

Experimental determination of quartz solubility in H₂O–CaCl₂ solutions at 600–900 °C and 0.6–1.4 GPa

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Abstract

Fluid-mediated calcium metasomatism is often associated with strong silica mobility and the presence of chlorides in solution. To help quantify mass transfer at lower crustal and upper mantle conditions, we measured quartz solubility in H₂O–CaCl₂ solutions at 0.6–1.4 GPa, 600–900 °C, and salt concentrations to 50 mol%. Solubility was determined by weight loss of single-crystals using hydrothermal piston-cylinder methods. All experiments were conducted at salinity lower than salt saturation. Quartz solubility declines exponentially with added CaCl₂ at all conditions investigated, with no evidence for complexing between silica and Ca. The decline in solubility is similar to that in H₂O–CO₂ but substantially greater than that in H₂O–NaCl at the same pressure and temperature. At each temperature, quartz solubility at low salinity ($X_{\text{CaCl}_2} < 0.1$) depends strongly on pressure, whereas at higher X_{CaCl_2} it is nearly pressure independent. This behavior is consistent with a transition from an aqueous solvent to a molten salt near $X_{\text{CaCl}_2} \sim 0.1$. The solubility data were used to develop a thermodynamic model of H₂O–CaCl₂ fluids. Assuming ideal molten-salt behavior and utilizing previous models for polymerization of hydrous silica, we derived values for the activity of H₂O ($a_{\text{H}_2\text{O}}$), and for the CaCl₂ dissociation factor (α), which may vary from 0 (fully associated) to 2 (fully dissociated). The model accurately reproduces our data along with those of previous work and implies that, at conditions of this study, CaCl₂ is largely associated (< 0.2) at H₂O density < 0.85 g/cm³. Dissociation rises isothermally with increasing density, reaching ~ 1.4 at 600 °C, 1.4 GPa. The variation in silica molality with $a_{\text{H}_2\text{O}}$ in H₂O–CaCl₂ is nearly identical to that in H₂O–CO₂ solutions at 800 °C and 1.0 GPa, consistent with the absence of Ca-silicate complexing. The results suggest that the ionization state of the salt solution is an important determinant of $a_{\text{H}_2\text{O}}$, and that H₂O–CaCl₂ fluids exhibit nearly ideal molecular mixing over a wider range of conditions than implied by previous modeling. The new data help interpret natural examples of large-scale Ca-metasomatism in a wide range of lower crustal and upper mantle settings.

Keywords: Metasomatism, quartz, silica, experimental, brines, fluids, halogens, solubility; Experimental Halogens in Honor of James Webster

Introduction

Fluid-mediated replacement of rock bodies with calcium silicate and/or carbonate assemblages (Ca-metasomatism) is an important process in the Earth's crust and upper mantle. Ca-metasomatized metamorphic rocks are found in various lithologies and grades, from surficial to deep-crustal and upper mantle parageneses. Examples include “epidosites” and prehnite-pumpellyite rocks after intermediate and mafic lithologies (Harper 1995), lawsonite-replaced blueschists and eclogites (Vitale Brovarone and Beyssac 2014), rodingite alteration of ultramafic rocks (Python et al. 2011), scapolite-rich rocks after granites, metasediments and sodic anorthosites (Oliver et al. 1994; Moecher et al. 1992), and fluid-induced formation of calcic clinopyroxene in low-Ca diamondiferous peridotites (Schulze 1995). Carbonated “megashear” terranes such as the Late Precambrian Attur Valley of southern India (Wickham et al. 1994) show replacement of up to 20% of the dominantly quartzofeldspathic country rocks by calcite or dolomite. Of considerable interest to economic

geology is the conspicuous involvement of Ca-metasomatism in the genesis of major Au, Cu, and rare-earth element deposits, as in the Cloncurry District of Queensland, Australia (Mark et al. 2006), the Zambian “Copperbelt” (Eglinger et al. 2014), and the porphyry Cu ore body at Yerington, Nevada (Carten 1986). The presence of Ca²⁺ ions in ore-forming fluids can facilitate disproportionation of an SO₂-bearing fluid to form anhydrite and sulfides (Mavrogenes and Blundy 2017).

Mobilization and transport of Ca is facilitated by chloride in aqueous solutions, as shown by fluid-inclusion studies of metasomatized rocks (De Jong and Williams 1995). These fluids promote high mobility of alkalis and alkaline earths in exchange processes involving feldspar, and pervasive replacement, consonant with the high “wetting” ability of chloride solutions (Holness 1992). However, little is known about the actual nature of the solutions: their concentrations, acid-base relations, accompanying cations and anions such as carbonate and sulfate, specific interaction with mineral assemblages, or mode of origin, whether magmatic (Mark 1998), diagenetic (Kendrick et al. 2008), or evaporitic (Oliver et al. 1994).

Ca metasomatism is commonly associated with substantial silica mobility. The combination of Ca and Si mobility with

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chloride-bearing fluids motivates examination of the nature of silica dissolution in the presence of Ca and Cl in solution. Measurements of the solubility of quartz in CaCl₂ solutions at high pressure (*P*) and temperature (*T*) are an important starting point. Shmulovich et al. (2006) measured quartz solubility in H₂O-CaCl₂ fluids over a wide range of temperature (400–800 °C), pressure (0.1–0.9 GPa), and salt concentration (50–100 mol% H₂O). They found that CaCl₂ causes a strong decrease of quartz solubility at all *P* > 0.2 GPa. The decrease in solubility is stronger than they observed in H₂O-NaCl fluids at the same *P*, *T*, and salt concentration. Quartz solubility in H₂O-NaCl exhibits initial increase at low NaCl (“salting in”) at *P* up to ~0.5 GPa (Novgorodov 1975, 1977; Xie and Walther 1993; Newton and Manning 2000; Shmulovich et al. 2006). At higher *P*, solubility declines monotonically with NaCl concentration but the decrease is subdued relative to that seen in solutions with inert diluents such as CO₂ (e.g., Newton and Manning 2000, 2009; Shmulovich et al. 2001, 2006). Shmulovich et al. (2006) showed that other alkali chlorides exhibit similar trends. Explanations for this behavior include density effects in the solvent (e.g., Fournier 1983; Akinfiev and Diamond 2009; Brooks and Steele-MacInnis 2019) and complexing between silica and salt components (e.g., Evans 2007; Newton and Manning 2010, 2016).

The difference in quartz solubility behavior in aqueous solutions of CaCl₂ vs. alkali halides revealed by the data of Shmulovich et al. (2006) has not been explained. Shmulovich et al. (2006) empirically fit their measurements at each *P* and *T* but did not attempt a more comprehensive model. Potential effects of silica speciation and complexing, and mixing properties of the fluid phase were not considered. To address these issues, we investigated the solubility of quartz in H₂O-CaCl₂ solutions at 0.6, 1.0, and 1.4 GPa from 600–900 °C. Our new data provide a framework for modeling silica dissolution in this geologically important fluid. The new results allow quantification of silica transport in Ca-metasomatic environments in a range of deep crustal and upper mantle settings.

Experimental methods

Starting materials and sample loading

Experimental methods generally followed those of Manning (1994) and Newton and Manning (2000), in which the weight loss of single crystals was used to measure solubility. Starting materials consisted of high-purity quartz from Brazil (Manning 1994), 18 MΩ cm deionized water, and EMD brand anhydrous CaCl₂. Fragments of 1–3 mm long quartz were initially rounded with a diamond file to remove sharp edges, then further rounded with 600 and then 400 grit sandpaper. The crystals were sonicated in ethanol or acetone to remove adhering debris and then heated in a 600 °C oven to purge organic residue. Starting crystal weights were ~0.5–14.0 mg. Unfractured run-product crystals were reused in successive experiments.

