# **@AGU**PUBLICATIONS

### Journal of Geophysical Research: Planets

### **RESEARCH ARTICLE**

10.1002/2016JE005059

#### Key Points:

- Van der Waals-type equations of state plausibly represent Si-O liquid-vapor speciation and phase relations
- Silica boils incongruently at high pressure enriching the liquid in reduced silicon
- The azeotropic boiling curve for SiO<sub>2</sub>-rich liquid is predicted from ambient pressure to its critical point

#### **Correspondence to:**

J. A. D. Connolly, james.connolly@erdw.ethz.ch

#### Citation:

Connolly, J. A. D. (2016), Liquid-vapor phase relations in the Si-O system: A calorically constrained van der Waals-type model, *J. Geophys. Res. Planets, 121,* 1641–1666, doi:10.1002/ 2016JE005059.

Received 21 APR 2016 Accepted 10 JUL 2016 Accepted article online 18 JUL 2016 Published online 16 SEP 2016

# Liquid-vapor phase relations in the Si-O system: A calorically constrained van der Waals-type model

**JGR** 

#### James A. D. Connolly<sup>1</sup>

<sup>1</sup>Earth Sciences Department, Swiss Federal Institute of Technology, Zurich, Switzerland

Abstract This work explores the use of several van der Waals (vW)-type equations of state (EoS) for predicting vaporous phase relations and speciation in the Si-O system, with emphasis on the azeotropic boiling curve of SiO<sub>2</sub>-rich liquid. Comparison with the observed Rb and Hg boiling curves demonstrates that prediction accuracy is improved if the *a*-parameter of the EoS, which characterizes vW forces, is constrained by ambient pressure heat capacities. All EoS considered accurately reproduce metal boiling curve trajectories, but absent knowledge of the true critical compressibility factor, critical temperatures remain uncertain by ~500 K. The EoS plausibly represent the termination of the azeotropic boiling curve of silica-rich liquid by a critical point across which the dominant Si oxidation state changes abruptly from the tetravalent state characteristic of the liquid to the divalent state characteristic of the vapor. The azeotropic composition diverges from silica toward metal-rich compositions with increasing temperature. Consequently, silica boiling is divariant and atmospheric loss after a giant impact would enrich residual silicate liquids in reduced silicon. Two major sources of uncertainty in the boiling curve prediction are the heat capacity of silica liquid, which may decay during depolymerization from the near-Dulong-Petit limit heat capacity of the ionic liquid to value characteristic of the molecular liquid, and the unknown liquid affinity of silicon monoxide. Extremal scenarios for these uncertainties yield critical temperatures and compositions of 5200–6200 K and  $Si_{1,1}O_2$ – $Si_{1,4}O_2$ . The lowest critical temperatures are marginally consistent with shock experiments and are therefore considered more probable.

#### 1. Introduction

Silicate liquid-vapor phase relations are of importance to understanding planet-forming processes associated with giant impacts. These processes include impact vaporization and melting [Benz et al., 1986; Stevenson, 1987], development of the instability that causes debris disks to spread beyond the Roche limit at which point satellites may coalesce [Thompson and Stevenson, 1988; Machida and Abe, 2004; Ward, 2012], and chemical fractionation caused by the atmospheric escape [Chen and Ahrens, 1997; Genda and Abe, 2003] or interactions between a protoplanet and its debris disk [Pahlevan et al., 2011]. Given the large uncertainties of astrophysical modeling, the silica system is often used as a first-order model for fluid behavior. The silica boiling point is at ~3150 K, and its boiling curve terminates at a critical point that has been estimated to lie at 5000-15,000 K and 0.2-2 GPa [Ahrens and O'Keefe, 1972; Bobrovskii et al., 1974; Stevenson, 1987; Melosh, 2007; Kraus et al., 2012; losilevskiy et al., 2014]. Such conditions, which can be realized after giant impacts [Canup, 2012; Reufer et al., 2012], preclude direct experimental observation except at pressures of ~10 Pa [Mysen and Kushiro, 1988] or by complex shock experiments [Kraus et al., 2012]. Because there would be no fractionation effects associated with turbulent convection between a supercritical proto-planet and its debris disk, the critical temperature is of particular importance for the hypothesis that the Earth-Moon system was homogenized by a brief, postimpact, period of planet-disk interaction [Stevenson, 1987; Pahlevan and Stevenson, 2007]. This importance motivates the present work which seeks to predict the critical condition for silica-rich fluid from equations of state (EoS). The effort differs from previous attempts in that it considers the vaporous of the entire Si-O system rather than just the  $SiO_2$  bulk composition; the advantage of this approach is that it offers more constraints on the predictive capacity of the EoS.

Most of the EoS parameterized for the purpose of predicting liquid-vapor equilibria and thermodynamic properties of silica fluid are wide-range EoS developed for hydrodynamic applications at extreme conditions. Wide-range EoS interpolate between a Mie-Gruneisen model [Kormer et al., 1962; Bobrovskii et al., 1974; de Koker and Stixrude, 2009; losilevskiy et al., 2014] for dense solid-like states and the Thomas-Fermi EoS for monatomic gases. The MANEOS [Melosh, 2007] is a wide-range EoS with an innovation to

©2016. American Geophysical Union. All Rights Reserved. account for the energetic effects of the formation of molecular clusters at densities intermediate between those of the low temperature liquid and monatomic vapor. The potential that causes critical phenomena in wide-range EoS is dependent on an interpolation function that is only constrained by the theoretical dense and monatomic gas limits. Thus, such models generally do not accurately represent the silica boiling curve *[Bobrovskii et al.,* 1974; *losilevskiy et al.,* 2014]. The MANEOS is exceptional in that its parameterization has been tuned to match a thermodynamic extrapolation of the boiling curve based on low-pressure data *[Schick,* 1960]. Because the MANEOS critical point is, likewise, adjusted to match an educated guess, the prediction is no better than the original guess. Additional limitations of wide-range EoS are that they make no provision for the uncertainty that may arise from compositional degrees of freedom and provide no information on speciation. Here these deficiencies are remedied by parameterizing van der Waals (vW)-type EoS to predict phase equilibria in the Si-O system to pressures adequate to complement the high-pressure predictive capacity of empirical Hugoniot equations [*Hicks et al.,* 2005] and/or wide-range EoS.

Computation of liquid-vapor compositions is routine at temperatures (1500–4000 K) of the primordial solar nebula [*Fegley and Cameron*, 1987; *Alexander*, 2002; *Fedkin et al.*, 2006] and the magma oceans that may be stable features on hot super-Earth exoplanets [*Schaefer et al.*, 2012; *Visscher and Fegley*, 2013]. In these computations the vapor is presumed to consist primarily of diatomic and monatomic species in accord with low-pressure mass spectroscopic observations [e.g., *Porter et al.*, 1955; *Nichols et al.*, 1998; *Shornikov and Archakov*, 2002]. In contrast, the liquid model includes polymerized molecular species (e.g., Si<sub>4</sub>O<sub>8</sub> and Mg<sub>2</sub>SiO<sub>4</sub>). This disparate speciation precludes description of critical phenomena at high temperature but is consistent with the low-pressure observation that Mg<sub>2</sub>SiO<sub>4</sub> boils congruently [*Nagahara et al.*, 1994]. There is ambiguity concerning the boiling of silica [*Mysen and Kushiro*, 1988]; however, it is invariably assumed in thermodynamic analysis [*Schick*, 1960; *Schnurre et al.*, 2004) that any deviation from congruent boiling is insignificant at ambient pressure. Given the multispecies nature of the vapor, congruent boiling requires that the liquid has no silicon in any oxidation state other than the 4+ state characteristic of the SiO<sub>2</sub> molecule.

Hugoniot temperatures predicted by the MANEOS are higher than, and diverge exponentially from, experimental determinations [*Hicks et al.*, 2005; *Kraus et al.*, 2012]. The reason for this discrepancy is that the experimental Hugoniot indicates a heat capacity for fluid silica significantly above the Dulong-Petit limit, which is taken as the heat capacity for the dense limit in the MANEOS. The anomalous heat capacity is attributed to bond-breaking during a continuous transformation from bonded liquid to monatomic fluid that culminates at ~30,000 K [*Hicks et al.*, 2006]. Evidence of this transformation is important because it suggests that at intermediate conditions significant amounts of silicon may be in the neutral and divalent oxidation state characteristic of Si and SiO in the vapor. Under such circumstances the liquid composition is not stoichiometrically constrained and univariant boiling is only possible if the liquid boils azeotropically. It is to be expected that the azeotropic liquid composition will be depleted in oxygen relative to the silica composition because oxygen should partition preferentially into the vapor during incongruent boiling. The model developed here permits assessment of this effect. The importance of incongruent boiling in seemingly stoichiometric oxide liquids has been demonstrated for UO<sub>2</sub> [*Iosilevski et al.*, 2001], and *Iosilevskiy et al.* [2014] acknowledge, but do not evaluate, the effect for silica.

Spectroscopic [*Mysen and Richet*, 2005; *Kalampounias et al.*, 2006] and molecular dynamic studies [*Trave et al.*, 2002; *Karki et al.*, 2007] show no evidence for molecular species in dense silica liquid or glass. However, molecular dynamic simulations have shown that Si-O coordination number in silica varies inversely with density and, specifically, that threefold coordinated silicon is present at the melting point [*Karki et al.*, 2007]. Thus, at the higher temperatures and lower densities of interest here, it is plausible that the Si-O coordination decreases to become consistent with a molecular model, i.e., Si-O coordination number  $\leq 2$ . The alternative that the vapor becomes increasingly polymerized and/or ionic as pressures increase along the boiling curve is not tractable because thermodynamic data for the potential species are lacking and because vW-EoS assume that interparticle forces decay more rapidly with distance than Coulombic forces.

Van der Waals-type EoS typically have a two-parameter isothermal potential consisting of a hard-sphere repulsive term and an attractive term accounting for vW forces between neutral species. Aside from the simplicity of the potential, which is desirable in view of the scarce information on high-temperature silicate fluids, the value of vW-EoS is that the potential of an impure fluid can be expressed as a function of the parameters of its constituent species. There is both precedent and justification for the use of vW-EoS, to predict the boiling curves and critical properties of both metals and oxides [*Young and Alder*, 1971; *losilevski et al.*, 2001; *Helffrich*, 2015]. *Ahrens and O'Keefe* [1972] applied this approach for silica but did not account for variations in speciation with the consequence that the predicted boiling curve is inconsistent with empirical constraints, and *losilevskiy et al.* [2014] predict both speciation and critical conditions along the SiO<sub>2</sub> boiling curve. A challenge to these efforts has been that in the absence of critical data, the repulsive and attractive potentials for the pure species are calibrated in terms of the density of the condensed phase and its evaporation energy. This approach is problematic for Si-O fluids, because silica evaporates to an impure gas and the consensus of current opinion is that there is no stable low-pressure form of condensed SiO [*Schnurre et al.*, 2004; *Ferguson and Nuth*, 2012; *Niu et al.*, 2015]. To circumvent these difficulties the vW potentials are calibrated here to match low-temperature phase equilibria and ambient pressure caloric equations of state. The benefit of relying on caloric data is that at high temperature the entropy of a molecular vapor can be estimated with confidence and the liquid adiabats are only weakly dependent on pressure and heat capacity. As the entropy of both phases must converge at critical conditions, caloric models provide robust constraints on the critical pressure and temperature [*Stevenson*, 1987].

This paper begins by reviewing the implications of the assumption that silica is a molecular liquid and outlining the ambient pressure calorimetric models to be used for its species. It is then demonstrated, by comparison with experimental data for Hg and Rb, that calorically constrained parameterization substantially improves the predictive capacity of vW-EoS for pure fluids and the problems in applying this method to impure and hypothetical pure fluids in the Si-O system are addressed. The final sections present predictions of the Si-O vaporous phase relations and discuss these in light of earlier predictions and shock experiments.

#### 2. The Molecular Model, Azeotropic Boiling, and Thermodynamic Data

Low-pressure observations indicate that the minimal set of molecular species necessary to describe Si-O fluids is {Si, O, SiO, O<sub>2</sub>, SiO<sub>3</sub>} [Schick, 1960; Nichols et al., 1998; Shornikov and Archakov, 2002]. The model pursued here assumes that both liquid and vapor Si-O phases can be described as mixtures of these molecular species, where, for brevity, license is taken in identifying monatomic Si and O as molecules. In contrast, microscopic considerations of the behavior of silica liquid at the comparatively moderate conditions of the present-day Earth generally suggest that the liquid is composed of large ionic clusters [Mysen and Richet, 2005; Ottonello et al., 2010], the stoichiometry of which is consistent with the 4+ silicon oxidation state. To distinguish this result from the molecular model pursued here, reactions between species that do not involve a change in oxidation state (e.g.,  $Si_9O_{18} = 2[Si_4O_7]^{2+} + [SiO_4]^{4-}$ ) are referred to as polymerization reactions, whereas the term speciation reaction is reserved for either molecular reactions (e.g.,  $SiO_2 = SiO + O$ ) that involve a change in silicon oxidation state or the disassociation reaction of diatomic oxygen (i.e.,  $O_2 = 2O$ ). Although it is indisputable that low-temperature silica and silicon liquids are polymerized, evidence that this polymerization decays with increasing temperature [McMillan, 2004; Hicks et al., 2006; Karki et al., 2007] lends credence to the assumption here that high-temperature silica fluids can be described as a mixture of neutral vapor-phase species. To distinguish such a fluid from a hypothetical single-species fluid, the latter are referred to as pure fluids. Given the distinction between polymerization and speciation, real Si and  $SiO_2$ liquids at ambient pressure are pure but polymerized. Standard chemical notation Si(I) and  $SiO_2(I)$  indicates the properties of the variably polymerized pure fluids. The present treatment assumes that the properties of Si(I) and SiO<sub>2</sub>(I) converge with those of the unpolymerized liquids at subcritical temperatures. In contrast to the liquid species Si(I) and SiO<sub>2</sub>(I), thermodynamic properties compiled for gaseous species correspond to those of the pure, unpolymerized, molecular gas [Schick, 1960].

#### 2.1. Azeotropic Boiling

Impure fluids do not, in general, exhibit critical behavior, rather for any given bulk composition the liquidvapor field defines a divariant envelope in pressure-temperature space. In the special case that reactions are possible among the species of an impure fluid, univariant boiling and therefore critical phenomena may occur for a particular fluid composition, i.e., an azeotropic composition. Azeotropic boiling occurs when the enthalpic benefit of forming a multicomponent species (e.g., SiO<sub>2</sub>) overwhelms its entropic cost, in terms of lost configurational entropy, in the liquid, but not in the vapor. This leads to a local maximum in the thermal stability of the liquid at the azeotropic composition, which is generally near to the composition of the multicomponent species. As a consequence of the maximum, a liquid with the azeotropic composition boils to form a vapor with the same bulk composition but different speciation.

#### 2.2. Ambient Pressure Properties of SiO<sub>2</sub>(I) and Si(I)

Although liquid thermodynamic data (Table A2) are not used directly for the prediction of Si-O phase relations, ambient pressure calorimetric and melting point properties for Si and SiO<sub>2</sub> liquids are used to parameterize the pure fluid EoS. For SiO<sub>2</sub>(I), the cristobalite melting point is taken to be 1999 K and the melting point liquid volume is estimated to be  $27.30 \pm 0.63$  J/MPa mol as described in Appendix A. For Si(I), calorimetric properties are taken as given in the HSC database together with the volume from *Sato et al.* [2000].

In petrological [*Richet and Bottinga*, 1984; *Lange and Navrotsky*, 1992] and high-temperature [*Schnurre et al.*, 2004; *Melosh*, 2007; *Kraus et al.*, 2012] applications it is assumed that the isobaric heat capacities of Si and SiO<sub>2</sub> liquids at ambient pressure are constant or weakly increasing functions of temperature (Table A2) approximately limited by the Dulong-Petit law. Such behavior is consistent with a microscopic model in which rotational, translational, configurational, and electronic contributions to the heat capacity are insignificant. *Ottonello et al.* [2010] suggest that the rotational and translational contributions account for most of measured heat capacity jump (~1R) across the silica glass transition, which *Richet and Bottinga* [1984] attributed to configurational disorder. The configurational contributions should rise with the onset of depolymerization and vanish in the molecular limit assumed here to apply at the critical condition. Although the changes in liquid structure observed in molecular dynamic simulations [*Karki et al.*, 2007] likely correspond to depolymerization, the highly anomalous heat capacity inferred from those simulations (~5nR, n is the number of atoms per molar formula unit) is excessive in light of experimental constraints. These highly anomalous values may reflect an exaggerated electronic contribution, which is expected to be negligible at 3000 K due to the large SiO<sub>2</sub> band-gap [*Kraus et al.*, 2012]. The silica Hugoniot heat capacity is also highly anomalous (~5nR), but this behavior is attributed to speciation rather than depolymerization [*Hicks et al.*, 2006].

