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Supporting Information for

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Compression of a multiphase mantle assemblage: Effects of undesirable stress and stress annealing on the iron spin-state crossover in ferropericlase

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Contents of this file

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Figures (S1-S6), Table S1 and additional evidence supporting our discussion given in the manuscript.

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Introduction

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Below we discuss previous literature data describing spin transition in ferropericlase with focus on critical pressure of the transition (Chapter 1).

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In addition to that we present characterization of the material by various techniques (Chapter 2).

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Finally, we present our estimation on Au-Pd alloy equation of state (Chapter 3).

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1   FERROPERICLASE ($Mg_{1-x}Fe_xO$ - Fp) IRON SPIN-STATE CROSSOVER

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26   Below we present a comparative analysis of ambient single crystal and powder data for Fp

27   phase with different concentrations of iron. Special attention is dedicated to imposing objective

28   constraints on the observed iron spin-state crossover critical pressures indicating start (P_{SSC}) and

29   end of the crossover (Figure S1).

30   All data, unless specified in a figure caption, is plotted according to original data given in

31   publications or in corresponding Supplementary Information. We increased reported pressure

32   range for data of Antonangeli et al. 2011 after comparing the data with Marquardt et al. 2009 and

33   Crowhurst et al. 2005. From the analysis of C_{44} compression behaviours, we find it clear that 70

34   GPa point from Antonangeli et al 2011 is on the edge of Fp LS state and that the material may

35   have residual contribution from HS state. We changed the originally proposed range for x=0.17

36   [*Lin et al.*, 2005]. The original range for spin-state crossover (60-70 GPa) was proposed relying

37   on conclusions from [*Badro et al.*, 2003], and thus, as we believe the actual transition range was

38   misinterpreted. Indeed, in the original publication Badro et al. [2003] detect changes of the XES

39   spectra from 49 to 75 GPa, which we will use in our analysis. Most of other suggested

40   corrections are based on comparison of literature data and F-f_E plots, modified below into F-P

41   plots for clarity.

42   Inconsistencies in the iron spin-state crossover phase diagram can be attributed to low

43   number of points, high scatter of points. However, in our paper we address a major problem,

44   when starting pressures and pressure ranges for spin-state crossover are inconsistent for similar

45   compositions.

Crowhurst et al. 2008
single crystal
$x_{Fe}=0.06$

K

G

C_{44}

Fp

used

original

Marquardt et al. 2009
single crystal (C_{44})
powder (F)
$x_{Fe}=0.10$

Fp

C_{44}

F

used

original

F was calculated using $V_0=75.62(A^3)$

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Irifune et al. 2010
polycrystalline mixture
Bm+Fp

$x_{Fe}=0.11$ for Fp
KD=0.8 and P=36.4 GPa

used

original

K_D, Iron partioning coefficient

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Figure (top-left): Lin et al. 2005, powder, $x_{Fe}=0.17$. F – Normalized stress (GPa) vs Pressure (GPa). *based on data of Badro et al. 2003. used / original*. V/V_0 as a function of P was digitized. F was calculated using $V_0=1$. Fp

Figure (top-right): Antonangeli et al. 2011, single crystal, $x_{Fe}=0.17$. Elastic properties (GPa) vs Pressure (GPa). C_{44}, F. used / original. F was calculated using $V_0=75.78 (A^3)$. Fp

Figure (bottom-left): Fei et al. 2007, powder, $x_{Fe}=0.2$. F – Normalized stress (GPa) vs Pressure (GPa). used / original. F was calculated using $V_0=76.16 (A^3)$. Fp

Figure (bottom-right): Lin et al. 2005, single crystal (X-ray Emission Spect.), $x_{Fe}=0.25$. Normalized Intensity (a.u.) vs Pressure (GPa). used / original. data was digitized. Fp

