Extinct ^{129}I in Halite from a Primitive Meteorite: Evidence for Evaporite Formation in the Early Solar System

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Halite crystals from the Zag H3-6 chondrite contain essentially pure (monoisotopic) xenon-129 (^{129}Xe) produced in the early history of the solar system by the decay of short-lived iodine-129 (^{129}I) (half-life = 15.7 million years). Correlated release of ^{129}Xe and ^{128}Xe, produced artificially from ^{127}I by neutron irradiation, corresponds to an initial (^{129}I/^{127}I) ratio of (1.35 ± 0.05) × 10^{-4}, close to the most primitive early solar system value. If the ^{129}Xe was produced by in situ decay, then the halite formed from an aqueous fluid within 2 million years of the oldest known solar system minerals.

The occurrence of halite has recently been reported in two primitive chondritic meteorites, Monahans (*1*) and Zag (*2*, *3*). Both meteorites are H group chondrites, indicating an origin on the same asteroidal parent body. Both are brecciated with light and dark lithologies commonly found in regolith breccias. The presence of halite suggests that heating of the parent body led to the dehydration of the interior and that leaching by the resulting hydrothermal fluids was followed by deposition of evaporite minerals, including halite. A Rb-Sr model age of 4.7 ± 0.2 billion years ago (Ga) reported for a halite crystal from Monahans (*1*) indicates that these processes occurred early in the history of the parent body.

We analyzed xenon isotopes extracted from a 10-μg halite crystal from Zag and found it to be essentially pure ^{129}Xe (Fig. 1) resulting from the decay of ^{129}I that was present in the early solar system. I-Xe and Ar-Ar experiments were subsequently performed on halite fragments ranging in weight from 8 to 40 μg and on milligram-sized whole rock chips of a light clast and gray matrix material (*4*). The I-Xe experiments on the halite were made possible by the uniquely high sensitivity of the RELAX resonance ionization mass spectrometer (*5*).

The I-Xe data (Table 1) show that apart from ^{129}Xe and ^{128}Xe, the amounts of other xenon isotopes released were barely distinguishable from blanks and, within error, are atmospheric in composition. Amounts of ^{132}Xe, for example, ranged from 1500 to 5000 atoms, whereas ^{124}Xe and ^{126}Xe were not detected. Small corrections for trapped ^{129}Xe and ^{128}Xe were made on the basis of the measured ^{132}Xe, assuming atmospheric values for ^{129}Xe/^{132}Xe and ^{128}Xe/^{132}Xe. The conversion factor from ^{127}I to ^{128}Xe was estimated from measurements on the Shallowater meteorite used as a neutron monitor (*6*), and initial ^{129}I/^{127}I ratios were inferred from the corrected ^{129}Xe/^{128}Xe ratio (hereafter denoted as ^{129}Xe*/^{128}Xe*) (Table 1). ^{129}I/^{127}I is low in the initial extractions because of either ^{129}Xe loss or addition of normal iodine after the decay of live ^{129}I. ^{129}Xe* and ^{128}Xe* are roughly correlated in the higher temperature extractions. Individual ^{129}I/^{127}I ratios range from (1.03 ± 0.04) × 10^{-4} to (1.83 ± 0.23) × 10^{-4}, with a weighted mean of (1.35 ± 0.05) × 10^{-4}. If interpreted in terms of chronology, this ratio would correspond to a formation time for the halite of 4.8 ± 0.9 million years (My) before the formation of the Bjurböle reference chondrite (*7*, *8*) and only 1.7 ± 0.9 My later than the earliest I-Xe age ever reported, that of magnetite in the Murchison meteorite, ^{129}I/^{127}I = (1.456 ± 0.006) × 10^{-4} (*9*). However, scatter of individual ratios about the mean value is significantly outside of the error, implying some kind of disturbance to the isotope system. The iodine contents of the two halite samples are 36 parts per billion (ppb) and 8 ppb, respectively. On the assumption of a similar bulk ^{129}Xe*/^{127}I ratio, the iodine content of the unirradiated sample (Fig. 1) is estimated to be 110 ppb.

