

## Structure of Cleaved Surfaces of Gypsum studied with Atomic Force Microscopy

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Atomic force microscopic (AFM) observation of cleaved surfaces of gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) clearly shows the arrangement of oxygen atoms belonging to sulphate groups and water molecules at the surface.

AFM<sup>1,2</sup> has a great advantage over scanning tunnelling microscopy (STM) in its applicability to non-conducting materials, giving us a wider selection of targets for study. Atomic scale images have been reported for insulators such as boron nitride<sup>3,4</sup> and a zeolite;<sup>5</sup> in addition to some conductors and semiconductors.<sup>6-8</sup>

Layered compounds such as graphite and molybdenite are

conveniently used as easy-to-handle and well-defined substrates in studying structures of molecules with STM and AFM. However, more hydrophylic substrates are sometimes required. We think that gypsum will make a good substrate for studying chemistry with AFM. In addition, the dissymmetry of its surface will facilitate the study of stereochemical features.

In this study a Digital Instruments Nanoscope II was used.

All experiments were performed in air at room temperature (295 K) and with a relative humidity of 55%.

The dehydration of gypsum has been widely studied in relation to its practical use, and crystal structures of a series of compounds with varying degrees of water content have been reported.<sup>9-13</sup> The single crystals of dihydrate used in this study are of natural origin (Kingman, AZ, USA). Its crystal structure consists of alternating layers of  $\text{CaSO}_4$  and water.<sup>10,11</sup> Cleavage occurs easily in the water layer connecting two  $\text{CaSO}_4$  layers by hydrogen bonds. The two opposite surfaces obtained are mirror images. Both surfaces must be checked using AFM in order to determine which side is being observed.

Fig. 1 shows a computer model of one of the cleaved surfaces studied. Calcium and sulphur atoms are located at the same level. Two oxygen atoms of each sulphate group protrude from the surface. Before cleavage, water molecules are located at a higher level. The positions of oxygen atoms are shown (denoted W) in Fig. 1. Each water molecule is coordinated to the nearest calcium ion and forms two hydrogen bonds, one with the nearest sulphate oxygen shown in Fig. 1, and another with a sulphate oxygen in the upper layer. The latter is broken when the upper layer is removed. On cleavage, the water molecule may desorb from the surface, or it may be stabilized at the surface by forming a new hydrogen bond with another oxygen atom in the lower layer.

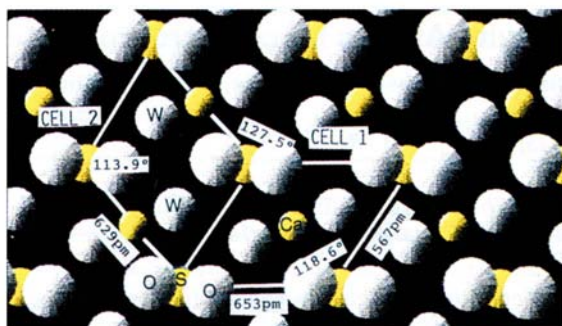
Two different surface unit cells are shown in Fig. 1. The cell dimensions were calculated from the data given in ref. 11. The cell 2 provides a common rhombic outer shape for the single crystals.<sup>14</sup>

Fig. 2 shows the AFM force image obtained in the 'constant height' mode. Poor quality at the right end is due to the change in the scan direction of the stylus, a common phenomenon in AFM. The parallelogram given in Fig. 2 corresponds to the unit cell 1 in Fig. 1. Two oxygen atoms of each sulphate group are observed separately with a distance of 230 pm, which is very close to 241 pm reported for the crystal.<sup>11</sup>

Since the sensitivities of the  $X$ - and  $Y$ -piezo scanners were not calibrated in atomic scales, distances measured from AFM images contain some uncertainties. Observed values for the cell dimensions were *ca.* 590 and 600 pm, implying an error of *ca.* 8%. The angle between the cell axes,  $115^\circ$ , was smaller than the theoretical value of  $118.6^\circ$ .

Within the unit cells shown in Fig. 2, less bright parts are noticed in addition to the sulphate oxygens. In order to check their mode of origin, the sample crystal was reset at a different angle on the sample stage. In the AFM observation the stylus is scanned in the horizontal direction and the 'ups-and-downs' of atoms are recorded. When two atoms are aligned in the scan direction with a short distance between them, they tend to be rather poorly resolved: rotation of samples often solves this problem.

