

1 **REVISION 1**

2 **Melting curve of NaCl to 20 GPa from electrical measurements of capacitive current**

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6 **ABSTRACT**

7 Using an in situ electrical method and the multi-anvil apparatus, we determined the melting  
8 curve of sodium chloride (NaCl) up to ~20 GPa, with an estimated uncertainty of  $\pm 40$  K. Our  
9 results agree well with the existing data up to 6.5 GPa. At higher pressures, the melting  
10 temperatures from this study are as much as 200 K higher than those from an experimental study  
11 using the diamond anvil cell (DAC), and are up to 500 K lower than those from theoretical  
12 studies using molecular dynamics (MD). The discrepancies may originate from surface melting  
13 in the DAC measurements, which underestimate the melting temperature, and from superheating  
14 in MD calculations, which over-predict the melting temperature. Fitting our results to the Simon  
15 equation yield  $(T/T_0)^{4.5} = (P - P_0)/1.6 + 1$ , where  $T$  and  $T_0$  are the melting temperatures at  $P$  and  
16  $P_0$ , respectively. The Simon equation fits the experimental data within uncertainties and therefore  
17 can be used to interpolate the melting curve. Using the equation of state (EoS) of NaCl at 300 K,  
18 the results are fitted to the Kraut-Kennedy equation in the form of  $T/T_0 = (V_0 - V)/V_0 \cdot 2.52 + 1$ ,  
19 where  $T$  and  $T_0$  are the melting temperatures at  $V$  and  $V_0$ , respectively. At pressures above 14  
20 GPa, the experimental data deviate from the Kraut-Kennedy equation fit towards lower  
21 temperatures, probably because the volume dependence of the Grüneisen parameter was ignored  
22 in the equation. The Gilvarry-Lindemann equation  $T_m \sim 0.00321 \cdot M \cdot \rho^2 \cdot \Theta_0^2 \cdot (V_0/V)^2 (\gamma - 1/3)$   
23 provides a satisfactory fit to the melting curve of NaCl between 0 GPa and 19 GPa if the

24 exponent  $q$  in the volume dependence of the Grüneisen parameter  $\gamma = \gamma_0 \cdot (V/V_0)^q$  is allowed to  
25 deviate from one. Given that the melting curve of NaCl up to 6.5 GPa is well established,  
26 monitoring the melting of NaCl offers an efficient alternative for pressure calibration of large-  
27 volume high-pressure apparatus for Earth science applications.

28       Keywords: Melting curve, high pressure, capacitive current, in situ electrical method,  
29 sodium chloride, Simon equation, Kraut-Kennedy equation, Lindemann's law

30

## 31 **INTRODUCTION**

32 Melting plays a critical role in planetary differentiation and dynamics. Knowledge of the  
33 pressure-dependent melting temperatures of Earth materials is of fundamental importance for  
34 constraining the Earth's thermal structure, understanding geochemical cycles, and interpreting  
35 seismic observations (Boehler 1996). Many experimental methods have been developed to  
36 investigate melting at high pressure. As a first order phase transition, melting is characterized by  
37 the loss of long-range atomic order, which manifests as the disappearance of reflections from  
38 lattice planes and appearance of diffuse scattering signal in X-ray diffraction patterns (Anzellini  
39 et al. 2013). Melting is associated with significant changes in lattice dynamics, which lead to  
40 vanishing Lamb-Mossbauer factor (Jackson et al. 2013). The latent heat of melting gives rise to  
41 enhanced absorption of heating power (Boehler et al. 1997; Lord et al. 2010) and may be  
42 detected through differential thermal analysis (DTA) (Akella et al. 1969). Furthermore, melting  
43 results in loss of shear strength and precipitous reduction in viscosity, which can be detected  
44 through textural change (Boehler 1997, Chen et al. 2008), from the sinking of a dense sphere  
45 marker (Dobson et al. 1996), or from discontinuous change in electrical resistivity (Brand et al.  
46 2006). Measuring the melting temperatures of materials at the pressure conditions of deep Earth  
47 poses considerable technical challenges and consequently experimental data are limited and  
48 often uncertain (e.g., Anzellini et al. 2013; Boehler 1996; Shen and Lazor 1995).

