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Appendix to article "Iridium geochemistry of volcanic ash layers from the early Eocene rifting of the northeastern North Atlantic and some other Phanerozoic events" by B. Schmitz and F. Asaro

Analyses with the Iridium Coincidence Spectrometer

The following describes in detail the analyses of the ashes from the Fur Formation in connection with the S-14 irradiation in 1994. The remaining analyses reported in this study were performed in a similar way in connection with other irradiations: Samples were ground to a powder, and about 30 mg of each were encapsulated with 0.020 cm thick high-purity (99.9999%) Al foil. Each capsule was thoroughly wiped twice with clean cotton swabs wetted with high-purity ethyl alcohol. The cleaned Al capsules were stacked in groups of about 40 in 8 quartz capsules, each about 10 cm high and 1.9 cm in diameter, and then heated at about 180 °C for several hours to drive off water. There were three 50 mg standards of DINO-1 (Alvarez and others, 1982b) used for calibration of Ir and Se abundances and another three, also 50 mg, of Standard Pottery (Perlman and Asaro, 1971), which were used to calibrate all of the other elements. There were later revisions in the abundances of Cr and Ni in Standard Pottery (Alvarez and others, 1982). The standards were all placed in the same quartz capsule with a DINO-1 and Standard Pottery sample at the bottom, middle and top. Then the quartz capsules were heat-sealed under vacuum with quartz tops. Each capsule was closely wrapped with 0.0025 cm thick Al (kitchen) foil to expedite heat transfer in the reactor and the 8 capsules were gathered together in a bunch, about 12 cm long and 7 cm in diameter, also wrapped in Al (kitchen) foil. The bunch was irradiated for 48 hours at a flux of 2.5×10^{13} neutrons/second/cm² at the

University of Missouri reactor in Research Park, Columbia, Missouri. It was rotated in the reactor during irradiation about its long axis, the same as the long axis of each quartz capsule. At any point on the long axis, the variation in reactor flux at a given radius was expected to be minimal because of the rotation of the bunch during irradiation. Neither was variation detected in the radial direction in any of our measurements, but there was sometimes variation along the long axis of about 10 % from one end of a capsule to the other. The calibration constants for each position in a quartz capsule (from 1-40) were interpolated for each element from the standards at the top, center and bottom, and calibration uncertainties due to sample position in a quartz capsule are expected to be less than 1 %.

Measurements of the samples were begun about 8 weeks after the end of the irradiation with the Iridium Coincidence Spectrometer (ICS) (Alvarez and others, 1988; Michel and others, 1990, 1991). Standards were measured in the next month, and 37 samples from Fur were measured first with a relatively short counting time and then again for a considerably longer period 2-3 months later. The counting times for each sample were adjusted to give an Ir counting error of about 39 parts-per-trillion (ppt). The ICS has two Ge detectors (A and B), each 5 cm in diameter by 5 cm long, with faces 20 mm apart. The irradiated sample (encapsulated in high-purity Al) sits (in air) between the two detector faces (which are under vacuum at liquid nitrogen temperatures). The position of the samples can vary about 1 mm from a given calibration for most singles measurements. (Coincidence measurements or Ni singles measurements, which use two detectors, are not sensitive to this effect). To compensate for this variation, the abundance of the prominent 1120.5 keV gamma ray of ^{46}Sc is counted in each detector and the relative count rates accurately determine the position of the sample with respect to the detector faces. (The accuracy is not very sensitive to variations in position in the radial direction). Surrounding the Ge detectors is a 12-15 inch shield of mineral oil doped with scintillator which can detect gamma radiation Compton-scattered from the detectors (as well as gamma rays emitted by the

