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| Authors | Experimental conditions | Thermodynamic results | Ksp−dol source | pKsp°−dol |
| **Solubility (experimental)** |
| Yanat’eva (1952) \* | 25°C, CO2=0.1 MPa,Water, 100 days, dissolution | $$Δ\_{f}G\_{298.15}^{°}=-2161.29 kJ mol^{-1}$$ | (Ca,Mg & Alk.) Sherman and Barak (2000)1Sherman and Barak (2000)2 (pH & CO2) Sherman and Barak (2000)1Sherman and Barak (2000)2Bénézeth and others (2018) | -17.8-18.4-18.5-19.3-18.37 |
| Kramer (1959) | 25°C, CO2=atmospheric, artificial seawater, variable salinity, dissolution | $$K\_{sp°-dol}= 1.5×10^{-17} ¶$$ | Sherman and Barak (2000)1 &Bénézeth and others (2018)Sherman and Barak (2000)2 | -16.8-17.2 |
| Garrels and others (1960) | 25°C, CO2=0.1 MPa,Water, 18 hours, dissolution | $$Δ\_{f}G\_{298.15}^{°}=-2175.26 kJ mol^{-1}$$from Garrels and others (1960)$$Δ\_{f}G\_{298.15}^{°}=-2173.08 kJ mol^{-1}$$using Table.3$$Δ\_{f}G\_{298.15}^{°}=-2161.7 kJ mol^{-1}$$per Bénézeth and others (2018) | (No grind) Sherman and Barak (2000)1 Sherman and Barak (2000)2 Bénézeth and others (2018)(Grind) Sherman and Barak (2000)Bénézeth and others (2018) | -19.3-19.4-19.34-16.5-16.44 |
| Rosenberg and Holland (1964) | 275-420°C, CaCl2-MgCl2 soln, precipitation & dissolution | $$log\_{10}(/)= \frac{-1000}{T(K)}+2.98 $$ | This study at 25°C | -16.58 |
| Langmuir (1965)Langmuir (1971) | 25°C, Water& MgCl2 soln.,dissolution | $$Δ\_{f}H\_{298.15}^{°}=-2320.69 kJ mol^{-1}$$ | Langmuir (1965) | -17.0 |
| Halla and Van Tassel (1965) | 21°C, CO2=0.1 MPa,Water, 546 days, dissolution |  | (Ca & Alk.) Sherman and Barak (2000)1Sherman and Barak (2000)2(pH &CO2) Sherman and Barak (2000)1Sherman and Barak (2000)2Bénézeth and others (2018) | -17.0-17.7-16.6-17.5-17.76 |
| Baker and Kastner (1981)† | 200°C, CaCl2-MgCl2 soln., 2 weeks, precipitation | $$-0.03< log\_{10}(/)<0.26$$ | This study at 200°C (using log$\frac{aCa^{2+}}{aMg^{2+}}$=0.12) | (-22.21±0.14) |
| Stoessell and others (1987) | 100-200°C, CaCl2, 300 bars, 7-8 weeks, dissolution | $log\_{10}(/)$ 100°C : 1.16 150°C : 1.37 200°C : 1.57 | This study at 100°C (using $log\_{10}(/)$=-0.35) | (-19.77) |
| Morrow and others (1994)† | 220-240°C, CO2 variable, CaCl2-MgCl2 soln., 300-600 hours,precipitation & dissolution | $$0.4< log\frac{aCa^{2+}}{aMg^{2+}}< 0.9$$ | This study at 230°C (using $log\_{10}(/)$ =0.65)  | (-24.06±0.25) |
| Usdowski (1967),Usdowski (1989),Usdowski (1994) | 60-180°C,CaCl2-MgCl2 soln.,< 372 weeks, precipitation & dissolution | $log\_{10}(/)$ 60°C : -0.35 90°C : 0.49 120°C : 0.83 180°C : 1.08 | This study at 60°C (using $log\_{10}(/)$ = - 0.35) | (-17.25) |
| Sherman and Barak (2000) | 25°C, CO2=0.101 MPa, Ca-Mg-HCO3/CO3 soln., 672 days, dissolution |  | Sherman and Barak (2000) | -17.2±0.2 |
| Rock and others (2001) | 25°C, Cd-Hg electrodes, CaCl2-MgCl2 soln., Electrochemical cell, dissolution | $$Δ\_{f}G\_{298.15}^{°}=-2147.82 \pm 2.20kJ mol^{-1}$$ | This study at 25°C | -14.65±0.39 |
| Gautelier and others (2007) | 80°C, HCL-NaHCO3 soln., dissolution |  | Gautelier and others (2007) at 80°C | (-17.95±0.1) |
| Bénézeth and others (2018) | 53-253°C, CO2=variable,NaCl soln.72-1320 hoursprecipitation & dissolution | $$Δ\_{f}G\_{298.15}^{°}=-2160.9 \pm 2.0 kJ mol^{-1}$$$$S\_{298.15}^{°}=156.9\pm 2.0 J mol^{-1}$$$$Δ\_{f}H\_{298.15}^{°}=-2323.1\pm 2.0 kJ mol^{-1}$$$$C\_{p 298.15}^{°}=154.2\pm 2.0 J mol^{-1} K^{-1}$$ | Bénézeth and others (2018)Möller and De Lucia (2020)1 Möller and De Lucia, (2020)2This study statistical reanalysis of activities determined by Bénézeth and others (2018) | -17.19±0.3-17.8-17.5-17.18±0.53 |
| Debure and others (2021) | Calcite-dolomite equilibrium, NaCl soln., 25°C & 80°C, up to 517 days | $log\_{10}(/)$ 25°C : -0.35 80°C : 0.49 |  |  |
| **Solubility (groundwater)** |
| Hsu (1963) | 22-27°C (n=28) | Average $\frac{[Ca^{2+}]}{[Mg^{2+}]}=0.78$ | Hsu (1963)Sherman and Barak (2000)This study | -16.7-17.1-17.07 |
| Barnes and Back (1964)$ ‡$ | No temperature reported (presumably 25°C) (n=87) | $K\_{sp°-dol}=(2.5\pm 0.5)×10^{-17} $$K\_{sp°-dol}=2.87×10^{-17}$$$K\_{sp°-dol}=2.89×10^{-17}$$ | Sherman and Barak (2000)Bénézeth and others (2018)This study | -16.5-16.54-16.60±0.09 |
| Hyeong and Capuano (2001) $ | 43 - 150°C (n=51) | $$Δ\_{f}G\_{298.15}^{°}=-2159.15 kJ mol^{-1}$$$$Δ\_{f}H\_{298.15}^{°}=-2318.77 kJ mol^{-1}$$*s* = 0.4 per eqs (129&130) of Helgeson and others (1978) | Hyeong and Capuano (2001) | -16.92 |