Uncertainty in the extrapolation of SiO<sub>2</sub>(I) heat capacity to high temperature is explored with two models. The reference model adopts, as in previous studies [*Melosh*, 2007; *Kraus et al.*, 2012], a near Dulong-Petit limit heat capacity function. Although this extrapolation has the virtue of simplicity, it is based on experimental observations of the low-temperature ionic liquid (Si-O CN ~4) and therefore of dubious relevance to the molecular limit. Structure energy calculations at 3000 K indicate that the heat capacity of molecular SiO<sub>2</sub> liquid is roughly half the Dulong-Petit limit [*Ottonello et al.*, 2010]. As an alternative to the reference model, a second model assumes that heat capacity of the liquid falls to the molecular value over the temperature interval of 3500–4500 K. As molecular dynamic results, albeit at superambient pressure, indicate that SiO<sub>2</sub>(I) is polymerized at such temperatures, this model is likely exaggeration of any real depolymerization effect; thus, the model is considered to illustrate the maximum destabilization of SiO<sub>2</sub>(I) attributable to caloric effects. A high heat capacity model is not considered because its effect would be opposite, i.e., stabilizing SiO<sub>2</sub>(I), but otherwise comparable to the low heat capacity model.

Silicon undergoes a continuous transition, which has been described by two-species models [*Deb et al.*, 2001], from bonded to metallic liquid with increasing temperature and pressure. Rather than include two Si species here, the ambient pressure heat capacity of Si(l) is taken to be constant as recommended by *Desai* [1986]. Because this approximation discounts the electronic and configurational components of the heat capacity, it may underestimate the stability of Si(l) and silicon solubility in high-pressure silica liquids. However, both previous [*losilevskiy et al.*, 2014] and present results suggest that the concentration of silicon in SiO<sub>2</sub>-rich liquid is unlikely to be important unless the error in this approximation is drastic.

#### 2.3. Ambient Pressure Data for Pure Si-O Gases

In view of the large extrapolations required, differences among the thermodynamic data in recent gas data compilations [*Chase*, 1998; *Schnurre et al.*, 2004; *Roine*, 2011; *Kraus et al.*, 2012] are insignificant. The data in the HSC database [*Roine*, 2011] (Table A1) are taken as the basis of a reference model. From low-pressure experiments, *Shornikov and Archakov* [2002] inferred both entropies and enthalpies of formation for gaseous SiO and SiO<sub>2</sub>. The entropies are consistent with the HSC data, but the enthalpies are significantly different. To assess the effect of these low-temperature enthalpic uncertainties, a variant on the reference model was constructed in which the Gibbs energies of SiO and SiO<sub>2</sub> are adjusted to match the enthalpies of *Shornikov and Archakov* [2002]. The adjustments stabilize SiO<sub>2</sub>, the dominant liquid species, and destabilize SiO, the

dominant vapor species; thus, this variant will extend the silica boiling curve to more extreme pressuretemperature conditions.

#### 3. Van der Waals-Type EoS

Van der Waals-type EoS represent pressure as the sum of a term  $(p^{r})$  that describes the variation in pressure solely due to packing density and a term  $(p^{a})$  that accounts the cohesive interparticle forces responsible for liquification [*Prausnitz*, 1969]. Many modern variants replace van der Waals original term

$$P_{\rm VW}^{\rm r} = \frac{{\rm R}T}{v-b},\tag{1}$$

where R is the gas constant, *T* is the temperature, *v* is the molar volume, and *b* is a measure of particle radius, with the Carnahan-Starling EoS

Ķ

$$p_{CS}^{r} = RT \left( 1 + \frac{b}{4v} + \frac{b^{2}}{16v^{2}} - \frac{b^{3}}{64v^{3}} \right) / \left[ v \left( 1 - \frac{b}{4v} \right)^{3} \right],$$
(2)

which has been found to represent fluids composed of noninteracting, spherical particles with near-perfect accuracy [Song et al., 1989]. There are numerous modifications of van der Waals original cohesive term

$$p_{\rm vW}^{\rm a} = -a/v^2, \tag{3}$$

among these the expression

$$p_{\rm RK}^{a} = -a / \left[ v(v+b)\sqrt{T} \right]$$
(4)

used in the Redlich-Kwong EoS ( $p = p_{vW}^r + p_{RK}^a$ ) has proven particularly successful. To abbreviate EoS names, vW is reserved for the van der Waals-type EoS in general, while four letter abbreviations (e.g., vWvW) are used to indicate specific EoS; in these, the first two letters identify the hard-sphere pressure term (i.e., vW for equation (1) and CS for equation (2)) and the second pair identifies the attractive term (i.e., vW for equation (3) and RK for equation (4)).

Modifications of the vWvW have largely been motivated by the observation that the critical compressibility factor

$$z_{\rm c} = \frac{p_{\rm c} v_{\rm c}}{{\rm R}T_{\rm c}},\tag{5}$$

obtained by solving  $\partial p/\partial v = \partial^2 p/\partial v^2 = 0$  for the vWvW is 0.375, whereas for pure low-temperature molecular fluids  $z_c$  is typically in the range of 0.22–0.31 [*Prausnitz*, 1969]. For the three EoS obtained in addition to the vWvW by combining the above expressions for  $p^a$  and  $p^r$ , the CSRK [*Vera and Prausnitz*, 1972], vWRK [*Redlich and Kwong*, 1949], and CSvW [*Young and Alder*, 1971], the critical compressibility factors are 0.316, 0.333, and 0.359, respectively. To assess the uncertainty that arises from using low-temperature data to predict critical conditions these equations and the vWvW are tested here against experimental constraints for Hg ( $z_c = 0.393 \pm 0.001$ ) and Rb ( $z_c = 0.23 \pm 0.02$ ), the compressibility factors of which span those of the four EoS. Additional grounds for choosing Hg and Rb are that among metals, they have the most accurately known critical conditions. A similar exercise was undertaken by *Young and Alder* [1971] with the CSvW and vWvW EoS, but their calibration is based partially on vaporous data; the intent here is to employ solidus data to maximize the use of experimental constraints for silica.

#### 3.1. Melting Point Parameterization

Given the thermodynamic properties of the liquid and gas of a pure substance, the vW *a* and *b* parameters can be determined requiring that at the melting point the EoS

$$p = p^{\rm r} + p^{\rm a} \tag{6}$$

reproduces the liquid volume and that the fugacity

$$= p_0 \exp\left(\int_{v_0}^{v} \frac{v}{\mathsf{R}T} \frac{\partial p}{\partial v} dv\right) \tag{7}$$

satisfies

f

Table 1.	Propert	ties of Rb,	Hg, and	I the Hypo	othetical I	Monospec	ies SiO <sub>2</sub> and	Si Fluids <sup>a</sup>										
				Melt	ting Point						Boiling Poir	ıt				Critica	l Point	
Hg <sup>b</sup> , T <sub>m</sub> = 234.	3 ± .0 K,	α 10 <sup>4</sup> /K	<i>К</i> GPa	c/R	s/R	$_{lpha K}^{lpha K}$ MPa/K	×	д <sub>b</sub> К	$^{lpha}_{10^4/\mathrm{K}}$	<i>К</i> GPa	c/R	s/R	α <i>K</i> MPa/K	×	д <sub>с</sub> К	р <sub>с</sub> МРа	T <sub>c</sub> /p <sub>c</sub> K/MPa	pc kg/m³
ρ <sub>m</sub> = 13,6 kg/m <sup>3</sup>	90 ± 2	<b>1.8 ± 0.0</b>	25 ± 1	3.42 ± 0.1	8.33±0.2	<b>4.5</b> ± 0.2	0.59 ± 0.05	630±0	<b>1.8 ± 0.0</b>	16 ± 1	3.27 ± 0.1	11.6±0.2	2.9±0.2	0.36 ± 0.05	1764±1	167 ± 3	10.6 ± 0.2	5800 ± 100
am	vww	1.6	106	20.9	9.88	17	0.97	673	2.0	25	2.75	12.7	5.0	0.12	2,099	154	13.6	4,725
	CSvW	9.4	21	27.6	3.44	20	4.8	560	8.4	5.8	6.78	10.3	4.9	0.73	1,247	52.4	23.8	2,826
	vWRK	3.3	55	43.8	-4.23	18	3.9	492	6.2	8.0	10.9	8.26	5.0	0.20	994	51.3	19.4	3,736
	CSRK	17	9.7	55.2	-9.43	16	24	459	19	1.9	16.2	7.21	3.6	17	7.99.7	21.4	37.4	2,054
a(T)	vwwv	1.7	106	3.42	8.33	18	0.08	621	2.4	23	3.59	11.4	5.5	0.19	1,545	114	13.6	4,725
	CSvW	8.1	21	3.42	8.33	17	-0.59	634	6.6	6.6	4.06	11.7	4.4	-0.046	1,368	57.5	23.8	2,826
	vWRK	2.3	55	3.42	8.33	13	0.21	643	3.6	10	3.96	11.8	3.6	0.46	1,439	74.3	19.4	3,736
	CSRK	11	9.7	3.42	8.33	11	-0.59	624	9.2	2.8	4.16	11.7	2.7	0.36	1,219	32.7	37.4	2,054
≻	vwwv	2.9	17	20.9	11.1	4.9	11.7	442	3.6	6.3	2.81	12.8	2.3	1.3	1,227	48.4	25.4	2,538
	CSvW	8.1	47	28.7	1.21	39	1.5	671	6.6	11	6.88	10.0	39	1.5	1,563	92.3	16.9	3,969
Rb <sup>c</sup> ,		ø	×			$^{\alpha K}$		$T_{\rm b}$	ø	×			αΚ		$T_{c}$	pc	T <sub>c</sub> /p <sub>c</sub>	β
$T_{\rm m} = 312.$	$4 \pm 0.1$ K,	10 <sup>4</sup> /K	GPa	c/R	s/R	MPa/K	х	×	10 <sup>4</sup> /K	GPa	c/R	s/R	MPa/K	X	¥	MPa	K/MPa	kg/m <sup>3</sup>
$\rho_{\rm m} = 1,46$	0 ± 50																	
kg/m <sup>3</sup>		$3.4 \pm 0.2$	2.1 ± 0.1	3.91 ± 0.2	$10.1 \pm 0.4$	$0.7 \pm 0.1$	25 ± 3	961 ± 1	7.8 ± 1.4 (	0.57 ± 0.2	$3.66 \pm 0.3$	14.3 ± 0.4	$0.45 \pm 0.2$	8.6 ± 28	2,093 ± 35	15.9±3.1	132 ± 23	346 ± 9
a <sup>m</sup>	www.	1.2	33	20.9	11.1	4.0	9.3	977	1.6	6.5	2.82	14.1	1.1	1.3	2,723	50.1	54.4	504
	CSvW	7.2	6.9	27.6	4.83	4.9	44	803	6.6	1.5	6.65	12.1	1.0	8.0	1,625	17.2	94.5	303
	vWRK	2.5	17	43.2	-2.58	4.2	37	701	5.2	2.0	10.2	10.3	1.0	29	1,301	16.8	77.4	399
	CSRK	13	3.1	54.5	-7.65	4.0	218	652	15	0.47	15.1	9.63	0.71	182	1,047	7.09	148	221
a(T)	vwwv	1.3	33	3.91	10.1	4.3	1.3	960	1.6	6.4	3.6	14.3	1.0	2.1	3,484	64.1	54.4	504
	CSvW	6.1	6.9	3.91	10.1	4.2	-3.8	961	4.2	2.0	3.83	14.4	0.83	2.1	2,374	25.1	94.5	303
	vWRK	1.7	17	3.91	10.1	3.0	2.5	962	2.4	3.1	3.85	14.4	0.73	4.7	2,625	33.4	77.4	399
	CSRK	8.0	3.1	3.91	10.1	2.5	-2.2	958	6.0	0.80	3.99	14.5	0.48	9.8	1,983	13.4	148	221
≻	~W^W	2.2	5.8	21.0	12.3	1.3	97	658	2.9	1.7	2.88	14.3	0.51	13	1,619	16.1	101	284
	CSvW	6.2	16	28.7	2.50	9.7	13	996	5.1	3.1	6.71	11.8	1.6	2.2	2,061	30.8	6.99	427

Table 1.	(continued	기)															
				Melti	ing Point						Boiling Poin	Ŧ				Critical Poin	Ŧ
$SiO_2^d$ , $T_m = 1,9$	90±10K,	$^{lpha}_{10^4/\mathrm{K}}$	K GPa	c/R	s/R	$^{lpha K}$ MPa/K	×	μ Κ	α 10 <sup>4</sup> /Κ	K GPa	c/R	s/R	<i>αK</i> MPa/K	×	τ <sub>c</sub> Κ	<i>P</i> c MPa	$ ho_c^{ ho_c}$ 3 kg/m <sup>3</sup>
$\rho_{\rm m} = 2,2$ kg/m <sup>2</sup>	- 150 -	0.6 ± 0.6	30 ± 20	9.87 ±0.2	$20.8 \pm 0.4$	1.8±2	0.13 ± 0.4	3,177 ± 115	5 0.6 ± 0.6	30 ± 20	$9.94 \pm 0.2^{f}$	$25.4 \pm 2^{f}$	1.8±2	$0.24 \pm 0.4$			
am	www.	0.22	356	61.1	28.1	7.7	0.19	U	0.23	196	61.8	31.6	4.6	0.23	15,540	616	764
	CSvW	1.2	79	67.2	22.4	9.4	0.86	υu	1.2	42	67.1	28.4	4.5	1.2	9,477	220	467
	vWRK	0.45	184	81.1	16.0	8.3	0.49	, u	0.65	57	72.8	26.3	3.7	0.93	7,711	215	605
E)e	CSRK	2.1	36 256	91.7	11.4 0.00	7.6	2.6	U U	2.2	12	77.8 C 11	25.3	2.7	5.3	6,260 6 770	94 240	342 76.4
(1)	MASU	1.3	0000 62	88.6	20.8	6.6	20.0	U	f. C	37	12.5	25.8	0	0.10	5.919	137	467
	vWRK	0.39	184	9.88	20.8	7.2	0.49	U	0.62	65	11.6	25.7	4.0	0.87	6,013	168	605
	CSRK	1.7	36	9.88	20.8	6.1	0.11	U	2.9	16	12.4	25.9	2.9	0:30	5,641	84	342
Si <sup>e</sup> ,		8	×			$\alpha K$		$T_{\rm b}$	8	×			$\alpha K$		$T_{c}$	pc	Pc 2
$T_{\rm m} = 1,60$	87 ± 2 K,	10 <sup>4</sup> /K	GPa	c/R	s/R	MPa/K	X	¥	10 <sup>4</sup> /K	GPa	c/R	s/R	MPa/K	X	¥	MPa	kg/m <sup>3</sup>
<i>د</i> ,2 = m <i>q</i> <sup>5</sup> kg/m	- 05 ± 0/	1.0 ± 0.4	49±4 3	3.27 ± 0.2	11.1 ± 0.4	4.9±0.2 (	).036 ± 0.005	3,564 ± 73	1.0±1	<b>41</b> ± 14	$3.27 \pm 0.2^{f}$	13.5 ± 0.5 <sup>f</sup>	<b>4.1</b> ± 3	0.025 ± 0.01			
am	WvWv	0.24	838	24.0	11.9	20.2	0.015	3,658	0.28	296	24.8	14.1	8.4	0.021	13,800	1,364	890
	CSvW	1.4	180	27.9	5.92	24.8	0.061	3,186	1.4	179	27.6	5.92	22	0.027	8,335	478	540
	vWRK	0.50	434	42.5	-0.89	21.8	0:050	2,896	0.78	111	32.4	8.54	8.6	0.091	6,735	468	705
	CSRK	2.5	80	53.3	-5.52	19.8	0.28	2,734	2.6	26	38.8	6.82	6.7	0.50	5,421	200	394
a(T)	www.	0.24	838	3.27	11.1	20.9	0.0014	3,568	0.31	286	3.60	13.4	8.8	0.00021	11,376	1,124	890
	CSvW	1.2	180	3.27	11.1	20.8	-0.0063	3,553	0.93	83	3.47	13.4	7.7	-0.0021	9,494	544	540
	CSRK	0.30 1.5	434 80	3.27		12.2	c200.0 0.0060	3,603 3,604	0.45 1.3	138 35	2.89 2.90	13.4 13.5	6.2 4.4	0.0028 0.0055	10,036 8,446	698 312	705 394
<sup>a</sup> Prec decreas ± 0.02 fu bMelt	lictions fro ing z <sub>c</sub> (i.e., or Rb [ <i>Dillo</i> ing and bo	the no $z_c^{vwvw} = (1, 1)$ in et al., 15 oiling poir	nregular 0.375, z <sup>CC</sup> 966]. The nt from <i>H</i>	ized and <sup>swv</sup> = 0.35 t predictic luber et al	regularize 9, z <sup>vwrk</sup> = 305 from t	ed versior - 0.333, z <sup>C</sup> - he vWvW ritical con	is of the vW <sup>SRK</sup> = 0.316), and CSvW   ditions from	EoS are in these com barameterii <i>Kozhevnik</i>	dicated by pare to the zations of ) ov et al. [15	a <sub>m</sub> and a e experim (oung and 96]; and e	(T), respective entally cons I Alder [1971 expansivity,	vely, in the strained va ] for Rb an bulk modu	: left-most lues of 0.3 d Hg are a ilus, and ca	column. In e 93 ± 0.001 fo Iso presented Ioric errors fi	ach catego r Hg [ <i>Kikoir</i> d (indicatec rom Ayrinho	ry, the EoS are l 1 and Senchenk, 1 by "Y" in the le ac et al. [2014]; c	isted in order of 1967] and 0.23 ftmost column). aloric data as in
Table A <sup>c</sup> Melt	1. ing and br	oiling poi	nts and	caloric da	ita from ∕	Ncock et a	ıl. [1994], cri	itical condi	tions from	Dillon et i	<i>а</i> І. [1966], т	ielting poii	nt bulk mo	- more from -	Jarzynski et	<i>al.</i> [1969], and	expansivity and
boiling Melt	point bulk ing and b	c modulus oiling poi	s estimat Int prope	ed from <i>l</i> vrties fron	reifer et כ ח Table A	1. [1979]. 1.											
<sup>e</sup> Melt mated k	ing and b by linear e	oiling poi xtrapolati	on of the	e tempera e tempera	ta from <i>D</i> ature dep	<i>esai</i> [1986 vendence	i), expansivi estimated fi	ty from Sati rom Alatas	<i>o et al.</i> [20( <i>et al.</i> [200:	00], meltir 5].	ng point bull	k modulus	from <i>Hosc</i>	kawa et al. [	2003], and ł	ooiling point bu	lk modulus esti-
Ē	Collinates		רנומר היו	ווויכמו.													

