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The NiSi melting curve to 70 GPa

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1 Abstract

2 The melting curve of NiSi has been determined to 70 GPa on the basis of laser-heated
3 diamond anvil cell (LH-DAC) experiments in which changes in the gradient of temperature vs. laser
4 power functions were used as the melting criterion. The melting curve was corroborated with *in situ*
5 X-ray diffraction experiments in both the LH-DAC and multi-anvil press in which the appearance
6 of liquid diffuse scattering in the diffraction patterns was used as the melting criterion. At all
7 pressures, the NiSi melting curve is lower than that of FeSi, with the difference in melting
8 temperature reaching a maximum of 900 K at 14 GPa. The location of the B31 + B20 + L triple
9 point has been constrained to 12 ± 2 GPa and 1550 ± 100 K and the B20 + B2 + L triple point to
10 28.5 ± 1.5 GPa and 2165 ± 60 K. On the basis of the *in situ* LH-DAC experiments the Clapeyron slope
11 of the B20 \rightarrow B2 transition is estimated at -67 MPa K⁻¹. Extrapolation of the B2-NiSi liquidus to
12 core-mantle boundary (CMB) conditions (135 GPa) suggests the melting point of NiSi (3700 ± 400
13 K) will be only marginally lower than that of isostructural FeSi (4000 ± 200 K). Thus any (Fe,Ni)Si
14 solid solution present within the D'' layer is expected to remain solid, with the possible exception of
15 the very hottest region adjacent to the CMB.

16

17 **Keywords:** NiSi, melting, high-pressure, *in situ*, LH-DAC

18 1. Introduction

19 Historically, the primary interest in nickel monosilicide (NiSi), an intermediate compound
20 along the Ni-Si binary (Massalski et al, 1990), owed to its usefulness as a contact material in
21 microelectronic devices (see e.g. Lavoie et al., 2006). Consequently, NiSi was studied extensively
22 at the conditions at which these devices are manufactured and operated, i.e. at ambient conditions
23 (e.g. Connétable & Thomas, 2009) and at high temperatures (e.g. Detavernier et al., 2003), where
24 NiSi has the MnP (B31) structure. In contrast, we are interested in NiSi because of its position as an
25 end-member in the Fe-Ni-Si system, of relevance to the cores of the terrestrial planets, not least that
26 of Earth. Geochemical models based on cosmochemical arguments suggest that Earth's core could
27 contain at least 5 wt.% nickel (e.g. Allègre et al., 1995) and up to 20 wt.% silicon (e.g. Allègre et al.
28 1995; Fischer et al. 2012; Balchan & Cowan, 1966). Attempts to reconcile experimental
29 measurements of sound velocities with 1-D seismic profiles (Badro et al., 2007) suggest that silicon
30 is an effective candidate for the light element required to explain Earth's core density deficit. More
31 recent *ab initio* determinations of sound velocities in FeSi exclude silicon as an inner core
32 component (Ono et al. 2013). However, this conclusion depends on the temperature at the inner
33 core boundary (ICB) being less than 6500 K, which is within error of current estimates and thus
34 may be in doubt (Anzellini et al., 2013; Sola & Alfè, 2009) and on the absence of any strong pre-
35 melting effects (Martorell et al., 2013). Recent measurements indicating that the silicon of the bulk
36 silicate Earth is isotopically heavy relative to the chondritic meteorites from which Earth is
37 postulated to have formed, lends further credence to the argument for a significant silicon reservoir
38 within the core (Armytage et al., 2011). As a result, several studies have been published concerning
39 the sub-solidus phase relations (e.g. Sakai et al., 2011) and melting behaviour (e.g. Morard et al.,
40 2011) of a range of ternary alloys within the Fe-Ni-Si system. The phase diagram of the FeSi end-
41 member has also been extensively studied (Lord et al. 2010; Santamaría-Pérez & Boehler, 2008;
42 Dobson et al. 2002; Vočadlo et al., 1999; Guyot et al. 1997), as have the physical properties of its

43 constituent phases (e.g. Sata et al. 2010; Dobson et al. 2003; Vočadlo et al., 1999). Recently, we
44 began an ongoing effort to study the NiSi end-member, the behaviour of which was entirely
45 unknown at the high-pressure, high-temperature conditions relevant to the interior of the Earth.
46 These efforts include static *ab initio* simulations that predicted a multitude of new high-pressure
47 phases at 0 K (Vočadlo et al., 2012) and complementary laser-heated diamond anvil cell (LH-DAC)
48 experiments (Lord et al., 2012) in which at least two of these were detected: the ϵ -FeSi (B20)
49 structure and the CsCl (B2) structure. Both studies also reported equations of state (EoS) for these
50 structures as well as for the room pressure phase, at 0 K (for the *ab initio* study), and 300 K (for the
51 LH-DAC study). A third installment (Wood et al., 2013) reported the discovery of another high-
52 pressure phase, with space group *Pmmn*, in multi-anvil press (MAP) experiments together with *ab*
53 *initio* simulations of this new structure, including a 0 K EoS. The present study, in which the
54 melting curve of NiSi is reported, forms a further part of this ongoing effort; it is accompanied by
55 Dobson et al. (submitted) in which the sub-solidus phase relations of NiSi are described using off-
56 line and *in situ* MAP experiments, in combination with the *in situ* LH-DAC experiments described
57 here.

58 Our primary motivation for studying the NiSi melting curve is to provide vital data for those
59 involved in continuing efforts to produce accurate thermodynamic descriptions of core liquids. The
60 composition of these liquids falls within a multi-component system, and their physical properties
61 can be determined by interpolation from the system end-members if the relevant physical properties
62 of those end-members are known. For example, by using the melting curves and room temperature
63 EoS of the end-members in the Fe-O-S system, Helffrich (2012) and Helffrich & Kaneshima (2010;
64 2004) constructed a thermodynamic model and calculated sound velocities for a range of possible
65 core liquids, and then constrained the composition of the liquid outer core by comparison with
66 seismically determined wave speeds. To make these models more realistic, additional components
67 must be added to the compositional space, with nickel and silicon being the most important. This

68 requires a more extensive database of end-member physical properties, with FeSi and NiSi being of
69 primary importance. For both FeSi and NiSi it is the B2 (CsCl) structured phase that is likely to be
70 relevant at the conditions of the deep Earth (Lord et al., 2012; 2010). The room temperature EoS
71 and melting curve of B2-FeSi (Sata et al., 2010; Lord et al., 2010) and the EoS of B2-NiSi (Lord et
72 al., 2012; Vočadlo et al., 2012) are already known; the melting curve of NiSi is the subject of this
73 study.

74 Additionally, we wanted to determine the effects of nickel on FeSi at the conditions of
75 Earth's core mantle boundary (CMB) region. Solid B2 structured FeSi may well be present within
76 Earth's lowermost mantle (the D'' layer; Lord et al., 2010). All pathways for the formation of FeSi
77 involve the iron-rich alloy of the underlying core, and so, given the expected solid solution between
78 the isostructural NiSi and FeSi phases, we would expect any silicide present to be iron-rich
79 (Fe,Ni)Si in the B2 structure (Lord et al., 2012). Knowing the melting curve for NiSi will give an
80 additional constraint on the stability of this material within D'', which depends on its melting curve
81 being above the geotherm.

82 Finally, this study is a further test of the accuracy of our primary method for determining
83 melting in the LH-DAC, namely the observation of changes in the gradient (i.e. plateaux) of
84 temperature vs. laser power curves. This method has been successfully adopted on a number of
85 occasions (Asanuma et al., 2010; Lord et al., 2010; 2009) but the underlying cause behind the
86 observed plateaux is still poorly understood (Geballe & Jeanloz, 2012) leading to inevitable
87 questions about its reliability. To address this issue, we present here not just off-line LH-DAC
88 melting data using this method, but also *in situ* experiments, in both the LH-DAC and the MAP in
89 which melting can be observed directly from the appearance of liquid diffuse scattering (LDS) in X-
90 ray diffraction (XRD) patterns acquired at simultaneous high-pressure, high-temperature conditions,
91 and even from visual identification of convective motion during *in situ* X-radiography.

92 2. Methods

93 This study consists of three sets of NiSi melting experiments. The first (see §2.1) was
94 performed off-line in the LH-DAC at the School of Earth Sciences, University of Bristol. The
95 second (see §2.2) consists of a pair of LH-DAC experiments coupled with *in situ* XRD
96 measurements at beam line ID-27 of the European Synchrotron Radiation Facility (ESRF) in
97 Grenoble, France. The final set (see §2.3) consists of a single MAP experiment, again coupled with
98 *in situ* XRD and X-radiography measurements, at beam line X17B2 of the National Synchrotron
99 Light Source (NSLS), Brookhaven National Laboratory, New York, USA. The NiSi starting
100 material was from the batch used in Lord et al. (2012). Additionally, two off-line experiments at
101 Bristol were performed on an Fe₈₅-Ni₅-Si₁₀ alloy (subscripts are in wt. %), from the batch used in
102 Morard et al. (2011).

