

**Experimental and Theoretical Considerations for
Proton Irradiation Processing
of Early Solar System Solids**

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Dedication

To Jen, Kelly, and Anna for their patience, support, and understanding

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ABSTRACT

The radiation environment of the early system was explored to understand how enhanced Solar Energetic Particles (SEP) could process early solar materials in a nebular environment. A series of proton irradiations using particle accelerators were performed on a suite of materials representative of primitive chondritic meteorite constituents: this included mineral fragments of olivine, feldspar, pyrite, and a weathered ordinary chondrite; sintered mixtures of olivine/gabbro, olivine/anorthosite, and olivine/corundum; and synthetic materials including forsterite, fused silica, and single crystalline Si wafers. Proton (p) irradiation conditions included energies between 50 keV-3.8 MeV, fluxes between 10^{12} - 10^{14} p/cm²-s, and fluences between 10^{14} - 10^{17} p/cm². The irradiated materials were examined using a variety of *insitu* and post-irradiation characterization techniques; *insitu* techniques included video monitoring, radiation detection using a Geiger-Mueller tube, and mass spectrometry using a Residual Gas Analyzer. Post-experimental examination included optical and electron microscopy and radiation count rate experiments.

The experimental results can be broadly classified into physical, chemical, and nuclear processing. Physical processing refers to mechanical fracture, melting, and radiation damage; chemical processing includes the formation of organic compounds, volatilization of certain elements and compounds, and the reduction of iron oxides to metal droplets; while nuclear processing include the formation of radioactive isotopes below energies typically investigated in spallation studies. The results provide several new mechanisms on how enhanced SEP events can process constituent chondrite components. Enhanced SEP processing could have a role in comminuting larger material to sub-mm sized fragments, melting fragments of chondrule precursors and chondrules, developing the igneous textures associated with some refractory inclusions (Calcium-Aluminum Inclusions, CAIs), annealing radiation damage, forming or modifying organic compounds found in the matrix of meteorites, volatilizing labile elements such as sodium and sulfur, reducing iron oxides to develop metals outside of the expected condensation sequence, and transmuting silicon and other isotopes from normal solar abundances

below traditionally examined energies. Collectively the results suggest that enhanced SEP interactions with early solar material may open up a new field of study in planetary sciences.

PREFACE

All rocks from Earth have a history of complex, multi-step processing which can include exposure to extremes in temperature and pressure, all over geologic time scales. By studying the mineralogy, chemistry, and texture of rocks, many of these processes can be deciphered; this includes an understanding of where the rocks were formed and how they have been altered over time. Collectively, by studying the suite of rocks formed on the Earth's surface and those formed in the interior that make it to the surface, models for the rock cycle, differentiation, and planet building can be developed.

Similar to terrestrial rocks, meteorites can share a complex history of exposure and cycling through a variety of processing conditions. While some meteorites can aid in understanding planet-building processes, others are a direct link to the conditions present in the solar nebula prior to and during star formation. As matter condenses in the high-temperature gaseous nebula, it is subject to processing conditions that are not present on terrestrial bodies. One such condition is exposure to intense fluxes of radiation in the form of photons, electrons, and particles from the developing Sun.

Stars such as our Sun are constantly ejecting particles, and as the Sun is made up primarily of hydrogen, the bulk of particles leaving the Sun are energetic hydrogen ions, or protons. Present evidence for this can be seen in the colorful *Aurora Borealis*, which represents the interaction of these particles with gasses in the upper atmosphere at the Earth's poles. But during star formation, particles are ejected with increased frequency and energy, and can interact with matter in a variety of ways. One such interaction is the transmutation of elements to different elements or isotopes by the highest-energy protons from the Sun. The elements formed in these transmutations are oftentimes unstable, and can decay to stable elements nearly instantaneously or over millions of years. As they decay, energy is released which may result in large-scale thermal metamorphism, melting, and differentiation which is critical to explaining the structure of the Earth.

A detailed understanding of the high-energy irradiation processes is necessary, as there are other possibilities for radioisotope formation and incorporation into future planetary material, a topic which is widely debated in literature. A key to understanding

the high-energy irradiation processes could be to study other interactions protons can have with matter. This is a novel concept, as most researchers have considered only how the highest-energy particles interact with matter, while in fact there is a considerably larger quantity of lower-energy particles coming from the Sun. If the lower-energy particles interact with matter in ways that are reflected in the meteorite record, it could further support the idea that unstable heat-generating isotopes are formed from high-energy particle reactions in the solar nebula.

In order to test how particles, specifically protons, interact with matter we conducted laboratory experiments using particle accelerators and meteorite analog materials to simulate conditions in the early solar nebula. The experiments considered the effects of energy, the total number of protons, and the exposure time. The results can be broadly classified into physical, chemical, and nuclear effects. Collectively, the results of the experiments have textural and chemical similarities to what is observed in some meteorite phases at both the macro and microscopic level. It may be that exposure to proton irradiation in the nebular environment was a significant processing mechanism in the early solar system.

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CHAPTER 1: INTRODUCTION

Astronomical observations and exotic isotope concentrations in primitive meteorites indicate the energetic particle environment in the early solar system was vastly different from that of the present day. Ground-based telescopes have a long history of recording stellar activity at various stages of protostar development. Seminal research from Herbig (1966) described the increase in luminosity and mass loss of the developing star FU Ori over several decades; these observations led to the classification of stars which display extreme changes in spectral output as FU Orionis type stars. More recent observations from the Hubble Space Telescope reveal detailed images of massive eruptions. For instance, Fig. 1 shows that large quantities of stellar matter can be ejected over decades and reach to distances of hundreds of AU (astronomical units) in a developing star system. Energetic stellar matter, primarily in the form of gaseous and ionized hydrogen, can interact with early solar material in a variety of ways.

Of longstanding interest is the role these energetic particles have in the formation of isotopic signatures which deviate from normal solar abundances; these are referred to as anomalous or exotic isotopes (Clayton et al., 1977; Fowler et al., 1962; Lee, 1978). These include, but are not limited to isotopes of lithium, beryllium, boron, oxygen, and neon, as well as the short-lived radionuclides (SLRs) including ^{41}Ca , ^{26}Al , and ^{60}Fe . The latter two isotopes are significant in their plausible roles as heat sources for asteroidal thermal alteration and planetary differentiation.

Considerable literature has addressed whether the various anomalous isotopes and SLRs have an external origin, seeded from a nearby supernova event, or have internal particle irradiation formation scenarios (Goswami et al., 2005; Gounelle et al., 2006; McKeegan et al., 2000; Trappitsch et al., 2018). The incorporation of live radiogenic nuclides into the solar nebula in an external model could be concurrent with the collapse of the nebular cloud or an infall event. Models indicate that the time scale between collapse of the molecular cloud and the incorporation of short-lived isotopes generated from explosive nucleosynthesis is on the order of 1 million years (Goswami et al., 2001; Wasserburg et al., 1995). This model suffers from the relatively tight time constraint

from production to incorporation of live short-lived isotopes. If significant quantities cannot be generated, transported, and incorporated live during this window, there will not be enough decay energy available to drive large-scale thermal metamorphism, melting, and differentiation in accreted bodies.

An alternative scenario is that exotic isotopes and SLRs can be produced through spallation by SEPs (solar energetic particles) concurrently with condensation and accretion during early stages of solar system evolution. Elements can be transmuted when incident energetic particles can overcome the repulsive force (Coulomb barrier) of the target nucleus and combine to form a new isotope. A hindrance to invoking an internal production model is that for a fixed flux (number of particles, per unit area, per second), is that it fails to produce the respective ratios of the suite of exotic isotopes measured in early refractory solar condensates (Goswami et al., 2005; Goswami et al., 2001; Gounelle et al., 2001). At present, conclusive evidence does not exist to singularly endorse an external seeding or internal production model for all anomalous isotopic signatures measured in primitive meteorites. For instance, production of ^{10}Be and ^7Be favors an internal model as external nucleosynthetic processes destroy these elements, while neutron-rich isotopes such as ^{60}Fe may have been produced in explosive nucleosynthetic *r-process* events (Leya et al., 2003; Trappitsch et al., 2018).