The AFM height image obtained in the 'constant deflection'



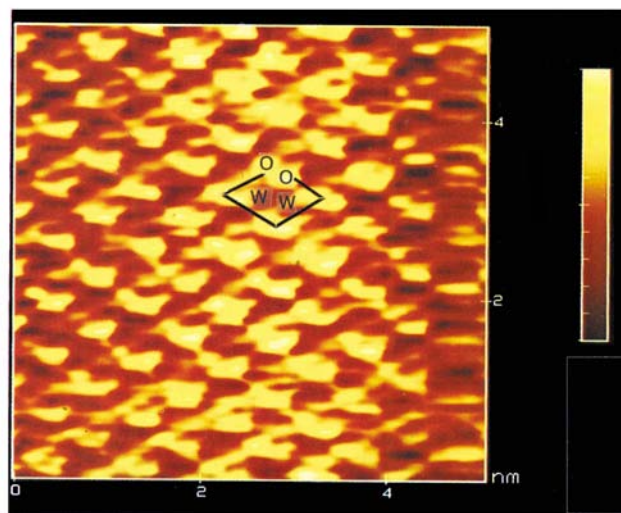
**Fig. 1** A model of cleaved  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  surface. Ca and S atoms are at the same height, while sulphate oxygens protrude from the surface. Water oxygens (denoted W) are located at even higher level before cleavage. Unit cell dimensions were calculated from the data in ref. 11. Fujitsu CRYSTRUCT graphic display system was used.

mode is shown in Fig. 3. The parallelogram given in Fig. 3 corresponds to the unit cell 2 in Fig. 1.

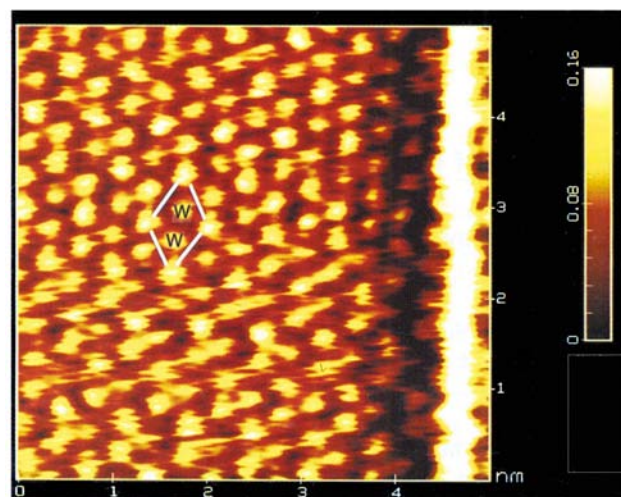
Because the oxygen atoms of each sulphate group are aligned horizontally in the scan direction, they only appear as a single bright spot instead of two separate spots. However, two additional spots are clearly observed within the unit cell.

Projected locations of oxygen atoms of a lower  $\text{CaSO}_4$  layer (not shown in Fig. 1) are close to the observed spots. However, they lie too low (239 pm below sulphate oxygens in the upper layer) to be observed. In addition the spot separation of 360 pm, observed in Fig. 3, is too large for sulphate oxygens.

The projected locations of water oxygens in Fig. 1 corresponds to the additional spots in Fig. 3. Most probably, therefore, the spots indicate the location of water molecules. As stated above, on cleavage, a hydrogen bond between each water molecule and the sulphate oxygen in the upper layer is broken. The molecule will thus not remain in the original position. However, the fact that water molecules are imaged as clear spots with AFM implies that the molecules adsorb rigidly onto the surface. It is likely that each water molecule is stabilized at the surface by coordination of the oxygen atom to



**Fig. 2** AFM force image (0.02 nN full scale, relative value) of one of the cleaved surfaces of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ . Unit cell 1 of Fig. 1 is shown. Sulphate oxygens are imaged as separate spots. 'W' denotes the location of the water oxygen in Fig. 1.



**Fig. 3** AFM height image (in nm unit) of cleaved  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ . Unit cell 2 of Fig. 1 is shown. Two sulphate oxygens appear as a single spot while water oxygens (denoted W) are separately observed.

a calcium ion and by hydrogen bonds to the oxygen atoms of two sulphate groups at the surface.

By carefully comparing Fig. 3 with Fig. 1, it can be seen that the spots are located closer to those cell edges having a central  $\text{Ca}^{2+}$  than to the edges without. It can also be seen from Fig. 3 that the two spots of the water oxygen on both sides of  $\text{Ca}^{2+}$  are often combined. This probably occurs because two water molecules are both coordinated to the same  $\text{Ca}^{2+}$ .

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