LASER ABLATION ICPMS: A POWERFUL NEW TOOL FOR MICROBEAM TRACE ELEMENT ANALYSIS Marc D. Norman, School of Earth Sciences, Macquarie University, North Ryde NSW 2109 Australia

A focused laser beam can be used to ablate small amounts of solid material which are then introduced into an inductively-coupled plasma mass spectrometer (icpms) for trace element and/or isotopic analysis. A laser ablation system has recently been installed in our laboratory and attached to a Perkin-Elmer ELAN 5100 icpms. Initial experiments on various operating conditions, and quantitative analyses of fused rock standards are reported. Despite problems with the fractionation of relatively volatile elements such as Pb and Zn during the course of a run, excellent results were obtained for a variety of more refractory elements, such as Sr, REE, Nb, U, and Th.

The ablation system and supporting software were designed and provided by Drs. S. Jackson and H. Longreach of Memorial University. The ablation system is based on a commercial Q-switched Nd:YAG laser with a fundamental wavelength of 1064 nm and a pulse width of 5 nsec. Two frequency doubling crystals provide access to 532 and 266 nm. The laser can be operated in single shot mode or continuously at repetition rates of 1-20 Hz (laser pulses per second). Pulse energies of 0.1 to 1 mJ typically are used for analysis, producing hemisphere diameters of about 20 to 100 μm, corresponding to about 10-1000 ng of ablated material. Oxide production in the icpms plasma is controlled by adjusting operating conditions (principally nebulizer gas flow) so that ThO/Th is <1%. At this rate, production of REE-oxides is considered negligible. Relative sensitivities of the elements are calibrated against an external standard such as the NIST glasses (e.g., 612), with each analysis normalized to an internal standard such as Ca which can be determined by electron microprobe prior to analysis. Detection limits of 0.1 to 0.01 μg/g are readily achievable.

The method is especially well suited for the determination of relatively refractory elements such as Sr and the REE. More volatile elements with high ionization potentials such as Zn, Au, and Pb present a particular problem as these elements tend to fractionate during a run. This fractionation can be reduced by using higher energies at the cost of larger spot sizes and more rapid consumption of sample. Operating conditions for our system are still being optimized, but initial results suggest that a lower pulse rate for a given energy gives a more sustained signal with less fractionation of the problem elements over the course of a run.

Fig. 1 shows results from a series of experiments using various energies and pulse rates to ablate a standard glass. These results illustrate the potential problems with fractionation of volatile elements during a run, and the effects of various energies and pulse rates on the signal. Note the convergence of the Pb signal with that of Ca, Sr, and U during the runs. This effect is especially pronounced in both of the 20 Hz runs. At a given energy, lowering the pulse rate, e.g., from 20 Hz to 4 Hz, reduces, but does not eliminate such fractionation. Lower pulse rates (e.g. 4 Hz vs. 20 Hz) also produce a more sustained signal. Higher energies tend to produce steadier, more intense signals, but the energy for a given application may be limited by the required spatial resolution and volume of material available for analysis. These observations appear to reflect general phenomena for the conditions which we have tested, but more experiments are needed to evaluate other variables such as matrix effects.

Table 1 gives the results of quantitative analyses of two USGS powdered rock standards (AGV, BIR) which were fused on Ir strips under an Ar atmosphere and quenched to a glass. The glasses were mounted in epoxy, polished, and analyzed by electron microprobe to evaluate homogeneity. They were found to be homogeneous with compositions closely matching those of the accepted compositions of these standards. For the trace element analyses, the mounted glasses were ablated using a 266 nm beam operated at 4 Hz and 1 mJ. Data were collected using 10 msec dwell times on each mass, 10 sweeps of the mass range per reading, and a total of 70 readings per analysis. For each analysis, backgrounds were collected for approximately 2 minutes prior to beginning ablation. A complete analysis took approximately 4.5 minutes. NIST glass 612 was used for external calibration, and the data were normalized to 42Ca as an internal standard, assuming 5.1% CaO in AGV and 13.4% CaO in BIR. These initial results compare well with the preferred values for these standards for a variety of elements.

Laser ablation ICPMS: Norman M.D.

