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| **TABLE S1. Experimental conditions in CdS(s) solubility and Cd-HS complexes studies** |
| **Reference, method** | **CdS(s) preparation, size of crystals (if known)** | **Solution composition** | **pH range** | **T°C** | **ΣSII** |
| This study, solubility  | Synthesis CdS+S in NH4Cl vapor; 0.5-3.0mm | H2O-HClO4-NaOH-H2S | 0.3-8.0 | 25-80°C | 10-7-0.75 mol/kgH2O |
| Wang and Tessier [1], solubility  | 1) Pretreated commercial power CdS(s); 0.2-5 μm;2) Precipitates Cd(NO3)2 + thioacetamide;3) Presipitates Cd(NO3)2+ Na2S | H2O±EDTA-NaNO3-pH buffers (2,4-lutidine for pH=6.5-7.5, imidazole for 8.0-9.0, acetate-acetic acid for 4.0-5.0) | 4.0-9.0 | 25°C | 10-6-0.1 mol/L |
| Al-Farawati and van den Berg [2], cathodic stripping voltammetry | not used | seawater  | 8 | 25°C | 10-6-10-7 mol/L |
| Zhang and Millero [3], cathodic stripping voltammetry | not used | seawater | 8 | 25°C | 10-7 mol/L |
| Daskalakis and Helz [4], solubility | Synthesis Cd+S10-100μm | H2O-DTPA-Mg(NO3)2-NH4H2PO4-NaCl-HCl-NaOH-H2S-pH buffers (acetate for pH = 4-5, 2,4-lutidine for pH=6.5-7.5, borate for pH=9) | 4-9 | 25°C | 10-3.4-4.4 mol/L |
| Van Hovell tot Westerflier et al.[5],solubility, radiotracer method | Precipitates CdCl2-H2SO4-H2S; 0.07-0.3 μm | H2O-H2SO4-HCl-NaOH | 1-14 | 25°C | 10-8-10-3.4 mol/L |
| Belcher [6], solubility and precipitation  | fresh precipitates; commercial powders and precipitates aged in:1) HCl2) HClO43) H2SO4;all agglomerates, 2-500 μm across | Precipitation experiments: Cd(ClO4)2-HCl/HClO4/H2SO4-H2O-H2S;Dissolution experiments: HCl, HClO4, H2SO4 | acidic media | 25°C | 10-4-10-2 mol/L |

**TABLE S1. (continued)**

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **Reference, method** | **CdS(s) preparation, size of crystals (if known)** | **Solution composition** | **pH range** | **T°C** | **ΣSII** |
| Ste-Marie et al. [7] solubility, radiotracer method | CdSO4-Na2S precipitates | CdSO4-NaClO4-Na2S-HCl-pH buffers (HClO4 for pH=1-2, acetic acid-acetate for ph = 3-6, imidazole for pH = 7-8, triethanolamine for pH = 8-9, monoethanolamine for pH = 9-10.5, piperidine for pH =10-12;NaOH for pH=12-14) | 1-14 | 25°C | 0.021 mol/L |
|  |  |  |  |  |  |

