Report on the EXAFS measurements

EXAFS data were collected at the GILDA beamline at the Cu, Zn and Cd K edges. The data were extracted with the ATHENA code and analyzed with the ARTEMIS code. Here we recall the main results:

Sites in Hydroxyl-apatite (HA)

There are two sited for Ca in HA (named Ca1 and Ca2) and the related local structure is shown in Table 1:

Table 1: Details of the sites Ca_1 and Ca_2 in the HA structure.

Ca1

Neighbor	Number	Dist
O	3	2.399
O	3	2.457
O	3	2.807
P	1	3.208
P	2	3.208
Ca1	1	3.425
Ca1	1	3.453
P	3	3.584

Ca2

Neighbor	Number	Dist
O	1	2.311
O	2	2.348
O	1	2.374
O	2	2.501
O	1	2.700
P	1	3.075
P	1	3.265
O	2	3.347
O	1	3.493
P	1	3.494
Ca1	2	3.961
O	2	3.986
O	1	3.988
Ca2	2	4.003
Ca1	2	4.045
Ca2	4	4.144

Both sites are highly coordinated with O (7 to 9) whereas Ca2 is more disordered than Ca1.

# Cd-K edge

Data were analyzed basing on a cluster consisting in a Cd ion substituted in HA. The results are shown in Table 2 and Figure 1:

Table 2: Quantitative analysis of the Cd-K edge EXAFS data. The errors on the last digit are indicated in brackets.

Sample	N_{Cd-O}	R_{Cd-O} (Å)	σ^2_{Cd-O} (Å^2)	N_{Cd-P}	R_{Cd-P} (Å)	σ^2_{Cd-P} (Å^2)
CdO	6.0(3)	2.345(5)	0.0039(2)			
50 ppm	4.1(3)	2.27(1)	0.009(1)	2.3(7)	3.52(3)	0.02
100 ppm	4.2(3)	2.27(1)	0.009(1)	2(1)	3.53(3)	0.02
200 ppm	4.1(3)	2.27(1)	0.009(1)	2(1)	3.51(3)	0.02(1)
300 ppm	4.0(2)	2.27(1)	0.008(1)	2.1(6)	3.51(3)	0.02
500 ppm	4.9(2)	2.27(1)	0.0090(6)	2.4(9)	3.52(3)	0.017(6)

Figure 1 EXAFS and Fourier Transforms data of Cd samples. Left: EXAFS data (line) and best fit curves for the Cd samples; right: Fourier Transforms of the EXAFS data (line) and best fit curves for the Cd samples. Transforms were carried out in the interval k=[2.0-9.4]Å^{-1} with a k^2 weight.
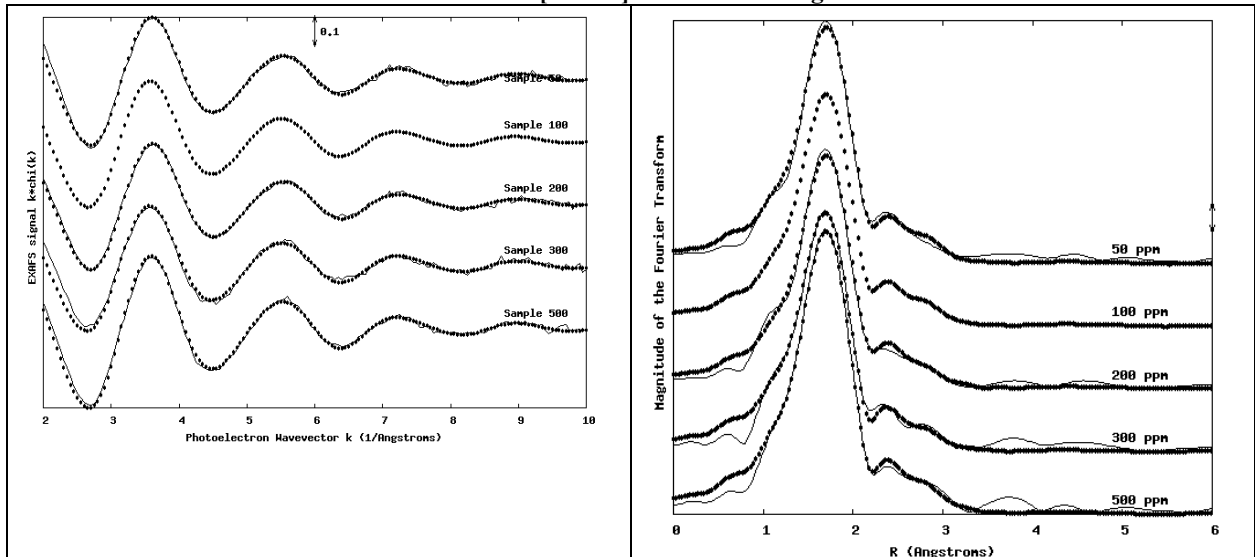