The experiments employed Pt capsules fabricated from tubing (3.5 mm OD, 0.25 mm wall thickness). After cleaning with acetone, the bottom of a ~1.6 cm long piece of tubing was crimped and welded using a graphite arc welder. A quartz crystal was first loaded into the tubing, followed by CaCl₂. To minimize H₂O absorption during loading of hydroscopic CaCl₂, the salt was stored in an oven at 600 °C, then loaded and weighed within 1–2 min of removal from the oven. Deionized water (10–40 mg) was then added with a microliter syringe. The top of the capsule was crimped with pliers and sealed by arc welding. Average weight loss upon sealing was 0.4 mg, all of which results from Pt evaporation based on numerous sealing tests on dry and H₂O-filled capsules. All weights were measured with a Mettler-Toledo UXM2 ultra micro balance with an uncertainty of 0.2 μg.

Piston-cylinder methods

Experiments were conducted in a 2.54 cm piston-cylinder apparatus at 0.6–1.4 GPa and 600–900 °C. Pressure was measured with a Heise bourdon tube gauge, and temperature was controlled on a Eurothem 2208e controller using type-S (Pt-Pt₉₀Rh₁₀) thermocouples. Pressure and temperature uncertainties are estimated to be ±0.03 GPa and ±3 °C, respectively. No correction was made for the effect of pressure on thermocouple emf.

The furnace assembly was similar to that in Figure 1a of Johannes et al. (1971), but with NaCl or NaCl/BN pressure media. An NaCl pressure medium was used in experiments at 600–800 °C. No pressure correction was applied (Johannes 1973; Mirwald et al. 1975). For experiments at 900 °C, an NaCl pressure medium was used in combination with 0.38 cm BN inserts placed above and below the sample to improve mechanical stability near the NaCl melting point. The BN-NaCl pressure medium required a pressure correction of ~60 MPa relative to the NaCl pressure medium, determined by comparison with quartz solubility in H₂O measured in NaCl-only pressure media (Manning 1994). The samples were heated resistively using cylindrical graphite heater sleeves of 3.18 cm in length, 1.50 cm outer diameter, and 0.165 cm wall thickness.

The capsule was loaded horizontally at the midpoint of the graphite furnace on either a 1.27 cm cylinder of compressed NaCl or on a 0.38 cm cylindrical piece of compressed BN on top of a 0.89 cm cylinder of compressed NaCl. The capsule was embedded in either NaCl or BN powder. A platinum disk of ~0.64 mm thickness was placed in contact with the capsule to prevent puncturing by the tip of the thermocouple. Slight indentation on quenched capsules proved thermocouple contact.

The cold piston-in technique was used for all experiments. *P-T* paths varied because of the relatively large range of *P-T* conditions investigated. For experiments at 600 °C and 0.6 GPa, the samples were pressurized to a nominal 0.3–0.5 GPa and then heated to 600 °C. Further pressurization was required to reach the target value. At 700–800 °C and 0.6 GPa the samples were pressurized to 0.35 GPa, followed by increasing the temperature to the target value. At these conditions, the temperature was high enough that the target pressure was reached or only minimal further pressurization was required. For experiments conducted at 1.0 GPa, the samples were cold pressed to ~30% below the target pressure and then heated to the final temperature. Gauge pressure rose to the final target value and was bled to maintain the desired pressure. For runs at 1.4 GPa, the samples were pressurized to 0.75 GPa, heated to 100 °C, and then further pressurized to 1.2 GPa. The samples were then heated to their target value, whereupon the pressure rose and was bled to maintain the final pressure. Run times for the experiments were typically about 20 h. Runs were quenched by turning off the power, dropping the temperature to <200 °C in ~30 s.

Solubility determination

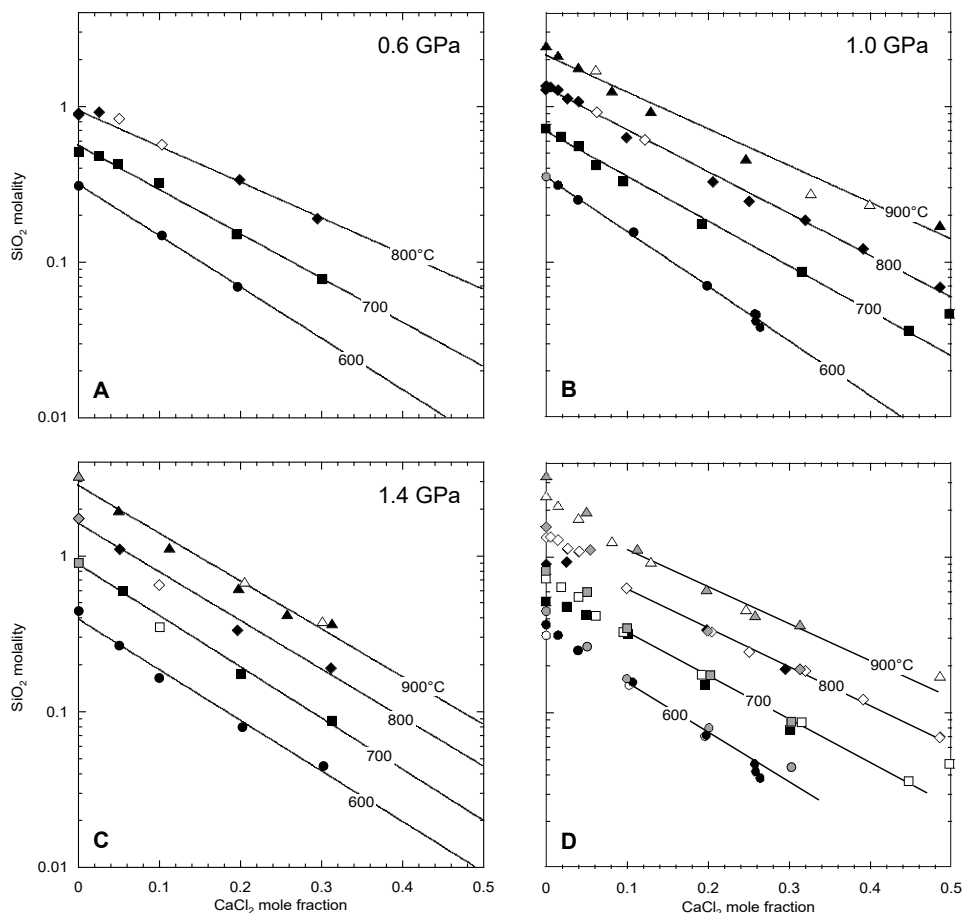
After each experiment, platinum capsules were cut open with a razor, placed in an agate mortar, and irrigated with water to remove the contents of the capsules. All crystals were carefully inspected using a binocular microscope. The quartz crystals were unbroken after most runs. Unbroken quartz crystals were sonicated in ethanol or water to remove adhered quench product and residual CaCl₂, then dried at 110 °C and weighed. For experiments in which the crystal broke, multiple irrigation steps were performed to remove all of the CaCl₂ from the solution. A platinum weighing boat of known mass was then immersed in water, and the crystals were transferred to it with pair of ultra-fine-tip tweezers. This was done under a binocular microscope to assure that all quartz fragments were collected. The platinum boat containing the crystal fragments was then dried at 110 °C and weighed. In all cases, solubility was taken to be the difference in crystal weight.

Results

The results of 78 experiments on quartz solubility in H₂O-CaCl₂ fluids are presented in Table 1. Quench pH was determined in selected experiments. All were neutral to slightly acidic (5.0–7.5).