| Vespasiano and others (2014) $ | 60.6°C (chalcedony geothermometer) (n=33) | $$Δ\_{f}G\_{333.75}^{°}=-2166.96 kJ mol^{-1}$$ 22% ordered dolomite per eq (10.2) of Anderson and Crerar (1993) | This study at 61°C | (-18.13) |
| Blasco and others (2018) $ | 87°C (combination geothermometer) (n=5) | $$Δ\_{f}G\_{360.15}=-2171.75 kJ mol^{-1} $$18.4% ordered dolomite per eq (10.2) Anderson and Crerar (1993) | This study at 87°C | (-18.93) |
| This study ¢ | 1.7-254.9°C (n=10,343) | Model J23$$Δ\_{f}G\_{298.15}^{°}=-2161.34\pm 8.26 kJ mol^{-1}$$$$Δ\_{f}H\_{298.15}^{°}=-2329.61\pm 0.51 kJ mol^{-1}$$$$C\_{p 298.15}^{°}=82.04\pm 12.17 J mol^{-1} K^{-1}$$Model J24 $$Δ\_{f}G\_{298.15}^{°}=-2161.40\pm 0.66 kJ mol^{-1}$$$$Δ\_{f}H\_{298.15}^{°}=-2332.67\pm 0.34 kJ mol^{-1}$$ | J24 – fixed $C\_{p 298.15}^{°}=157.51 J mol^{-1} K^{-1}$ | -17.27±0.35-17.28±0.35 |
| **Thermal decomposition** |
| Rossini and Rossini (1952)\* |  | $$Δ\_{f}G\_{298.15}^{°}=-2169.3 kJ mol^{-1}$$ | Sherman and Barak (2000) | -18.6 |
| Stout and Robie (1963) | Bomb calorimetry | $$S\_{298.15}^{°}=155.18 J mol^{-1} K^{-1}$$$$C\_{p 298.15}^{°}=157.53 J mol^{-1} K^{-1}$$ | Sherman and Barak (2000)Bénézeth and others (2018) | -18.7-18.2 |
| Karpov and others (1971) \* |  | $$Δ\_{f}G\_{298.15}^{°}=-2170.0 kJ mol^{-1}$$ | Sherman and Barak (2000) | -18.7 |
| Naumov and others (1974) \* |  | $Δ\_{f}G\_{298.15}^{°}=-2151.9 kJ mol^{-1}§$ $Δ\_{f}G\_{298.15}^{°}=-2121.9 kJ mol^{-1}§$  | Sherman and Barak (2000) | -15.6 |
| Helgeson and others (1978) SUPCRT92 – slop07.dat Johnson and others (1992)  | Method of Navrotsky and Loucks (1977). Using data from Goldsmith and Heard (1961) | Disordered$$Δ\_{f}G\_{298.15}^{°}=-2157.49 kJ mol^{-1}$$$$Δ\_{f}H\_{298.15}^{°}=-2316.70 kJ mol^{-1}$$$$S\_{298.15}^{°}=166.69 J mol^{-1}$$$$C\_{p 298.15}^{°}=157.74 J mol^{-1}$$Ordered(Natural) ¥$$Δ\_{f}G\_{298.15}^{°}=-2166.31 kJ mol^{-1}$$$$Δ\_{f}H\_{298.15}^{°}=-2328.94 kJ mol^{-1}$$$$S\_{298.15}^{°}=155.18 J mol^{-1}$$$$C\_{p 298.15}^{°}=157.74 J mol^{-1}$$ | This studySherman and Barak (2000) ◆Bénézeth and others (2018)This study | -16.60-18.09-18.15-18.14 |
| Wagman and others (1982) |  | $$Δ\_{f}G\_{298.15}^{°}=-2163.4 kJ mol^{-1}$$$$Δ\_{f}H\_{298.15}^{°}=-2326.3 kJ mol^{-1}$$$$S\_{298.15}^{°}=155.18 J mol^{-1}$$$$C\_{p 298.15}^{°}=157.53 J mol^{-1}$$ | Sherman and Barak (2000)This study | -17.6-17.63 |
| Navrotsky and Capobianco (1987)Morrow and others (1994) | HCl solution, 358K | Disordered$$Δ\_{f}G\_{298.15}^{°}=-2166.31 kJ mol^{-1}$$$$Δ\_{f}H\_{298.15}^{°}=-2328.94 kJ mol^{-1}$$Ordered$$Δ\_{f}G\_{298.15}^{°}=-2167.02 kJ mol^{-1}$$$$Δ\_{f}H\_{298.15}^{°}=-2315.89 kJ mol^{-1}$$ | This studyThis studySherman and Barak, 2000 | -15.82-18.26-18.2 |
| Chernosky and Berman (1989) |  | $$Δ\_{f}G\_{298.15}^{°}=-2162.4 kJ mol^{-1}$$ | Sherman and Barak, 2000 | -17.4 |
| Knacke and others (1991) \* |  | $$Δ\_{f}H\_{298.15}^{°}=-2327.9 kJ mol^{-1}$$ | Sherman and Barak, 2000 | -17.8 |
| Chai and Navrotsky (1993) | PbO-B2O3 melt, 973K | $$Δ\_{f}H\_{298.15}^{°}=-2332 \pm 3 kJ mol^{-1}$$ | Sherman and Barak (2000) | -18.5 |
| Barin (1995) |  | $$Δ\_{f}G\_{298.15}^{°}=-2163.57 kJ mol^{-1}$$$$Δ\_{f}H\_{298.15}^{°}=-2326.30 kJ mol^{-1}$$$$S\_{298.15}^{°}=155.23 J mol^{-1}$$$$C\_{p 298.15}^{°}=157.53 J mol^{-1}$$ | This studySherman and Barak, 2000 | -17.66-17.6 |
| Robie and others (1978) Hemingway and Robie (1994)Robie and Hemingway (1995) | 300.15K, HCl soln. | $$Δ\_{f}G\_{298.15}^{°}=-2161.3\pm 1.7 kJ mol^{-1}$$$$Δ\_{f}H\_{298.15}^{°}=-2324.5\pm 1.6 kJ mol^{-1}$$$$S\_{298.15}^{°}=155.2 J mol^{-1}$$$$C\_{p 298.15}^{°}=157.51 J mol^{-1}K^{-1}$$ | Robie and others (1978) & Hemingway and Robie (1994)1) Sherman and Barak (2000)2) Sherman and Barak (2000)Bénézeth and others (2018)This study | -17.09±0.37-17.1-17.2-17.1217.26± 0.3 |
| **Database** |
| Holland and Powell (1990) |  | $$Δ\_{f}H\_{298.15}^{°}=-2325.72 kJ mol^{-1}$$$$S\_{298.15}^{°}=155.2 J mol^{-1}$$$$C\_{p 298.15}^{°}=157.52 J mol^{-1}K^{-1}$$ | Sherman and Barak, 2000 | -17.4 |
| Holland and Powell (1998) |  | $$Δ\_{f}G\_{298.15}^{°}=-2161.51 kJ mol^{-1}$$$$Δ\_{f}H\_{298.15}^{°}=-2324.56 kJ mol^{-1}$$$$S\_{298.15}^{°}=156.0 J mol^{-1}$$$$C\_{p 298.15}^{°}=157.28 J mol^{-1}K^{-1}$$ | This Study | -17.30 |
| Blanc and others (2012)Thermoddem v.2017 |   |   | DolomiteOrdered DolomiteDisordered Dolomite | -17.12-17.90-16.35 |
| Miron and others (2017) |  |  | New aqueous model using Holland and Powell (1998) mineral data | -17.0 |

