AGU PUBLICATIONS

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Supporting Information for

Spin transition of iron in δ-(Al,Fe)OOH induces thermal anomalies in Earth's lower mantle

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Introduction

There are four figures and two tables that provide supporting information to the section of **Materials and Experimental Methods** in the main text. Figure S1 illustrates example comparison of the pressures obtained by the Raman spectra of ruby and diamond anvil at about 94 and 102 GPa. Figure S2 presents example TDTR data for δ-$(Al_{0.85}Fe_{0.15})OOH$ at 94 GPa along with thermal model fitting. Figure S3 shows the tests of sensitivity of our thermal model to input parameters. Figure S4 illustrates the calculated constant pressure heat capacity C_P of δ-AlOOH at 300 K under pressure. Table S1 lists the pressure dependence of the molar volume and volumetric heat capacity C_p of δ-AlOOH at 300 K by first-principles calculations. Table S2 tabulates the input parameters for the thermal model at 94 GPa.

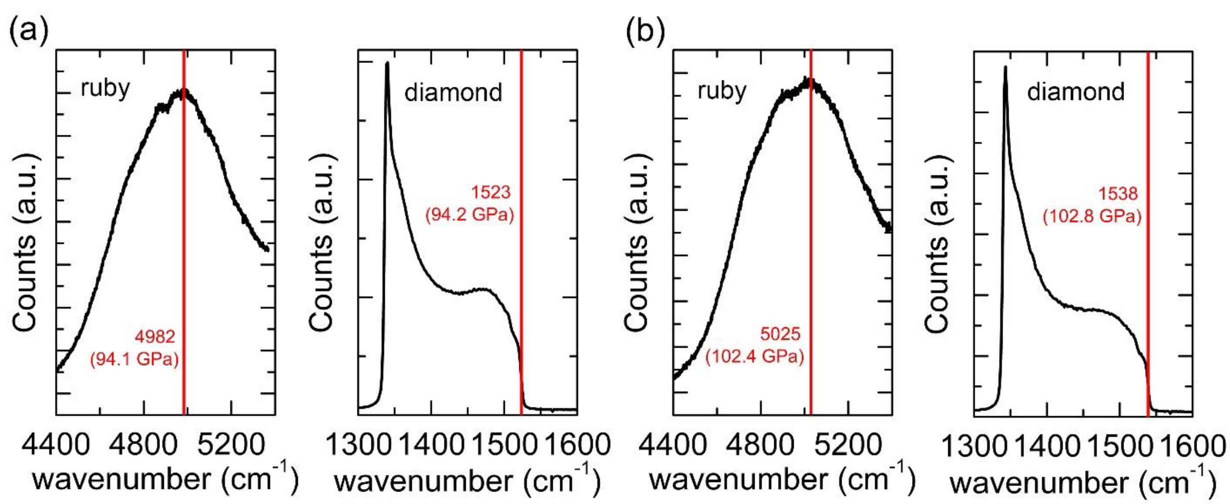

Figure S1. Comparison of example Raman spectra of ruby and diamond anvil at about (a) 94 GPa and (b) 102 GPa, respectively. Red vertical lines indicate the wavenumber positions of the ruby peak and diamond anvil edge, whose values and the corresponding pressures are labeled next to the vertical line. The uncertainty of pressure due to the uncertainty of the wavenumber positions of the peak and edge is typically less than 2–3 GPa.