We note that the coordination of Cd is 4 and the Cd-O distance is 2.27 Å. This value is considerably contracted respect to the value observed in the 6-coordinated CdO (R_{Cd-O}=2.345 Å) although longer than the sum of the tetrahedrally radii tabulated in ref (R_{Cd-O}=1.405+0.678 = 2.083 Å). Both parameters evidence the presence of low-coordinated Cd that results from a heavy structural rearrangement around the impurity. The fit can be improved by adding a further Cd-P shell.

Zn-K edge

In this case we compared the data from the samples with reference compounds for tetrahedrally coordinated Zn (Wurtzite ZnO) and octahedrally coordinated Zn (Zn^{2+} ion in water solution). The results are shown in Figure 2 and Table 3:

Figure 2: EXAFS and Fourier Transforms data of Zn samples. Left: EXAFS data (line) and best fit curves for the Zn samples; right: Fourier Transforms of the EXAFS data (line) and best fit curves for the Zn samples. Transforms were carried out in the interval k=[2.5-11.0]$Å^{-1}$ with a k^2 weight.
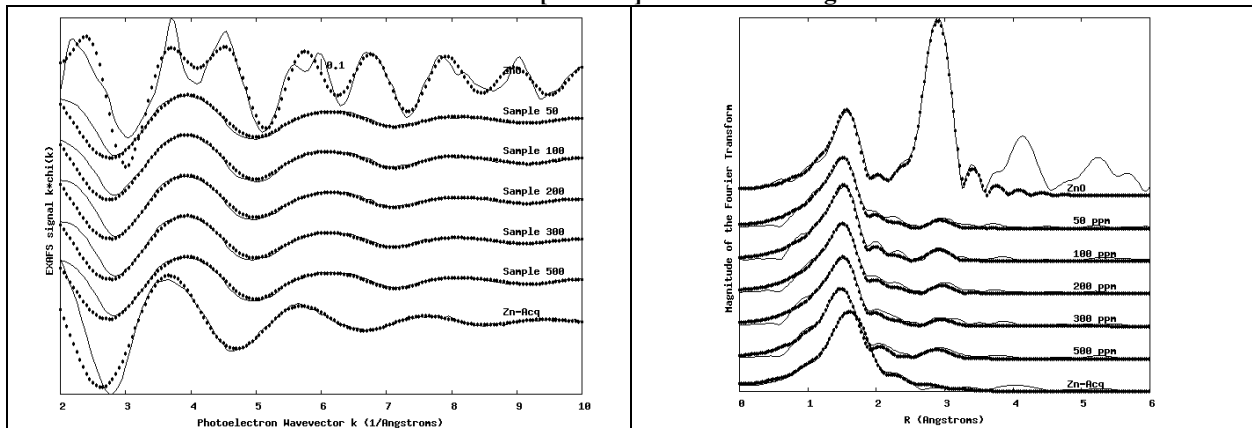
Table 3: Quantitative analysis of the Zn-K edge EXAFS data. The errors on the last digit are indicated in brackets.

Sample	N_{Zn-O}	R_{Zn-O} (Å)	σ^2_{Zn-O} ($Å^2$)	N_{Zn-Ca}	R_{Zn-Ca} (Å)	σ^2_{Zn-Ca} ($Å^2$)
ZnO	4.0(1)	1.966(5)	0.0042(6)			
50 ppm	3.1(3)	1.96(2)	0.006(1)	0.6(5)	3.37(4)	0.005
100 ppm	3.1(3)	1.97(2)	0.005(1)	0.8(6)	3.36(3)	0.005
200 ppm	3.2(3)	1.97(2)	0.006(1)	0.5(5)	3.38(4)	0.005
300 ppm	3.2(3)	1.97(2)	0.006(1)	0.6(8)	3.38(4)	0.005
500 ppm	3.1(3)	1.96(2)	0.005(2)	0.8(9)	3.36(3)	0.005
Zn-Acq	6.0(3)	2.09(1)	0.0088(9)			

The comparison with the reference compounds shows that Zn is low-coordinated to O both from the value of Oxygen nearest neighbors and the R_{Zn-O} bond length (1.97 Å in the samples against 2.09Å in the octahedral ion and 1.966 Å in the tetrahedrally coordinated Zn). Note that 6-coordinated Zn in the high pressure FM3-M phase[1],[2] has a R_{Zn-O} bond length of 2.13 Å. An additional Zn-Ca coordination can be added to account for the small peak at 3Å in the FT but the error bars on the coordination number Zn-Ca are quite important. An alternative model attributing that peak to a small contribution from ZnO clusters (10% of the total Zn) is also compatible with the data.

