

Oxidised iron in garnets from the mantle transition zone

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Extended Data Table 1. **Hyperfine parameters of the garnet inclusions.**

Components	JF-1A		JF-9A		JF-37A		JF-37B	
	Fe ²⁺	Fe ³⁺	Fe ²⁺	Fe ³⁺	Fe ²⁺	Fe ³⁺	Fe ²⁺	Fe ³⁺
	X-site	Y-site	X-site	Y-site	X-site	Y-site	X-site	Y-site
CS (mm/s)	1.285(3)	0.34(4)	1.282(5)	0.26(6)	1.280(5)	0.35(7)	1.278(4)	0.28(6)
FWHM (mm/s)	0.26(2)	0.25(17)	0.27(3)	0.2(2)	0.25(3)	0.25	0.24(2)	0.4(3)
Int (%)	87(3)	13(3)	88(3)	12(3)	91(5)	9(5)	86(3)	14(3)
QS (mm/s)	3.547(6)	0.33(8)	3.55(1)	0.48(8)	3.551(9)	0.2(2)	3.552(7)	0.4(1)
a12	0.480(7)	–	0.48(1)	–	0.481(9)	–	0.477(9)	–

Components	JF-39A		JF-42A		JF-44B		JF-50A	
	Fe ²⁺	Fe ³⁺	Fe ²⁺	Fe ³⁺	Fe ²⁺	Fe ³⁺	Fe ²⁺	Fe ³⁺
	X-site	Y-site	X-site	Y-site	X-site	Y-site	X-site	Y-site
CS (mm/s)	1.259(3)	0.282(15)	1.279(4)	0.34(4)	1.290(7)	0.38(5)	1.279(2)	0.31(3)
FWHM (mm/s)	0.20(2)	0.21(15)	0.25(2)	0.28(13)	0.23(5)	0.2(2)	0.236(16)	0.20(13)
Int (%)	77.9(12)	22.1(12)	81(2)	19(2)	83(4)	17(4)	90.8(15)	9.2(15)
QS (mm/s)	3.524(6)	0.39(2)	3.545(7)	0.45(5)	3.519(13)	0.30(9)	3.548(5)	0.35(6)
a12	0.487(7)	–	0.471(8)	–	0.475(14)	–	0.474(5)	–

Components	JF-55A		JF-58A		JF-58B		JF-84A	
	Fe ²⁺	Fe ³⁺	Fe ²⁺	Fe ³⁺	Fe ²⁺	Fe ³⁺	Fe ²⁺	Fe ³⁺
	X-site	Y-site	X-site	Y-site	X-site	Y-site	X-site	Y-site
CS (mm/s)	1.248(6)	0.31(2)	1.273(3)	0.32(3)	1.282(9)	0.320	1.275(6)	0.320
FWHM (mm/s)	0.25(4)	0.14(6)	0.25(2)	0.29(14)	0.24(7)	0.34(24)	0.23(4)	0.2(2)
Int (%)	67(3)	33(3)	83(2)	17(2)	71(5)	29(5)	84(4)	16(4)
QS (mm/s)	3.516(12)	0.42(3)	3.528(7)	0.30(8)	3.52(2)	0.3(1)	3.545(12)	0.51(8)
a12	0.477(13)	–	0.484(8)	–	0.50(2)	–	0.459(12)	–

Components	JF-22A		
	Fe ²⁺	Fe ³⁺	Fe ²⁺
	X-site	Y-site	cpx
CS (mm/s)	1.226(12)	0.27(7)	1.15(8)
FWHM (mm/s)	0.26(8)	0.3(2)	0.300
Int (%)	47(5)	29(4)	24(4)
QS (mm/s)	3.493(25)	0.300	2.07(16)
a12	–	–	–

CS: centre shift relative to α -Fe, FWHM: full width at half maximum of the absorber line, Int: relative area, QS: quadrupole splitting, a12: doublet area asymmetry.

