EXPERIMENTAL DETERMINATION OF THE ^{129}I/^{127}I RATIO IN THE EARLY SOLAR SYSTEM.

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Introduction: The abundances of short-lived radionuclides in the early Solar System (ESS) are values of considerable interest, constraining the course of nucleosynthesis and defining the time-interval between its cessation and the formation of refractory minerals. The existence of live ^{129}I in the ESS was discovered in 1960 [1], with the estimated abundance level, relative to ^{127}I, of ~1.2×10^{-4} [2] (at the time of CAIs formation [3]). ^{129}I, which decays into ^{129*}Xe (15.7 Myr half-life), provides a sensitive ESS chronometer. The I-Xe dating method involves neutron irradiation of meteoritic samples resulting in ^{127}I(n,γβ)^{128*}Xe reaction. The observed correlation of ^{128*}Xe with radiogenic ^{129*}Xe forms the basis of I-Xe chronology [4].

Although the actual value of the initial $(^{129}$I/^{127}I$)_0$ ratio in the sample is of no importance for I-Xe dating since only relative values are needed, it can be estimated if the conversion factor (σΦ) of ^{127}I to ^{128*}Xe is known (σ - neutron capture cross section, Φ - neutron fluence). However, there is a complication since resonance capture plays a large role for ^{127}I. The earlier estimations of the initial $(^{129}$I/^{127}I$)_0$ ratios in Bjurböle were done using KI salt as an irradiation monitor [5, 6]. Meteoritic iodine is at ppb levels, billions of times less than in KI salt. The large resonance capture cross sections for ^{127}I and the high iodine concentration in KI, yield mean capture lengths for resonance neutrons of less than a few microns, much smaller than KI grains size. Neutrons at the resonance energies will be rapidly removed as captures in the outer layers of these monitors, producing gaps in the neutron energy spectra. This self-shielding reduces the effective capture cross sections for such iodine salts, making them unsuitable as irradiation monitors.

Moreover, 1mg of KI, irradiated with 2×10^{19} n/cm^2, would produce ~ 3×10^{13} atoms of ^{128*}Xe from thermal neutrons alone, and twice this much when resonance captures are included. A comparable amount of atmospheric ^{128}Xe for proper isotopic dilution would require an air spike of about 50 cm^3 STP [5]. Even after removal of chemically active species, the gas pressure will be so high as to be in the viscous, rather than the molecular flow regime, making complete mixing a very serious problem. Although mixing by repetitive exchange between two activated charcoal fingers, by sequential application of liquid nitrogen and heating, was used to obtain reproducible values for initial iodine in 3 Bjurböle samples, resulting in $(^{129}$I/^{127}I$)_0$ = $(1.095 \pm 0.029)\times10^{-4}$ [6, 7], that value most probably is too low due to the self-shielding effects.

In order to properly measure the effective σΦ of an irradiation, iodine monitors with ppm-ppb levels of iodine must be utilized. To address this problem we irradiated and analyzed 2 natural standards from the Geological survey of Japan (Table 1) with known ppb levels of iodine.

Table 1. Concentrations of iodine in standard obsidian rocks JR-1 and JR-2 as determined by [8, 9].

	Iodine, ppb			
	[8]	[9]		[9]wt.ave
JR-1	80 ± 6	97 ± 10	91 ± 11	94 ± 4
JR-2	67 ± 7	61 ± 7	70 ± 10	66 ± 4

Experimental: Two aliquots of different weight for each standard were sealed under vacuum in quartz ampules. Samples, along with the Shallowater absolute age standard [10], were irradiated with thermal neutrons in the Missouri University Research Reactor (MURR), receiving ≈ 2×10^{19} n/cm^2. The samples were placed in a fixed horizontal plane at the center of the vertical neutron profile in the pool of the reactor to minimize any vertical gradient of the neutron flux and the capsule was continuously rotated to minimize any x-y gradient. Irradiated samples were transferred into the Pt boats and kept for 6 month under high vacuum in the sample system of the mass-spectrometer. To extract noble gases samples were heated in a W-coil; released gases were cleaned from the chemically active species. The heavy noble gases were separated from He, Ne, and Ar; their isotopic composition measured by high transmission mass-spectrometer [11].

Cold blank with the first sample (JR-1a) in the furnace was measured following the standard analytical procedures [10] and was ~2×10^{-15} ^{132}Xe cm^3 STP. Xenon isotopic composition in JR-1a was then measured in 200–800–1000–1200–1400–1770°C temperature steps in order to estimate the release profile of ^{128*}Xe and optimize the measurement protocol for the remaining samples. The abundance and the isotopic composition of Xe at 200°C were undistinguishable from the cold blank values. Hot blanks, measured after melting of each sample with an empty coil at 1800°C (5 min), were about ~1.5×10^{-14} ^{132}Xe cm^3 STP and approximately atmospheric in

composition. The atmospheric standard corresponding to ~ 3.06×10^7 atoms of ^{132}Xe was routinely measured during the course of the analyses (Fig. 1).

