The speciation of Cd in Cd-Fe co-precipitates: Does Cd substitute for Fe in goethite structure?

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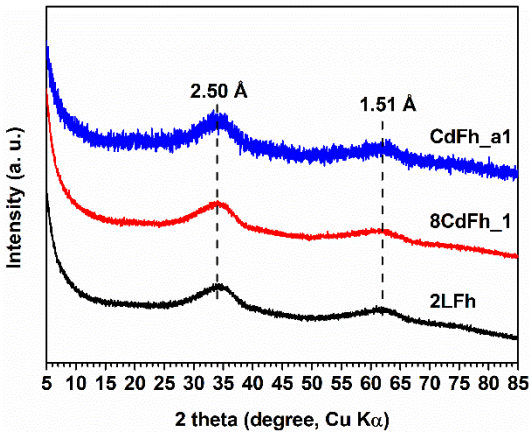

Figure S1. The powder XRD patterns of the synthesized ferrihydrite standards, including 2-line ferrihydrite (2LFh), Cd-coprecipitated 2-line ferrihydrite (8CdFh_1), and Cd-adsorbed 2-line ferrihydrite (CdFh_al). These patterns matches well with that of 2-line ferrihydrite (ICSD 158475). For clarity the intensity for CdFh_al was multiplied by a factor of 10.

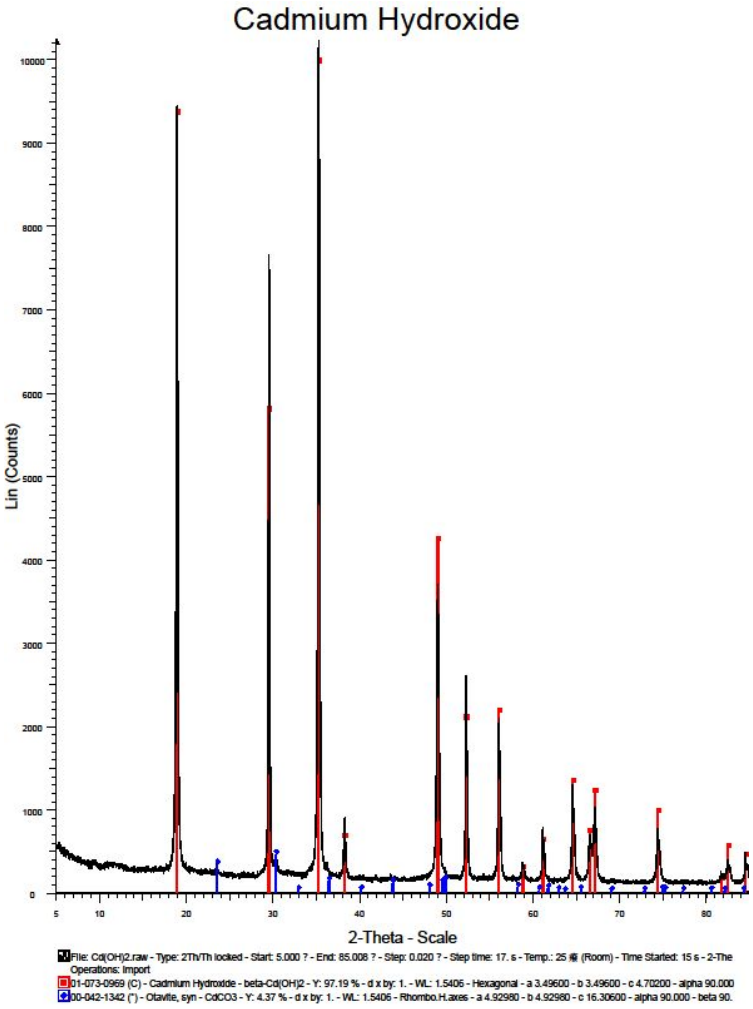

Figure S2. The powder XRD pattern of the synthesized $Cd(OH)_2$. It matches well with that of β-$Cd(OH)_2$ (JCPDF 73-0969), except a minority of $CdCO_3$ impurity (JCPDF 42-1342).