Supplementary Table 2 Literature reported standard state thermodynamic properties of dolomite and pKsp°−dol values largely compiled from Sherman and Barak (2000) and Bénézeth and others (2018). Minor discrepancies between the two are due mostly to differing methods and reference thermodynamic data sets used during calculation from the sources. We report the original author pKsp°−dol, pKsp°−dol values where they differ from those recalculated by Sherman and Barak (2000) or Bénézeth and others (2018), and any recalculations by this study (using reference data from table 1) that represent or entirely new values or significant refinements (change in pKsp°−dol > 0.1). Estimates for pKsp−dol that are not at reference temperature (25°C) are reported in parentheses. Some entries, such as Robie and Hemingway (1995) and Johnson and others (1992), represent notable significant recalculations of original experimental data (Robie and others (1978) and Helgeson and others (1978) in this case respectively) and multiple studies are listed in the ‘authors column’ that synthesize and reflect the heritage of the more frequently referenced analyses; the pKsp°−dol value for the most recent study is given in the pKsp°−dol column. Sherman and Barak (2000) present multiple recalculations of pKsp°−dol using different methods/data sources and these are reported here in the order they appear in the original source. Apart from Kramer (1959), unique in using a synthetic seawater composition, experimental solubility is determined using distilled/pure water (‘Water’) or a solution (‘soln.’) consisting of a specific electrolyte (e.g. MgCl2).

