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Tritium Release and Gamma Activity of Various Lithium Ceramics Irradiated by Fast and Thermal Neutrons (COMPLIMENT Experiment)

Abstract

In the COMPLIMENT experiment the various ceramic breeder materials ($LiAlO_2$, Li_2O, Li_2ZrO_3, Li_2SiO_2 and Li_4SiO_4) studied within the European Fusion Technology Program were irradiated in parallel with epithermal neutrons in the HFR Petten and with thermal neutrons in the OSIRIS reactor at Saclay up to a total damage of 2 dpa (displacements per atom). The objectives of this irradiation were

1. to compare the radiation damage effects caused by fast neutrons and by the charged particles of the $^6Li(n, \alpha)$ t - reaction and
2. to compare the irradiation behavior of the various ceramics in an identical test environment.

Tritium release of the irradiated samples was studied by out-of-pile annealing. These studies indicate that the tritium release kinetics is not significantly affected by

- the specific tritium inventory (i.e. the release process is first order)
- the Li-burnup (up to 2 %)
- the type of radiation damage (induced by fast neutrons or charged particles)

The gamma activity of the investigated ceramics was found to be mainly due to stainless steel contaminations and sample impurities. The activity of the main constituents was comparatively small, even for zirconate.

Some of the ceramics decomposed into pieces or particles, especially during the 425 °C, high power density ($\approx$ 60 W/cm^3) and high Li-burnup (2 %) OSIRIS irradiation. This unexpected observation requires further irradiations under DEMO-relevant conditions to qualify the reference ceramic materials.

Tritiumfreisetzung und Gammaaktivität verschiedener, mit schnellen und thermischen Neutronen bestrahlten Lithium-Keramiken (COMPLIMENT-Experiment)

Zusammenfassung

Im COMPLIMENT-Experiment wurden die verschiedenen, innerhalb des Europäischen Fusionstechnologie-Programms untersuchten Brutkeramik-Materialien ($LiAlO_2$, Li_2O, Li_2ZrO_3, Li_2SiO_2 und Li_4SiO_4) parallel mit epithermischen Neutronen im HFR Petten und mit thermischen Neutronen im OSIRIS-Reaktor in Saclay bis zu einer Gesamtschädigung von 2 dpa ("displacements per atom") bestrahlt. Die Ziele des Bestrahlungsexperiments waren:

1. Vergleich der durch schnelle Neutronen und der durch die geladenen Partikel von der $^6Li(n, \alpha)$ t - Reaktion hervorgerufenen Strahlenschäden
2. Vergleich des Bestrahlungsverhaltens der verschiedenen Materialien unter identischen Testbedingungen.

Die Tritiumfreisetzung der bestrahlten Proben wurde durch out-of-pile-Ausheizen untersucht. Die Untersuchungen zeigen, daß die Tritiumfreisetzungs-Kinetik nur unmerklich von folgenden Parametern abhängt:

- Spezifisches Tritiuminventar (d.h. die Freisetzungsprozesse sind erster Ordnung)
- Li-Abbrand (bis 2 %)
- Art der Strahlenschäden (durch schnelle Neutronen oder durch geladene Teilchen verursacht)

Ein Teil der Proben zerfiel während der Bestrahlungen in Stücke bzw. Partikel. Dies gilt insbesondere für die Bestrahlung im OSIRIS-Reaktor (hohe Leistungsdichte $\approx$ 60 W/cm^3 und hoher Abbrand $\approx$ 2 %) bei 425 °C. Dieses überraschende Ergebnis zeigt, daß weitere Bestrahlungen unter DEMO-relevanten Bedingungen für eine Qualifizierung der Referenz-Brutmaterialien notwendig sind.

Contents

1. Introduction

The various ceramic breeder materials studied within the European Fusion Technology Program were irradiated in parallel in an epithermal neutron field (behind a cadmium screen) in the HFR reactor at Petten and in a thermal neutron field in the OSIRIS reactor at Saclay up to a total damage of about 2 dpa (displacements per atom), corresponding to about 3 months operation of a 1 MW/m^2 blanket [1, 2]. The objectives of this irradiation, named COMPLIMENT (comparison of lithium materials damage effects by fast neutrons and ^{6}Li(n, α) t - reactions) were

1. to compare the radiation damage effects caused by fast neutrons and by the charged particles of the ^{6}Li(n, α) t-reaction and
2. to compare the irradiation behavior of the various ceramics in an identical test environment.

The neutron field and the induced radiation damage in the HFR is representative for the inner regions near the first wall, those of OSIRIS for the outer regions of a fusion reactor blanket.

2. Irradiation conditions and sample characteristics

Details of the irradiations have been described previously [1, 2], important characteristics are summarized in table 1.

The ceramics were irradiated in 6 mm outer, 5.24 mm inner diameter and 100 mm total length tubes made of 1.4970 grade stainless steel. The breeder material occupied about half of the tube volume, the remaining volume constitutes a gas plenum. The ceramics were thoroughly dried, filled into the tubes under a dry helium atmosphere at 300 °C and the tubes were closed by a welded end cap.

In table 2 sample characteristics and irradiation conditions of all tested samples are summarized. Each irradiation tube is identified by a sample number. In addition, sample material, sample type (P pellets, MS molten and SS sintered spheres), density (% theoretical density) and the supplying laboratories are indicated.

All pellet samples were fabricated by cold pressing and sintering of chemically precipitated powder. The orthosilicate spheres were produced either by a melting process (MS) or by granulation, spherodization and sintering (SS). While the pellets are foreseen for the "breeder in tube (BIT)" blanket concept, the spheres or pebbles are used in the "breeder out of tube (BOT)" concept.

For the samples fabricated by Casaccia and by KfK, additional data are available and are given in table 3 [3 - 5, 12]. For the KfK samples the measured densities differ somewhat from the specified values used to identify the samples.

3. Experiments

The sample tubes have been examined by neutron radiography at HFR Petten and by gamma radiography at OSIRIS Saclay and were then returned to KfK for dismantling. After dismantling a few samples were sent to Casaccia and Saclay, the bulk stayed at KfK for post irradiation examination.

3.1 Irradiation behavior

Radiographic results (swelling) and KfK observations from visual inspection, from ceramography and concerning compatibility with stainless steel have been compiled in [4, 5], KfK results from mechanical tests and on chemical reactivity in [6, 7].

The microstructure of the KfK silicate samples changed remarkably during irradiation: the grain size of all samples increased (table 3), whereas the amount of open porosity decreased for the molten (MS), but increased for the sintered (SS) spheres [4].

Irradiation induced dimensional and weight changes for the KfK pellets are compared in the table below:

Sample type	no	Irradiation	Change (%) Stack length	Pellet diam.	Pellet height	Pellet weight
Li_4SiO_4 90 % P	109	HFR 400 °C	+ 1.0	+ 1.1	+ 1.0	- 0.6
	110	HFR 650 °C	+ 1.3	+ 2.8	- 1.0	- 4.4
Li_2SiO_3 90 % P	101	HFR 400 °C	+ 2.5	+ 1.5	+ 0.8	+ 2.3
	102	HFR 650 °C	+ 3.0	+ 3.1	+ 2.9	+ 2.0
	104	OSIRIS 650 °C	+ 3.3	+ 2.9	+ 2.8	+ 1.9

Except for sample number 110, where the height of two from three pellets decreased during irradiation, the radiographically determined changes in stack length [4] are in reasonable agreement with the diameter and height change of

the three pellets studied here (table 8). Values for the unirradiated pellets are given in [3]. Usually some weight loss is observed for ceramics which are kept at elevated temperatures for longer times. In contrast to this, a remarkable weight increase was consistently found for the Li_2SiO_3 pellets.

The mechanical stability of the ceramics decreased remarkably during irradiation [6]. This was already indicated by the visual inspection after dismantling [4, 5] and during handling in the tritium release tests (table 4 to 7). The state of specimens after irradiation is indicated in table 2 behind the sample number: "st" means the sample had got stuck to the tube and could not be removed, "pi" sample decomposed into large pieces and "pa" into small particles or dust. Especially for the 400 °C OSIRIS irradiation, a large fraction of the samples, including all KfK samples, decomposed. This is probably due to the high power density and/or thermal transients during reactor trips. Power densities induced by the ^6Li (n, α) t-reaction have been calculated according to q_n [W/cm^3] = 7.66 x 10^{-13} x p [1/cm^{3}s] [4] (p tritium production rate) and are given for some representative samples in the table below. The gamma heating in both irradiations (HFR and OSIRIS) was $\leq$ 5 W/cm^3.

Sample type	no.	Irradiation	p (10^{12}/cm^{3}s)	q_n (W/cm^3)
$LiAlO_2$ 84 % P	142	HFR 400 °C	4.6	3.5
	150	OSIRIS 400 °C	100	78
Li_4SiO_4 98 % MS	173	HFR 400 °C	5.7	4.4
	175	OSIRIS 400 °C	75	57
Li_4SiO_4 85 % SS	113	HFR 400 °C	4.5	3.4
	115	OSIRIS 400 °C	72	55

In table 4 conditions and state of samples after irradiation for previous high power density and high burnup irradiations are summarized [7 - 10, 15 - 17]. As can be seen, COMPLIMENT was the first irradiation where a massive decomposition of the molten and sintered Li_4SiO_4 spheres was observed, although in some previous irradiations (ALICE-3, SIBELIUS) both, the power density and the burnup were comparable or even higher. The reason for the serious mechanical failure of most samples in the COMPLIMENT irradiation is yet unclear. A tentative explanation are steep temperature transients caused by trips in the OSIRIS reactor. As the power density in the OSIRIS irradiation was comparable to that in a DEMO fusion

reactor ($\approx$ 50 W/cm^3), the OSIRIS results indicate that further irradiations under DEMO-relevant conditions concerning power density and burnup are necessary to quality the reference breeder ceramics.

3.2 Tritium release

Annealing was performed in a device described earlier [14]. The main characteristics are: the sample chamber is connected by a short, heated line ($\approx$ 300 °C) to a Zn reductor (390 °C). The reductor transforms any tritium water to tritium gas. This avoids problems with tritium water adsorption and allows quantitative tritium measurements. The tritium activity is measured in parallel with a ionization chamber and a proportional counter. In all cases, the agreement between the two detectors was excellent. Therefore only the ionization chamber data are given.

The samples were purged with 50 standard-cm^3/min He + 0.1 % H_2 (purity 99.9999 %). Two heating procedures were used: linear ramps with 5 °C/min (occasionally with 10 °C /min) or fast, stepwise temperature increase holding each temperature level for about 2 h, up to a final temperature of 850 °C, which was hold for $\geq$ 3 h.