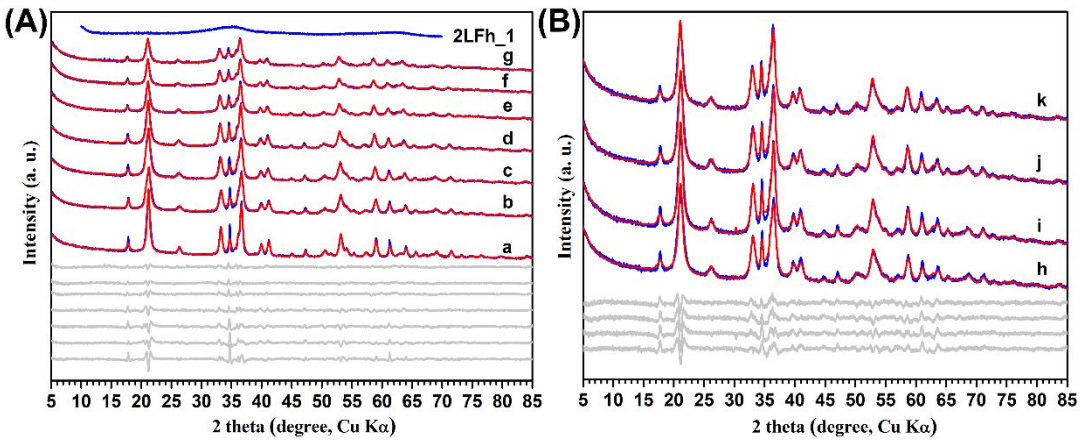

Figure S3. Powder XRD patterns of Cd-Fe coprecipitates after pretreatment with oxalic acid/ammonium oxalate solution (NCd_o samples, A) and those further treated with nitric acid solution (NCd_n samples, B), overlapped with the best fitting results of quantitative phase analysis using goethite (ICSD 71810) and ferrihydrite (ICSD 158475) as end members (the blue lines are experimental data, the red lines are the best fits, and the light gray lines are the difference patterns). In panel (A) a pattern of 2-line ferrihydrite, 2LFh_1 from our previous paper,[1] is present to show that in the spectra of these Cd-Fe coprecipitates the "humps" located at ~35 º and ~62 º correspond to the contribution from 2-line ferrihydrite phase.

(a)Goe, (b)1Cd_o, (c)2Cd_o, (d)3Cd_o, (e)4Cd_o, (f)5Cd_o, (g)6Cd_o, (h)3Cd_n, (i)4Cd_n, (j)5Cd_n, (k)6Cd_n.

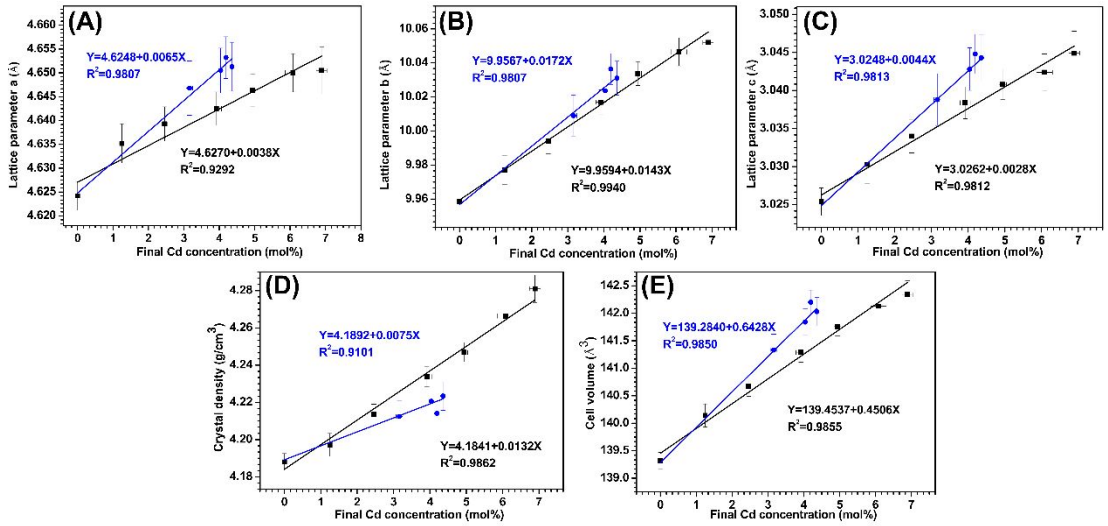

Figure S4. Variations of lattice parameters (A) a, (B) b, (C) c, (D) calculated crystal density and (E) cell volume of the obtained Cd-Fe coprecipiate samples, based on Rietveld structure refinement using a goethite model (ICSD 71810). The black squares correspond to the NCd_o (N=1-6) samples and the pure goethite (Goe), and the blue squares correspond to NCd_n (N=3-6) samples. The black solid lines are best linear fits to Goe and NCd_o (N=1-6) samples while the blue solid lines are best linear fits to Goe, NCd_o (N=1-2) and NCd_n (N=3-6) samples.

