatite structural unit with a chain of silica tetrahedra linked to magnesium octahedra can be seen in Model F6a. Release of silica chains on leaching of Mg^{2+} ions from the enstatite structure is shown in Model F6b. Part of a hornblende structure can be seen in Model F7a, with a complex arrangement of silica chains, Mg/Fe in octahedral and Ca and Na in 8-fold coordination. Weathering of the mineral, resulting in removal of Na^+ and Ca^{2+} ions, would not completely disrupt the structure (F7b), which would be held together by the rows of silica tetrahedra and magnesium octahedra. Biotite structure may be viewed in Model F8a and the altered product obtained after interlayer cation removal is shown in Model F8b.

Students can be encouraged to simulate weathering reactions by selective removal of cations from the crystal structures and visualise the effect on the crystal. Larger crystals can also be drawn to study surfaces and possible adsorption sites. Neoformation reactions can be carried out by building up silica sheets and stacking octahedral layers (Model F9). The possibilities are immense and limited only by the imagination of the student or researcher.

Acknowledgements

The work presented here is the outcome of quite a few Masters degree dissertations in Agricultural Chemistry and Soil Science of the University of Calcutta, each delivering at the most three-four structures. Their contribution is particularly praiseworthy because before the software is utilised, the 3D structure is to be manually depicted on a 2D plane with the help of basic geometric knowledge. In addition to hard labour, this is possible only when one sees the crystal before him.

References

Deer, W.A., Howie, R.A. and Zussman, J. 1975. *Rock-Forming Minerals. Volume 1. Ortho- and Ring Silicates*. Longmans, London.

Grim, R.E. 1968. *Clay Mineralogy*. McGraw-Hill, New York, USA.

On-line models

F1a-f : Silica tetrahedra with number of shared oxygens, 0, 1, 2, 2.5, 3 & 4.

F2a-d : Gibbsite, boehmite, goethite & hematite.

F3a-b : Silica tetrahedron & aluminium octahedron

F4a-b : Olivine & weathered olivine

F5a-b : Epidote & weathered epidote

F6a-b : Enstatite & weathered enstatite

F7a-b : Hornblende & weathered hornblende

F8a-b : Biotite & weathered biotite

F9 : Neoformation of kaolinite

LEGENDS TO FIGURES

Fig. 1 : (a) Projection of a tetrahedron.
(b) Section of a tetrahedron along the plane containing Si.

Fig. 2 : (a) 3D view of a tetrahedron.
(b) 3D view of an octahedron.

Fig. 3 : Olivine structure parallel to 100 plane. Large circles are oxygens; small circles are Mg atoms at
positions 0 and $\frac{1}{2}$.

Fig. 4 : (a)-(c) Sections of the olivine structure in Fig. 3.