We ensured that run durations were sufficient to attain equilibrium by conducting a time series at 600 °C, 1.0 GPa, and *X*_{CaCl₂} = 0.26. These conditions represent the lowest temperature and one of the higher salt contents investigated. Run times in four experiments varied between 1.5 and 18 h (Table 1). The 1.5 h run returned slightly lower solubility than the three longer runs, which gave similar results independent of time and were therefore assumed to have equilibrated. This is consistent with Newton

Figure 1. Results of experiments on quartz solubility in H₂O-CaCl₂ solutions at 0.6 GPa (a), 1.0 GPa (b), and 1.4 GPa (c). Data are from Table 1; 2 σ errors are smaller than symbol size. Symbols indicate temperature of experiment: circles, 600 °C; squares, 700 °C; diamonds, 800 °C; triangles, 900 °C. Filled symbols indicate solubility measurements from crystals that were unfractured, whereas unfilled symbols indicate a maximum solubility because the crystal broke or new crystals grew in the experiment. Gray symbols indicate pure-H₂O solubility from Hunt and Manning (2012). The linear trends in the log-linear plots show that solubility of quartz decreases exponentially with increasing mole fraction of CaCl₂ in solution. Figure 2d shows data at each temperature. Filled symbols, 0.6 GPa; open symbols, 1.0 GPa; gray symbols, 1.4 GPa. At each temperature, data at $X_{\text{CaCl}_2} < 0.1$ vary slightly with pressure, but at > 0.1 are independent of pressure. This is interpreted to indicate a transition to fused salt behavior in the solvent (see text).



and Manning (2000), who found equilibration times of ~ 2 h for quartz dissolution in aqueous NaCl solutions at 700 °C and 1.0 GPa. Based on these considerations, all runs at 600 °C were at least 17.5 h. Some runs at higher T had shorter run times, but none were shorter than the minimum duration of the time series.

The experimental results are presented in Figure 1. The starting crystal was chipped or broken in 10 runs (13% of experiments). In all cases, the pieces could be recovered and weighed; however, the chance that a few stray fragments were missed means that these runs strictly provide only a maximum constraint on solubility. In run QzC-56, several minute euhedral quartz crystals were interpreted to have grown during the run though the crystal showed no evidence of mechanical failure. In this case, the crystals were collected, and their mass was included with the final quartz weight in determining solubility. As with runs in which the crystal broke, this experiment is taken as a maximum solubility constraint. Figure 1 shows that maximum-solubility results agree well with the rest of the data at any given P and T . Nevertheless, these data were omitted from all fitting and modeling described below.

Table 1 includes new data on quartz solubility in pure H₂O, which are in good agreement with previous predictions (Manning 1994; Dolejš and Manning 2010; Hunt and Manning 2012; Sverjensky et al. 2014). Our new pure-H₂O data are used to establish the trends in Figure 1 and in modeling; however, where

we did not conduct new experiments in pure H₂O, we used the solubility equation of Hunt and Manning (2012) in preference to those of Manning (1994), Dolejš and Manning (2010), or the DEW model (Sverjensky et al. 2014) because it provides the best agreement with experimental results at 900 °C while yielding accuracy similar to the other models at lower temperature.

The results show that, at all of the investigated P and T , quartz solubility is highest in pure H₂O but declines exponentially with increasing mole fraction of CaCl₂, as indicated by the isobaric-isothermal linear trends in Figures 1a–1c. Fitted linear slopes are broadly independent of pressure and become less negative with rising temperature. No evidence for salt saturation was observed.

At some conditions, quartz solubility in NaCl-H₂O fluids increases slightly before declining at low NaCl concentrations (Xie and Walther 1993; Newton and Manning 2000; Shmulovich et al. 2006). This effect was not observed here, except possibly at the lowest pressure of 0.6 GPa and 800 °C (Fig. 1a). At any given temperature, quartz solubility is nearly independent of pressure for CaCl₂ mole fraction (X_{CaCl_2}) more than ~ 0.1 (Fig. 1d). This behavior is similar to quartz solubility in concentrated NaCl solutions and is consistent with a transition from an aqueous solution dominated by the effects of solvent H₂O, to a solution, which behaves more like a molten salt dominated by the CaCl₂ component (Newton and Manning 2000).

Table 1. Experimental results

Run no.	<i>P</i> (GPa)	<i>T</i> (°C)	<i>t</i> (h)	H ₂ O (mg)	CaCl ₂ (mg)	Δ <i>w</i> _{quartz} (mg)	<i>X</i> _{CaCl₂}	<i>m</i> _{SiO₂} (mol/kg H ₂ O)	Notes
QzC-47	0.6	600	22.0	19.662	0.000	0.366(1)	0.000	0.310(1)	
QzC-52	0.6	600	18.0	28.311	20.017	0.254(1)	0.103	0.149(1)	
QzC-36	0.6	600	22.0	14.976	22.512	0.063(1)	0.196	0.070(1)	
QzC-39	0.6	700	22.0	15.767	0.000	0.488(2)	0.000	0.515(2)	
QzC-76	0.6	700	23.0	20.926	3.287	0.608(1)	0.025	0.483(1)	
QzC-46	0.6	700	20.0	26.690	8.497	0.687(1)	0.049	0.429(1)	
QzC-54	0.6	700	22.0	20.457	14.021	0.398(1)	0.100	0.324(1)	
QzC-57	0.6	700	24.5	14.174	21.201	0.129(2)	0.195	0.152(2)	
QzC-45	0.6	700	28.5	10.792	28.596	0.051(2)	0.300	0.078(3)	
QzC-35	0.6	800	4.0	24.916	0.000	1.321(1)	0.000	0.883(1)	
QzC-40	0.6	800	22.0	24.841	0.000	1.353(2)	0.000	0.906(1)	
QzC-74	0.6	800	22.0	15.580	2.511	0.864(2)	0.025	0.923(2)	
QzC-56	0.6	800	14.5	37.115	11.994	1.871(2)	0.050	0.839(1)	max (2)
QzC-37	0.6	800	21.0	20.110	14.170	0.689(3)	0.103	0.570(1)	max (1)
QzC-41	0.6	800	20.5	23.662	36.169	0.484(1)	0.199	0.340(1)	
QzC-43	0.6	800	22.5	10.639	27.371	0.122(2)	0.295	0.191(3)	
QzC-108	1.0	600	69.0	10.692	0.972	0.200(1)	0.015	0.312(1)	
QzC-107	1.0	600	69.0	7.968	1.962	0.120(1)	0.038	0.252(3)	
QzC-16	1.0	600	23.0	40.060	29.726	0.375(1)	0.107	0.156(1)	
QzC-19	1.0	600	63.0	16.365	24.861	0.070(1)	0.198	0.071(1)	
QzC-28	1.0	600	1.5	21.959	47.450	0.060(1)	0.260	0.046(1)	TS
QzC-95	1.0	600	4.5	7.218	15.464	0.018(2)	0.258	0.042(2)	TS
QzC-97	1.0	600	9.0	17.112	37.769	0.039(1)	0.264	0.038(1)	TS
QzC-96	1.0	600	18.0	9.592	20.401	0.027(1)	0.257	0.047(1)	TS
QzH2O-1	1.0	700	4.0	23.951	0.000	1.040(1)	0.000	0.722(1)	
QzH2O-2	1.0	700	4.0	15.030	0.000	0.654(1)	0.000	0.724(1)	
QzC-3	1.0	700	22.5	24.598	2.794	0.950(1)	0.018	0.643(1)	
QzC-110	1.0	700	23.5	11.956	3.022	0.399(1)	0.039	0.556(1)	
QzC-9	1.0	700	47.0	17.366	6.903	0.438(1)	0.061	0.420(1)	
QzC-4	1.0	700	20.5	24.667	15.864	0.493(1)	0.095	0.332(1)	
QzC-5	1.0	700	23.0	22.386	32.609	0.238(2)	0.191	0.177(1)	
QzC-6	1.0	700	22.5	15.063	42.589	0.079(1)	0.315	0.088(1)	
QzC-91	1.0	700	22.0	8.882	44.128	0.019(1)	0.446	0.036(1)	
QzC-115	1.0	700	3.0	5.122	31.410	0.014(1)	0.499	0.046(3)	
QzC-112	1.0	800	3.8	9.271	0.000	0.759(1)	0.000	1.363(1)	
QzC-104	1.0	800	4.0	10.411	0.000	0.805(1)	0.000	1.287(1)	
QzC-101	1.0	800	4.0	23.156	0.767	1.863(1)	0.005	1.339(1)	
QzC-102	1.0	800	4.0	11.645	1.063	0.891(2)	0.015	1.273(2)	
QzC-98	1.0	800	4.0	18.575	3.158	1.256(1)	0.027	1.125(1)	
QzC-99	1.0	800	4.0	15.781	4.095	1.026(2)	0.040	1.083(2)	
QzC-10	1.0	800	21.0	29.454	11.978	1.624(2)	0.062	0.918(1)	max (1)
QzC-92	1.0	800	4.0	29.403	19.893	1.118(1)	0.099	0.633(1)	
QzC-15	1.0	800	23.0	29.393	25.065	1.077(2)	0.122	0.610(1)	max (1)