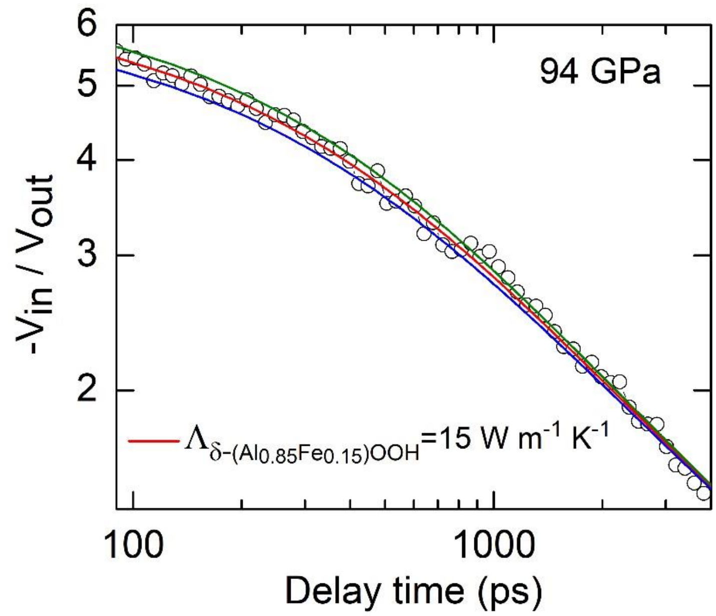

Figure S2. Example TDTR data for the temporal variation of ratio $-V_{in}/V_{out}$ (open circles) for δ-($Al_{0.85}Fe_{0.15}$)OOH at 94 GPa along with the fitting by the calculation of heat diffusion model (red curve). A thermal conductivity $\Lambda_{\delta\text{-}(Al0.85Fe0.15)OOH}$ =15 W m^{-1} K^{-1} provides a best-fit to the data using input parameters listed in Table S2. Under our experimental conditions, the ratio $-V_{in}/V_{out}$ is sensitive to the $\Lambda_{\delta\text{-}(Al0.85Fe0.15)OOH}$ during delay time of few hundred picoseconds, in particular, between 100 and 500 ps [*Cahill andWatanabe*, 2004; *Zheng et al.*, 2007]. A 10% variation in Λ (green curve with Λ=16.5 W m^{-1} K^{-1} and blue curve with Λ=13.5 W m^{-1} K^{-1}) shows a clear deviation from the best-fit to the data, indicating the heat diffusion model fitting and the derived $\Lambda_{\delta\text{-}(Al0.85Fe0.15)OOH}$ are precise and reliable due to the high quality data and sample geometry.