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| **TABLE S2. Stability constants of cadmium hydrosulfide complexes at 25°C and 1 bar** |
| **Reaction** | **log10K(25°C)** | **Reference** |
| Cd2+ + HS- = CdHS+ | 7.38±0.68 | Selected in this study, Wang and Tessier [1] |
|  | 7.84, 9.13±0.2, 7.63-8.43 | Al-Farawati and Van Den Berg [2] and corrections[1] |
|  | 6.3±0.2 | Zhang and Millero [3] |
|  | 7.63-9.13 | Racalculated [2] from Zhang and Millero [3] |
|  | ≤ 7.66 | Daslkalakis and Helz [4]  |
|  | ≤ 8.22 | Recalculated [1] from Daskalakis and Helz [4] |
|  | 8.41±0.16 | Recalculated to I=0 from Ste-Marie (7.55±0.16I=1.0) [7]  |
|  |  |  |
| Cd2+ + 2HS- = Cd(HS)20(aq) | 14.43±0.01 | Selected in this study, Wang and Tessier [1] |
|  | ≤ 13.36 | Daskalakis and Helz [4] |
|  | 14.24, 14.99-15.69 | Al-Farawati and Van Den Berg [2] and corrections [1] |
|  | ≤ 13.92 | Recalculated [1] from Daskalakis and Helz [4] |
|  | 15.91±0.16 | Recalculated to I=0 from Ste-Marie (14.61±0.16I=1.0) [7]  |
|  |  |  |
| Cd2+ + 3HS- = Cd(HS)3- | 16.26±0.58 | Selected in this study, Wang and Tessier [1] |
|  | 16.44±0.36 | Daskalakis and Helz [4] |
|  | 17.00 | Recalculated [1] from Daskalakis and Helz [4] |
|  | 17.81±0.20 | Recalculated from Ste-Marie (16.49±0.20I=1.0) [7] |
|  |  |  |
| Cd2+ + 4HS- = Cd(HS)42- | 18.43±0.05 | Selected in this study, Wang and Tessier [1] |
|  | 17.89±0.01 | Daskalakis and Helz [4] |
|  | 18.45 | Recalculated [1] from Daskalakis and Helz [4] |
|  | 19.77±0.20 | Recalculated from Ste-Marie (18.85±0.20I=1.0) [7] |
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| **TABLE S3. Thermodynamic properties of greenockite CdS(hexagonal) reported in thermodynamic handbooks** |
| **kJ/mol** | **kJ/mol** | **J/(mol·K)** | **cm3/mol** | **J/(mol·K)** |  **equation** **(T(K) range)** | **Reference** |
| -151.355*±0.300* | -154.889 | 72.18 | 29.93 | 47.29 | 35.38 + 1.50·10-2·T - 5.33·105·T-2 + 2.36·102·T-0.5 - 2.40·10-6·T2 (298-1100 K) | This study, recommended |
| -156.500 | -161.900 | 64.9 | NA | NA | NA | CRC Handbook [8] |
| -146.100*±1.300* | -149.600*±1.300* | 72.2*±1.3* | 29.93 | 47.39 | 35.38 + 1.50·10-2·T - 5.33·105·T-2 + 2.36·102·T-0.5 - 2.40·10-6·T2 (298-1100 K) | Robie and Hemingway [9] |
| -145.185 | -149.369 | 72.2 | NA | 47.29 | 48.92 + 0.6176·10-2·T - 0.3088·105·T-2(298-1100 K) | Pankratz et al. [10] |
| -156.500 | -161.900 | 64.9 | NA | NA | NA | NBS Tables [11] |
| NA | -149.369*±2.092* | 69.036*±1.300* | NA | 48.68 | 44.56 + 1.38·10-2·T (298-1200 K) | Mills [12] |
| -147.300 | NA | 68.199 | NA | 49.96 | 53.97 + + 3.76·10-2·T (298-1200 K) | Naumov et al. [13] |
| -153.159 | -156.900*±4.184* | 71.128*±2.092* | NA | 47.32*±0.418* | NA | TKV database [14] |
|  |  |  |  |  |  |  |

NA = not available

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| **TABLE S4. Thermodynamic properties of greenockite CdS(hexagonal), original measurements** |
| **Data**  | **Method** | **Reference** |
| **, kJ/mol** |
| -151.50*±0.30* | Solubility product | This study |
| -150.36*±0.17* | Solubility product, treated CdS | Wang and Tessier [1] |
| -147.96*±0.34* | Solubility product, fresh precipitated CdS (Cd(NO3)2+thiacetamide) | Wang and Tessier [1] |
| -146.53*±0.34* | Solubility product, fresh precipitated CdS (Cd(NO3)2+Na2S) | Wang and Tessier [1] |
| -151.54 | Solubility product, aging experiments in HCl | Calculated from Belcher [6] |
| -140.23 | Precipitation experiments at 20°C | Recommended in Belcher [6] |
|  |  |  |
| -149.800*±2.000* | Galvanic cell measurements, DTA calorimetry | Nasar and Shamsuddin [15] |
|  |  |  |
| **, kJ/mol** |
| **-155.784** | Solubility product | This study |
| -148.790*±4.130* | Oxide melt solution calorimetry | Deore and Navrotsky [16] |
| -153.300*±2.800* | Galvanic cell measurements, DTA calorimetry | Nasar and Shamsuddin [15] |
| -145.603 | Calorimetric determination of heat of synthesis | Kapustinskii and Korshunov [12] |
| -149.369 | Solution calorimetry | Adami and King [12] |
| -149.369 | Dissolution pressure data, Third Low analysis | Munir [12] |
| -147.695*±2.092* | Dissolution pressure data, Third Low analysis | Boev et al. [12] |
| -158.574*±2.092* | Dissolution pressure data, Third Low analysis | Veselovskii [12] |
| -156.482*±2.092* | Dissolution pressure data, Third Low analysis | Pogorelyi [12] |
| -166.314*±2.092* | Dissolution pressure data, Third Low analysis | Spandau and Klaberg [12] |
| -159.201*±2.092* | Dissolution pressure data, Third Low analysis | Goldfinger and Jeunnehomme [17] |
| -158.155*±2.092* | Dissolution pressure data, Third Low analysis | Isakova and Nesterov [12] |
| -142.256 | Galvanic cell measurements, Third Low analysis | Makolkin [12] |
| -151.879*±2.092* | Galvanic cell measurements, Second Low analysis | Newns [12] |
| -154.808*±0.418* | Galvanic cell measurements, Third Low analysis | Newns [12] |
|  |  |  |
| **, J/(mol·K)** |
| 72.18*±0.26* | Critically selected | This study |
| 69.0*±6.0* | Solubility product | Estimated in this study |
| 72.0 | Recalculated from experimental values of and  | Nasar and Shamsuddin [15] |
| 72.18*±0.26* | Cp measurements (5-300 K) | Bayer et al. [18] |
| 68.2*±0.8* | Cp measurements (50-310 K) | Shaulov and Kostina [12] |
| 68.2*±0.8* | Cp measurements (55-300 K) | Demidenko [12] |
| 70.5*±0.8* | Recalculated using (S°55-S°0)=2.98cal/(molK) by extrapolation using Debye and Einstein functions | Demidenko [12] |
| 69.2*±0.8* | Galvanic cell measurements Second Low analysis | Makolkin [12] |
| 73.4 | Galvanic cell measurements, Second Low analysis | Newns [12] |
| 77.4 | Galvanic cell measurements, Third Low analysis, using dH°298 = -35.7 | Newns [12] |
| 77.4 | Dissociation pressure measurements, Third Low analysis using dH°f=-35.7kcal/mol | Goldfinger and Jeunehomme [12] |
|  |  |  |
| **, J/(mol·K)** |
| 47.3 | Cp measurements (5-300 K) | Bayer et al. [18] |
| 48.7 | Cp measurements (50-310 K) | Shaulov and Kostina [12] |