49 As a simple ionic compound, sodium chloride (NaCl) has been investigated extensively in  
50 an attempt to gain insights into its melting mechanism and melt structure (e.g., Clark 1959;  
51 Boehler et al. 1997; An et al., 2006). In high-pressure research, NaCl is widely used as a thermal  
52 insulating material and pressure marker in diamond-anvil cell (DAC) experiments, and therefore  
53 knowledge of its melting curve helps to assess its applicable ranges of pressure and temperature

54 (e.g., Shen et al. 2001). Furthermore, monitoring the melting of NaCl offers an appealing  
55 alternative for pressure calibration of large-volume apparatus such as the piston-cylinder  
56 apparatus and multi-anvil press (e.g., Leinenweber et al. 2012), with several advantages  
57 including 1) melting occurs much more rapidly than solid-state phase transition; 2) melting can  
58 be readily recognized using a sinking marker such as a Pt sphere; 3) high-purity NaCl is readily  
59 available and less expensive than gold, the melting curve of which has been used for pressure  
60 calibration.

61 Earlier studies have determined the melting curve of NaCl to 6.5 GPa using the piston-  
62 cylinder apparatus and DTA method (Clark 1959; Pistorius 1966; Akella et al. 1969). The  
63 pressure coverage was subsequently extended to 100 GPa using the diamond anvil cell technique  
64 (Boehler et al. 1997). On the other hand, molecular dynamics (MD) calculations have been  
65 performed to constrain the high-pressure melting curve of NaCl (e.g., Belonoshko and  
66 Dubrovinsky 1996; Vočadlo and Price 1996; Chen et al. 2004; Cheng et al. 2003; An et al.  
67 2006). At 20 GPa the calculated melting temperatures from MD simulations exceed the  
68 measured values by as much as 25% and the discrepancies were attributed to superheating and  
69 surface melting effects (An et al. 2006; Vočadlo and Price 1996).

70 Melting of an ionic compound is accompanied by an abrupt and large increase in  
71 conductivity, when ions locked in the crystal lattice are freed and become capable of carrying  
72 charges. If an alternating voltage is applied through two electrodes and the voltage stays below  
73 the thresholds of oxidizing or reducing the ions at the electrodes, an ionic melt can support  
74 capacitive current, with ions move back and forth between the two electrodes, resembling the  
75 charging and discharging of a capacitor (Rieger 1994). At sufficiently high voltage, ionic  
76 conduction and redox reactions at the electrode would produce Faradic current instead. In this

77 study, we developed an in situ electrical method to determine the melting temperature of  
78 compressed NaCl by monitoring sudden rise in the capacitive current. We aimed to establish the  
79 melting curve of NaCl up to ~ 20 GPa using the multi-anvil apparatus and to examine if the  
80 Simon equation (Simon 1929), the Kraut-Kennedy equation (Kraut and Kennedy 1966), and the  
81 Gilvarry-Lindemann equation (Gilvarry 1956, 1966; Poirier 2000) can adequately describe the  
82 melting behavior of ionic compounds at high pressures.

### 83 **METHODS**

84 High-pressure experiments were conducted using the 1000-ton Walker-style multi-anvil  
85 apparatus at the University of Michigan. For experiments at pressures up to 10 GPa, we used  
86 Fansteel tungsten carbide cubes with 8-mm truncation edge length (TEL) and octahedron-shaped  
87 pressure medium casted from Aremco 584 old-style material (Walker 1991). For experiments at  
88 pressures up to 21 GPa, we used Toshiba-Tungaloy F-grade tungsten carbide cubes with 5-mm  
89 TEL and the COMPRES 10/5 assembly (Leinenweber et al. 2012), which was modified for the  
90 electrical measurements (Fig. 1a). The relation between the sample pressure and applied ram  
91 pressure was established using the Bi I-II, II-III and III-V transitions at room temperature  
92 (Decker et al. 1972) and the known phase boundaries at 1473 K including quartz-coesite-  
93 stishovite (Bohlen and Boettcher 1982; Zhang et al. 1996), CaGeO<sub>3</sub> garnet-perovskite (Susaki et  
94 al. 1985) and forsterite-wadsleyite- ringwoodite transitions (Katsura and Ito 1989). The sample  
95 pressure ( $P$ ) is calculated from the ram force ( $p$ ) according to the following formulae:

$$96 \quad P \text{ (GPa)} = -0.03 + 3.21 \cdot 10^{-2} \cdot p \text{ (US ton)} - 1.40 \cdot 10^{-5} \cdot p^2 \text{ for 8-mm TEL}$$

$$97 \quad P \text{ (GPa)} = 5.65 \cdot 10^{-2} \cdot p \text{ (US ton)} - 3.80 \cdot 10^{-5} \cdot p^2 \text{ for 5-mm TEL.}$$

98 The precision in pressure calibration is estimated at  $\pm 5\%$  on the basis of duplication experiments  
99 and does not include the effect of temperature, which will be discussed later.

