The Li and trace element budget of Acfer 094 matrix. I. Lyon, N. Spring, A. King, T. Henkel and D. Rost. The University of Manchester, SEAES, Williamson Bldg. Oxford Rd., Manchester, M13 9PL, UK, Ian.Lyon@manchester.ac.uk.

Introduction: The unique chondrite Acfer 094 is thought to contain primary condensates from the solar nebula that have not been altered by subsequent aqueous alteration on primordial parent bodies as in most other chondritic meteorites [1,2]. This meteorite also contains the highest known abundance of presolar interstellar grains [3]. In a recent study, [4] Bland et al. found that a 50µm×50µm area of Acfer 094 matrix contained a diverse range of minerals including a sub-micrometer Li-bearing phase that they speculated was a Li Cr oxide. We here report on a Time-Of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS) analysis of a similar sized area of Acfer094 matrix that contains a rich diversity of minerals including 2, ~micrometer-sized grains of a mineral that is highly enriched in Li, Na, Cr and Mn.

Experimental: In 2007, we equipped one of our TOF-SIMS instruments [5] with a 25 kV Au Liquid Metal ion gun.

Secondary ion mass spectra can be acquired with a lateral resolution down to ~300nm, (although there were some small vibrations during the course of these measurements which have degraded the spatial resolution to ~0.7µm). We have also recently developed elaborate software tools that allow for correcting instrumental drift and varying mass calibrations throughout the measurement as well as depth profiling - that is following the intensities of selected ion species throughout the measurement. Elemental abundances were quantified by using relative sensitivity factors derived by measuring known elemental abundances in a range of silicate standards. [5,6]

Results and discussion:

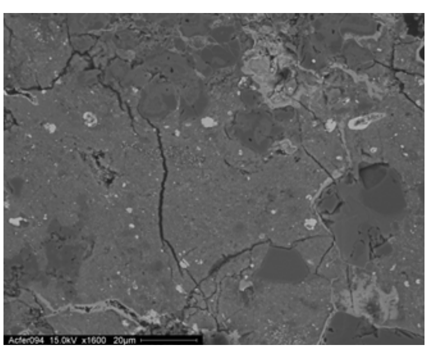

Figure 1. Approximately 120µm × 100µm area of Acfer 094, back scattered electron image.

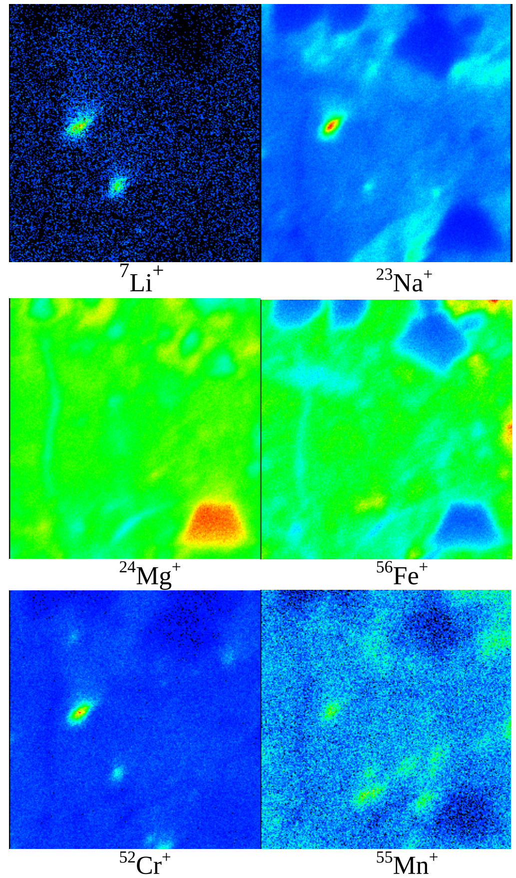

Figure 2. Selected secondary ion images of the central part of the area of figure 1. Image size ~50µmx50µm Large field of view shown for context to compare with figure 1. (Warmer colors indicate higher abundance).

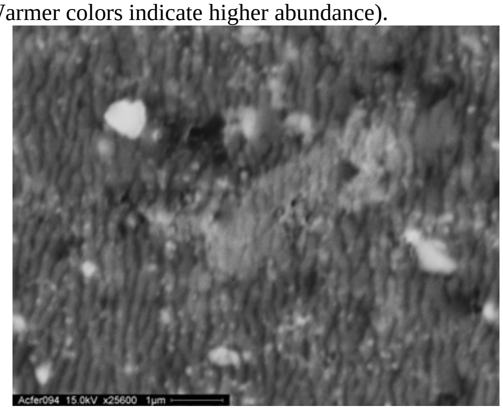

Figure 3. Back scattered electron image of the ~3µmx1µm long lithium-bearing mineral (slightly lighter area to centre of the image). (Corrugated appearance of the surface is due to sputtering by Au^{+} ions).