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| **TABLE S5. Thermodynamic properties of cadmium aqueous ion Cd2+ reported in thermodynamic handbooks** |
|  |  |  |
|  **kJ/mol** |  **kJ/mol** |  |  **J/(mol·K)** |  |  **cm3/mol** |  **J/(mol·K)** | **Reference** |
| -77.73 | -75.92 |  | -72.80 |  | -16.0 | -14.22 | This study |
| -77.60 | -75.90 |  | -73.20 |  | NA | NA | CRC Handbook [8] |
| -77.57 | NA |  | -71.80*±1.4* |  | NA | NA | Archer [19] |
| -77.65 | -75.90 |  | -72.802 |  | -16.0 | -14.22 | GEOPIG database [20,21] |
| NA | -75.92*±0.60* |  | -72.80*±1.5* |  | NA | NA | CODATA [22] |
| NA | -75.92*±0.60* |  | -72.80*±1.5* |  | NA | NA | Robie and Hemingway [9] |
| -77.864±0.209 | -75.563 |  | -71.128*±4.184* |  | NA | 4.184 | Naumov et al. [13] |
| -77.655±0.209 | -75.312*±0.836* |  | -70.906*±2.886* |  | NA | -20.083*±7.112* | TKV database [14] |
|  |  |  |  |  |  |  |  |

NA = not available

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| **TABLE S6. Logarithms of the stability constants for Cd–HS complexes formation as a function of temperature at saturation vapor pressure calculated using modified Ryzhenko–Bryzgalin model (Table 6, main text)** |
| **Reaction** | **5°C** | **25°C** | **50°C** | **80°C** | **100°C** | **150°C** | **200°C** |
| Cd2+ + HS- = CdHS+ | 7.42 | 7.38 | 7.46 | 7.66 | 7.84 | 8.38 | 9.07 |
| Cd2+ + 2HS- = Cd(HS)20(aq) | 14.92 | 14.43 | 14.03 | 13.76 | 13.67 | 13.68 | 13.97 |
| Cd2+ + 3HS- = Cd(HS)3- | 16.68 | 16.26 | 15.99 | 15.89 | 15.92 | 16.27 | 16.94 |
| Cd2+ + 4HS- = Cd(HS)42- | 19.53 | 18.43 | 17.29 | 16.21 | 15.61 | 14.43 | 13.63 |

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| **TABLE S7. Standard thermodynamic properties of simple substances used in this study** |
|  | **Δ*f*G0298.15 kJ/mol** | **Δ*f*H0298.15 kJ/mol** | **S0298.15 J/(mol·K)** | **Reference** |
| **Cd(s)** | 0 | 0 | 51.80 ± 0.15 | CODATA[22] |
| **H2(g)** | 0 | 0 | 130.680 ± 0.003 | CODATA[22] |
| **S(s) rhomb** | 0 | 0 | 32.054 ± 0.050 | CODATA[22] |
| **H+** | 0 | 0 | 0 | Reference substance |

