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Loyd, D. H.

Vogel, J. S.

Trumbore, S.

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LITHIUM CONTAMINATION IN AMS MEASUREMENTS OF ^{14}C

D. H. LOYD¹, J. S. VOGEL¹ and SUSAN TRUMBORE

Center for Accelerator Mass Spectrometry, University of California
Lawrence Livermore National Laboratory, Livermore, California 94550 USA

ABSTRACT. High count rates of lithium ions in an AMS measurement system for ^{14}C were traced to the lithium content in the quartz tubes used in the graphitization of the samples. The lithium contamination was nearly eliminated by the use of borosilicate glass reaction tubes at a lower reaction temperature. The ion beam current and the measurement precision of the isotope ratio were not affected.

INTRODUCTION

Since the initial work of Nelson, Korteling and Stott (1977), AMS laboratories have observed variable amounts of lithium and "di-lithium" (two Li^{2+} ions entering the detection system simultaneously) in the ^{14}C spectra of AMS measurements, when using the even charge states of carbon from a tandem Van de Graaff accelerator. Both species of detected lithium are injected into the accelerator as a negative Li_2 ion at mass 14. The molecule is dissociated at the terminal stripper, and Coulomb repulsion separates the two atomic ions. A fraction of possible repulsion geometries allows the two ions to enter the detector simultaneously. More of the separated ions are on projections that bring only one of the pair to the detector.

The M/q analysis of the positive ions eliminates these lithium ions in AMS systems using the +3 or +5 charge states of carbon. We prefer to analyze +4 carbon ions to obtain higher system efficiency at our 6-7 MV operating voltage. At these energies, the lithium contamination is easily discriminated from the voltage pulses due to true ^{14}C counts in a multiple-anode gas ionization detector. However, bursts of lithium ions have occasionally caused count rates in excess of 25,000 cps. Our data-collecting software applies livetime corrections at 0.3- to 0.5-second intervals, and such bursts do not affect the overall measurement to more than 0.2%. The more usual rates of 500-2000 cps have no effect on the analyzed data. However, the variability of the lithium content among different samples drove us to discover its source, and led us to a simplification of our graphitizing procedures.

LITHIUM CONTAMINATION

Our first difficulties with di-lithium were traced to a jar of activated charcoal, which was used in testing the CAMS spectrometer before graphite-production facilities were complete. Perhaps the charcoal was activated in an alkali wash that contained large amounts of lithium. Also, our original bench for loading the AMS samples was close to the area used for coating filaments with lithium hydride for use in a direct extraction ion source. Better handling protocols prevent this lithium from entering the AMS sputter source. However, the detector spectra continued to show varying lithium contamination in prepared samples.

Typical spectra from a single anode are shown in Figure 1, for samples with little lithium and for those with contamination. The lithium peak in most spectra is small and constant for repeated measurements of the same sample. In other cases, the lithium is intense and does not change over

¹Permanent address: Department of Physics, Angelo State University, San Angelo, Texas 76909 USA

