

# SEM Post-Irradiation Examinations of Weapons-Derived MOX Fuel at ORNL

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**Abstract**—Mixed-oxide fuels, made from weapons-derived plutonium with and without a gallium-removal treatment, have been irradiated to 40 GWd/MT (about 4.2% burnup). The as-prepared fuels contained a population of plutonium-rich agglomerates which, after irradiation, are characterized by high local porosity and a surrounding clear “halo region.” Elevated levels of solid fission products such as Ru, Pd, and Nd have been imaged within the agglomerates while Xe was present in the halo spaces. Fuel/clad contact gave rise to a discontinuous oxide layer on the inner surface of the Zircaloy-4 cladding, and this layer was both thicker and subject to minor fuel penetration at sites where an agglomerate was adjacent to the clad interface. All the above effects are part of normal fuel behavior and represent no compromise with fuel pin integrity or performance.

## I. INTRODUCTION

The Fissile Materials Disposition Program (FMDP) is investigating the use of weapons-derived or weapons-grade (WG) plutonium in mixed oxide (MOX) fuel for light-water reactors. Commercial MOX fuel has been successfully used in overseas reactors for many years and a large data base has been generated for MOX fuel applications; however, weapons-derived fuel differs from the commercial fuel in two ways. First, the isotopics of the fuel are different. Weapons-derived fuel contains greater amounts of  $^{239}\text{Pu}$  and smaller amounts of the higher plutonium isotopes. Second, fuel derived from weapons material may contain trace amounts of gallium as an impurity. It is the primary purpose of a current series of irradiation tests to demonstrate that the substitution of weapons-derived plutonium for the reactor grade plutonium used in commercial MOX fuel does not degrade the performance of the fuel system and, thus, the commercial database is applicable. The method of the test program is to fabricate, assemble, and irradiate small test capsules containing MOX fuel formulated from weapons-derived plutonium to both the expected and to higher-than-expected average powers (up to 33 kW/m).

Post-irradiation examinations (PIE) of the fuel capsules have been conducted, including segmenting of the fuel pins, optical ceramography, scanning electron microscope/microprobe (SEM) examination, and radiochemical analysis of the fuel and the clad. Several new and interesting microstructural developments have been observed.

## II. IRRADIATION TEST DETAILS

### II.1. Fuel Types

Two fuel types, which differ in their treatment of the same weapons-derived  $\text{PuO}_2$  source, are included in the tests. Fuel type B was fabricated with plutonium dioxide that was subjected to a thermal treatment (“TIGR”) for gallium removal prior to pellet fabrication. Fuel type A was fabricated with plutonium dioxide that was not treated. Ten pellets of each batch were analyzed at ORNL for gallium content. Batch A had an average gallium content of 2.97 ppm (mass) while Batch B had an average gallium content of 1.33 ppm (mass). The 95% confidence interval for Batch A is 1.00 to 4.95 ppm and for Batch B, 0.79 to 1.88 ppm. Both batches of fuel contain 5% plutonium by weight. The gallium content of the unirradiated Zircaloy clad averaged 0.59 ppm.

The fabrication of both batches of fuel achieved high density in part due to the extended sintering schedule. Average immersion densities of 94.5% TD and 95.3% TD were measured on fuel types A and B, respectively. Essentially no density change was achieved during a subsequent 24-hour thermal densification test. The porosity distribution includes a uniform distribution of fine pores. The average grain size was 10 $\mu\text{m}$  (fuel type A) and 11  $\mu\text{m}$  (fuel type B).

### II.2. Irradiation Capsules

Fifteen fuel pellets, each 8.3 mm diameter by 10.1 mm long, were sealed inside a Zircaloy-4 clad fuel pin that was then enclosed in a close-fitting stainless steel

capsule. A total of eleven capsules have been irradiated in the reflector region of the Advanced Test Reactor (ATR) at Idaho National Engineering and Environmental Laboratory (INEEL). The ultimate burnup goal is 50 GWd/MT for three capsules [still in reactor]; the other capsules were removed in pairs after 9, 21, 30, and 40 GWd/MT. It is the capsule pair (one with each fuel type) irradiated to 40 GWd/MT (or approximately 4.2% burnup) which has furnished the present results. This pair was in reactor for thirty ATR operational cycles, accumulating 904 effective full-power days and 42 thermal cycles.

All the capsules were uninstrumented except for containing flux monitor wires. Calculated fuel pellet temperatures indicate a maximum of 1600 C (more than 1000 C below the fuel melting temperature) occurring at about 10 GWd/MT, decreasing to less than 1100 C for all exposures after about 20 GWd/MT.

### *II.3. Post-irradiation Examination Methods*

The irradiated capsules and corresponding fuel pins were subjects for dimensional measurements, qualitative gamma scans, and puncturing by a custom drilling apparatus to measure fission gas pressure and quantity ( $^{85}\text{Kr}$ ). The fission gas release was found to be in the range of 8.4 to 9.5% (based on  $^{85}\text{Kr}$ ).

Segmenting the fuel pins provided samples for microstructural studies, radiochemistry (to determine the gallium content of fuel and clad), and for testing of clad ductility. Fuel/clad segments obtained by low-speed, dry sectioning with a diamond-blade saw were mounted in Araldite epoxy, smoothed by vibratory polishing through 3 $\mu\text{m}$  diamond paste, and examined by a shielded optical metallograph.

Specimens for SEM/microprobe examination were ground down to 0.25-0.60 mm thick (to minimize the mass of radioactive material) before polishing and sputtering on an extremely thin gold conductive film. The examination was carried out in an unshielded Jeol JXA-840A SEM/microprobe fitted with two wavelength-dispersive x-ray spectrometers (WDS) and operated at 20 kV.