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| **TABLE S8. Standard thermodynamic properties and HKF parameters of major sulfur species, used in this study** |
|  | **HS-** | **H2S0(aq)** | **NaOH0(aq)** |  |
| **NΔ*f*G0298.15 cal mol-1** | 2863 | -6673\* | -99900 |  |
| **Δ*f*H0298.15 cal mol-1** | -3847 | -9001\* | -112300 |  |
| **S0298.15 cal mol-1 K-1** | 19.953 | 30.000\* | 10.7 |  |
| **Cp0298.15 cal mol-1 K-1** | -20.746 | 42.7\* |  |  |
| **V0298.15 cm3/mol** | 21.166 | 35\*\* |  |  |
| **a1 × 10, cal mol-1 bar-1** | 5.4467 | 6.5097\*\* | 2.2338 |  |
| **a2 × 10-2 , cal mol-1 bar-1** | 5.9833 | 6.7724\*\* | -2.3287 |  |
| **a3, cal mol-1 bar-1** | 1.1229 | 5.9646\*\* | 6.6683 |  |
| **a4 × 10-4, cal mol-1 bar-1** | -3.4623 | -3.0590\*\* | -2.6826 |  |
| **c1, cal mol-1 K-1** | -33.7048 | 27.8951\* | 4.0146 |  |
| **c2 × 10-4, cal mol-1 K-1** | 13.6786 | 6.7164\* | -3.6863 |  |
| **ɷ× 10-5, cal mol-1** | 1.6105 | -0.1471\* | -0.030 |  |
| **z** | -1 | 0 | 0 |  |
|  |  |  |  |  |
| **Reference** | Calculated according to Ref [23] and theoretical correlations HKF [24], see also FigS1. | \*Ref [23], \*\*calculated using correlation from Ref [25] | Ref. [20] |  |

Equation for the activity coefficients used in this study is:

where *m* is the sum of moles of all compounds per 1 kg of H2O.



**Figure S1.** Comparison logK values for the reaction H+ + HS- = H2S0(aq) according to Table S8, classical HKF database [26] and experimental data [24]



**Figure S2.** Comparison between total dissolved Cd concentrations measured in experiments and calculated using thermodynamic data derived in this study. The highest and the lowest experimental *m*Cd values at 80°C, pH = 1.9 - 3.9 and *m*S = 0.05 were excluded from thermodynamic analysis.

**Thermodynamic uncertainty evaluation**

The derivation of the thermodynamic data on grenockite CdS(s) and Cd-HS complexes (Table 4-6, main text) is subject of different types of uncertainties. First of all, the primary source of errors comes from the experimental data including Cd and reduced S concentrations and pH. Please note that *m*Cd, *m*S and pH(25°C) were measured independently. However, in the case of NaHS-H2S-H2O solutions, the *m*H2S and pH(25°C) are interdependent and thus can be also controlled by the thermodynamic calculations. The uncertainty in logK values related to possible errors *m*Cd, *m*S and pH increases in near-neutral pH where CdS solubility is low and possible errors in *m*S and pH are high. Thus the uncertainty 0.5 log units in *m*Cd results in 0.5 log units uncertainty for K(3), 50% in *m*S – in 0.3 log units fork(3). In the same time, due to several points used (range of mS, pH and mCd conditions), the final uncertainty for K(3) is estimated to be 0.4 log units. Potential source of uncertainties stems also from the choice of the thermodynamic parameters of the major species and activity coefficients of neutral and charged species. The highest uncertainties of this type are expected for the concentrated solutions, i.e. for 0.575*m* HClO4 and 0.466*m* and 0.753*m* NaOH. We believe that this type of errors does not exceed 0.1 log units in the final K values. The uncertainties on the logK values in Tables 4-6 in the main text (reported at 2 sigma probability level) were evaluated using error propagation analysis and taking into account all possible errors cited above. The uncertainties in G, H and S values were evaluated as a function of possible errors in logK values without taking into account uncertainties of standard reference species properties. The entropy values for Cd-HS were estimated with the high uncertainty, more experimental data are required for their more accurate determination. The accuracy of the extrapolation to higher temperatures using Ryzhenko-Bryzgalin model is believed to not exceed 0.5 log units in *m*Cd at 150-200°C, but calculations at higher *T* are more uncertain. Further experimental data on Cd-HS complexes stability at *T* above 200°C are required for accurate modeling of Cd transport at such high *T*.



**Figure S3.** Cadmium speciation in seawater at pH = 7.9 as a function of H2S concentration at 5°C. Under CdS saturation, the concentration of Cd2+ species decreases with increasing H2S at all *m*H2S. At lower Cd concentration, the mCd2+species is H2S-independent when Cd-Cl complexes predominate (below ~ 10-6*m* H2S), but decreases with increasing H2S when Cd-HS complexes predominate (above ~ 10-6*m* H2S).

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