Ar-Ar analyses were also carried out on two separate halite fragments, on two fragments of gray matrix, and on a light clast (*10*). The data are too extensive to present here in full. Key features are summarized in Table 2 and in Fig. 2. The whole rock Ar-Ar release patterns show well-developed age plateaus from the lowest temperature steps with the characteristic high-temperature decrease interpreted as an artifact of recoil (*11*). Ages based on the plateaus are indistinguishable (Table 2), with a mean value of 4.25 ± 0.03 Ga. This is presumed to represent the time of lithification of the breccia. The major release of radiogenic Ar from the (furnace heated) dark fragment occurs between 400° and 600°C from a phase with a K/Ca ratio of 0.32, probably K-feldspar. This identification is supported by diffusion characteristics of the low-temperature release that correspond to an activation energy of 100 ± 8 kJ mol^{-1} K^{-1}. The two halite fragments both yielded age plateaus, but with distinct ages of 4.03 ± 0.05 and 4.66 ± 0.08 Ga. Factor of two differences in K/Cl and the different apparent ages may reflect the presence of a minor, easily mobilized K-bearing phase such as sylvite.

High concentrations of trapped ^{36}Ar in

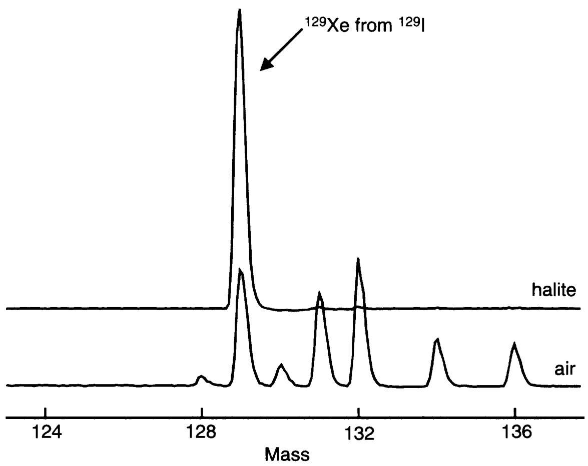

Fig. 1. Comparison of the mass spectrum of Xe released from unirradiated Zag halite with that of the terrestrial atmosphere. The spike of ^{129}Xe in the halite results from the decay of now extinct ^{129}I.

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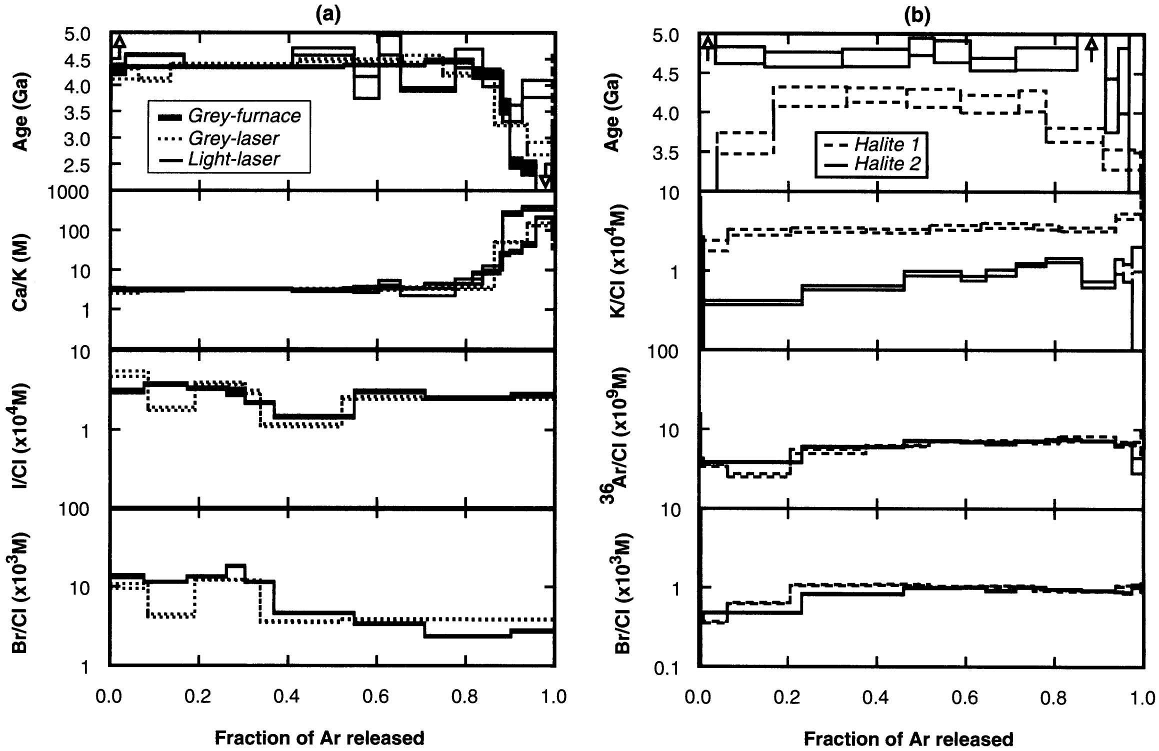