Extended Data Table 2. **Crystal structure data of garnet inclusions**

Inclusion	JF-1A	JF-9A	JF-22A	JF-37A	JF-37B	JF-39A	JF-42A	JF-44B
Chemical formula	Al _{1.925} Ca _{0.478} Fe _{0.777} Mg _{1.82} Si ₃ O ₁₂	Al _{1.952} Ca _{0.474} Fe _{0.838} Mg _{1.736} Si ₃ O ₁₂	Al _{1.847} Ca _{0.444} Fe _{0.702} Mg _{2.006} Si ₃ O ₁₂	Al _{1.948} Ca _{0.501} Fe _{0.78} Mg _{1.77} Si ₃ O ₁₂	Al _{1.938} Ca _{0.497} Fe _{0.792} Mg _{1.773} Si ₃ O ₁₂	Al _{1.886} Ca _{0.45} Fe _{0.631} Mg _{2.033} Si ₃ O ₁₂	Al _{1.875} Ca _{0.883} Fe _{0.808} Mg _{1.435} Si ₃ O ₁₂	Al _{1.893} Ca _{0.616} Fe _{0.716} Mg _{1.775} Si ₃ O ₁₂
Crystal system, space group	Cubic, $la\bar{3}d$							
Temperature (K)	293							
<i>a</i> (Å)	11.54866 (9)	11.54697 (8)	11.56570 (8)	11.55093 (7)	11.55114 (8)	11.54816 (9)	11.61383 (8)	11.57482 (7)
<i>V</i> (Å ³)	1540.26 (2)	1539.59 (2)	1547.09 (2)	1541.17 (2)	1541.25 (2)	1540.06 (2)	1566.49 (2)	1550.75 (2)
<i>Z</i>	8							
<i>F</i> (000)	1717	1723	1706	1719	1720	1695	1746	1719
Radiation type	Synchrotron, $\lambda = 0.29464$ Å							
μ (mm ⁻¹)	0.26	0.27	0.25	0.26	0.26	0.24	0.28	0.26
Crystal size (mm)	0.16 × 0.10 × 0.03	0.16 × 0.10 × 0.02	0.11 × 0.07 × 0.02	0.13 × 0.10 × 0.05	0.17 × 0.10 × 0.05	0.23 × 0.15 × 0.05	0.12 × 0.12 × 0.07	0.08 × 0.08 × 0.02
No. of measured, independent and observed [<i>I</i> > 3σ(<i>I</i>)] reflections	4006, 464, 398	3184, 456, 398	4116, 448, 417	4296, 443, 394	3477, 439, 376	3614, 438, 380	4095, 447, 381	3970, 448, 381
<i>R</i> _{int}	0.021	0.028	0.030	0.026	0.023	0.015	0.023	0.025
θ values (°)	$\theta_{\max} = 16.8,$ $\theta_{\min} = 1.8$	$\theta_{\max} = 16.9,$ $\theta_{\min} = 1.8$	$\theta_{\max} = 16.9,$ $\theta_{\min} = 1.8$	$\theta_{\max} = 16.9,$ $\theta_{\min} = 1.8$	$\theta_{\max} = 16.8,$ $\theta_{\min} = 1.8$	$\theta_{\max} = 17.0,$ $\theta_{\min} = 1.8$	$\theta_{\max} = 16.9,$ $\theta_{\min} = 1.8$	$\theta_{\max} = 16.7,$ $\theta_{\min} = 1.8$
(sin θ/λ) _{max} (Å ⁻¹)	0.982	0.985	0.984	0.985	0.982	0.989	0.984	0.975
Range of <i>h</i> , <i>k</i> , <i>l</i>	<i>h</i> = -21→19, <i>k</i> = -19→9, <i>l</i> = -21→21	<i>h</i> = -16→6, <i>k</i> = -20→19, <i>l</i> = -17→21	<i>h</i> = -16→19, <i>k</i> = -21→20, <i>l</i> = -21→16	<i>h</i> = -8→17, <i>k</i> = -18→20, <i>l</i> = -19→19	<i>h</i> = -20→21, <i>k</i> = -21→19, <i>l</i> = -15→9	<i>h</i> = -14→19, <i>k</i> = -21→20, <i>l</i> = -21→17	<i>h</i> = -21→20, <i>k</i> = -5→15, <i>l</i> = -20→20	<i>h</i> = -21→13, <i>k</i> = -19→18, <i>l</i> = -21→18
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.023, 0.030, 1.60	0.027, 0.033, 1.89	0.028, 0.037, 2.38	0.020, 0.031, 1.85	0.022, 0.030, 1.56	0.026, 0.035, 1.95	0.022, 0.031, 1.70	0.024, 0.032, 1.86
No. of parameters	20							
No. of restraints	0							
No. of constraints	8							
CCDC reference No.	1588374	1588375	1588376	1588377	1588378	1588379	1588380	1588381