Mao et al. 2011
powder
$x_{Fe}=0.25$

Fp

used
original

F was calculated using $V_0=76.34(A^3)$

Chen et al. 2012
powder
$x_{Fe}=0.35$

Fp

used
original

F was calculated using $V_0=77.24(A^3)$

Fei et al. 2007
powder
$x_{Fe}=0.39$

Fp

used
original

F was calculated using $V_0=77.48(A^3)$

Zhuravlev et al. 2010
powder
$x_{Fe}=0.39$

Fp

used
original

F was calculated using $V_0=77.4(A^3)$

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Figure S1. Literature data used for construction of Fp iron spin state crossover phase diagram. Unless otherwise stated, the data was taken from tables provided in the publications main text or in the corresponding Supplementary Information. We use the following notations: F − Normalized stress, P − pressure, V - volume, K − bulk modulus, G − shear modulus, C_{44} − crystal lattice elastic constant and $K_D = (Fe/Mg)_{Mg-Bm}/(Fe/Mg)_{Mw}$ is the iron partitioning coefficient between magnesium silicate perovskite (Bm) and Fp. The data on iron partitioning coefficient K_D was taken from [*Irifune et al.*, 2010]. For data x=0.58 of [*Fei et al.*, 2007a] we feature material phase transition from cubic to rhombohedral phase occurring at lower pressures compared with HS-LS crossover. Labels placed on figures describe iron concentration in Fp. Red shading together with region highlighted by horizontal red bar labeled as 'used' indicates iron spin state crossover used for construction of the phase diagram presented in the manuscript body. Horizontal black bar indicates pressure range originally suggested in the publications. Black lines are the eye guides.

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2 SAMPLE PREPARATION AND CHARACTERIZATION

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54   Below we show a scanning electron microphotograph of the synthesized K1297 material.

55   Image was obtained in the center of the capsule using a backscattered electrons sensor (K.E.

56   Developments) installed on XL30 Scanning Electron Microscope (SEM) at Yale University.

57   Brighter and darker areas correspond to iron rich magnesium ferropericlase phase (Fp) and

58   iron poor magnesium silicate perovskite phases (Bm), respectively.

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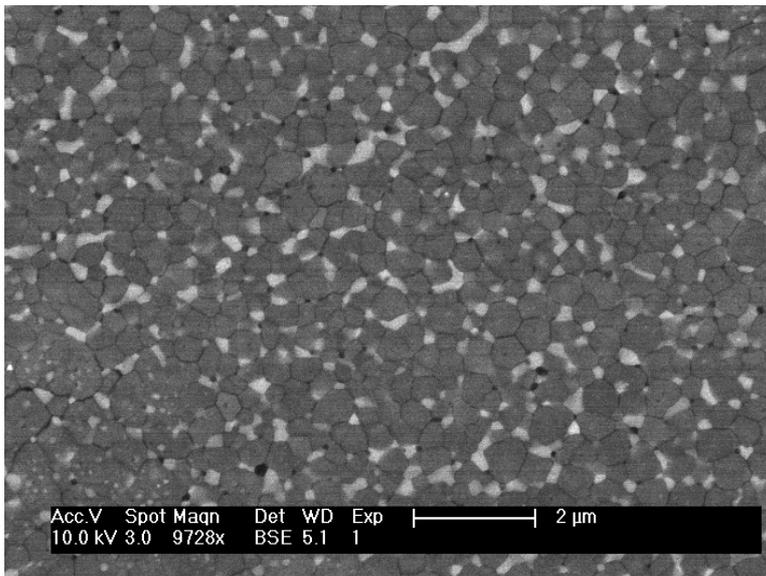
Figure S2. SEM image of the prepared material (K1297). High contrast image collected in backscattered electrons mode features two phases quenched from high pressure - high temperature conditions, namely, Bm (dark gray) and Fp (light grey). Higher brightness of Fp grains is a result of higher Fe concentration.

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61   We present additional information from our TEM EELS study and Mössbauer spectroscopy

62   study on sample characterization in the figures and table shown below.