Cu-K edge

The data were fitted with a single Cu-O shell model starting from the structure of CuO oxide. No evidence for other coordination shells was found.

Figure 3: EXAFS and Fourier Transforms data of Zn samples. Left: EXAFS data (line) and best fit curves for the Zn samples; right: Fourier Transforms of the EXAFS data (line) and best fit curves for the Zn samples. Transforms were carried out in the interval k=[2.5-11.0]Å^{-1} with a k^2 weight.
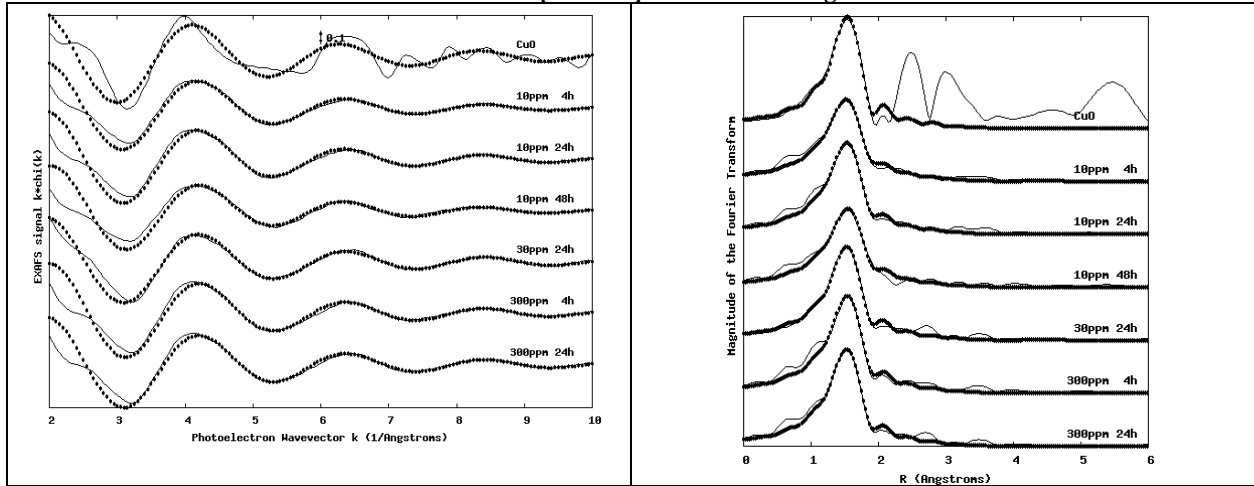
Table 4: Quantitative analysis of the Zn-K edge EXAFS data. The errors on the last digit are indicated in brackets.

Sample	N_{Cu-O}	R_{Cu-O} (Å)	σ^2_{Cu-O} (Å^2)
CuO	4.0(5)	1.95(1)	0.003(1)
10 ppm 4h	3.9(3)	1.94(1)	0.006(1)
10 ppm 24h	4.0(4)	1.94(1)	0.005(1)
10 ppm 48h	3.5(4)	1.96(1)	0.006(1)
30 ppm 24h	3.6(3)	1.93(1)	0.004(1)
300 ppm 4h	3.9(5)	1.94(1)	0.005(2)
300 ppm 24h	3.8(3)	1.94(1)	0.004(1)

The Cu-O coordination number (4) and the bond length (1.94 Å) are typical of the Cu^{2+} ion. The other possibility could be Cu^+ ion but in that case the coordination number should go to 2 or 3 and the bond length to 1.85 Å: these values are largely outside the error bars then the presence of Cu^+ can be ruled out. Also in this case no farther shell is visible so details on the precise site occupied cannot be given: at any rate the reorganization of the crystal around the impurity is quite marked as even the first shell bond lengths are by far shorted than those of the unperturbed crystal.

Conclusion

In general no precise statements can be done on the site occupancy of the ions because only a first shell is visible in the spectra (the case of Cd is an exception). In all cases the metal-oxygen bond length is much shorter than the Ca-O in the pristine crystal and the metals tend to be 4

coordinated. The bond length value observed in all cases agrees with this coordination value and the occurrency of ≥6 coordinations can be safely ruled out. Considering that both in the cases of Ca1 and Ca2 sites there is a high coordination of the metal with the oxygens, the structure undergoes a strong rearrangement when incorporating the divalent metal.

References

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[2] Bates, C.H.;White, W.B. Science (1962) **137**, 993-993.