Because of the relatively-high specimen radiation level and the lack of standards for certain elements (Pu, Xe), the goal was to acquire moderate-magnification (100-2500x) images of microstructural features using secondary electrons (SE) and back-scattered electrons (BE) together with qualitative, spatial-distribution views of the major constituents and major fission products by WDS x-ray mapping.

## III. RESULTS

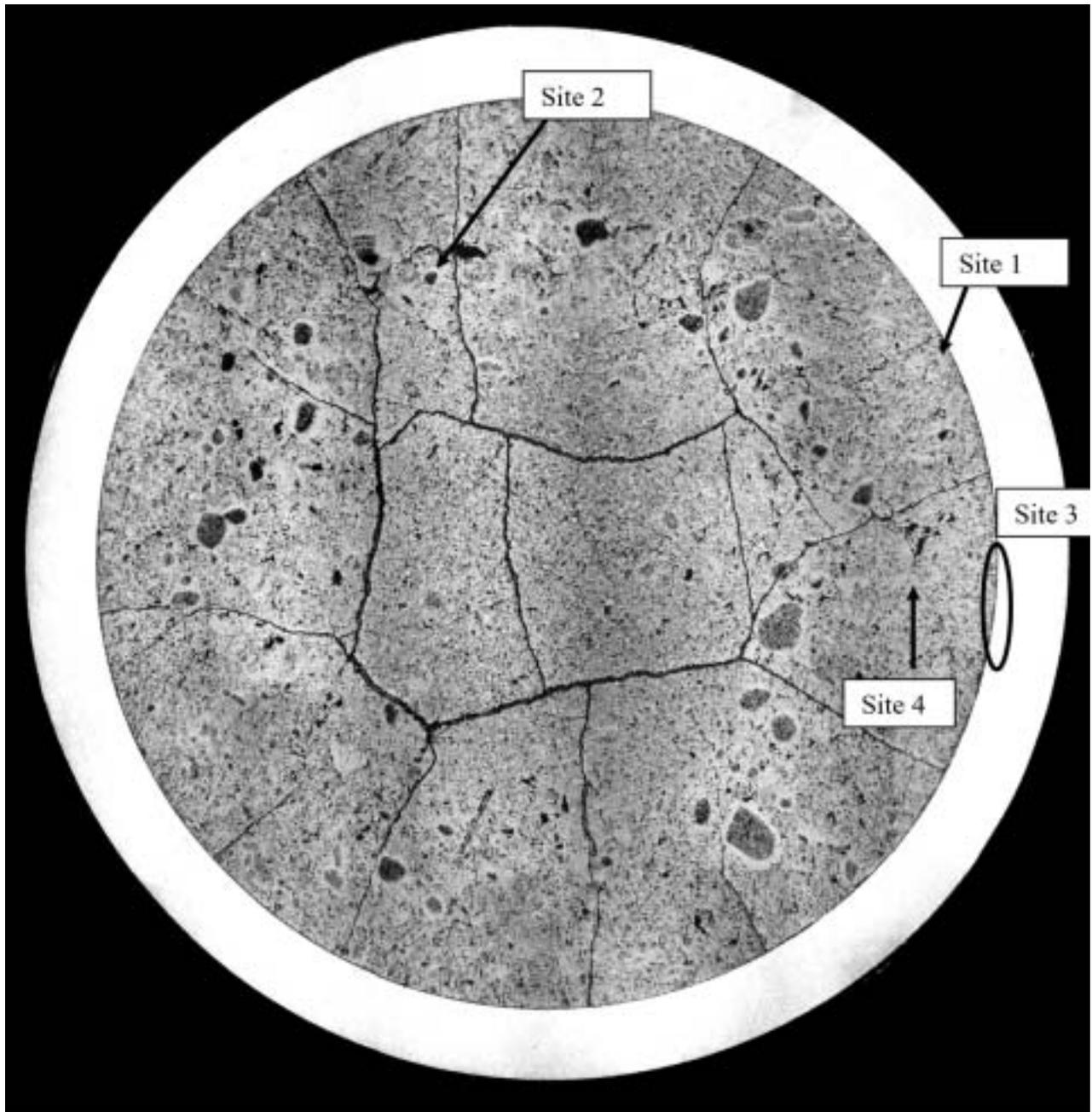
### *III.1. Agglomerates*

A view of a full-diameter section of fuel plus clad is given in Fig. 1 (actually a composite of 25 overlapping images each taken at 40x). The material here is the MOX fuel not subjected to the special preirradiation Ga-reducing process. Consistent with the thermal history, there is no indication of centerline melting, and radial cracking is representative of the thermal cycling imposed during irradiation. Fig. 1 reveals a population of "agglomerates" with a wide range of sizes, up to 500–600  $\mu\text{m}$  in diameter. The agglomerates were present in the as-fabricated pellets and the few with large sizes are indicative of less-than-optimum powder mixing. They have an average local content of about 30%  $\text{PuO}_2$  (six times the overall Pu concentration) and are several times larger than those in modern commercial fuel. The agglomerates are prominently visible in the outermost region of the pellet section, and are only weakly evident within the central half-radius.

Another conspicuous feature is the clear "halo"-like region around each agglomerate. Considering first a typical "internal" agglomerate [not adjacent to the fuel-clad interface] such as "site 2" in Fig. 1, a set of electron images and elemental (x-ray) maps is given in Fig. 2. The agglomerate exhibits a dense local population of small cavities (presumably fission gas bubbles) and a depleted concentration of uranium – the uranium map is darker there relative to the area outside the agglomerate. Plutonium and neodymium are notably enhanced within the agglomerate, and metallic fission products like ruthenium (and palladium, not shown but very similar) are present in discrete precipitates. The fission gas xenon presents a stronger x-ray signal from the surrounding (halo) region compared to the agglomerate interior [see Discussion to follow].