A corollary of an irradiation environment capable of transmuting elements into exotic isotopes, is that material would be subjected to a much larger flux of lower-energy particles. Irradiated material may be in the form of gas, early nebular condensates such as calcium-aluminum-rich inclusions (CAIs), precursor chondrule material, chondrules, and dust and larger grains which are remnants of past supernovae. The physical and chemical composition of the irradiated material, as well as the irradiation environment, will be functions of time in the protostar development sequence and distance from the star. For instance, internal production models proposed by Shu et al. (1997) and Lee et al. (1998) consider distances associated with reconnection rings (x-wind) which are fractions of an AU, whereas more conventional production distances are on the order of 2 AU (Goswami et al., 2001). Exploring how the larger-flux of lower-energy particles can

interact with early solar material should first consider the nature of the particle environment, early types of matter present, and how particles interact with solids.

1.1 Nature of the Particle Environment in Space

Energetic particles in the cosmos have an energy distribution, flux, elemental composition, and an irradiation duration which are variable over time; any discussion of irradiation effects must include these variables. Here we define *flux* as the number of particles incident over an area for a duration of time (e.g. particles/cm²-s), and *fluence* as the total number of particles incident over an area (e.g. particles/cm²) irrespective of time. We will reserve the use of *dose* to specifically refer to energy deposition (e.g. J/kg). To understand the radiation environment in the early solar system, the present day particle environment should first be examined.

The dominant source of energetic particles in the present solar system are low-energy protons in the solar wind. The solar wind is a stream of particles emanating from the sun in all directions at a relatively constant flux (Parker, 1958). The energy and atomic species distribution of the solar wind was reviewed by Bennett et al. (2013). Dominant species of the solar wind include hydrogen (97%), helium (2.5%), and the remainder which includes order of magnitude similar amounts of oxygen, iron and silicon. The collective solar wind at 1 AU has a velocity of approximately 500 km s⁻¹, which conveniently works out to atomic species possessing ~1 keV/nucleon of energy. The flux of protons at this distance is approximately 4x10⁸ p/cm²-s. In addition to the solar wind, higher-energy particles are present in the solar system; these include solar flares, galactic cosmic rays (GCRs), and solar cosmic rays (SCRs). GCRs and SCRs are typically indistinguishable and are collectively referred to as GCRs and poses energies > 100 MeV. The solar wind particles are by far the most abundant, but have the lowest energy, while SCR and GCRs have the highest energy but the lowest abundance. Solar flares have intermediate energies and abundances several orders of magnitude greater than SCRs, but considerably lower than the solar wind.

Early attempts to understand the particle environment of the early solar system used isotopic ratios from extinct radiogenic nuclides in primitive solar material such as CAIs and chondrules. Here a radiogenic nuclide is defined as the direct transmutation product and or the decay product from a spallation event. Historically, the invocation of SEP as a mechanism for the production of radiogenic nuclides began after the discovery of live ^{26}Al in CAIs (Gray and Compston, 1974; Lee et al., 1976). Heymann and Dziczkaniec (1976) made preliminary calculations to determine the proton particle flux required to transmute ^{26}Mg to ^{26}Al via a (p,n) reaction ($^{26}\text{Mg}(\text{p},\text{n})^{26}\text{Al}$). Their results indicated that a flux between 10^{10-12} p/cm²-s of 1 MeV protons is required to produce the respective positive and negative anomalies observed in ^{26}Mg . However, if the irradiation conditions suggested by Heymann and Dziczkaniec for ^{26}Al were applied to other low-atomic number elements, there would exist an incongruent relationship between predicted and measured isotopic ratios. This is particularly true in the case of calcium, where flux values used to predict the $^{26}\text{Al}/^{27}\text{Al}$ ratio overproduced the $^{41}\text{Ca}/^{40}\text{Ca}$ by a factor of 2 (Leya et al., 2003). Early hypothesis attempted to rectify this incongruent relationship by suggesting a calcium poor rim, and a magnesium rich core, however this texture is not supported in the meteorite record (Gounelle et al., 2001). Work by Leya et al. (2003) has resolved much of the discordance by considering the contribution of ^3He and ^4He in addition to protons. However, several isotopic species still do not align with irradiation production conditions, suggesting non-homogeneous irradiation conditions or injection from nearby supernovae.

Astronomical studies of developing stars can further elucidate the particle environment of the early solar system. Studies indicate that the proton flux associated with X-ray bursts from the pre-main sequence Sun may be $10^{1.5}$ more powerful and $10^{2.5}$ more frequent than the largest contemporary flare events. This may result in proton fluxes 10^5 greater than contemporary levels (Feigelson et al., 2002; Feigelson and Montmerle, 1999); however, the authors admit exact mechanisms for the flux increase have not been developed. When integrated over a range of energy, the 10^5 enhancement of the measured flux at 10 MeV, ~ 1 p/cm²-s (Caffee et al., 1988), becomes $\sim 10^{12}$ p/cm²-s. This treatment considers a simple linear relationship between flux and energy. However;

it is predicted that the flux of particles increases substantially with decreasing energy (Caffee et al., 1988; Reedy and Arnold, 1972; Reedy et al., 1983); this will be developed further in the Discussion section .

1.2 Early Solar Material

Interpreting the history of the early solar system can be made possible by studying the chemical and physical properties of the most abundant class of meteorites, chondrites. Named for the millimeter-sized droplets of silicate materials ubiquitous within the microstructure, chondrites consist of an assemblage of components that collectively have an elemental signature similar to the Sun (McSween and Huss, 2010). Chondrite components consist of refractory inclusions, chondrules, metal, sulfides and dust; all cemented in a fine grained predominately siliceous and carbon containing matrix.

The formation of individual chondrite components is likely accomplished by the cooling of a hot nebular gas, for which pure elements can condense directly or interact with other gaseous species to form compounds. A condensation sequence can be developed that is based on the overall volatility of the component elements and compounds found in chondrites which operates over temperatures between ~ 1700 -650 K and partial pressures of $\sim 10^{-3}$ atm (Davis and Richter, 2003; Ebel, 2006; Grossman and Larimer, 1974). Individual components can combine and ultimately accrete to form larger bodies, which become the source material for asteroid and planet building. However, a simple condensation model does not accurately predict all chondrite components, nor do those phases which are well-predicted avoid secondary alteration both in the nebula or on the parent body of the asteroid for which they accrete (Brearley, 2003; Krot et al., 1995; Messenger et al., 2010) . This is particularly true in the case of chondrules.

An enormous body of literature addresses the formation and alteration mechanisms of chondrules based on numerous observed and theoretical considerations (Boss, 1996; Ciesla, 2005; Grossman et al., 1988). A generalized chondrule mineral composition would include fayalite (Fe_2SiO_4), forsterite (Mg_2SiO_4), clinoenstatite

(MgSiO_3), albite ($\text{NaAlSi}_3\text{O}_8$), anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$), and smaller amounts of cristobalite (SiO_2), diopside ($\text{MgCaSi}_2\text{O}_6$), Fe metal and sulfides. (Wasson, 1996). As many chondrules record evidence for multiple complete and partial melting events, the temperatures chondrules experience should approach and exceed that of forsterite. The Mg-rich endmember of olivine has the highest melting temperature of all minerals listed above at approximately 2100 K. The lower limit associated for chondrule formation is the temperature at which Fe metal interacts with sulfur to form sulfides such as troilite (FeS) and pyrrhotite (Fe_{1-x}S) at approximately 650 K. As chondrules are a dominant feature in the meteorite record, understanding their formation and processing mechanisms has the ability to further elucidate the conditions present during the formation of our solar system.

As it has been proposed that high-energy particles from the Sun can result in the formation of anomalous isotopic signatures, it is reasonable to assume that some collateral effects may occur when constituent mineral phases are exposed to the entire energy spectrum of energetic particles coming from the developing Sun.

1.3 Ion Solid Interactions

For the purposes of exploring ion-solid interactions in space, it is practical to focus discussion on protons as they are the dominant source of particles from the Sun. Here we use the term *target* to refer to the stationary atom, and *incident* as the energetic irradiating particle. Proton interactions with matter can occur in the following:

- Sputtering- the ejection of target atoms from solids due to interaction with incident energetic particles
- Scattering- a change of momentum of the incident particle due to coulomb repulsion with a target nucleus
- Radiation damage- displacement of target atoms from their normally occupied lattice sites by incident radiation and the breaking of bonds

- Compound formation- implanted species forming compounds with target atoms, i.e. the formation of a hydroxide when a proton is implanted into an oxygen bearing compound
- Nuclear reactions- result of an incident and target nucleus interaction above the coulomb threshold resulting in the formation of a new nucleus.