Table 1. — Continued

Run no.	<i>P</i> (GPa)	<i>T</i> (°C)	<i>t</i> (h)	H ₂ O (mg)	CaCl ₂ (mg)	Δ <i>w</i> _{quartz} (mg)	<i>X</i> _{CaCl₂}	<i>m</i> _{SiO₂} (mol/kg H ₂ O)	Notes
QzC-14	1.0	800	20.0	22.939	36.542	0.453(2)	0.205	0.329(1)	
QzC-12	1.0	800	25.0	14.634	30.060	0.217(2)	0.250	0.246(3)	
QzC-27	1.0	800	2.0	15.301	44.206	0.172(2)	0.319	0.187(2)	
QzC-87	1.0	800	22.0	12.567	49.656	0.092(1)	0.391	0.122(1)	
QzC-89	1.0	800	17.0	10.143	59.182	0.042(1)	0.486	0.068(1)	
QzC-105	1.0	900	4.5	14.877	0.000	2.210(1)	0.000	2.473(1)	
QzC-103	1.0	900	4.5	12.869	1.209	1.655(1)	0.015	2.140(1)	
QzC-106	1.0	900	4.5	17.658	4.436	1.896(1)	0.039	1.787(1)	
QzC-25	1.0	900	1.5	44.871	17.823	4.662(2)	0.061	1.729(1)	max (1)
QzC-100	1.0	900	4.5	14.673	7.925	1.119(1)	0.081	1.269(1)	
QzC-17	1.0	900	2.5	30.023	27.301	1.685(1)	0.129	0.934(1)	
QzC-20	1.0	900	26.0	13.645	27.402	0.379(1)	0.246	0.463(1)	
QzC-24	1.0	900	19.5	17.136	51.042	0.286(3)	0.326	0.278(3)	max (1)
QzC-90	1.0	900	3.0	13.681	55.937	0.194(2)	0.399	0.237(3)	max (1)
QzC-88	1.0	900	4.0	11.099	64.505	0.116(1)	0.485	0.174(2)	
QzC-49	1.4	600	25.0	19.497	0.000	0.522(1)	0.000	0.445(1)	
QzC-73	1.4	600	72.0	23.139	7.469	0.370(1)	0.050	0.266(1)	
QzC-65	1.4	600	20.0	47.055	31.966	0.468(1)	0.099	0.165(1)	
QzC-66	1.4	600	71.0	14.757	22.980	0.071(2)	0.202	0.080(2)	
QzC-51	1.4	600	17.5	19.613	52.239	0.053(1)	0.302	0.045(1)	
QzC-71	1.4	700	51.0	37.575	13.347	1.345(1)	0.055	0.596(1)	
QzC-67	1.4	700	24.0	40.148	27.538	0.843(3)	0.100	0.349(1)	max (1)
QzC-70	1.4	700	21.0	23.985	36.910	0.252(1)	0.200	0.175(1)	
QzC-60	1.4	700	22.0	12.329	34.514	0.065(2)	0.312	0.088(1)	
QzC-72	1.4	800	18.0	23.293	7.612	1.550(1)	0.050	1.107(1)	
QzC-68	1.4	800	20.0	19.550	13.261	0.764(3)	0.099	0.650(2)	max (1)
QzC-63	1.4	800	23.5	21.050	31.598	0.423(2)	0.196	0.334(1)	
QzC-59	1.4	800	21.5	13.375	37.237	0.154(1)	0.311	0.191(1)	
QzC-75	1.4	900	23.0	25.619	8.202	3.018	0.049	1.960(1)	
QzC-69	1.4	900	20.0	18.727	14.564	1.277	0.112	1.135(3)	
QzC-83	1.4	900	5.0	15.717	23.790	0.589	0.197	0.623(1)	
QzC-61	1.4	900	22.5	23.771	37.673	0.977	0.205	0.684(14)	max (1)
QzC-84	1.4	900	5.0	17.435	37.254	0.445	0.258	0.425(1)	
QzC-58	1.4	900	21.5	12.464	33.039	0.287	0.301	0.383(4)	max (1)
QzC-85	1.4	900	4.5	16.141	45.314	0.359	0.313	0.370(2)	

Notes: Quartz solubility results reported as weight change in single quartz crystals (Δ*w*_{quartz}). Parenthetical entries in Δ*w*_{quartz} and SiO₂ molality are 1σ uncertainty in last digit(s) based on propagated weighing errors; propagated errors in fluid compositions (*X*_{CaCl₂}) are too low to be reported at this level. Entries in notes column: TS = time series used to determine minimum run times; max (1) = maximum solubility because crystal broke; max (2) = maximum solubility because run products include several minute vapor transport crystals.

Discussion

Thermodynamic model

A thermodynamic framework for explaining quartz solubility in CaCl₂ solutions can be developed by comparison to quartz solubility behavior in H₂O-NaCl and H₂O-CO₂. Figure 2a shows the change in quartz solubility at 800 °C and 1 GPa as NaCl (Newton and Manning 2000), CO₂ (Newton and Manning 2000, 2009), or CaCl₂ (this study) are added to H₂O. In each case, the solubility declines as the concentration of the added component increases. Notably, the extent of the decline differs depending on the component, with the decline associated with adding CaCl₂ slightly greater than for the same molar amount of CO₂, and significantly greater for NaCl. Various models have been developed to explain such differences at high *P* and *T*. Largely empirical approaches based on solvent density have been successful for H₂O-CO₂ and/or H₂O-NaCl (e.g., Shmulovich et al. 2006; Akiniev and Diamond 2009; Brooks and Steele MacInnis 2019). An alternative framework is based on solvent mixing models and solute-solvent interaction (e.g., Newton and Manning 2009, 2010, 2016). However, both approaches pose problems for the present data set because of uncertainty

in the properties and behavior of H₂O-CaCl₂ solutions at high *P* and *T*. Ivanov and Bushmin (2019) have proposed a model for H₂O-CO₂-CaCl₂ fluids at conditions relevant to this study. Their model reproduces ternary phase-equilibrium experiments; however, its accuracy for H₂O activity and CaCl₂ speciation on the H₂O-CaCl₂ binary is unknown. Here we use our new quartz solubility data to simultaneously develop a provisional model for quartz solubility and H₂O activity in H₂O-CaCl₂ solutions at high *P* and *T*.

