

Analysis of calcium oxygen coordination environment using Ca K-edge XANES

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The structural chemistry of calcium is of widespread importance to understanding materials as diverse as cements, dental materials and high temperature ceramic superconductors. Compounds of calcium are also of significant biological interest, fulfilling a wide range of roles in living organisms: from bone, teeth and shell formation to calcium binding proteins such as Troponin and Parvalbumin.

Many of these biological systems involve materials, which are either non- or “poorly” crystalline and are therefore well suited to structural investigations using X-ray absorption spectroscopy. Whilst the use of extended X-ray absorption fine structure (EXAFS) at the calcium K-edge is well documented in the literature for a wide range of fields [1a-f], there are relatively few studies of the X-ray absorption near edge structure (XANES).

In order to analyse calcium oxygen coordination environment, the XANES of a wide range of ‘model’ (i.e. well characterised, crystalline) calcium compounds and minerals were collected and these spectra were correlated to the known calcium/oxygen coordination environment, in order to generate a means by which calcium K-edge XANES spectra from compounds of unknown structure might be more fully interpreted.

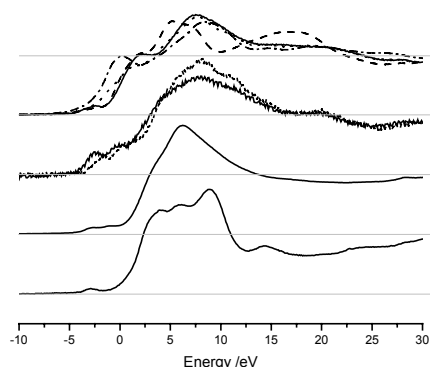
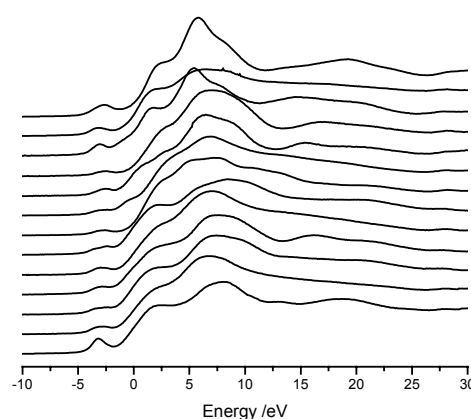


Figure 1: Xanes spectra of compounds with well defined coordination shells. From top: 6-coordinate, Okenite (solid), calcium carbonate (dashed), calcium hydroxide (dotted) and calcium oxide (dash/dot), 8-coordinate calcium molybdate (solid) and calcium tungstate (dotted), 9-coordinate calcium nitrate, 12-coordinate $\text{CaAl}_{12}\text{O}_{19}$. All spectra have been normalised to an absorbance edge jump of 1, indicated by the grey horizontal lines. Energy scale normalised to the Ca K-edge (4086 eV).

Figure 2. Xanes spectra of compounds with complex Ca-O coordination shells. From top, and with the coordination number shown in brackets: Calcium titanate (12), hydroxyapatite (8.4), calcium zirconate (8), calcium dihydrogen phosphate hydrate(8), Pseudowollastonite(8), calcium acetate (7.5), calcium hydrogen phosphate (7.5), Wollastonite (6.67), CaSiO_3 (6.67), Xonotlite (6.5), Gyrolite (6.3), Foshagite (6.25) and Grossite (5).



A clear correlation has been found between edge position and Ca-O coordination environment (Figure 3) for compounds with up to nine coordinate Ca-O environments. For compounds with Ca-O higher coordination the correlation breaks down, however, the overall *shape* of the post-edge spectral envelope is evidently indicative of high coordination. It may be seen in Figure 3 that the post edge spectral features samples having Ca in lower coordination environments continues out to ~22 eV beyond the edge before dropping below the normalised post-edge level of unity. As the coordination number increases, this envelope falls below unity by ~16 eV to the high energy side of the edge for 8-coordinate compounds, and at ~11 eV

beyond the edge for 12-coordinate compounds. In other words, the immediate post-edge features become narrower as the Ca-O first shell coordination number increases.

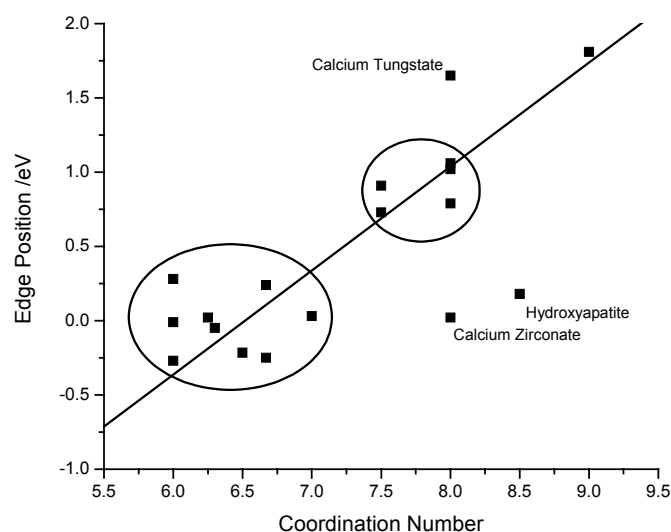


Figure 3. Correlation between XANES edge position and coordination number.

It is possible to use XANES at the Ca K-edge to determine average oxygen coordination numbers of up to nine atoms. Compounds with a higher coordination number have a distinctive shape in the post edge region and can be identified on this basis. In compounds with average coordination numbers up to and including nine, the edge position is diagnostic for coordination number via a shift of 0.7 ± 0.1 eV per atom. When the measured edge position is used in conjunction with a qualitative analysis of the post-edge absorption spectrum shape it is possible to comment with a high degree of confidence on the Ca-O coordination environment in more complex (e.g. amorphous) materials. The associated EXAFS data remains under analysis.

References

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