100 High temperature was generated using cylindrical-shaped foil of rhenium, with a thickness  
101 of 0.0015 inch or 0.038 mm for 8-mm experiments and 0.0025 inch or 0.064 mm for 5-mm  
102 experiments. A standard type-C thermocouple (W26%Re and W5%Re, 0.005 inch or 0.127 mm  
103 in diameter) was used to monitor the temperature. The uncertainty in the measured temperature  
104 is estimated at  $\pm 1\%$  for experiments up to 15 GPa and 2600 K, which includes the precisions in  
105 the thermocouple calibration and the positioning of the thermocouple junction relative to the  
106 sample (Li et al. 2003) and does not include the effect of pressure on the electromotive force  
107 (emf), which will be discussed later.

108 For the electrical measurements, a pair of 200  $\mu\text{m}$ -thick Pt wires were inserted into a four-  
109 bore alumina holder and used as the electrodes (Fig. 1b). The electrode tips and thermocouple  
110 junction were placed along the rotational axis of the cylindrical-shaped heater and at the same  
111 distance to the equator of the heater, in order that the thermocouple measured the same  
112 temperature where the electrode tips sit, and they were kept within the middle third of the heater  
113 length, where the temperature variation was expected to be less than 100 K (Leinenweber et al.  
114 2012). The measurement circuit consisted of a Mastech variac power supply, which converted  
115 110 V, 60 Hz AC voltage from the wall outlet to 0.1 to 1 V, 60 Hz AC voltage, and a Fluke 289  
116 multi-meter, which recorded the current through the sample. For most measurements, the AC  
117 voltage was set to 0.1 V to prevent electrolysis reactions and irreversible changes in sample  
118 composition. In order to avoid the electromagnetic perturbation from the heating current and the  
119 motor for pressure control, the voltage was occasionally raised to 1 V, which was found to be  
120 still below the threshold for electrolysis reactions.

121 Powder of NaCl from Aldrich (99.99%, #38,886-0) was dried in a vacuum oven at  $\sim 400$  K  
122 for more than one week before being packed inside a Pt tubing, which served as the sample

123 container and helped to reduce the temperature gradient. The complete assembly was dried in the  
124 vacuum oven at 400 K for at least 24 hours before loading into the multi-anvil apparatus. In a  
125 typical high-pressure experiment, the ram pressure was increased at the rate of 100 US ton per  
126 hour during compression, and decreased at the rate of 35 US ton per hour during decompression.  
127 Data were acquired at several target pressures along the compression path. At each target  
128 pressure the assembly was heated at the rate of 60 K per minute until melting was detected, and  
129 then cooled rapidly to 1000 K and heated again at the same rate of 60 K per minute to replicate  
130 melting detection at least once. At the highest pressure and temperature of each run, we  
131 quenched the sample by turning off the power. The run products were recovered and inspected  
132 for the positioning of the electrode tips and thermocouple junctions with a Zeiss microscope with  
133 the reflected light and 10x magnification objective lens. A number of run products were  
134 examined for chemical contamination through semi-quantitative energy-dispersive spectroscopy  
135 analyses using the CAMECA SX100 electron microprobe at the University of Michigan.

136 To test the validity of the in situ electrical measurements, we performed two experiments  
137 using Pt sphere markers, one quench experiment at the University of Michigan and another  
138 synchrotron radiography experiment at GSECARS, the Advanced Photon Source at the Argonne  
139 National Laboratory. The quench experiment used the 8-mm configuration and was run at 6 GPa  
140 and 1923 K, following similar pressure and temperature paths as described above. The  
141 synchrotron experiment used the COMPRES 10/5 on-line design with graphite-filled linear slots  
142 in the lanthanum chromite sleeve as windows for X-ray diffraction and radiography  
143 measurement (Chen et al. 2008; Leinenweber et al. 2012). The experiment was compressed at  
144 room temperature to the target oil load and then heated to 750 K at the rate of 60 K per minute,  
145 where an X-ray diffraction pattern was collected on crystalline NaCl sample for in situ pressure

146 determination. During further heating at the rate of 60 K per min, we monitored the X-ray  
147 radiograph until the Pt marker sank and then quenched the experiment by turning off the power.