### *III.2. Fuel-Clad Interface*

Two views of the fuel-clad interface for which there is no nearby agglomerate are shown in Fig. 3. The backscatter electron images (on the left) provide a basic material discrimination because electrons back-scatter more strongly from higher-Z materials. The near-white regions are fuel, the medium-gray [at far left] is the Zircaloy-4 clad metal, the intermediary dark gray layer is zirconium oxide and the black layer is epoxy (hydrocarbon). As is evident both from these BE images as well as from the corresponding zirconium maps on the right, the oxide



**MXR83142**

**6218**

**500µm**  
as polished

Fig. 1. Composite photograph of clad and fuel pellet not treated for reduced gallium.

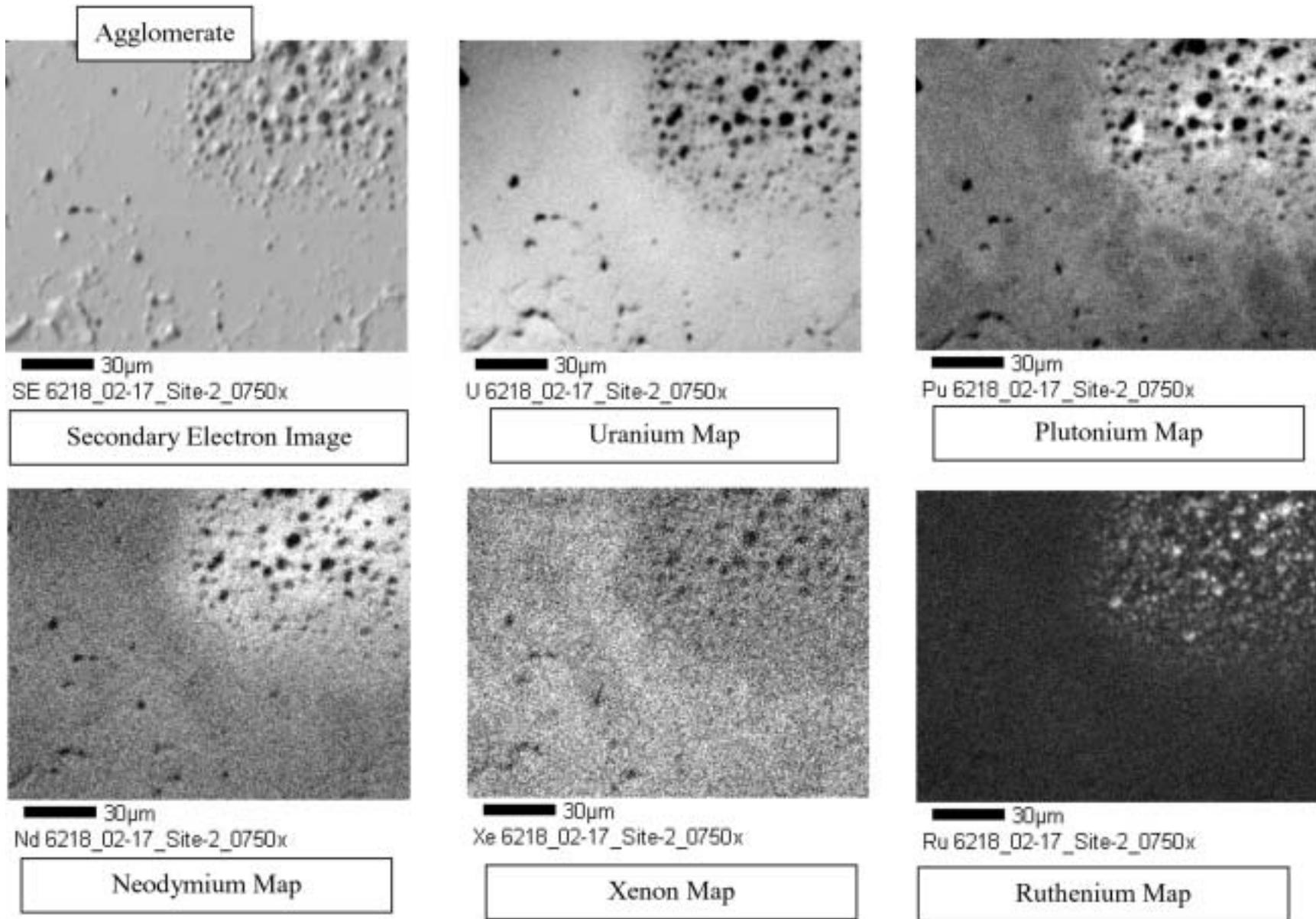
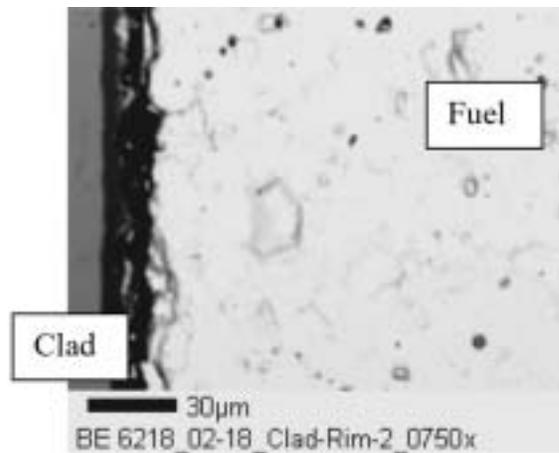
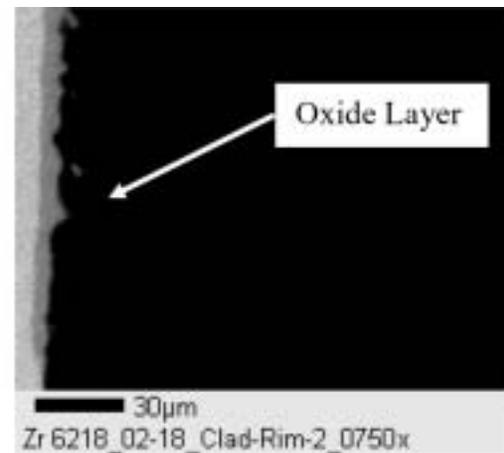


Fig. 2. SEM/Microprobe scans for an internal agglomerate at Site 2 (Fig. 1).