103

104 2.1 Off-line LH-DAC melting experiments, University of Bristol

105 These experiments were performed in Princeton-type symmetric DACs using anvils with
106 200-250 µm diameter culets. Rhenium gaskets were used, pre-indented to 25 GPa and drilled
107 centrally to create a sample chamber $\frac{1}{3}$ the diameter of the culet. Between 1 and 5 densified foils
108 (Lord et al., 2012) of the starting material, 10-40 µm in diameter and 5-10 µm thick, were loaded
109 into the sample chamber between discs of NaCl the same diameter as the sample chamber and ~15
110 µm thick. These form-fitting discs, which act as both pressure medium and thermal insulation, were
111 cut using an automated UV (266 nm) laser ablation unit (New Wave Research, LUV series) from
112 sheets produced by compressing powder, either between a pair of diamond anvils or between steel
113 plates in a hydraulic press. Form-fitting pressure media eliminate void space in the sample chamber,
114 helping to maintain the sample geometry during compression. In addition, this ensures a near
115 identical thickness of insulation on either side of the sample, which makes equalizing the
116 temperatures on the two sides by varying the laser power significantly easier. Several sub-micron

117 Cr:Al₂O₃ (ruby) grains were placed between the sample and NaCl on one side, to allow the pressure
118 to be monitored by ruby fluorescence spectroscopy before and after heating. Each cell was held for
119 1 hour under a N₂ atmosphere at 120°C before being sealed under the same conditions to remove
120 any adsorbed water.

121 Once at pressure, samples were heated in a double-sided geometry using two 100 W diode
122 pumped TEM₀₀ (Gaussian mode) fiber lasers (model R4, SPI lasers Ltd., Southampton, UK)
123 operating at 1070 nm. If used in their raw state, the Gaussian energy distribution of the lasers
124 inevitably results in strong Gaussian temperature gradients on the sample surface (Fig. 1) that can
125 lead to overestimates of temperature when measured using spectroradiometry due to chromatic
126 aberration imparted by the refractive optics (Walter & Koga, 2004). Furthermore, strong
127 temperature gradients increase the sensitivity of the measured temperature to misalignment of the
128 emitted light with the aperture of the spectrometer and so can result in underestimates of
129 temperature. Finally, they can promote thermally induced (Soret) diffusion in the sample (Sinmyo
130 & Hirose et al., 2010). To minimize these problems, we have employed beam-shaping optics
131 (focal- π Shaper, AdlOptica, Berlin, Germany), which convert the Gaussian energy distribution into a
132 distribution with a flat-topped profile (Fig. 1; Prakapenka et al., 2008). Subsequent variable beam
133 expansion optics (model 56-30-2-8X, Special Optics Inc., New Jersey, USA) allow the diameter of
134 the spot to be varied up to ~30 μ m.

135 Long working distance infinity-corrected apochromatic near infra-red objective lenses (M
136 Plan Apo NIR 10x, Mitutoyo) were employed to focus the laser light onto and collect the
137 incandescent light from the sample. These lenses absorb a small proportion of the IR radiation
138 causing them to heat up, flex, and change their focal length. Consequently we have found it
139 necessary to water cool the lenses as well as the LH-DAC. These lenses significantly reduce
140 chromatic aberration compared to the optics used in previous studies (Fig. 2a; Lord et al. 2010;
141 2009). As a result, it is no longer necessary to eliminate the most aberrant non-paraxial rays using f-

142 stops, thus making temperature measurement feasible at lower temperatures (down to 1400 K).
143 While the shorter focal length of these objectives increases the magnification (50x vs. 20x
144 previously) and ideal system resolution ($0.5\ \mu\text{m}$ vs. $1.25\ \mu\text{m}$ previously), the system is diffraction
145 limited to $1.0 - 1.5\ \mu\text{m}$ across the spectral range available for temperature fitting ($570 - 840\ \text{nm}$).
146 This is confirmed by measurement of the width of a sharp interface focused onto the CCD, which
147 indicates an actual resolution of $\sim 1\ \mu\text{m}$. Optical aberrations, especially of the chromatic variety,
148 reduce the effective spectroradiometric resolution further (Walter and Koga, 2004). On the basis of
149 the measured focal deviations of our system (a maximum of $\sim 10\ \mu\text{m}$ at the image plane over the
150 $200\ \text{nm}$ spectral window used for temperature fitting), we calculate an actual system temperature
151 measurement resolution of $\sim 3\ \mu\text{m}$ at the sample surface (object plane). Thus, a temperature
152 calculated from the spectrum recorded by a single row of the CCD (e.g. every $0.5\ \mu\text{m}$ at the object
153 plane), must be viewed as a temperature representing an integration of light from a $\sim 9\ \mu\text{m}^2$ region.
154 This integration will lead to errors in the measured temperature that are a function of the
155 temperature gradient at the sample surface (Walter and Koga, 2004), minimized in this study by the
156 use of beam-shaping optics. The degree of chromatic aberration is reflected in the precision of the
157 spectral fits to the ideal greybody Wien function (Fig. 2a; Walter & Koga, 2004), which in the case
158 of this study was typically 2-5K (Fig. 1 and 2b), a significant improvement over the 3-13K reported
159 previously (Lord et al. 2010). All things considered, we conservatively estimate the error associated
160 with optical aberrations at less than 50 K. As in our previous publications, we do not attempt to
161 assign uncertainties due to the unknown emissivity of the sample. Ambient pressure calibration
162 experiments on a range of metals indicate that this uncertainty does not exceed 200 K (Lord et al.
163 2010; 2009).

164 To minimize uncertainties due to radial pressure gradients, pressures were measured after
165 heating as close as possible to the location of melting. No correction for the effects of thermal
166 pressure can be made to the off-line melting data (cf. §2.2) because we have insufficient *in situ* data

167 to accurately determine the empirical relationship between the thermal pressure and the factors that
168 control its magnitude. These include the specific geometry of each assembly, the physical properties
169 of the sample and pressure medium (both of which undergo phase transitions within the range of
170 our data), the degree of compression and the melting temperature (e.g. Errandonea et al. 2003). The
171 *in situ* experiments (§2.2) indicate maximum thermal pressures of 6 GPa. The resulting
172 overestimate in the melting temperature never exceeds ~200 K, is <100 K by ~60 GPa and becomes
173 insignificant at the pressures relevant to the deep Earth.

174 We use the ruby pressure scale of Dewaele et al. (2008), which falls approximately in the
175 middle of several recent calibrations, with a range of ~4 GPa at 100 GPa (see their Fig. 4a); we add
176 an uncertainty to our pressure measurements encompassing this range. Additional uncertainty terms
177 of ± 0.5 -1.0 GPa (to take account of radial pressure gradients) and ± 0.2 GPa (the analytical error on
178 the position of the R_1 ruby fluorescence line) are also included.

179

180 2.2 *In situ* LH-DAC melting experiments, ESRF

181 Sample assemblies were identical to those used off-line (§2.1), except that no ruby grains
182 were placed in the sample chamber, to simplify XRD analysis. Instead, pressure was monitored
183 using the measured unit cell volumes of NaCl, in either the B1 or B2 structures, and their known
184 thermal EoS (Dorogokupets & Dewaele, 2007). The total pressure at high temperature was
185 determined using the method of Campbell et al. (2009). However, to ensure comparability between
186 all datasets, the melting pressures reported in Table 1 for the *in situ* data are also post-heating
187 pressures determined at room temperature.

188 Laser heating was performed using a double-sided, off-axis geometry with heated spots 20-
189 30 μm in diameter. The incandescent light from the sample was collected using reflective optics
190 while a $2 \times 2 \mu\text{m}$ area centered on the heated spot was selected using a pinhole and analysed
191 spectroradiometrically to determine the sample temperature. Temperatures were measured on both
192 sides of the sample before the start of the experiment to allow the temperatures to be equalized by
193 varying the laser power, but on the upstream side only during the melting run due to the necessity of
194 removing the light collecting optics from the path of the diffracted X-rays. For further details see
195 Schultz et al. (2005).

196 The $3 \times 3 \mu\text{m}$ X-ray beam ($\lambda = 0.3738 \text{ \AA}$) was co-aligned with the laser-heated spot using
197 the X-ray induced fluorescence of the NaCl pressure medium. Diffracted X-rays were collected on
198 a MAR345 CCD with exposure times of 2-10 seconds. The distance between the sample and
199 detector was calibrated using a LaB₆ standard. For further details of the beam-line see Mezouar et
200 al. (2005). The resulting 2-D diffraction patterns were carefully masked to remove any saturated
201 spots and then integrated into 1-D diffraction patterns using the Fit2D program (Hammersley,
202 1997). The 1-D patterns were in turn fitted and analysed using the Le Bail method (Le Bail *et al.*,
203 1988) as implemented in the GSAS suite of programs (Larson & Von Dreele, 2000; Toby, 2001).

204

205 2.3 *In situ* MAP melting experiment, NSLS

206 This experiment was performed in a cubic DIA type apparatus. The cylindrical sample
207 chamber contained three compartments, separated with Re foil, the first containing NiSi, the second
208 an NaCl + BN pressure standard with a 10:1 ratio by weight and the third containing a mixture of
209 elemental nickel and silicon in a 1:1 atomic ratio. The sample was surrounded by a BN sleeve,
210 followed by a cylindrical graphite heater separated from the 6 mm pyrophyllite cube with an Al₂O₃
211 sleeve. A D-type thermocouple (W/3 % Re-W/25 % Re) was inserted through the furnace and BN
212 sleeve, with the contact just inside the pressure standard.