Common to all these effects is the deposition of energy, which is the result of the proton losing energy as it is slowed in the solid; the resultant energy loss is accompanied by a temperature gain in the solid. The degree to which the above affects can be resolved is largely due to the total number of interactions (fluence), and the rate at which interactions occur (flux). Energy deposition from particle-solid interactions resulting from a small number of events over a long time period are typically unresolvable. For instance, the low-proton flux associated with the solar wind (4×10^8 p/cm²-s) has virtually no measurable instantaneous effects. While the total integrated energy deposition in this case may be high, the rate of heat gain can be negated by conductive, convective, and radiative heat loss so that minor temperature gain may result. If solids are irradiated by significantly higher fluxes of protons, the energy deposition may result in heating and even melting of early solar system solids.

1.4 Literature Review

Considerable literature exists on the interactions of solar wind particles (~1 keV protons) with solids (Bennett et al., 2013; Hapke, 2001; Loeffler et al., 2009). When combined with micrometeorite impacts, “space weathering transforms surfaces through comminution (crushing/shattering), agglutination (aggregation by impact-induced melting), particle sputtering/ vaporization, vapor deposition, ionization, ion implantation, melt-quench cycles, and potential loss of volatile components” (Ichimura et. al., 2012). A product of space weathering is a mineral surface which is both compositionally and morphologically different than its interior.

In contrast to space weathering, virtually no literature experimentally investigates solar flare equivalent energy and fluxes; this of course excludes literature directed to understand nuclear cross-sections in order to understand isotope transmutations (Leya et al., 1998; Michel et al., 1997; Reedy, 2013). Feigelson and Montmerle suggest that energetic photons and protons from Young Stellar Objects (YSOs) may account “for long-standing findings in meteorites that are quite difficult to explain” (Feigelson and Montmerle, 1999); this includes the ability of YSOs to melt chondrules (Feigelson et al., 2002). The authors further state that, “There has also been inadequate study of the effects of flare shocks and energetic particles on solids. Further accelerator experiments with X-rays and particles should be pursued actively. The final evaluation of the astrophysical importance of energetic processes in YSOs awaits these future investigations” (Feigelson and Montmerle, 1999). The collective astronomical observations from these two articles become the foundation for other researchers to perform production calculations to examine the source of anomalous isotopes and SLRs (Goswami et al., 2005; Gounelle et al., 2006; Leya et al., 2003).

1.5 Thesis Statement

In this work, we perform some of the first experimental work to understand the collateral effects of invoking an internal production model for the formation of anomalous isotopes and SLRs. We subject chondrite constituent analog materials to the predicted enhanced SEP as suggested by Feigelson et. al. (Feigelson et al., 2002; Feigelson and Montmerle, 1999). Leya et al. (2003) published the following article, “*The Predictable Collateral Consequences of Nucleosynthesis by Spallation Reactions in the Early Solar System.*” We like the use of the term “collateral” in the article; however, in our text we use the term to explore the physical, chemical and nuclear effects associated with the lower-energy/higher-flux portion of an enhanced SEP.

Previous preliminary experimental work (Wetteland et al., 2013; Wetteland et al., 2016; Wetteland et al., 2015) using particle accelerators have indicated that irradiating silicates with high-energy/flux protons can process these solids in the

following ways: (i) catastrophically fragment cm-sized grains forming sub-millimeter sized fragments, (ii) deposit significant amounts of energy that can melt and even vaporize materials, and (iii) preferentially deposit low-concentrations of organic compounds from a high-vacuum environment ($\sim 10^{-6}$ Torr) onto the surface. In addition to these physical and chemical observations, the authors noted that silicates irradiated with 2 MeV protons emit considerable amounts of short-term radiation in the form of γ -rays. (Wetteland et al., 2016). This radiation represents nuclear transmutations that could result in exotic isotope signatures.

In this investigation, we consider collateral radiation effects which can occur in early solar system material from exposure to the lower-energy/higher-flux portion of enhanced SEP. To accomplish this, a series of experiments using particle accelerators were conducted to simulate early solar system conditions. A variety of analog minerals representing chondritic meteorite components were irradiated using keV-MeV hydrogen ions. The experiments investigate the effects of energy, flux, and total fluence, with results compared to primitive meteorites to explore the possibility that energetic protons could be responsible for processing early solar system solids. Results will be presented that address the collective physical, chemical, and nuclear processing of protons with chondrule component analogs using energies 2 MeV and below.

CHAPTER 2: EXPERIMENTAL

2.1 Sample Selection

A suite of materials was chosen to represent a wide temperature regime of minerals predicted to sequentially condense from a hot nebular gas; the sequence represents the start of planet building in the solar system (Ebel, 2006; Larimer, 1967; McSween and Huss, 2010). Cooling followed by condensation and grain growth develops distinct minerals which can be cemented together to form meteorites. Prior to cementation, these constituent mineral phases can be exposed to energetic particles as well as other types of nebular processing (Brearley, 2003; Krot et al., 1995; Messenger et al., 2010).

Constituent minerals examined in this work are detailed below:

- Calcium-Aluminate-Inclusions (CAIs)- Condensing at approximately 1700 K, CAIs are the most refractory minerals found in meteorites. CAIs include minerals such as corundum (Al_2O_3), hibonite ($\text{CaAl}_{12}\text{O}_{19}$), perovskite (CaTiO_3), melilite ($\text{Ca}_2(\text{Al}_2, \text{MgSi})\text{SiO}_7$), and Al rich spinels ($(\text{Fe}, \text{Mg}, \text{Cr}, \text{Al}, \text{Ti})_3\text{O}_4$). The condensation of CAIs is the established beginning, or birth of our solar system. They have limited occurrences in meteorites, found only in meteorites which escaped thermal and aqueous alteration after large-scale agglomeration.
- Olivine-Olivine is a solid solution between the high- melting temperature forsterite end-member (Mg_2SiO_4) and the lower-temperature end-member fayalite (Fe_2SiO_4); it condenses over a series of temperatures beginning around 1450 K. Olivine is the major mineralogical component of chondrules. Other minerals found in chondrules include pyroxenes and feldspars; the latter will be additionally investigated in this study.
- Metals-Metals come from two different distinctive temperature regimes in the condensation sequence. Small metal nuggets found in CAIs include the most refractory elements such as iridium, osmium, ruthenium, molybdenum, tungsten, and rhenium; these nuggets are also known as Fremdlinge. An intermediate condensation temperature regime contains Fe, Ni, Co alloys, which form within and on the rims of

chondrules. These alloys essentially condense at the same temperature of olivine at ~1400 K. The formation of the lower temperature metals will be investigated in this study.

- Sulfides-Sulfide minerals represent one of the lowest-temperature, non-organic, constituents found in meteorites. The formation of sulfides is predicted to occur below ~650 K when previously condensed Fe metal reacts with sulfur to form minerals such as troilite (FeS). The ~650 K temperature can be thought of as a closure temperature which describes the lowest-temperature non-organic constituent phase of chondrite meteorites.

2.2 Sample Preparation

Mineral fragments of San Carlos olivine, alkali feldspar, pyrite, and a weathered, thermally metamorphosed ordinary chondrite were sliced into slabs of various thickness (0.5-2 mm) and progressively ground to 800 grit using silicon carbide. Forsterite pellets were synthesized by mixing SiO₂ and MgO in a 1:2 molar ratio in isopropanol using a zirconia ball mill canister for 20 minutes. The pellets were dry pressed in a 13 mm stainless steel die and sintered in air at 1823 K for 12 hours; x-ray diffraction (XRD) measurements yielded a homogenous and model forsterite pattern. Pellets from mineral fragments and rock were generated by ball milling the material with isopropyl in a zirconia canister for two hours. Powders were subsequently combined and mixed in the ball mill. Mixed compositions by weight included: (i) 80% San Carlos olivine and 20% of a Nain Gabbro, (ii) 80% San Carlos olivine and 20% of a Stillwater anorthosite, and (iii) 50% San Carlos olivine and 50% synthetic Al₂O₃. After mixing, powders were similarly pressed as above then sintered in a vacuum furnace at 5×10^{-6} Torr at 1423 K for 12 hours. Sintering in vacuum was required as minerals containing iron would oxidize if processed in air. XRD patterns before ball milling and after sintering indicate the mineralogy of the original mixture was preserved; e.g. no chemical reactions occurred during sintering.