## 148 **RESULTS and DISCUSSION**

149 The melting temperatures of NaCl were determined between 1.8 and 21 GPa (Table 1). In a  
150 typical experiment, we saw a rise in the current during heating from a few  $\mu\text{A}$  at temperatures  
151 below 1000 K to a few hundred  $\mu\text{A}$  upon melting (Fig. 2). Assuming that melting leads to the  
152 sharpest rise in the measured current, we took the starting point of the steepest segment of the  
153 current-temperature curve as the melting point. As the heating cycle was repeated multiple times  
154 in the same experiment, melting was detected within  $\pm 5$  K. The measured melting temperatures  
155 from duplicate experiments at the same condition agree within  $\pm 30$  K. At pressures below 4 GPa,  
156 the measured melting temperature sometimes shifted up by 10 to 40 K during the first two or  
157 three heating cycles, which may result from thermal relaxation of internal stress in the assembly.  
158 In these cases heating cycles were repeated until the melting temperature reached a stable value,  
159 except at 1.8 GPa where the electrodes failed shortly after melting during the first heating cycle  
160 (Fig. 2). The current-temperature relation was reversed upon cooling at up to 20 K lower in  
161 temperature (Fig. 2). The hysteresis between the heating and cooling cycle can be attributed to  
162 super-cooling, which is caused by kinetic barrier in nucleation, but there is not a counterpart  
163 effect upon melting (Galiński et al. 2006), so the melting temperatures in the study were all  
164 picked up from heating ramps.

165 Electron microprobe analyses of several recovered samples showed no contamination from  
166 the four-bore alumina, which was in direct contact with the sample, or from any other  
167 components in the assembly, which might diffuse into the sample. Optical inspection of the  
168 experimental products revealed that in Experiment 071614 the thermocouple junction was



169 positioned further away from the center of the heater than the electrode tips (Fig. 1c). As a result,  
170 the measured temperatures from this experiment shifted systematically to lower values (Table 1).  
171 These data were not included in the fitting of melting equations.

172 The melting temperature of NaCl was found to increase continuously with pressure from ~  
173 1100 K at 1.8 GPa to ~ 2300 K at 19 GPa (Table 1, Fig. 3a). In the synchrotron radiography  
174 experiment (Experiment T1103), melting was detected between 1643 and 1648 K at 4.2 GPa,  
175 whereas the quench sinking sphere experiment (Experiment 012411) indicated that melting  
176 occurred below 1923 K at 6.0 GPa. These results are consistent with the in situ electrical  
177 measurements.

178 As mentioned earlier, our measurements are subject to uncertainties arising from the effect  
179 of pressure on the emf of thermocouple, which is poorly known and hence not corrected. Limited  
180 data suggest that the type C thermocouple underestimates the temperature with a systematic error  
181 that generally increases with pressure and temperature and could amount to tens of degrees or  
182 even more than 100 K at 15 GPa and above 2000 K (Li et al. 2003). Consequently, our melting  
183 temperatures may need to be corrected upwards by tens to 100 K, especially at high pressures.

184 Another source of uncertainty in the data may result from pressure drift during heating.  
185 Recent synchrotron experiments showed that the sample pressure at constant applied ram  
186 pressure drifted upwards or downwards as temperature increased from 1473 to 2273 K (Fei et al.  
187 2004a, 2004b; Leinenweber et al. 2012). The direction and magnitude of the pressure drift varied  
188 with the TEL, configuration, temperature, pressure and heating history in a complicated manner,  
189 making it difficult to correct for the effect of temperature on pressure calibration. For the  
190 COMPRES 10/5 assembly, on which our experiments were based, available data showed that  
191 upon heating from 1473 K to 1800 K the sample pressure drifted downwards by 0.2 GPa at 20