CONNOLLY

$$g^{\rm I} = g^{\rm g} + {\rm R}T \ln \frac{f^{\rm I}}{f^{\rm g}}, \qquad (8)$$

where *g* is the molar Gibbs energy, superscripts I and g identify properties of the liquid and gas, and  $v_0$  is the molar volume in the ideal gas limit  $f \rightarrow p$ . For present purposes it is assumed that the ideal gas limit is realized at ambient pressure  $(p_0)$ , an assumption justified by the high temperatures of interest. The molar entropy  $(s^I)$  and isobaric heat capacity  $(c^I)$  of the liquid can then be computed from equation (8) and gas phase calorimetric properties as

$$s^{l} = s^{g} - R\left(\ln\frac{f^{l}}{\rho_{0}} + T\frac{\partial\ln f^{l}}{\partial T}\right)$$
(9)

$$c^{\mathsf{I}} = c^{\mathsf{g}} - \mathsf{R}T\left(2\frac{\partial \mathsf{ln}\,f^{\mathsf{I}}}{\partial T} + T\frac{\partial^{2}\,\mathsf{ln}\,f^{\mathsf{I}}}{\partial T^{2}}\right). \tag{10}$$

Comparison of the liquid properties and boiling ( $T_b$ ) and critical conditions predicted by the four EoS for Hg and Rb (Table 1) suggests that the characteristic critical compressibility factor of the EoS is proportional to *s*,  $c^{-1}$ ,  $T_b$ ,  $T_c$ ,  $p_c$ , and  $\rho_c$ . With the possible exception of the vWvW prediction for Hg, the predicted properties are haphazard and in some cases nonphysical, i.e., negative entropy. For the limited *p*-*T* range of concern, the accuracy of the predicted boiling curve is determined largely by the ability of the EoS to reproduce the boiling point entropy but is insensitive to second-order properties. In contrast, the location of the critical point along the boiling curve is defined by the condition

$$\chi = v \left(\frac{c}{TK} - va^2\right) = \infty,\tag{11}$$

where *K* is the isothermal bulk modulus,  $\alpha$  is the isobaric expansivity, and  $\chi$  is required to be positive for stable states of a pure substance [*Tisza*, 1961]. Condition (11) suggests that an accurate EoS can be distinguished from one which fortuitously predicts plausible critical conditions by comparing the predicted and observed values of  $\chi$  at the melting and boiling points. This criterion correctly identifies the vWvW and CSvW as accurate predictors for Hg and Rb, respectively.

In principle, comparison of the present results with those of *Young and Alder* [1971] should illustrate the beneficial effect on the critical point prediction of parameterization on the basis of vaporous rather than solidus properties. Instead, that no such benefit is evident (Table 1) illustrates the unfortunate consequence of relying on independent estimators of *a* and *b*. Specifically, while *Young and Alder* [1971] estimated *a* from evaporation energies, *b* was estimated from the melting point liquid density using the Percus-Yevick hardsphere equation, which is accurately approximated by the Carnahan-Starling EoS. Because the CSvW is formed by adding the  $p_{vW}^a$  term to the Carnahan-Starling, the resulting equation cannot reproduce the liquid density from which it is parameterized. This inconsistency is more pronounced for the vWvW, because the vW hard-sphere potential is a poor approximation of the Percus-Yevick equation. Consequently, Young and Alder's parameterization has the peculiar result that if pressure, temperature, and density are considered individually, then the best critical point prediction (CSvW for Hg, vWvW for Rb) is obtained with the EoS that maximizes the discrepancy between the real and predicted  $z_c$ . There is no doubt that the strategy used here would provide better critical point predictions if it were based on boiling point rather than melting point properties, but the boiling point properties of silica are based almost exclusively on extrapolation of data measured at, or below, the melting point.

#### 3.2. Caloric Regularization

Inaccurate caloric properties are a prominent failing in vW EoS if the *a* parameter is taken to be a constant (Table 1). Because *a* enters linearly in the EoS, from equations (9) and (10), the predicted melting point entropy can be adjusted arbitrarily, without affecting the melting point Gibbs energy, by treating  $\partial a/\partial T$  as a free parameter. Likewise, once the desired entropy has been obtained, the heat capacity can be adjusted by treating  $\partial^2 a/\partial T^2$  as a free parameter. These adjustments are implicit if *a* is fit as a function of temperature to satisfy equations (6) and (8) assuming the value of *b* obtained by the melting point parameterization.

Although assigning a temperature dependence to *a* is justified by perturbation theory [*Vera and Prausnitz*, 1972; *de Santis et al.*, 1974; *Holloway*, 1977; *losilevski et al.*, 2001], the motivation here is purely empirical as in some previous applications [*Desantis et al.*, 1976; *Kerrick and Jacobs*, 1981]. For the vWvW, *a*(*T*) initially falls

		a ( <del>J/Pa-mol</del> )	b (J/MPa-mol)	Т <sub>b</sub> (К)	<i>Т</i> <sub>с</sub> (К)	р <sub>с</sub> (МРа)	$\rho_{\rm c}$ (kg/m <sup>3</sup> )
02	exptl <sup>b</sup>			90.18	154.6	5.045	436.9
	vWRK	1.50438	19.078	91.22	154.6	5.837	436.9
	CSRK	1.71661	6.102	98.88	154.6	5.395	436.9
SiO <sub>2</sub> (1, 3)	VWRK	f <sub>1</sub> <sup>c</sup>	25.7967	3568	6131	171.2	605.4
	CSRK	f <sub>5</sub> <sup>c</sup>	5.61723	3567	5692	87.87	352.2
SiO <sub>2</sub> (2)	VWRK	f <sub>2</sub> <sup>c</sup>	25.8380	3646	6300	175.6	604.4
SiO <sub>2</sub> (4)	VWRK	$f_3^{c}$	25.7967	3550	5586	156.0	605.4
	CSRK	f <sub>6</sub> <sup>c</sup>	5.61723	3557	5583	86.19	352.2
SiO <sub>2</sub> (5)	vWRK	$716.590 \pm 36$	25.7967±.6	$3471\pm63$	$7711 \pm 133$	$215.3\pm8.8$	$605.4\pm4.6$
SiO (1, 2, 4)	vWRK	44.0972	5.34948	1476	3431	454.4	2145
	CSRK	1.40178	2.62942	1446	2764	91.15	552.0
SiO (3)	vWRK	220.544	16.0618	2170	4821	216.2	713.4
	CSRK	3.44422	3.48000	2169	4174	104.0	417.1
Si (1–4)	vWRK	f4 <sup>c</sup>	10.3579	3550	9768	679.5	604.4
	CSRK	f <sub>7</sub> <sup>c</sup>	2.27702	3754	14444	550.0	404.9
Si (5)	vWRK	$234.970 \pm 8$	$10.3579 \pm .4$	$2897\pm9$	$6737\pm16$	$468.5\pm19$	$704.8\pm27$

Table 2. vW Parameters and Critical Properties of the Hypothetical Monospecies Fluids Used for Model Variants (1) HSC, (2) Shornikov, (3) SiO(I), and (4) Low-c With the vWRK and CSRK EoS (Section 4.1)<sup>a</sup>

<sup>a</sup>For Si and SiO<sub>2</sub>, properties (Variant 5), are also given for the unregularized melting point parameterizations computed with the HSC data. The caloric properties for these variants (Table 1) are inconsistent with thermodynamic assess-

puter with the rise cata. The caloric properties for these variants (Table 1) are inconsistent with thermodynamic assessments but illustrate the minor influence of the melting point volumetric uncertainty. <sup>b</sup>Kaye and Laby [1995]. <sup>c</sup> $f_i = a_0 + a_1T + a_2T^{3/2} + a_3T^2 + a_4/T + a_5\ln(T) + a_6T^{1/2} + a_7T^{5/2} + a_8/T^{1/2} + a_9/T^2$ ; when no value for a coefficient is specified the coefficient is zero; for i = 1, { $a_0 = -3743.37$ ,  $a_1 = -1.15993$ ,  $a_2 = 2.04563 \cdot 10^{-2}$ ,  $a_3 = -1.25367 \cdot 10^{-4}$ ,  $a_4 = -47.8704$ ,  $a_5 = 717.244$ , T = 1400-6000 K}; for i = 2, { $a_0 = -3707.97$ ,  $a_1 = -1.11182$ ,  $a_2 = 1.94790 \cdot 10^{-2}$ ,  $a_3 = -1.18805 \cdot 10^{-4}$ ,  $a_4 = -46.8778$ ,  $a_7 = 710.713$ , T = 1400-6000 K}; for i = 3,  $a_7 = -1.111224$ ,  $a_7 = -2.27266$  $\begin{array}{l} a_{4}=-47.8704, \ a_{5}=717.244, \ r=1400-6000 \text{ K}; \ \text{ for } r=2, \ \{a_{0}=-3707.97, \ a_{1}=-1.1182, \ a_{2}=1.94790\cdot10^{-7}, \ a_{3}=-1.1182, \ a_{2}=-1.94790\cdot10^{-7}, \ a_{3}=-1.011583, \ a_{2}=-1.24090\cdot10^{-2}, \ a_{3}=-2.61410\cdot10^{-4}, \ a_{5}=42.7563, \ a_{6}=-17.0393, \ a_{7}=-3.80259\cdot10^{-7}, \ a_{8}=1.51371, \ T=1000-9000 \text{ K}; \ \text{for } i=5, \ \{a_{0}=-18973.3, \ a_{1}=-6.40617, \ a_{2}=0.109170, \ a_{3}=-6.07460\cdot10^{-4}, \ a_{4}=-746587, \ a_{5}=3380.73, \ a_{9}=7.46213\cdot10^{8}, \ T=1000-5400 \text{ K}; \ \text{for } i=6, \ \{a_{0}=-29.412.5, \ a_{1}=-10.3678, \ a_{2}=0.175421, \ a_{3}=-9.57158\cdot10^{-4}, \ a_{4}=-1,111.990, \ a_{5}=5213.03, \ a_{9}=11.1144\cdot10^{8}, \ T=1000-5300 \text{ K}; \ \text{for } i=7, \ \{a_{0}=-1626.75, \ a_{1}=-0.366288, \ a_{2}=7.11091\cdot10^{-3}, \ a_{3}=-0.399047\cdot10^{-4}, \ a_{4}=-113.427, \ a_{5}=302.051, \ a_{9}=0.956758\cdot10^{8}, \ T=1000-5300 \text{ K}; \ \text{for } i=7, \ \{a_{0}=-1626.75, \ a_{1}=-0.366288, \ a_{2}=7.11091\cdot10^{-3}, \ a_{3}=-0.399047\cdot10^{-4}, \ a_{4}=-113.427, \ a_{5}=302.051, \ a_{9}=0.956758\cdot10^{8}, \ T=1000-5300 \text{ K}; \ \text{for } i=7, \ \{a_{1}=-10.3678, \ a_{2}=0.75678\cdot10^{8}, \ T=1000-5300 \text{ K}; \ \text{for } i=7, \ a_{1}=0.956758\cdot10^{8}, \ T=1000-5300 \text{ K}; \ \text{for } i=7, \ a_{1}=0.956758\cdot10^{8}, \ T=1000-5300 \text{ K}; \ \text{for } i=7, \ a_{1}=0.956758\cdot10^{8}, \ T=1000-5300 \text{ K}; \ \text{for } i=7, \ a_{1}=0.956758\cdot10^{8}, \ T=1000-5300 \text{ K}; \ \text{for } i=7, \ a_{1}=0.956758\cdot10^{8}, \ T=1000-5300 \text{ K}; \ \text{for } i=7, \ a_{1}=0.956758\cdot10^{8}, \ T=1000-5300 \text{ K}; \ \text{for } i=7, \ a_{1}=0.956758\cdot10^{8}, \ T=1000-5300 \text{ K}; \ \text{for } i=7, \ a_{1}=0.956758\cdot10^{8}, \ T=1000-5300 \text{ K}; \ \text{for } i=7, \ a_{1}=0.956758\cdot10^{8}, \ T=1000-5300 \text{ K}; \ \text{f$ 1000-5300 K}.

as temperature increases beyond the melting point, but remains within 10% of the melting point value  $a_m$ . For the other EoS, a(T) is roughly parabolic rising to a maximum of  $\sim 2a_m$  at temperatures roughly halfway between those of the boiling and critical points. It emerges that the variation in  $a(T)/a_m$  for SiO<sub>2</sub> and Si is smaller than for Rb and Hg but shows the same patterns (Table 2). The parabolic form of a(T) suggests that it could be parameterized entirely on the basis of the heat capacity and entropy of the liquid at the melting point; this approach was not pursued because it generally does not reproduce boiling point caloric properties within the estimated uncertainties. The choice of an arbitrary analytical expression for a(T) precludes exact reproduction of the heat capacity of the liquid assumed for the parameterization, but the boiling and melting point caloric properties of Hg and Rb are generally within experimental uncertainty (Table 1). Consequently, caloric regularization substantially improves predicted boiling curve trajectories (Figure 1). The effect on critical point prediction is more subtle. Critical density is solely a function of b and is therefore unaffected by the temperature dependence of a; likewise, the ratio  $p_c/T_c$  predicted by vW EoS (Table 1) is mathematically constrained. However, the  $p_c$ - $T_c$  predictions cluster closer to the experimentally determined coordinates, suggesting that in the absence of knowledge of the true value of  $z_{cr}$  regularization improves critical point prediction. In contrast to the unregularized EoS, the predicted critical pressure and temperature are proportional to  $K^{i}$  rather than  $z_{cr}$  presumably because allowing greater degrees of freedom in a emphasizes the role of the hard-sphere term in determining  $K^{l}$ . The greatest benefit of caloric regularization is that accurate reproduction of boiling curve trajectories effectively eliminates uncertainty in the critical pressure as a function of temperature. Thus, while the critical pressure predictions vary over half an order of magnitude, this variation is due almost entirely to the logarithmic dependence of pressure on boiling curve temperature.