Fig. 2. Ar-Ar ages and elemental ratios in (**A**) whole rock and (**B**) halite fragments from Zag. In (A), age and Ca/K are plotted against potassium-derived $^{39}Ar_K$, and Br/Cl and I/Cl are plotted against chlorine-derived $^{38}Ar_{Cl}$. In (B), age is plotted against $^{39}Ar_K$; the other plots are against $^{38}Ar_{Cl}$.

the gray matrix (Table 2) are consistent with solar wind implantation in an asteroidal regolith. Cosmogenic ^{38}Ar ($^{38}Ar_C$) was released at high temperatures and is distinguished from the trapped and chlorine-derived ^{38}Ar on the basis of a high- temperature correlation with Ca-derived ^{37}Ar. The implied $^{38}Ar_C$/Ca ratio is (10.5 ± 0.5) × 10^{-7} cm^3 standard temperature and pressure (STP) g^{-1}. In contrast, trapped and cosmogenic Ar concentrations were much lower in the light phase, with $^{38}Ar_C$/Ca = (1.2 ± 0.3) × 10^{-7} cm^3 STP g^{-1} of Ca. On the basis of a nominal 4π production rate of 2.8 × 10^{-8} cm^3 STP g^{-1} of Ca My^{-1} (*12*), the $^{38}Ar_C$/Ca ratio of the light phase corresponds to an exposure duration of 4.3 ± 1.0 My. We interpret this as indicating the ejection time of Zag from its parent asteroid and note its correspondence with the well-established cluster at 4 million years ago (Ma) in H-chondrite exposure ages (*13*). The difference between $^{38}Ar_C$/Ca for gray matrix and light phases corresponds to an additional 2π exposure duration of 66 My, which we interpret as indicative of precompaction exposure in the asteroidal regolith. The halite samples have identical ^{36}Ar/Cl ratios of (6.9 ± 0.9) × 10^{-9} mole ratio (M), corresponding to relatively high concentrations of ^{36}Ar, (2.6 ± 0.3) × 10^{-6} cm^3 STP g^{-1}. The absence of a corresponding high concentration of trapped ^{132}Xe in the halite leads us to infer that the most likely source is by way of the reaction ^{35}Cl(n,γβ)^{36}Ar, induced by cosmic ray secondary neutrons. Zag is a relatively large meteorite, and the inferred thermal neutron fluence, 2 × 10^{14} neutrons cm^{-2}, is consistent with irradiation in transit to Earth (*14*). It is also possible that this neutron exposure occurred in the asteroidal regolith. Soil samples from the lunar regolith typically exhibit exposure to neutron fluences ranging from <10^{15} to 10^{17} neutrons cm^{-2} and cosmic ray exposure ages typically in the range of 100 to 500 Ma (*15*).

Chlorine is detected predominantly in the gray matrix material, consistent with the observation that halite appears to be confined to this phase. Br/CI (7.6 × 10^{-3} M) and I/Cl (3.5 × 10^{-4} M) in the matrix are comparable to Cl chondritic values (2.1 × 10^{-3} M and 4.7 × 10^{-4} M, respectively) (*16*). Br/Cl in the light phase (1.0 × 10^{-3} M) and halite (0.9 × 10^{-3} M) are lower, whereas I/Cl in the halite [(0.4 to 5.1) × 10^{-8} M] is four to five orders of magnitude lower. This latter observation is consistent with halite formation by brine evaporation, during which process I is largely excluded from the halite lattice (*17*).