Development of the model begins with consideration of the nature of dissolved silica. In the absence of strong shifts from neutral pH, dissolved silica exists as neutral species in varying states of polymerization (Zhang and Frantz 2000; Zotov and Keppler 2000, 2002; Newton and Manning 2002, 2003). For most deep crustal conditions, the monomer and the dimer predominate in pure H₂O (Newton and Manning 2008; Huang and Sverjensky 2019). Both can be modeled as hydrous species containing both structurally bound OH groups as well as molecular H₂O of solvation. Water activity in mixed fluids can therefore be expected to play an important role in the stability of silica species and hence in quartz solubility. This is seen by considering homogeneous equilibrium between the monomer and dimer:

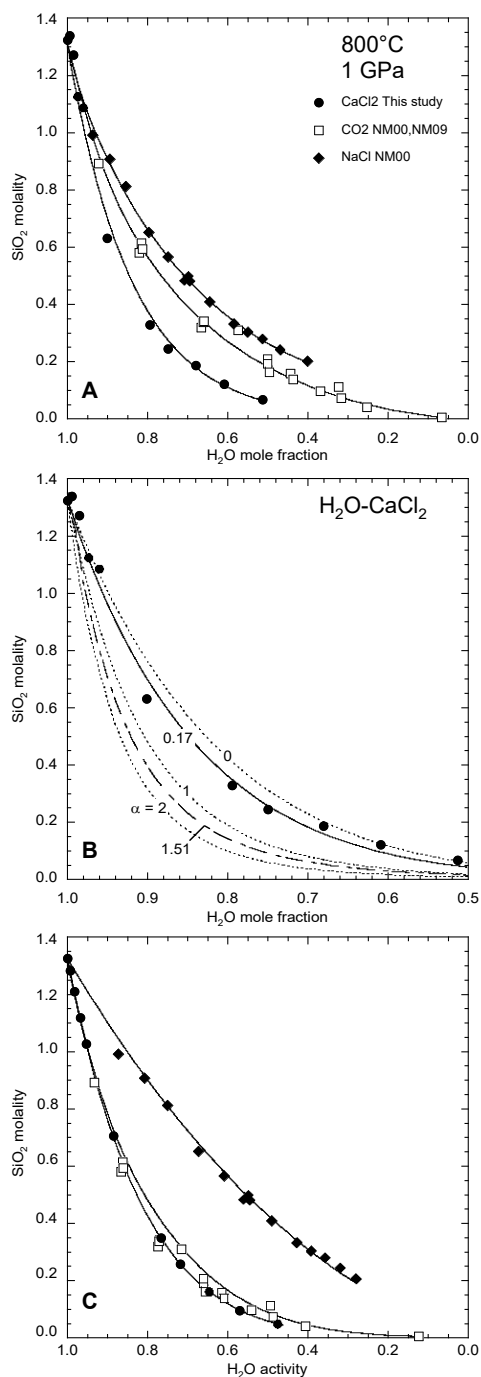
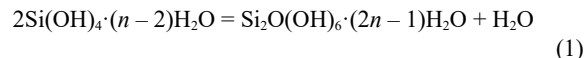


Figure 2. Quartz solubility at 800 °C, 1 GPa. **(a)** Solubility variation with H₂O mole fraction in H₂O-CaCl₂ (circles, this study), H₂O-CO₂ (squares, Newton and Manning 2000, 2009), and H₂O-NaCl (diamonds, Newton and Manning 2000). **(b)** Solubility in H₂O-CaCl₂ along with representative values of $\alpha = 0, 1$ and 2 (dotted lines). A best-fit value of 0.17 (solid line) implies that CaCl₂ is nearly fully associated at this P and T . The model of Ivanov and Bushmin (2019) gives $\alpha = 1.51$ (dash-dot line), which does not reproduce the data. **(c)** As in **a**, except the x-axis is H₂O activity. The similar dependence of solubility on H₂O activity in the H₂O-CaCl₂ and H₂O-CO₂ systems suggests negligible calcium silicate complexing, in contrast to the H₂O-NaCl system.



in which n is the “hydration number” of dissolved silica (e.g., Walther and Orville 1983; Newton and Manning 2009), reflecting the sum of H₂O necessary to form OH groups and molecular H₂O tightly solvated to the complex. The equilibrium constant for monomer-dimer equilibrium (K_{md}) in Equation 1 is:

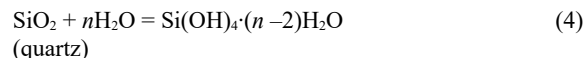
$$K_{\text{md}} = (a_d a_{\text{H}_2\text{O}}) / (a_m^2) \quad (2)$$

where a denotes activity and m and d stand for the monomer and dimer. Newton and Manning (2002) compared solubilities of SiO₂-buffering assemblages to show that, at conditions of the present experiments, values of K_{md} are accurately represented by:

$$\log K_{\text{md}} = 1.48 + 0.0012T + (0.000119T - 0.1685)P \quad (3)$$

with T in kelvin and P in kbar. Equation 3 yields silica speciation that is consistent with experimental solubility and spectroscopic results of Zhang and Frantz (2000), Zotov and Keppler (2000, 2002), and Newton and Manning (2002, 2003), but not with data from Sverjensky et al. (2014). Moreover, the latter source yields unrealistic results when extrapolated to low pressure, so Equation 3 was used in preference. It is important to note that the model results described below do not depend strongly on the silica speciation model.

Equilibrium between quartz and the monomer can be written as:



for which the equilibrium constant, K_{qm} , is:

$$K_{\text{qm}} = (a_m) / (a_{\text{H}_2\text{O}}^n). \quad (5)$$

At a given P and T , K_{qm} may be obtained from quartz solubility in pure H₂O and the speciation model, assuming ideal mixing of species, a standard state for quartz and H₂O of unit activity of the pure phase at any P and T , and a standard state for total silica in solution (a_{SiO_2}) of unit activity of the hypothetical pure solution of the monomer (Newton and Manning, 2002, 2003, 2009). This leads to:

$$a_m = X_m = a_{\text{SiO}_2} = \gamma_{\text{SiO}_2} X_{\text{SiO}_2} \quad (6)$$

and

$$a_d = X_d \quad (7)$$

where X denotes mole fraction and γ_{SiO_2} is the activity coefficient for total dissolved SiO₂:

$$\gamma_{\text{SiO}_2} = \frac{(1 + 8X_{\text{SiO}_2} K_{\text{md}} / a_{\text{H}_2\text{O}})^{1/2} - 1}{4X_{\text{SiO}_2} K_{\text{md}} / a_{\text{H}_2\text{O}}} \quad (8)$$

(e.g., Newton and Manning, 2009).