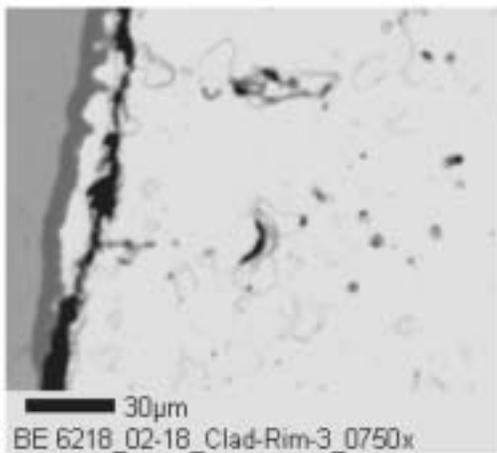
Back Scatter Electron Image

Fuel/clad region with no adhesion to clad. Note the uniform oxide layer



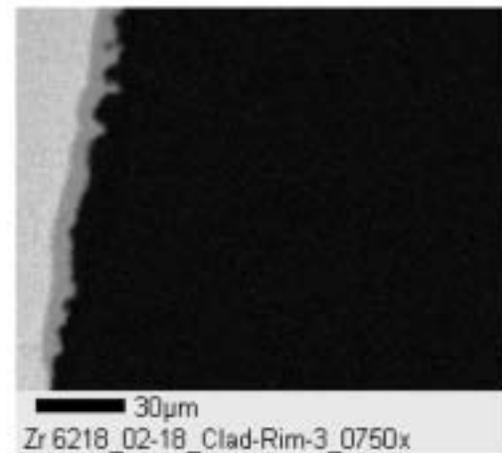
Zirconium Map

**Agglomerate-free pellet/clad interfaces**



Back Scatter Electron Image

Fuel/clad region with adhesion to clad.



Zirconium Map

Fig. 3. SEM/Microprobe scans for a fuel/clad region, Site 3 (Fig. 1), having no nearby agglomerate.

layer has a relatively uniform 5 to 10  $\mu\text{m}$  thickness and this is true whether there is a fine gap or, instead, intimate contact between fuel and clad.

Such an oxide layer was not present everywhere around the entire inner clad circumference, however. It was discontinuous, being absent where the fuel-clad gap was greater. And at sites where a Pu-rich agglomerate was adjacent to the clad, such as the small ( $\sim 50\ \mu\text{m}$ ) triangular agglomerate denoted “site 1” in Fig. 1 and shown in detail in Fig. 4, the oxide layer was both thicker ( $\sim 20\ \mu\text{m}$ ) and had interpenetrating “fingers” of fuel material (both U and Pu). Otherwise the elemental spatial distributions are like those of the internal agglomerates.

### III.3. Grain Boundary Features

The polishing process to prepare a ceramographic specimen occasionally caused pull-out of one or more grains, thereby exposing the faces of several other grains below the polished surface. “Site 4” noted on Fig. 1 is such a case, and in the high-magnification SEM image of Fig. 5 one can discern dimples and grooves on many of the grain faces. These are proposed to be signs of intergranular collections of fission gases such as xenon and krypton.

### III.4. Comparison Between Fuel Types

Post-irradiation measurements determined that the fuel stock which had received initial gallium-removal thermal treatment (TIGR) had slightly greater fission gas release (9.5% based on  $^{85}\text{Kr}$ ) relative to that of the untreated fuel (8.4%). However, there was little difference in the high burnup structure between the two fuel types. Fig. 6 is a full-section optical view of a “Type B” fuel irradiated to the same fluence and temperature as the Fig. 1 sample and it shows similar agglomerate distributions. The electron and x-ray signal maps of Fig. 7, in which two small agglomerates are at the fuel pellet-cladding interface, reveal the same influences on the clad oxide layer for this treated fuel as was seen with Fig. 4 for the “Type A” untreated fuel.

### III.5. Agglomerates at Central vs. Outer Regions of the Fuel

During the irradiation, the edge regions of a pellet were always cool enough for the agglomerates’ radiation microstructure to develop. However, only during the last portion of the irradiation did the central part of these pellets become cool enough for this structure to form. It is useful to compare these two regions. From Fig. 8 one can see that an outer-region agglomerate (on the left) has a more complex structure and a higher density of smaller cavities. The central region agglomerates lack the complex structure, owing to the much higher fission product

diffusion rates that were due to the higher temperatures experienced over most of their history.

### III.6. Gallium Analysis

Multiple samples of irradiated fuel pellet and clad materials [for both fuel types] were submitted to the Radioactive Materials Analysis Laboratory of ORNL for determination of their gallium contents. The mass averages for each pellet were found to be comparable to the previously measured unirradiated values: 2.68 ppm (irradiated) vs. 2.97 ppm for the untreated fuel type, and 1.05 ppm (irradiated) vs. 1.33 ppm for the TIGR fuel.