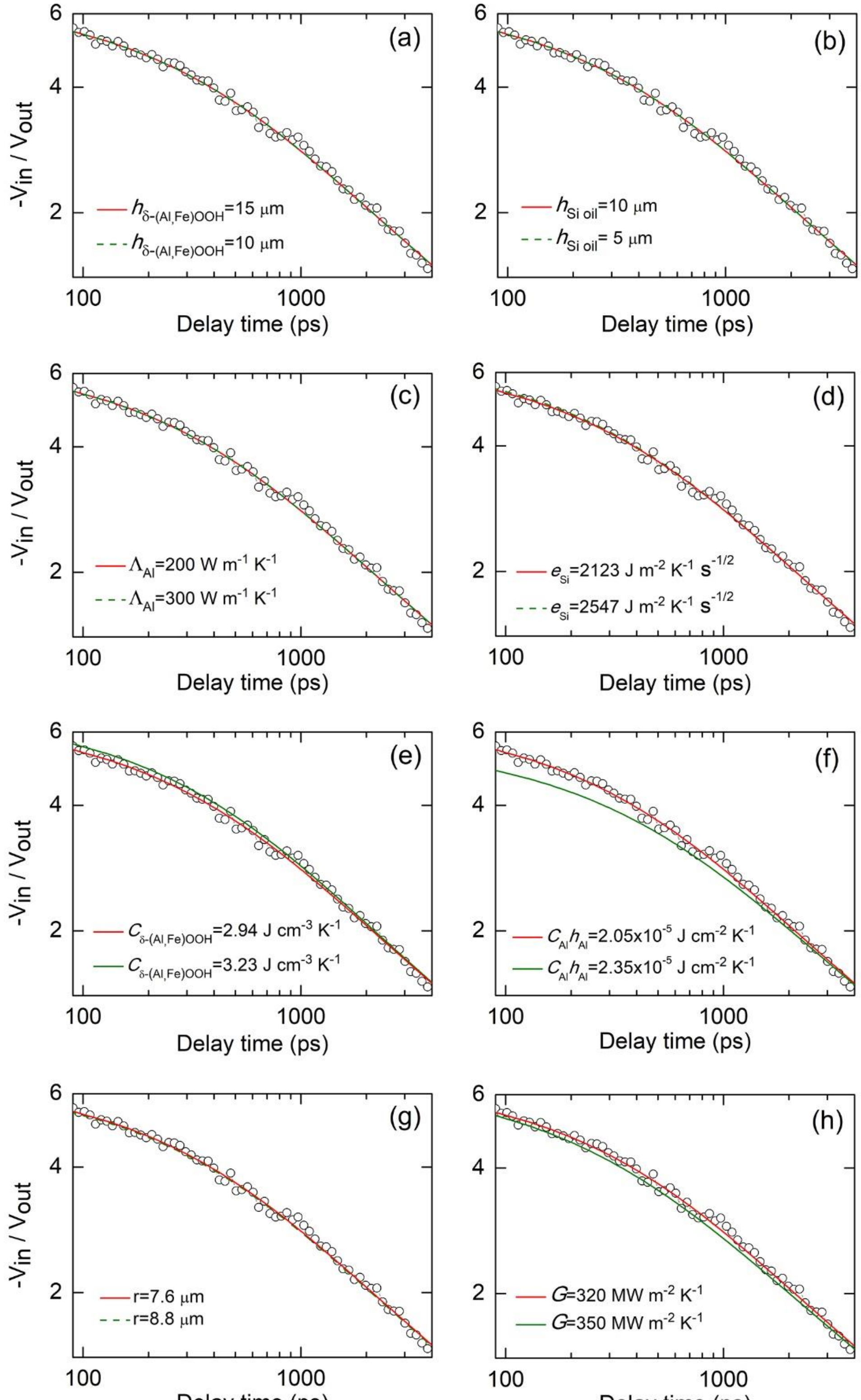

Figure S3. Tests of sensitivity of the thermal model to input parameters for δ-($Al_{0.85}Fe_{0.15}$)OOH at 94 GPa . Here we fix the δ-($Al_{0.85}Fe_{0.15}$)OOH thermal conductivity $\Lambda_{\delta\text{-(Al0.85Fe0.15)OOH}}$ to be 15 W m^{-1} K^{-1}, as derived in Fig. S2, using input parameters listed in Table S2. (a) and (b) Assuming variations in the thicknesses of δ-$(Al_{0.85}Fe_{0.15})OOH$ ($h_{\delta\text{-}(Al0.85Fe0.15)OOH}$) and silicone oil ($h_{Si\ oil}$), respectively, were as large as 50%, our heat diffusion model calculations show identical fits to the data, indicating that the derived $\Lambda_{\delta\text{-}(Al0.85Fe0.15)OOH}$ is not affected by uncertainties in the $h_{\delta\text{-}(Al0.85Fe0.15)OOH}$ and $h_{Si\ oil}$. (c) With a large Al thermal conductivity, Λ_{Al}, it has essentially no effect on the derived $\Lambda_{\delta\text{-}(Al0.85Fe0.15)OOH}$. (d) An example 20% variation in the thermal effusivity of the pressure medium silicone oil, $e_{Si}=(\Lambda_{Si}C_{Si})^{1/2}$, still shows nearly identical model calculation, indicating that its uncertainty does not affect the derived $\Lambda_{\delta\text{-}(Al0.85Fe0.15)OOH}$. (e) An example 10% uncertainty in the volumetric heat capacity of δ-$(Al_{0.85}Fe_{0.15})OOH$, $C_{\delta\text{-}(Al0.85Fe0.15)OOH}$, (2.94 to 3.23 J cm^{-3} K^{-1}) only slightly deviates the model calculation from the data, which requires $\Lambda_{\delta\text{-}(Al0.85Fe0.15)OOH}$ to decrease slightly to 13.8 W m^{-1} K^{-1} to re-fit the data, i.e., propagating approximately 8% uncertainty to the derived $\Lambda_{\delta\text{-}(Al0.85Fe0.15)OOH}$. (f) The major measurement uncertainty is from the uncertainty in Al heat capacity per unit area (product of volumetric heat capacity and thickness, $C_{Al}\,h_{Al}$) since the ratio $-V_{in}/V_{out}$ at few hundred ps delay time scales inversely with the $C_{Al}\,h_{Al}$[*Zheng et al.*, 2007]. An example 15% uncertainty requires approximately 20% change in the $\Lambda_{\delta\text{-}(Al0.85Fe0.15)OOH}$ to re-fit the data. (g) Laser spot size changed by as large as 15% (7.6 to 8.8 μm) still offers identical model calculation, i.e., the uncertainty in laser spot size does not affect the derived $\Lambda_{\delta\text{-}(Al0.85Fe0.15)OOH}$. (h) Variations in the thermal conductance of Al/δ-$(Al_{0.85}Fe_{0.15})OOH$ interface and Al/silicone oil interface, *G*, only slightly affect the derived $\Lambda_{\delta\text{-}(Al0.85Fe0.15)OOH}$. Variations in *G* mostly change the slope of model calculation at delay times longer than 1000 ps [*Cahill andWatanabe*, 2004; *Zheng et al.*, 2007]. An example 10% uncertainty has already caused the model calculation deviating from the data, in particular after 1000 ps. The uncertainty in *G* is typically less than 10%, which only produces 2% uncertainty in the derived $\Lambda_{\delta\text{-}(Al0.85Fe0.15)OOH}$.