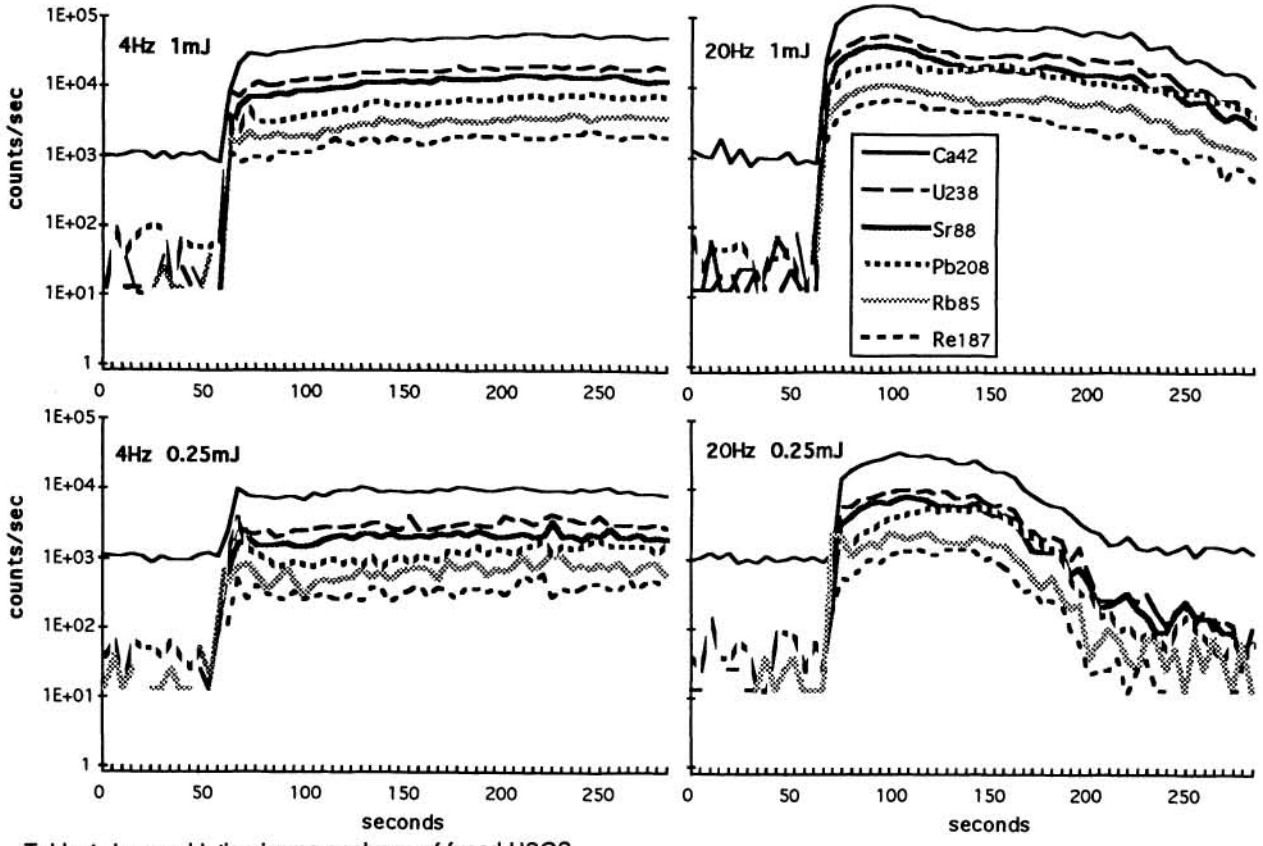

Table 1. Laser ablation icpms analyses of fused USGS standards compared to their preferred values (PV).

	AGV (ppm)	1σ η=3	PV	BIR (ppm)	1σ η=3	PV
V	128	4	121	353	88	313
Co	17.6	0.3	15.3	62	1	51
Ni	19.0	0.4	16	205	4	185
Sr	677	2	660	111	2	110
Y	18.0	0.9	20	13.6	0.7	16
Zr	213	12	248	15	3	16
Nb	15.0	0.6	15	0.7	0.1	0.6
Ba	1322	22	1200	7.2	0.5	6.6
La	40.3	1.6	37.6	0.59	0.07	0.62
Ce	74.0	1.2	70	1.86	0.18	1.91
Pr	8.8	0.3	8.5	0.34	0.06	0.35
Nd	32.7	1.3	32	2.21	0.30	2.41
Sm	5.98	0.29	5.78	1.13	0.16	1.12
Eu	1.64	0.08	1.57	0.48	0.02	0.53
Gd	4.63	0.35	4.68	1.66	0.06	1.90
Dy	3.61	0.19	3.54	2.39	0.14	2.62
Ho	0.67	0.04	0.68	0.51	0.02	0.59
Er	1.80	0.10	1.81	1.62	0.16	1.66
Yb	1.73	0.06	1.71	1.53	0.13	1.70
Lu	0.26	0.03	0.25	0.23	0.02	0.26
Hf	5.2	0.2	5.2	0.71	0.08	0.60
Ta	0.90	0.07	0.9	0.05	0.04	0.07
Th	6.3	0.2	6.5	0.027	0.006	0.03
U	1.7	0.5	1.9	0.013	0.006	0.01