192 GPa, and by 1 GPa at 15 and 17 GPa. On the other hand, the sample pressure was found to drift  
193 upwards by 2 GPa when heated from 1473 K to 2273 K at 23 GPa after experiencing a previous  
194 heating cycle (Fei et al. 2004a). Synchrotron experiments may be more susceptible to pressure  
195 drifts because the cell configurations were modified to allow X-ray access to the sample, which  
196 introduced additional heat sinks and mechanical weakness. In this study, the melting temperature  
197 at 3.6 GPa was found 30 K higher in the second heating cycle, probably because the sample  
198 pressure shifted up by about 0.3 GPa. On the other hand, experiments above 4 GPa yielded  
199 consistent melting temperatures (within  $\pm 5$  K) among multiple heating cycles, indicating little  
200 pressure drift. For these reasons, we expect that the sample pressures in this study deviate from  
201 the calibration curve at 1473 K by less than 1 GPa at 15GPa and by less than 2 GPa at  $\sim 20$  GPa,  
202 no greater than synchrotron experiments mentioned above. At low pressures where the melting  
203 temperature increases rapidly with pressure at a rate of  $\sim 200$  K per GPa, any pressure drift would  
204 lead to large errors in the measured melting temperature. Fortunately, pressure drift generally  
205 scales with temperature (e.g., Fei et al. 2004b), and therefore smaller pressure drifts are expected  
206 at lower pressures where the melting temperatures are lower. At high pressures where the rate  
207 drops to 20 K per GPa at  $\sim 15$  GPa and 10 K per GPa at  $\sim 20$  GPa, a pressure drift of  $\pm 1$  GPa at  
208 15GPa or  $\pm 2$  GPa at 20 GPa would introduce an additional error of  $\pm 20$  K. The combined  
209 uncertainties in the measured melting temperature, including the precision of the type C  
210 thermocouple, the reproducibility within a single experiment and among duplicate experiments,  
211 and the pressure drift at high temperature, are estimated at  $\pm 40$  K, assuming that the sources of  
212 uncertainties are random and independent.

### 213 **Comparison with existing data**

214 The melting curve of NaCl determined in this study agrees well with the existing  
215 experimental results at pressures up to 6.5 GPa and is marginally consistent with those at higher  
216 pressures (Fig. 3a). The results reproduced the existing data from piston-cylinder experiments  
217 (Akella et al. 1969) within  $\pm 20$  K, suggesting that emf correction and melting temperature  
218 change caused by pressure drift are smaller than  $\pm 20$  K within the relevant pressure and  
219 temperature ranges, unless the two effects cancel out. At pressures above 12 GPa, the melting  
220 temperatures determined in this study exceed the DAC results (Boehler et al. 1997) by 100 K to  
221 200 K. The discrepancies between the two sets of data, however, generally fall within the  
222 estimated uncertainty of  $\pm 40$  K in this study and the reported uncertainties of  $\pm 50$  K up to 15  
223 GPa and  $\pm 100$  K up to 20 GPa in the DAC study. Heating-induced pressure drifts in the positive  
224 direction would bring our results into better agreements with the DAC data, whereas emf  
225 corrections and pressure drifts in the negative direction are expected to do the opposite. Further  
226 studies are necessary to quantify the effect of pressure on emf and to reduce the uncertainties in  
227 sample pressure, for example, by using an internal pressure marker. Vočadlo and Price (1996)  
228 suggested that DAC measurements tend to underestimate the melting temperature because of  
229 observational biases under extreme conditions. If corrected upwards by about 10% to account for  
230 surface melting effect (Cheng et al. 2003), the DAC data would agree well with the results of this  
231 study.

232 Compared with the latest theoretical results (An et al. 2006), the melting temperatures  
233 reported here are in agreement at 5 GPa, 100 K lower at 10 GPa, and 150 K lower at 20 GPa  
234 (Fig. 3a). Earlier results from MD simulations exceed that from DAC experiments by as much as  
235 500 K at 20 GPa, well beyond the estimated uncertainty of  $\pm 100$  K using the supercell  
236 methodology (Vočadlo and Price, 1996). Cheng et al. (2003) proposed that the melting

237 temperature from simulation should be corrected downward by about 20% to account for  
238 superheating effect resulting from small system size and short time scale. More recent MD  
239 simulation (An et al. 2006) yielded substantially lower melting temperatures for NaCl, which  
240 requires no more than 5% correction for superheating to match the melting temperature at 20  
241 GPa determined in this study.

#### 242 **Fitted melting equations**

243 The empirical Simon equation has been widely used to fit pressure-dependent melting  
244 temperature in the form of  $(T/T_0)^c = (P-P_0)/A + 1$ , where  $A$  and  $c$  are constants with values  $\geq 1$ ,  
245  $T_0$  and  $T$  are the melting temperatures at the reference pressure  $P_0$  and  $P$ , respectively. The  
246 Simon equation stands out in its simplicity and has the advantage of not requiring any knowledge  
247 of the equation-of-state (EoS) of the solid phase. It has the drawbacks that the fitting parameters  
248  $A$  and  $c$  have no clear meanings and that they correlate with each other. Consequently, the  
249 equation works well for interpolation but cannot be used for extrapolating melting temperatures  
250 beyond the experimental pressure range. Indeed, the parameters that fitted data up to 6.5 GPa  
251 (Akella et al. 1969) differ considerably with that of this study (Table 2) and the melting curve  
252 extrapolated from the low-pressure fitting over-predicts the data by nearly 100 K at 20 GPa (Fig.  
253 3a).