Extended Data Table 2. **Crystal structure data of garnet inclusions (continued).**

Inclusion	JF-50A	JF-55A	JF-58A	JF-58B	JF-84A
Chemical formula	Al _{1.938} Ca _{0.377} Fe _{0.815} Mg _{1.871} Si ₃ O ₁₂	Al _{1.855} Ca _{0.57} Fe _{0.56} Mg _{2.015} Si ₃ O ₁₂	Al _{1.894} Ca _{0.36} Fe _{0.886} Mg _{1.86} Si ₃ O ₁₂	Al _{1.882} Ca _{0.355} Fe _{0.89} Mg _{1.873} Si ₃ O ₁₂	Al _{1.908} Ca _{0.493} Fe _{0.722} Mg _{1.877} Si ₃ O ₁₂
Crystal system, space group	Cubic, $la\bar{3}d$				
Temperature (K)	293				
<i>a</i> (Å)	11.53228 (7)	11.57663 (7)	11.53956 (7)	11.54779 (18)	11.55837 (9)
<i>V</i> (Å ³)	1533.72 (2)	1551.48 (2)	1536.62 (2)	1539.91 (4)	1544.15 (2)
<i>Z</i>	8				
<i>F</i> (000)	1715	1698	1721	1721	1712
Radiation type	Synchrotron, $\lambda = 0.29464$ Å				
μ (mm ⁻¹)	0.26	0.23	0.27	0.27	0.25
Crystal size (mm)	0.22 × 0.18 × 0.08	0.20 × 0.10 × 0.08	0.30 × 0.30 × 0.30	0.18 × 0.10 × 0.03	0.09 × 0.06 × 0.02
No. of measured, independent and observed [<i>I</i> > 3σ(<i>I</i>)] reflections	3646, 420, 366	4193, 438, 392	3732, 440, 394	4173, 440, 361	4306, 412, 357
<i>R</i> _{int}	0.022	0.021	0.034	0.021	0.026
θ values (°)	$\theta_{\max} = 16.8,$ $\theta_{\min} = 1.8$	$\theta_{\max} = 16.8,$ $\theta_{\min} = 1.8$	$\theta_{\max} = 17.0,$ $\theta_{\min} = 1.8$	$\theta_{\max} = 16.7,$ $\theta_{\min} = 1.8$	$\theta_{\max} = 16.9,$ $\theta_{\min} = 1.8$
(sin θ/λ) _{max} (Å ⁻¹)	0.983	0.983	0.992	0.974	0.984
Range of <i>h</i> , <i>k</i> , <i>l</i>	<i>h</i> = -6→15, <i>k</i> = -21→22, <i>l</i> = -21→21	<i>h</i> = -21→22, <i>k</i> = -22→21, <i>l</i> = -13→6	<i>h</i> = -22→15, <i>k</i> = -21→21, <i>l</i> = -15→20	<i>h</i> = -22→21, <i>k</i> = -21→20, <i>l</i> = -17→12	<i>h</i> = -18→9, <i>k</i> = -22→21, <i>l</i> = -21→22
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.027, 0.036, 2.09	0.027, 0.036, 2.34	0.023, 0.032, 1.81	0.031, 0.038, 2.07	0.022, 0.029, 1.77
No. of parameters	20				
No. of restraints	0				
No. of constraints	8				
CCDC reference No.	1588382	1588383	1588384	1588385	1588386

The chemical formula is the obtained model (see Methods) used for the crystal structure refinement. The constraints are (i) fixed amount of Ca, (ii) identical anisotropic displacement parameters (ADP), and (iii) fixed total occupation number (equal to 1) for atoms populating the same crystallographic position.