Pellets were sliced into mm thick slabs and coarsely ground to thicknesses of approximately 0.5 mm using silicon carbide. Scanning Electron Microscopy (SEM) with a Backscatter Electron Detector (BSE) of the pellet surfaces indicates a poorly densified microstructure with minimal sintering. Representative microstructures can be observed in Fig. 2, while Table 1 describes the materials, compositions, sources, and processing conditions investigated, with A detailed list of irradiations performed is compiled in Appendix 2.

2.3 Irradiations

Irradiation experiments were split between two different facilities using three accelerators; 2 MeV experiments were performed at the University of Wisconsin-Madison (UW) using a 1.7 MV NEC 5-SDH tandem accelerator (Field et al., 2013), while 1.8-3.8 MeV experiments were performed at Los Alamos National Laboratory (LANL) with a 3 MV NEC 9-SDH tandem. Lower energy (50-150 keV) experiments were conducted using a Varian ion implanter at LANL.

2.3.1 UW Experiments

Experiments at UW were conducted in a custom fabricated stainless steel end station operating at $\sim 10^{-6}$ Torr vacuum pressure. Pellets and slabs were mounted on a stainless steel holder, with a thin stainless steel washer between the target and holder to minimize surface contact. The target holder was electrically isolated, which allowed beam current measurement with a Brookhaven Instruments (BIC) charge integrator. Measured charge using the unbiased holder agreed well with Faraday cup measurements at the entrance of the chamber. The irradiations were conducted using un-scanned 2 MeV protons with a variety of fluxes between 10^{12-14} protons/cm²-s (p/cm²-s) to several different fluences on the order of 10^{15-17} p/cm². The size of the beam was controlled by a tantalum slit system and was kept on the order of 0.1 cm².

During irradiation, targets were monitored with a digital microscope, a Stanford Research Systems (SRS) 300 atomic mass unit (amu) Residual Gas Analyzer (RGA), and

a Vernier VRM-BTD Geiger-Mueller (G-M) tube. The digital microscope allows external monitoring of the target to confirm the beam is properly located and assure that the sample remained intact over the course of the entire radiation. The RGA is a specialized mass spectrometer, which is capable of measuring gaseous species that can become evolved during the irradiation. A turbo pump pulls some portion of the gaseous species past a hot filament. The filament ionizes the particles which can then be accelerated, separated, and collected.

Radiation generated during the experiment (prompt radiation) was measured using the Vernier G-M tube. The detector is located outside the chamber, which would only allow the measurement of γ -rays. Two complementary radioactive decay experiments were performed on an un-doped single crystal silicon wafer and an olivine-gabbro pellet. In the first experiment, the targets were monitored during the irradiation with the Vernier G-M tube. Immediately following the irradiation, the target was removed from the chamber and placed 2 cm below the detector. The decay rate as a function of time was measured with a Vernier data acquisition module. In the second experiment, a Si single crystal and olivine-gabbro pellet were irradiated using identical conditions. However, immediately after irradiation the target was removed from the chamber and taken to a Na-I counting station. The count station is significantly more sensitive to low-levels of radiation as compared to the Geiger-Mueller tube, and is capable discriminating energy of the γ -rays collected.

2.3.2 LANL Experiments

Low-energy proton irradiations were conducted on Los Alamos's Varian ion implanter under two different flux conditions; scanned and un-scanned. Un-scanned beam conditions allowed targets to be irradiated with higher-fluxes than the scanned beams. Scanning the beam allows for the most uniform fluence over the entire sample area. Charge collected with un-scanned beams was performed using a singular Faraday cup before the target and timing the irradiation to get the desired fluence. Scanned experiments made use of a four Faraday cup system which measures both the fluence and

uniformity directly during the irradiation. Samples were adhered to threaded alumina and stainless steel screws using high-temperature cement to determine what role the heating and or electrical charging may have on physical changes. The alumina screw provides both thermal and electrical isolation, while the stainless steel provided only thermal isolation. Low-energy irradiations varied the flux between 10^{12-14} p/cm²-s using 50 and 80 keV/amu energy protons.

High-energy experiments were performed at LANL to track prompt γ -radiation produced from nuclear reactions between the incident protons and the target elements; this was performed at 1.8, 2.8, and 3.8 MeV. Irradiations were performed using a scanned beam over an area of 0.25 cm², with a proton flux of 9×10^{13} p/cm²-s to a fluence of 2×10^{16} p/cm². A Princeton Gamma-Tech liquid nitrogen cooled, high-purity germanium detector (IGC40200) biased to +300V was positioned 40 cm from the target to measure γ -ray emission from the targets.

Additional post-irradiation characterization included optical microscopy, SEM with BSE detector, and energy dispersive x-ray spectroscopy (EDXS). The irradiation conditions and testing are summarized in Table 2.

CHAPTER 3: RESULTS

Results are presented in the following format: (1) characterization of low- energy irradiations, (2) characterization of high-energy irradiations, (3) experiments which resulted in volatilization, (4) and experiments which yielded nuclear transformations.

3.1 Low-Energy-Irradiations

3.1.1 Visual Observation and Handling Post Irradiation

During irradiation, the silicate targets exhibit varying degrees of scintillation or fluorescence. In the case of the un-scanned irradiations, targets transition from fluorescence to thermal emission when exposed to a threshold flux and fluence. Scanned beams fluoresce, but less vibrantly than un-scanned beams. The scanned targets do not thermally emit, but rather lose their fluorescing ability to a large degree over the course of the irradiation.

Targets spall or fracture consistently during irradiation based on whether the beam is scanned or un-scanned, and if mineral fragments or polycrystalline samples were irradiated. For instance, catastrophic fracture only results when single crystalline mineral fragments are irradiated with un-scanned beams above a threshold current. Polished polycrystalline pellets do not explode, but rather crack during irradiation. Targets that do not crack often completely break up into mm-sized or smaller fragments when removed from the sample holder post-irradiation. In some cases, irradiated samples were so friable that they disintegrated between optical and SEM examination. No visual difference in spalling or fracturing for samples mounted on the stainless steel or alumina screws was observed. Visually all irradiated targets appear darker or exhibit a black coating after irradiation.

3.1.2 Synthetic Forsterite Irradiations

Preliminary experiments were performed on synthetic forsterite using un-scanned beams. The targets scintillated vibrantly, which clearly outlined a non-circular beam

spot. The targets were irradiated to a fluence of 1.1×10^{17} p/cm² with fluxes of 6.24×10^{13} (1800 sec.), 3.12×10^{14} (360 sec.), 6.24×10^{14} (180 sec.) p/cm²-s using 50 keV protons and examined with optical and SEM. The lower two fluxes, when observed with SEM, were unremarkable as compared to the un-irradiated (native) microstructure, minus the dark coating. However, the highest-flux irradiation showed a gradient of melt texture from the center of the beam spot to the native microstructure over ~5 mm in length as observed in Fig. 3. The sample was extremely friable, and fractured surrounding the most intense area of the beam spot; it ultimately split the fragment again at the center of the spot. Higher-magnification images, EDXS area scans (500 μ m x 500 μ m), and point scans (positions 1 & 2, Fig. 4) indicate the chemical composition of the melt area differs from the native microstructure, as can be observed in Table 3. The redistribution of elements can further be examined in higher-magnification images and EDXS line scans, as seen in Fig. 4. The images profile the chemistry both between and within the grains, detailing the differences between the bulk chemistry observed in the respective area scans. Significant zirconium zoning in the higher-magnification images both inside and outside of the forsterite grains can be observed. Many of the forsterite grains show sharp straight edges which further accentuate the zirconium zoning.