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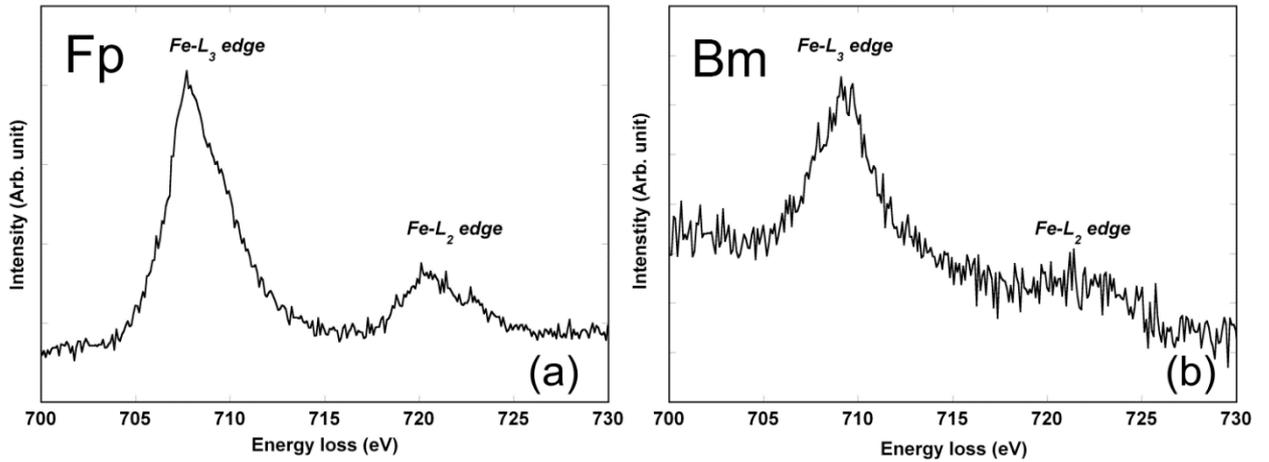
Figure S3 Fe $L_{2,3}$-edge ELNES spectra of Fp grain (a) and Bm grain (b) found in K1297 sample.
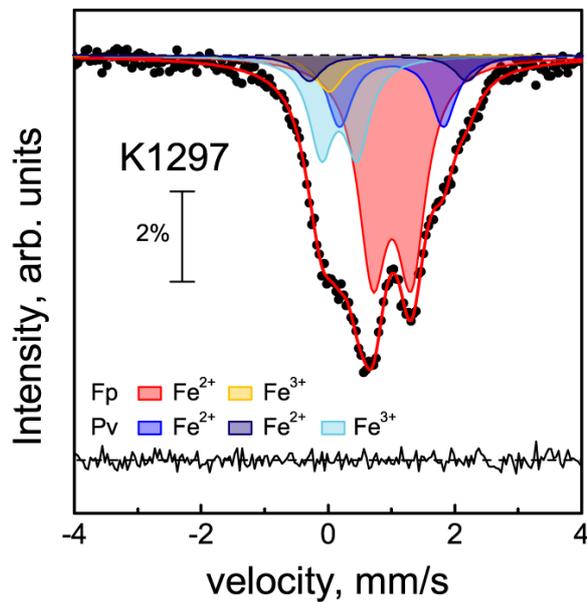
Figure S4. Mössbauer spectrum of K1297 sample collected at ambient conditions. Data points are black, and red line passing through the points represents the fit. We highlight the following contributions. Red and yellow shaded area correspond to ferrous iron and ferric iron incorporated into Fp, respectively. Blue, dark blue and light blue areas correspond to two ferrous iron positions and one ferric iron position in Bm, respectively. Black line at the bottom features the fit residuals.

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Table S1. Mössbauer parameters for sample K1297. Isomer shift (IS) values are given relative to the iron foil. QS represents quadrupole splitting. Values marked with stars were fixed or constrained during the fit of the spectrum. Area of the yellow subspectrum was constrained to 9% of the red subspectrum area during the fit and is identified by an asterisk. At the same time isomer shift of yellow subspectrum was fixed to 0.13 mm/s. This is a reasonable value for ferric iron in Fp [*Otsuka et al.*, 2010] synthesized in the multianvil at ~1800 K.

Subspectrum	Phase	IS, mm/s	QS, mm/s	Area, %
Red	Fp Fe^{2+}	1.12(1)	0.61(1)	52.8(19)
Yellow	Fp Fe^{3+}	0.13		4.8*
Blue	Bm Fe^{2+}	1.06(1)	2.48(7)	5.7(9)
Dark Blue	Bm Fe^{2+}	1.11(1)	1.63(5)	15.9(18)
Light blue	Bm Fe^{3+}	0.29(1)	0.57(2)	20.8(9)

3 AU-PD EQUATION OF STATE

In our study we employed (75wt% Au and 25wt% Pd) as capsule material in multianvil

synthesis from glass material. Composition of the material is confirmed by x-ray diffraction and

energy dispersive x-ray spectroscopy mode of scanning electron microscope XL30. Finite

amount of Au-Pd was incorporated into synthesized K1297 material and, respectively, into S2

sample.