Extended Data Table 3. **X-ray refinement of Fe³⁺ content of sample JF22a.**

X-site	Y-site	Fe ³⁺ /ΣFe (%)
Fully occupied Ca amount fixed to microprobe data Mg occupancy refined	Fully occupied Mg, Si, Al refined as single Al atom	21.8(4)
Fully occupied Mg amount fixed to microprobe data Ca occupancy refined.	Fully occupied Mg, Si, Al refined as single Al atom	21.7(4)
Fully occupied Mg occupancy refined Fe occupancy refined	Fully occupied Mg, Si, Al refined as single Al atom	21.5(4)
Fully occupied Ca amount fixed to microprobe data Mg occupancy refined	Fully occupied Mg and Si amount fixed to microprobe data Al and Fe occupancy refined	22.3(4)
Fully occupied Ca amount fixed to microprobe data Mg occupancy refined	Fully occupied Al amount fixed to microprobe data Mg and Si constrained to have same abundance Fe and (Mg+Si) amounts refined	22.1(4)

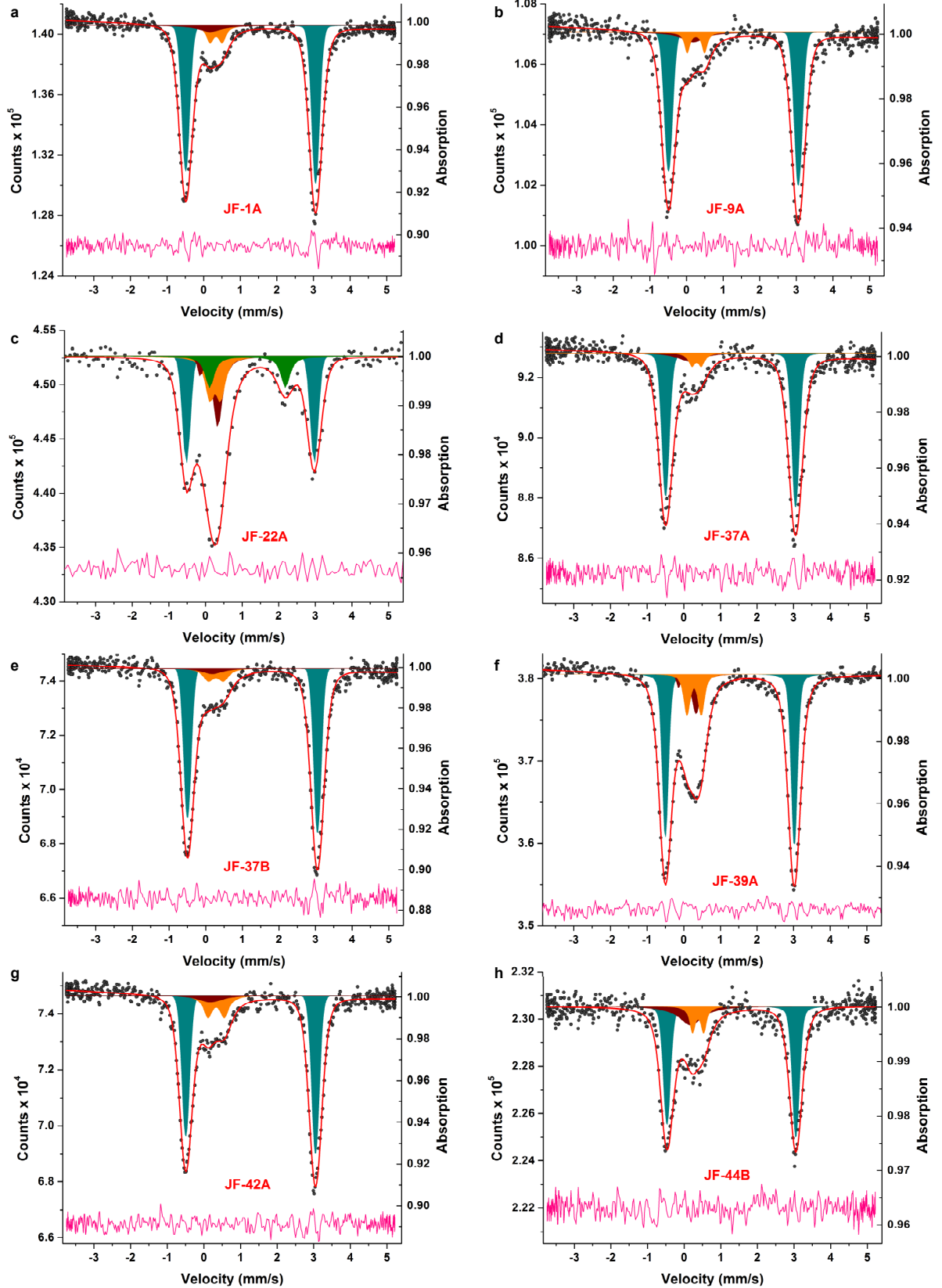
Rows indicate different refinements of single crystal diffraction data using the indicated constraints.