3.1.3 Multicomponent Irradiations

A series of scanned irradiations was performed on a more chemically diverse set of targets; this included the 80 wt.% San Carlos and the 20 wt.% portions of either Nain gabbro, Stillwater anorthosite, or synthetic alumina or corundum. The scanned experiments provide a more uniform irradiation, as compared to un-scanned beams. However, as the beam is scanned over a greater area the total flux of the beam is significantly decreased. Table 4 details the series of irradiations and general results performed using 160 keV H₂⁺ ions (80 keV/amu). In scan mode, the implanter was unable to generate beam currents similar to the fluxes used in the un-scanned experiments. To achieve a flux beyond 5.0×10^{13} p/cm²-s, the scan area had to be

reduced, and the overall fluence calculated using time and corrected for the reduction in area.

Several remarkable changes in the microstructure were observed among the four irradiations. The olivine-gabbro, olivine-anorthosite, and olivine-corundum exhibited no microstructural changes during the 5×10^{13} p/cm²-s, 2.0×10^{16} p/cm² fluence irradiation. For the 5×10^{13} p/cm²-s, 2.3×10^{17} p/cm² fluence irradiation, the olivine-anorthosite, and olivine-corundum remained unchanged, but the olivine-gabbro exhibited an approximately 8 mm x 4 mm dark spot as observed in Fig. 5. Further investigation indicated the spot had a microstructure consisting of the porous native structure adjacent to glassy carbon-rich texture. EDXS spot measurements, Table 5, from three locations in Figs. 5a and 5c, indicate the respective bulk chemistry.

No combination of flux or fluence yielded a melt region similar to that observed in the synthetic un-scanned forsterite irradiations. However, one remarkable observation was made in the highest-flux/fluence (1.25×10^{14} p/cm²-s to 2.5×10^{16} p/cm²) irradiation on the olivine-corundum target. SEM examination of the surface at higher-magnifications found regions of the surface peppered with a higher-atomic number phase. The phase is associated with and best observed on the larger olivine grains and has a droplet-like morphology. This is in contrast to angular zirconia fragments from ball milling. EDXS K_α X-ray maps indicate the droplet phase is rich in Fe and Ni; Fig. 6 details the microstructure and EDXS results on the olivine-corundum pellet.

3.2 High-Energy Irradiations

3.2.1 Visual Observation and Handling Post Irradiation

Similar to low-energy experiments, mineral fragments exposed to fluxes of 5×10^{13} p/cm²-s and above catastrophically fracture, while sintered pellets crack during irradiation or often fall apart during removal from the target holder. Cracking was nearly always associated with the center of the beam; this occurred whether the beam was located in the center of the pellet or towards an edge. As in the case of low-energy irradiations, the un-scanned beam in the high-energy irradiations can be non-uniform and

thus result in areas exposed to a distribution of flux and fluence over the irradiated area. Similar to low-energy experiments, pellets examined post irradiation exhibit various amounts of a dark coating or residue on the surface. Higher-fluence targets exhibit the coating around the periphery of the beam spot, where lower fluence irradiations display a coating many times larger than the beam. Figure 7 shows the dark coating developed as the beam is moved across a target.

3.2.2 Optical and SEM

Optical and BSE images of three olivine-gabbro pellets irradiated with a 2 MeV flux of 2×10^{14} p/cm²-s to respective fluences of 5×10^{15} (24 sec), 1×10^{16} (48 sec), and 2×10^{16} (96 sec) p/cm² can be observed in Fig. 8. The pellets show progressive amounts of macroscopic damage with increasing fluence. At the microscopic level, the greatest fluence alters the surface from one that exhibits a large degree of porosity to a texture where isolated mineral grains are surrounded by a glassy phase. The melt texture is maximized at the center of the beam spot and decreases further from the irradiated center. Outside the immediate area of the beam, no melt texture was observed. EDXS line and spot scans indicate the grains are the olivine component and the glassy matrix is rich in calcium and aluminum. The melt texture is nearly identical to microstructure observed in the low-energy experiment.

Further SEM interrogation of the 1×10^{16} and 2×10^{16} p/cm² pellet resulted in discovery of Fe-Ni metal droplets similar to the low-energy experiments. The medium fluence irradiation had a minimal distribution of droplets, located on the periphery of the beam spot. The size and concentration were comparable to those observed in the low-energy experiments. The features were identified due to the drastic change in contrast from the relatively low average atomic number of the silicate. The relative spacing of the droplets allowed for EDXS line scans, which indicated the droplets had a Fe/Ni ratio of 4/1. However, due to the relative size of the droplets and excitation volume of the beam this value is approximate.

The subsurface of the high-fluence target (Fig 8c) was exposed during post-irradiation handling of the pellet, which was aided by the cracking process. This target had a considerable larger concentration of smaller droplets as can be observed in Fig. 9. The droplets that were observed would have been under the surface at the direct center of the irradiation. In contrast to the isolated pockets of droplets discovered in the medium fluence, the high-fluence target had a droplet concentration that was readily observable. The region is significantly brighter due to the large abundance of droplets that appear to be “sweating” from the olivine grains.

An identical series of three irradiations was performed on the olivine-anorthosite mixture. The same 2×10^{14} p/cm²-s flux had similar results in terms of fracturing and surface darkening; however, the 2×10^{16} p/cm² fluence did not exhibit the melt morphology observed in the 2×10^{16} p/cm² olivine-gabbro irradiation. A melt texture similar to the 2×10^{16} p/cm² fluence was only observed when the olivine-anorthosite was irradiated to 2×10^{17} p/cm² using a 2×10^{14} p/cm²-s flux. Both olivine-gabbro and olivine-anorthosite targets did thermally emit under the highest flux conditions.

3.3 Chemical and Physical Alteration

3.3.1 Volatile Products Measurement

A series of irradiation experiments was performed to investigate the volatility of several chondrule analog phases exposed to 2 MeV protons with various fluxes. The targets irradiated include olivine-gabbro, olivine-anorthosite, a polished slab of alkali feldspar, and a polished slab of pyrite. The data are presented with time on the abscissa and partial pressure on the ordinate. The spectrometer is capable of measuring up to 8 different mass species simultaneously. As mass spectrometers separate ions based on their mass over charge (m/q), care needs to be taken in interpreting spectra. For instance, diatomic nitrogen would look identical to $^{28}\text{Si}^+$, and $^{40}\text{Ar}^{2+}$ would look identical to $^{20}\text{Ne}^+$. Furthermore, a cadre of contaminants, mostly oils from pumps, machining, and handling reside in vacuum chambers and are ubiquitous in mass spectra. The data are presented assuming that the identified elements are the dominant m/q species measured.

Figure 10 shows the effects of three different fluxes on the olivine-gabbro mixtures as measured with the RGA. The fluxes include 6.2×10^{13} , 1.2×10^{14} , and 2.5×10^{14} p/cm²-s, which correlate to beam currents of 1, 2, and 4 μ A respectively. Multiple species were measured, with m/q values which were interpreted to be H₂O, Na, Mg, Ca, and Fe. Each species has a background level that indicates the general equilibrium vapor pressure. For instance, all three measurements show the background pressure of water prior to irradiation is consistently the highest. Furthermore, the figures indicate that an order-of-magnitude change or greater in the pressure is observed for water when the beam is applied to the target, while the other species show variable effects to the incident beam. Targets irradiated with higher-fluxes show a sharper decrease in signal when the beam is turned off as compared to lower fluxes.

The highest flux from above (2.5×10^{14} p/cm²-s) was used to further investigate the effects on the olivine-anorthosite and a slab of polished alkali feldspar, as can be observed in Fig. 11. The olivine-anorthosite spectrum is similar to the olivine-gabbro mixture above, minus a small increase in all of the species when the beam was turned off. In contrast to the respective Nain and Stillwater mixtures, the polished slab of feldspar had significantly less water. Furthermore, the Na signal exhibits a behavior different from the other species. The spectrum shows a sharp, almost two order-of-magnitude increase in the signal for approximately 60 sec, with little observable signal above background beyond the initial peak. Fe and Mg show an increase in pressure with the application of the beam, followed by a relatively constant signal over the course of the irradiation; a sharp drop in the signal is observed after the beam is turned off. Visible analysis of the target post irradiation shows a glassy bubble feature at the beam spot. Optical images shown in Fig. 12 detail the size and texture of the bubble.