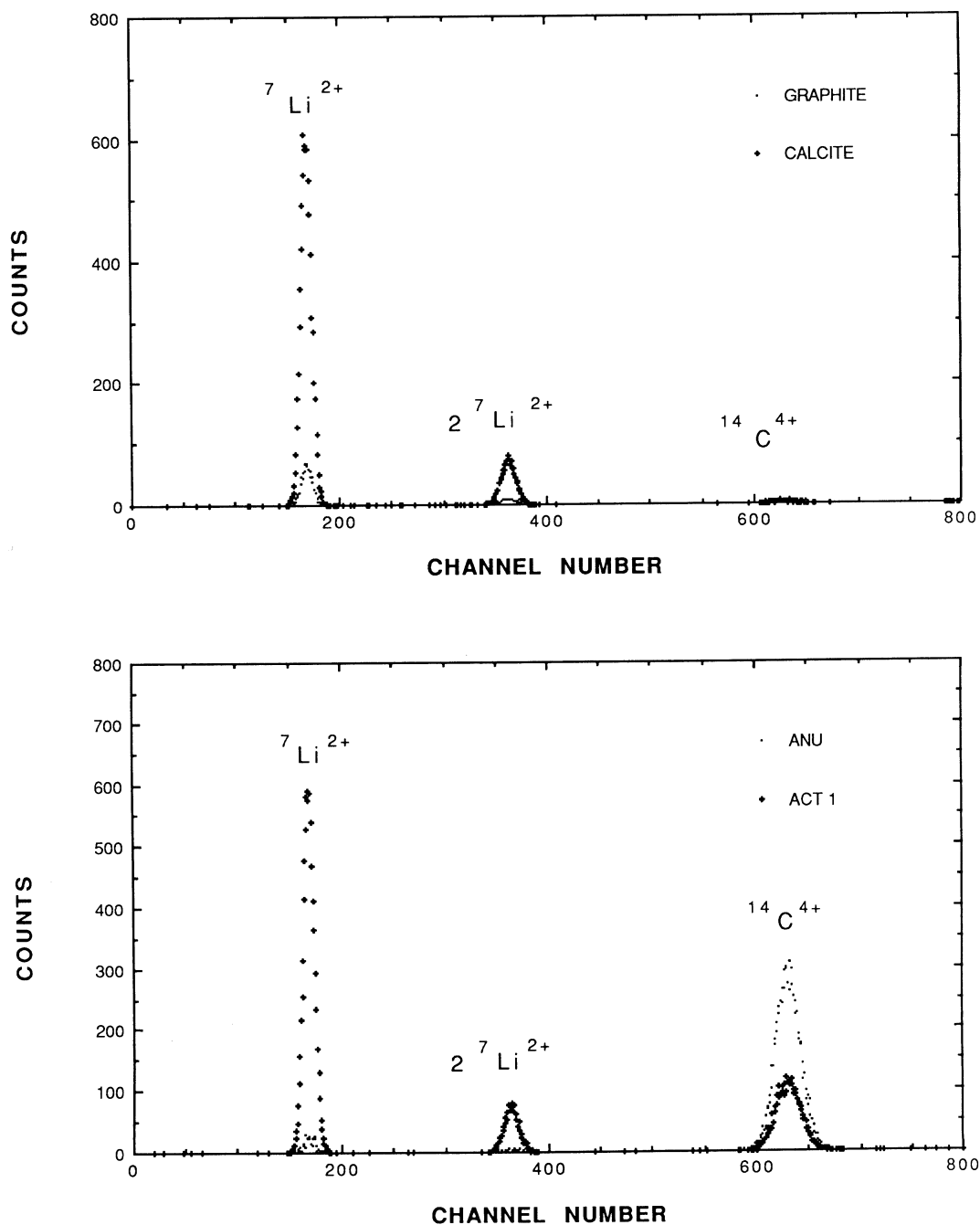


Fig. 1. Energy deposition spectra are shown for 4 samples, 2 of which (ACT-1 and Calcite), have lithium contamination in the prepared graphite. The prepared graphite made from ANU sugar and the unprepared geological graphite show low levels of lithium contamination, which may arise in the ion source rather than in the graphite preparation. In all spectra, the first peak arises from ${}^7\text{Li}^{2+}$, the second peak is caused by two simultaneous ${}^7\text{Li}^{2+}$, and the third peak is due to ${}^{14}\text{C}^{4+}$. All spectra are normalized to the counts in 100 seconds.

the several measurements. Another behavior shows a moderate or low lithium contamination that suddenly becomes very intense. The intense contamination may quickly disappear or last through several measurements. The lithium is not associated with the ion source itself, or as a contaminant in the sputtering cesium, since all behaviors are observed in neighboring samples placed in the ion source in quick succession. The cobalt catalyst used in the graphitization process does not produce lithium beams when it is placed directly into the ion source. We do not observe an increase of lithium in graphites stored for over a year. However, we find that geological graphite increases lithium emission by a factor of five over a period of several hours, indicating that memory effects in the ion source can contribute a small amount of lithium. The ratio of di-lithium to lithium varies from 1:1.5 to 1:15, and a ratio of 1:4 is most common. The ratio is not an apparent function of ion current or system control settings.

Graphites readily form intercalation compounds with alkali metals (Hennig 1959), and the continuous emission of lithium from some samples indicates its uniform distribution, which must arise chemically in the preparation of filamentous graphite. No lithium compounds have sufficiently high vapor pressures to survive the cryogenic purification and transport of the gases produced by sealed-tube combustion (Vogel, Nelson & Southon 1987). Thus, the contamination must arise during the graphitization, which involves only the catalyst, the purified CO₂, hydrogen and the reaction vessel. The catalyst and the gases have been ruled out, but one possible source of lithium is the fused quartz of the reaction tube itself.