All KfK materials and in addition $LiAlO_2$ 84 % P Sayclay, $LiAlO_2$ "P" 80 % P Casaccia, Li_2O P Springfield, Li_2ZrO_3 80 % P Springfield and Li_2SiO_3 82 % P Mol have been studied. Usually three pellets from each of these stacks have been annealed. The geometrical data, the mass before and after annealing and the tritium release per sample and per g are given in table 5 to 8. In addition it is indicated if the samples were decomposed after irradiation or after annealing. The specific tritium release of pellet number 1, located at the end of the stack, is generally remarkably higher (up to a factor two) than that of pellets (number 3 to 6) from the central region of the stack. This is probably due to the temperature drop at the end of the stack.

In table 9 and 10 irradiation data and specific tritium release data are summarized for the HFR and OSIRIS irradiation, respectively. Irradiation data for the HFR (temperature, damage, tritium production and burnup) have been reported in [4, 8, 9].

For the OSIRIS irradiation until now no measured temperatures are available. Damage and tritium production are from [10] and burnup has been calculated from the tritium production.

In purged inpile tests under steady-state conditions, the tritium residence time is equal to the ratio of tritium inventory and tritium production rate. The residence times determined by this relation for the closed capsule irradiation studied here are generally about two orders of magnitude higher than the inpile residence times. Evidently the stainless steel walls constitute effective barriers for tritium permeation, leading to high tritium tritium partial pressures in the gas plenum and to high inventories in the samples. This is consistent with the observation that the tritium inventory in the gas plenum is of the same order of magnitude as that in the samples. Accordingly, the ratios of released tritium (tritium inventory) to tritium production are pretty high and ly

for	HFR 400 °C	in the range	7 - 23 %
"	HFR 650 °C	"	0.3 - 5 %
"	OSIRIS 400 °C	"	20 - 45 %
"	OSIRIS 650 °C	"	1 - 3 %

Exceptional high inventories were observed for Li_4SiO_4 98 % MS KfK in HFR 400 °C (42 %) and for Li_2SiO_3 90 % P KfK in all irradiations ($\approx$ 100 % in OSIRIS 400 °C). Exceptional low was the inventory of Li_2O 82 % P Springfield in OSIRIS 400 °C (2.5 %). Generally, the inventories at 650 °C are more than one order of magnitude smaller than that at 400 °C. This is not the case for Li_2ZrO_3 80 % P Springfield in HFR and for Li_2O P Springfield in OSIRIS.

In the table below tritium release determined in Casaccia [12, 13] is compared with results of this study:

Sample type	no	Irradiation	Tritium release (10^{10} Bq/g) Casaccia	This work
$LiAlO_2$ "P" 80 % P Casaccia	117	HFR 400 °C	0.333	0.782
	155	OSIRIS 400 °C	15.91	14.949
Li_4SiO_4 90 % P KfK	109	HFR 400 °C	1.465	2.171

Taking into account the scatter of individual values from the same stack (table 5 to 8), the agreement is very satisfactory.

In fig. 1 to 8 the release rates (per sample) and the temperatures as function of time are shown for the 5 °C/min ramp annealing tests. Irradiation conditions, sample and pellet number and specific tritium release are indicated. In some tests

with high inventories the ramp was terminated before the 850 °C final temperature was achieved to avoid overloading of the ionization chamber amplifier. The achieved temperature was hold for several hours and two or more runs were necessary to achieve the final temperature of 850 °C in these cases. In fig. 9 and 10 tritium release during stepwise temperature increase (350, 450, and 650 °C) is shown for samples irradiated at 400 °C in the HFR.

As can be seen from fig. 1 to 8 the release curves have a quite complex structure indicating that tritium release from ceramics can be considered as desorption from different sites, each characterized by the number of sites and an activation energy [14, 15]. These hitherto unknown parameters would be required for a quantitative description of tritium release. Because of this lack in modeling capability, a quantitative comparison of tritium release from closed capsule tests with purged inpile tests is not possible.

Nevertheless , a qualitative ranking with respect to tritium release kinetics based on the temperature at which the bulk of the tritium is released during the ramp tests yields:

Li_2O, Li_2ZrO_3	bulk tritium release at	$\leq$ 500 °C
Li_4SiO_4 SS	"	$\approx$ 550 °C
$LiAlO_2$, Li_4SiO_4 MS, P	"	$\approx$ 600 °C
Li_2Si_O3	"	$\approx$ 650 °C

This ranking is consistent with the temperature-step annealing (fig. 9, 10) and with results of purged inpile tests [16, 17].

Comparing the general shape and the temperature of maximum release of the ramp tests and the fractional release and the slope of the release at the different temperatures in the temperature step tests, no remarkable difference could be observed for the same specimens irradiated under different conditions. From this we conclude, in agreement with Casaccia's COMPLIMENT study [12], that the tritium release kinetics is not significantly affected by

1. the specific inventory (i.e. the release rate was observed to be proportional to the specific inventory, indicating that the release process is first order),
2. the Li-burnup (up to about 2 %)
3. the type of radiation damage (induced by fast neutrons or by the charged particles from the $^6Li(n, \alpha)$ t-reaction).

These conclusions are in agreement with earlier work [15], where it is also claimed that tritium release is essentially a first order process and with the observation of the EXOTIC-6 inpile test, that the tritium residence times of $LiAlO_2$, Li_2ZrO_3 and Li_4SiO_4 are not affected by a Li-burnup of up to 3 % [17].

3.3 Gamma activity

The dose rate (per pellet) in different distances and the gamma spectrum have been determined for several pellets October/November 1992, i.e. nearly four years after irradiation. For the gamma spectrum measurements, performed with a calibrated Ge(Li)-semiconductor detector, the pellets were enclosed in an aluminum capsule with 1 mm wall thickness. In table 11 the results are summarized. The dose rate refer to the whole pellet, the gamma activity values of the different lines have been transformed to specific values using the pellet mass, both sets of data refer to October/November 1992.

Li_2ZrO_3 has the highest dose rate and this is mainly due to Eu impurities, whereas the activity of the major component Zr is pretty small. In contrast to the other ceramics, the zirconate pellet irradiated in the epithermal HFR spectrum exhibits a higher activity than that irradiated in the thermal OSIRIS spectrum. The pretty high activity of $LiAlO_2$ "P" pellets is mainly due to Zn and Sb impurities, in accordance with a previous neutron activation analysis ($LiAlO_2$ "P": Zn 92 ppm, Sb 0.10 ppm, $LiAlO_2$ "A2": Zn 3.1 ppm, Sb 0.034 ppm [19]). For all other pellets the main activities are Co and Mn, which are probably due to stainless steel contamination caused by machining and/or contact with the stainless steel tubes during irradiation.

4. Conclusions

COMPLIMENT was the first irradiation, where a massive decomposition of the molten and sintered Li_4SiO_4 spheres was observed, although in some previous irradiations both, the power density and the burnup were comparable or even higher. A tentative explanation are steep temperature transients caused by reactor trips. Further irradiations under DEMO-relevant conditions concerning power density and burnup are required to quality the reference breeder ceramics.

The tritium release kinetics of the various ceramics investigated is not significantly affected by

- the specific tritium inventory (indicating that the release process is first order)
- the Li-burnup (up to 2 %)
- the type of radiation damage (induced by fast neutrons or by the charged particles from the $^{6}Li(n, \alpha)$ t-reaction).

The gamma activity of all investigated ceramics is mainly due to stainless steel contaminations (from machining and/or from contact with the cladding during irradiation) and due to sample impurities. The activity of the main constituents is, even for the zirconate, comparatively small.

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Table 1 COMPLIMENT irradiation data

Reactor Neutron spectrum	HFR Petten Cd-screened	OSIRIS Saclay Thermal
Irradiation	April 88 - January 89	October 88 - February 89
Full power days	178	77
Temperature *	400 - 450 °C 650 - 700 °C	
Lithium burnup*	≈ 0.25 %	≈ 1 %
Radiation damage*		
fast neutrons	1.6 dpa	1.1 dpa
d + t	0.2 dpa	0.7 dpa
total	1.8 dpa	1.8 dpa

*Pre-irradiation estimation

Table 2 Sample characteristics and irradiation conditions

Identification of samples. P = sintered pellets, MS = molten spheres and SS = sintered spheres

	ELIMA 2/HFR-Petten								DELICE 03/OSIRIS-Saclay								Sum of samples
	Matrix I 400–450 °C				Matrix II 650–700 °C				Matrix III 400–450 °C				Matrix IV 650–700 °C				
CEA, Saclay	$LiAlO_2$	78% [a]	P	139 [b] pi [c]	$LiAlO_2$	78%	P	143	$LiAlO_2$	78%	P	147 st	$LiAlO_2$	78%	P	151	
	$LiAlO_2$	78%	P	140 st	$LiAlO_2$	78%	P	144 st	$LiAlO_2$	78%	P	148 st	$LiAlO_2$	78%	P	152 st	
	$LiAlO_2$	62%	P	141 pa	$LiAlO_2$	62%	P	145 st	$LiAlO_2$	62%	P	149 st	$LiAlO_2$	62%	P	153 st	
	$LiAlO_2$	84%	P	142 pa	$LiAlO_2$	84%	P	146	$LiAlO_2$	84%	P	150 pa	$LiAlO_2$	84%	P	154	16
ENEA, Casaccia	$LiAlO_2$	80%	P	117	$LiAlO_2$	80%	P	120	$LiAlO_2$	80%	P	155 pi	$LiAlO_2$	80%	P	158	
	$LiAlO_2$	80%	P	118	$LiAlO_2$	80%	P	121	$LiAlO_2$	80%	P	156	$LiAlO_2$	80%	P	159	
	$LiAlO_2$	80%	P	119	$LiAlO_2$	80%	P	122	$LiAlO_2$	80%	P	157	$LiAlO_2$	80%	P	160	12
UKAEA, Springfields	Li_2O	83%	P	131	Li_2O	80%	P	133	Li_2O	79%	P	135 pi	Li_2O	82%	P	137 pi	
	Li_2O	79%	P	132 st	Li_2O	82%	p	134 st	Li_2O	81%	P	136 st	Li_2O	82%	P	138 st	8
	Li_2ZrO_3	80%	P	123	Li_2ZrO_3	80%	P	125 st	Li_2ZrO_3	80%	P	127 st	Li_2ZrO_3	80%	p	129 st	
	Li_2ZrO_3	80%	p	124	Li_2ZrO_3	80%	p	126	Li_2ZrO_3	80%	p	128 pi	Li_2ZrO_3	80%	p	130 pi	8
CEN, Mol	Li_2SiO_3	82%	P	161	Li_2SiO_3	82%	P	162 st	Li_2SiO_3	82%	P	167 pi	Li_2SiO_3	82%	P	168 st	
	Li_2SiO_3	82%	P	163 st	Li_2SiO_3	75%	P	166 st	Li_2SiO_3	82%	P	169 st	Li_2SiO_3	75%	P	172 st	10
	Li_2SiO_3	75%	P	165	Li_2ZrO_3	80%	P	164	Li_2SiO_3	75%	P	171 st	Li_2ZrO_3	80%	P	170	2
KfK, Karlsruhe	Li_4SiO_4	98%	MS	173	Li_4SiO_4	98%	MS	174	Li_4SiO_4	98%	MS	175 pa	Li_4SiO_4	98%	MS	176	4
	Li_4SiO_4	85%	SS	113 pa	Li_4SiO_4	85%	SS	114	Li_4SiO_4	85%	SS	115 pa	Li_4SiO_4	85%	SS	116	4
	Li_4SiO_4	90%	P	109	Li_4SiO_4	90%	P	110	Li_4SiO_4	90%	P	111 pa	Li_4SiO_4	90%	P	112 pa	4
	Li_2SiO_3	90%	P	101	Li_2SiO_3	90%	P	102	Li_2SiO_3	90%	P	103 pa	Li_2SiO_3	90%	P	104	4
Sum		18				18				18				18			72