213 The sample was compressed at room temperature to an end load of 70 tons (a sample
214 pressure of 7 GPa) and then heated in increments of 50-100 K up to 1523 K. At each step, all three
215 samples were analysed using an incident white X-ray beam with a diameter of 50 μm. The
216 diffracted X-rays were collected using a 10 element energy-dispersive detector (Weidner et al.
217 2010) with a 2θ angle of ~6.6° calibrated using the diffraction pattern of Al₂O₃ recorded at 1
218 atmosphere. By widening the slits collimating the incident X-ray beam, radiographic images were
219 recorded regularly to monitor sample geometry. Once melting was determined from the appearance
220 of LDS, this imaging mode was used to produce X-ray videography of the sample at 10 frames per
221 second to monitor the sample for evidence of convection.

222

223 2.4 Melt detection

224 In the *in situ* MAP and LH-DAC melting experiments, the appearance of LDS during XRD
225 was the primary melting criterion. In the off-line LH-DAC experiments however, melting was
226 detected by the appearance of plateaux in the laser power vs. temperature function (Figs. 2c, 3, and
227 9) generated during automated linear incremental ramping of the power to the lasers, coupled with
228 regular temperature measurements (also automated). Lord et al. (2009) suggested that plateaux
229 would be expected at any invariant melting point as the laser power provides the latent heat of

230 melting. However, it has since been suggested that this explanation of the observed plateaux is
231 unlikely because the magnitude of the latent heat involved in the melting of such small samples is
232 dwarfed by the heat provided by the laser (Geballe & Jeanloz, 2012; Lord et al, 2010). It is likely
233 that several factors contribute to the observed thermal perturbations, including differences in the
234 optical and thermal properties of the liquid and solid phases. For example, convection in the liquid
235 rapidly moves excess heat from the melt pool (upon which the laser is incident) to the solid/liquid
236 boundary, where it promotes further melting, thus moving the boundary further away from the
237 center of the heated spot without significantly increasing the temperature. This process continues
238 until the whole sample is molten or, more likely, until the boundary is sufficiently far from the
239 incident laser beam that any additional power is lost by conduction to the surroundings rather than
240 promoting further melting. At this point, the molten part of the sample often becomes super-
241 liquidus, its temperature rising linearly with increasing laser power, until a second plateaux is
242 reached, often within error of the known melting curve of the surrounding NaCl pressure medium
243 (Fig. 3a; Boehler et al., 1997). Alternatively, the melt may become mechanically unstable and flow,
244 leading to sudden variations in temperature. Whatever the underlying process, the key point is that
245 this melting criterion has been used to successfully detect melting in a broad range of metallic and
246 intermetallic compounds, including Fe, Pt, Pb, FeS, Fe₃C, Fe₇C₃, the Fe-Fe₃C eutectic (Lord et al.
247 2009) and FeSi (Lord et al. 2010). All of these data either match closely with LH-DAC melting
248 data, published by other research groups and produced using a range of different melting criteria
249 (Fe, Pt, Pb, FeS, FeSi) including *in situ* XRD (Fe, Pb, FeSi) or have been corroborated at low
250 pressures using large volume press (LVP) apparatus based on *ex situ* textural analysis (Fe₃C, Fe₇C₃,
251 the Fe-Fe₃C eutectic and FeSi; see Lord et al., 2010; 2009 and references therein). The present
252 study provides two additions to this list: firstly, the melting curve of NiSi corroborated using *in situ*
253 XRD in both the LH-DAC and the MAP and secondly, two offline melting experiments on an Fe₈₅-
254 Ni₅-Si₁₀ alloy, for which *in situ* melting data already exist (Morard et al. 2011).

255 In the case of the off-line experiments, the uncertainties in the melting temperatures reported
256 here are a sum of: 1) the analytical precision in the blackbody spectral fitting (typically ± 2 -5 K; see
257 §2.2); 2) the standard deviation of the temperatures within the melting plateau (typically ± 50 -150
258 K); and 3) an additional estimate of the temperature variations within the central part of the hotspot
259 from which the temperature is determined (typically ± 25 -50 K; see Fig. 1a) leading to total
260 uncertainties of ± 80 -200 K. In the case of the *in situ* experiments, the reported uncertainties are
261 simply chosen to encompass the temperatures of the two XRD analyses that bracket the appearance
262 of LDS plus the maximum estimated uncertainty in the temperature measurements (± 150 K; e.g.
263 Morard et al. 2011).

264 3. Results

265 The NiSi data are listed in Table 1, and plotted as a function of pressure in Fig. 4a, and as a
266 function of isothermal compression, relative to the ambient pressure volume of B31-NiSi in Fig. 5.

267 At ambient pressure, NiSi melts congruently from the MnP (B31) structure but undergoes a
268 series of solid-state phase transitions with increasing pressure. The next liquidus phase on increase
269 in pressure has the ϵ -FeSi (B20) structure, with the transition initially bracketed at 12.5 ± 4.5 GPa
270 and 1550 ± 150 K on the basis of the XRD analysis of LH-DAC experiments (Lord et al. 2012). The
271 Clapeyron slope of this transition has since been refined from the XRD analysis of off-line MAP
272 experiments (Fig. 4a; Dobson et al. submitted). All melting data below this transition have been
273 fitted separately, using two methods. Firstly, the P - T data (Fig. 4a) are fitted using the Simon-
274 Glatzel equation $T_m = [(P_m/A + 1)]^{1/C} \times T_0$, where T_m is the melting temperature at pressure P_m ,
275 T_0 is the ambient pressure melting point and A and C are fitting parameters (Simon & Glatzel, 1929;
276 see Table 2). Secondly, the melting temperatures are plotted as a function of isothermal
277 compression, $(V_0 - V)/V_0$, using the EoS for B31-NiSi (Lord et al., 2012) and fitted using the
278 Kraut-Kennedy equation $T_m = T_0(1 + C(V_0 - V)/V_0)$ where V_0 is the ambient pressure volume of
279 B31-NiSi, and V is the volume of the liquidus phase at the pressure of melting (Fig. 5; Kraut &
280 Kennedy, 1966). This approach is justified because the data are linear in T vs. $(V_0 - V)/V_0$ space.
281 Both fits pass within error of the off-line LH-DAC data and the single *in situ* MAP melting point at
282 5.5 GPa. In the latter experiment melting was not only detected by the onset of LDS in the XRD
283 patterns, but is also clearly demonstrated by the appearance of convective motion in an X-
284 radiographic video acquired after the onset of LDS (see Supplementary video). The invariant point
285 at which our newly determined B31-NiSi liquidus intersects the B31 \rightarrow B20 transition line (Dobson
286 et al., submitted) defines the B31 + B20 + L triple point (TP1; 12 ± 2 GPa, 1550 ± 100 K).

287 Fig. 6 shows the first of the *in situ* LH-DAC experiments at the ESRF (experiment 31A)
288 while Fig. 7 shows selected diffraction patterns. Before heating the sample consists of pure B31-
289 NiSi (Fig. 7a). Up to 1700 K the assemblage consists of B20-NiSi plus the orthorhombic *Pmmn*
290 phase (Fig. 6a and 7b; Wood et al., 2013) which are known to share a broad two-phase region. The
291 *Pmmn* phase has been found to be stable above a pressure of ~ 13 GPa and below a temperature of
292 ~ 1100 K (Dobson et al., submitted). At a constant laser output of 26.5% the temperature of the
293 sample rose from 1650 K to 1850 K, during which time the *Pmmn* phase disappeared, leaving B20-
294 NiSi plus several, small, unidentified peaks (Fig. 7c). From this point up to 29% laser power these
295 unidentified peaks diminish in both number and intensity, while temperature increases linearly,
296 followed by a sudden jump and then a plateau that yields a melting temperature of 2180 ± 30 K. At
297 30% laser power, while on the plateau, LDS was observed during XRD (Fig. 6b), with the
298 magnitude of the LDS signal increasing as laser power is increased while the temperature remains
299 approximately constant. In this experiment, the B2-NiSi phase appeared simultaneously with the
300 onset of melting, suggesting that this run fortuitously intersected the B20 + B2 + L triple point
301 (TP2). After heating (Fig. 7d), the quenched assemblage consists of B20-NiSi + B2-NiSi while two
302 of the unidentified peaks, both very small, persist. Given that the integrated area under these peaks
303 is only 0.8% that of the peaks from the indexed NiSi phases, we are confident that the molten
304 system is close to the NiSi stoichiometry. Nevertheless, a detailed discussion of the nature of these
305 peaks can be found in the supplementary material. Using the post-heating pressure for this run, the
306 triple point is thus defined as 28.5 ± 1.3 GPa and 2165 ± 61 K.

307 The melting data that fall within the narrow pressure range where B20-NiSi is the liquidus
308 phase, between TP1 and TP2, were too few to fit. Instead, we have opted to connect the two triple
309 points with a slightly convex upward curve in P - T space to prevent Schreinemaker's rules being
310 contravened (Fig. 4a; Zen, 1966) and by a straight line in V - T space (Fig. 5).