\*The original source for Yanat’eva (1952), Rossini and Rossini (1952), Karpov and others (1971), Naumov and others (1974), Knacke and others (1991) were not available and we report the data as sourced from Sherman and Barak (2000) and Bénézeth and others (2018).

 ¶The data for Kramer (1959) reported by Sherman and Barak (2000) and Bénézeth and others (2018) this study believes is in error, and instead Ksp°−dol=1.5×10−17 is reported from the original source.

†Baker and Kastner (1981) and Morrow and others (1994) do not regress the high temperature experimental data to reference state conditions and instead report experimental ranges; a single average value determined by this study is used to represent the pKsp°−dol.

 ‡The value of Ksp°−dol= 2.89 × 10−17 reported by Sherman and Barak (2000) appears to be a transcription error. Barnes and Back (1964) present a range (Ksp°−dol = 2-3 × 10−17) over which they interpret Ksp°−dol. The value Ksp°−dol=2.87 × 10−17 represents the maximum ion activity product for dolomite as reported by Barnes and Back (1964) and corresponds to the pKsp°−dol reported by Bénézeth and others (2018).

 §There is likely a transcription error on the part of either Sherman and Barak (2000) ($Δ\_{f}G\_{298.15}^{°}=-2151.9 kJ mol^{-1}$) or Bénézeth and others (2018) ($Δ\_{f}G\_{298.15}^{°}=-2121.9 kJ mol^{-1}$).

◆ The pKsp°−dol from Sherman and Barak (2000) uses the original Helgeson and others (1978) thermodynamic properties not reported here.

¢ Reported uncertainties associated with the thermodynamic properties are derived using the standard error otherwise uncertainties associated pKsp°−dol values are computed using 95% confidence intervals.

$ There are two distinct (but related) methods of estimating ordering parameter; a) the standard Helgeson and others (1978) method as used by Hyeong and Capuano (2001) and easily relatable to crystallographic measurements and b) the Anderson and Crerar (1993) % of ordered dolomite method as used by Vespasiano and others (2014) and Blasco and others (2018). However the Anderson and Crerar (1993) method, though initially easier to calculate is not easily converted to *s* values (and is not attempted here as this study discounts the influence of natural dolomite order and favoring dolomite stoichiometry). Equilibrium $log\_{10}(/)$ values are higher for both Vespasiano and others (2014) and Blasco and others (2018) compared to Hyeong and Capuano (2001) which classically suggests the presence of a ‘more ordered’ or, as this study interprets, a more stoichiometric dolomite phase.

¥ - Most databases, such as slop07, have the same properties for the ordered and natural (i.e. just ‘Dolomite’) phases suggesting the natural (*s*=0.7) phase has fallen out of usage though Blanc and others (2012) preserved a natural dolomite phase which we presume is related to the Helgeson (1978) phase.