254 The Kraut-Kennedy melting equation describes how the melting temperature scales with  
255 volume and it can be written in the form of  $T/T_0 = C \cdot \Delta V/V_0 + 1$ , where  $\Delta V = V_0 - V$  is the volume  
256 reduction of the solid resulting from compression,  $T$  and  $T_0$  are the melting temperatures at  $V$  and  
257  $V_0$  respectively,  $C$  is a constant that relates to the vibrational Grüneisen parameter  $\gamma_0$  at  $V_0$  and it  
258 equals to  $2 \cdot (\gamma_0 - 1/3)$ . In this equation  $V$  and  $V_0$  refer to the 300 K volumes of the solid phase at a  
259 given pressure and 0 GPa, respectively. For NaCl, we used the EoS parameters from Birch

260 (1986) to calculate  $V$  from  $V_0$  and found that  $\gamma_0$  is  $2.52 \pm 0.05$ . These values are in general  
261 agreement with existing results (Table 2). For example, by using the EoS parameters from  
262 Bridgman (1940), Akella (1969) reported a  $\gamma_0$  value of 2.78, which is similar to the fitted value of  
263  $2.62 \pm 0.02$  using the EoS parameters from Birch (1986).

264 Lindemann's law (1910) provides a semi-empirical scaling relation to fit discrete  
265 measurements of melting temperatures for interpolation, and in the absence of data it is often  
266 used together with an equation of state to predict  $T_m$  at high pressures (Poirier, 2000). Given that  
267 Lindemann (1910) only used the equation to calculate the vibrational frequency of a solid from  
268 its melting point, and that Gilvarry (1956, 1966) developed the theory of melting from  
269 Lindemann's law, we will call it Gilvarry-Lindemann melting equation. The equation takes the  
270 form  $T_m \sim 0.00321 \cdot M \cdot f^2 \cdot \Theta_D^2 \cdot V^{2/3}$ , where  $M$  (the molar mass in grams) and  $f$  (the critical  
271 Gilvarry-Lindemann factor) are independent of pressure, and  $\Theta_D$  (the Debye temperature) varies  
272 with  $V$  (the molar volume in cubic centimeter). The volume dependence of  $\Theta_D$  can be described  
273 by the vibrational Grüneisen parameter  $\gamma = -\partial \ln \Theta_D / \partial \ln V$ . It is commonly assumed that  $\gamma$  itself  
274 scales with volume in the form  $\gamma / \gamma_0 = (V/V_0)^q$ , where  $\gamma$  and  $\gamma_0$  are the Grüneisen parameters at  $V$   
275 and  $V_0$ , respectively, and  $q$  is a constant that is usually assumed to be one in shock wave data  
276 reduction (Fei et al. 2004b). The equation can then be expressed as  $T_m \sim$   
277  $1.689 \cdot f^2 \cdot \Theta_0^2 \cdot (V_0/V) (2\gamma_0 (V_0/V)^q - 1/3)$ , where  $\Theta_0$  is the Debye temperature at  $V_0$ . In this form, the  
278 equation has four fitting parameters ( $f$ ,  $\Theta_0$ ,  $\gamma_0$ ,  $q$ ), all of which may be obtained from or compared  
279 with independent measurements, and an isothermal EoS at 300 K is used to calculate the volume  
280 at a given pressure.

281 By using the EoS parameters from Birch (1986), two sets of fitting parameters were  
282 obtained: one for a fixed  $q$  at 1, and the other allowing  $q$  to be fitted by the data (Table 2). The

283 parameters  $f$  and  $\Theta_0$  correlate with each other and cannot be uniquely fitted. With  $\Theta_0$  fixed at 302  
284 K (Poirier, 2000), the fitted Gilvarry-Lindemann factor  $f \sim 0.08$  is lower than the known value of  
285 0.11 for alkali halides (Martin and O'Connor, 1977). If  $f$  is fixed at 0.11, the fitted  $\Theta_0$  value is 228  
286 K, which is closer to  $279 \pm 11$  K, which is cited in Decker (1971). We found that holding  $q$  at 1  
287 failed to reproduce the curvature of the melting curve between 0 and 20 GPa, whereas a good fit  
288 is obtained when  $q$  is allowed to vary. Recent experimental and theoretical studies on MgO  
289 demonstrated that variable  $q$  is required to satisfy the high  $P$ - $T$  static and shock wave data (Fei et  
290 al. 2004b). For NaCl, a volume-dependent  $q$  value may be needed to describe the thermoelastic  
291 behavior, or it may indicate that extending the Gilvarry-Lindemann melting equation to ionic  
292 crystals does not work well because the Debye-Waller theory is limited to monoatomic solids  
293 (Gilvarry, 1956).