Table S1. Unit cell parameters, cell volume, and calculated crystal densities of the Cd-Fe coprecipitates obtained by Rietveld structure refinement using a goethite model (ICSD 71810).

Sample	Lattice parameters				Crystal Density (g/cm^3)	R_{wp} (%)
	a (Å)	b (Å)	c (Å)	V ($Å^3$)		
Goe	4.6242(30)	9.9586(62)	3.0254(18)	139.32(15)	4.1880(46)	4.64
1Cd_o	4.6352(41)	9.9772(85)	3.0303(25)	140.14(21)	4.1972(62)	4.17
2Cd_o	4.6393(36)	9.9942(75)	3.0340(22)	140.67(18)	4.2135(55)	3.90
3Cd_o	4.6425(35)	10.0169(72)	3.0384(21)	141.29(18)	4.2338(53)	3.51
4Cd_o	4.6463(34)	10.0337(70)	3.0408(20)	141.76(17)	4.2469(52)	2.78
5Cd_o	4.6500(40)	10.0465(83)	3.0424(24)	142.13(20)	4.2663(61)	2.74
6Cd_o	4.6505(49)	10.052(10)	3.0449(29)	142.34(25)	4.2810(74)	2.79
3Cd_n	4.6468(57)	10.009(12)	3.0388(34)	141.33(29)	4.2124(86)	4.13
4Cd_n	4.6505(47)	10.0236(96)	3.0428(28)	141.84(24)	4.2206(71)	4.22
5Cd_n	4.6513(51)	10.031(10)	3.0443(30)	142.03(26)	4.2234(77)	4.08
6Cd_n	4.6532(44)	10.0364(91)	3.0448(26)	142.20(22)	4.2141(66)	3.54

Table S2. Results of quantitative phase analysis of these Cd-Fe coprecipitates using goethite (ICSD 71810) and ferrihydrite (ICSD 158475).

	Goe	1Cd_o	2Cd_o	3Cd_o	4Cd_o	5Cd_o	6Cd_o	3Cd_n	4Cd_n	5Cd_n	6Cd_n
Goethite (%)	98.98(14)	99.17(15)	98.51(13)	98.02(18)	86.0(28)	78.8(29)	75.9(26)	98.85(15)	99.03(15)	98.56(14)	98.61(13)
Ferrihydrite (%)	1.02(14)	0.83(15)	1.49(13)	1.98(18)	14.0(28)	21.2(29)	24.1(26)	1.15(15)	0.97(15)	1.44(14)	1.39(13)
Rwp (%)	4.4	4.17	3.85	3.31	2.8	2.72	2.86	3.77	3.94	3.79	3.27

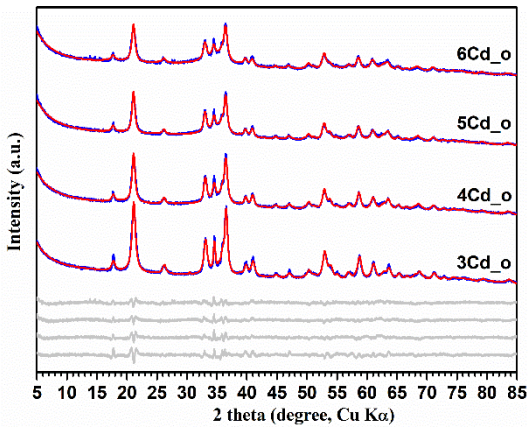

Figure S5. Powder XRD patterns of Cd-Fe coprecipitates after pretreatment with oxalic acid/ammonium oxalate solution (NCd_o samples), overlapped with the best fitting results of quantitative phase analysis using goethite (ICSD 71810) and ferrihydrite (ICSD 158475) as end members (the blue lines are experimental data, the red lines are the best fits, and the light gray lines are the difference patterns). During these analysis Cd partitions between 2-line ferrihydrite and goethite obtained by linear combination fitting (LCF) of Cd K-edge EXAFS analysis were taken into consideration. The obtained R_{wp} values are 3.35%, 2.80%,2.74% and 2.86% for 3Cd_o, 4Cd_o, 5Cd_o and 6Cd_o respectively.