311 The melting data above TP2 have also been fitted separately using the Simon-Glatzel and
312 Kraut-Kennedy equations (Table 2). In this case the Simon-Glatzel equation has been modified
313 such that $T_m = [((P_m - 28.5)/A + 1)]^{1/C} \times T_0$ in order to force the melting curve through the triple
314 point. The Kraut-Kennedy equation is also modified, such that $T_m = T_0[1 + (C(V_0 - V)/V_0) -$
315 $0.104557)]$.

316 The pair of off-line melting experiments performed on Fe₈₅-Ni₅-Si₁₀ are presented as a
317 function of pressure in Fig. 8 with the raw data in Fig. 9. Both points fall within error of the melting
318 curve of Morard et al. (2011), which is defined by two brackets determined from the appearance of
319 LDS in *in situ* LH-DAC experiments. Our data also agree with those of Fischer et al. (2013) on a
320 similar composition (Fe₉₁Si₉) in which both LDS and plateaux in temperature vs. laser power
321 functions were used as melting criteria.

322

323 4. Discussion & conclusions

324 4.1 The NiSi phase diagram

325 The data reported here and in Dobson et al. (submitted) provide additional constraints on the
326 NiSi phase diagram, including the melting curves of all three liquidus phases (B31, B20, B2) and
327 the positions of both triple points. It is clear from Figs. 4a and 5 that the inflection associated with
328 TP1 is much larger than that associated with TP2. This is probably related to the fact that the
329 volume change across the B31 \rightarrow B20 transition (-6%) is significantly larger than that across the
330 B20 \rightarrow B2 transition (-0.8%) as is clear from Fig. 5. Although there are insufficient data to
331 determine the liquidus for B20-NiSi by fitting, the constraints on the two triple points are
332 independent and thus the slope is tightly constrained, and clearly significantly steeper than that of
333 B31-NiSi, but similar to that of B2-NiSi (Fig. 5).

334 The *in situ* LH-DAC experiments allow us to refine our estimate of the Clapeyron slope of
335 the B20 \rightarrow B2 transition. Our initial estimate of \sim -105 MPa K⁻¹ was based on an experimental
336 bracket at 46 \pm 3 GPa and 1900 \pm 150 K (Lord et al., 2012) and a prior *ab initio* study (Vočadlo et al.,
337 2012) which determined that B2-NiSi would become stable relative to the preceding Pnma-II
338 structure at 247 GPa and 0 K. Wood et al. (2013) have since shown that at 0 K the B2 structure
339 becomes stable at 264 GPa, from the newly discovered Pmmn structure. However, if we use the
340 more relevant B20 \rightarrow B2 transition pressure of 170.5 GPa at 0 K from Vočadlo et al. (2012), the
341 Clapeyron slope decreases to \sim -67 MPa K⁻¹. The new *in situ* data (TP2 plus an additional bracket at
342 1715 \pm 35 K and 58.5 \pm 1 GPa from the second of the two experiments) yield an identical value
343 (Dobson et al., submitted). This new slope passes within the bracket reported by Lord et al. (2012)
344 and extrapolates to 173 GPa at 0 K, in excellent agreement with the 0 K B20 \rightarrow B2 transition
345 pressure of 170.5 GPa from Vočadlo et al. (2012). This new estimate is preferred because the
346 previous estimate was constructed assuming a linear boundary between the pressure at which the

347 B2 phase becomes stable at 0 K and the experimental value from Lord et al. (2012); in fact there are
348 likely to be additional phase boundaries in between, leading to inflections in the transition to the B2
349 phase (Dobson et al., submitted). This explains the difference between the 0 K stabilization pressure
350 of B2-NiSi predicted by the *ab initio* simulations (264 GPa; Wood et al., 2013) and the pressure that
351 would be expected from a linear extrapolation of the experimentally determined Clapeyron slope
352 (173 GPa). This new value confirms that the B2 structure is the relevant one for NiSi at Earth's core
353 conditions given that no further phase transitions are expected at higher pressures (Wood et al.,
354 2013; Vočadlo et al., 2012).

355

356 4.2 Comparison with FeSi

357 The NiSi phase diagram has two significant differences from the phase diagram of FeSi
358 (Lord et al., 2010). Firstly, it exhibits a greater degree of polymorphism at pressures and
359 temperatures below the B20 \rightarrow B2 transition, with at least two additional stable phases (B31 and
360 *Pmmn*) and perhaps several more (Wood et al., 2013; Lord et al., 2012; Vočadlo et al., 2012).
361 Secondly, its liquidus is considerably lower in temperature, by 425 K at 1 atmosphere and by a
362 maximum of \sim 900 K at 12 GPa (TP1). On the other hand, the B20 \rightarrow B2 transition, shared by both
363 compositions, involves a very similar reduction in volume (0.8% for NiSi vs. 1.1% for FeSi, at 300
364 K; Lord et al., 2012) and has a very similar Clapeyron slope (-67 MPa K^{-1} for NiSi compared to -56
365 MPa K^{-1} for FeSi; Lord et al., 2010). In fact if the FeSi phase diagram were shifted in pressure such
366 that the B20 + B2 + L triple points for both compositions coincided, the B2 liquidus and B20 \rightarrow B2
367 transitions would be almost indistinguishable (Fig. 4a). However, the more recent *in situ* FeSi phase
368 diagram (Fischer et al., 2013) contradicts this conclusion (see their Fig. 1d). In that study, a two-
369 phase loop was observed in which the assemblage B20 + B2 is stable (the compositions of which
370 must be non-stoichiometric but complementary), followed by a near vertical transition at 40 GPa to

371 single phase, B2-FeSi. Presumably this two-phase region is bounded at lower pressures by a
372 transition to single-phase B20-FeSi at a pressure below the lower limit of their experiments.
373 Looking at the phase diagram presented in Fig. 2 of Lord et al. (2010), this interpretation could
374 explain the majority of the data. Although the results of *ex situ* MAP synthesis experiments
375 published by Dobson et al. (2002), in which pure B2-FeSi was observed at 24 GPa and 2023 K,
376 appear to contradict this new interpretation, those experiments purposefully used non-stoichiometric
377 starting material ($\text{Fe}_{52}\text{Si}_{48}$). This slight metal excess is known to stabilize the B2 structure in both
378 FeSi and RuSi (Dobson et al., 2002) and might explain its appearance at lower pressures in the
379 MAP experiments. However, it seems unlikely that an iron excess of 2% could reduce the pressure
380 at which B2-FeSi becomes the sole polymorph by such a large extent (18 GPa). Furthermore,
381 Dobson et al. (2002) found that at 24 GPa the width of the two-phase loop is less than 4 wt. % (i.e.
382 pure B20 at $\text{Fe}_{48}\text{Si}_{52}$ and pure B2 at $\text{Fe}_{52}\text{Si}_{48}$), which is hard to reconcile with the width of 28 GPa in
383 pressure space reported by Fischer et al. (2013). In light of this contradiction, we have chosen to
384 present both of the proposed boundaries in Fig. 4.

385 It has been predicted that FeSi could be present within the D'' region, either as a reaction
386 product between the (Mg,Fe)SiO₃ perovskite or post-perovskite of the lower mantle and the Fe-Ni
387 alloy of the outer core (Knittle & Jeanloz, 1991) or as a result of exsolution from the core during
388 secular cooling (Buffett et al., 2000). Based on its melting curve and estimates of the geotherm
389 within the D'' region (Lord et al., 2010), it is expected that any FeSi present would be solid at the
390 top of the D'' region, but almost certainly molten toward the bottom (with the depth of the transition
391 dependent on the geotherm), making it a potential candidate for a component of the partial melts
392 postulated to explain the seismic ultra-low velocity zones (ULVZs) observed at the CMB (e.g.
393 Idehara, 2011; Buffett et al., 2000). A recent *in situ* XRD study on FeSi confirms that the B2
394 structure is stable to at least 150 GPa and 2200 K (Fischer et al., 2013) while no further phase

395 transitions are expected in NiSi on the basis of extensive *ab initio* simulations on a range of possible
396 polymorphs (Wood et al., 2013; Vočadlo et al., 2012). FeSi and NiSi are therefore likely to be
397 isostructural at CMB conditions probably forming the end-members of a simple binary solid
398 solution. Given this assumption and that the core contains at least 5 wt.% Ni (e.g. Allègre et al.,
399 1995), any silicide produced would be expected to be B2 structured (Fe,Ni)Si, with a liquidus
400 temperature falling somewhere between the two end-members. If we extrapolate our Simon-Glatzel
401 fit of the B2-NiSi melting data to the CMB pressure of 135 GPa we find an NiSi melting
402 temperature of 3700 ± 400 K, well within error of the value for FeSi of 4000 ± 200 K (Lord et al.
403 2012). Employing our Kraut-Kennedy fit yields essentially the same result. Combined with the fact
404 that any (Fe,Ni)Si phase is likely to be iron-rich, largely reflecting the composition of the core, the
405 present results strongly indicate that the incorporation of Ni has little effect on the conclusions
406 discussed in Lord et al. (2010).