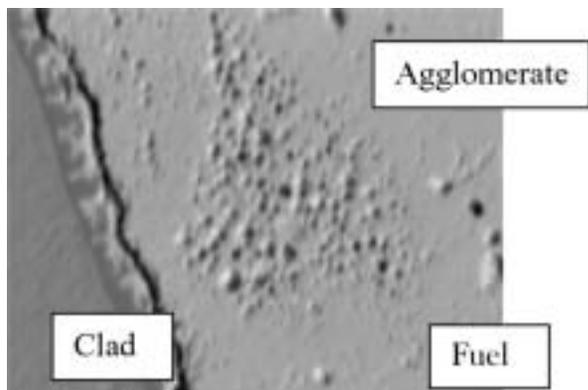
For the clad samples, the post- vs. preirradiation measurements indicate negligible transfer of gallium to the cladding, with the specimen average gallium concentrations of 0.60 (pin with untreated fuel) and 0.70 (TIGR fuel) being within 20% of the unirradiated value.

## IV. DISCUSSION AND CONCLUSIONS

The most prominent feature of both types of fuel after irradiation is the plutonium-rich and high burnup microstructure of the agglomerates. The WDS x-ray maps confirm (qualitatively) their elevated local concentrations of Pu and various solid fission products. The situation for xenon is a bit more complex, since it presents a higher signal in the “halo” region just outside an agglomerate than within it. The agglomerate is clearly the source of the xenon, but there is cause to believe that the signal associated with the presence of xenon within the agglomerate is weakened due to its collection into bubbles there. Prior work<sup>1</sup> has determined that when fission gases collect in bubbles larger than 2 nm in diameter, the detectable x-ray intensity is reduced and the magnitude of this signal reduction increases with bubble size.

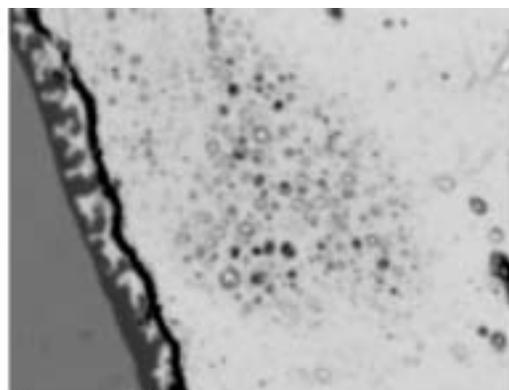
Agglomerates of widely varying sizes all display the “halo”: a clear region that is visibly different from either the porous agglomerate or the fuel matrix. It appears that a combination of athermal (fission recoil) and thermal diffusion of fission products such as xenon from the agglomerate has altered the adjacent matrix in a manner that responds differently to polishing (than the general matrix) and makes these regions visible. The fact that the halos around small or large agglomerates are of approximately constant thickness argues against their arising from local stress effects that should scale with agglomerate size. Further evidence for the accumulation and transport of fission gases exists in the observations of dimples and grooves on grain interfaces that were occasionally exposed by polishing-induced pull-out.

Thin (a few microns) corrosion layers were discerned on the clad inner surface at areas of pellet-clad contact. These oxide layers were notably wider and displayed some partial-thickness fuel diffusion whenever an agglomerate was immediately adjacent. It must be



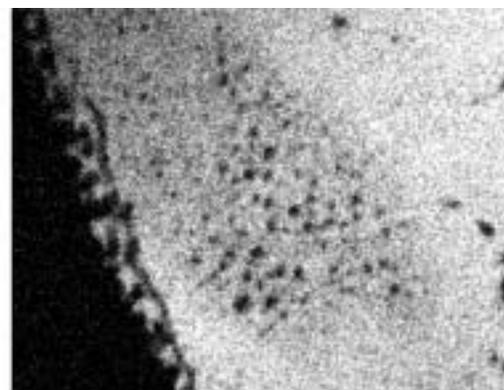
30µm  
SE 6218\_02-13\_Site-1\_0750x

Secondary Electron Image



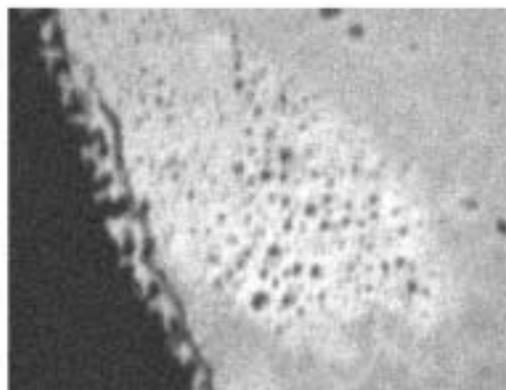
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BE 6218\_02-14\_Site-1\_0750x

Back Scatter Electron Image



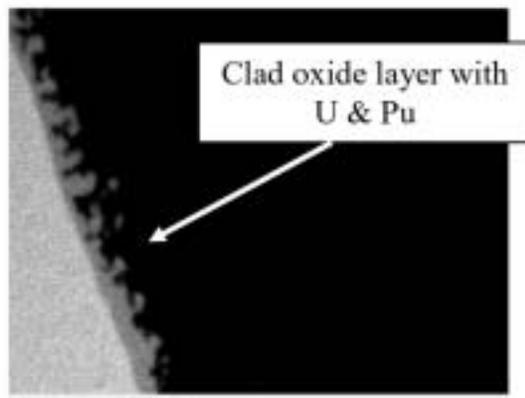
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Uranium Map



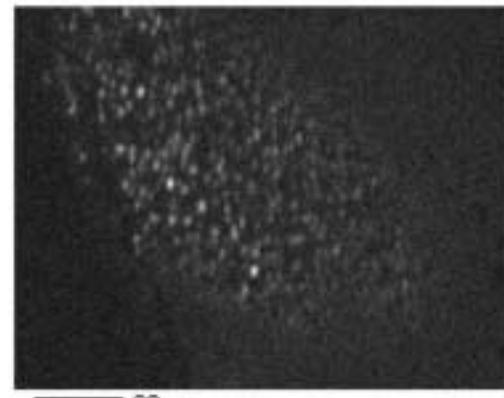
30µm  
Pu 6218\_02-13\_Site-1\_0750x

Plutonium Map



30µm  
Zr-PET 6218\_02-14\_Site-1\_0750x

Zirconium Map



30µm  
Pd 6218\_02-13\_Site-1\_0750x

Palladium Map

Fig. 4. SEM/Microprobe scans of Site 1 (Fig. 1).