This framework can be used to constrain H₂O activity and CaCl₂ dissociation in H₂O-CaCl₂ fluids. We assume that n is a

constant equal to 4 for a wide range of P and T , based on measurements of quartz solubility in H₂O-CO₂ solutions (Newton and Manning 2009). H₂O-CaCl₂ mixing is modeled following Aranovich and Newton (1996, 1997), who showed that in H₂O-NaCl and H₂O-KCl solutions at high P and T , there is a marked decrease in $a_{\text{H}_2\text{O}}/X_{\text{H}_2\text{O}}$ that occurs at P greater than about 0.3 GPa. They interpreted this to result from pressure-induced ionization of the alkali chlorides (e.g., Quist and Marshall 1966). This led Aranovich and Newton to adopt an ideal fused-salt model for H₂O activity in salt solutions, in which:

$$a_{\text{H}_2\text{O}} = X_{\text{H}_2\text{O}}/(1 + \alpha X_{\text{salt}}) \quad (9)$$

where α is the dissociation parameter which nominally varies from zero for an undissociated salt to one for a single salt such as NaCl fully dissociated to Na⁺ and Cl⁻. CaCl₂ dissociates in two steps via formation of CaCl⁺ + Cl⁻ followed by Ca²⁺ + 2Cl⁻. Thus, for consistency with the fused salt model, we set α for CaCl₂ to vary from 0 to 2. The mole fraction of silica is related to the experimentally determined SiO₂ molality (m_{SiO_2} , Table 1) by:

$$X_{\text{SiO}_2} = X_{\text{m}} + 2X_{\text{d}} = \frac{m_{\text{SiO}_2}}{m_{\text{SiO}_2} + 55.51 \left(1 + \frac{(1 + \alpha)X_{\text{CaCl}_2}}{1 - X_{\text{CaCl}_2}} \right)} \quad (10)$$

Values of α in the fused salt model are constants independent of concentration (e.g., Aranovich and Newton 1996). In the context of this study, α can be interpreted to be an average over an experimentally investigated concentration range.

We used Equations 5–10 in combination with experimental results (Table 1) to derive values of α at each investigated P and T by weighted least-squares regression. Figure 2b shows an example result at 800 °C, 1 GPa, where $\alpha = 0.17$ yields the best fit to the data. Solubility behavior for $\alpha = 0, 1$, and 2 is shown for reference, along with predicted solubility using $\alpha = 1.51$ calculated from the model of Ivanov and Bushmin (2019). At 800 °C and 1 GPa, the Ivanov and Bushmin model predicts that CaCl₂ is strongly dissociated, yielding a_{SiO_2} and m_{SiO_2} that are too low to be consistent with observed quartz solubility. The solubility data instead imply that CaCl₂ is only slightly dissociated at these conditions.

The modeling approach described above assumes that $a_{\text{H}_2\text{O}}$ is the sole control on quartz solubility, which is justified because dissolved silica species are hydrated (Eq. 1). If $a_{\text{H}_2\text{O}}$ is the only controlling factor, the array of solubility values at a constant T and P plotted against H₂O (or salt) mole fraction correspond to lines of constant α , as in Figure 2b. If, however, SiO₂ complexes with the salt component, there is an additional increment of solubility or “enhancement.” This leads to contrasting solubility behavior in plots of H₂O activity vs. SiO₂ concentration. For example, there is no evidence for complexing between SiO₂ and CO₂ in H₂O-CO₂ fluids (e.g., Walther and Orville 1983; Newton and Manning 2009), which leads to a strong decline in quartz solubility with $a_{\text{H}_2\text{O}}$ (Fig. 2c). In contrast, quartz solubility declines less strongly with $a_{\text{H}_2\text{O}}$ in H₂O-NaCl (Fig. 2c), which can be interpreted as a consequence of Na-SiO₂ complexing (e.g., Evans 2007; Newton and Manning 2016) and is consistent with the extreme solubility of Na silicates. In this case, mass balance (Eq. 10) must be modified such that:

$$X_{\text{SiO}_2} = X_{\text{m}} + 2X_{\text{d}} + \sum v_i X_i \quad (11)$$

where i refers to the additional silica complexes and v_i is the number of Si in a complex.

The low solubility of wollastonite (CaSiO₃) in pure H₂O at 800 °C, 1 GPa (Newton and Manning 2006) suggests negligible of SiO₂-Ca complexing. This is confirmed by the lower solubility of quartz in CaCl₂-H₂O than in H₂O-CO₂ (Fig. 2a). Figure 2c shows that the predicted variation in quartz solubility with $a_{\text{H}_2\text{O}}$ with no SiO₂-Ca complexing is nearly identical in the H₂O-CaCl₂ and H₂O-CO₂ systems. The much higher solubility of quartz in NaCl solutions (Fig. 2c) of the same H₂O activity is consistent with the inferred strong Na-SiO₂ complexing in that medium.

Best-fit values of the dissociation factor, α , were found to increase with P at constant T , and to decrease with T at constant P (Table 2). These values were fitted to polynomial function of P and T , which supplied smoothed values of α for fitting to a logistic function of the form:

$$\alpha = \frac{2}{1 + e^{-k(\rho_{\text{H}_2\text{O}} - \rho_{\text{H}_2\text{O}}^*)}} \quad (12)$$

where $\rho_{\text{H}_2\text{O}}$ is H₂O density in g/cm³. Equation 12 forces α to vary from zero to two, consistent with the fused salt model. Least-squares regression gave optimal values of the parameters k and $\rho_{\text{H}_2\text{O}}^*$ as functions of P (GPa):

$$k = 75.26 - 36.94P. \quad (13)$$

$$\rho_{\text{H}_2\text{O}}^* = 0.665 + 0.4268P - 0.1196P^2. \quad (14)$$

Values of $\rho_{\text{H}_2\text{O}}$ were from Holland and Powell (1991), and all parameters were assigned dimensions consistent with dimensionless α . In Equation 12, $\rho_{\text{H}_2\text{O}}^*$ may be regarded as a characteristic density of the solution, and the parameter k determines the span and the slope of the α function. Values of α derived from Equation 12 are given in Table 2.

Figure 3 compares solubilities from Equation 12 with experimental results. Overall the model reproduces the data well. However, in detail, the fits are somewhat poorer at the highest temperatures at each pressure. This could be a consequence of some combination of the appearance of low concentrations of more polymerized silica at these conditions (Newton and Manning 2008; Hunt and Manning 2012), less accurate experimental results where solubilities are highest, and the slim possibility of SiO₂-Ca complexing leading to “salting in” at 0.6 GPa, 800 °C, and the lowest X_{CaCl_2} (run QzC-74).

Table 2. Values of α from experiments and models

P (GPa)	T (°C)	Regression of experimental data	Equation 13
0.6	600	0.781	0.563
0.6	700	0.139	0.043
0.6	800	-0.162	0.003
1.0	600	1.232	1.183
1.0	700	0.585	0.449
1.0	800	0.173	0.116
1.0	900	0.258	0.027
1.4	600	1.554	1.393
1.4	700	0.603	1.000
1.4	800	0.395	0.617
1.4	900	0.487	0.339