Journal of Geophysical Research: Planets



**Figure 1.** Critical and boiling points predicted by the melting point parameterizations of the vW EoS for Hg, Rb, and hypothetical monospecies SiO<sub>2</sub> and Si fluids. The experimentally constrained boiling curves for Hg [*Huber et al.*, 2006] and Rb [*Dillon et al.*, 1966; *Pfeifer et al.*, 1979] and "ideal" boiling curves are shown for comparison. The ideal curves are computed assuming that the volume of the liquid is insignificant, the ideal gas law for the vapor, and the calorimetric data in Table A1. The ideal model should underestimate the Clapeyron slope of the boiling curve and therefore provide an upper bound on boiling curve temperature as illustrated by the curves for Rb and Hg, which also show that the ideal model provides a good approximation to the real boiling curves. The critical point predictions of the regularized vW EoS are consistent with the trends indicated by the ideal models, whereas the unregularized vW EoS predictions are scattered and, in the case of SiO<sub>2</sub>, lie consistently on the high-temperature side of the ideal boiling curve.

In view of the goals of this paper, it is desirable to identify accurate EoS from melting point properties of the liquid. As the melting point calibration and caloric regularization allow for essentially exact reproduction of  $v^{l}$ ,  $s^{l}$ , and  $c^{l}$  these properties provide no accuracy information, leaving  $\alpha^{l}$  and  $K^{l}$  as the only candidates for this purpose. In vW EoS the singularity that arises in the limit  $b \rightarrow v$  has the consequence that  $K^{l}$  increases more rapidly as temperature falls to the melting point than in real liquids. On the basis Hg and Rb liquid behavior, the EoS melting point predictions of  $K^{l}$  are roughly twice as high they would be without the influence of the singularity. Thus, an otherwise accurate vW EoS will overestimate  $K^{l}$ . Despite this effect, the proximity of the predicted product  $\alpha^{l}K^{l}$  to the real liquid values does correlate with the accuracy of the critical point prediction (Table 1).

#### 3.3. Application to the Pure Si-O Species

The melting point vW parameterizations obtained with the reference models for SiO<sub>2</sub>(I) and Si(I) (section 2.1) illustrate similar patterns to those for Rb and Hg. For both SiO<sub>2</sub> and Si,  $\alpha' K'$  predicted by regularized parameterizations of the CSRK and vWRK most closely match experimentally constrained estimates (Table 1). For this reason the other EoS are not considered further. Taking into account that the vW EoS overestimate  $K^{1}$  at the melting point and assuming that the behavior of impure SiO<sub>2</sub>-rich liquid will primarily reflect the properties of the metastable pure SiO<sub>2</sub> liquid, the CSRK should yield a low estimate of the critical condition, while the vWRK is expected to yield a high estimate. While data for SiO<sub>2</sub>(I) are poorly constrained compared to those for Rb(I) and Hg(l), if it is accepted that vW estimates of the melting point  $K^{I}$  are too high by a factor of ~2, then the regularized vW EoS, and in particular the CSRK and vWRK, provide better fits for SiO<sub>2</sub>(I) than they do for the liquid metals. That SiO<sub>2</sub>(I) is well described by these EoS is supported by the relatively moderate variation in a(T) required for the regularization; i.e., a(T) rises to a maximum that is only 5–15% above  $a_m$ . Although the near Dulong-Petit heat capacity of the reference model is usually assumed to extrapolate to high temperature, there is no experimental data to support this extrapolation. Thus, three variants on the reference model are parameterized to illustrate the uncertainties in this extrapolation, a low heat capacity model, a high enthalpy model, and a nonregularized model (Table 2). Because Si does not emerge as a significant species, only two models for pure Si are presented, the reference model and the nonregularized model. In both cases,

**RAGU** 

the nonregularized models are included only to illustrate the minor influence of the uncertainty in melting point properties on the critical point prediction and are not discussed further.

#### 3.3.1. Pure SiO

The combined calorimetric-phase equilibrium method used to estimate vW parameters for Si and SiO<sub>2</sub> cannot be used for SiO because it has no stable liquid or solid state except at extreme pressure (~500 GPa [Niu et al., 2015]); rather, SiO condenses to a submicroscopic mixture of silicon and SiO<sub>2</sub>-glass or cristobalite [Ferguson and Nuth, 2012] at low pressure, and at ambient pressure thermodynamic analysis indicates that SiO condenses to a mixture of immiscible Si-rich and SiO<sub>2</sub> liquids [Schnurre et al., 2004]. Two approaches were taken to estimate the SiO vW parameters. In one, taken as the reference model, the relations between the vW parameters of SiO and SiO<sub>2</sub> were assumed to be identical to those CO and CO<sub>2</sub>, which were computed from the corresponding critical conditions [Prausnitz, 1969]. In the fully parameterized models these estimates yield an oxygen solubility in Si-rich liquid coexisting with SiO<sub>2</sub>-rich liquid at 2000–2100 K and 0.1 MPa comparable to that observed experimentally (~ $10^{-4}$  mol [Schnurre et al., 2004]). Because SiO<sub>2</sub> is the dominant O-bearing species in Si-rich liquid at these conditions, the experimental constraint is indirect and implies only that this parameterization does not overestimate the liquid affinity of SiO. In the second approach, the vW parameters of SiO were derived to fit a hypothetical boiling curve coincident with the amorphous SiO vapor pressure curve [Ferguson and Nuth, 2012] at 0.01 MPa and 1935±50 K and 0.1 MPa and 2170±50 K. This approach provides a model that predicts the maximum stability of SiO(I) consistent with the absence of SiO(I) in low-pressure experiments. For the vWRK parameterization both a and b were derived by fitting the hypothetical boiling curve. This strategy was not possible for the CSRK because of its strong nonlinearity; therefore, for the CSRK  $b_{SiO}$  was estimated as  $b_{CO}(d_{SiO}/d_{CO})^3$ , where  $d_{SiO}$  and  $d_{CO}$  are the bond lengths of gaseous SiO (150 pm) and CO (112.9 pm) and only  $a_{SiO}$  was fit.

#### 3.3.2. Pure O<sub>2</sub> and O

The vW parameters for O and  $O_2$  are of little consequence because the conditions of interest are far beyond the  $O_2$  critical condition, which is assumed to be identical to that of a hypothetical O fluid. The parameters are estimated from the  $O_2$  critical volume and temperature (Table 2).

#### 3.4. Impure Fluids

The vW parameters of a multispecies fluid are usually computed by averaging the corresponding parameters of the pure species. It can be shown by virial theory that *b* should be the mean of the species values weighted by their molar proportions  $y_i$  [*Prausnitz*, 1969]. Similarly, *a* is required to be the sum of pair-wise interaction terms

$$a = \sum_{i} \sum_{j} y_{i} y_{j} \langle a_{ij} \rangle, \tag{12}$$

where the pure limit defines  $\langle a_{ij} \rangle \equiv a_i$  and in the case of nonpolar species or interactions between a nonpolar and polar species  $\langle a_{ij} \rangle$  is well approximated by the geometric mean of  $a_i$  and  $a_i$  as originally proposed by van der Waals provided that there are no interspecies chemical interactions [*de Santis et al.*, 1974; *Holloway*, 1977]. This approximation can be tested by comparison with an empirical macroscopic model for Si-rich liquid [*Schnurre et al.*, 2004]. Over the temperature range of the calibration, 1700–1850 K, the vW models indicate that such liquid are approximately binary Si-SiO<sub>2</sub> mixtures. Making this approximation, the values of  $\langle a_{Si-SiO_2} \rangle$  necessary to reproduce the Henryian limit of the macroscopic model with the vWRK are 495 J/Pa at 1700 K and 329 J/Pa at 1850 K. These values compare reasonably to the (geometric, harmonic) averages of (490, 462) and (506, 480) J/Pa at the corresponding temperatures. As large values of  $\langle a_{ij} \rangle$ favor the stability of *i*-*j* liquid, the deviation between the microscopic and macroscopic models indicates that the geometric mean may overestimate miscibility and the solubility of subordinate species. To minimize this effect, unless otherwise noted,  $\langle a_{ij} \rangle$  is estimated by the harmonic mean.

#### 4. Predicted Phase Equilibria and Thermodynamic Properties

The speciation of Si-O vW fluids is found as a function of bulk composition, pressure, and temperature by solving for the conditions of the interspecies equilibria  $2 O = O_2$ , O + Si = SiO, and  $2 O + Si = SiO_2$  subject to mass balance and closure constraints. Stable heterogeneous phase equilibria are then computed by Gibbs energy minimization [*Connolly*, 2009]. At a given pressure, the temperature-composition coordinates of the SiO<sub>2</sub>-rich

**AGU** Journal of Geophysical Research: Planets



**Figure 2.** Isobaric (0.1 MPa) Si-O phase diagram predicted by the HSC-vWRK parameterization. The phase relations differ insignificantly from those predicted by other parameterizations discussed in the text and/or the CSRK EoS. The compositional variable  $X_{\rm O}$  is the atomic fraction of oxygen. The red circles locate invariant conditions from the analysis of *Schnurre et al.* [2004]. Although not visible at the scale of the diagrams, the oxygen-solubility predicted in Si-rich liquid is consistent with that analysis.

azeotropic boiling curves were taken to be those of the first point found during a search initiated from the O-rich side of the azeotrope, at which the liquid and vapor field were separated by a temperature interval of  $<10^{-5}$  K. This procedure is complicated at near-critical conditions because the density difference between liquid and vapor becomes comparable to the computational resolution. Therefore, critical temperatures were estimated by extrapolating the limbs of the liquid-vapor field in temperature-density space by making use of the critical exponent estimated from the last welldetermined segment of the liquidvapor field.

#### 4.1. Model Variants

The uncertainty associated with extrapolating from low-temperature phase equilibrium constraints and thermodynamic data is likely much greater than the experimental error

associated with the constraints and data. For this reason no attempt is made to systematically propagate experimental errors through the phase equilibrium calculations. Instead, four configurations are considered to illustrate various sources of error. In each case calculations were made for both the vWRK and CSRK. As phase relations and speciation patterns are qualitatively similar in both cases, complete results are presented only for the vWRK. The Hg and Rb systematics (section 3.2) suggest that the vWRK likely overestimates the critical pressure and temperature of the silica-rich boiling curve, while the CSRK underestimates these conditions. The four configurations (Tables 2 and A1) are: (1) HSC; the reference model. The vW parameters for SiO are assumed to be proportional to those of SiO<sub>2</sub>, and HSC data are used for all ambient pressure calorimetric properties of the gas. (2) Shornikov. This configuration illustrates the impact of enthalpic error by using enthalpies and vW parameters for SiO and SiO<sub>2</sub> consistent with the experiments of Shornikov and Archakov [2002] (section 2.3). That this impact is minor is anticipated by the small differences in the predicted boiling and critical points for the hypothetical pure SiO<sub>2</sub> liquid (Table 2). (3) SiO(l). This configuration uses vW parameters for SiO deduced by assuming that the SiO boiling curve is coincident with the low-temperature vaporpressure curve of amorphous SiO [Ferguson and Nuth, 2012] (section 3.3.1). This configuration maximizes the concentration of SiO in silica liquid and consequently maximizes the stability of SiO<sub>2</sub>-rich liquid relative to vapor. (4) Low-c. This configuration uses vW parameters for SiO<sub>2</sub> deduced by assuming that heat capacity of SiO<sub>2</sub>(I) falls to the values comparable to that of the molecular liquid [Ottonello et al., 2010] with increasing temperature (section 3.3). This configuration minimizes the stability of the SiO<sub>2</sub> molecule and consequently minimizes the stability of SiO<sub>2</sub>-rich liquid relative to vapor.

#### 4.2. Low-Temperature Properties and T-X<sub>0</sub> Phase Relations

The HSC-vWRK parameterization accurately reproduces the 0.1 MPa optimized Si-O phase diagram of *Schnurre et al.* [2004] (Figure 2). Similar results are obtained with the alternative parameterizations because the extrapolation from the melting point to the vaporous is relatively moderate at ambient pressure. With the exception of vapor entropy, the SiO<sub>2</sub> boiling point calorimetric properties (Table 3) of all the vW models are within the estimated error bounds [*Kraus et al.*, 2012]. The boiling point vapor entropy of *Kraus et al.* [2012] incorrectly neglects configurational entropy; if the configurational entropy is added, then the result, 7477  $\pm$  12 J/K-kg, is identical to the HSC value. At subambient pressure, the vW boiling curves lie well within

	5 1		Tb	s <sub>b,l</sub>	s <sub>b,g</sub>	T <sub>c</sub>	pc	$\rho_{c}$	s <sub>c</sub>		N <sub>c</sub>		n <sub>c</sub>
			К	J/K-kg	J/K-kg	К	MPa	kg/m³	J/K-kg	X <sub>c</sub>	g/mol	Z <sub>C</sub>	at/mol
Present vW-EoS estimates	HSC	vWRK	3,130	3,554	7,477	6,074	930	1,036	5,382	0.352	50.8	0.903	2.51
		CSRK	3,131	3,564	7,479	5,548	419	555	5,322	0.350	51.0	0.834	2.52
	SiO(I)	vWRK	3,130	3,554	7,477	5,675	373	782	5,404	0.403	48.8	0.493	2.34
		CSRK	3,131	3,564	7,479	5,298	229	485	5,375	0.383	49.8	0.534	2.41
	Low-c	vWRK	3,134	3,445	7,482	5,543	663	932	5,161	0.350	51.6	0.797	2.55
		CSRK	3,137	3,601	7,486	5,452	391	554	5,233	0.350	51.4	0.801	2.53
	Low-c + SiO(I)	vWRK	3,134	3,446	7,482	5,324	282	745	5,280	0.409	48.8	0.436	2.33
		CSRK	3,137	3,601	7,486	5,243	222	486	5,322	0.382	49.9	0.523	2.42
	Shornikov	vWRK	3,143	3,559	7,535	6,242	1,148	1,126	5,419	0.353	50.1	0.984	2.47
Empirical estimates	HSC		3,119	3,504	7,460								
	HP + HS	C	3,122	3,494	7,464								
	Stevenso	n	2,700	2,800	7,000	5,500	1,000		4,600				
	Kraus		3,177	3,552	7,254	<4,961			<5,798				
			±115	± 70	±8 <sup>d</sup>	± 559			± 277				
	Melosh-Shi	ck <sup>b</sup>	3,158			5,423	220	650		0.3	40*	0.30 <sup>*</sup>	2 <sup>*</sup>
Previous EoS estimates	Ahrens & O'ł	Keefe	4,926			13,386	624	622	4,721	0.3	40 <sup>*</sup>	0.36	2*
	Bobrovsk	dii	2,723			5,400	540	741		0.3			
	losilevskiy-S	AHA	3,270			6,303	305	650	5,919	0.3	44.87	0.18	2.24
	losilevskiy-MF	QEOS	1,740			4,862	551	650		0.3			
	losilevskiy-lor	ic-MD	5,473			11,976	200	580		0.3			
	MANEOS-N	Лie				6,214	444	690	6,200	0.3	40	0.50	2
	MANEOS-Mo	orse <sup>c</sup>				5,071	24	73	5,900	0.3	40	0.31	2
	MANEOS-N	/lie <sup>*</sup>	3,157	3,443	7,240 <sup>d</sup>	5,398	189	549	4,789	0.3	40 <sup>*</sup>	0.31 <sup>*</sup>	2*
	MANEOS-Kr	aus				5,130	130	508	5,150	0.3			

#### Table 3. vW Critical and Boiling Point Properties and Various Other Recent Estimates<sup>a</sup>

<sup>a</sup>Subscripts b and c indicate, respectively, boiling and critical points; subscripts I and g indicate liquid and gas state. Asterisks indicate models or properties that are based on assumed critical properties. "Kraus" is the constraint on the critical *s*-*T* coordinate derived by assuming that the decompression isentrope for the highest shock pressure experiment of *Kraus et al.* [2012] intersects the vapor-rich side of the boiling envelope (Figure 4a); their estimated boiling point and entropies are also shown. "HSC" is the boiling point based on the HSC database [*Roine*, 2011], and "HSC + HP" is the boiling computed using the liquid data from *Holland and Powell* [2011] with HSC vapor data. "Melosh-Shick" is the empirical critical point estimate (described in the text) of *Melosh* [2007]. "MANEOS-Mie" is the unbiased on a Mie-like interatomic potential [*Melosh*, 2007]; "MANEOS-Morse" is the MANEOS prediction based on the Morse potential [*Melosh*, 2007]; "MANEOS-Mie" is the parameterization of *Kraus et al.* [2012] obtained by adjusting six parameters of the "MANEOS-Mie" to fit their estimate of the boiling point conditions ("Kraus").