These observations can be understood by the following sequence of events. On the basis of the I-Xe analyses, the halite formed soon after parent body accretion by evaporation of a brine. The relatively low neutron fluence experienced by the halite and the absence of solar wind ^{132}Xe suggest that it was not part of the regolith when the gray matrix acquired its solar wind and spallation components. This period of regolith evolution lasted for around 66 My sometime within the first 300 My of solar system history. At about 4.25 Ga, a large impact brought together the halite, the regolith component, and the light phase. The retention of a high ^{129}Xe*/^{127}I ratio implies that the halite has not been subjected to substantial dissolution and recrystallization in the 4.5 billion years since its formation. This in turn suggests that the processes that led to aqueous activity in the asteroidal parent body may have ended early in solar system history after evaporation of water into space. This interpretation supports recent modeling of aqueous transfer within early planetesimals subjected to heating by now extinct ^{26}Al (*18*). The younger, 4.0-Ga Ar-Ar age of one halite sample is difficult to understand in view of the well-defined 4.25-Ga "cooling age" of the host unless one assumes that the potassium-bearing phase, possibly sylvite, was mobilized by mild heating or moisture in a way that left the K-feldspar in the host phase unaffected.

An alternative interpretation of the halite I-Xe and Ar-Ar data is that the ^{129}Xe and possibly some ^{40}Ar represent an "inherited" component leached from the interior of the parent asteroid along with sodium, chlorine, and iodine. In this case, the correlation between ^{129}Xe and ^{127}I would require semiquantitative extraction and trapping of both xenon and iodine from primitive precursors. This process is common on Earth, where ore minerals and hydrothermal quartz veins commonly contain inherited ^{40}Ar trapped in fluid inclusions (*19*). However, these terrestrial fluids also contain significant quantities of dissolved atmo-

Table 1. Xenon isotopes from irradiated Zag halite (amounts in atoms). The data represent successive releases by laser stepped heating. Temperatures were not determined directly, but the first extraction is estimated to be on the order of 300° to 400°C. The last extraction releasing measurable gas is presumed to be above the fusion point of halite, 800°C.

	^{128}Xe	^{129}Xe	^{132}Xe	$^{129}I/^{127}I$ ($\times 10^{-4}$)
		Zag h1 (9 μg) I = 36 ppb		
1	56,300 ± 1,000	44,900 ± 1,000	4,340 ± 550	0.63 ± 0.02
2	49,250 ± 1,000	75,200 ± 1,250	2,420 ± 450	1.29 ± 0.03
3	14,000 ± 600	30,650 ± 950	1,430 ± 450	1.83 ± 0.10
4	12,600 ± 550	17,900 ± 750	3,310 ± 450	1.03 ± 0.07
5	5,020 ± 450	10,520 ± 700	2,150 ± 550	1.50 ± 0.19
Total	137,170 ± 1,200	179,170 ± 1,600	13,650 ± 810	1.06 ± 0.01
		Zag h4 (40 μg) I = 8 ppb		
1	92,800 ± 950	11,900 ± 500	2,330 ± 400	0.09 ± 0.01
2	55,200 ± 750	95,900 ± 1,050	1,500 ± 350	1.49 ± 0.03
3	37,360 ± 650	59,200 ± 850	2,210 ± 350	1.33 ± 0.03
4	3,830 ± 250	10,240 ± 400	2,730 ± 300	1.80 ± 0.16
5	2,020 ± 250	7,180 ± 400	5,000 ± 350	1.14 ± 0.27
6	2,970 ± 350	6,740 ± 550	2,730 ± 500	1.26 ± 0.23
Total	141,250 ± 1,050	191,160 ± 1,200	16,500 ± 680	1.08 ± 0.01

Table 2. Element abundances based on Ar-Ar analyses. Errors are 1σ; ND, not determinable.