407 The present data do not cover a sufficient pressure range to allow a reliable extrapolation of
408 the NiSi melting curve to ICB conditions (330 GPa). The likelihood that FeSi and NiSi will be
409 isostructural at inner core conditions means that the melting temperature of any iron-rich B2
410 structured (Fe,Ni)Si phase at the ICB pressure of 330 GPa is likely to be only slightly lower than
411 the value of 6200 K determined for FeSi (Lord et al., 2010). Consequently, such a phase could be a
412 stable solid at inner-core conditions, given favorable sub-solidus phase relations in the Fe-Ni-Si
413 system, which are largely unknown at these conditions. However, most recent experimental data
414 (Fischer et al., 2013; Brosh et al., 2009) and *ab initio* simulations (Zhang & Oganov, 2010) in the
415 Fe-Si system suggest that if the inner core contains more than 4 wt. % Si, as predicted by most
416 experimental and modeling studies (e.g. Allègre et al. 1995; Fischer et al. 2012; Balchan & Cowan,
417 1966) an assemblage of hcp + B2 structures will be stabilized. These results contradict earlier
418 experimental studies (e.g. Asanuma et al., 2008; Kuwayama et al., 2009) which suggested that such
419 bulk compositions would stabilize a single, hcp-structured alloy phase. An alternative inner core

420 model containing 1-2 wt.% Si and 4-5 wt.% Ni, based on sound velocity measurements, has been
421 proposed by Antonangeli et al. (2010). In this case, the phase diagram proposed by Fischer et al.
422 (2013) would also predict a single phase, hcp-structured inner core.

423

424 *4.3 Melting criteria*

425 The data described here provide additional evidence that plateaux in temperature vs. laser
426 power curves are a reliable proxy for melting in those materials that we have tested to date. The
427 close correspondence between the MAP experiment and LH-DAC experiments suggests that our
428 spectroradiometric temperature measurements are accurate and that the temperature gradients
429 within our LH-DAC experiments, minimized by beam shaping, are not an issue. This is because, in
430 the MAP experiment, temperature was measured directly using a thermocouple while the
431 temperature gradient is expected to be small due to the external heating geometry.

432 The *in situ* LH-DAC experiments are particularly informative, because they afford us the
433 opportunity to measure the temperature vs. laser power function simultaneously with an
434 independent and direct determination of the melting temperature from the appearance of LDS. In
435 run 31A (Fig. 6a) LDS does not appear until some way into the plateau, either because there is too
436 little liquid within the diffracted volume to produce a visible signal, or because of slight
437 misalignments between the laser heated spot and the X-ray beam. Once the LDS signal appears,
438 however, its magnitude increases with increasing laser power while the temperature remains
439 constant, which strongly suggests that the additional power is causing an increase in the volume of
440 melt rather than increasing the temperature. This behaviour is to be expected given the axial
441 temperature gradients within the sample (likely less than 100 K; see Campbell et al. 2009). The
442 melt volume appears to reach a maximum by 33% laser output and in the next measurement, at
443 34%, the temperature has risen above the plateau, suggesting that the sample was fully molten
444 within the laser-heated volume and that the additional laser power was forcing the melt into the

445 super-liquidus region, but the experiment was halted before this relationship had become
446 convincing. The observation that LDS is coincidental with a plateau in the temperature vs. laser
447 power function confirms that the observed plateaux are the result of progressively increasing melt
448 volumes rather than of sub-solidus transitions.

449 The jump in temperature at the onset of the melting plateau (indicated by the arrow in Fig.
450 6a), sometimes observed (cf. Fig. 2c), may be the result of the difference in emissivity or laser
451 absorption between the solid and liquid phase. Similar behaviour has been observed in an $\text{Fe}_{82}\text{Si}_{18}$
452 alloy (see Fig. 1 of Asanuma et al., 2010), but not in FeSi (see Fig. 1 of Lord et al. 2010). Given
453 these inconsistencies, no definitive explanation of this behaviour can yet be made.

454 The good agreement between the published *in situ* melting curves of $\text{Fe}_{85}\text{Ni}_5\text{Si}_{10}$ (Morard et
455 al., 2011) and $\text{Fe}_{91}\text{Si}_9$ (Fischer et al. 2013) and the two off-line melting points on $\text{Fe}_{85}\text{Ni}_5\text{Si}_{10}$
456 reported here indicates that the correspondence between the *in situ* and off-line measurements on
457 NiSi is not a material-specific coincidence. Visual inspection of samples after laser heating provides
458 an additional, secondary, melting criterion. Fig. 9c shows a photomicrograph of experiment 41
459 (sample $\text{Fe}_{85}\text{Ni}_5\text{Si}_{10}$) after laser heating. The two dark spots at the bottom and top right of the
460 sample foil were observed to have formed at the locations of melting runs 41A and 41B
461 respectively. A third heating cycle in which a temperature of 2000 K was maintained for 10 minutes
462 (the white circle in Fig. 9c) produced no change in the sample surface compared to adjacent
463 unheated regions. The exact cause of this discoloration is not known, but it is unlikely to be the
464 result of reaction between the sample and its environment, given the lack of evidence of carbides or
465 other extraneous compounds in diffraction patterns collected on quenched samples of various
466 compositions (Fig. 7d; Lord et al., 2010).

467 Further examples of the reliability of discontinuities in temperature vs. laser power curves as
468 a melting criterion are provided by two recent studies performed by independent groups. Firstly,
469 Fisher et al. (2013) report melting data for $\text{Fe}_{91}\text{Si}_9$ based on the appearance of LDS during *in situ*

470 XRD. At 88 GPa (3648 ± 149 K) and 101 GPa (3662 ± 224 K), the appearance of LDS coincides with
471 clear plateaux in temperature vs. laser power curves (see their Fig. 4). Fischer et al. (2013) also
472 report a single *in situ* melting bracket for FeSi that closely matches our previously published off-
473 line melting curve (Fig. 4b; Lord et al. 2010) but is ~ 600 K above the melting curve of Santamaría-
474 Pérez & Boehler (2008) in which melting was determined from visual observations of changes in
475 laser speckle patterns. The second example comes from the new melting curve for iron reported by
476 Anzellini et al. (2013). In Fig. 1c of their paper the authors report a clear example of a discontinuity
477 in the rate of change in temperature as a function of time (equivalent to power given the linear ramp
478 rate) at 4100 K. This matches exactly their LDS based melting curve. Anzellini et al. (2013) note
479 that discontinuities in their temperature vs. power curves are not always apparent (as in their Fig.
480 1d), but that this non-appearance is associated with thicker samples. These two examples indicate
481 that although it is preferable to determine melting curves from the appearance of LDS during *in situ*
482 XRD, in lieu of such data, discontinuities in temperature vs. laser power curves are a useful and
483 accurate alternative approach. In contrast, Anzellini et al. (2013) make clear that earlier
484 measurements of the iron melting curve based on visual observations of motion in laser speckle
485 patterns presumed to represent convection in the liquid considerably underestimated the iron
486 melting curve, as was also the case for FeSi (described above). Anzellini et al. (2013) suggest that
487 these visual methods can potentially misidentify dynamic recrystallization in the solid as melt
488 convection. Therefore it appears that plateaux in temperature vs. laser power curves provide the
489 more accurate criterion in off-line melting experiments.

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634 Figure Captions

635

636 Figure 1:

637 (a) Temperature cross-sections measured by spectroradiometry across an NiSi sample at 25 GPa.

638 The beam shaping optics used in the present study produce relatively isothermal conditions over

639 wide areas (± 35 K over $10\ \mu\text{m}$; blue circles); without them, much larger gradients are created by the

640 Gaussian energy profile of the laser (red squares).

641

642 Figure 2:

643 Results from experiment 25D at 27 GPa. (a) Thermal emission spectra collected from the left hand

644 side, plotted as normalized intensity (J) versus normalized wavelength (ω) where $c_1 = 2\hbar c^2$ and

645 $c_2 = \hbar c/k$ (c , speed of light; \hbar , Planck's constant; k , Boltzmann's constant). Each line represents

646 the spectrum from a point along a transect across the laser heated spot. The straightness of the data

647 leads to very low fitting errors (1.6 K in this case) and indicates the successful minimization of the

648 effects of chromatic aberration, which would be manifested as curvature in the data. (b) Selected

649 temperature cross-sections collected from the left hand side of the sample during the melting

650 experiment (in this case, the sample is larger than the heated spot) and (c) the resulting temperature

651 vs. laser power function showing a clear melting plateau on the left side (open circles) and right

652 side (closed circles). Temperatures in (c) represent the maxima of the cross-sections in (b). The grey

653 bars represent \pm one standard deviation of the data in the plateau, which is defined by the arrows

654 in (c). The uncertainty reported in Table 1 is larger than that reported here because it includes

655 additional terms (see text). All figures are colour coded as a function of laser power.

656

657 Figure 3

658 Further examples of melting induced plateaux in temperature vs. laser power functions in NiSi. (a)
659 Experiment 25B at 21 GPa, (b) experiment 40B at 30 GPa, (c) experiment 28C at 42 GPa, (d)
660 experiment 28E at 54 GPa and (e) experiment 29A at 69 GPa. The small kink in (a) at 62 % laser
661 output is due to a slight adjustment made to the positioning of the laser on the right hand side. Open
662 circles: left hand side; filled circles: right hand side; filled square: melting point of NaCl from the
663 melting curve of Boehler et al. (1997).