<sup>b</sup>*Melosh* [2007] reports slightly different critical conditions (219 MPa, 5397 K), probably due to round-off error.

 $c_{\rm T}^{\rm C}$  That  $z_{\rm c}$  for this model appears to coincide with that of *Melosh*'s [2007] critical point correction may indicate the prediction was biased.

<sup>d</sup>The boiling point vapor entropy of *Kraus et al.* [2012] is the sum of the vapor species entropies and does not to include configurational entropy. For the speciation in that paper, the correct boiling point vapor entropy is 7477 ± 12 J/K-kg, essentially identical to the present results. It is probable that *Melosh*'s [2007] boiling point vapor entropy is incorrect for the same reason.

the error of thermodynamic and experimental boiling curve extrapolations (±125 K [Schick, 1960; Mysen and Kushiro, 1988]).

Although nonstoichiometric boiling of SiO<sub>2</sub>-rich liquid is not apparent at 0.1 MPa, with increasing pressure the azeotropic composition shifts to progressively more Si-rich compositions as anticipated from the consideration that the O<sub>2</sub> and O species are more volatile than SiO and Si species. For the HSC parameterization (Figures 3a–3c), the azeotropic composition reaches Si<sub>1.10</sub>O<sub>2</sub> at the critical point, corresponding to a 9.2 mol% enrichment in Si relative to the SiO<sub>2</sub> composition. The SiO(I) parameterization (Figures 3d–3f), which maximizes SiO liquid affinity, yields a Si-enrichment of 27.3 mol% at its critical point (Si<sub>1.37</sub>O<sub>2</sub>). The SiO(I) parameterization is unique in predicting the stability of SiO-rich liquid. At high temperature and moderate pressures, this liquid is miscible with SiO<sub>2</sub>-rich liquid (Figure 3d). At ambient pressure, the liquid is stable between 2170 K and 2060 K. The existence of such a liquid cannot be precluded on the basis of direct observation.

The *T*-*X*<sub>O</sub> phase relations (Figures 2 and 3) were computed using the harmonic mean to estimate  $\langle a_{ij} \rangle$  in equation (12). It is not possible to discriminate between results obtained with the geometric and harmonic means on the basis of data, but for all model variants, harmonic averaging reproduces the essentially stoichiometric behavior of SiO<sub>2</sub>-rich liquid generally assumed in ambient pressure thermodynamic analysis. It is shown subsequently that the difference in critical point predictions resulting from the different averages is small in comparison to the differences among the model variants.



**Figure 3.** Isobaric Si-O phase diagrams at elevated pressure predicted by the HSC- and SiO(I)-vWRK parameterizations. Phase relations predicted by the CSRK are similar but shifted to lower temperature. The vaporous geometry is defined by the SiO-rich azeotrope that forms as a consequence of the stability of molecular SiO in the vapor at  $X_0 \sim 0.5$  and the SiO<sub>2</sub>-rich negative azeotrope at  $X_0 \sim 0.3$ . (a, b, d, and e) At 10–100 MPa, the vaporous is continuous from Si to compositions at which, formally, supercritical O-rich fluids (F<sub>4</sub>) are stable. The SiO<sub>2</sub>-rich negative azeotrope (L<sub>2</sub> = V) lies to the Si-rich side of the SiO<sub>2</sub> composition. The SiO(I) parameterization predicts stability of an SiO-rich liquid (L<sub>2</sub>). At 10 MPa (Figure 3d) the invariant reactions involving this liquid, with increasing temperature, L<sub>1</sub> + L<sub>2</sub> = L<sub>1</sub>' (O-rich Si-liquid), L<sub>2</sub> + L<sub>3</sub> = V and L<sub>2</sub> = L<sub>1</sub> + V, the L<sub>1</sub> + L<sub>1</sub>' and L<sub>1</sub>' + L<sub>2</sub> fields at ~3100–3200 K are not labeled, and at 100 MPa (Figure 3e) the reactions are L<sub>2</sub> = V and L<sub>2</sub> = L<sub>1</sub> + V. The critical point for the SiO<sub>2</sub>-rich azeotropic boiling curve occurs at pressures between 100 MPa (Figures 3b and 3d) and (c and f) 1 GPa (Table 3). The Shornikov and Low-c parameterization phase relations are similar to the HSC result.

#### 4.3. The SiO<sub>2</sub>-Rich Azeotropic Boiling Curve

None of the predicted SiO<sub>2</sub>-rich azeotropic boiling curves (Figure 5) is displaced by more than a few hundred kelvin from the boiling curve estimated by Schick [1960], which was computed by neglecting the liquid heat capacity and volume and assuming a vapor composed entirely of SiO and O<sub>2</sub> molecules. The success of the Shick's extrapolation reflects the minor influence of heat capacity at high temperature, that silica vapor is essentially diatomic and ideal (Figures 6a and 6c), and that to within 1000 K of the critical temperature the deviation in the composition of the azeotropic liquid from  $SiO_2$  is insignificant (Figure 5b). Taking the HSC results for reference, the Shornikov and SiO(I) parameterizations favor liquid stability, whereas the Low-c parameterization reduces liquid stability. While an effect that destabilizes the liquid, as in the Low-c parameterization, must lower the critical pressure; effects that stabilize the liquid may either raise or lower the critical pressure. Thus, the SiO(I) parameterization, which increases liquid impurity, increases the volatility of the liquid and lowers the critical pressure, whereas the Shornikov parameterization stabilizes SiO<sub>2</sub> relative to SiO and raises the critical pressure. Among the effects considered, the lowest critical p-T coordinate and maximum deviation from stoichiometric boiling are obtained by combining the effects represented by the Low-c and SiO(I) parameterizations (SiO(I) + Low-c in Figures 5 and 4). Although not explicitly evaluated, the effect of adopting an anomalously high  $SiO_2(I)$  heat capacity of 5nR, comparable to the values reported from molecular dynamic simulations [Karki et al., 2007], on the boiling curve trajectory is illustrated by the ideal-gas + high-c model (Figure 5a). As high SiO<sub>2</sub>(I) heat capacity would stabilize the liquid by reducing its volatility, such an effect favors high critical pressure and would likely lead to critical temperatures in excess of 6000 K.

## **AGU** Journal of Geophysical Research: Planets





That the CSRK EoS predicts lower critical *p*-*T* coordinates than the vWRK is consistent with the Rb and Hg systematics, which indicate predicted critical pressure correlates with the melting point bulk modulus of the liquid. Other factors being equal, as in the HSC parameterization, the CSRK predicts a slightly greater Clapeyron slope because it predicts larger liquid expansivities than the vWRK. This difference in expansivity accounts for the notably lower densities predicted by the CSRK along the liquid limb of the azeotropic  $\rho$ -*T* boiling envelope (Figure 4b). With the exception of the Shornikov parameterization, the displacements of the boiling point intercepts of the liquid limb of the azeotropic *s*-*T* boiling envelopes (Figure 4a) reflect vicissitudes of the parameterizations. Most prominently, in the Low-*c* vWRK parameterization, the SiO<sub>2</sub>(I) heat capacity drops beneath the Dulong-Petit limit at temperatures below the boiling point, whereas in the

**AGU** Journal of Geophysical Research: Planets



**Figure 5.** The (a) SiO<sub>2</sub>-rich azeotropic boiling curves and corresponding (b) fluid speciation predicted by various vW parameterizations. The small filled circles indicate the vWRK critical point predictions obtained by using the geometric mean mixing rule rather than the harmonic mean. Previous predictions indicated by crosses (critical and/or boiling points) and/or thin dashed curves. In Figure 5b the solid and dashed curves indicate, respectively, liquid and vapor speciation; the fine dashed line patterns near the critical temperature indicates where results have been extrapolated. The estimated boiling curve (dashed green) of *Schick* [1960], used by *Melosh* [2007] to locate the MANEOS critical point (magenta x symbol), neglects the liquid volume and speciation, the liquid is assumed to be pure SiO<sub>2</sub>, and the gas is assumed to be ideal and consist of 67 mol% SiO + 33 mol% O<sub>2</sub>. The "ideal + vWRK SiO<sub>2</sub>(I)" boiling curve is computed from the HSC parameterization, assuming a pure SiO<sub>2</sub> vWRK liquid in equilibrium with an ideal multispecies vapor. The "ideal + high *c*" boiling curve computation assumes a constant volume, high heat capacity (5*n*R) model for the liquid, and ideal (HSC) multispecies vapor. This boiling curve illustrates the effect that the anomalously high heat capacities reported by *Karki et al.* [2007] would have on the vW EoS predictions of the boiling curve trajectory.

Low-*c* CSRK parameterization the heat capacity of  $SiO_2(I)$  is actually slightly higher than that of the HSC parameterization at the boiling point. The Shornikov parameterization is distinct because it is based on different reference state Gibbs energies (Table A1).

Compared to the use of the harmonic mean to estimate  $\langle a_{ij} \rangle$  (section 3.4), the geometric mean increases the influence of subordinate species on the critical condition. Thus, for the SiO(I) parameterization, for which SiO is the dominant species at the critical condition (Figure 5b), the geometric rule decreases the volatility of the liquid shifting the critical point to higher pressure and temperature (small filled circles in Figures 4 and 5). SiO<sub>2</sub> is the dominant species at the critical condition for all other parameterizations; thus, for these models the geometric rule shifts the critical conditions to lower pressure and temperature. These effects are minor in comparison those attributable to the choice of parameterization and EoS.



**Figure 6.** (a–g) Various properties of liquid (solid curves) and vapor (dashed curves) along the SiO<sub>2</sub>-rich azeotropic boiling curves predicted by the HSC and SiO(I) vWRK parameterizations. As the liquid is nearly a binary SiO-SiO<sub>2</sub> mixture, the mole fraction of SiO in the liquid is approximately  $(1 - 2 X_{Si})/X_{Sir}$ , where  $X_{Si}$  is the bulk composition in Figure 6d.

The anomalous ambient pressure heat capacity ratio (Figure 6f) of the azeotropic liquid is likely an artifact of inaccuracy in the melting point bulk modulus predicted by the vWRK (Table 1). With increasing temperature along the boiling curve, a necessary condition for critical phenomena is that the expansivity of the liquid begins to rise rapidly while that of the vapor falls rapidly toward the critical singularity. These rapid variations in expansivity lead, in turn, to anomalous heat capacities (Figures 6e and 6f) and bulk moduli (Table 4). In a multispecies fluid, the effect of the variation in expansivity is superimposed on the effect of the convergent speciation required to produce critical phenomena. Calculations of secondorder properties in which speciation is fixed (Table 4) suggest that while speciation effects are minor at ~1000 K below the critical temperature of the SiO<sub>2</sub>-rich liquid boiling curve, the effects dominate the behavior of the system in the immediate vicinity of the critical point. Variable speciation has the consequence that the vW *a* and *b* parameters are implicit functions of volume; therefore, the mathematical constraints on  $z_c$  and  $p_c/T_c$  for pure vW liquids do not apply to azeotropic liquids. As strong variations in speciation **Table 4.** Effect of Speciation on Thermodynamic Properties Along the SiO<sub>2</sub>-Rich Azeotropic Boiling Curve for the HSC vWRK Parameterization<sup>a</sup>

р				ρ	n	Ν			К,		
MPa	X <sub>Si</sub>	State	s/[nR]	kg/m <sup>3</sup>	at/mol	g/mol	Speciation	αT	MPa	c/[3nR]	c/c <sub>v</sub>
5.012	0.3341	Ι	9.334	1960	2.999	60.07	on	0.3601	3223	1.013	1.744
							off	0.3604	3224	1.013	1.746
		v	16.56	6.151	2.015	40.36	on	1.704	4.767	2.414	1.234
							off	1.690	4.772	2.406	1.230
107.2	0.3355	I	10.13	1719	2.979	59.75	on	1.037	9624	1.319	3.761
							off	1.037	9620	1.317	3.757
		v	15.48	106.3	2.059	41.30	on	1.959	97.93	2.214	1.345
							off	1.724	100.4	2.093	1.083
741.3	0.3565	I	12.12	1256	2.707	54.90	on	16.51	621.5	21.88	6.328
							off	4.102	1506	7.752	1.553
		v	14.09	718.3	2.295	46.54	on	16.00	267.1	16.27	5.006
							off	2.835	728.1	4.239	1.357
	р МРа 5.012 107.2 741.3	p MPa         X <sub>Si</sub> 5.012         0.3341           107.2         0.3355           741.3         0.3565	p MPa         X <sub>Si</sub> State           5.012         0.3341         I           v         v           107.2         0.3355         I           v         v         v           741.3         0.3565         I           v         v         v	p MPa         X <sub>Si</sub> State         s/[nR]           5.012         0.3341         I         9.334           v         16.56           107.2         0.3355         I         10.13           v         15.48         v         15.48           741.3         0.3565         I         12.12           v         14.09         14.09	p MPa         X <sub>Si</sub> State         s/[nR] $μ g/m^3$ 5.012         0.3341         I         9.334         1960           v         16.56         6.151           107.2         0.3355         I         10.13         1719           v         15.48         106.3         106.3           741.3         0.3565         I         12.12         1256           v         14.09         718.3         1409         1409	p MPa         X <sub>Si</sub> State         s/[nR] $\rho$ kg/m <sup>3</sup> n at/mol           5.012         0.3341         I         9.334         1960         2.999           v         16.56         6.151         2.015           107.2         0.3355         I         10.13         1719         2.979           v         15.48         106.3         2.059           γ         15.48         106.3         2.059           γ         15.48         106.3         2.059           γ         15.48         106.3         2.059           γ         12.12         1256         2.707           γ         14.09         718.3         2.295	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$

<sup>a</sup>In the nonreactive ideal gas limit  $\alpha T \rightarrow 1$  and  $K \rightarrow p$ , vapor properties computed without speciation effects are close to these limits. At ~4000 K, the effect of speciation on second-order properties is insignificant; by ~6000 K speciation effects dominate these properties.  $c_V$  is the isochoric heat capacity.

are intrinsic to azeotropic critical phenomena, this behavior demonstrates that there is no reason to expect that the critical compressibility factors of real azeotropic liquids should be comparable to those observed for pure liquids.

#### 4.4. The SiO<sub>2</sub> Divariant Boiling Envelope

Azeotropic boiling of SiO<sub>2</sub>-rich liquid has the consequence that boiling in the silica system is incongruent (Figure 7). The onset of boiling corresponds to the point in an isobaric *T*-*X*<sub>O</sub> phase diagram (Figure 3) at which the most oxygen-rich SiO<sub>2</sub>-rich liquid composition falls below  $X_O = 0.6$ . As neither Si nor oxygen species have significant liquid concentrations (Figure 5b), this point is determined by SiO liquid affinity; thus, the SiO(I) parameterization results in an enlarged liquid + vapor field. Because the vaporous is only weakly temperature-dependent over a wide compositional interval about the azeotropic boiling point (Figures 2 and 3), the high-temperature limit of the liquid + vapor field lies below but is nearly coincident with the azeotropic boiling curve. This geometry has the consequence that the amount, and bulk Si-content, of the vapor rises rapidly toward the high-temperature limit of the two-phase field. However, even in the SiO(I) model, at subcritical conditions the vapor volumetric fraction only becomes comparable to the liquid fraction within 100–200 K of the high-temperature limit. Thus, given the generally large liquid-vapor density differences, from a volumetric perspective the amount of boiling that occurs at temperatures more than a few hundred kelvin below the azeotropic boiling curve is insignificant.