source). The ICS can be used to measure the abundance of radioactive isotopes, (and hence elements) by both singles and coincidence measurements of their gamma rays with or without rejection of Compton-scattered gamma rays. Rejection of the Compton scattered radiation removes part of the background underneath peaks and is therefore useful for better counting statistics. If there are significant abundances of gamma rays coincident with the detected singles radiation, however, the shield will also reject part of the desired radiation. The radioactive species measured for each element are shown in Table 1. Also shown are the energies of the gamma rays measured, whether singles or coincidence techniques were used and whether Compton-scattered radiations were rejected. Chromium, Fe, Ni (determined from ^{58}Co), Ta and Th (determined from ^{233}Pa) were measured by counting individual gamma rays with rejection of scattered radiation. All but Ni were counted in Detector B which has better resolution than Detector A. The Ni detected by ^{58}Co radiation is produced by the reaction $^{58}\text{Ni}(n,p)^{58}\text{Co}$. With the Missouri reactor, the fast neutron flux, (which produces the ^{58}Co) is sufficiently low that both detectors are needed to obtain the best precision for the Ni abundance. Cobalt, Cs and Sb were measured from individual gamma rays without rejection of the Compton background because they have significant coincident radiations. Iridium, Sc, Hf, and Se were measured by coincidence techniques utilizing two gamma rays. One gamma ray (e.g. 316.5 keV of ^{192}Ir) was counted in detector A, while another (e.g. the 468.1 keV of ^{192}Ir) was counted simultaneously (within the resolving time of the electronics) in Detector B. In each detector the other gamma ray was also counted and coincidences between those were also determined. Coincidence measurements give increasingly better sensitivity for measurement of an element as its radiation becomes progressively smaller with respect to background. For 30 ppt iridium in a sample the coincidence technique provides results 500 times faster than the singles methods (without chemical separation), and Sc coincidence measurements are even more effective. The ICS can become

contaminated if some of the encapsulated samples are not sealed completely tight or if a thin coat of irradiated powder is on the outside of the capsules. The ICS contamination level for iridium was negligible for the measurements reported here. Other contaminants (e.g. 0.08 ppm Co for a 100 mg sample) were subtracted from each measurement. The high purity Al foil used to encapsulate the samples had significant amounts of Sc, about 0.201 ppm for a 100 mg sample, and Sb, about 0.045 ppm for a 100 mg sample, as well as lesser amounts of other elements. Corrections for all detected contaminants, inversely corrected for sample weight, were subtracted from each measurement with the assumption that the contamination level in the Al foil was constant. Although interference corrections have been extensively studied at the Lawrence Berkeley Laboratory in the past (e.g. Perlman and Asaro, 1969), the ICS detectors have considerably higher efficiency than formerly used for conventional neutron activation analysis (NAA), and the irradiation times are much longer (a factor of 6). The higher geometry can result in larger interference corrections, e.g. coincident gamma rays in a single detector would have higher sum peaks than before. The higher geometry and longer irradiation times are also reflected by smaller counting errors for many elements, particularly Co, Cs, Fe, Th and Sb. Count rates are over an order of magnitude higher than in past conventional NAA studies and appropriate corrections as a function of count rate also had to be determined. Coincidence measurements remove the interference problems to a large extent. But calibration is more complex, particularly in determining the count rate dependence. Coincidence measurements also have a dependence on the timing of the two coincidence pulses and the coincidence efficiency for low energy gamma rays can become rather low (and possibly variable). Earlier work (in press) had demonstrated that the ICS could reproduce abundance ratios measured by conventional techniques down to a precision of about 1-1.5 %. In the present S14 study two measurements, averaging about 82 days apart, were made on each sample. For each element and each sample in which the counting

errors were about 1.5 % or smaller in both measurements, the mean and standard deviation of the two measurements were calculated and the Coefficient of Variation in percent ($\text{Standard Deviation}/\text{Mean} \times 100$) was then determined. The Coefficients of Variation were averaged for each element and these are shown in Table 1. Six elements had precisions of 0.5-0.7 %, 4 had values of 1.0-1.1 % and one, Hf, was 1.7 %. There are systematic errors which would not appear in these determinations, e.g. errors in weighing samples and precision errors in measuring the standards (which were only done once). Weighing samples of 30 mg should be done better than 1 %, and the precision in measuring the standards should be comparable to the measured precision of the unknowns. Also residual (uncorrected) interferences between gamma rays of isotopes of very long half-lives or similar half-lives would not be detected. As there is considerable decay in the samples over the period of the measurements, however, errors due to improper count rate corrections would have been determined. The accuracy of the measurements depends not only on the precisions but also on the accuracy of the abundances values in the standards (Alvarez and others, 1982b; Perlman and Asaro, 1971). These are also shown in Table 1. Generally the uncertainty in the standard is much greater than the precision of measurement. Selenium is calibrated versus DINO-1 in each irradiation, but the original measurement (Alvarez and others, 1980) of DINO-1 was calibrated versus a flux monitor and hence was rather uncertain. Also, Se (in contrast to Ir) may fractionate in DINO-1, and the overall uncertainty is probably about 25 %. The abundance used in this study for Se in DINO-1 is 27.6 ppm. The various conditions and techniques used for other irradiations reported in this work were roughly comparable to those of S14.