In order to exploit this material as an X-ray diffraction pressure standard, we need to know

the relations connecting its unit cell volume and pressure, for example, its Birch-Murnaghan

equation of state. Assuming an fcc cubic lattice and ideal solid solution [*Okamoto and*

Massalski, 1985], we can estimate isothermal bulk modulus of our Au-Pd alloy through Voigt-

Reuss-Hill (VRH) and Hashin and Shtrikman bounds (HS) [*Watt et al.*, 1976]. The physical

meaning of HS bounds corresponds to a case of 'composite sphere assemblage' justifying our

approach. In order to calculate bulk modulus for the alloy, we need end-member ambient

temperature parameters, namely, isothermal bulk modulus (K_0), shear modulus (G), volume (V_0)

and bulk modulus pressure derivative (K'). We used the following parameters for gold:

87   K_0^{Au}=167 GPa, V_0^{Au}= 67.85 Å^3, $K^{,Au}$=5.77, G^{Au}=27 GPa [*Duffy et al.*, 1999; *Fei et al.*, 2007b],

88   and the following for palladium: K_0^{Pd} =193 GPa, V_0^{Pd}=58.88 Å^3, $K^{,Pd}$=5, G^{Pd}=53.3 GPa [*Rayne*,

89   1960; *Okamoto and Massalski*, 1985; *Weller et al.*, 1991].

90   In figures below we show values of bulk modulus and variation of crystallographic unit cell

91   for Au-Pd alloys as a function of Pd content at ambient conditions.

92   We calculate K_0^{Au-Pd} using Hashin and Shtrikman equations and show the corresponding

93   values (Figure S5). Volume fractions of Au and Pd end members are calculated according to a

94   linear approximation of Au and Pd contribution to the Au-Pd alloy volume. This approach is

95   justified by very small deviation of Au-Pd unit cell parameters from the Vegard's rule and by

96   insignificant error introduced by using the assumption that volume of the alloy is a linear

97   function of Au and Pd concentrations. For pressure determination using Au-Pd alloy as a

98   standard, we compute the following parameters: K_0^{Au-Pd}=176.5 GPa, V_0^{Au-Pd}= 64.29Å^3,

99     $K^{,Ad-Pd}$=5.5.

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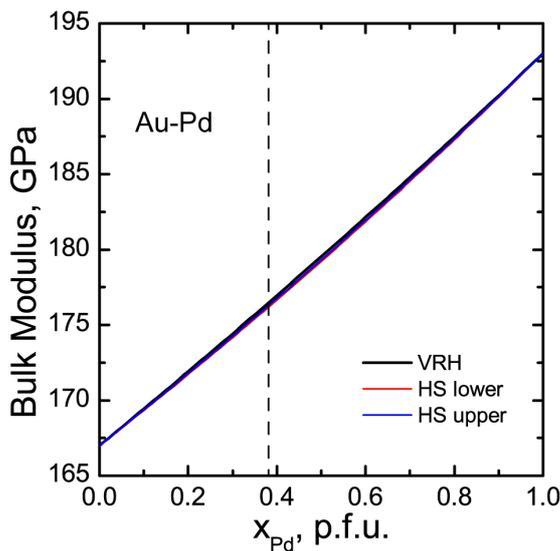
Figure S5. Variation of K_0^{Au-Pd} as a function of Pd concentration calculated within VRH, HS approximations. Vertical dashed line corresponds to our 75wt% Au and 25wt% Pd composition. Note similarity of the values calculated using Hashin-Shtrikman (HS) and Voigt-Reuss-Hill (VRH) approaches.

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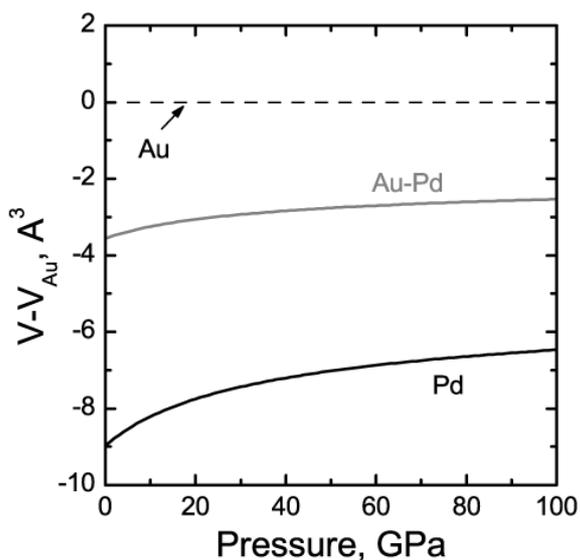
Figure S6. Relative difference of Au-Pd (75wt% Au and 25wt% Pd), Pd and Au unit cell volumes as a function of pressure. We take pure Au as a reference (dashed line).

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