Although isochores and isentropes are presented only for the vWRK-HSC parameterization (Figures 7b and 7c), it can be deduced that the CSRK liquid isochores are displaced to higher temperature but parallel to the vWRK isochores because the CSRK predicts higher expansivities but comparable  $\alpha K$ , i.e.,  $(\partial p/\partial T)_v$ . In contrast, vWRK and CSRK liquid adiabats must extrapolate to similar temperatures at ambient pressure due to the caloric regularization, but because the adiabatic slope  $(\partial p/\partial T)_s = c/(v\alpha T)$ , the CSRK predicts slightly flatter liquid adiabats. As the vapor is ideal except in the vicinity of critical condition, vapor isochores predicted by the CSRK and vWRK EoS are essentially identical.

#### 5. Discussion

Thermodynamic data for Si-O vapor species can be extrapolated to extreme temperatures with confidence because spectroscopic studies confirm the molecular character of the low-temperature vapor [*Schick*, 1960; *Shornikov and Archakov*, 2002]. In contrast, the only resemblance between low-temperature silica liquid and a liquid composed of SiO<sub>2</sub> molecules is that both liquids are consistent with the Si<sup>4+</sup> oxidation state [*Mysen and Richet*, 2005]. Thus, the relevance of molecular models for Si-O fluids is open to question. Given that the ionic character of the liquid is implicit in conventional extrapolation of low-temperature data, the likely effect of introducing ionic clusters, or more polymerized molecular species, into a silica fluid model

## **AGU** Journal of Geophysical Research: Planets



**Figure 7.** Pressure-temperature phase diagram section for (a) the silica composition with corresponding (b) isochores and (c) isentropes for the HSC-vWRK parameterization. Because the temperature of the Si-O vaporous is not a strong function of composition in the vicinity of the SiO<sub>2</sub>-rich azeotrope (Figure 3) the upper temperature limit of the  $L_2 + V$  field is essentially coincident with the azeotropic boiling curve, which is superimposed on the section (thick solid curve). Thin red curves in Figure 7a outline the  $L_2 + V$  field for the SiO(I) vWRK parameterization. The spreading of the isochores over an interval of 100–200 K at the high-temperature limit of the  $L_2 + V$  field indicates conditions over which divariant boiling is mechanically significant. In Figures 7b and 7c, thin dashed curves show the MANEOS [*Melosh*, 2007] boiling curve, isentropes, and isochores for stoichiometric silica.

would be to stabilize vapor, yielding a boiling curve with higher Clapeyron slope and more moderate critical conditions than predicted here. The SAHA EoS [*losilevskiy et al.*, 2014], which accounts for both molecular species and simple ions in stoichiometric silica, indicates that at the critical condition the most abundant ionic species is 4 orders of magnitude less abundant than the least abundant molecular species. This result appears to support a molecular model.

In the context of speciation models for silica, true critical behavior is only possible if the  $SiO_2$  species is significant at the critical condition and truly congruent boiling is only possible if all other species are insignificant. Thus, models that assume diatomic critical speciation formally cannot be correct. In light of the relative volatilities of silicon and oxygen, it is unsurprising that the vW EoS predict that the boiling azeotrope of SiO<sub>2</sub>-rich fluids becomes progressively enriched in silicon with increasing temperature. This enrichment is accomplished almost entirely by the reduction of  $SiO_2$  to SiO, the molecular proxy for divalent silicon. Solubility of SiO in SiO<sub>2</sub>-rich liquid has been considered as both an implicit [Melosh, 2007; Kraus et al., 2012] and explicit [losilevskiy et al., 2014] phenomenon in recent EoS for silica. By imposing the constraint that the liquid is stoichiometric, these treatments require that the net molecular oxygen solubility is comparable to that of SiO and, implausibly, that silica boils congruently. The maximum SiO solubility is constrained by the negative observation that liquid SiO is not stable on the Si-O vaporous at ambient pressure [Schnurre et al., 2004]. Despite SiO concentrations approaching 50 mol% ( $X_{Si} \sim 0.4$ ; Figure 6d), the physical consequences of incongruent silica boiling are likely to be minor for most applications because the amount of vapor produced is volumetrically insignificant at conditions more than a few hundred kelvin below the azeotropic boiling curve. Likewise, the displacement between the azeotropic boiling curve and that predicted for the boiling of stoichiometric silica in equilibrium with an ideal multispecies gas is insignificant at low pressure and differs by only a few hundred kelvin at the critical condition.

A key assumption of the vW models is that the observed properties of the ionic liquid approximate the hightemperature properties of the molecular liquid. The uncertainty of this approximation has been evaluated with the Low-*c* parameterization, in which the heat capacity of the liquid falls to value characteristic of the molecular state [*Ottonello et al.*, 2010] at ~4200 K. The parameterization is extremal in that it neglects enthalpic effects and implies a more rapid transition from ionic to molecular liquid with decompression than is suggested by molecular dynamic simulations [*Karki et al.*, 2007] at densities ~10% higher than the upper limit relevant here. In contrast to other effects, the Low-*c* parameterization influences the Clapeyron slope of the boiling curve at lower pressure and, ultimately, displaces the curve to lower temperatures by as much 500 K compared to models that assume a near-Dulong Petit limit for the heat capacity of SiO<sub>2</sub>(l). This result suggests that the uncertainty due to the heat capacity extrapolation dwarfs the uncertainty associated with the low-temperature properties of pure silica liquid.

#### 5.1. Shock Relaxation Experiments

The s-T coordinates inferred by Kraus et al. [2012] offer the only experimental constraints on the silica boiling curve at superambient pressure. In the experiments a silica disk was shocked to a supercritical fluid, and as the sample decompressed, the temperature on the low-pressure side of the sample was recorded for 10–20 ns. Assuming that this temperature is representative of vapor-liquid equilibrium and that the decompression is isentropic, then the relatively well-constrained entropy of the shocked state defines the entropy of the boiling curve at the observed temperature. The first assumption is problematic. Kraus et al. [2012] argue that the trend of weakly rising temperature with entropy (Figure 4a) indicates that the decompression isentropes for their high entropy experiments intersected the vapor-rich side of the boiling envelope and that, due to optical effects, the temperatures recorded for these experiments place an upper bound on the critical temperature ("Kraus"; Table 3). Only the Low-c CSRK parameterizations match this constraint. The argument of Kraus et al. [2012] is based on a complex model of optical effects. Without this model the critical temperature is unconstrained and the consequence of the effects is that experiments at  $s < s_c$  place a lower bound on the temperature of the boiling envelope, while those at  $s > s_c$  provide an upper bound. If this interpretation is accepted, the SiO(I) and Low-c vW-EoS parameterizations are consistent with all the experimental constraints. While it may seem that this consistency lends credibility to the vW EoS, comparisons based only on caloric data are not sufficient to justify an EoS. Such comparisons are also tenuous because it is conceivable that in shock-relaxation experiments silica fluid supercools relative to the boiling curve [Boslough, 1988]. In this most pessimistic interpretation, the experiments provide only a lower bound on the critical temperature, i.e.,  $T_c > 4400$  K.

#### 5.2. Molecular Dynamic Simulations

Although molecular dynamic simulations have not been reported on the low-density side of the silica melting point isochore, extrapolation of high-temperature isochores [*Karki et al.*, 2007] to zero pressure should approximate the liquid densities along the silica boiling envelop [*Iosilevskiy et al.*, 2014]. The resulting densities are substantially higher than both present and previous EoS estimates (Figure 4b) but are consistent with the anomalously high heat capacities obtained from the simulations. While it is difficult to reconcile the heat capacities with low-temperature measurements (section 2.2), taken at face value the simulations imply that the EoS predictions underestimate the liquid stability and, consequently, the critical pressure-temperature conditions.

#### **5.3. Previous Predictions**

Both *Stevenson* [1987] and *Melosh* [2007] used thermodynamic extrapolations to estimate silica critical conditions (Table 3) without assuming an EoS. Stevenson's strategy was similar to the caloric regularization advocated here, and the discrepancy in his prediction and the present results is attributable to improvements in the caloric data. Melosh's estimate is the analytical consequence of assuming: a critical density of 650 kg/m<sup>3</sup>; a mean molecular weight of 40 g/mol, i.e., that the fluid is diatomic, that the critical compressibility factor  $z_c = p_c N/(\rho_c RT_c) = 0.3$ , and that the critical point occurs along the ideal boiling curve estimated by *Schick* [1960]; Figure 5a). Although the assumptions are neither consistent nor well justified for the critical fluid, the result is in good agreement with the conditions predicted here. The reason for this agreement is that the vW EoS predict an abrupt transition from pure liquid to essentially diatomic vapor; thus, assumptions based on either limiting behavior are true in close proximity to the critical condition.

Given the limited data for silica, it is not possible to identify accurate critical point predictions; however, it is possible to identify EoS predictions that are dubious because the boiling curve is inconsistent with the relatively well-constrained boiling point. This standard eliminates all predictions except those from the SAHA-EoS and MANEOS. The SAHA is calibrated on the basis of higher boiling point that is nonetheless within the uncertainty of the boiling point estimate [*Kraus et al.*, 2012]. Its boiling curve suggests that the SAHA entropies are comparable to those of the Shornikov parameterization. Thus, the SAHA prediction corresponds to a more extreme variant of the Shornikov parameterization, which was intended to illustrate uncertainties due to ambient pressure enthalpic data. As the SAHA, a derivative of the Carnahan-Starling EoS, indicates densities intermediate between the vWRK and CSRK (Figure 4b) it is seems probable based on vW pure fluid

systematics (sections 3.2,3), that if similar boiling points were assumed, then the SAHA prediction would lie between those of the vWRK and CSRK and be most closely matched by the CSvW.

Although the MANEOS has, unlike vW EoS, the desirable feature that it interpolates between theoretical limits, the intermolecular potential responsible for its prediction of critical phenomena at intermediate conditions is dependent on the interpolation shape function, which is chosen for mathematical convenience. Consequently, MANEOS critical phenomena are sensitive to a number of parameters that are not directly constrained. Melosh [2007] explored this sensitivity with Morse and Mie-like potential functions and obtained discrepant critical conditions (MANEOS-Mie and MANEOS-Morse; Table 3 and Figures 4 and 5). To arrive at his preferred parameterization (MANEOS-Mie\*), Melosh adjusted the Mie-like version to match his estimate of the critical conditions. While this result is a fit rather than a prediction, the estimate is reasonable in that it is intermediate between the unprejudiced MANEOS models and consistent with the experimental s-T shock coordinates [Kraus et al., 2012] (Figure 5a). Comparison of the isochores and isentropes predicted by the MANEOS and the HSC-vWRK parameterization for the silica system (Figures 7b and 7c) reveals few significant differences with the possible exceptions that the bulk compressibility of divariant system is evidently greater than the univariant system at pressures immediately above the boiling curve and that the MANEOS indicates more realistic compressibilities for dense supercritical fluid. The discrepancies between the vWRK and MANEOS vapor adiabats reflect simplifying assumptions of the MANEOS and an error in the boiling point vapor entropy used for its calibration. Because the MANEOS boiling point entropy for the liquid was inconsistent with their estimate, Kraus et al. [2012] adjusted six parameters of Melosh's preferred parameterization to obtain a slightly different critical point (MANEOS-Kraus\*). Although they do not detail their procedure, it is evident that they relaxed Melosh [2007] assumptions on density and compressibility factor.

The relatively flat slope of the liquid limb of the MANEOS *s*-*T* boiling envelopes reflects liquid heat capacities (4–8 *n*R; Figures 4a and 7c) that are in excess of, and inconsistent with, the heat capacity used to derive the melting point entropy assumed for calibration. The anomalous heat capacities are caused by the interpolation function required to simulate vaporization, an effect that corresponds to incipient vapor speciation in the liquid, and in the specific case of silica, to the formation of SiO. However, the SiO(I) vW parameterizations suggest that significant concentrations of SiO in ambient pressure silica liquid can only be realized if an SiO-rich liquid, for which there is no evidence [*Schnurre et al.*, 2004], is stable on the Si-O vaporous (Figure 3d). While the overestimation of the liquid heat capacity and SiO liquid affinity have no important consequence for first-order thermodynamic properties, the location of the critical point is determined by second-order properties (equation (11)). Thus, there is little reason to expect that wide-range EoS that represent speciation implicitly have intrinsic capacity for accurate critical point prediction.

#### 5.4. Planetary Context

Comparisons of hydrodynamic simulations of the giant impact scenario for the formation of the Moon suggest that the initial (~1 day) postimpact relaxation is insensitive to the choice of EoS because the process is dominated gravitational torques rather than pressure gradients [Wada et al., 2006; Canup et al., 2013]. Consequently in the giant impact context the primary importance of an EoS is in predicting the state of the postimpact debris disk. Recent impact models [Cuk and Stewart, 2012; Canup, 2012; Reufer et al., 2012] show that the present-day angular momentum of the Earth-Moon system does not preclude high-energy collisions that result in postimpact temperatures far in excess of the estimated silica critical temperature (Table 3). Thus, it appears reasonable to admit the possibility that the postimpact Earth and its debris disk were supercritical for a substantial period of time (10-100 years). Under such conditions the absence of a distinct atmosphere would presumably reduce chemical fractionation by atmospheric blow-off [Chen and Ahrens, 1997]. The consequences for disk dynamics are uncertain. Wada et al. [2006] suggest that a supercritical gaseous disk would be unstable and quickly (~5 day) rain down on the proto-Earth, a suggestion that would again substantially restrict the energy of Moon-forming impact scenarios. The results of Wada et al. [2006] have been questioned [Nakajima and Stevenson, 2014; Canup et al., 2013]. In part, this criticism has been based on the use of the Tillotson EoS by Wada et al. [2006], but the present results provide no grounds to question the applicability of polytropic EoS to the supercritical gaseous state. If it emerges that supercritical gaseous disk may persist on the appropriate time scale, then it is tempting to postulate that mass transfer between the supercritical proto-Earth and its disk explains the isotopic similarity of the Earth-Moon system [Stevenson, 1987]. Two objections to this postulate are that mass transfer on the requisite scale is physically implausible [*Melosh*, 2014] and that chemical fractionation during condensation of lunar material from the gaseous disk would invert the problems discovered by *Pahlevan et al.* [2011]; i.e., the Moon would likely be depleted in silica and oxidized iron and show unacceptable isotopic differences relative to the Earth's mantle.

Given the uncertainties of impact models, differences in the state of a silica protoplanetary disk [e.g., Reufer et al., 2012] as predicted by the MANEOS or vW EoS are unlikely to be significant. However, most giant impact simulations [e.g., Canup et al., 2013; Nakajima and Stevenson, 2014] use a parameterization of the MANEOS for Mg<sub>2</sub>SiO<sub>4</sub> that has not been discussed in the literature. The Mg<sub>2</sub>SiO<sub>4</sub> MANEOS (as reported in Nakajima and Stevenson [2014]) predicts a critical point at comparable entropy (~5300 J/K-kg), but much higher temperature (~8800 K) than estimated for silica. Since postimpact relaxation is approximately isentropic [Ahrens and O'Keefe, 1972], the similar critical entropy has the consequence that the amount of vapor predicted by either parameterization will be comparable for a given isentrope, but an Mg<sub>2</sub>SiO<sub>4</sub> model disk will be significantly hotter than a silica disk. High temperatures accelerate heat transfer and thermally activated processes and reduce chemical fractionation during the subsequent evolution of the disk and, because the gas phase species dissociate, lower the molecular weight of the gas and, thereby, reduce the disk surface density [Thompson and Stevenson, 1988]. Thus, if real, the difference in critical temperatures between silica and Mg<sub>2</sub>SiO<sub>4</sub> may have significant consequences for models of disk evolution. There is even less data for Mg<sub>2</sub>SiO<sub>4</sub> than silica, but a reason to question the high Mg<sub>2</sub>SiO<sub>4</sub> critical temperature is that in an empirical potential molecular dynamic study of silicate liquids over a wide compositional range, including Mg-rich olivine, critical behavior was reported at 5000-5500 K [Guillot and Sator, 2007]. Additionally, it is to be expected that ambient pressure calorimetric extrapolation of the properties of the low-temperature liquid to the critical temperature yields an entropy that is less than critical entropy. This expectation is borne out in the case of silica, where calorimetric extrapolation of the liquid properties yields an entropy of ~4400 J/K-kg at 5500 K [Holland and Powell, 2011; Ghiorso et al., 2002]. However, in the case of Mg<sub>2</sub>SiO<sub>4</sub>, the entropy of the metastable dense liquid is ~6200 J/K-kg at 8800 K, well above the MANEOS critical entropy.

