

ATTEMPTS TO PRODUCE CARBON-FREE SILICA AEROGEL FOR MICROMETEOROID CAPTURE CELLS; I.P.Wright, H-P.Huang and C.T.Pillinger, Dept. of Earth Sciences, Open University, Walton Hall, Milton Keynes MK7 6AA, UK.

In applications where intact micrometeoroids are to be collected from space, it is widely thought that silica aerogel [1,2] offers the best hope for a suitable collection medium [e.g. 3]. For this material to obtain the universal seal-of-approval it should ideally satisfy the constraints of all potential investigations. Thus far it would appear that the implantation of synthetic micrometeoroids into aerogels has been successful [e.g. 4] and, furthermore, the material is chemically pure with respect to its trace element chemistry [5]. However, since a major proportion of micrometeoroids are likely to be carbon-rich or CHON-like, it is imperative that any aerogel selected for a collection cell should not impart any light element contamination to the prospective particles. Since it is known already that aerogel can become coated onto the surfaces of particles during ground-based impact studies [6,7,8], the collection medium itself needs to be free of light element contaminants.

There are two immediate problems with the usage of aerogel. Firstly, by the very nature of its highly porous structure, it tends to adsorb atmospheric water vapor. Fortunately this can be largely removed by heating at relatively low temperatures (a process that has no deleterious effects on the aerogel structure). Secondly, it is clear from a knowledge of the preparation procedures used to manufacture silica aerogel, which commonly involve a substance like tetramethoxysilane, $(\text{CH}_3\text{O})_4\text{Si}$, and various solvents such as alcohol, $\text{CH}_3\text{CH}_2\text{OH}$, that complete removal of residual carbon-bearing molecules is difficult. Indeed, a previous study of the carbon contents of aerogel has shown that the element can be present at up to 3.3 % by weight [9]; the exact nature of the compounds has been studied using thermogravimetric analysis and laser desorption-mass spectrometry [10]. Attempts have been made to reduce the carbon content of existing aerogels using either heating [9,10], or a technique known as supercritical fluid extraction [11]. Simple heating techniques (pyrolysis under vacuum conditions) can release about 50% of the total volatile content of aerogel, while supercritical fluid extraction, under optimal conditions, seems to remove >90% of the total carbon content, and presumably most of the water as well.

The biggest challenge for the development of a totally suitable aerogel collection cell is to devise ways of, not only removing the volatiles, but also keeping the material clean once the extraction has been completed. In this respect, simply reducing the concentration of the volatile constituents may not necessarily be what is required because, upon re-exposure of the aerogel to the atmosphere, contaminants may be added to the highly active and clean surfaces of the porous material. Rather, the overall success of a clean-up procedure needs the contemporaneous addition of an inert substance to the aerogel structure during volatile removal. This should then act to terminate any broken bonds, or fill any newly created void spaces, of the devolatilised aerogel. The obvious choice here is oxygen since its addition will effectively purify the Si-O material. For this reason it was decided to evaluate the usage of a combustion technique. A measure of the efficacy of this approach can then be gained by studying the volatiles removed during combustion and then re-appraising the material after exposure to air (in this study, the carbon chemistry of aerogel is used as the monitor). While in principle the idea of combustion sounds fairly straightforward it should be pointed out that previous attempts to remove volatiles from aerogels by heating in air were largely unsuccessful [10]. Furthermore, preliminary experience [9,11] with combusting aerogel by a sealed tube method at high temperature showed that while carbon could indeed be satisfactorily removed, the aerogel structure itself generally collapsed to form a hard coherent material of no value whatsoever, as a collection medium. In the new study, aerogel has been combusted by an

CARBON -FREE SILICA AEROGEL; Wright, I.P. *et al.*

incremental heating technique, using 50°C temperature steps of 40 minutes duration each, from ambient to 1000°C. The benefit of using a stepped combustion technique is that the heating rate experienced by the aerogel is sufficiently slow enough to allow any accompanying structural rearrangements to take place without causing cracking or shrinkage. Indeed, using the technique herein, the aerogel remains, visibly at least, unchanged at the end of a normal experiment.