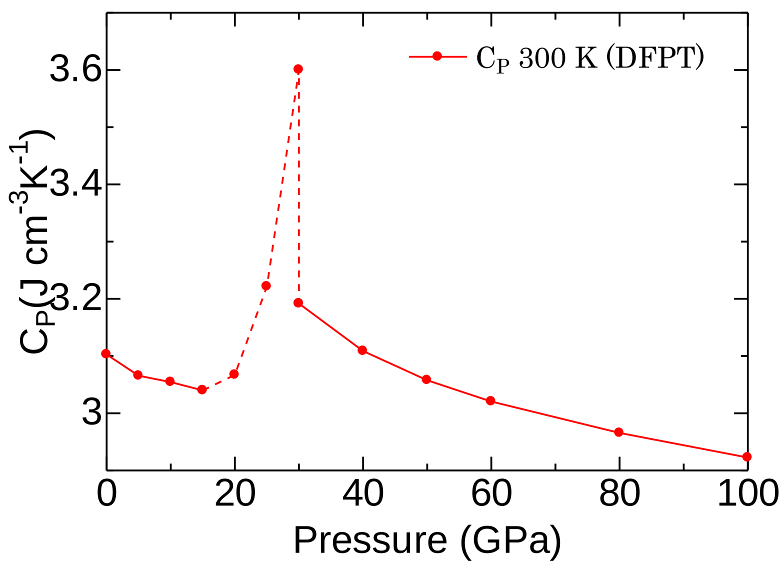

Figure S4. The calculated constant pressure heat capacity C_P of δ-AlOOH at 300 K under pressure. The anomalous results due to the invalidity of QHA are indicated by dashed line at 15–30 GPa.

Table S1. Pressure dependence of the molar volume and volumetric heat capacity C_p of δ-AlOOH at 300 K by first-principles calculations.

P (GPa)	Volume (cm^3 mol^{-1})	C_p (J cm^{-3} K^{-1})
0	17.43924596	3.102732
5	16.92477701	3.065517
10	16.47870993	3.054462
15	16.11754168	3.039949
20	15.78309324	3.067219
25	15.48102816	3.221479
30	15.2305234	3.600329
30	15.2305234	3.191781
40	14.79359593	3.108771
50	14.40854389	3.057658
60	14.06633442	3.020453
80	13.47318625	2.965579
100	12.97673403	2.922546

Table S2. Input parameters for the bi-directional heat diffusion model at 94 GPa

P	$C_{\delta\text{-(Al0.85Fe0.15)OOH}}$	C_{Al}	h_{Al}	$e_{si} =(\Lambda_{Si}C_{Si})^{1/2}$	r	$h_{\delta\text{-(Al0.85Fe0.15)OOH}}$/ $h_{Si\ oil}$	Λ_{Al}	G
GPa	J cm^{-3} K^{-1}	J cm^{-3} K^{-1}	nm*	J m^{-2} K^{-1} $s^{-1/2}$	µm	µm	W m^{-1} K^{-1}	MW m^{-2} K^{-1}
94	2.94	2.684	76.2	2123	7.6	15/10	200	320

*In this experimental run, the Al thickness at ambient pressure is 93.1 nm measured by *in situ* picosecond acoustics.

$C_{\delta\text{-(Al0.85Fe0.15)OOH}}$: δ-$(Al_{0.85}Fe_{0.15})OOH$ heat capacity (calculated in this study), C_{Al}: Al heat capacity [*Hsieh et al.*, 2009], h_{Al}: Al thickness (calculated from Ref [*Chen et al.*, 2011]), e_{si}: silicone oil thermal effusivity [*Hsieh*, 2015], r: laser spot size (measured in this study), $h_{\delta\text{-(Al0.85Fe0.15)OOH}}$: δ-$(Al_{0.85}Fe_{0.15})OOH$ thickness (measured in this study), $h_{Si\ oil}$: silicone oil thickness (measured in this study), Λ_{Al}: Al thermal conductivity [*Hsieh et al.*, 2009], G: Thermal conductance of Al/δ-$(Al_{0.85}Fe_{0.15})OOH$ and Al/silicone oil interfaces (measured in this study).