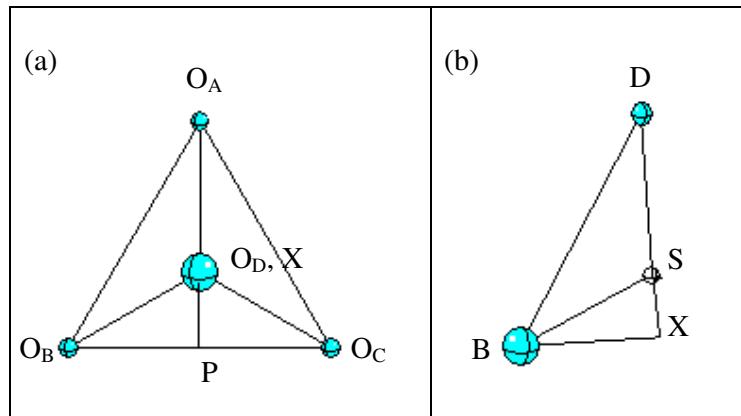


Fig 1

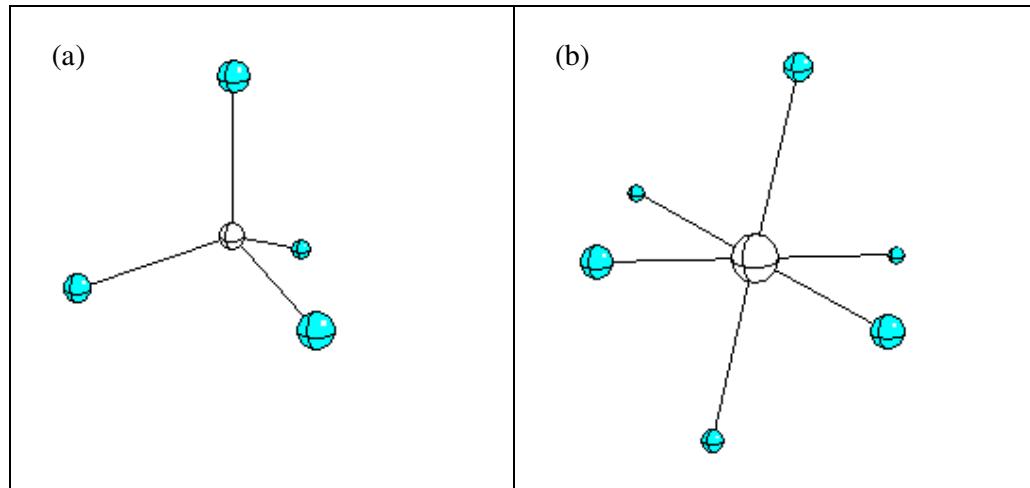


Fig 2

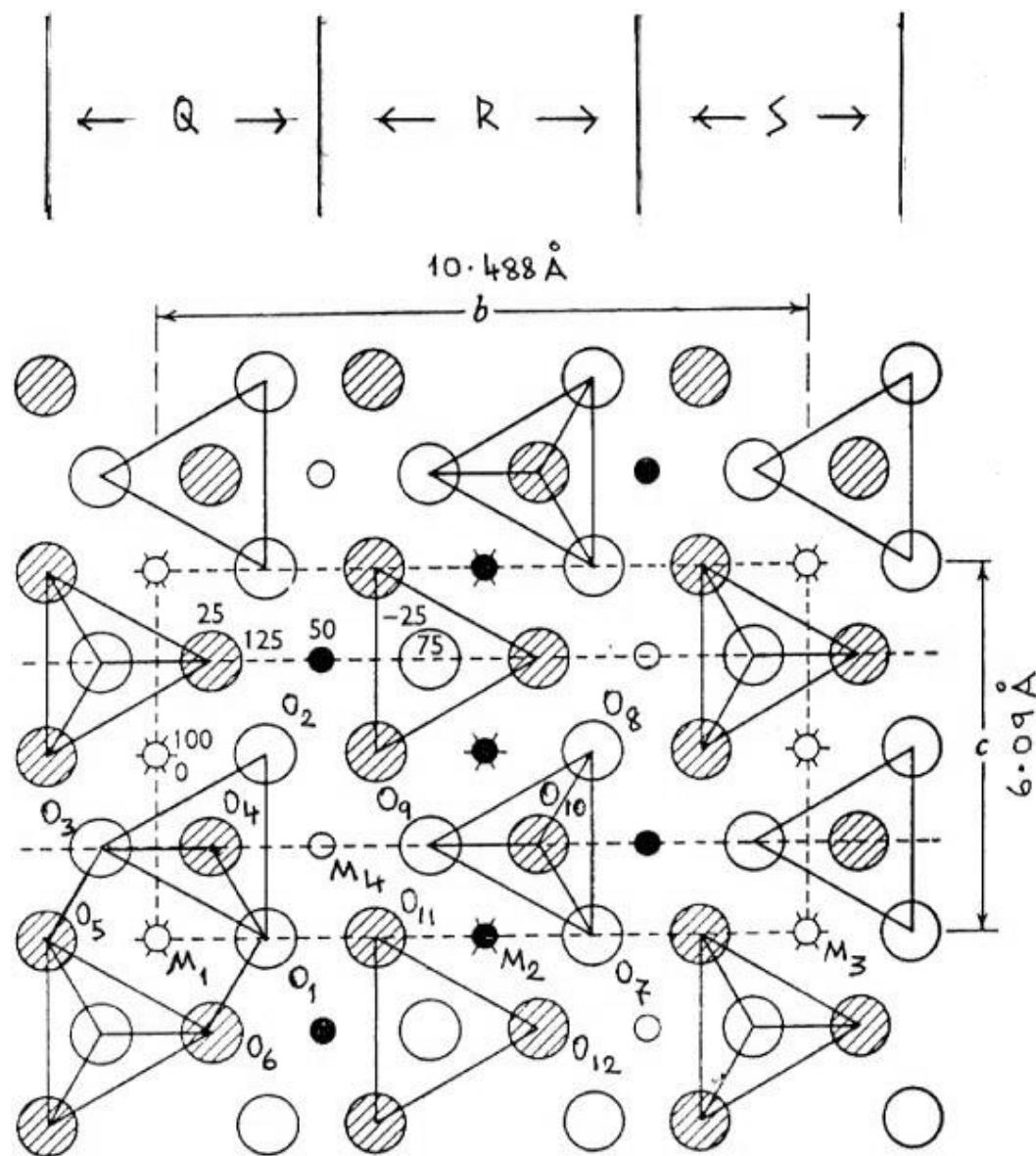


Fig. 3.

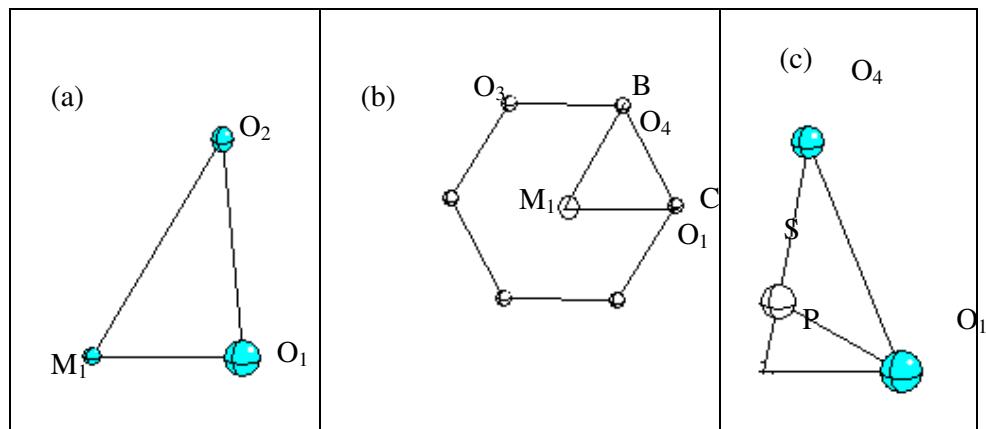


Fig 4