664

665 Figure 4

666 (a) The NiSi phase diagram above 900 K (black lines). Filled circles: off-line LH-DAC melting
667 points (Bristol); open black (grey) triangles: *in situ* LH-DAC melting brackets determined at the
668 ESRF without (with) thermal pressure included; filled triangles: *in situ* MAP melting bracket
669 determined at the NSLS; filled diamonds: B20 → B2 transition bracket from Lord et al. (2012);
670 open diamond: ambient pressure melting point (Massalski et al. 1990). For the *in situ* experiments,
671 the appearance of LDS was the melting criterion, with the downward pointing arrow representing
672 its first appearance and the upward pointing arrow representing the preceding measurement. The
673 solid grey lines and text relate to the FeSi phase diagram of Lord et al. (2010) while the dashed grey
674 line represents the B20 + B2 → B2 transition determined by Fischer et al. (2013). The sub-solidus
675 parts of the NiSi phase diagram reported here are from Dobson et al. (submitted). (b) The FeSi
676 phase diagram. Lines are as in (a) except for the dot-dash line, which indicates the melting curve of
677 Santamaría-Pérez & Boehler (2008). The solid triangles represent the *in situ* melting bracket from
678 Fischer et al. (2013).

679

680 Figure 5

681 The same melting data shown in Fig. 4, plotted as a function of isothermal compression ($(V_0 -$
682 $V)/V_0$ where V is the volume of the liquidus phase at the pressure of melting and V_0 is the ambient
683 pressure volume of B31-NiSi (open circles). The horizontal error bars are asymmetric because they
684 include a contribution equivalent to the maximum measured thermal pressure of +6 GPa. Solid lines
685 represent fits to the Kraut-Kennedy equation for, from left to right, B31-NiSi (red), B20-NiSi
686 (green) and B2-NiSi (blue). The solid circles represent the two triple points, each of which appears
687 twice because of differences in the EoS parameters of the two solid phases which define each triple
688 point, while the size of the gaps between them are proportional to the magnitude of the volume
689 decrease across the two transitions. Note: the fit to the B20 liquidus is constrained to pass through
690 both triple points.

691

692 Figure 6

693 *In situ* LH-DAC experiment 31A at 29 GPa. (a) Temperature vs. laser power plot. Open circles with
694 plus sign: *Pmmn* + B20-NiSi; Solid black circles: B20-NiSi + unknown trace phase (see text). The
695 dashed line represents the temperature above which the *Pmmn* phase was no longer observed and
696 the grey bar represents the melting temperature determined from the points within the melting
697 plateau, which are colour coded as a function of laser output. The open circles represent XRD
698 patterns in which LDS was observed. (b) XRD patterns colour coded to match (a). The black
699 dashed line represents the background fit to the pattern collected immediately before LDS was
700 observed. Tick marks from top to bottom represent B1-NaCl, B2-NaCl, B20-NiSi and the
701 unidentified trace phase (see text).

702

703 Figure 7

704 XRD patterns (black crosses) from experiment 31A (29 GPa) fitted with the LeBail method using
705 GSAS (red lines). (a) before heating, (b) at 1650 K, (c) at 1710 K and (d) after heating. Tick marks

706 from top to bottom represent B1-NaCl, B2-NaCl, B2-NiSi, B20-NiSi, B31-NiSi and the *Pmmn*
707 phase. The arrows denote the peaks associated with the unidentified trace phase (see text).

708

709 **Figure 8**

710 Melting data for selected Fe-Ni-Si alloys. The solid line is a fit to the *in situ* LH-DAC melting data
711 for Fe₉₁Si₉ of Fischer et al. (2013) that includes melting brackets, in which the appearance of LDS
712 was the melting criterion (open triangles), and melting points in which plateaux in temperature vs.
713 laser power curves were used (solid circles). The dashed line is a fit to the *in situ* LH-DAC melting
714 brackets (solid triangles) for Fe₈₅Ni₅Si₁₀ of Morard et al. (2011). Open circles are the melting data
715 for Fe₈₅Ni₅Si₁₀ from this study in which plateaux in temperature vs. laser power curves were used to
716 define melting.

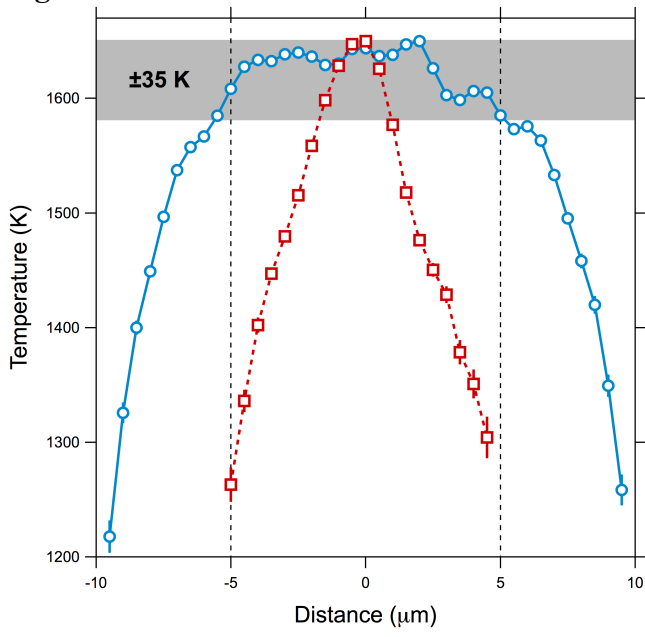
717

718 **Figure 9**

719 Melting plateaus from off-line LH-DAC experiment 41 (Fe₈₅Ni₅Si₁₀) with symbols as in Fig. 3. (a)
720 Run 41A at 47 GPa. Only the right side is plotted due to a fault on the left side. (b) Run 41B at 49
721 GPa. The small (~80 K) difference in the plateaux temperature between the left and right sides is
722 most likely due to small misalignments between the heated spot and the spectrometer. (c)
723 Photomicrograph of the left side of the sample taken after laser heating. The dark spot resulting
724 from runs A and B are marked by the arrows. The white circle represents the location of a third
725 heating run, halted at 2000 K. Note the lack in the latter position of any change in the nature of the
726 sample surface.