[a] % Theoretical density.
[b] KfK rod number.
[c] st sample had got stuck in tube, could not be removed
pi sample decomposed into (large) pieces
pa sample decomposed into (small) particles or dust

Table 3 Characteristics of Casaccia and KfK samples

Laboratory	Sample	% theor. density	Spec. surface (m^2/g)	Mean grain size (µm)
Casaccia [12]	$LiAlO_2$ "P" 80 % P	80	2.6	0.6
KfK [3 - 5]	Li_4SiO_4 98 % MS 0.5 mm ∅ (type Schott 86, temp.)	93.3 (57*)	5.9	19 (32**)
	Li_4SiO_4 85 % SS 0.5 mm ∅	91.6 (51*)	2.1	36 (62**)
	Li_4SiO_4 90 % P	90.0	1.54	45 (76**)
	Li_2SiO_3 90 % P	93.7	0.67	19 (37**)

KfK samples: porosity ≈ 100 % open

* density of sphere bed

** after irradiation [4, 5]

Table 4 Irradiation behavior of KfK Li_4SiO_4 and Li_2ZrO_3 samples

Irradiation Reactor	Sample	Irradiation conditions			Sample state after irradiation
		Temp. (°C)	Power dens. (W/cm³)	Li-burnup (%)	
BEATRIX-I, FUBR-1B[a] [18]	Li_4SiO_4 92 % P, 9.5 mm ∅	≤ 550	30 - 60	6	Appear intact
EBR-II, 560 FPD, 1988 - 89	Li_4SiO_4 85 % SS, 1 mm ∅	≤ 475	30 - 60	6	
ALICE-3[a] [11]	Li_4SiO_4 96 % MS, 0.5 mm ∅ (Schott 89/3,7)	600	74	2.7	Intact
OSIRIS, 46 FPD, 1990 - 91	Li_4SiO_4 85 % SS, 0.5 mm ∅	600	70	2.7	Intact
	Li_2ZrO_3 86 % SS, 0.5 mm ∅ (HITEC)	600	51	3.8	Some dust
SIBELIUS[b] [11]	Li_4SiO_4 98 % MS, 0.5 mm ∅ (Schott 86 temp.)	270 - 470	68	1.8	Intact
SILOE, 70 FPD, 1990	Li_4SiO_4 90 % P, 8 mm ∅	≈ 550	117	2.2	Intact
EXOTIC.6[b] [16, 17]	Li_4SiO_4 95 % MS, 0.5 mm ∅ (Schott 90/1 temp.)	430 - 640	≈ 40	3.1	Intact
HFR, 200 FPD, 1991 - 92	Li_2ZrO_3 86 % SS, 0.5 mm ∅ (HITEC)	400 - 640	≈ 30	3.1	Intact
COMPLIMENT[a]	Li_4SiO_4 98 % MS, 0.5 mm ∅ (Schott 86 temp.)	400 - 450	≈ 60	1.8	50 % dust
OSIRIS, 77 FPD, 1988 - 89	Li_4SiO_4 85 % SS, 0.5 mm ∅	400 - 450	≈ 60	2.0	70 % dust

a) Sample capsule closed
b) Sample capsule purged

Table 5 Saclay and Casaccia $LiAl_2O_3$ pellets

Sample type	Irradiation Reactor	T (°C)	Sample No.	Pellet No.	Annealing Date	type	Pellet Dim (mm) Diam.	Height	Mass (g) before	after	Released Tritium per sample (MBq)	per g (MBq/g)	Remarks a.i. = after irradiation a.a. = after annealing
$LiAlO_2$ 84 % P Saclay	HFR	400	142	5 c	24.7.90	S	5.0955	≈6.1	0.2230	0.2223	1245	5583	2 pieces a.i.
				5 b	9.8.90	R	5.1090	≈4.5	0.1499	0.1494	816	5444	
				5 a	12.3.91	R	5.0975	≈9.5	0.3686	0.3682	2027	5449	
	OSIRIS	400	150	1	15.3.91	R	-	-	0.1712	0.1710	41145	240333	Particles + dust a.i.
$LiAlO_2$ "P" 80 % P Casaccia	HFR	400	117	2	18.7.90	R	4.8130	5.3360	0.2025	0.2019	1583	7817	
	OSIRIS	400	155	1	25.3.91	R	4.8655	5.0385	0.1898	0.1882	28373	149489	

Purge gas: 50 SCCM He + 0.1 % H_2

S: temperature steps 350, 450, 600, 850 °C

R: linear ramp 5 °C/min to 850 °C

R*: linear ramp 10 °C/min to 850 °C

Table 6 Springfield pellets

Sample type	Irradiation Reactor	T (°C)	Sample No.	Pellet No.	Annealing Date	type	Pellet Dim (mm) Diam.	Height	Mass (g) before	after	Released Tritium per sample (MBq)	per g (MBq/g)	Remarks a.i. = after irradiation a.a. = after annealing
Li_2O P Springfield	HFR	400	131 (83 %)	1	4.10.90	R	4.6958	5.0460	0.1222	0.1015	1697	16605	
				2	9.10.90	S	4.8380	5.1980	0.1297	0.1291	1613	12436	
				3	7.3.91	R	4.8675	4.9345	0.1275	0.1264	1475	11569	
		650	133 (80 %)	1	10.4.91	R	4.4625	4.3040	0.1094	0.1076	≈130	≈1200	
				2	11.4.91	R*	4.4220	4.7745	0.1201	0.1187	89	741	
				3	15.4.91	S	4.4590	4.9945	0.1281	0.1267	101	788	
	OSIRIS	400	135 (79 %)	-	13.7.92	R	-	-	0.0205	0.0197	726	35415	Pieces a.i.
				-	15.7.92	S	-	-	0.0166	0.0159	523	31506	
		650	137 (82 %)	1	18.3.92	R	-	-	0.0808	-	1165	14418	Pieces a.i., 100 % dust
				2	19.3.92	S	-	-	0.0989	0.0985	1392	14075	2 pieces a.i., 4 pieces a.
				3 - 8	24.3.92	R*	-	-	0.1849	0.1835	1890	10222	Particles a.i.
Li_2ZrO_3 80 % P Springfield	HFR	400	124	3	31.1.91	R	4.9710	4.9865	0.3275	0.3260	1519	4638	
				5	6.2.91	R	4.9840	4.8840	0.1341	0.3126	1432	4559	
				6	12.2.91	S	4.9810	4.9520	0.3190	0.3178	1239	3884	
		650	126	1	17.4.91	R	4.9850	4.8705	0.3084	0.3084	1128	3658	
				2	19.4.91	R*	4.9980	4.8950	0.3034	0.3033	634	2090	
				3	22.4.91	S	4.9975	4.9230	0.3120	0.3120	537	1721	
	OSIRIS	400	128	1	30.1.92	S	5.0830	5.0210	0.3171	0.3160	≈35000	≈110000	
				2	11.3.92	R	-	-	0.0192	0.0192	1257	65469	Pieces a.i.
				"	13.3.92	S	-	-	0.0214	0.0213	1243	58084	
				3	23.4.92	R	5.0250	4.9160	0.3037	0.3009	26090	85907	
		650	130	1	4.2.92	R	-	-	0.2627	0.2622	3366	12813	2 pieces a.i.
				2	6.2.92	S	5.0120	4.9185	0.3104	0.3100	1660	5348	
				3	11.2.92	R*	5.0155	4.9875	0.3228	0.3244	1830	5669	

Purge gas: 50 SCCM He + 0.1 % H_2
S: temperature steps 350, 450, 600, 850 °C
R: linear temperature ramp 5 °C/min to 850 °C
R*: linear temperature ramp 10 °C/min to 850 °C

Table 7 Mol Li_2ZrO_3 pellets and KfK Li_4SiO_4 spheres

Sample type	Irradiation: Reactor	Irradiation: T (°C)	Sample No.	Pellet No.	Annealing: Date	Annealing: type	Pellet: Dim (mm) Diam.	Pellet: Dim (mm) Height	Pellet: Mass (g) before	Pellet: Mass (g) after	Released Tritium: per sample (MBq)	Released Tritium: per g (MBq/g)	Remarks (a.i. = after irradiation, a.a. = after annealing)
Li_2SiO_3 82 % P Mol	HFR	400	161	1	15.1.90	R	4.9950	6.4960	0.2571	0.2567	1783	6935	
				2	28.2.91	R	5.0040	6.5170	0.2594	0.2587	2578	9938	
				3	5.3.91	S	5.0160	6.4740	0.2592	0.2586	3139	12110	
	OSIRIS	400	167	2	2.3.92	R	-	-	0.0188	0.0187	523	27819	} 3 pieces a.i.
				"	6.3.92	S	-	-	0.0261	0.0259	877	33602	
				1	9.4.92	R	-	-	0.2524	0.2516	11865	47009	2 pieces a.i.
				3	13.4.92	R	-	-	0.2605	0.2508	6760	25950	
Li_4SiO_4 98 % (57 %) MS KfK	HFR	400	173	-	13.11.90	R	-	-	0.1854	0.1843	8981	48441	
				-	19.11.90	S	-	-	0.1952	0.1940	9429	48304	
		650	174	-	13.6.91	R	-	-	0.2104	0.2093	462	2196	
				-	17.6.91	S	-	-	0.2064	0.2055	469	2272	
	OSIRIS	400	175	-	13.2.92	R	-	-	0.0250	0.0244	4064	162560	} 50 % dust a.i.
				-	17.2.92	S	-	-	0.0237	0.0230	3945	166456	
		650	176	-	21.6.91	R	-	-	0.2108	0.2102	1212	5750	
				-	12.8.91	S	-	-	0.2191	0.2182	1249	5701	
Li_4SiO_4 85 % (51 %) SS KfK	HFR	400	113	-	25.10.90	R	-	-	0.1234	-	2747	22261	} 50 % dust a.i.
				-	5.11.90	S			0.1358	0.1352	3053	22482	
		650	114	-	6.6.91	R	-	-	0.1985	0.1962	218	1098	
				-	10.6.91	S	-	-	0.2021	0.2005	135	668	
	OSIRIS	400	115	-	20.2.92	R	-	-	0.0204	0.0200	2588	126863	} 70 % dust a.i.
				-	25.2.92	S	-	-	0.0216	0.0208	3350	155093	
		650	116	-	27.1.92	R	-	-	0.1023	0.1018	1075	10508	
				-	28.1.92	S	-	-	0.1110	0.1102	1135	10225	