Figure 13 shows an RGA scan of mass 64, S₂, from an irradiated polished slab of FeS₂. At an elapsed time of 360 seconds, a flux 6.2×10^{13} p/cm²-s was applied to the target; no change in the RGA spectrum was observed. However, at 720 seconds the flux was increased to 9.5×10^{13} p/cm²-s, and a significant change in the S₂ signal was detected. The scan in Fig. 13 shows a steady increase in the S₂ signal for approximately 720 seconds before it begins to level out. At approximately 1500 sec, the signal exhibited a

drastic increase again; in this case, there was no change in the beam current. At approximately 1600 sec, the beam was turned off and the S_2 signal decreased rapidly, then slowly decayed toward background over 1000 sec before the measurement was stopped. The sample was observed post irradiation with optical microscopy and SEM, as shown in Figs. 14a and 14b. An EDXS line scan in Fig. 14c across the surface shows the relative concentrations of Fe and S. The irradiated area indicates sulfur loss, while the inner region reveals the expected FeS_2 stoichiometry.

3.4 Nuclear Transmutations

3.4.1 Gamma-Ray Spectroscopy

Previous work had indicated that all silicate materials exhibit short-term radioactivity when irradiated with protons above 2 MeV (Wetteland et al., 2016; Wetteland et al., 2015). Based on this work, a series of silicon-based targets were irradiated to determine if residual radioactivity was limited to silicon and or other elements; the measurement of the instantaneous γ -ray yield can indicate elements which undergo nuclear reactions as a function of incident proton energy. Targets included an undoped Si single crystal (University Crystal), fused silica (MTI Corporation), an olivine-gabbro pellet, and an extremely weathered ordinary chondrite; the data can be observed in Fig. 15. The targets were irradiated with a constant flux of 9×10^{13} p/cm²-s to a common fluence of 2×10^{16} p/cm² using 1.8, 2.8, and 3.8 MeV protons. The data collection system was designed to measure γ -rays generated from various nuclear reactions during the irradiation. Fig. 15 indicates discrete reactions, peaks, are occurring over the series of energies examined. As energy increases, the number of γ -rays associated for a specific reaction increases as well as new reactions occurring as evidenced by additional peaks. Upon completion of the experiment, no signal could be measured from the target with the detector (40 cm away). However, standard protocol for removing irradiated materials from experimental chambers requires radiation monitoring. Samples irradiated in all experiments using protons with energy greater than 1.8 MeV exhibited residual radiation activity as measured with a pancake style Geiger-

Mueller (GM) tube. This requires controlled storage until radiation levels reach background. This remnant activity can be measured for minutes to hours with the GM tube.

3.4.2 Geiger-Mueller Tube Counting Station

To explore this residual radiation, a primitive radiation count station was fabricated using a GM tube. The count station is capable of measuring the prompt radiation during the experiment, as well as the residual activity once removed from the vacuum chamber. Fig. 16 shows radiation data generated during the experiment, as well as remnant activity from a 2 MeV, 4×10^{14} p/cm²-s irradiation of undoped silicon performed at UW. These data show two distinct levels of γ -ray emission. The first being from prompt γ -rays generated during the experiment (15-280 sec.) with the detector external to the chamber. A constant level of radiation is detected over the course of the irradiation, which instantly becomes unmeasurable when the beam is turned off (280 sec). If the sample is immediately removed from the vacuum chamber and placed 2 cm below the detector, a decay curve can be generated; the process to remove the sample takes approximately one minute. Fig. 17 shows the decay of the target over approximately 500 sec and a best fit exponential decay curve with the exponent equal to -0.008 s^{-1} .

3.4.3 Sodium-Iodide Counting Station

To further elucidate the nature of the decay post irradiation, a similar 2 MeV, 4×10^{14} p/cm²-s irradiation of undoped silicon and olivine-gabbro mixture was performed, followed by direct measurement of γ -rays in a Na-I count station. Approximately 4 min are required to remove the target from the vacuum chamber and transport to the count station. Figure 18 shows a representative γ -ray spectrum for the olivine-gabbro target with background radiation subtracted. The most dominant peak in this spectrum is the 0.511 MeV γ -ray; the result of electron-positron annihilation. The 0.511 MeV peak from the undoped Si irradiation was integrated at 10-sec intervals and plotted with time versus

counts and subsequently curve fit using an exponential function to determine a decay constant of -0.0045 s^{-1} as observed in Fig. 19.

3.5 Summary of Experimental Results

Experimental results indicate that silicate pellets exposed to certain energy, flux, and fluence conditions are subject to mechanical, chemical, and nuclear changes. A summary of experimental results is as follows:

- Surface Darkening
 - All irradiations resulted in the darkening of the surface to various degrees.
- Scintillation
 - All silicate targets, except the meteorite, vibrantly scintillate in the visible during irradiation.
 - Un-scanned targets irradiated with a critical flux and fluence transition from scintillation to thermal emission.
 - Scanned targets did not thermally emit.
 - In both scanned and un-scanned irradiations, significant decreases in scintillation luminosity occur over the course of the irradiation.
- Mechanical Fracture and Modification
 - Un-scanned irradiations of mineral fragments above a critical flux using both low and high-energy beams can result in explosion into sub-mm sized fragments.
 - Polycrystalline samples do not explode, but rather crack and fracture.
 - Scanned targets do not explode in either case.
- Melting
 - Low-energy irradiations determined that with 50 keV protons, a critical flux of greater than $3.12 \times 10^{14} \text{ p/cm}^2\text{-s}$ and fluence of $1.1 \times 10^{17} \text{ p/cm}^2$ are required to partially melt synthetic forsterite.

- High-energy irradiations determined that mixtures of San Carlos olivine/Nain gabbro, and San Carlos olivine/Stillwater anorthosite can be partially melted.
 - Partial melting was accomplished in an un-scanned irradiation of olivine-gabbro mixture using 2 MeV protons with a respective flux and fluence of 2×10^{14} p/cm²-s and 2×10^{16} p/cm². For the same flux, an order of magnitude more fluence was required to melt the olivine-anorthosite mixture.
 - An alkali feldspar formed a surface melt bubble that exhibited a glassy texture using a flux of 2×10^{14} p/cm²-s and a fluence of 2×10^{16} p/cm².
- Metal Droplet Formation
 - Scanned low-energy and un-scanned high-energy irradiations with a critical flux and fluence resulted in the formation of Fe-Ni metal droplets on the surface and subsurface of the pellet.
- Volatilization
 - Above critical flux values, certain elements and molecular species can become volatilized as measured with a mass spectrometer.
 - During irradiation both S₂ and Na were volatilized from a pyrite and feldspar target respectively.
 - Chemical analysis of pyrite post irradiation indicated that the surface was reduced from FeS₂ to FeS_{2-x}.
- γ -ray Production and the Formation of Short-Lived Radionuclides
 - Sample activation and the formation of short-lived radioisotopes occurred above a threshold energy.
 - A direct relationship exists between the γ -ray yield and flux/energy.
 - In all the compounds irradiated, nuclear transitions in silicon were the dominant γ -rays measured.

- Transmutations in silicon resulted in isotopes that emit γ -rays and β particles, which decay over minutes to hours.

CHAPTER 4: DISCUSSION AND APPLICATION OF RESULTS

Observed results will be classified and discussed in the following order; physical, chemical, and nuclear. The effects will be examined in terms of their cosmochemical significance with additional experiments proposed to further elucidate irradiation-processing mechanisms. Results will reference figures from multiple sections to explore the physical, chemical and nuclear effects; as such, the reader will be directed to figures multiple times and sometimes apparently out of sequence. It should be noted that all references to *irradiation* refer to “proton irradiation” unless specified otherwise.