Although it is not widely acknowledged that silica boils incongruently (Figures 3 and 7a), the importance of incongruent boiling in more complex silicate liquids is well established from petrological models of the silicate atmospheres that develop above magma oceans. Typically, in these models each element exists in the liquid with only one oxidation state; thus, boiling of a simple oxide such as silica is constrained to be congruent and the models cannot predict the metal enrichment by zeotropic boiling illustrated here (Figure 6b). The Si-O system may be unusual in this regard because metal enrichment is effected by the stability of an intermediate oxide (SiO). No such oxide exists for MgO, and in the case of FeO the stability of Fe<sub>2</sub>O<sub>3</sub> may even favor the formation of oxygen-rich azeotropes. The high temperatures required to achieve significant metal concentrations in SiO<sub>2</sub>-rich liquids may mitigate the importance of metal enrichment by zeotropic boiling in planetary processes.

#### 6. Concluding Remarks

Calorically regularized vW EoS parameterized from melting point properties provide plausible representations of Si-O vaporous phase relations and critical phenomena along the azeotropic boiling curve of SiO<sub>2</sub>-rich liquid. Given the paucity of high-temperature data, it would be disingenuous to discriminate among the various predictions obtained here and in other recent efforts. However, the tests made on Rb and Hg fluids show that vW EoS are surprisingly accurate. The value of the vW formulation is that it provides a practical framework for assessing effects that are ad hoc in wide-range EoS formulations and this is accomplished with far fewer free parameters than current formulations that neglect compositional degrees of freedom.

The present work is unique among treatments of silica in that it accounts for incongruent boiling. Although it emerges that this effect is unlikely to have profound consequences for astrophysical modeling, its incorporation is important because it adds to the available calibration constraints and, thereby, to the reliability of the result. Specifically, the negative observation that SiO is not stable as a liquid constraints the abundance of divalent silicon in silica liquid, this constraint is obscured if boiling is assumed to be congruent. This work has also explored the uncertainty in critical conditions associated with the choice of specific forms of vW EoS, the heat capacity model for the liquid used for regularization, and the reference state enthalpies. The choice of EoS is the greatest source of uncertainty. Based on the, albeit brief, analysis of the behavior of pure

**Table A1.** Reference State (298.15 K, 0.1 MPa) Gibbs Energies, Third-Law Entropies, and Isobaric Heat Capacity Functions for Rb, Hg, and Si-O Gas Species<sup>a</sup>

	g <sup>0</sup> (J/mol)	s <sup>0</sup> (J/mol-K)	c (J/mol-K)
Hg(l)	-22,667	76.02	$f_1^{b}$
Hg(g)	9,213	174.97	20.77
Rb(I)	-22,812	82.22	$f_2^{b}$
Rb(g)	30,221	169.98	20.79
SiO <sub>2</sub> (g) (1, 3, 4)	-390,292	228.72	$f_3^{b}$
SiO <sub>2</sub> (g) (2)	-378,938	u	"
SiO(g) (1, 3, 4)	-166,014	211.60	$f_4^{b}$
SiO(g) (2)	-163,668	u	".
Si(g)	405,554	167.98	$f_{5}^{b}$
O <sub>2</sub> (g)	-61,165	205.15	$f_{6}^{b}$
O(g)	201,154	161.06	$f_7^{b}$

<sup>a</sup>Data for Hg from HSC data-base, except that the gas heat capacity is taken to be constant and the liquid heat capacity is fit to single function over the temperature interval of 234–2000 K. Data for Rb from *Alcock et al.* [1994] with the heat capacity function modified to avoid unreasonable extrapolation. Data for Si-O gas species from the HSC database [*Roine*, 2011], the properties are similar to the values summarized by *Schnurre et al.* [2004] and *Chase* [1998]. Two variants are listed for SiO<sub>2</sub> and SiO. Variant (1) is the unmodified HSC data. Variant (2) is based on the experimentally constrained enthalpies of *Shornikov and Archakov* [2002]; these differ significantly from the HSC values. In Variant (2), the HSC entropies were not modified because within experimental uncertainty, the *Shornikov and Archakov* [2002] entropies do not differ from the HSC values.

 ${}^{b}f_{i} = a_{0} + a_{1}T + a_{2}/T^{2} + a_{3}T^{2} + a_{4}T^{3} + a_{5}T^{4}$ ; when no value for a coefficient is specified the coefficient is zero; for i = 1,  $\{a_0 = 31.61420,$  $a_1 = 19.20722 \cdot 10^{-3}$  $a_3 = 27.16711 \cdot 10^{-6}$ ,  $a_4 = -14.01547 \cdot 10^{-9}$  $a_1 = 19.20722 \cdot 10^{-3}$ ,  $a_3 = 27.16711 \cdot 10^{-6}$ ,  $a_4 = -14.01547 \cdot 10^{-7}$ ,  $a_5 = 2.604180 \cdot 10^{-12}$ , T = 234-2000 K}; for i = 2,  $\{a_0 = 34.42277$ ,  $a_1 = -7.114854 \cdot 10^{-3}$ ,  $a_3 = 3.076733 \cdot 10^{-6}$ , T = 298-2000 K}; for i = 3,  $\{a_0 = 27.28805, a_1 = 71.29955 \cdot 10^{-3}, a_2 = -25104, a_3 = -47.78965 \cdot 10^{-6}$ , T = 298-400 K;  $a_0 = 43.14959$ ,  $a_1 = 26.20858 \cdot 10^{-3}$ ,  $a_2 = -636805$ ,  $a_3 = -10.35122 \cdot 10^{-6}$ , T = 400-1100 K;  $a_0 = 62.321$ ,  $a_2 = -4147181$ , T =1100–8000 K}, for i = 4, { $a_0 = 23.80206$ ,  $a_1 = 21.78592 \cdot 10^{-3}$ ,  $a_2 = 43740$ ,  $a_3 = -10.07503 \cdot 10^{-6}$ , T = 298-800 K;  $a_0 = 37.02928$ ,  $a_1 = 0.29472 \cdot 10^{-3}$ ,  $a_2 = -1550846, \quad a_3 = 1.456 \cdot 10^{-8}, \quad T = 800 - 4100 \text{ K}; \quad a_0 = 73.41891, \\ a_1 = -11.88528 \cdot 10^{-3}, \quad a_2 = -101.467.529, \quad a_3 = 1.1742 \cdot 10^{-6}, \quad T = 100.467.529, \quad a_3 = 100.567.529, \quad a_3 = 100.57.529, \quad$ 4100–6000 K;  $a_0 = 41.55976$ , T = 6000-8000 K; for i = 5,  $\{a_0 = 21.04075, a_0 = 20.04075, a_0 = 21.04075, a_0 = 21.040$  $a_1 = -0.75852 \cdot 10^{-3}, a_2 = 123608, a_3 = 5.8354 \cdot 10^{-7}, T = 298 - 2000$  K;  $a_0 = 22.56649, a_1 = 4.8505 \cdot 10^{-4}, a_2 = -5524340, a_3 = -6.694 \cdot 10^{-8}, T = 2000-5500 \text{ K}; a_0 = 33.13343, a_1 = -2.5732 \cdot 10^{-3}, a_2 = -42235756, a_3 = 1.7995 \cdot 10^{-7}, T = 5500-8000 \text{ K}; \text{ for } I = 6.$  $a_3 = 1.7995 \cdot 10^{-7}$ , T = 5500 - 8000 K; for l = 6,  $\{a_0 = 22.05955, a_1 = 20.88672 \cdot 10^{-3}, a_2 = 162056, a_3 = -8.20733 \cdot 10^{-6}, T = 298 - 700$  K;  $a_0 = 29.79298, a_1 = 7.91038 \cdot 10^{-3}, a_2 = -619384, a_3 = -2.2036 \cdot 10^{-6}$ , T = 700 - 1200 K;  $a_0 = 34.85945,$   $a_1 = 1.31218 \cdot 10^{-3},$   $a_2 = -1,414,037,$  $a_3 = 1.6256 \cdot 10^{-7}$ , T = 1200 - 2500 K;  $a_0 = 32.69336$ ,  $a_1 = 3.13735 \cdot 10^{-3}$ ,  $a_2 = -1730230$ ,  $a_3 = -2.1417 \cdot 10^{-7}$ , T = 2500 - 4500 K;  $a_0 = 18.48998$ ,  $a_1 = 6.56662 \cdot 10^{-3}$ ,  $a_2 = 65,405,977$ ,  $a_3 = -4.38 \cdot 10^{-7}$ , T = 4500, 8000 K  $a_{1} = 6.56662 \cdot 10^{-3}, a_{2} = 65,405,977, a_{3} = -4.38 \cdot 10^{-7}, T = 4500-8000 \text{ K};$ for i = 7, { $a_{0} = 21.16715, a_{1} = -6.2024 \cdot 10^{-4}, a_{2} = 78643, a_{3} = 2.531 \cdot 10^{-7}, T = 298-1500 \text{ K}; a_{0} = 20.07968, a_{1} = 1.3599 \cdot 10^{-4}, a_{2} = 1,089,287, a_{3} = 3.825 \cdot 10^{-8}, T = 1500-6000 \text{ K}; a_{0} = 24.85874, a_{1} = -9.62 \cdot 10^{-5}, a_{2} = -72,290,558, a_{7} = -7.7 \cdot 10^{-10}, T = 6000-8000 \text{ K}$ }.

metals, it is anticipated that the vWRK and CSRK EoS, respectively, overestimate and underestimate the critical temperature leading to an uncertainty of ±250 K. In combination, enthalpic and caloric effects roughly double this uncertainty. A curious feature of vW EoS predictions is that while critical density is ~30% of boiling point liquid density, as typical of pure liquids, the critical compressibility factor is much larger in the azeotropic case. The chief limitation of vW EoS is that parameterizations based on melting point properties overestimate the stiffness of the liquid. Consequently, the resulting parameterization has poor accuracy at pressure-temperature conditions on the high-pressure side of the melting point isochore.

The application to the Si-O system here leads to two results that are likely robust. The first is that at superambient pressure silica boils incongruently, with the consequence that the residual liquid is depleted in oxygen. The second is that the *p*-*T* trajectory of the azeotropic boiling curve for SiO<sub>2</sub>-rich liquid does not deviate significantly from that predicted for the equilibrium of pure silica liquid and a multispecies ideal vapor; thus, excepting critical behavior, conventional petrological models [Fealey and Cameron, 1987; Ghiorso, 2004; Green et al., 2012; Visscher and Fegley, 2013] are adequate to predict boiling curve trajectories and vapor speciation. The vW framework can easily be extended to incorporate volatile elements such as C, S, and H because thermodynamic data are available for the relevant species. Evidence that Mg<sub>2</sub>SiO<sub>4</sub> boils azeotropically [Nagahara et al., 1994] suggests that treating refrac-

tory elements such as Mg, Fe, and Al would be more complicated because it entails estimating the properties of polymerized gas species, e.g., Mg<sub>2</sub>SiO<sub>4</sub>.

An accidental consequence of this work has been to draw attention to the importance of the continuous transition between low-temperature ionic silicate liquids and high-temperature molecular gases. The key to understanding this transition is likely to lie in the liquid structure at conditions intermediate between the melting point isochore and boiling curve.

	T <sub>m</sub>	g <sub>m</sub> (J/mol)	s <sub>m</sub> (J/mol-K)	v <sub>m</sub> (J/mol-MPa)	c <sub>m</sub> (J/mol-K)
SiO <sub>2</sub> (I) Schnurre et al. [2004]	1999		173.28 174.02	27.30 ± 0.63	82.12 <sup>b</sup> 79.01 <sup>c</sup>
Hudon et al. [2012] Hudon et al. [2002]		-1,126,826	172.17 ± 3.9 173.11 173.28	27.58	83.25 ± 4.1 85.77 82.50
Ghiorso et al. [2002] Ghiorso [2004]		-1,127,095	184.15	27.30 26.70 27.19	82.6
Si(I)	1,687	-68,583	91.92	$10.92 \pm 0.34$	27.20

Table A2. Melting Point Molar Gibbs Energies, Third-Law Entropies, Volumes, and Heat Capacities for SiO<sub>2</sub>(I) and Si(I)<sup>a</sup>

<sup>a</sup>Additional estimates for SiO<sub>2</sub>(I) properties at 1999 K illustrate uncertainty.

<sup>b</sup>The  $a_{SiO2}$  functions for Variants (1–3) given in Table 1 were computed with  $c(J/mol-K) = c_2(c_0 + c_1T)/(c_0 + c_1T + c_3)$ , where  $c_0 = -251,807$ ,  $c_1 = 942.971$ ,  $c_2 = 83.5100$ , and  $c_3 = 27,579.3$ . For Variant (4), at T > 1999 K, this heat capacity function was replaced by the sigmoid function  $c = c_m - (c_m - c_{molecular})(1 + \tau/(1 + \tau^2)^{1/2})/2$  with  $\tau = 9(T - T_m)/3000 - 6$  chosen so that the *c* falls from 99% of  $c_m$  at 3000 K to 99% of the assumed molecular heat capacity ( $c_{molecular} = 45.4$  J/mol-K [Ottonello et al., 2010]) at 5000 K.

<sup>C</sup>Kraus et al. [2012] and Schnurre et al. [2004] use functions that increase weakly with temperature.

#### **Appendix A: Thermodynamic Data**

Thermodynamic data for gaseous species and SiO<sub>2</sub>(I) and Si(I) are summarized in Tables A1 and A2. For SiO<sub>2</sub>(I) liquid, the melting point Gibbs energy was equated to Gibbs energy of cristobalite as given by *Holland and Powell* [2011], its entropy and volume are likewise from *Holland and Powell* [2011], and its heat capacity function was fit to values given by *Richet and Bottinga* [1984] at 300 (44.25 J/mol-K) and 1600 K (81.37 J/mol-K), *Lange and Navrotsky* [1992] at 1999 K (82.6 J/mol-K) and an assumed value of 10R at 5000 K. The resulting volume and entropy of fusion, 4.58 J/K-mol and -0.15 J/MPa-mol, are essentially identical to those recommended by *Mysen and Richet* [2005] and yield a Clapeyron slope of -0.033 K/MPa. For comparison, recent assessments [*Hudon et al.*, 2002; *Ghiorso*, 2004; *Schnurre et al.*, 2004; *Mysen and Richet*, 2005] locate the melting point within 10 K of 1999 K; give ranges on the entropy and volume of cristobalite at the melting point of 168.31–168.89 J/K mol and 27.450–27.448 J/MPa mol, a range of 4.04-5.12 J/K mol for the entropy of fusion; and Clapeyron slopes for the melting reaction in the range of -0.146 to -0.022 K/MPa. The only direct observation of cristobalite melting indicates a Clapeyron slope of  $\pm 0.1$  K/MPa [*Jackson*, 1976]. From the ranges in Clapeyron slope and entropy of fusion, the uncertainty in the liquid volume at the melting point is  $\pm 0.63$  J/MPa mol.

#### Acknowledgments

This work was supported by Swiss National Science Foundation grant 200021\_146872; its presentation benefited from informal reviews and/or discussions with George Helffrich, Eleanor Green, Igor Iosilevskiy, and Bruce Fegley, and four anonymous formal reviews. All data may be found in the text, appendix, and tables.

#### References

Ahrens, T. J., and J. D. O'Keefe (1972), Shock melting and vaporization of lunar rocks and minerals, *Earth Moon Planets*, *4*, 214–249.

- Alatas, A., A. H. Said, H. Sinn, E. E. Alp, C. N. Kodituwakku, B. Reinhart, M.-L. Saboungi, and D. L. Price (2005), Elastic modulus of supercooled liquid and hot solid silicon measured by inelastic X-ray scattering, J. Phys. Chem. Solids, 66, 2230–2234.
- Alcock, C. B., M. W. Chase, and V. P. Itkin (1994), Thermodynamic properties of the group IA elements, J. Phys. Chem. Ref. Data, 23, 385–497.
- Alexander, C. (2002), Application of melts to kinetic evaporation models of feo-bearing silicate melts, *Meteorit. Planet. Sci.*, 37, 245–256. Ayrinhac, S., M. Gauthier, L. E. Bove, M. Morand, G. Le Marchand, F. Bergame, J. Philippe, and F. Decremps (2014), Equation of state of liquid

mercury to 520 K and 7 GPa from acoustic velocity measurements, J. Chem. Phys., 140, 244, 201–1.

