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# Quantitative Study of Electron Radiation Damage by in Situ Observation of the Phase Transformation from $CaCO_3$ to CaO as a Function of the Accelerating Voltage (20-300 kV)

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$CaCO_3$ (calcite) is one of the important systems in the field of biomineralisation and the most common carbonate of the earth crust inevitable for the manufacture of cements. Limestone is the chief raw material, which when heated about 900° C forms CaO (lime) by the reaction: $CaCO_3 \rightarrow CaO + CO_2\uparrow$. Apparently $CaCO_3$ undergoes the same phase transformation to CaO by electron-radiation damage. Therefore the new challenge arises to search for conditions and instrumental settings especially the applied accelerating voltage to study in situ the phase transformation on an atomic scale. The radiation damage can be caused on the one hand by thermal heating or on the other hand by knock on damage. The influence of knock on damage is studied by reducing the accelerating voltage from 300 kV down to 20 kV by using a CM20 operating at 200 kV, equipped with a LaB6 cathode, a TITAN operating at 300 kV and 80 kV equipped with a field emission gun and an imaging-side Cs-corrector and the newly developed SALVE prototype microscope equipped with a field emission gun, an image-side Cs-corrector and a monochromator [1] operating at 20, 40 and 80 kV. At high accelerating voltages the radiation damage of $CaCO_3$ is starting immediately with the electron-radiation and can be divided up in three stages first the amorphisation of the crystalline structure, then producing holes and at least recrystalisation in a polycrystalline structure with significant volume and correlated mass loss during the reaction time. Figure 1 a), b) show a $CaCO_3$ crystal and the correlated FFT, where the lattice planes can be imaged without any radiation damage. Figure 2 c), d) show the same crystal after 25 min radiation with a dose rate of $4x10^4$ e/nm$^2$s, where a polycrystalline structure is grown with lattice spacing fitting the CaO structure. Exemplary a starting image taken with the Titan and a dose rate of $4x10^4$ e/nm$^2$s at 300kV accelerating voltage is presented in Figure 2 e), where the radiation damage is visible by producing immediately a hole. Beside that hole the single crystal structure of the original calcite is still present in the FFT of the cut-out. We found that reduced accelerating voltages below 80 kV slows down the radiation damage and gives the freedom to align the instrument to obtain information on the atomic scale before significant beam damage effects appear. The quantitative studies of volume-loss at 20, 40 and 80 kV delivered increasing volume loss with decreasing accelerating voltages. This disadvantage of low accelerating voltages is counterbalanced by increasing contrast which allows the use of decreasing dose rates. To determine the mass loss the chemistry has to be known, therefore additionally EELS spectra were taken. Figure 2 show spectra taken with the SALVE microscope at 80kV of the C K, Ca $L_{23}$ and O K-edge where the fading out signal of carbon confirm the phase transformation. The high stability of the instrument enables additionally to measure in situ with ELNES the bond length variation of Ca in the pm range during the phase transformation.

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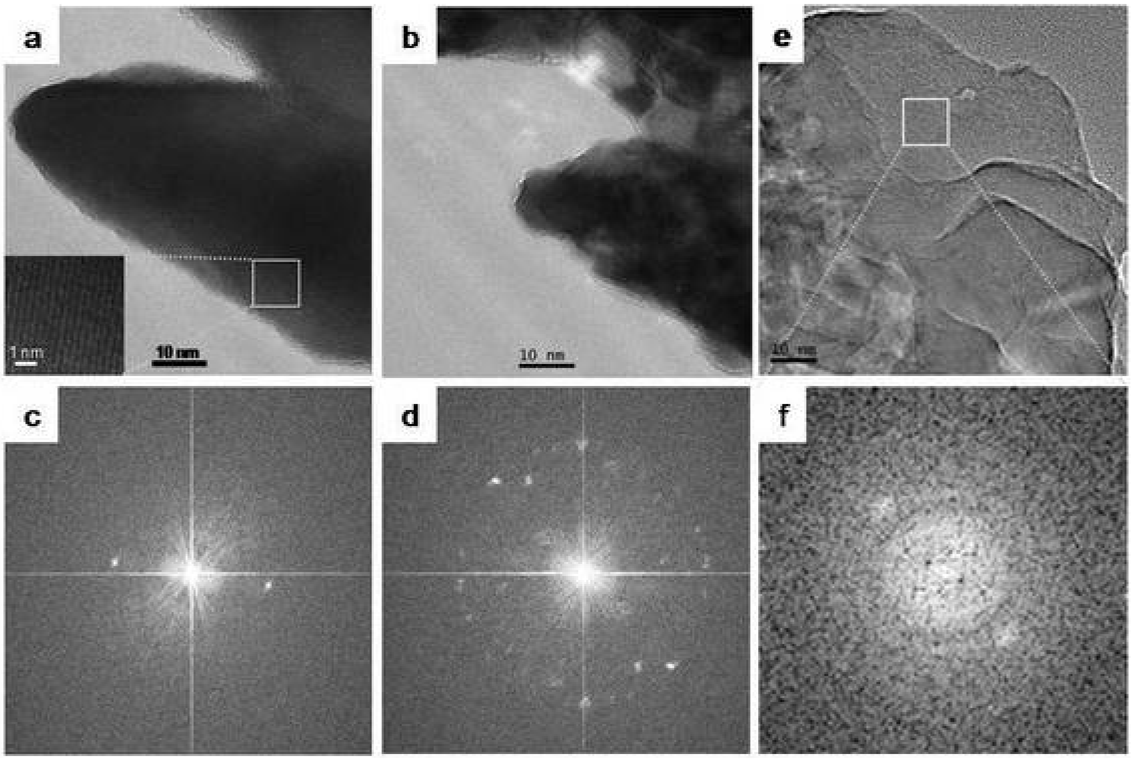