4.1 Astrophysical Context

To fully explore the cosmochemical significance of the above results, some context relating the above experimental conditions to predicted energy/flux relationships in the early solar system is required. There has been limited experimental work to address irradiation effects outside those caused by the solar wind; however, extensive theoretical work has been conducted in predicting spallation reactions in the early solar system. Leya et al. (2003) considered a range of integrated flux values > 10 MeV for determining spallation reactions. These values ranged from 2×10^6 - 2×10^{12} particles/cm²-s for irradiation scenarios which occurred over 1 Myr and 1 year respectively. The authors additionally proposed hypothetical “ultra-high-flux SEP” events with upwards of 10^{16} particles/cm²-s in nonisotropic irradiation scenarios. Both these irradiations include helium nuclei as they result in generating the entire suite of isotopic anomalies known to occur in meteorites. Gounelle et al. (2006) considered a >10 MeV flux of 2×10^{10} proton/cm²-s, and cited reconnection rings from the X-wind model (Lee et al., 1998) as the astrophysical setting. Trappitsch and Ciesla (2015) uniquely investigated the low-energy end of the energy spectrum by modeling a monoenergetic 10 keV flux of protons between ~ 2 - 5×10^{14} protons/cm²-s in order to investigate amorphization conditions in dust. In all cases, the authors did not consider the integrated flux over a range of energy. For instance, the integrated flux between 0-10 MeV should be orders of magnitude larger

than the multiple values proposed by Leya et al. for protons above 10 MeV (Leya et al., 2003).

As discussed earlier, if a simple linear extrapolation of flux from 0-10 MeV was considered, the integrated flux would be $\sim 10^{12}$ p/cm²-s. However, the general energy/flux relationship favors an increase in particle flux as the energy decreases (Caffee et al., 1988; Reedy and Arnold, 1972). A more complete description of the flux/energy relationship for solar flares and GCRs follows a power law distribution when considering the kinetic energy of the particles, and as an exponential in rigidity which considers momentum per unit charge (Caffee et al., 1988). The kinetic (E = energy) and rigidity (R = momentum per unit charge) relationships with flux can be respectively expressed as follows:

$$\frac{dN}{dE} = \text{constant} \times E^{-\gamma} \quad \text{Eq. 1}$$

$$\frac{dN}{dR} = \text{constant} \times e^{-R/R_0} \quad \text{Eq. 2}$$

where γ and R_0 range between 2-4 and 50-200 MeV respectively (Caffee et al., 1988; Reedy and Arnold, 1972). If considering the exponential of rigidity, expanding the variable R in Eq. 2 yields:

$$R = \frac{\sqrt{2m}}{Ze} \sqrt{E} \quad \text{Eq. 3}$$

where m is the mass of the particle, Ze is the net charge, and E is the energy of the particle in eV. Eq. 2 then takes the form of:

$$\frac{dN}{dR} = a \cdot \exp\left(-\frac{\sqrt{2m}}{Ze \cdot R_0} \cdot \sqrt{E}\right) \quad \text{Eq. 4}$$

This formula can be simplified for protons using m equal to 1.67×10^{-27} kg, Ze equal to the fundamental electron charge (1.602×10^{-19} coulombs), R_0 equal to 100 MeV, with a as a constant. A value for the constant a , can be determined by setting dN/dR equal to 1 p/cm²-s at 10 MeV as extrapolated from Caffee et al. (1988). Equation 4 can then be rewritten as:

$$\frac{dN}{dR} = 9.04 \times 10^4 \cdot \exp(-0.0036 \cdot \sqrt{E}) \quad \text{Eq. 5}$$

Figure 20 displays flux versus energy values for three different solar flare conditions at 1 AU using Eq. 5; a present-day flare displaying the predicted exponential relationship, a solar flare with the 10^5 enhancement as predicted by Feigelson et al. (2002) with a simple linear relationship, and the same 10^5 enhancement but with the exponential relationship.

When integrated from 0-10 MeV the curves yield total fluxes of approximately 10^{10} , 10^{12} , 10^{15} p/cm²-s respectively. The linear extrapolation could be referred to as the minimum solar flare output, while a working upper limit of the proton flux could be the 10^{15} . This value could move up or down if R_0 is changed; the value used in the above calculations was suggested by multiple researchers (personal communications with (RR, 2016; RT, 2016)).

It is reasonable that the integrated flux for early SEP could occur between the linear and exponential values given. Our experimental results included fluxes on the order of 10^{14} , therefore we feel confident our data can be discussed within a true astrophysical context.

4.2 Physical

4.2.1 Mechanical Fracture

The most likely cause of mechanical failure during irradiation in these systems is differential thermal expansion associated with rapid heating of the near-surface in relation to the bulk. The thermal and electrical properties of forsterite are well known

and have been exploited for use as refractory firebrick and in applications where metal-ceramic interfaces are needed (Kingery et al., 1954; Kingery, 1960). Thermal conductivity in forsterite is extremely low as compared to other ceramics, as can be observed in Fig. 21 (Kanamori et al., 1968; Kingery et al., 1954; Schatz and Simmons, 1972). Nearly an order-of-magnitude difference in thermal conductivity exists between alumina and forsterite at room temperature, with spinel exhibiting intermediate behavior. At higher-temperature, all three materials converge within a factor of 3.

Thermal expansion in forsterite is considerable when compared to other ceramics. This lends its use as a technical ceramic for applications which require minimal thermal expansion mismatch, such as in ceramic-metal interfaces (Kingery, 1960). Volumetric thermal expansion values were compiled for forsterite, corundum, spinel, and quartz, as seen in Fig. 22 (Ackermann and Sorrell, 1974; Bouhifd et al., 1996; Fiquet et al., 1999). The plot indicates that forsterite exhibits greater expansion over similar temperature ranges as compared to spinel and corundum. For comparison, quartz undergoes a displacive transformation associated with an ~4% volume expansion at the $\alpha \rightarrow \beta$ transition (846 K). Wetteland et al. (2013) found that single crystal quartz cracked in 6 sec when exposed to a 1.8 MeV flux of 1×10^{14} p/cm²-s. Single crystal olivine mineral fragments cracked ~ 60 sec later than quartz when exposed to a similar flux of protons. Single crystal alumina was exposed to a 2.5 times greater flux and did not crack over several minutes of irradiation, while fused silica exposed to the same 2.5×10^{14} p/cm²-s flux displayed a “melt” droplet on the surface.

The timescales for cracking in quartz is directly related to the low-temperature phase transformation. With a flux on the order of 2×10^{14} p/cm²-s, reaching a temperature of 846 K occurred very rapidly. Corundum escaped mechanical fracture because (i) it remains in the singular α phase until its melting point at 2324 K, and (ii) it exhibits a relatively high-thermal conductivity. Transmitting heat can allow for a smoother temperature profile between the surface and the bulk, eliminating differential expansion; this is not the case for forsterite. The inability of a mineral to conduct heat would create a discontinuity in temperature between the near-surface and bulk. Following from the quartz example, if an ~4% change in volume is required for fracture, forsterite would

need to be heated to ~1400 K. As it has been demonstrated that irradiation can induce melting in forsterite (Figs 3 & 8), it is therefore expected that the surface can reach the required temperatures for the 4% expansion.

To summarize, fracture of olivine fragments during irradiation is due to a rapid rise of temperature in the near-surface, a relatively low-degree of heat transfer into the bulk, followed by surface expansion and cracking/spalling.

4.2.1.1 Cosmochemical Significance of Mechanical Fracture of Early Condensates

Mechanical fracture or comminution to produce small particles of material could be a possible mechanism to destroy or disaggregate primary or first-generation chondrules, which could develop the feedstock for secondary chondrules and the fine-grained material found in chondrite matrix. It may be that some CAI phases could be completely destroyed, effectively removing their formation history from the meteorite record. The below discussion will specifically address the development of chondrule precursor material.

It is difficult to determine if a mechanical fracture/spalling scenario could be active in the early solar system. Based on the experimental observations; (i) the irradiation scenario would require a sufficient flux of protons to heat the near-surface, (ii) the target mineral fragment would need to have a bulk temperature low-enough to develop the thermal expansion mismatch, and (iii) the mineralogy of the fragment should consist of the phases which exhibit relatively poor thermal conductivity and high-thermal expansion. If the above conditions were applied to accreted objects, and flux values were in accordance to those predicted, then the result may be the formation of sub-mm-sized particles. This comminution scenario could potentially develop the feedstock material for chondrules from previously accreted material.

A succinct model has not been fully developed for the size of the body or the change in temperature (ΔT) between the surface and the bulk that would result in surface spalling. Objects closer to the Sun would be hotter, and the ΔT between the surface and bulk may not be great enough to lead to fracture during irradiation. However, the flux can

change by orders of magnitude as irradiated materials approach the Sun. This could drive up the ΔT rapidly regardless of the initial temperatures.

