ARTICLE

Supplementary material

Boltzmann plot

For the purposes of laser induced plasma temperature determination the well-known Boltzmann equation can be rewritten in the following form:

$$\ln\frac{{}^{q}I_{ij}^{S}}{g_i^S A_{ij}^S} = \frac{-E_i^S}{k_B T} + \ln\frac{n^S}{{}^{q}U^S(T)}, \qquad (1)$$

where ${}^{q}I_{ij}^{S}$ (photons cm^{-3} s^{-1}) is the intensity of atomic or ionic line of element S, q is the ionization stage, i,j are the indexes of the higher and lower energetic quantum states of the same ionization stage q, n^S (cm^{-3}) is the total number density of species S, A_{ij}^S (s^{-1}) is the transition probability of upper level of species S, g_i^S (dimensionless) is the statistical weight of upper level, E_i^S (eV) is the excitation energy of upper level, T (K) is the temperature, k_B (eVK^{-1}) is the Boltzmann constant and ${}^{q}U^S(T)$ $(dimensionless)$ is internal partition function of selected species at temperature T (K):

$${}^{q}U^S(T) = \sum_i g_i e^{-E_i^S/k_B T} . \qquad (2)$$

If the left side of the equation (1) is represented as a function of energy of the upper level for different transitions the result should leads to a linear plot. The plasma temperature may be then obtained from the slope of the plot.

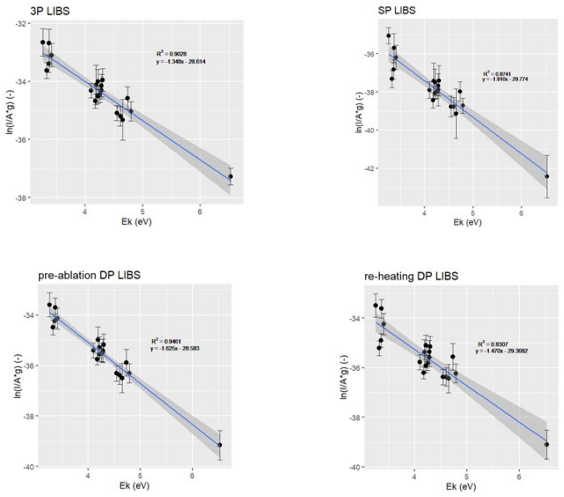

Figure S1 Examples of Boltzmann plot in the SP LIBS, DP LIBS (pre-ablation and re-heating) and 3P LIBS.

Table S1 List of Fe I spectral lines utilized for Boltzmann plot

Central_wavelength	Ek (eV)	Ak*g (s^{-1})
367.9913	3.37	12400000
368.7456	4.22036	72000000
371.9934	3.332	178000000
372.2563	3.4169	24800000
372.7618	4.2833	112000000
373.4863	4.1777	991000000
373.7131	3.3683	127000000
374.3361	4.3013	78000000
374.9485	4.2204	687000000
375.8232	4.2562	444000000
376.3788	4.2833	272000000
376.5538	6.5283	1430000000
375.8232	4.2562	444000000
382.0425	4.1034	600000000
382.7822	4.7955	525000000
387.2501	4.1909	52500000
389.9707	3.2657	12900000
390.2945	4.7331	150000000
400.5242	4.652	102000000
404.5812	4.5485	776000000
406.3594	4.6076	466000000

Signal enhancement

Table S2 Signal enhancement as a ratio of both DP LIBS configurations and 3P LIBS spectral line intensity to corresponding spectral line intensity of SP LIBS.

Wavelength (nm)	Signal enhancement (-)			Upper level energy (eV)
	Pre-ablation	Re-heating	3P LIBS	
Fe I 367.99	14±2	11±4	44±6	3.37
Fe I 368.75	17±3	13±6	53±8	4.22
Fe I 372.25	22±2	14±6	55±8	3.41
Fe I 372.76	23±2	17±5	67±6	4.28
Fe I 373.71	63±2	21±5	108±7	4.3
Fe I 382.78	34±3	19±3	80±11	4.10
Fe I 387.25	11±5	10±2	36±5	3.26
Fe I 389.97	27±2	23±6	86±7	4.19
Fe I 390.29	15±3	13±3	49±6	3.22

Fe I 404.58	43±3	24±5	85±9	4.65
Fe I 406.36	36±3	22±5	85±10	4.54
Fe II 259.94	196±7	138±7	243±15	12.5
Fe II 261.38	190±8	98±6	228±12	12.69
Mn I 403.08	31±2	14±5	60±7	3.07
Cr I 425.43	20±3	11±5	53±7	2.91
Cu I 324.75	28±3	25±4	74±6	3.81
Ni I 341.476	25±2	14±5	63±8	3.65

Crater diameters

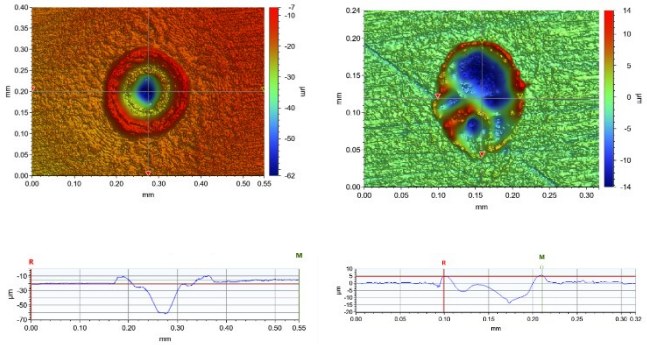

Figure S2 Pictures of ablation craters obtained from 3D optical microscope. Crater on right site is for 3P LIBS with 10 mJ laser pulse energy and the crater on the left is for SP LIBS with 100 mJ. The optical emission intensity from both laser-induced plasmas is comparable. Under each ablation crater is the X axis profile.