Purge gas: 50 SCCM He + 0.1 % H_2
S: temperature steps 350, 450, 600, 850 °C
R: linear temperature ramp 5 °C/min to 850 °C
R*: linear temperature ramp 10 °C/min to 850 °C

Table 8 KfK pellets

Sample type	Irradiation: Reactor	Irradiation: T (°C)	Sample No.	Pellet No.	Annealing: Date	Annealing: type	Pellet: Dim (mm) Diam.	Pellet: Dim (mm) Height	Pellet: Mass (g) before	Pellet: Mass (g) after	Released Tritium: per sample (MBq)	Released Tritium: per g (MBq/g)	Remarks (a.i. = after irradiation, a.a. = after annealing)
Li_4SiO_4 90 % P KfK	HFR	400	109	5	9.4.90	R	5.0330	5.0190	0.1998	0.1969	4602	23033	
				6	20.4.90	S	5.0320	5.1375	0.2060	0.2030	5091	24714	
				3	6.6.90	R	5.0170	5.1130	0.2060	0.2048	3579	17374	
		650	110	5	16.5.90	R	5.1081	4.9831	0.1931	0.1929	520	2693	
				6	22.5.90	S	5.1153	4.8771	0.1921	0.1920	567	2952	
				3	25.6.90	R	5.1120	4.9845	0.1917	0.1913	484	2525	
	OSIRIS	400	111	-	3.7.92	R	-	-	0.0204	0.0200	2409	118088	Pieces and particle a.i.
				-	7.7.92	S	-	-	0.0230	0.0225	2837	123348	
		650	112	-	25.6.92	R	-	-	0.2134	0.2112	4062	19035	Particles and dust a.i.
				-	30.6.92	S	-	-	0.2157	0.2145	3861	17900	
Li_2SiO_3 90 % P KfK	HFR	400	101	5	17.4.90	R	4.8455	5.1285	0.2142	0.2135	13520	63119	
				6	25.4.90	S	4.8830	4.9175	0.2076	0.2068	14126	68044	
				3	19.6.90	R	4.8610	5.0645	0.2122	0.2113	12276	57851	
		650	102	5	29.5.90	R	4.9588	5.0671	0.2104	0.2103	440	2091	
				6	31.5.90	S	4.9426	5.3261	0.2189	0.2186	468	2138	
				3	27.6.90	R	4.9218	5.4218	0.2214	0.2212	528	2385	
	OSIRIS	400	103	1	26.3.92	R	-	-	0.0203	0.0202	10937	538768	Particles a.i.
				"	2.4.92	S	-	-	0.0237	0.0237	11801	497932	
		650	104	1	24.4.91	R	4.9255	4.7195	0.1943	0.1941	10635	54735	
				2	24.5.91	S	4.9020	4.8750	0.1996	0.1993	8881	44494	
				3	29.5.91	R*	4.9340	4.8860	0.2015	0.2014	7720	38313	

Purge gas: 50 SCCM He + 0.1 % H_2
S: temperature steps 350, 450, 600, 850 °C
R: linear temperature ramp 5 °C/min to 850 °C
R*: linear temperature ramp 10 °C/min to 850 °C

Table 9 HFR, irradiation conditions and tritium release

Sample type	Sample no.	Position level/hole	Temp. (°C)	Li-burnup (%)	Damage (dpa)		Tritium		
					n	α + t	Production 10^{19} T/g	Release 10^{10} Bq/g	Release 10^{19} T/g
$LiAlO_2$ 84 % P Saclay	142	2/6	474	0.36	2.18	0.07	3.2	0.551	0.31
$LiAlO_2$ "P" 80 % P Casaccia	117	2/7	474	0.36	2.18	0.07	3.2	0.782	0.44
Li_2O 83, 80 % P Springfield	131	1/7	458	0.27	0.88	0.11	10.9	1.354	0.76
	133	4/6	686	0.38	1.21	0.16	15.2	0.091	0.051
Li_2ZrO_3 80 % P Springfield	124	2/2	474	0.45	2.27	0.11	3.6	0.436	0.25
	126	4/8	686	0.37	1.85	0.09	2.9	0.249	0.14
Li_2SiO_3 82 % P Mol	161	1/1	458	0.35	1.80	0.08	4.7	0.966	0.54
Li_4SiO_4 98 % MS KfK	173	1/4	458	0.35	1.60	0.10	6.5	4.837	2.72
	174	3/4	637	0.46	2.10	0.14	8.5	0.223	0.13
Li_4SiO_4 85 % SS KfK	113	1/5	458	0.31	1.41	0.09	5.7	2.237	1.26
	114	3/5	637	0.41	1.87	0.12	7.5	0.088	0.050
Li_4SiO_4 90 % P KfK	109	1/6	458	0.28	1.29	0.08	5.3	2.171	1.22
	110	3/6	637	0.38	1.70	0.11	7.0	0.272	0.15
Li_2SiO_3 90 % P KfK	101	1/3	458	0.36	1.90	0.08	4.9	6.301	3.55
	102	4/1	686	0.37	2.73	0.09	5.0	0.221	0.12

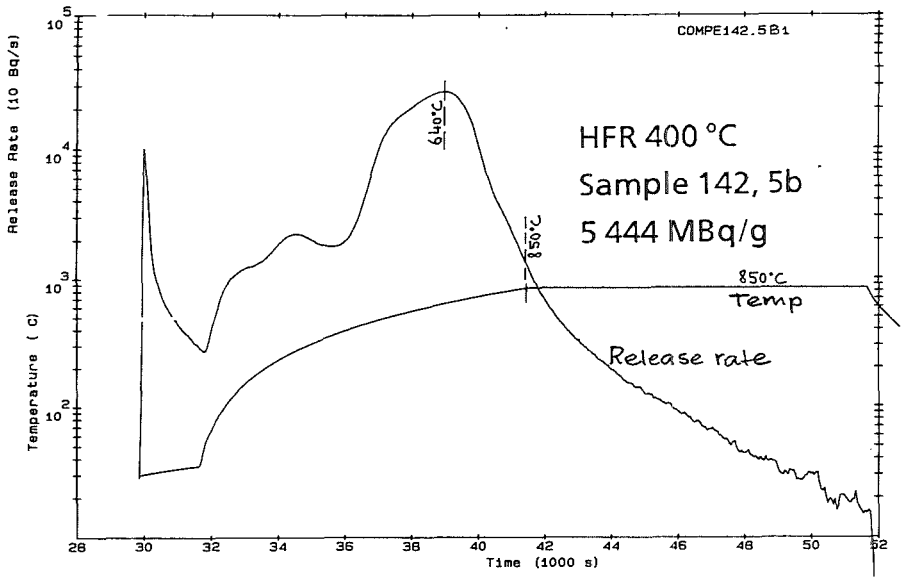
Table 10 OSIRIS, irradiation conditions and tritium release

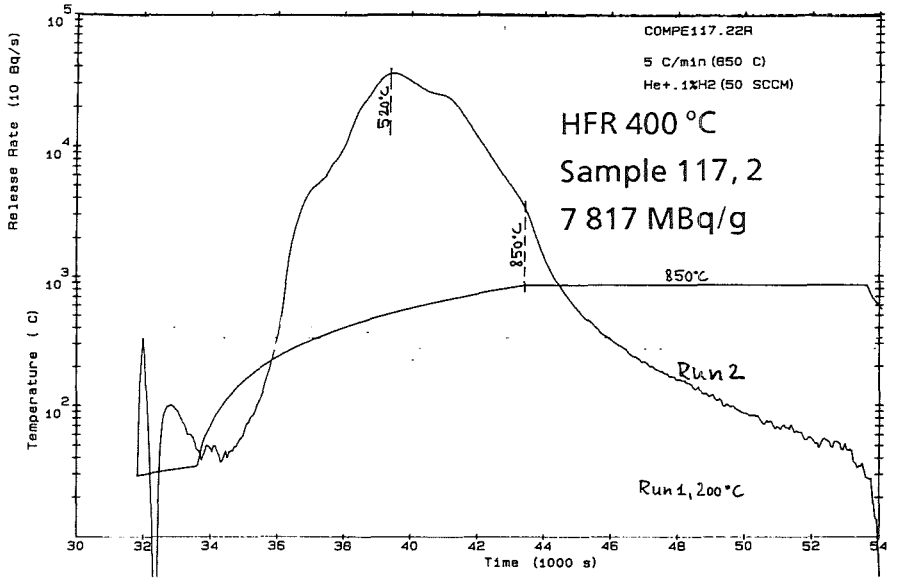
Sample type	Sample no.	Position level/hole	Temp. (°C)	Damage (dpa)		Tritium Production 10^{19} T/g	Li-burnup (%)	Tritium Release	
				n	α + t			10^{10} Bq/g	10^{19} T/g
$LiAlO_2$ 84 % P Saclay	150	8/2	425	1.69	0.75	30.2	3.3	24.033	13.5
$LiAlO_2$ "P" 80 % P Casaccia	155	7/5	425	1.73	0.82	34.3	3.8	14.949	8.37
Li_2O 79, 82 % P Springfield	135	10/4	425	0.74	0.85	73.7	1.8	3.346	1.87
	137	2/3	675	0.51	0.50	43.1	1.1	1.291	0.72
Li_2ZrO_3 80 % P Springfield	128	10/6	425	0.87	0.66	20.1	2.6	7.987	4.47
	130	5/6	675	0.94	0.62	18.9	2.4	0.794	0.44
Li_2SiO_3 82 % P Mol	167	10/2	425	1.24	0.69	31.7	2.4	3.360	1.88
Li_4SiO_4 98 % MS KfK	175	11/3	425	0.91	0.71	36.8	1.8	16.451	9.21
	176	4/3	675	1.02	0.65	34.0	1.7	0.573	0.32
Li_4SiO_4 85 % SS KfK	115	11/5	425	0.91	0.66	39.4	2.0	14.098	7.89
	116	4/5	675	1.02	0.61	36.7	1.8	1.037	0.58
Li_4SiO_4 90 % P KfK	111	12/4	425	0.76	0.56	31.5	1.6	12.072	6.76
	112	4/1	675	1.02	0.62	35.3	1.8	1.847	1.03
Li_2SiO_3 90 % P KfK	103	11/1	425	1.08	0.69	29.1	2.2	51.835	29.0
	104	1/2	675	0.69	0.34	14.1	1.1	4.585	2.57