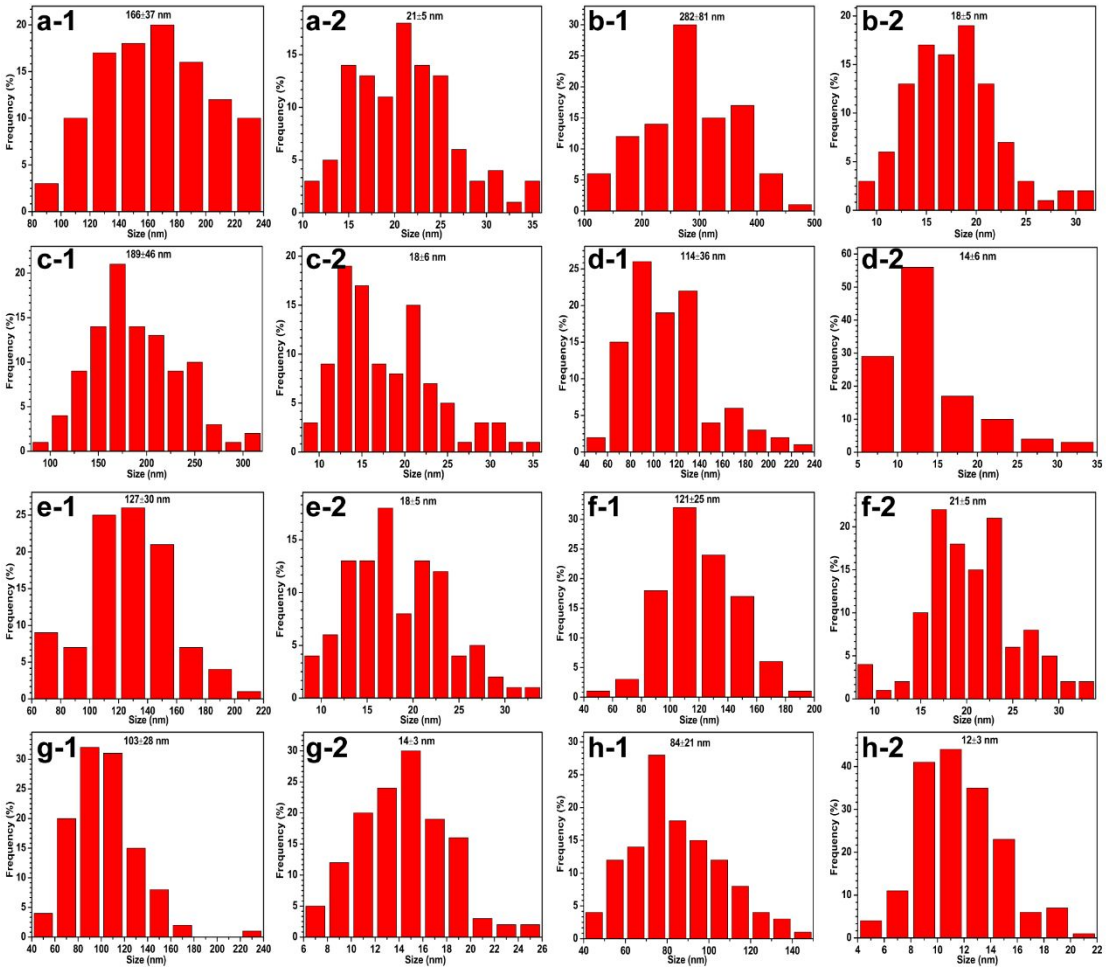

Figure S6. Length and width distribution histograms of typical Cd-Fe coprecipitate samples after oxalic acid/ammonium oxalate solution pretreatment (Goe (a), 2Cd_o (b), 4Cd_o (c), 6Cd_o (d)) and samples after further nitric acid pretreatment (3Cd_n (e), 4Cd_n (f), 5Cd_n (g), 6Cd_n (h)). The length and width are statically average values by analyzing 100 crystals.