	Gray matrix	Light clast	Halite 1	Halite 2
Wt (mg)	2.48	0.79	0.0085	0.0358
Ca (wt %)	1.33	4.52	0.115	0.135
K (ppm)	880	1050	2290	560
Cl (ppm)	59	5	≡60.7 (wt %)	≡60.7 (wt %)
Br (ppm)	1.01	0.011	1300	1140
I (ppb)	74	<2	ND	ND
^{36}Ar (cm^3 STP g^{-1})*	9.2×10^{-7}	$\leq 4 \times 10^{-9}$	2.6×10^{-6}	2.6×10^{-6}
^{132}Xe (cm^3 STP g^{-1})	7.0×10^{-10}	$\leq 4 \times 10^{-12}$	($\leq 5 \times 10^{-11}$)†	
Ca/K (M)	14.7 ± 0.2	42.1 ± 0.9	0.5 ± 0.1	2.4 ± 0.6
K/Cl (M)	14 ± 2	190 ± 50	0.0033 ± 0.0001	0.0008 ± 0.0001
Br/Cl (× 10^3 M)	7.6 ± 1.0	1.0 ± 0.5	0.95 ± 0.05	0.81 ± 0.05
I/Cl (× 10^{4}M)	3.5 ± 0.5	ND	ND	ND
Exposure age (Ma)	66 ± 3‡	4 ± 1‡	ND	ND
Ar-Ar age (Ga)	4.25 ± 0.03	4.29 ± 0.03	4.03 ± 0.05	4.66 ± 0.08

*Trapped solar wind ^{36}Ar for gray matrix and light clast, secondary neutron induced for halite (see text). †Based on analysis of a different halite fragment. ‡Age for light clast is based on 4π exposure. Age for gray matrix is additional 2π preexposure (see text).

spheric gases, and if the Zag xenon and iodine correlation were inherited in an analogous way, one might expect to see substantial quantities of planetary ^{132}Xe, inherited from the passage of the fluid through the parent body. Its absence argues against this second interpretation.