727

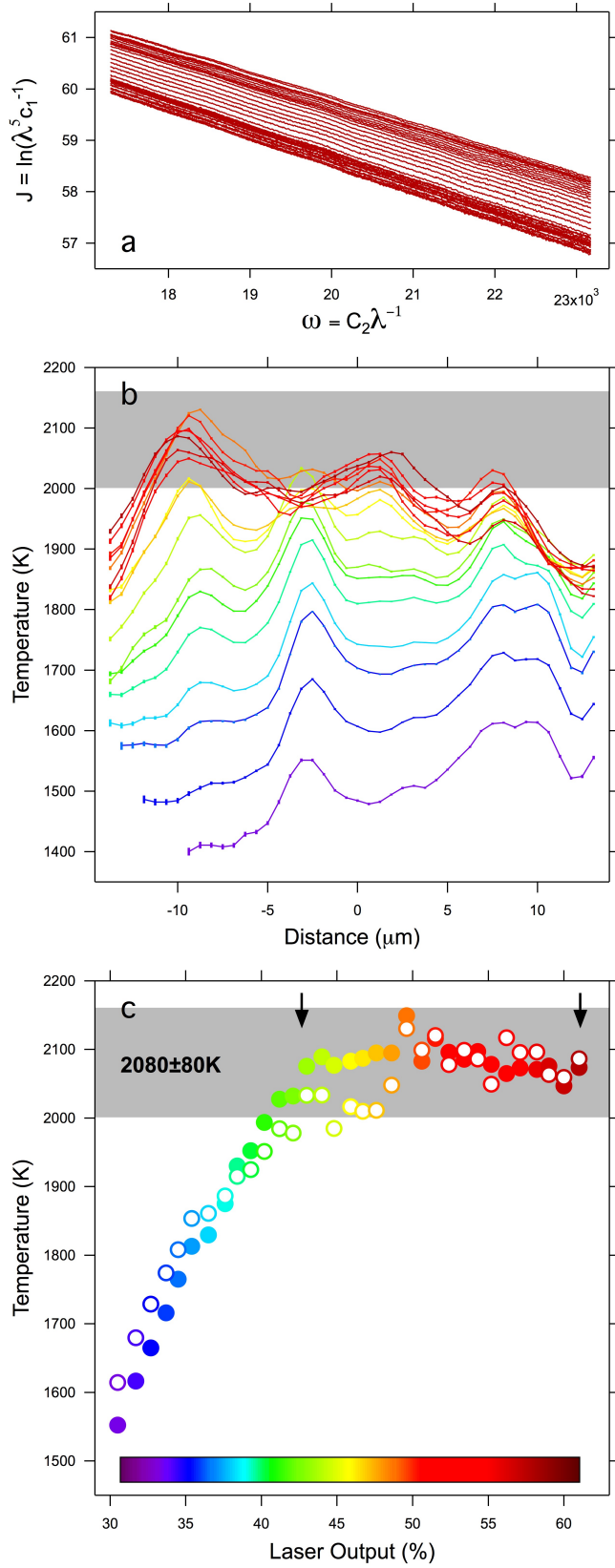
728 **Figure 1:**



729

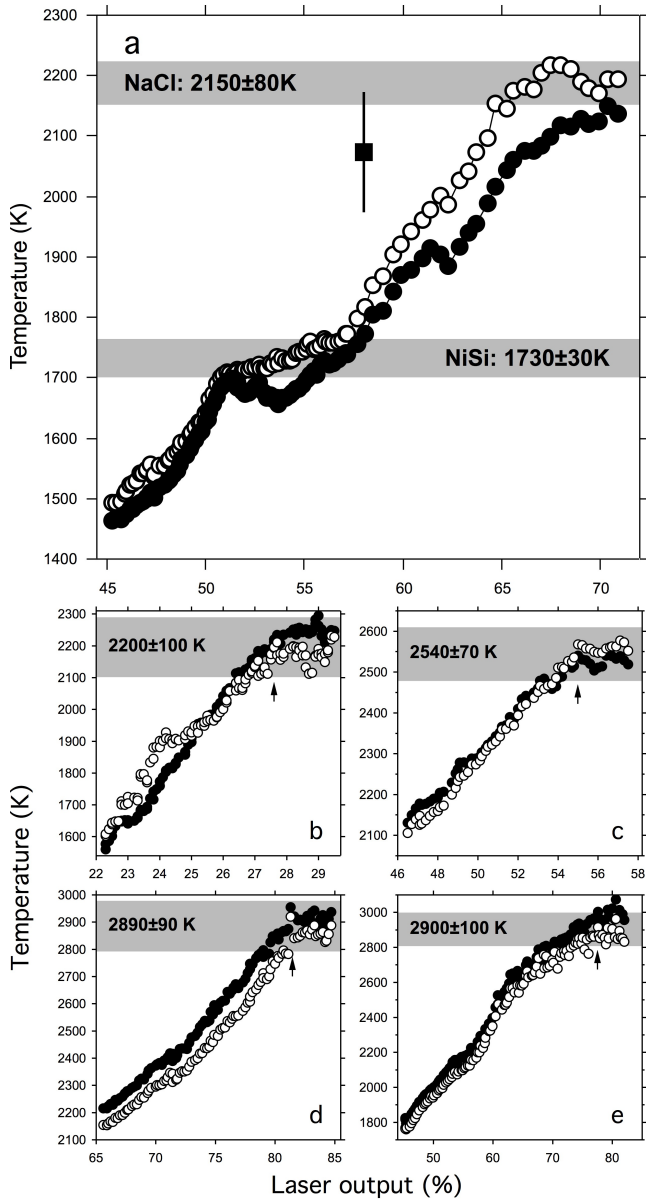
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731 **Figure 2:**



732

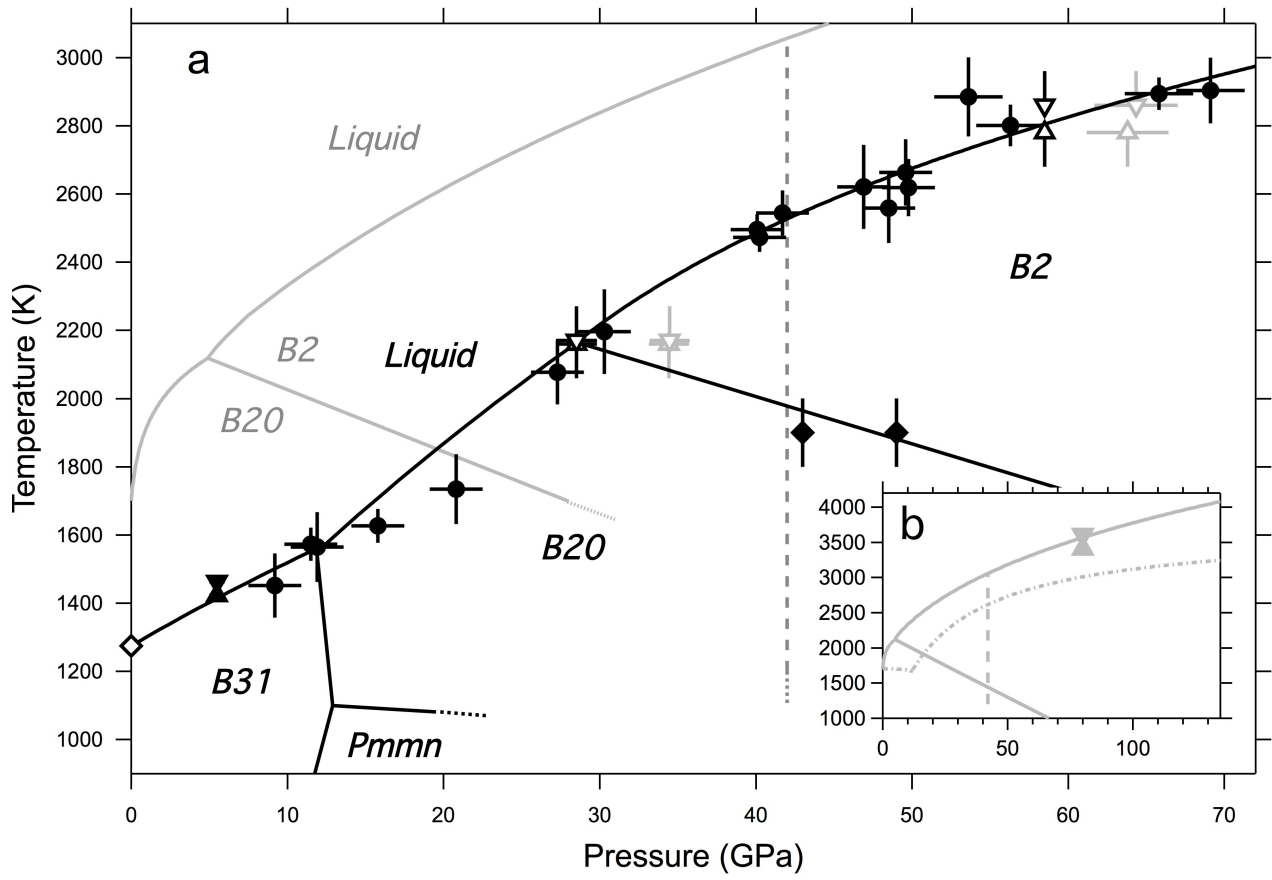
733 **Figure 3**



734

735

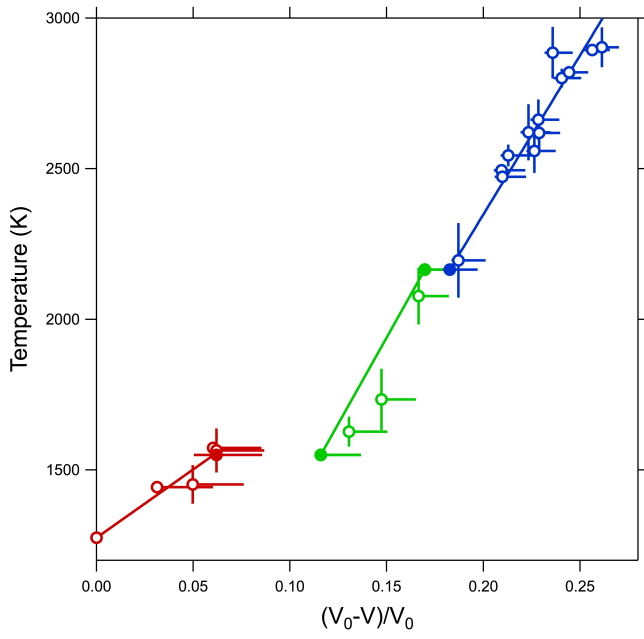
736 **Figure 4**



737

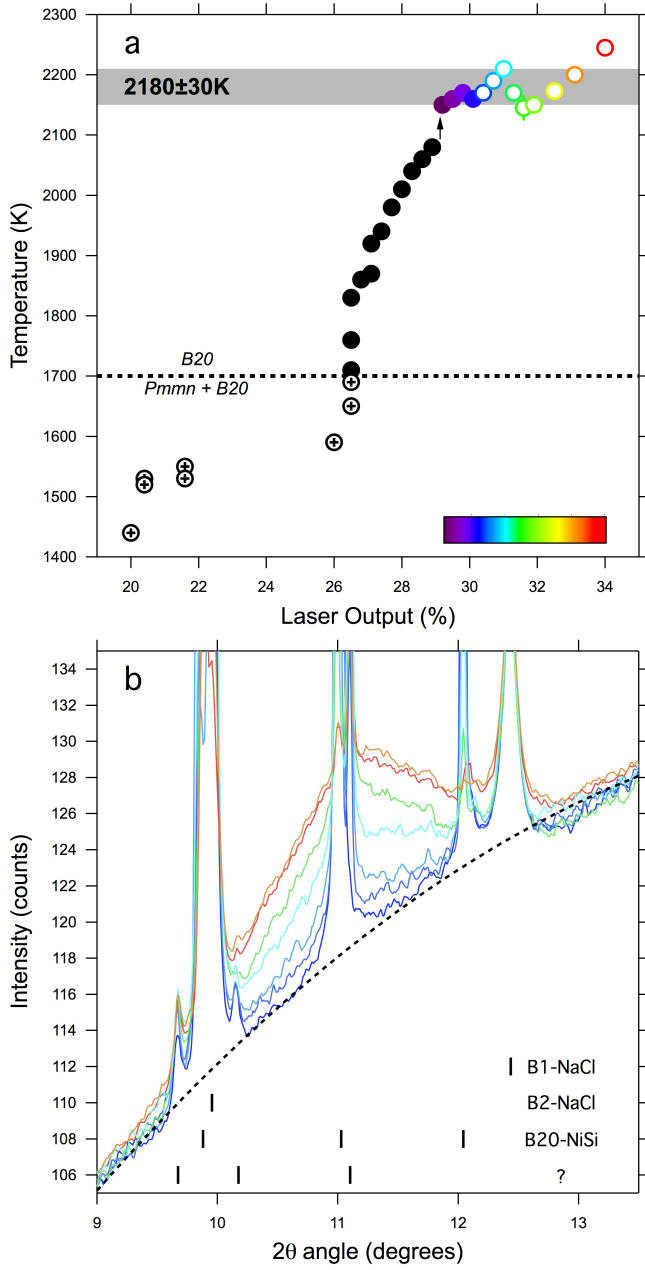
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739 **Figure 5**