Benz, W., W. L. Slattery, and A. G. W. Cameron (1986), The origin of the Moon and the single-impact hypothesis. 1, *Icarus*, 66, 515–535.
Bobrovskii, S. V., V. M. Gogolev, B. V. Zamyshlyaev, and V. P. Lozhkina (1974), Spalling rate in a solid medium subjected to a strong shock-wave, *Combust. Explos. Shock Waves*, 10, 799–805.

Boslough, M. B. (1988), Postshock temperatures in silica, J. Geophys. Res., 93, 6477-6484, doi:10.1029/JB093iB06p06477.

Canup, R. M. (2012), Forming a Moon with an Earth-like composition via a giant impact, *Science*, 338, 1052–1055, doi:10.1126/ science.1226073.

Canup, R. M., A. C. Barr, and D. A. Crawford (2013), Lunar-forming impacts: High-resolution SPH and AMR-CTH simulations, *lcarus*, 222(1), 200–219, doi:10.1016/j.icarus.2012.10.011.

Chase, M. W. (1998), NIST-JANAF thermochemical tables, J. Phys. Chem. Ref. Data Monogr., 9, 1951.

Chen, G. Q., and T. J. Ahrens (1997), Erosion of terrestrial planet atmosphere by surface motion after a large impact, *Phys. Earth Planet. In.*, 100, 21–26, doi:10.1016/s0031-9201(96)03228-1.

Connolly, J. A. D. (2009), The geodynamic equation of state: What and how, *Geochem. Geophys. Geosyst.*, 10, Q10014, doi:10.1029/2009GC002540.

Cuk, M., and S. T. Stewart (2012), Making the Moon from a fast-spinning Earth: A giant impact followed by resonant despinning, *Science*, 338, 1047–1052, doi:10.1126/science.1225542.

de Koker, N., and L. Stixrude (2009), Self-consistent thermodynamic description of silicate liquids, with application to shock melting of MgO periclase and MgSiO<sub>3</sub> perovskite, *Geophys, J. Int., 178*, 162–179.

de Santis, R., G. J. F. Breedveld, and J. M. Prausnitz (1974), Thermodynamic properties of aqueous gas-mixtures at advanced pressures, Ind. Eng. Chem. Process Des. Dev., 13, 374–377.

Deb, S. K., M. Wilding, M. Somayazulu, and P. F. McMillan (2001), Pressure-induced amorphization and an amorphous-amorphous transition in densified porous silicon, *Nature*, 414, 528–530.

Desai, P. D. (1986), Thermodynamic properties of iron and silicon, J. Phys. Chem. Ref. Data, 15, 967-983.

Desantis, R., F. Gironi, and L. Marrelli (1976), Vapor-liquid-equilibrium from a hard-sphere equation of state, Ind. Eng. Chem. Fund., 15, 183–189.

Dillon, I. G., P. A. Nelson, and B. S. Swanson (1966), Measurement of densities and estimation of critical properties of alkali metals, J. Chem. Phys., 44, 4229.

Fedkin, A. V., L. Grossman, and M. S. Ghiorso (2006), Vapor pressures and evaporation coefficients for melts of ferromagnesian chondrule-like compositions, *Geochim. Cosmochim. Acta*, 70, 206–223.

Fegley, B., and A. G. W. Cameron (1987), A vaporization model for iron silicate fractionation in the mercury protoplanet, *Earth Planet. Sci. Lett.*, 82, 207–222.

Ferguson, F. T., and J. A. Nuth (2012), Vapor pressure and evaporation coefficient of silicon monoxide over a mixture of silicon and silica, J. Chem. Eng. Data, 57, 721–728.

Genda, H., and Y. Abe (2003), Modification of a proto-lunar disk by hydrodynamic escape of silicate vapor, *Earth Planets Space*, 55, 53–57. Ghiorso, M. S. (2004), An equation of state for silicate melts. I. Formulation of a general model, *Am. J. Sci.*, 304, 637–678.

Ghiorso, M. S., M. M. Hirschmann, P. W. Reiners, and V. C. Kress (2002), The pmelts: A revision of melts for improved calculation of phase relations and major element partitioning related to partial melting of the mantle to 3 GPa, *Geochem. Geophys. Geosyst.*, 3, 1–35, doi:10.1029/2001GC000217.

Green, E. C. R., T. J. B. Holland, and R. Powell (2012), A thermodynamic model for silicate melt in CaO-MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> to 50 kbar and 1800°C, J. Metamorph. Geol., 30, 579–597.

Guillot, B., and N. Sator (2007), A computer simulation study of natural silicate melts. Part I: Low pressure properties, *Geochim. Cosmochim.* Acta, 71, 1249–1265, doi:10.1016/J.Gca.2006.11.015.

Helffrich, G. R. (2015), The hard sphere view of the outer core, Earth Planets Space, 67, doi:10.1186/s40623-015-0238-7.

Hicks, D. G., T. R. Boehly, P. M. Celliers, J. H. Eggert, E. Vianello, D. D. Meyerhofer, and G. W. Collins (2005), Shock compression of quartz in the high-pressure fluid regime, *Phys. Plasmas*, *12*, 082702.

Hicks, D. G., T. R. Boehly, J. H. Eggert, J. E. Miller, P. M. Celliers, and G. W. Collins (2006), Dissociation of liquid silica at high pressures and temperatures, *Phys. Rev. Lett.*, 97, 025502.

Holland, T. J. B., and R. Powell (2011), An improved and extended internally consistent thermodynamic dataset for phases of petrological interest, involving a new equation of state for solids, J. Metamorph. Geol., 29, 333–383.

Holloway, J. R. (1977), Fugacity and activity of molecular species in supercritical fluids, in *Thermodynamics in Geology*, edited by D. G. Frazer, pp. 161–181, Springer, Berlin.

Hosokawa, S., W. C. Pilgrim, Y. Kawakita, K. Ohshima, S. Takeda, D. Ishikawa, S. Tsutsui, Y. Tanaka, and A. Q. R. Baron (2003), Sub-picosecond dynamics in liquid Si, J. Phys.-Condens. Mat., 15, L623–L629.

Huber, M. L., A. Laesecke, and D. G. Friend (2006), Correlation for the vapor pressure of mercury, Ind. Eng. Chem. Res., 45, 7351–7361.

Hudon, P., I. H. Jung, and D. R. Baker (2002), Melting of beta-quartz up to 2.0 GPa and thermodynamic optimization of the silica liquidus up to 6.0 GPa, *Phys. Earth Planet. Int.*, 130, 159–174.

losilevski, I., G. J. Hyland, C. Ronchi, and E. Yakub (2001), Equation of state of UO<sub>2</sub>, Int. J. Thermophys., 22, 1253–1264.

losilevskiy, I., V. Gryaznov, and A. Solovev (2014), Properties of high-temperature phase diagram and critical point parameters in silica, High Temp.-High Press., 43, 227–241.

Jackson, I. (1976), Melting of silica isotypes SiO2, BeF2 and GeO2 at elevated pressures, Phys. Earth Planet. Inter., 13, 218–231, doi:10.1016/0031-9201(76)90096-0.

Jarzynski, J., J. R. Smirnow, and C. M. Davis (1969), Isothermal compressibility and structure factor of liquid alkali metals, *Phys. Rev.*, 178, –288.

Kalampounias, A. G., S. N. Yannopoulos, and G. N. Papatheodorou (2006), Temperature-induced structural changes in glassy, supercooled, and molten silica from 77 to 2150 K, J. Chem. Phys., 124, 014504.

Karki, B. B., D. Bhattarai, and L. Stixrude (2007), First-principles simulations of liquid silica: Structural and dynamical behavior at high pressure, *Phys. Rev. B*, *76*, 104205.

Kaye, G. W. C., and T. H. Laby (1995), *Tables of Physical and Chemical Constants*/originally compiled by G. W. C. Kaye and T. H. Laby; now prepared under the direction of an editorial committee, 611 pp., Longman, New York.

Kerrick, D. M., and G. K. Jacobs (1981), A modified Redlich-Kwong equation for H<sub>2</sub>O, CO<sub>2</sub>, and H<sub>2</sub>O-CO<sub>2</sub> mixtures at elevated pressures and temperatures, Am. J. Sci., 281, 735–767.

Kikoin, I. K., and A. Senchenk (1967), Electrical conductivity and equation of state of mercury in temperature range 0–2000°C and pressure range of 200–5000 atm, *Phys. Met. Metallogr.-Ussr*, 24, 74.

Kormer, S. B., A. I. Funtikov, V. D. Urlin, and A. N. Kolesnikova (1962), Dynamic compression of porous metals and the equation of state with variable specific heat at high temperatures, Sov. Phys. Jetp-Ussr, 15, 477–488.

Kozhevnikov, V., D. Arnold, E. Grodzinskii, and S. Naurzakov (1996), Phase transitions and critical phenomena in mercury fluid probed by sound, *Fluid Phase Equilib.*, 125, 149–157.

Kraus, R. G., et al. (2012), Shock vaporization of silica and the thermodynamics of planetary impact events, J. Geophys. Res., 117, E09009, doi:10.1029/2012JE004082.

Lange, R. A., and A. Navrotsky (1992), Heat capacities of Fe<sub>2</sub>O<sub>3</sub>-bearing silicate liquids, Contrib. Mineral. Petrol., 110, 311–320.

Machida, R., and Y. Abe (2004), The evolution of an impact-generated partially vaporized circumplanetary disk, *Astrophys. J., 617*, 633–644. McMillan, P. F. (2004), Polyamorphic transformations in liquids and glasses, *J. Mater. Chem., 14*, 1506–1512.

Melosh, H. J. (2007), A hydrocode equation of state for SiO<sub>2</sub>, Meteorit. Planet. Sci., 42, 2079–2098.

Melosh, H. J. (2014), New approaches to the Moon's isotopic crisis, *Phil. Trans. R. S. Math. Phys. Eng. Sci.*, 372, doi:10.1098/rsta.2013.0168. Mysen, B., and P. Richet (2005), *Silicate Glasses and Melts: Properties and Structure*, Elsevier, Amsterdam.

Mysen, B. O., and I. Kushiro (1988), Condensation, evaporation, melting, and crystallization in the primitive solar nebula—Experimental-data in the system MgO-SiO<sub>2</sub>-H<sub>2</sub> to  $1.0 \times 10^{-9}$  bar and 1870°C with variable oxygen fugacity, *Am. Mineral.*, *73*, 1–19.

Nagahara, H., I. Kushiro, and B. O. Mysen (1994), Evaporation of olivine: Low-pressure phase-relations of the olivine system and its implication for the origin of chondritic components in the solar nebula, *Geochim. Cosmochim. Acta*, 58, 1951–1963.

Nakajima, M., and D. J. Stevenson (2014), Investigation of the initial state of the Moon-forming disk: Bridging SPH simulations and hydrostatic models, *Icarus*, 233, 259–267, doi:10.1016/j.icarus.2014.01.008.

Nichols, R. H., R. T. Grimley, and G. J. Wasserburg (1998), Measurement of gas-phase species during Langmuir evaporation of forsterite, *Meteorit. Planet. Sci.*, 33(4), A115–A116.

Niu, H., A. R. Oganov, X.-Q. Chen, and D. Li (2015), Prediction of novel stable compounds in the Mg-Si-O system under exoplanet pressures, Sci. Rep., 5, doi:10.1038/srep18347.

Ottonello, G., M. V. Zuccolini, and D. Belmonte (2010), The vibrational behavior of silica clusters at the glass transition: Ab initio calculations and thermodynamic implications, *J. Chem. Phys.*, 133, 104508.

Pahlevan, K., and D. J. Stevenson (2007), Equilibration in the aftermath of the lunar-forming giant impact, *Earth Planet. Sci. Lett.*, 262, 438–449, doi:10.1016/j.epsl.2007.07.055.

Pahlevan, K., D. J. Stevenson, and J. M. Eiler (2011), Chemical fractionation in the silicate vapor atmosphere of the Earth, Earth Planet. Sci. Lett., 301, 433–443.

Pfeifer, H. P., W. Freyland, and F. Hensel (1979), Equation of state and transport data on expanded liquid rubidium up to 1700°C and 400 bar, Berichte Der Bunsen-Gesellschaft-Phys. Chem. Chem. Phys., 83, 204–211.

Porter, R. F., W. A. Chupka, and M. G. Inghram (1955), Mass spectrometric study of gaseous species in the Si-SiO<sub>2</sub> system, *J. Chem. Phys.*, 23, 216–217. Prausnitz, J. M. (1969), *Molecular Thermodynamics of Fluid-Phase Equilibria*, 523 pp., Prentice-Hall, Englewood Cliffs, N. J.

Redlich, O., and J. N. S. Kwong (1949), On the thermodynamics of solutions. 5. An equation of state. Fugacities of gaseous solutions, *Chem. Rev.*, 44, 233–244.

Reufer, A., M. M. Meier, W. Benz, and R. Wieler (2012), A hit-and-run giant impact scenario, *lcarus*, 221, 296–299.

Richet, P., and Y. Bottinga (1984), Glass transitions and thermodynamic properties of amorphous SiO<sub>2</sub>, NaAlSi<sub>n</sub>O<sub>2n + 2</sub> and KAlSi<sub>3</sub>O<sub>8</sub>, *Geochim. Acta, 48,* 453–470.

Roine, A. (2011), HSC chemistry, version 7.11, Outokumpu Research Oy, Pori, Finland.

Sato, Y., T. Nishizuka, K. Hara, T. Yamamura, and Y. Waseda (2000), Density measurement of molten silicon by a pycnometric method, Int. J. Thermophys., 21, 1463–1471.

Schaefer, L., K. Lodders, and B. Fegley (2012), Vaporization of the Earth: Application to exoplanet atmospheres, Astrophys. J., 755, 41.

Schick, H. L. (1960), A thermodynamic analysis of the high-temperature vaporization properties of silica, Chem. Rev., 60, 331–362.

Schnurre, S. M., J. Grobner, and R. Schmid-Fetzer (2004), Thermodynamics and phase stability in the Si-O system, J. Non Cryst. Solids, 336, 1–25.

Shornikov, S. I., and I. Y. Archakov (2002), A mass spectrometric determination of the enthalpies and entropies of Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> melts, *Russ. J. Phys. Chem.*, *76*, 1054–1060.

Song, Y. H., E. A. Mason, and R. M. Stratt (1989), Why does the Carnahan-Starling equation work so well, *J. Phys. Chem.*, *93*, 6916–6919. Stevenson, D. J. (1987), Origin of the Moon—The collision hypothesis, *Annu. Rev. Earth Planet. Sci.*, *15*, 271–315.

Thompson, C., and D. J. Stevenson (1988), Gravitational-instability in 2-phase disks and the origin of the Moon, *Astrophys. J.*, 333, 452–481. Tisza, L. (1961), The thermodynamics of phase equilibrium, *Ann. Phys.*, 13, 1–92.

Trave, A., P. Tangney, S. Scandolo, A. Pasquarello, and R. Car (2002), Pressure-induced structural changes in liquid SiO<sub>2</sub> from ab initio simulations, *Phys. Rev. Lett.*, *89*, 245504.

Vera, J. H., and J. M. Prausnitz (1972), Generalized van der Waals theory for dense fluids, Chem. Eng. J., 3, 1-13.

Visscher, C., and B. Fegley Jr. (2013), Chemistry of impact-generated silicate melt-vapor debris disks, Astrophys. J. Lett., 767, L12.

Wada, K., E. Kokubo, and J. Makino (2006), High-resolution simulations of a Moon-forming impact and postimpact evolution, *Astrophys. J.*, 638, 1180–1186, doi:10.1086/499032.

Ward, W. R. (2012), On the vertical structure of the protolunar disk, Astrophys. J., 744, 140–155.

Young, D. A., and B. J. Alder (1971), Critical point of metals from vanderwaals model, Phys. Rev. A, 3, 364–371.