The extraction system used for the stepped combustion experiments is different to that used in a previous study in the following ways: a wider diameter sample holder is used (8mm i.d. versus 4mm), and a loading stage has been added that enables the sample under investigation to be admitted to the extraction system and evacuated, prior to admission to the combustion furnace. The increased dimensions of the holder mean that with a typical sample size of ~70mg, the depth of aerogel required is only 1-2cm, compared with >5cm in the previous work. This is an important advance since the combustion furnace used previously, and in this study, is only 15cm long, and so a sample depth greater than 3cm is subjected to a large temperature gradient. This could result in volatiles being removed from one part of the aerogel and at the same time becoming adsorbed into another. Loading the aerogel into the extraction system, rather than directly into the reaction vessel as used previously, enables the combustion system to be properly blanked out before the experiment begins (which can now be done without having to open the vessel to the atmosphere).

All experiments were carried out using an aerogel of 0.12 g cm⁻³ density (supplied from L.W.Hrubesh, Livermore, via M.E.Zolensky, NASA-JSC). The carbon released upon stepped combustion is clearly present in two major forms. One variety has a $\delta^{13}\text{C}$ of about -28‰ and is released at temperatures less than 500°C. This carbon is certainly not merely a system blank, which would characteristically be present at 2 orders of magnitude lower amounts. The temperature of combustion and the $\delta^{13}\text{C}$ value are suggestive of normal atmospheric (hydrocarbon) contamination. The second form of carbon is released above 500°C and has $\delta^{13}\text{C}$ of about -36‰; the high temperature of combustion strongly implicates carbon that is in some way bonded to the aerogel (presumably remnant tetramethoxysilane). The ratio of low to high temperature forms of carbon is 0.48.

When removed from the extraction system the aerogel was found to have undergone a 16% loss in weight; since carbon only accounts for 0.1% it is fairly certain that the rest is due to water. Interestingly after exposure to air for 48 hours the weight of the aerogel only increased by ~1%, which seems to imply that only a minimal amount of water was re-adsorbed over this period. Upon re-examination for carbon it was found that the high temperature form of carbon had been effectively removed, while that released at low temperature was present in roughly the same amounts as in the original extraction. Thus, having identified a way of removing the structural carbon with no apparent damaging effects on the aerogel itself, it is now necessary to develop a method of preventing the re-adsorption of low-temperature carbon. In this regard, it was found that simply leaving the material in the extraction system, under vacuum, was not successful. Presumably the aerogel acts to cleanse the vacuum system itself, a possible future application of the material in low carbon blank extraction systems.

References: [1] Kistler, S.S. (1931), *Nature*, 127, 741; [2] Fricke, J. and Emmerling, A. (1992), In: *Chemical Processing of Advanced Materials* (eds. L.L.Hench and J.K.West), 3-17; [3] Barrett, R.A. *et al.*, (1992), *Proc Lunar Planet. Sci.*, 22, 203-212; [4] Brownlee *et al.*, (1993), *LDEF Newsletter*, 4 (3), 4-18; [5] Flynn, G.J. and Sutton, S.R., (1990), *Lunar Planet. Sci.*, XXI, 371-2; [6] Lurance, M.R., (1989), *Lunar Planet. Sci.*, XX, 560-1; [7] Zolensky, M.E. *et al.*, (1989), *Lunar Planet Sci*, XX, 1251-2; [8] Zolensky, M.E. *et al.*, (1990), *Lunar Planet Sci*, XXI, 1381-2; [9] Gibson, J.E. *et al.*, (1991) *Lunar Planet Sci.*, XXII, 441-2; [10] Hartmetz, C.P. *et al.*, (1990), *Lunar Planet. Sci.*, XXI, 463-4; [11] Huang, H-P. *et al.*, (1993), *Lunar Planet. Sci.*, XXIV, 679-80.