Extended Data Table 4. **Inclusion compositions.**

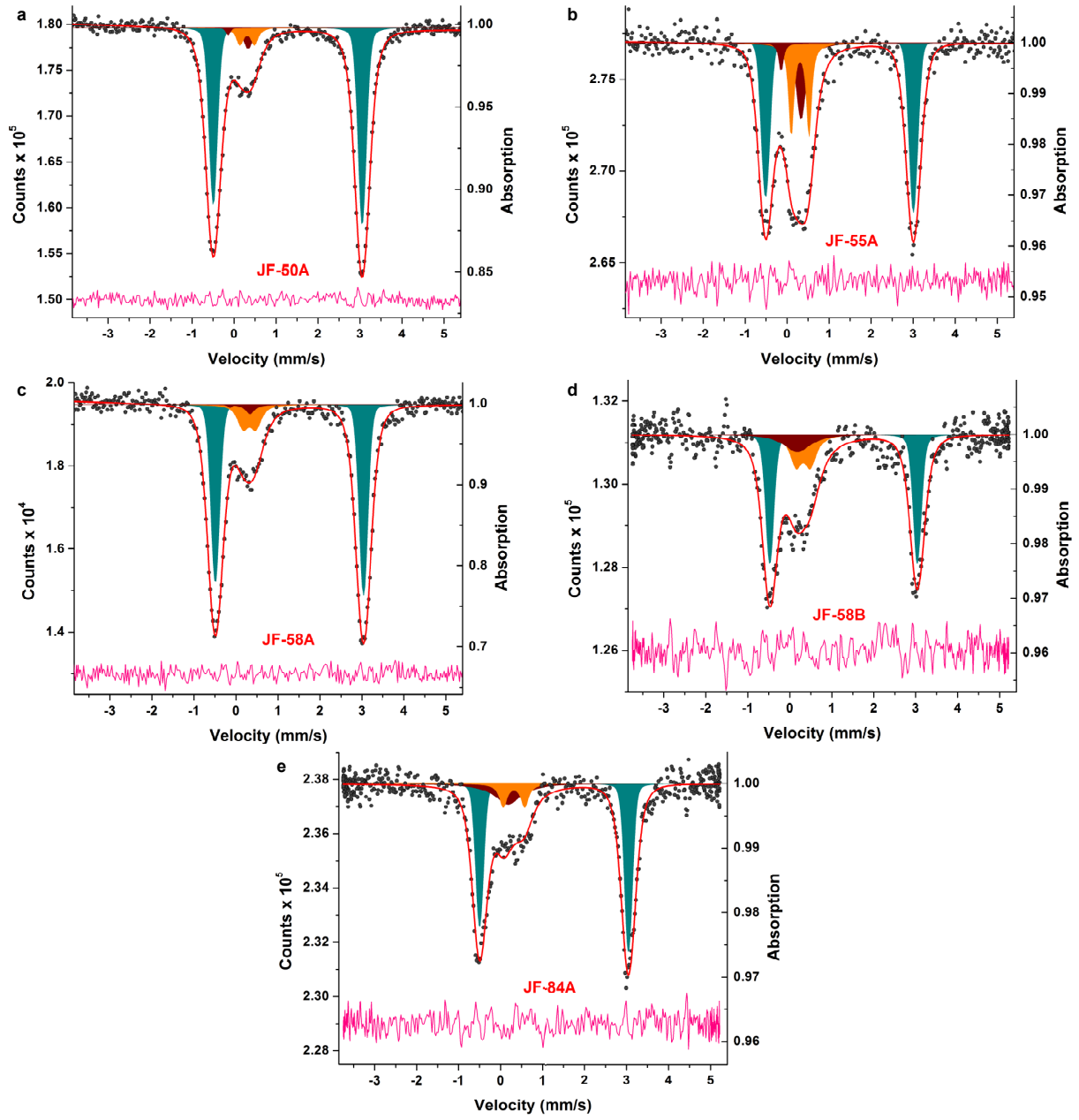
Sample	Pressure (GPa)	Si (pfu)	Mg (pfu)	Al (pfu)	Ca (pfu)	Fe (pfu)	Fe by XRD (pfu)	Fe ³⁺ /Fe _{tot} by MS (%)	Y-site Fe/Fe _{tot} by XRD (%)	Fe ³⁺ /Fe _{tot} by EMPA (%)
JF-37B	7.7	3.08(3)	1.82(2)	1.77(2)	0.50(1)	0.79(1)	0.79	12(3)	7.8(4)	11(6)
JF-37A	7.7	3.08(3)	1.83(2)	1.77(2)	0.50(1)	0.79(1)	0.78	8(5)	6.7(4)	11(6)
JF-09A	7.9	3.08(3)	1.75(2)	1.80(2)	0.48(1)	0.86(1)	0.84	11(3)	5.7(3)	10(6)
JF-50A	7.9	3.08(3)	1.91(2)	1.79(2)	0.38(1)	0.80(1)	0.82	8(1)	7.6(4)	10(6)
JF-01A	8.1	3.11(3)	1.90(2)	1.71(2)	0.48(1)	0.77(1)	0.78	12(2)	9.7(4)	13(7)
JF-58B	9.9	3.16(3)	1.99(2)	1.57(2)	0.36(1)	0.89(1)	0.89	27(5)	13.3(3)	17(10)
JF-44B	10.2	3.19(3)	1.91(2)	1.52(2)	0.62(1)	0.71(1)	0.72	15(3)	14.9(3)	14(8)
JF-58A	10.3	3.16(3)	1.98(2)	1.56(2)	0.36(1)	0.90(1)	0.89	15(2)	12.0(3)	18(11)
JF-84A	11.5	3.21(3)	2.04(2)	1.48(1)	0.49(1)	0.71(1)	0.72	15(4)	12.7(3)	16(9)
JF-42A	13.0	3.22(3)	1.48(1)	1.52(2)	0.89(1)	0.80(1)	0.81	17(3)	15.5(4)	12(7)
JF-39A	13.5	3.32(3)	2.22(2)	1.30(1)	0.45(1)	0.66(1)	0.63	20(1)	18.0(4)	17(10)
JF-55A	15.6	3.44(3)	2.35(2)	1.01(1)	0.57(1)	0.57(1)	0.56	30(3)	25.9(5)	29(18)
JF-22A	17.9	3.55(4)	2.36(2)	0.83(1)	0.45(1)	0.72(1)	0.70	27(3)	21.7(4)	22(14)

Cation abundance based on 12 oxygen anions calculated from major element compositions from electron microprobe data reported in Ref. 32. XRD: X-ray diffraction, MS: Mössbauer spectroscopy, EMPA: calculation based on electron microprobe data assuming stoichiometry

Extended Data Figure 1. **Mössbauer spectra of garnet inclusions JF-1A, JF-9A, JF-22A, JF-37A, JF-37B, JF-39A, JF-42A and JF-44B.** The bluish-green doublet corresponds to Fe^{2+} on the X-site and the orange doublet indicates Fe^{3+} located on the Y-site. The dark red component corresponds to iron in the X-ray optics on ID18 at ESRF. The green doublet in c with smaller splitting corresponds to Fe^{2+} in clinopyroxene. The pink line indicates the residual of the fit.



Extended Data Figure 2. **Mössbauer spectra of garnet inclusions JF-50A, JF-55A, JF58A, JF-58B and JF-84a.** The colours are the same as in Extended Data Figure 1.



Extended Data Figure 3. **Photos of garnet inclusions.** Epoxy mount with seven inclusions (marked by red circles) is shown on the left. The right image shows inclusion JF-55A under higher magnification. The photos were made on a Leica M205 C stereo microscope equipped with a Leica DFC450 digital camera.