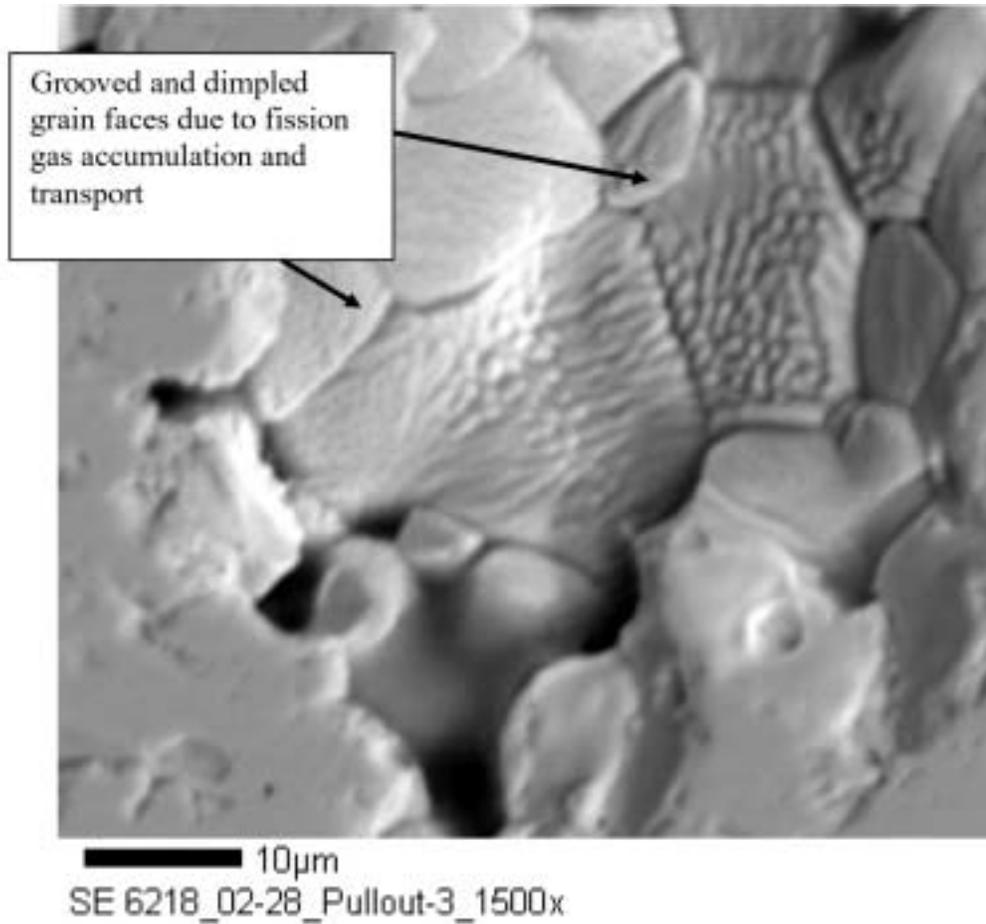
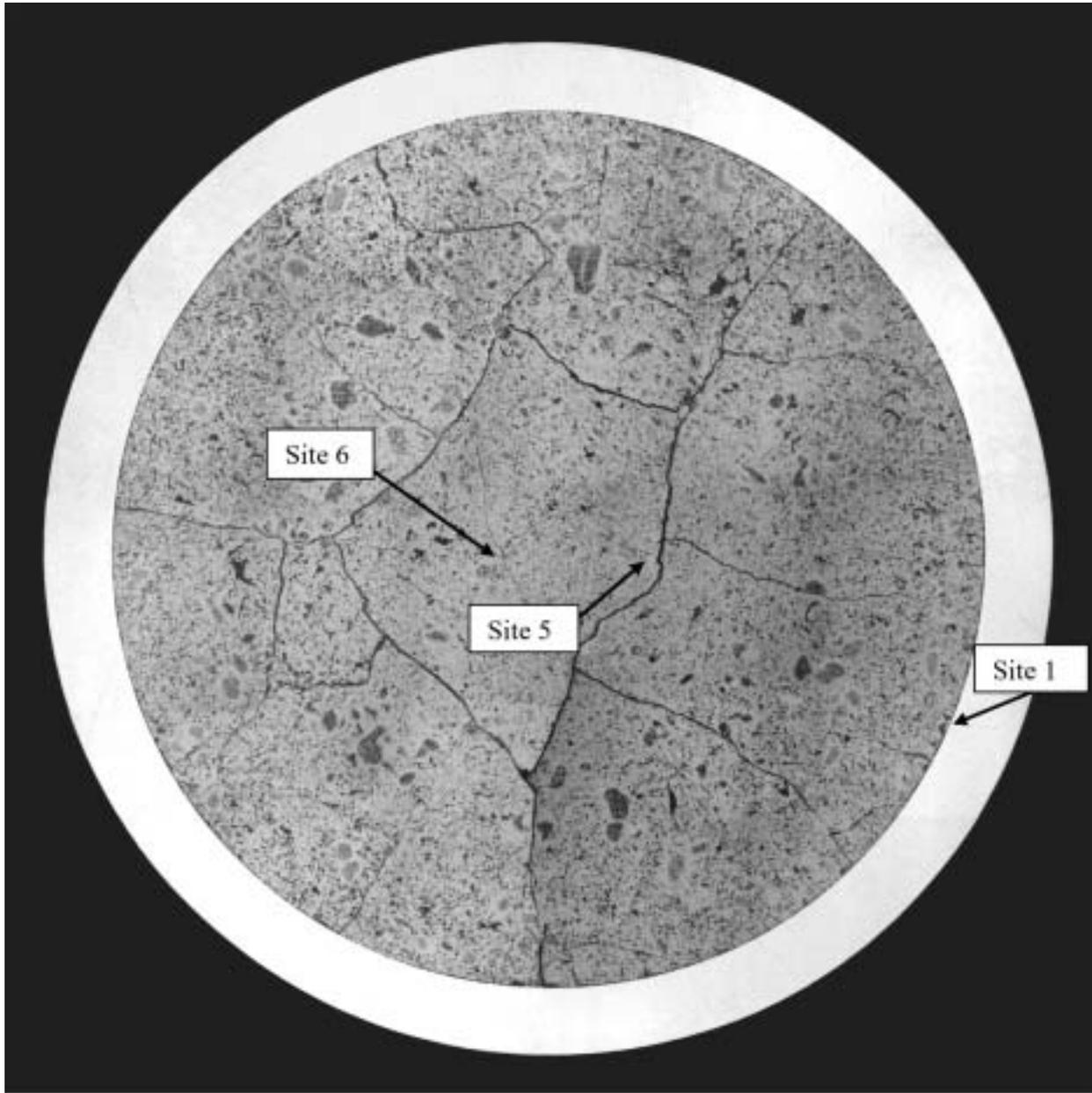