740

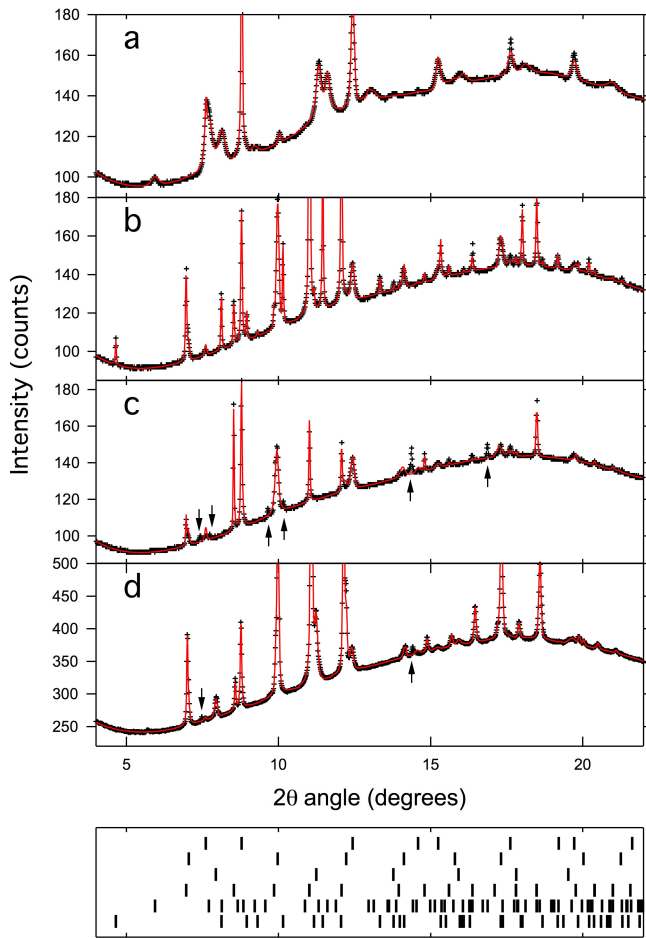
741 **Figure 6**



742

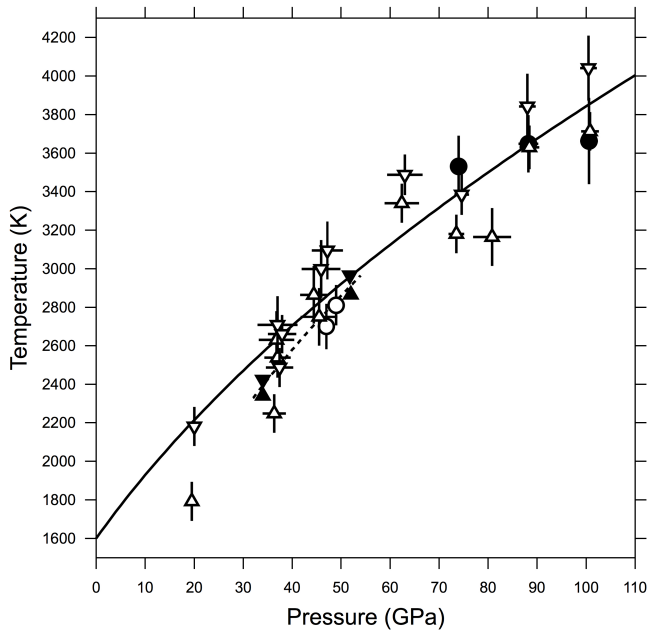
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744 **Figure 7**



745

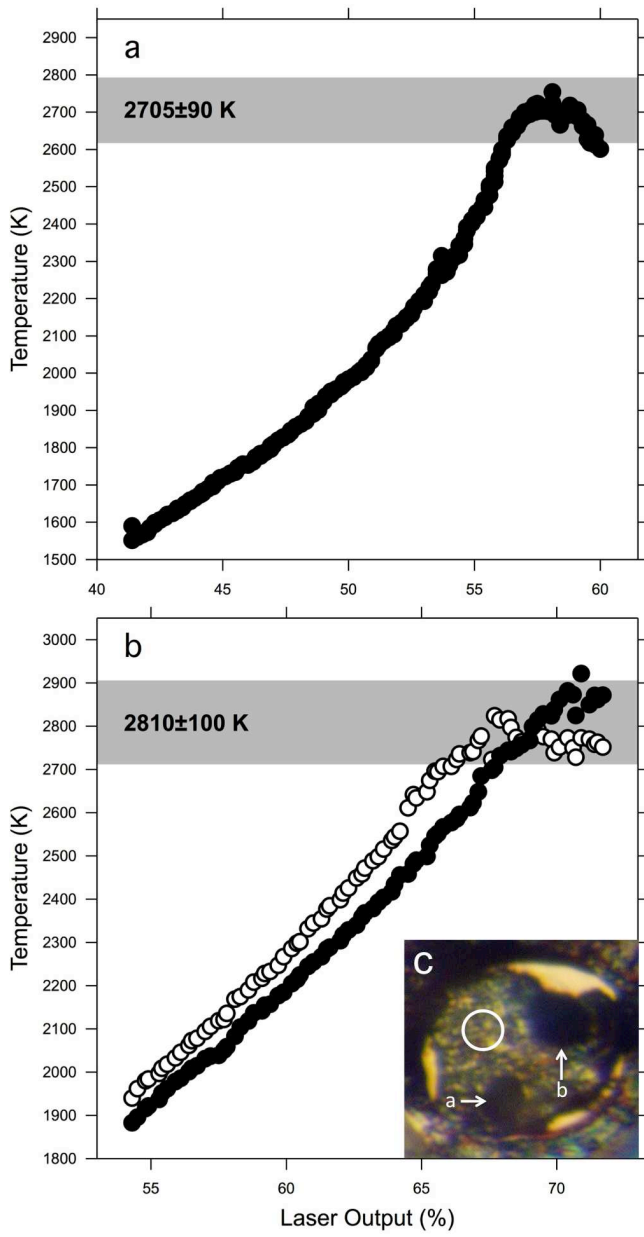
746 **Figure 8**



747

748

749 **Figure 9**



750

751

752 **Table 1:** NiSi melting data

Code	Pressure (GPa)	Temperature (K)
Off-line LH-DAC experiments (NiSi)		
24A	9.2±1.7	1452±94
26B	11.5±1.7	1573±49
26C	11.9±1.7	1565±103
25A	15.8±1.7	1627±50
25B	20.8±1.7	1734±102
25D	27.3±1.7	2077±94
40B	30.3±1.7	2196±124
57A	40.1±1.7	2495±45
57B	40.2±1.7	2473±42
28C	41.7±1.7	2544±66
25E	46.9±1.7	2621±123
28D	48.5±1.7	2559±103
57D	49.6±1.7	2663±97
57E	49.8±1.7	2619±84
28E	53.6±2.2	2885±116
57F	56.3±2.2	2801±61
57I	65.8±2.2	2894±48
29A	69.1±2.2	2903±96
<i>in situ</i> LH-DAC experiments (NiSi)		
31A	28.5±1.3	2165±61
31B	58.5±0.3	2780±92
<i>in situ</i> MAP experiments (NiSi)		
NiSi-04	5.5±1.7	1443±50
Off-line DAC experiments (Fe ₈₅ Ni ₅ Si ₁₀)		
41B	47±1.7	2705±118
41C	49±1.7	2810±136

753

754

755 **Table 2:** Fitting parameters

Phase	Simon-Glatzel			Kraut-Kennedy	
	T ₀ (K)	A (GPa)	C	T ₀ (K)	C
MnP (B31)	1275 ^{a,b}	10±5	4±1	1275 ^{a,b}	3.5±0.2
CsCl (B2)	2165 ^{a,c}	12.8±6.1	4.7±1.4	2165 ^{a,c}	4.9±0.2

^aParameters kept constant during fitting

^b(Massalski et al. 1990)

^cValue of T₀ taken from the B20 + B2 + L triple point (TP2) defined by *in situ* experiment 31A (§3).

756