294 As widely recognized the Kraut-Kennedy melting equation can be derived from the  
295 Lindemann equation by assuming that the volume dependence of melting temperature is constant  
296 and equals to the value at  $V_0$  (e.g. Akella et al. 1969). This approximation does not apply at  
297 higher pressures, where the measured melting temperatures deviated from the fitted curve  
298 towards lower temperatures due to the volume dependence of gamma (Akella et al. 1969). In our  
299 study, the measured melting temperature began to deviate from a linear trend at pressures above  
300 14 GPa, where the Grüneisen parameter is expected to be higher because of the reduced volume.

### 301 **IMPLICATIONS**

302 The melting temperatures of NaCl between 0 and  $\sim 20$  GPa, determined using a newly  
303 developed in situ capacitive current method and the multi-anvil apparatus and, reproduce existing  
304 data up to 6.5 GPa but show considerable discrepancies with both diamond-anvil-cell and  
305 theoretical results at higher pressures. The discrepancies suggest that superheating effect in

306 molecular dynamic calculations may be as much as 150 K at about 20 GPa. Alternatively, the  
307 discrepancies may originate from pressure effect on the emf of type C thermocouple, which was  
308 expected to underestimate the melting temperatures and are uncertain at pressures above 4 GPa  
309 (e.g., Li et al. 2003; Fei et al. 2004b). In high-pressure experiments, temperatures are commonly  
310 measured with a thermocouple or spectral radiometry. While the thermocouple method is subject  
311 to poorly constrained pressure effect on emf, the spectral radiometry also suffers from limited  
312 knowledge of wavelength dependent emissivity and optical aberration (Shen et al., 2001),  
313 leading to errors that are more than 100 K (Campbell, 2008). An independent evaluation of the  
314 pressure effect on emf remains a challenge.

315       The capacitive current method can be applied to determine the melting temperatures of ionic  
316 compounds at high pressures. This method uses Pt as the electrodes and sample container and is  
317 applicable below the melting point of Pt, which increases from 2042 K at 0 GPa to 2600 to 2900  
318 K at 20 GPa (Belonoshko and Rosengren 2012). Compared with the existing methods (e.g.,  
319 Anzellini et al. 2013; Jackson et al. 2013; Boehler et al. 1997; Chen et al., 2008; Akella et al.  
320 1969), the capacitive current approach is characterized by its high signal/noise ratio and high  
321 efficiency. The experimental procedure has been optimized to generate non-destructive  
322 capacitive current through the sample so that it can be melted more than 20 times before failure  
323 because of electrodes shorting in a single experiment to yield results that are reproducible within  
324  $\pm 5$  K at a given pressure. By using this approach, we can repeat measurements at each pressure  
325 and collect data at multiple pressures in each experiment. The melting curve of NaCl may be  
326 used for hot pressure calibration of piston cylinder and multi-anvil apparatus up to about 7 GPa.  
327 At higher pressures, the melting slope becomes rather shallow, increasing by only 20 K per GPa  
328 at 15 GPa. Considering the weak dependence of melting temperature on pressure and significant

329 uncertainties the melting temperature of NaCl, the melting curve of NaCl does not appear to be a  
330 good candidate for pressure calibration above 10 GPa.

331 In this study the frequency of the test voltage is 60 Hz, which is readily available and  
332 adequate for detecting melting. In impedance spectroscopy studies, a wide range of frequencies  
333 from 1 Hz to 1 MHz have been used (e.g., Gaillard et al. 2008; Yoshino et al. 2010). The  
334 signal/noise ratio may improve at higher frequencies that match ionic relaxation more closely. In  
335 future development, a waveform generator may be used to optimize the frequency of the test  
336 voltage. The design of the pressure assembly can also be modified to further reduce the random  
337 errors in temperature by improving the positioning precision and minimizing the size of the  
338 thermocouple junction. Finally, this approach may be integrated with other high-pressure devices  
339 such as diamond anvil cells to extend the pressure coverage.

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- 451

452 **FIGURE CAPTIONS**

453 **Fig. 1** Experimental configurations for melting detection using capacitive current method.

454 a. Schematic configuration of the 5-mm assembly used in this study.

455 b. Illustrations of the platinum electrodes in four-bore alumina in opaque and translucent views.