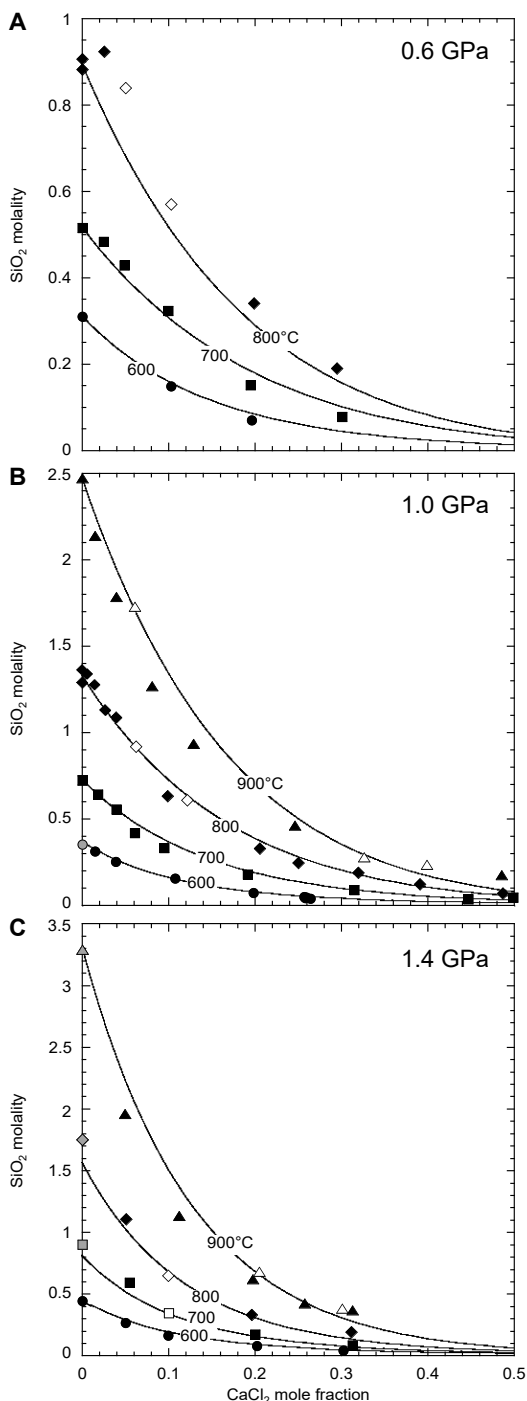


Figure 3. Quartz solubility in H₂O-CaCl₂. As in Figure 1, except solid lines are calculated using α derived from Equations 12–14.

Comparison to previous results

Shmulovich et al. (2006) determined quartz solubility in H₂O-CaCl₂ fluids at selected conditions in the range 0.1–0.9 GPa, 400–800 °C. Figure 4 shows their results at conditions similar to those of the present study. They modeled their solubility data in a form similar to that of Setchenow (1892):

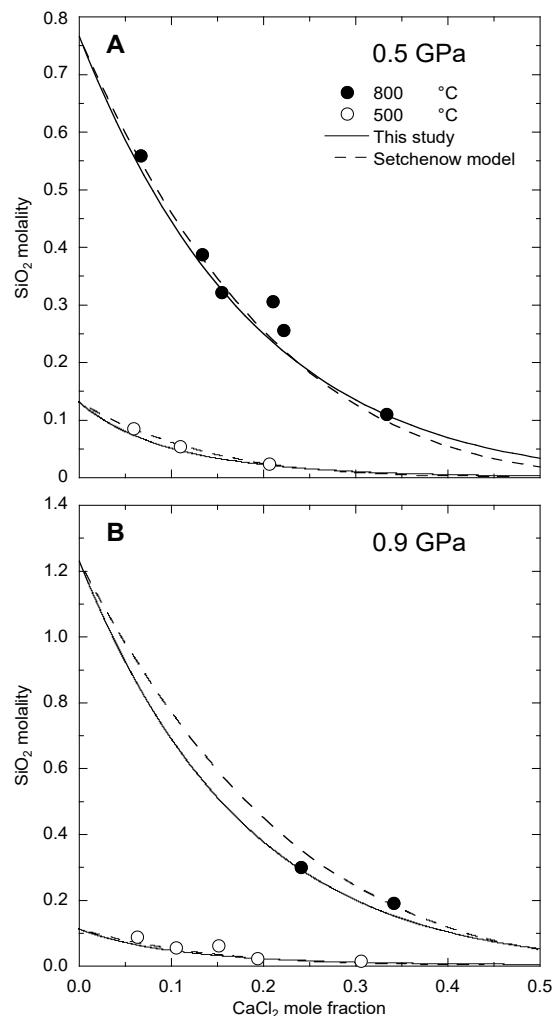


Figure 4. Results of Shmulovich et al. (2006) on quartz solubility in H₂O-CaCl₂ at 0.5 GPa (a) and 0.9 GPa (b). Dashed lines show solubility based on their Setchenow model (Eq. 15); solid lines calculated using α (Eqs. 12–14).

$$\log m_{\text{SiO}_2} = 3.5 \log X_{\text{H}_2\text{O}} + a \cdot m_{\text{salt}}^b \quad (15)$$

where the m denotes molality. The coefficient 3.5 is similar to the hydration number n (Eqs. 1 and 4), but differs in detail because $X_{\text{H}_2\text{O}}$ rather than $a_{\text{H}_2\text{O}}$ is used. Shmulovich et al. (2006) derived empirical constants a and b , which are unique to each P , T , and salt in their study, but they did not identify any systematics in their variations. Nevertheless, this empirical approach accurately represents their data, as shown in Figure 4.

Figure 4 also illustrates quartz solubility predicted by Equation 12. The Shmulovich et al. (2006) data are reproduced by our model with accuracy comparable to their Setchenow parameters.

Thermodynamic modeling using data from Huang and Sverjensky (2019) suggests that the aqueous calc-silicate complex, $\text{Ca}(\text{H}_3\text{SiO}_4)^+$, contributes significantly to total dissolved silica, such that predicted quartz solubility initially rises with the addition of minor CaCl₂ at all P and T of our study. This is not seen in our results (Figs. 1 and 3), and thus the experimental data require

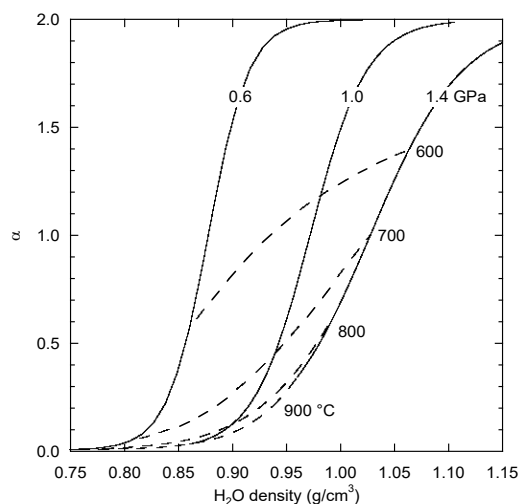


Figure 5. Variation in α with H₂O density (Eqs. 12–14). Solid lines show isobars, dashed lines show isotherms. Model results suggest that at lower crustal and upper mantle pressures, decreasing temperature results in significant CaCl₂ ionization.

substantially lower stability of any such calc-silicate complex at the conditions investigated. The neutral to slightly acidic quench pH of the present solutions (5–7.5) suggests that the deprotonated silica dimer [Si₂O₄(OH)⁻], inferred by (Aranovich et al. 2020) for