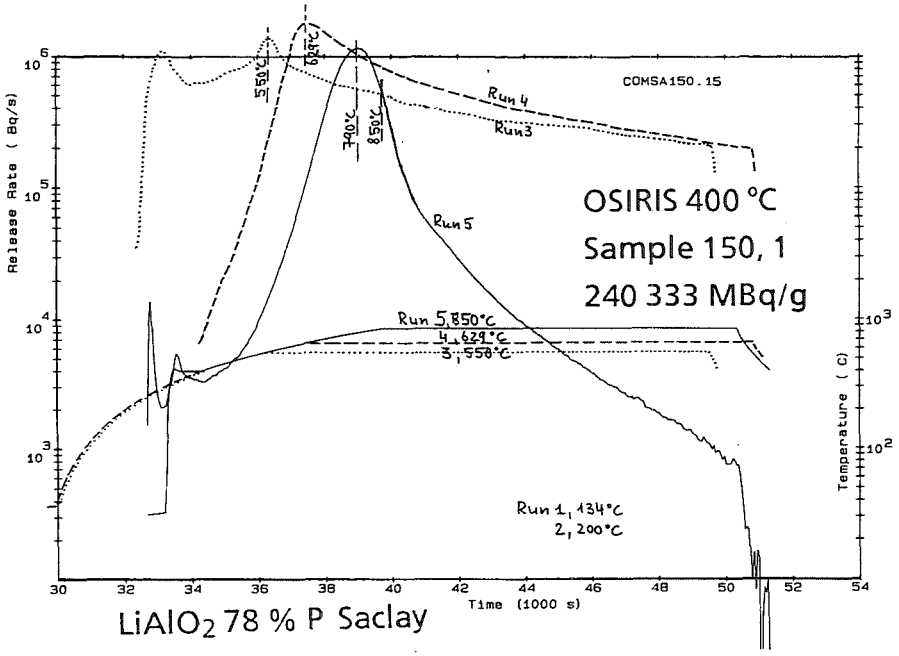
Table 11 Dose rate and specific gamma activity

(reference time October/November 1992)

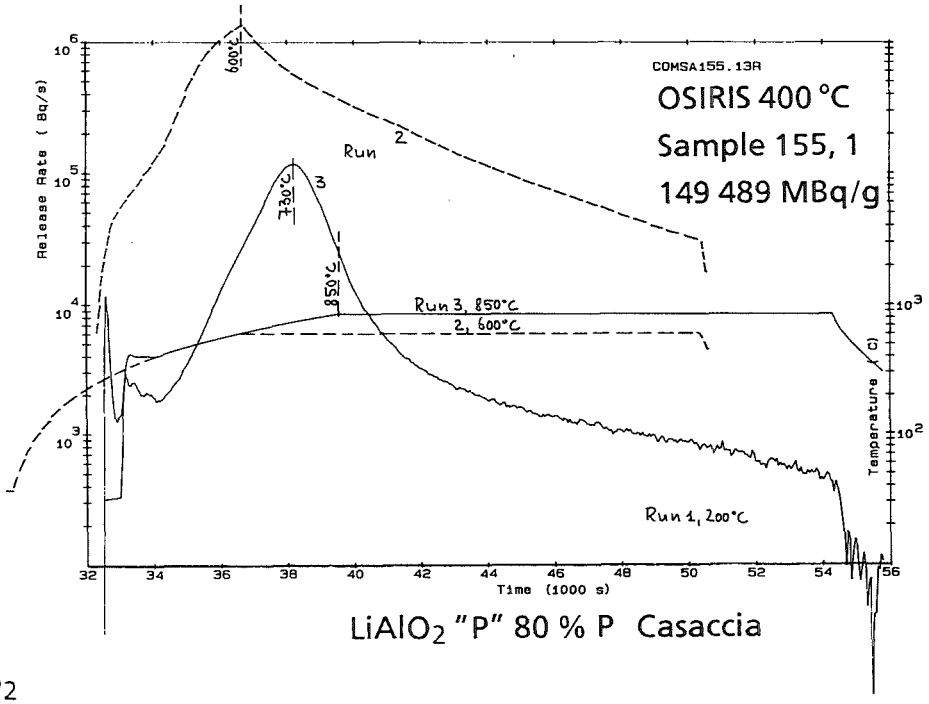
Sample type	no.	Irradiation	Pellet no	Pellet mass (g)	Dose rate (µSv/h) Contact	5	10	15 cm	Specific gamma activity (10^4 Bq/g) Mn 54	Co 60	Zn 65	Zr 95	Ag 110	Sb 125	Ba 133	Cs 134	Cs 137	Eu 152	Eu 154	Ta 182
Casaccia	118	HFR 400 °C	3	0.1926	16	1.9	0.6	0.2	0.81	2.4	5.2	-	-	4.1	-	0.28	-	-	0.37	-
$LiAlO_2$ "P"	155	OSIRIS 400 °C	1	0.1887	62	5.7	1.9	0.9	1.6	12	9.0	-	-	5.6	-	0.56	-	-	0.27	-
Casaccia	119	HFR 400 °C	2	0.2089	8.6	0.6	0.3	0.1	0.51	2.0	0.25	-	0.03	0.08	-	-	-	-	0.03	-
$LiAlO_2$ "A2"	156	OSIRIS 400 °C	1	0.2036	36	3.8	1.1	0.4	1.0	9.1	0.63	-	0.04	0.13	-	-	0.06	-	-	--
Spring-field	124	HFR 400 °C	2	0.3221	218	23	7.3	3.9	0.29	0.58	-	0.41	-	-	-	-	-	38	38	2.0
Li_2ZrO_3	128	OSIRIS 400 °C	3	0.3010	46	4.7	1.0	0.8	0.27	1.2	-	0.13	-	-	-	-	-	1.9	9.8	0.96
Mol Li_2SiO_3	161	HFR 400 °C	4	0.2577	10	1.1	0.4	0.1	0.09	2.1	0.18	-	0.02	0.07	-	0.04	-	-	-	-
KfK Li_4SiO_4, P	109	HFR 400 °C	4	0.2017	4.9	0.4	0.2	0.1	0.27	1.2	0.41	-	0.02	0.05	0.02	-	-	-	-	-
KfK	101	HFR 400 °C	4	0.2078	7.5	0.7	0.3	0.1	0.31	1.7	0.49	-	0.01	0.17	-	0.11	-	-	-	-
Li_2SiO_3, P	103	OSIRIS 400 °C	3	0.2053	18	1.5	0.3	0.1	0.45	4.3	1.3	-	-	0.34	0.02	0.12	-	-	-	-







LiAlO$_2$ 78 % P Saclay



LiAlO$_2$ "P" 80 % P Casaccia

Fig. 1 Tritium release of LiAlO$_2$
Ramp 5 °C/min, purge gas He + 0.1 % H$_2$

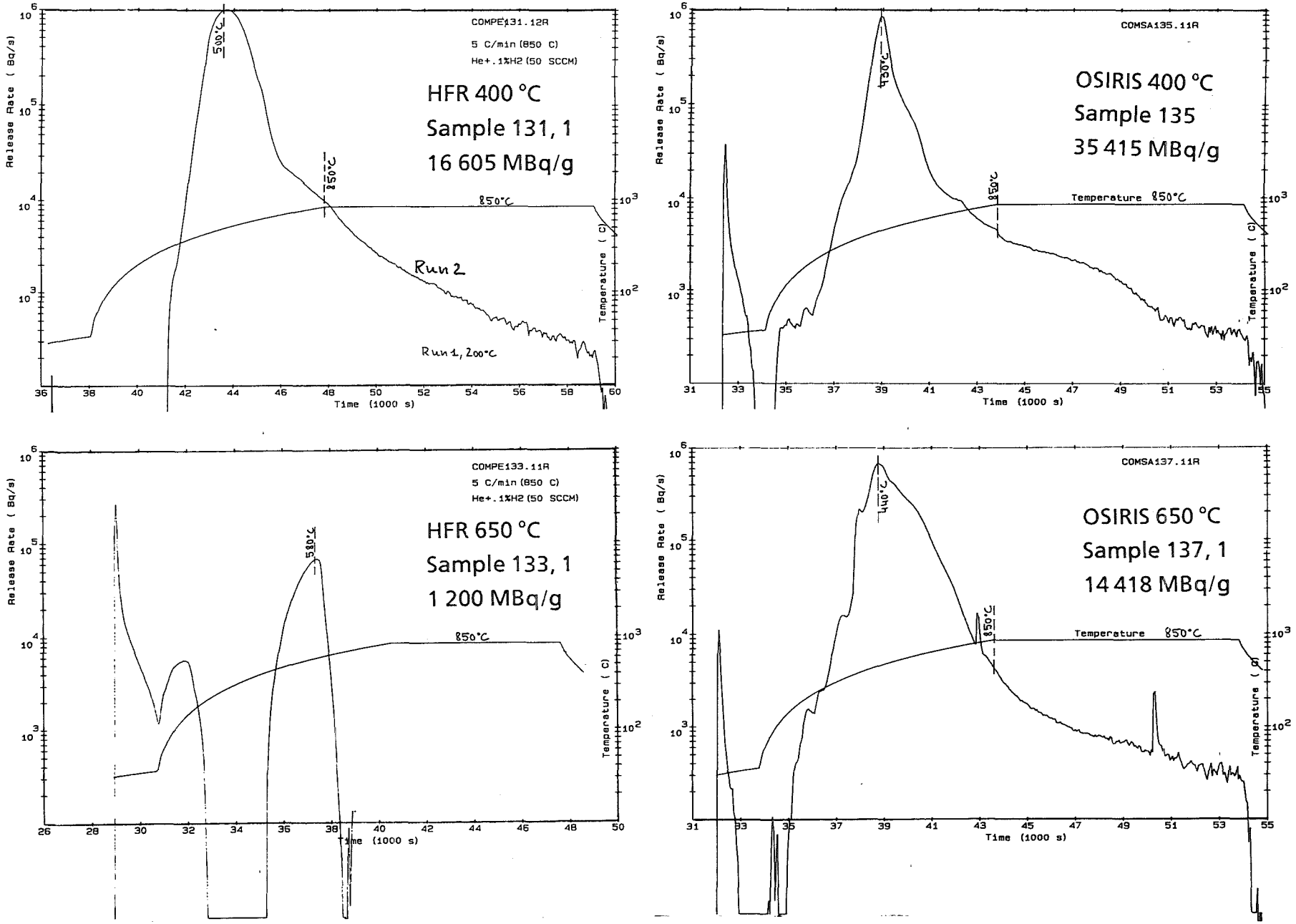


Fig. 2 Tritium release of $Li_2O \approx 80\ \%$ P Springfield
Ramp 5 °C/min, purge gas He + 0.1 % H_2