Fig. 5. SEM/Microprobe scans for a grain boundary at Site 4 (Fig. 1).

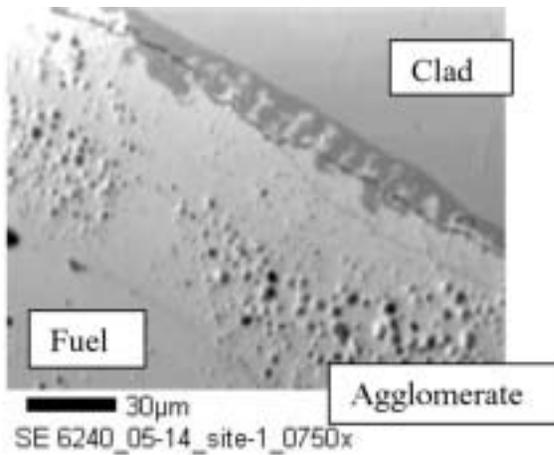


**MXR83182**

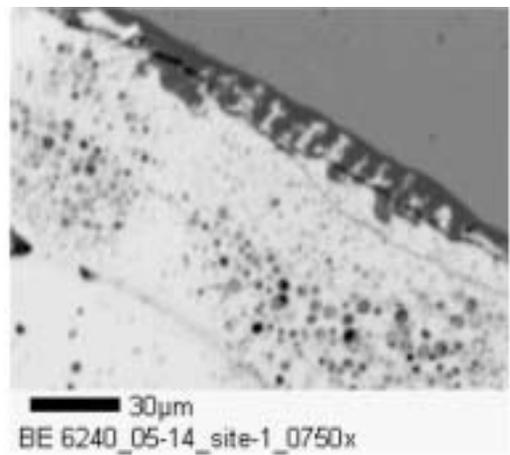
**6240**

500µm  
As Polished

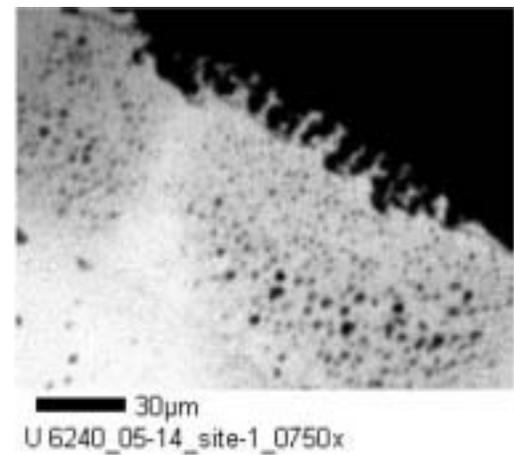
Fig. 6. Composite photograph of a reduced-gallium fuel pellet.