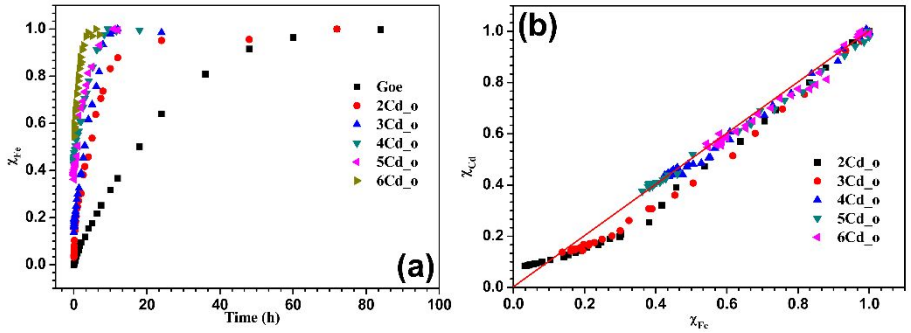

Figure S7. Dissolution of Fe (χ_{Fe}) over time (a) and congruency of Fe and Cd dissolution (b) in Cd-Fe coprecipitates after oxalic acid/ammonium oxalate solution pretreatment. The 1:1 line is shown by a red solid line in panel (b). Dissolution condition: 3M HCl, 50 ^{o}C.

Table S3. Fitting parameters of the χ_{Fe}-t and χ_{Cd}-t curves of the oxalic acid/ammonium oxalate solution treated samples dissolving in 3M HCl solution at 50 °C or in 2M HCl solution at 25 °C using Kabai equation[2], χ_{Fe} or χ_{Cd} =1-exp(-(kt)$^{\alpha}$).

Experiment conditions		χ_{Fe}-t					χ_{Cd}-t				
		k	error	α	error	R^2	k	error	α	error	R^2
3 M HCl, 50 °C	Goe	0.0434	0.0008	1.0936	0.0236	0.9979	-	-	-	-	-
	2Cd_o	0.1885	0.0090	0.7462	0.0341	0.9851	0.137	0.0096	0.861	0.0658	0.9613
	3Cd_o	0.2742	0.0282	0.6715	0.0610	0.9213	0.2145	0.0188	0.9510	0.1014	0.9225
	4Cd_o	0.7215	0.1522	0.2779	0.0286	0.8022	0.5871	0.1414	0.2721	0.0314	0.7569
	5Cd_o	0.5287	0.1019	0.3387	0.0331	0.8311	0.6078	0.1141	0.3294	0.0319	0.8239
	6Cd_o	5.7357	1.1077	0.2234	0.0215	0.8200	5.1730	1.1419	0.2213	0.0245	0.7736
2HCl, 25 °C	3Cd_o	0.0144	0.0016	0.4890	0.0315	0.9597	0.0102	0.0014	0.5559	0.0562	0.9094
	4Cd_o	0.0597	0.0105	0.2719	0.0177	0.9238	0.0333	0.0101	0.2160	0.0221	0.7798
	5Cd_o	0.1170	0.0199	0.2430	0.0145	0.9384	0.2481	0.0781	0.1553	0.0156	0.7889
	6Cd_o	0.2619	0.0471	0.2226	0.0146	0.9255	1.5546	0.4981	0.1180	0.0116	0.7892

Table S4. Linear combination fitting results of Fe and Cd K-edge EXAFS spectra of samples after $H_2C_2O_4/(NH_4)_2C_2O_4$ treated and HNO_3 treated, by using 4Cd_n as goethite standard, 2LFh as ferrihydrite standard for Fe K-edge EXAFS spectra analysis, and using 4Cd_n as Cd-substituted goethite standard and 8CdFh as Cd associated with ferrihydrite standard for Cd K-edge EXAFS spectra analysis respectively.