456 c. Reflected light microscopic images of recovered charges of Experiment 021314 (left) showing

457 symmetric placement of the electrode tips and thermocouple (TC) junction (circles) with respect

458 to the equator of the heater (horizontal line) and the sample position (box), and Experiment

459 071614 (right) showing that the TC junction is located further away from the equator of the

460 heater than the electrode tips.

461 **Fig. 2** Representative current-temperature curves at selected pressures. Melting is located the

462 abrupt take-off point of each blue curve (Experiment 021314), or as the starting point of the

463 steepest segment for each yellow curve (Experiment 100313). The black curve represents data

464 collected along the cooling path at 15 GPa in Experiment 021314. The down-going part of the

465 red curve (Experiment 092613) indicates instability of the electrodes before they failed by

466 contacting each other or with adjacent Pt capsule.

467 **Fig. 3** Fittings of experimental data to melting equations. Results from this study (Table 1) are

468 shown as narrow diamonds for 8-mm experiments 092613 (blue) and 100313 (Red), regular

469 diamonds for 5-mm experiments 021314 (red) and 070114 (black), and solid triangles for the

470 experiments using Pt sphere markers. Open triangles and circles represent experimental data

471 from Akella et al. (1969) and Boehler et al. (1997), respectively. Bars and pounds represent

472 theoretical results from Belonoshko and Dubrovinsky (1996) and An et al. (2006), respectively.

473 a. Simon's equation fittings for data from this study (black thick solid curve) and for those of

474 Akella et al. (1969) (gray thin solid curve).

475 b. Kraut-Kennedy equation fittings for data from this study (black thick solid line), for those of  
476 Akella et al. (1969) (gray thin solid curve), and those of Boehler et al. (1997) (gray thin dashed  
477 line).

478 c. Gilvarry-Lindemann equation fittings for data from this study with  $q$  fitted by the data (black  
479 thick solid line) or  $q$  fixed at 1 (gray thick solid line), for those of Akella et al. (1969) (gray thin  
480 solid curve), and those of Boehler et al. (1997) (gray thin dashed line).

481

**Table 1 Experimental condition and results**

Experiment ID	Pressure, GPa	Melting T, K
071614_5 <sup>1</sup>	5.0	1738
	9.0	1963
	12.0	2064
	15.0	2129
	18.0	2181
	21.0	2215
070114_5	5.0	1789
	9.0	2027
	12.0	2058
	15.0	2130
021314_5	9.0	2031
	12.0	2140
	15.0	2205
	17.0	2233
	19.0	2268
100313_8 <sup>2</sup>	3.6	1552
	4.5	1719
	5.4	1791
	6.3	1850
	7.2	1911
	8.1	1955
	9.0	1993
092613_8	1.8	1348
<u>Synchrotron Pt marker</u>		
T1103	4.4 at 300 K 4.2 at 780 K	1643 to 1648
<u>Quench Pt marker</u>		
012411_8 <sup>3</sup>	6	1923

<sup>1</sup>Data from this experiment were not used for fitting because the thermocouple junction was located at a significantly colder position than the electrode tips.

<sup>2</sup>At 3.6 GPa, the melting temperature is taken from the second heating cycle and it is higher than that from the first heating cycle by 40 K.

<sup>3</sup>The marker sank at this temperature.



**Table 2 Fitting parameters of melting equations**

<u>Simon equation</u>				
	This study	Akella et al. 1969 <sup>1</sup>	Pistorius 1966	Clark 1959
$A$	1.6(5)	0.94(4)	1.5	1.62
$c$	4.5(4)	3.65(8)	2.969	2.81
<u>Kraut-Kennedy equation</u>				
	This study	Akella et al. 1969 <sup>2</sup>		
$g$	2.52(5)	2.62(2)		
<u>Gilvarry-Lindemann equation</u>				
	This study	This study	Akella et al. 1969 <sup>2</sup>	Boehler 1997 <sup>2</sup>
$Q_0, K$	302 (fixed)	302 (fixed)	302 (fixed)	302 (fixed)
$f$	0.082(1)	0.087(1)	0.0835(1)	0.0841(1)
$g_0$	2.9(2)	1.93(9)	2.75(3)	2.4(2)
$q$	1.9(1)	1 (fixed)	2.27(5)	1.9(2)

<sup>1</sup>Fitted for the reported data.

<sup>2</sup>Fitted for the reported data using Birch (1986) EoS parameters.  
Numbers in parentheses are uncertainties on the last digits.