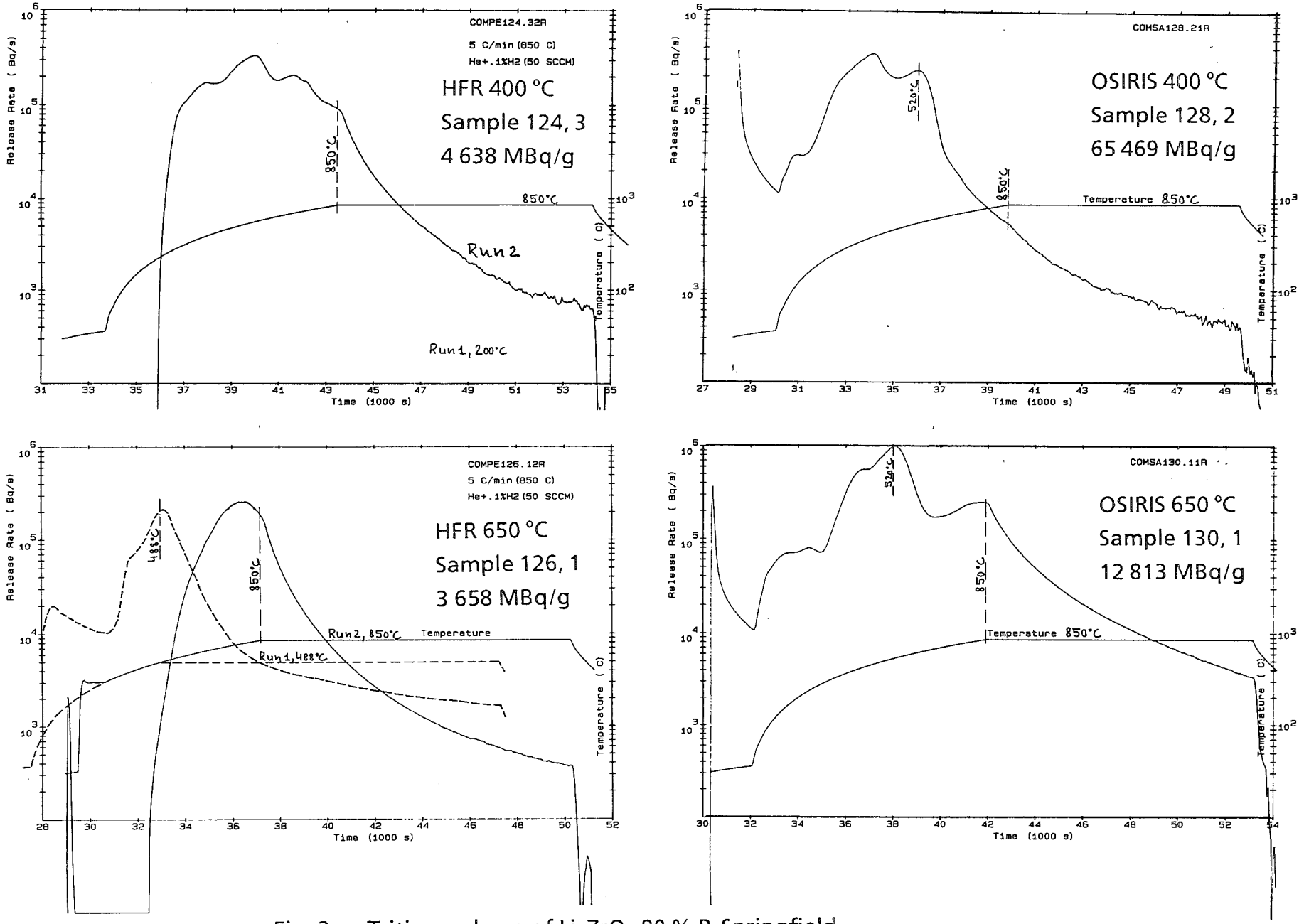


Fig. 3 Tritium release of Li_2ZrO_3 80 % P Springfield
Ramp 5 °C/min, purge gas He + 0.1 % H_2

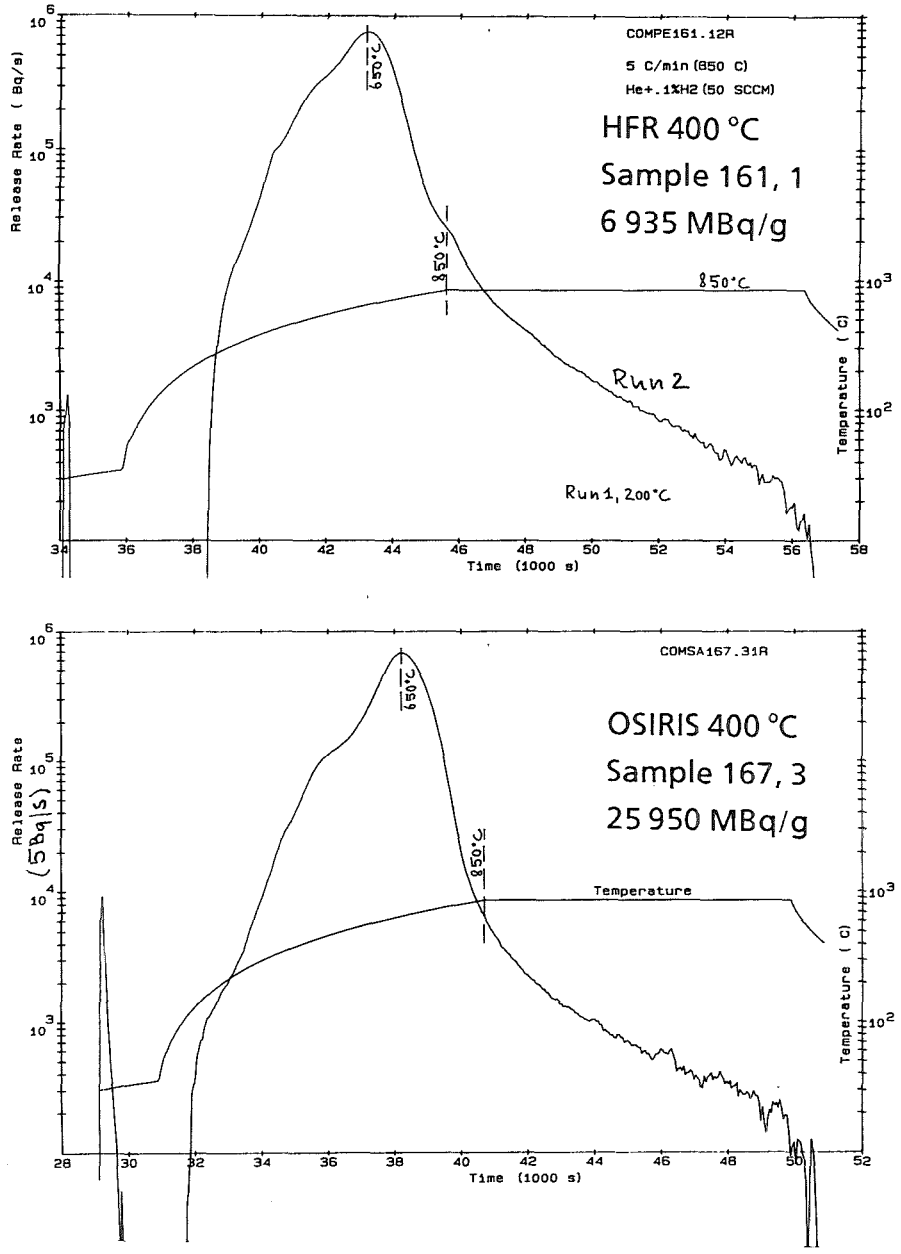


Fig. 4 Tritium release of Li_2SiO_3 82 % Mol
Ramp 5 °C/min, purge as He + 0.1 % H_2
(different ordinate scale in lower figure)

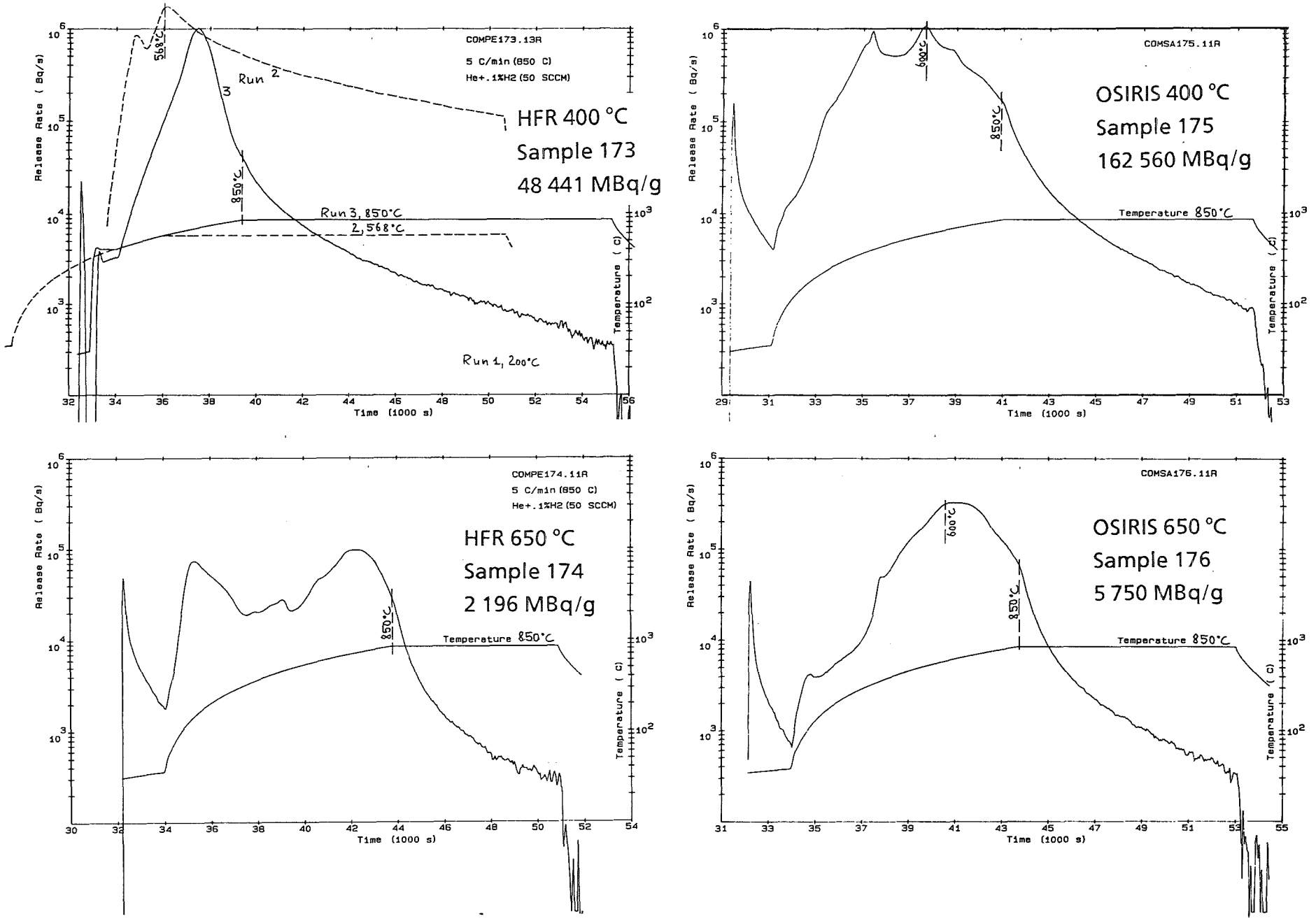


Fig. 5 Tritium release of Li_4SiO_4 98 % MS KfK
Ramp 5 °C/min, purge gas He + 0.1 % H_2