**Figure 1.** In situ study of calcite recorded with the SALVE at 20 kV (a-d) and Titan at 300kV (e,f) accelerating voltage and the corresponding FFTs, which shows the change of a single crystal structure to a polycrystalline structure by electron-irradiation damage.

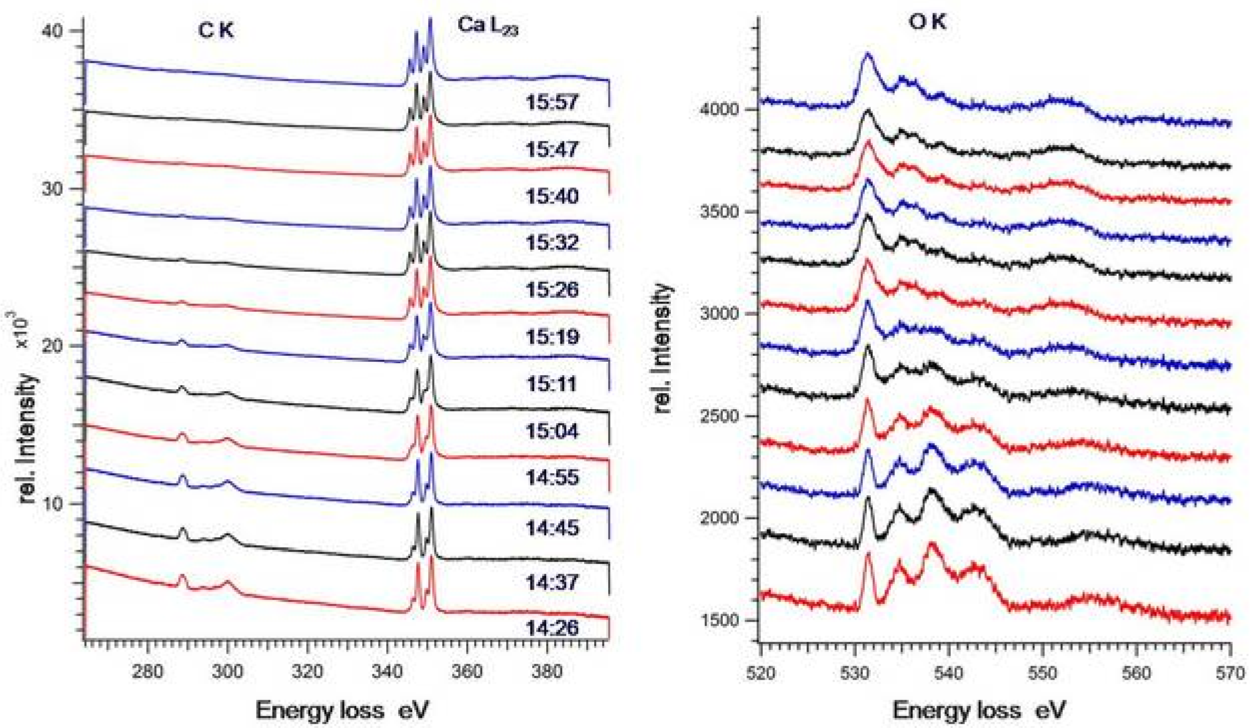


**Figure 2.** Electron energy loss spectra taken at 80kV during one phase transformation series of the C K, Ca $L_{23}$ and O K-edge

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