	contents	1Cd_o	2Cd_o	3Cd_o	4Cd_o	5Cd_o	6Cd_o	3Cd_n	4Cd_n	5Cd_n	6Cd_n
Fe	Fh (%)	6(1)	7 (1)	21(1)	42(2)	47(2)	50(2)	16(1)	21(2)	21(1)	25(2)
	Goe (%)	94(1)	93(1)	79(1)	58(2)	53(2)	50(2)	84(1)	79(2)	79(1)	75(2)
	R	0.0066	0.0063	0.0140	0.0297	0.0378	0.0376	0.0127	0.0222	0.0172	0.0228
	Reduced χ^2	0.0015	0.0014	0.0028	0.0053	0.0065	0.0064	0.0026	0.0043	0.0033	0.0045
Cd	Cd-Fh (%)	-	-	44(4)	58(2)	66(2)	74(2)	-	-	1(7)	27(4)
	Cd-goe (%)	-	-	56(4)	42(2)	34(2)	26(2)	-	-	99(7)	73(4)
	R	-	-	0.0842	0.0450	0.0343	0.0382	-	-	0.1634	0.1152
	Reduced χ^2	-	-	0.0113	0.0048	0.0033	0.0037	-	-	0.0375	0.0180

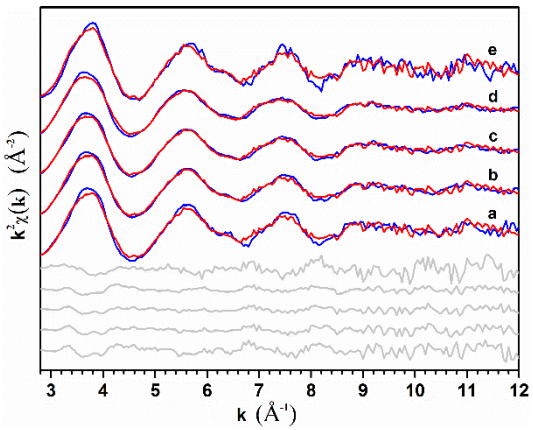

Figure S8. Cd K-edge EXAFS spectra of typical samples after $H_2C_2O_4/(NH_4)_2C_2O_4$ treatment and after nitric acid treatment, overlapped with the best linear combination fittings with 4Cd_n as Cd-substituted goethite standard, 8CdFh as Cd-associated ferrihydrite standard, and $Cd(OH)_2$ standard (the blue lines are experimental curves, the red lines are the best-fit linear combinations, and the light gray lines are the differences).

(a) 3Cd_o, (b) 4Cd_o, (c) 5Cd_o, (d) 6Cd_o and (e) 6Cd_n.

Table S5. Fitting results of Cd K-edge EXAFS spectra of samples after $H_2C_2O_4/(NH_4)_2C_2O_4$ treating and nitric acid treat using 4Cd_n as Cd-substituted goethite standard, 8CdFh as Cd-associated ferrihydrite standard, and $Cd(OH)_2$ standard.

	3Cd_o	4Cd_o	5Cd_o	6Cd_o	6Cd_n
Cd-Fh(%)	41(4)	55(3)	63(2)	68(2)	22(5)
Cd-goe(%)	56(4)	42(2)	34(2)	25(2)	72(4)
$Cd(OH)_2$(%)	3(6)	3(4)	3(3)	8(3)	6(7)
R	0.0836	0.0443	0.0334	0.0331	0.1130
Reduced χ^2	0.0113	0.0047	0.0033	0.0032	0.0178

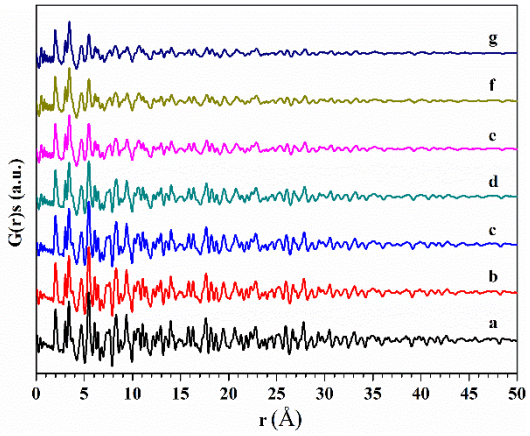

Figure S9. Pair distribution functions [G(r)s] of the Cd-Fe coprecipitate samples after pretreatment with 0.2 mol·L^{-1} oxalic acid/ammonium oxalate solution at pH3. (a) Goe, (b) 1Cd_o, (c) 2Cd_o, (d) 3Cd_o, (e) 4Cd_o, (f) 5Cd_o and (g) 6Cd_o.

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