We observed that samples that contained small chips of quartz (a result of not fire-polishing the open end of a series of reaction tubes) produced large and fluctuating amounts of lithium contamination: up to 120 times the lithium found in geological graphite. The samples showed points of light during sputtering, where the non-conducting quartz chips were heated in the cesium beam. Such spot heating causes observable fractionation (Vogel, Southon & Nelson 1987). Many glasses, including the precursors of high-temperature glasses, are composed of silicate mixed with sodium (and hence, other alkali) compounds. These elements are chemically bound in most glasses, but can exist in high-temperature glasses as interstitial elements left from the etching process (Nordberg 1944). The quartz chips are an obvious source of the sporadic lithium contamination, but the uniformly distributed lithium is not as easily understood. High-temperature glasses, such as fused quartz and Vycor, are more porous than borosilicate glasses (Eitel 1966). We hypothesize that lithium migrates out of the quartz reactor tubes in the vacuum of the nearly complete reaction at temperatures over 600°C. Initial baking of the quartz tubes in air to 900°C does not eliminate this lithium. Variations in lithium between samples may be related to initial gas pressures or to detailed temperature histories of the tubes, but we have no data to firmly establish this. Instead, we decided to test the hypothesis by using a different glass for the reactors.

BOROSILICATE GLASS REACTION TUBES

Although we measured more lithium in borosilicate glass than in fused quartz (secondary ion mass spectrometry using a Kameca IMS-3F, D. Phinney, personal communication), we investigated whether the contamination could be reduced by using borosilicate glass for the reaction tubes. The resulting graphite samples have 20 to 50 times less lithium than those produced in quartz, and only 2 to 10 times the lithium found in geological graphite. The use of borosilicate glass tubes for the reactors requires only slight modification of our preparation protocols, and produces filamentous graphite of the same quality as that from quartz reactors.

Regardless of its relationship to the amount of lithium in the spectra, the use of borosilicate glass tubes is attractive, from the standpoint of reduced cost and effort in the production of AMS sam-