The two obvious Li-bearing grains are enriched in Li by factors of approximately 100 and 10 relative to comparable sized volumes of average matrix and also by similar factors in Cr. These grains therefore constitute a significant reservoir of lithium and chromium in the meteorite. Further analyses will allow us to ascertain the distrubution of the Li-rich grains although 2 grains appearing in a randomly selected area implies a considerable abundance throughout the meteorite. The two grains have similar bulk compositions but there are significant differences between them in their minor element chemistry. The lithium in the larger grain yields a value of $^7Li/^6Li$ = 11.9 (2σ~100‰) which is of solar system normal isotopic composition ($^7Li/^6Li$=12.18). The Li in the other Li-rich grain and in the matrix is also solar system normal within error.

The major element composition of the two lithium-rich spots is very similar to that of the surrounding matrix as seen in table 1. The figures in table 1 were calculated from analyses of smaller fields of view, focused on the grains with a better spatial resolution than shown in figure 2. A decrease in abundance of Fe and Mg is seen at the position of the grain but element maps for Ca, Al and Si show uniform intensity across the position of the grain compared with surrounding matrix. We therefore infer that although there may be some contribution to the elemental abundances calculated for the grains in the table below caused by the primary beam picking up a contribution from major elements in the matrix, that nevertheless, the grains have a silicate rich composition, not a silicon free composition such as an oxide.

	Upper Li grain		Lower Li grain		Matrix near grains	
	/Si (CI)	/Si	/Si (CI)	/Si	/Si (CI)	/Si
Li	436	0.03	270	0.015	36	2×10^{-3}
B	32	7×10^{-4}	45	1×10^{-3}	14	3×10^{-4}
O	0.6	4.5	0.4	3.3	0.4	3.1
Na	4.3	0.25	1.3	0.08	0.8	0.05
Mg	1.6	1.7	1.8	1.9	1.8	1.9
Al	1.4	0.1	2.0	0.2	1.6	0.1
Si	1.0	1.0	1.0	1.0	1.0	1.0
K	6.3	0.02	8.8	0.03	6.7	0.03
Ca	5.1	0.3	6.0	0.4	5.1	0.3
Ti	1.7	4×10^{-3}	2.0	5×10^{-3}	1.7	4×10^{-3}
V	3.6	1×10^{-3}	2.0	6×10^{-4}	1.5	4×10^{-4}
Cr	19	0.26	6.1	0.08	2.2	0.03
Mn	4.0	0.04	3.1	0.03	1.6	0.02
Fe	1.5	1.4	2.0	1.8	1.7	1.6
Ni	1.3	0.06	1.6	0.07	1.5	0.08

Table 1. Elemental abundances measured in the two lithium-rich spots and nearby average matrix. The columns labelled /Si (CI) contains at% of the element ratioed to at%Si and then normalized to CI abundances. The columns labelled /Si are at% abundances normalized to Si to show which elements are quantitatively the most abundant in the minerals. Systematic errors may amount to as much as a factor of 2 in calculating absolute abundances of these elements.

The two Li-rich grains do not differ very much in major element chemistry from nearby average matrix being composed mainly of Mg,Fe silicate with small quantities of Ca and Al. The larger Li-rich grain (labelled 'upper' in table 1 and shown in figure 3), does have significant Cr in its major element composition and this may account for the slightly lighter appearance of the grain in the back scattered electron image shown in figure 3.

Bland et al. [4] speculated that the ~0.5μm Li-rich grain observed by them may have been a Li,Cr rich oxide. Indeed, Li,Cr,Mn spinel is a common mineral with useful properties as a cathode for Lithium ion batteries [7,8]. The work here however suggests that it is a silicate mineral in most respects near-identical to matrix grains that surround it, possibly only with some substitution of Li, Na and Cr for Fe and Mg. Its isolated nature in the matrix suggests that it must have acquired its high Li abundance before condensation with other matrix grains. To hold high Li and Cr abundances, the grains must have either been formed in an environment in which these elements were strongly enriched or, alternatively, but less likely, that there are some mineralogical differences which allow Li and Cr to enter the lattice of this grain in preference to average matrix silicates. Further work will allow us to constrain the properties of the unusual minerals in Acfer 094 more accurately.

References: [1]Greshake A. (1997) GCA 61, 437-452. [2] Nuth et al., (2005) Workshop Chondrules Protoplanetary Disk. SOEST pub. No. 04-03, 675-700. [3]Newton et al., (1995) Meteoritics 30, 47-56. [4] Bland et al., (2007) MAPS 42, 1417-1427. [5] Henkel et al. (2007) J. Sci. Inst. 78, 055107. [6] King et al., in prep. [7] Lu et al., (2003) J. Material Sci. Lett. 22, 615-618; [8] Yonemura et al., (2004) J. Materials Chemistry **14**, 1948-1958.

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