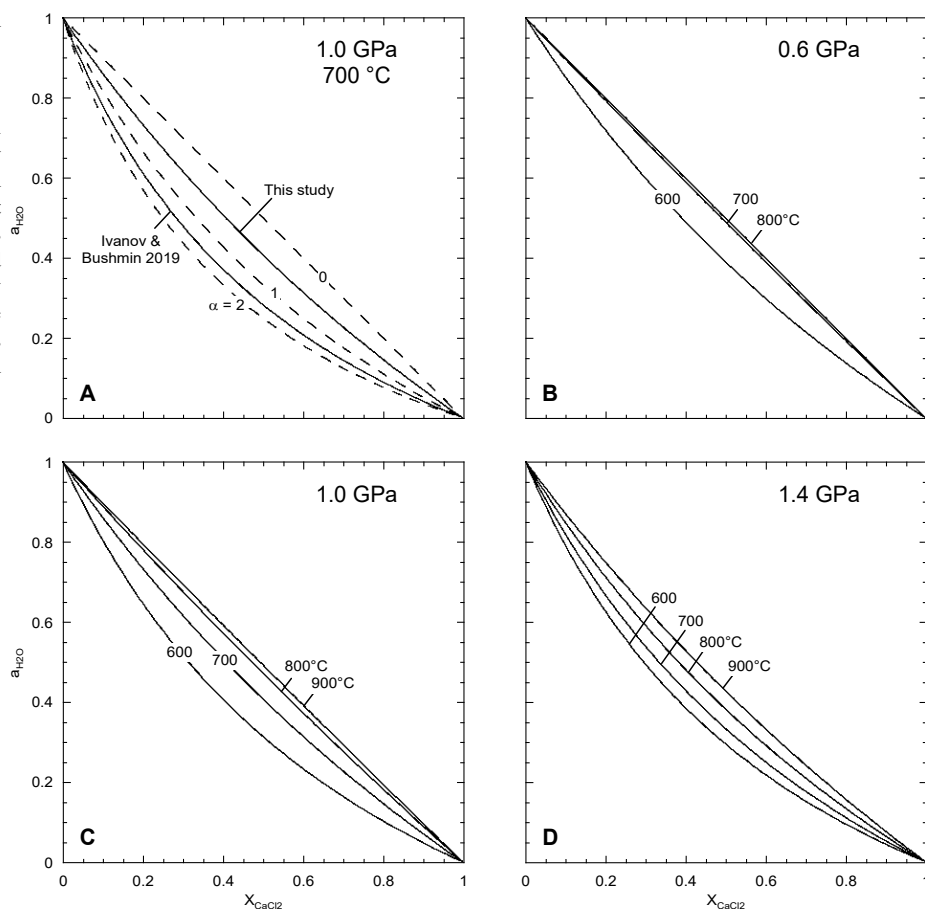
quartz solubility in Na₂CO₃ solutions at 0.4 GPa, is not a major species in CaCl₂-H₂O solutions.

Implications for H₂O-CaCl₂ fluids

Figure 5 illustrates the variation in α consistent with our experiments at mid- to lower-crustal and upper-mantle conditions. At these conditions, our model suggests that CaCl₂ is largely associated ($\alpha = 0$) at $\rho_{\text{H}_2\text{O}}$ below ~ 0.8 . Dissociation becomes significant at higher density along any isotherm or isobar. Our results contrast with predicted α in the model of Ivanov and Bushmin (2019), in which the transition from associated to largely dissociated CaCl₂ occurs at a much lower density, leading to near-constant predicted α of 1.5 ± 0.1 over the conditions of this study.

Variations in α can be used to assess activity-composition relations in H₂O-CaCl₂ fluids. Figure 6 shows $a_{\text{H}_2\text{O}}$ vs. $X_{\text{H}_2\text{O}}$ (Eq. 10) at the conditions of our experiments. In the ideal fused salt model, $a_{\text{H}_2\text{O}} = X_{\text{H}_2\text{O}}$ where $\alpha = 0$ is consistent with ideal molecular mixing. Maximum negative departures of $a_{\text{H}_2\text{O}}$ from $X_{\text{H}_2\text{O}}$ occur where $\alpha = 2$, corresponding to the ideal mixing of a fully dissociated double salt. Figure 6a illustrates a - X relations at 1.0 GPa and 700 °C. At this P and T , we obtain $\alpha = 0.45$, consistent with only a small negative departure from $a_{\text{H}_2\text{O}} = X_{\text{H}_2\text{O}}$; i.e., comparatively minor dissociation. The model of Ivanov and Bushmin (2019) gives $\alpha = 1.53$, implying more extensive dissociation and stronger departure from the 1:1 line. At each pressure, our results indicate a progressive approach to ideal molecular mixing (increasing

Figure 6. Predicted variation in H₂O activity with H₂O mole fraction, based on Equations 9 and 12–14. (a) 700 °C, 1 GPa, with values of $\alpha = 0, 1$, and 2 for reference, along with results from this study and Ivanov and Bushmin (2019). Values of α in the latter work are nearly constant at $\alpha \sim 0.15$ over all P and T of this study. For clarity, they are omitted from (b, c, and d), which show calculated a - X relations based on the present model. Our model predicts significant variation in the ionization state of CaCl₂ at these conditions, such that $a_{\text{H}_2\text{O}}$ depends strongly on P and T at any X_{CaCl_2} .



association, decreasing α) with rising temperature (Figs. 6b–6d). Isothermal pressure increases cause α to rise, yielding progressively greater departures from the 1:1 line.

Applications to petrology

Our results on the solubility of quartz in H₂O-CaCl₂ fluids may be useful in modeling silica metasomatism in settings showing evidence for calcium and other chlorides in the solution. For example, in the Cloncurry District of Queensland, conversion of metabasic and metapelitic lithologies to actinolite-titanite-clinopyroxene-rich rocks along with possibly metasomatic quartzites record high silica mobility, and fluid inclusions in the quartz contains high levels of both CaCl₂ and NaCl (De Jong and Williams 1995). The observations are consistent with regional-scale scapolite alteration in the district (Edwards and Baker 1953).

Alpine eclogites and blueschists of Corsica have undergone conversion to lawsonite-rich rocks containing as much as 13 wt% CaO and 12 wt% H₂O, with strong silica depletion and almost total removal of K₂O (Vitale Brovarone and Beyssac 2014). Metasomatic scapolite is a striking feature of the Bamble Shear Belt of southern Norway (Touret and Nijland 2013). This region also features extensive wholesale metasomatic replacement of silicate rocks by dolomite (Dahlgren et al. 1993). Depletion of silica is profound in this occurrence. At very high pressures and temperatures, i.e., upper mantle conditions, CaCl₂ can coexist with alkali chlorides in the dissociated state in concentrated solutions comparable to fused salt mixtures, as in fluid inclusions in cloudy diamonds (e.g., Izraeli et al. 2001). The metasomatizing potential of these fluids is, as yet, undefined but must be substantial.

The important inference that can be drawn from these natural occurrences is that in light of the decrease in quartz solubility with increasing CaCl₂ (this study) and NaCl (Fig. 1; Newton and Manning 2000), integrated fluid fluxes must have been very high to generate the observed Si removal or redistribution. This effect is only enhanced if CO₂ is also involved, as it also reduces quartz solubility (Fig. 2).

Implications

- Quartz solubility declines exponentially as CaCl₂ is added to H₂O at all P and T investigated.
- The decreases in solubility imply that there is no complex formation between SiO₂ and the salt. This contrasts with H₂O-NaCl, where complexing appears to cause solubility enhancement. Instead, where data exist for comparison, silica concentration is nearly the same as in CO₂-H₂O at the same H₂O activity, signaling negligible silica-Ca interaction. This holds at nearly all P - T conditions investigated, with the possible exception of the dilute solutions at 0.6 GPa and 800 °C.
- The monomer-dimer model for silica speciation leads to evidence for P - T dependent dissociation of CaCl₂. Our model implies substantial dissociation of CaCl₂ at low T and high P . Transition to undissociated CaCl₂ takes place over a relatively narrow temperature interval at each pressure nearly independently of CaCl₂ concentration at a given P and T . This feature could exert important influence on solubilities and stabilities of mineral assemblages in the presence of CaCl₂-bearing fluids by virtue of the associated large changes of H₂O activity.
- Important avenues for further investigation include solubil-

ity studies of quartz and major rock-forming minerals, including feldspars and magnesian silicates in mixed solutions of Ca, Na, and K chlorides and carbonates, at P - T conditions spanning ranges covering the middle crust to the upper mantle.

Acknowledgments and Funding

Our experimental program investigating the role of salts in fluids, melts, and their interactions with minerals has been inspired in part by contributions and intellectual leadership of Jim Webster. We thank J. Blundy, L. Aranovich, and N. Akinfiev for helpful reviews. This work was supported by National Science Foundation grants EAR 1732256 and 2124650 to C.E.M.

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Manuscript received November 15, 2021

Manuscript accepted December 15, 2022

Accepted manuscript online January 5, 2023

Manuscript handled by Daniel E. Harlov