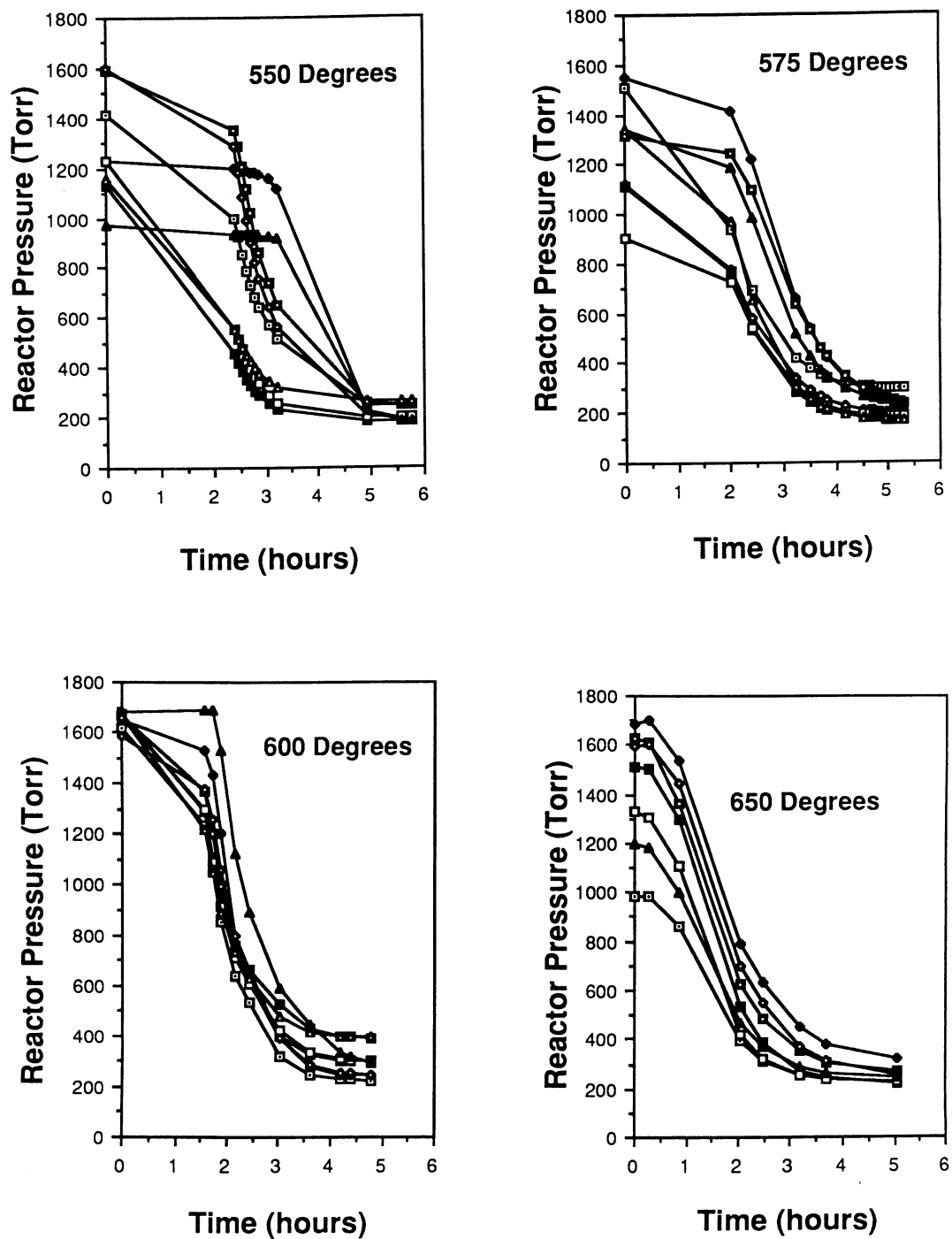


Fig. 2. The pressure *versus* time plots are shown for 4 different reaction temperatures in 8 different reactors. The asymptotic approach of the gas pressure to a constant low level is taken as an indication of the completion of the reaction. Many reactions are complete after 4 or 5 hours, but reactions at the coolest temperature, 550°C, occasionally do not proceed for 3 or 4 hours.

ples. The quartz tubes were either purchased from professional glassblowers at considerable expense, or else produced 'in house' with less uniformity in quality. We now use standard 6 mm \times 50 mm biological culture tubes, which are available from several manufacturers for approximately 10¢ each. We purchase clean, sealed packages of the tubes, which are used once before disposal. The tubes are available with both thin walls or thick walls. The thin-walled tubes soften and partially collapse during heating, and the temperature must be reduced to a maximum of 575°C for the thick-walled tubes. At this temperature, we still observe occasional softening of the tubes.

Graphs of gas pressures in eight reactors at different temperatures show (Fig. 2) the times at which the pressures approach a constant value, taken as a sign that the reaction is complete. Contrary to the evidence of Kromer *et al.* (1987), we see an increase in the time required for the reaction to proceed to completion from even these small changes in operating temperature. Our reaction vessels are much smaller, however, and gas diffusion or pressure effects may dominate. We also observe slight differences in the reaction times between reactors and on different days. At 575°C, the reaction is usually done in five hours, and is almost always complete in six hours. Note that at 550°C, several of the reactions do not even begin to precipitate carbon for almost three hours, and we do not allow our temperatures to decrease to that level. Samples smaller than 100 μg can take considerably longer than six hours to finish, however, and we continue to use quartz reactors at higher temperatures for them. Other than the lower temperature, all other operating parameters have been outlined previously (Vogel, Nelson & Southon 1987; Vogel, Southon & Nelson 1987).

CONCLUSION

We have found that disposable, inexpensive, borosilicate glass culture tubes can be used reliably at lower temperatures to replace quartz reaction tubes, when producing filamentous graphite for AMS sample preparation. The culture tubes are uniform in manufacture and do not chip during handling. Glass chips in a sample produce high amounts of lithium ions, but the frequency of these chips is greatly reduced by using the glass tubes. Similarly, small pieces of glass wool are sources of lithium in a sample, and sample holders should not be cleaned with glass filter paper or glass wool. The lithium that was uniformly distributed through graphite samples, and that had become a contamination in a large fraction of our samples, has been eliminated.

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