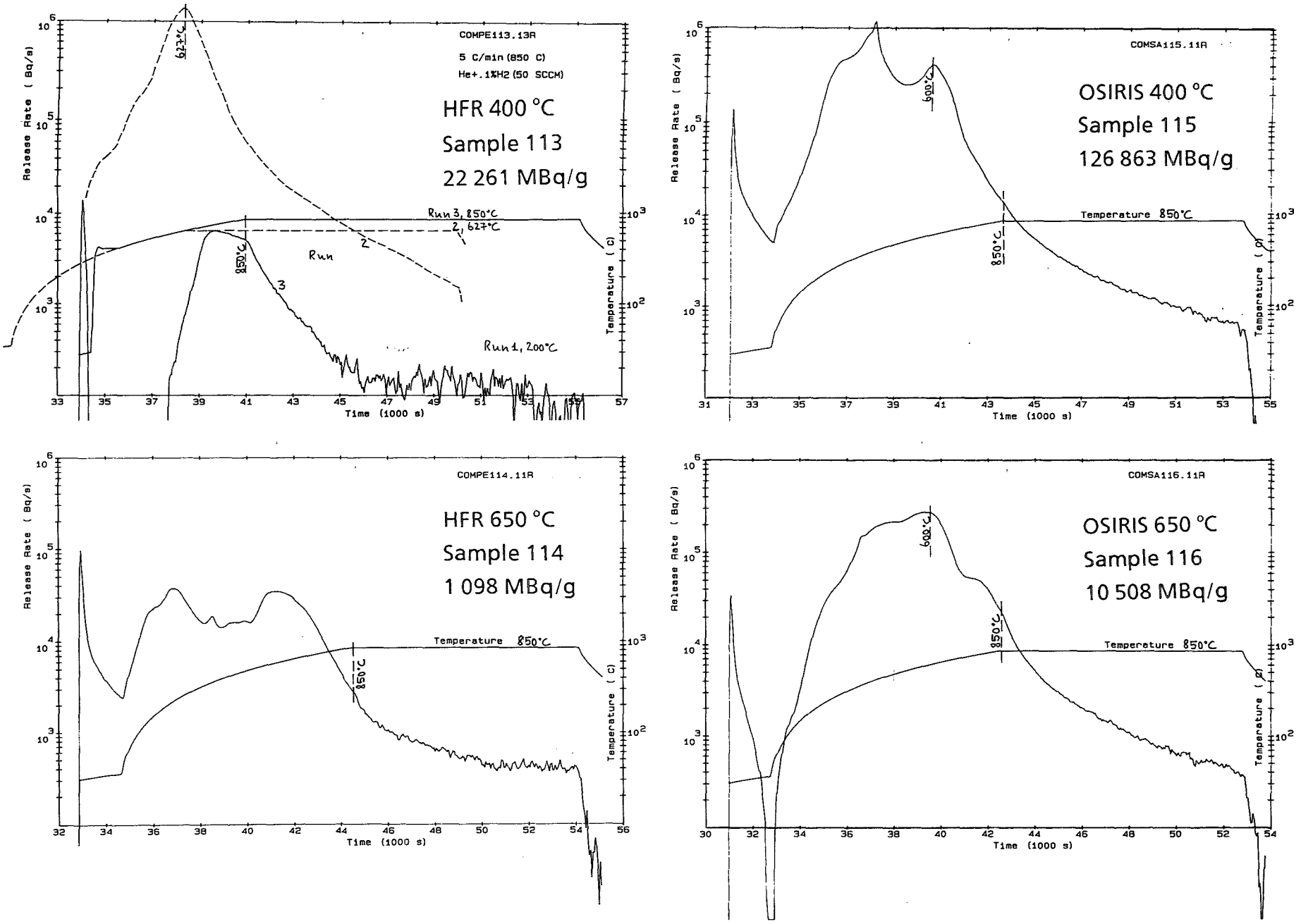


Fig. 6 Tritium release of Li_4SiO_4 85 % SS KfK
Ramp 5 °C/min, purge gas He + 0.1 % H_2

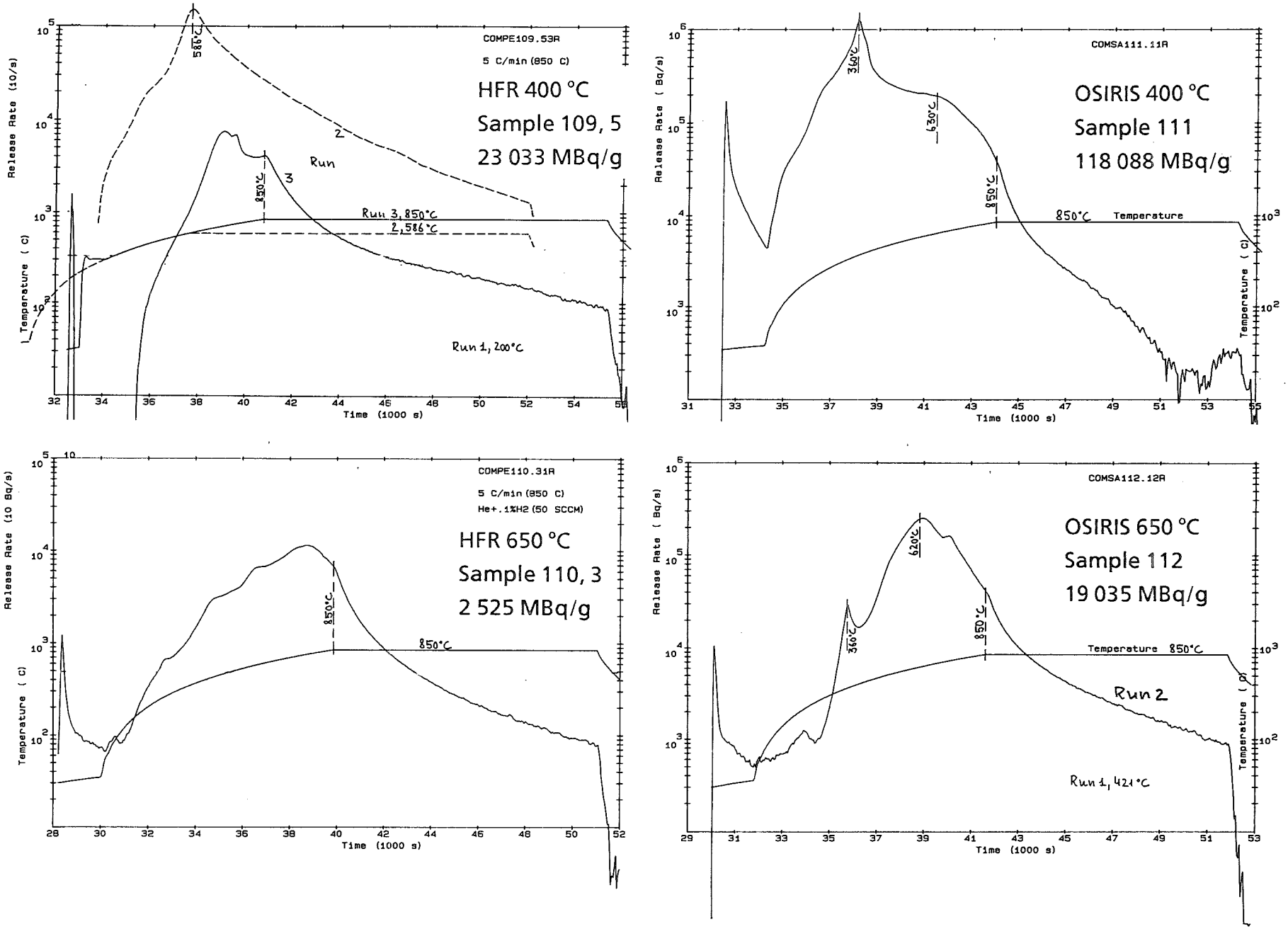


Fig. 7 Tritium release of Li_4SiO_4 90 % P KfK
Ramp 5 °C/min, purge gas He + 0.1 % H_2