References and Notes

1. M. E. Zolensky *et al.*, *Science* **285**, 1377 (1999).
2. J. N. Grossman, *Meteorit. Planet. Sci.* **34** (suppl.), A182 (1999).
3. M. E. Zolensky, R. J. Bodnar, A. E. Rubin, *Meteorit. Planet. Sci.* **34** (suppl.), A124 (1999).
4. This study used material separated from a 15 cm by 10 cm cut slice of Zag (Natural History Museum specimen 1999, M34). The meteorite slice shows a brecciated texture and consists of about 70% light-colored, crystalline clasts of petrographic type 6 and 30% surrounding gray matrix of petrographic type 4 that contains recognizable chondrules. Lesser amounts of a third dark clast type that has not yet been sectioned are also present in the hand specimen. Ten halite grains (≤3 mm diameter) have been identified on the cut surfaces of the Zag specimen, and four others have been found in thin sections; all fourteen are within the gray matrix. The grains are not present along obvious veins, although some of their outlines (i.e., rhombohedral in the case of the largest one) indicate that they crystallized within opening fractures. Some of the halite grains also show signs of having undergone subsequent fracturing and recrystallization. Both the matrix and light clasts were found to be weakly shocked—S3 by the classification of (*20*). The halite grains have mottled colors varying from colorless to blue (predominant) and dark blue. Zolensky *et al.* (*1*) suggested that similar colors seen in Monahans (H5) halite grains—also present within a gray matrix—were a result of exposure to cosmic rays before the meteorite fall. No other minerals within Zag that might have a related paragenesis to the halite, e.g., carbonates, sulfates, or clay veins, have been found; the textures and major mineral assemblages seen in thin section are typical of equilibrated H group chondrite. There are no signs of any reaction between the halite and surrounding silicate phases. The halite was found to contain primary and secondary fluid inclusions, and these are the subject of a separate study. Olivine and pyroxene mineral compositions (Hitachi 2500 SEM/EDS, 15 kV, 2 nA) are equilibrated Fo82, En83 in the light clasts and the matrix. However, the meteorite has previously been classified as H3-6 (*2*), indicating the presence of unequilibrated material. Therefore, Zag is heterogeneous on a coarse scale in respect to the range of petrographic types present within its components. The halite is nearly pure NaCl as K, S, and Ca were not detected (on the basis of multiple analyses within two separated grains and three grains in thin section; Cameca SX50 wds probe, 15 kV, 20 nA).
5. J. D. Gilmour, I. C. Lyon, W. A. Johnston, G. Turner, *Rev. Sci. Instrum.* **65**, 617 (1994).
6. Six fragments of halite from three distinct grains were packaged for irradiation individually in 3-mm outer diameter quartz tubes with aluminum foil plugs. A larger diameter quartz tube was used to hold fluence monitors and standards (three aliquots of Hb3gr hornblende, an aliquot of potassium sulfate, an aliquot of calcium fluoride, and three aliquots of the Shallowater meteorite) together with two fragments of gray matrix material and two fragments of light clast material. All discrete samples were wrapped in aluminum foil, which was removed before analysis, and the tube was evacuated and sealed. The package was irradiated in the Vertical Irradiation Facility position of the DR3 reactor at the Riso National Laboratory, Denmark, with a nominal thermal fluence of 7×10^{18} neutrons cm^{-2}. A conversion factor $[(^{129}Xe^*/^{127}I)/(^{129}Xe^*/^{128}Xe^*) = 0.87 \times 10^{-4}]$ was determined from measurements on Shallowater.
7. G. Turner, *J. Geophys. Res.* **70**, 5433 (1965).
8. C. M. Hohenberg and B. M. Kennedy, *Geochim. Cosmochim. Acta* **45**, 251 (1981).
9. R. S. Lewis and E. Anders, *Proc. Natl. Acad. Sci. U.S.A.* **72**, 268 (1975). Following a recent analysis of Orgueil magnetite, C. M. Hohenberg *et al.* {*Lunar Planet. Sci. Conf.* **31** (abstract number 1958) (2000) [CD-ROM]} have argued that the $^{129}I/^{127}I$ values of Lewis and Anders are systematically high.
10. Noble gases were extracted from meteorite and halite samples with a Nd–yttrium-aluminum-garnet laser defocused to a spot diameter of 3 mm. Stepped heating of the sample was achieved by sequentially increasing the laser power until fusion. Each step was of 1-min duration followed by a further 4 min of purification with a hot (400°C) Zr-Al getter. Gas from one sample of the gray matrix was extracted with a resistance furnace over the temperature interval 300° to 1400°C. Isotopic measurements were performed on Ar, Kr, and Xe. Corrections for blanks, background, mass discrimination, and interfering nuclear reactions were applied but are only significant for Ar data. Hb3gr and the Shallowater meteorite were used to monitor Ar, Kr, and Xe isotope production from Ca, K, Cl, Br, and I (*21*).
11. G. Turner and P. H. Cadogan, *Proceedings of the Fifth Lunar Conference, Geochim. Cosmochim. Acta* **2** (Suppl. 5), 1601 (1974).
12. G. Turner, J. C. Huneke, F. A. Podosek, G. J. Wasserburg, *Earth Planet. Sci. Lett.* **12**, 19 (1971).
13. K. Marti and T. Graf, *Annu. Rev. Earth Planet. Sci.* **20**, 221 (1992).
14. D. D. Bogard *et al.*, *J. Geophys. Res.* **100**, 9401 (1995).
15. G. Crozaz, *Phys. Chem. Earth* **10**, 197 (1977).
16. E. Anders and N. Grevesse, *Geochim. Cosmochim. Acta* **53**, 197 (1989).
17. W. T. Holser, in *Marine Minerals*, vol. 6 of *Reviews in Mineralogy*, R. G. Burns, Ed. (Mineralogical Society of America, Washington, DC, 1979), chap. 9.
18. E. D. Young, R. D. Ash, P. England, D. Rumble III, *Science* **286**, 1331 (1999).
19. S. Kelley, G. Turner, A. W. Butterfield, T. J. Shepherd, *Earth Planet. Sci. Lett.* **79**, 303 (1986).
20. D. Stöffler, K. Keil, E. R. D. Scott, *Geochim. Cosmochim. Acta* **55**, 3845 (1991).
21. L. H. Johnson, R. Burgess, G. Turner, J. W. Harris, J. H. Milledge, *Geochim. Cosmochim. Acta* **64**, 131 (2000).

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