Figure1. Typical count rates of ^{132}Xe in air standards measured prior to each JR-1b extraction (1σ).
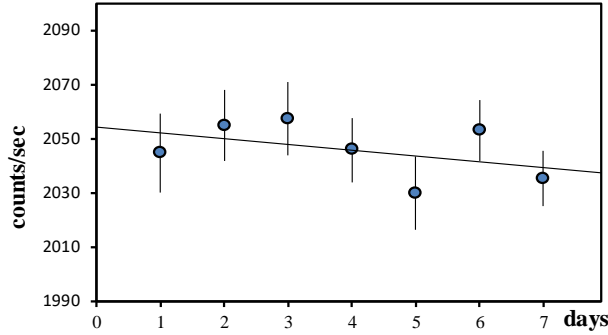
Results: Xe isotopic composition in irradiated JR standards consisted of atmospheric, ^{235}U fission, I-derived and Ba-derived Xe. Concentrations of radiogenic ^{128*}Xe, were calculated as excesses over atmospheric ^{128}Xe/^{130}Xe values (Table 2). The conversion factor (although referred to here as $\sigma\Phi$, it is really the resonance integral over the reactor neutron spectrum) of ^{127}I to ^{128*}Xe in JR-1 and JR-2 was calculated based on the official "preferable" values for these standards [8] and on the average of the later data [9] (Table 2). The ($\sigma\Phi$) values show better agreement when calculated based on the earlier official iodine concentrations [8].

Table 2. Concentrations of radiogenic ^{128*}Xe for JR-1 and JR-2 and corresponding ($\sigma\Phi$) values, derived here from different iodine concentrations reported by [8, 9].

	Weight, mg	Atoms $\times 10^9$	($\sigma\Phi$)[8], $\times 10^{-4}$	($\sigma\Phi$)[9], $\times 10^{-4}$
JR1-a	20.401	58.92 ± 0.24	1.54	1.32
JR1-b	102.316	56.74 ± 0.22	1.50	1.27
JR2-a	27.516	45.02 ± 0.13	1.42	1.44
JR2-b	99.197	49.24 ± 0.35	1.55	1.57

Considering lower iodine inhomogeneity in larger samples (10% at 100 grams *versus* 26% at the 20 gram), we adopted 1.53×10^{-4}, an average ($\sigma\Phi$) value for JR-1b and JR-2b in this irradiation (Table 2). Using this value we estimated the initial (^{129}I/^{127}I)$_0$ ratio in the absolute I-Xe age standard Shallowater, irradiated with these samples. Xe in Shallowater was released in 14 temperature extractions. The ^{129*}Xe/^{128*}Xe ratio for Shallowater of 0.8829 ± 0.0056 is the slope of the linear correlation defined by 8 experimental points

(Fig. 2). Using ($\sigma\Phi$) = 1.53×10^{-4}, the initial iodine ratio (^{129}I/^{127}I)$_0$ in Shallowater is $(0.8829 \pm 0.0056) \times 1.53 \times 10^{-4}$, or $\approx 1.35 \times 10^{-4}$.

Figure 2. Three-isotope plot for Shallowater. Red numbers are extraction temperatures in °C. 1σ error bars are smaller than the experimental point's symbols.
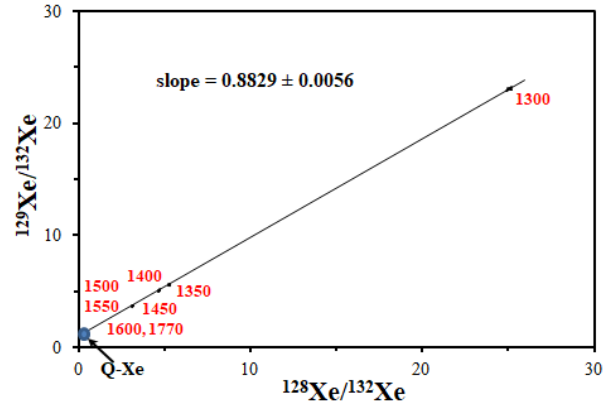
The absolute age of Shallowater, 4562.3 ± 0.3 Ma, was determined from the correlation of Pb-Pb and I-Xe ages in a number of samples, where I-Xe and Pb-Pb systems closed simultaneously [10]. Considering an age difference of 5 Ma between the formation of CAIs (4567.30 ± 0.16 Ma [3]) and the I-Xe system closure in Shallowater, the ^{129}I/^{127}I ratio at the time of CAI formation is 1.7×10^{-4}, about 1.5 times higher than the currently accepted ESS value [2]. The uncertainty of this value is limited by the level of precision of the iodine concentration in JR-1 and JR-2.

References: [1] Reynolds J. H. (1960) *Physical Review Letters 4*, 8–10. [2] Brazzle R. H. et al. (1999) *Geochim. et Cosmochim. Acta 63*, 793–760. [3] Connelly J. N. et al. (2017) *Geochim. et Cosmochim. Acta 201*, 345–363. [4] Jeffery P. M. and Reynolds J. H. (1961) *J. Geophys. Res. 66*, 3582–3583. [5] Lewis R. S. and Anders E. (1975) *Proc. National Academy of Sci. 72*, 268–273. [6] Kennedy B. M. (1981); Ph. D. Thesis, Washington Univ., St. Louis. [7] Hohenberg C. M. and Kennedy B. M. (1981) *Geochim. et Cosmochim. Acta 45*, 251–256. [8] Imai N. et al. (1995) *Geostandards Newsletter 19*, 135–213. [9] Ozaki H. and Ebihara M. (2007) *Analytica Chimica Acta 583*, 384–391. [10] Pravdivtseva O. et al. (2017) *Geochim. et Cosmochim. Acta 201*, 320–330. [11] Hohenberg C. M. (1980) *Rev Sci Instrum. 51*, 1075–1082. [12]