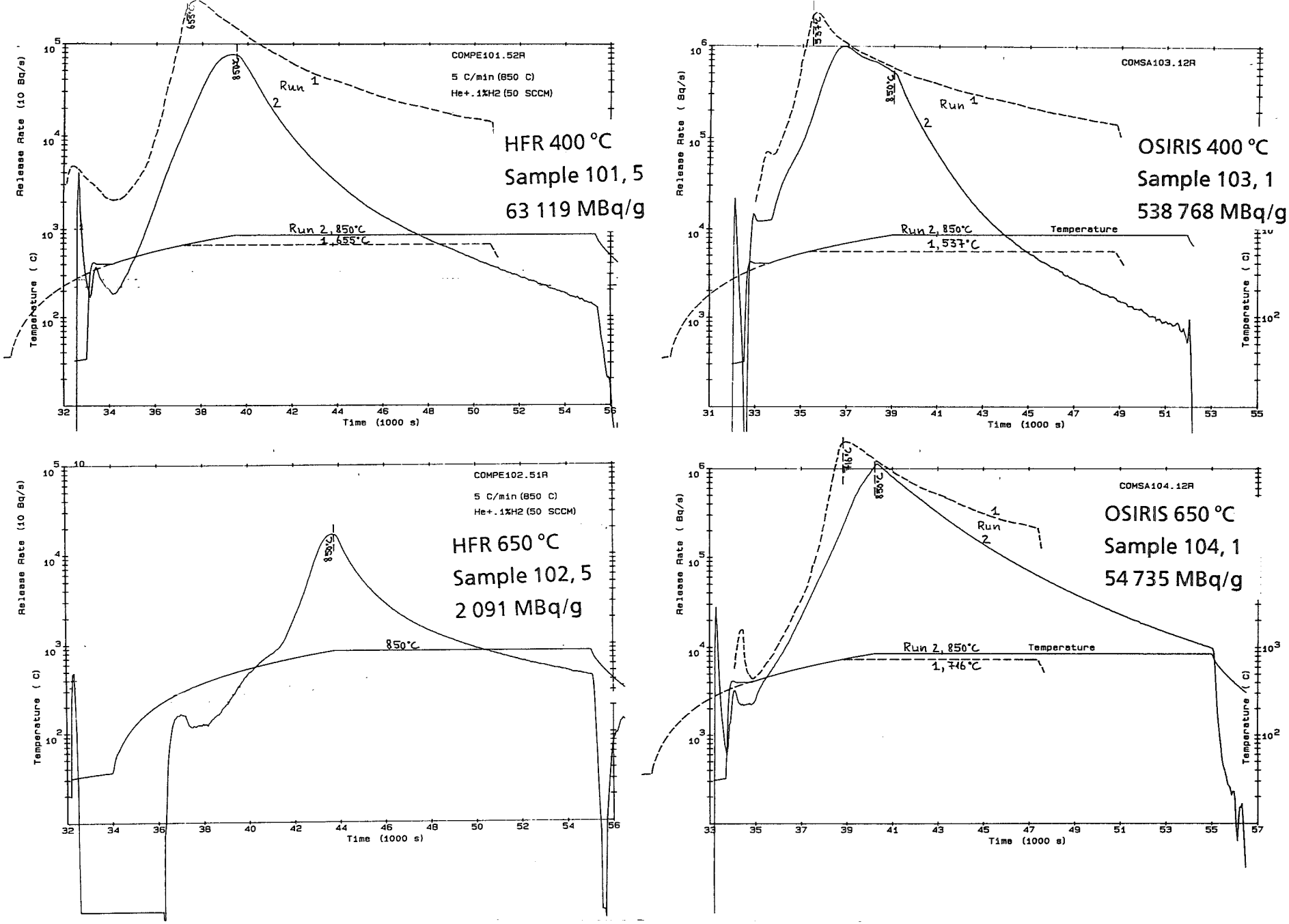


Fig. 8 Tritium release of Li_2SiO_3 90 % P KfK
Ramp 5 °C/min, purge gas He + 0.1 % H_2

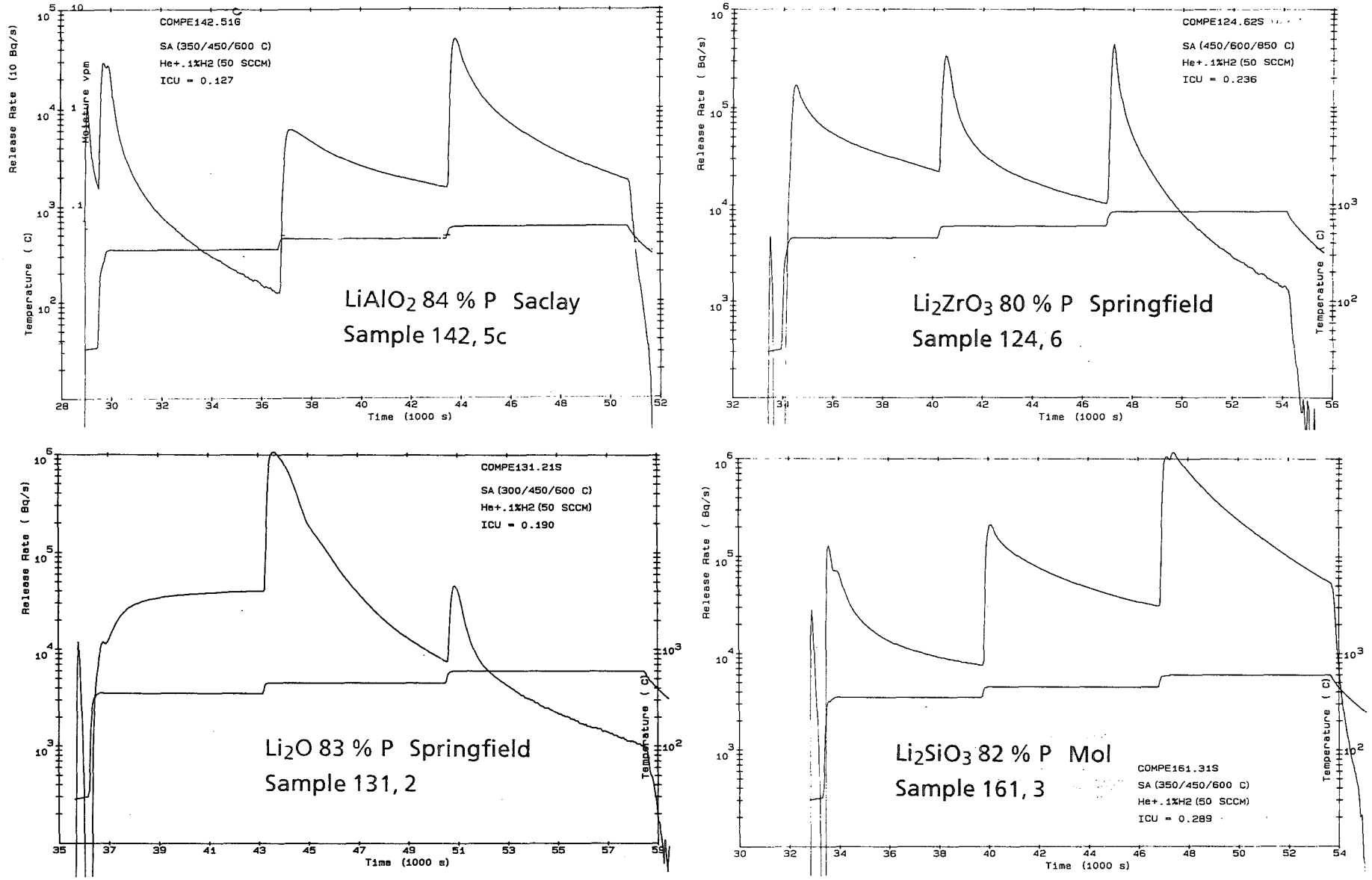


Fig. 9 Tritium release of various ceramics irradiated in HFR at 400 - 450 °C. Temperature steps (350, 450, 600 °C), purge gas He + 0.1 % H_2

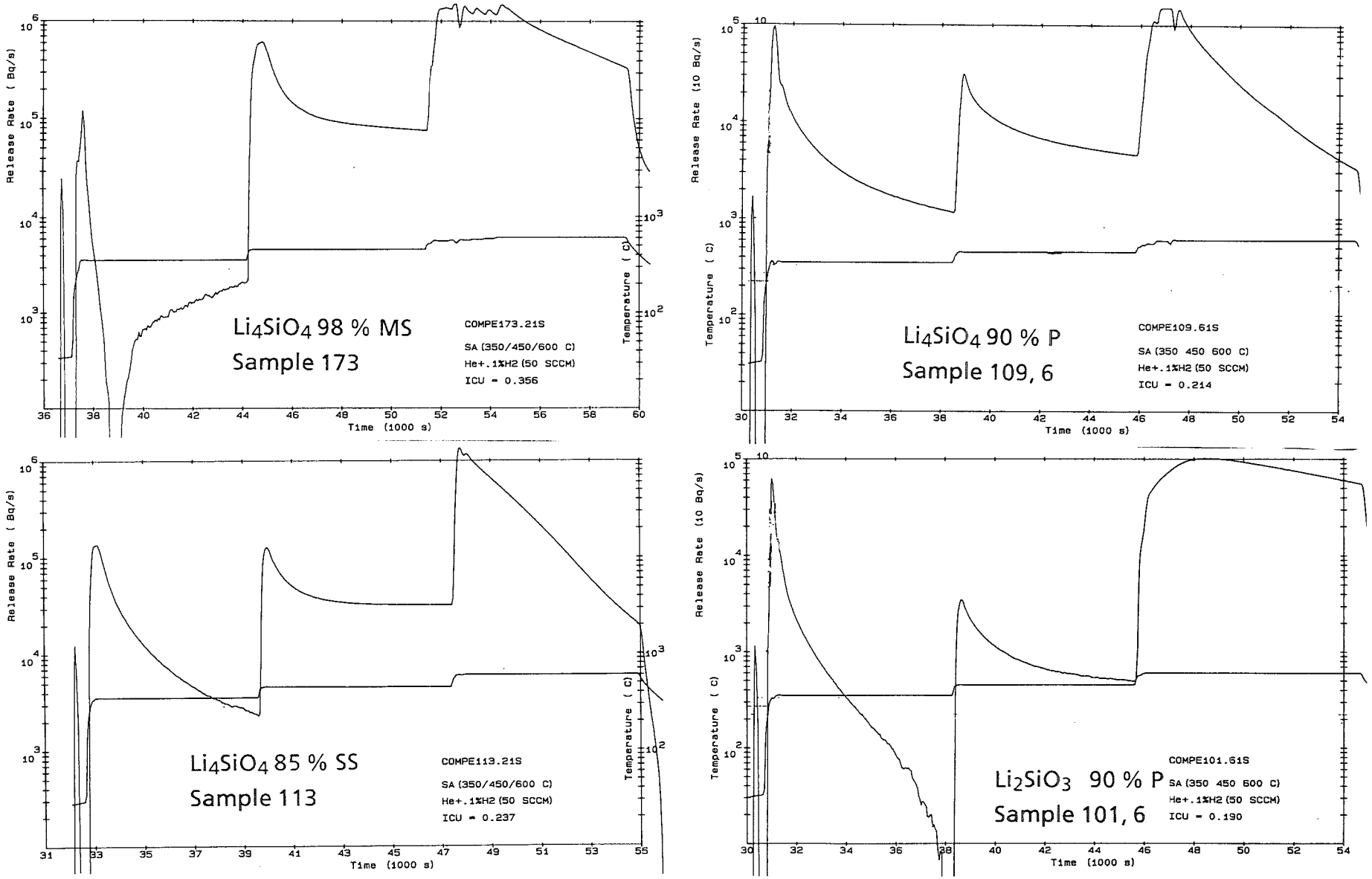


Fig. 10 Tritium release of KfK ceramics irradiated in HFR at 400 - 450 °C.
Temperature steps (350, 450, 600 °C), purge gas He + 0.1 % H_2