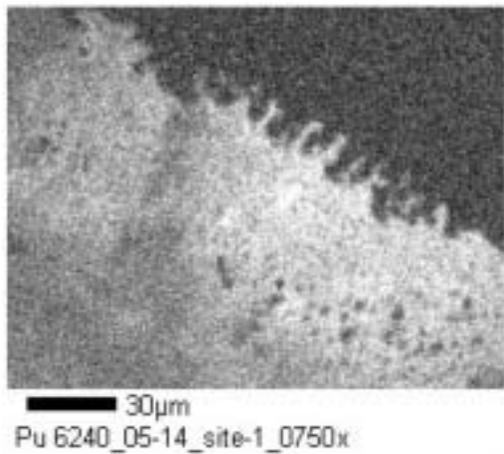
Secondary Electron Image



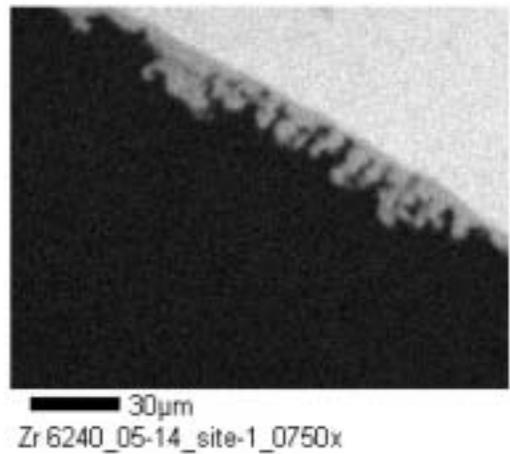
Back Scatter Electron Image



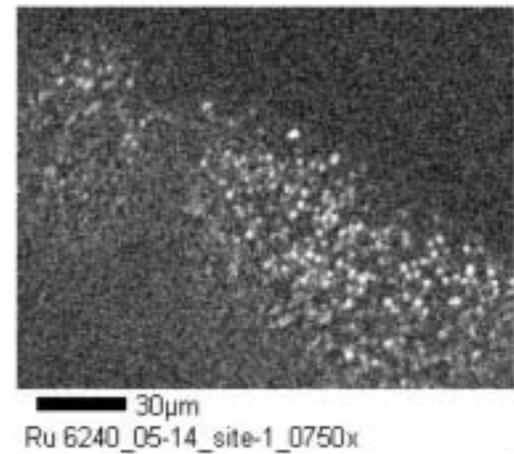
Uranium Map



Plutonium Map



Zirconium Map



Ruthenium Map

Fig. 7. SEM/Microprobe scans of Site 1 (Fig. 6).

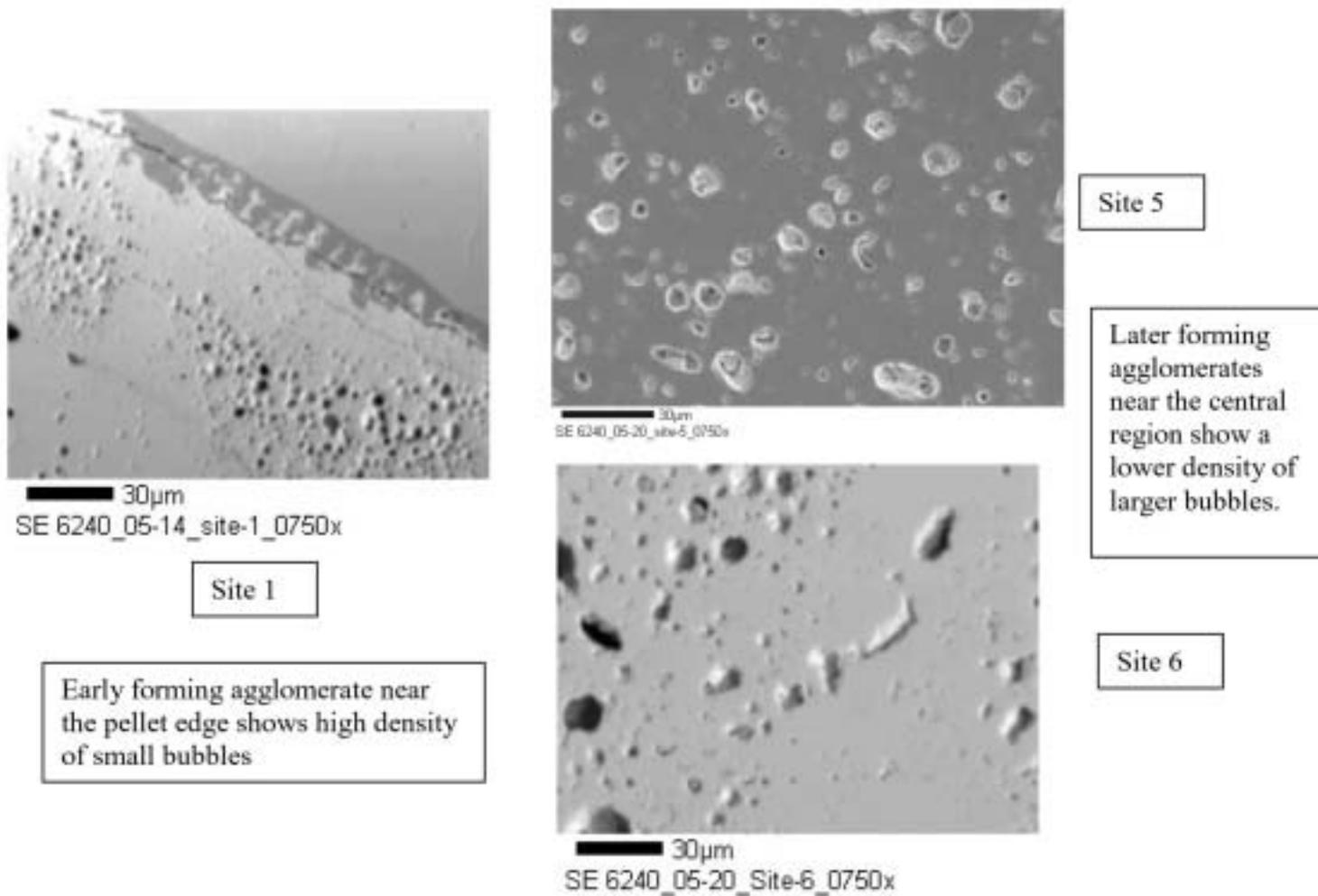


Fig. 8. Comparison of internal and edge agglomerates at sites 1, 5, and 6 (Fig. 6).

emphasized, however, that both these clad-oxide effects as well as the anomalies associated with the agglomerates were fine-scale phenomena and do not present any compromise of fuel performance. Also, post-irradiation radiochemical analyses determined any gallium migration from fuel to cladding to be insignificant. Overall, the tested two versions of MOX fuel prepared with weapons-derived plutonium have behaved as expected out to the relatively-high exposure of the present results.

#### ACKNOWLEDGMENTS

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#### REFERENCES

1. C. RONCHI and C. T. WALKER, "Determination of Xenon Concentrations in Nuclear Fuels by Electron Microprobe Analysis", *J. Phys. D: Appl. Phys.* **13** 2175 (1980)