Recent literature has addressed the long-standing argument that the first chondrules formed 1-3 Myr after CAIs, producing a CAI-chondrule gap (Bollard et al., 2017; Crowther et al., 2018). These works discuss the possibility that *primary* chondrules condensed simultaneously with CAIs and were the precursor material for planetary accretion. It may be that comminution of primary chondrules and early planetary objects could develop the feedstock for secondary chondrules, which were reworked over the remaining lifetime of the planetary disk.

The same comminution mechanism could be responsible for destruction of some CAI phases. For instance, other CAI phases may not share the same physical properties as corundum, and thus be more susceptible to cracking/spalling under irradiation. This could result in some CAI phases being reduced to small enough particles that they become more susceptible to secondary processing in the nebula or on planetary bodies, and thus absent in the meteorite record. CAI irradiation could also result in the variety of observed textures beyond those predicted for condensates. This will be explored in the following section.

4.2.2 Melting

Figures 3 and 4 indicate that synthetically produced forsterite exposed to a 50 keV flux of 6.24×10^{14} p/cm²-s to a fluence of 1×10^{17} p/cm² exhibited a melt texture. The shapes of the mineral grains and redistribution of the incompatible element Zr indicate that temperatures were high enough for melting, followed by grain growth to form larger euhedral grains. If the starting powder was finer, and melting occurred over greater time periods, more redistribution of Zr could have occurred. Under these conditions, the forsterite grain in Fig. 4c would have exhibited a more homogenous Zr free chemical signature with an even more defined Zr layer around the perimeter.

Figure 8 revealed that a similar melt texture was developed when a mixture of olivine and gabbro was exposed to a 2 MeV flux of 2×10^{14} p/cm²-s to a fluence of 2×10^{16} .

A mixture of San Carlos olivine and Stillwater anorthosite melted, but only after exposure to an order of magnitude higher-fluence.

Chemical analysis from both the high- and low-energy irradiations indicate a distribution of elements not observed in the native microstructure; see Table 3. The elements forming the glassy matrix had an overall higher average atomic number as observed in both SEM and EDXS. These elements are likely contaminants found in the detergents used to clean the ball milling canisters, minus the Zr and Yt which are from the canister itself. The elements become mobile and redistribute during heating, filling pores from incomplete sintering.

Figure 12 showed that alkali feldspar exhibited a glassy texture in the form of a bubble which protruded from the surface after exposure to a 2 MeV flux of 2×10^{14} p/cm²-s. Multiple mechanisms may be responsible for bubble formation in the feldspar, as the temperature during irradiation should significantly exceed the melt temperature. The evolution of gasses from the silicate as well as water present in the rock could allow for foaming or the protrusion of the glass bubble from the surface (Cable and Rasul, 1967; Rasul and Cable, 1966).

The melting temperature for forsterite is 2150 K, with sintering experiments of the olivine and gabbro mixture indicating that partial melting occurs at ~1500 K. The mineralogy of the Nain gabbro includes plagioclase with ~An₅₀ (Xue and Morse, 1993) and pyroxene as observed in hand specimen. The Stillwater anorthosite was predominately plagioclase with An₆₀₋₈₀ (McCallum et al., 1980). End-member melting temperatures in feldspar are 1826 K for anorthite, 1523 K for orthoclase, and 1473 K for albite; other chondrite minerals such as enstatite and pyrite melt at 1830 K and 1450 K respectively. The synthetic forsterite was only melted during the highest-flux experiments; this despite the fact the energy of the beam was 200 times less than the 2 MeV experiments. Melting occurred at a lower fluence in the olivine-gabbro mixture than in the olivine-anorthosite. This is not surprising based on the melting temperatures of the constituent mineral phases of the gabbro and anorthosite respectively.

Collectively, the data indicate that melting can occur during both low- (50 keV) and high- (2 MeV) energy proton irradiations when critical flux and fluence conditions

are met. The flux conditions required to melt forsterite and olivine-gabbro mixtures in both the low- and high-energy experiments were on the order of 10^{14} p/cm²-s, with fluences $\sim 10^{16}$ p/cm². The threshold values to melt should ultimately consider heat flow in and out of the irradiated region. If energy input is greater than heat flow out, then the temperature should increase and reach melting given sufficient time. Furthermore, as expected, the energy input required to melt the respective mixtures is directly related to the melt temperature of the constituent mineral phases.

4.2.2.1 Cosmochemical Significance of Melting Chondritic Constituents

The definitive processing conditions which resulted in the melting of chondrules remain one of the most elusive data in meteoritics. The following discussion supports a novel mechanism which considers melting from an enhanced flux of protons in the early solar system.

Early solar system processes which can rapidly heat silicate mixtures above 1600 K are candidates for chondrule formation mechanisms. Wasson (1996) determined the energy required to heat and melt a weighted mixture of chondrule silicates (enstatite, forsterite, fayalite, and albite) in order to investigate conditions necessary to melt chondrules. He determined that approximately 1630 J/g were required to heat chondrule precursors from 500 to 1900 K, whereas only 1080 J/g would be necessary if the starting temperature were 1000 K. To melt the entire mixture, an additional 480 J/g are necessary to account for the heat of fusion. This generalized treatment for the four minerals is possible due to their relatively similar specific heat values; only the heat of fusion for albite differs significantly. The net result is that a total of **~2110 J/g** is required to completely melt a mixture of chondrule precursor silicates. Wasson further stated that the 2110 J/g value is likely conservative, because of heat loss due to volatilization of the near-surfaces as well as heating the surrounding gaseous nebular atmosphere. He estimated that **35,300 J/g** may be a more realistic value for large-scale chondrule melting, or approximately 15x the theoretical value.

Heating from irradiation can be determined by considering the flux, energy, time, and irradiated mass, which can then be converted to energy deposition via the following equation:

$$dose = \frac{beam\ energy \times flux \times time}{mass} \quad Eq. 6$$

Energy deposition per volume, or dose, can be reported in J/kg or the SI unit Gray (Gy). Chemical and biological fields use this unit to describe absorbed radiation dose in both organic and inorganic systems. Additionally, the Gy is the fundamental unit that is weighted to determine radiation dose in various biological tissues, i.e. the sievert. Units and the conversion factor applied to Eq. 6 can be reported as:

$$Gy = \frac{eV \times \frac{p}{m^2 \cdot sec.} \times sec. \times 1.602 \times 10^{-19} J/eV}{kg (irradiation\ volume \times density\ (kg/m^3))} \quad Eq. 7$$

where the numerator is experimentally determined, minus the conversion factor, the denominator is the product of the area of the beam multiplied by the range or depth the particles travel into the sample. The volume is then multiplied by the density to determine mass. To be consistent with Wasson and other literature data addressing the energetics of chondrule formation, our discussion and calculations will use the units of J/g.

The range or depth a particle travels in a solid is governed by coulombic interactions with both electrons and the nucleus. This is referred to as electronic and nuclear stopping respectively. The degree of each stopping component ultimately determines the ion range. Software packages such as SRIM (Stopping and Range of Ions in Matter, (Ziegler et al., 2010) use Monte Carlo methods to readily determine ion ranges and the relative degree of electronic and nuclear stopping. Figure 23 provides SRIM calculated ranges as a function of proton energy for several chondrule constituents. From the figure, proton range is most directly related to electron density or average atomic

number. As the energy of the incident proton increases, the respective range differences become more apparent. Coulombic interactions are suppressed at higher-energies; this results in a non-linear relationship between energy and range.

Using Eq. 7 above, energy deposition can be determined for a mono-energetic source of 2 MeV protons considering a flux of 2×10^{14} p/cm²-s, a 10 second exposure, an area of 1 cm², with an average silicate range and density of 25 μ m and 4 g/cm³ respectively. This calculation yields **64,000 J/g** which is roughly an additional factor of 2 greater than Wasson's predicted requirement. Using Eq. 7, several radiation scenarios are presented in Table 6 to bound conditions for energy deposition in an early solar system environment. The upper limit for time of 1000 sec is on the high-end of exposure for generally accepted chondrule formation mechanisms. Should chondrules be melted for an extended time, they would completely vaporize. The table indicates that a variety of radiation scenarios can provide the energy requirements to melt chondrule mineral components. It is reasonable to only consider the fluence and energy for determining the energy deposition, as differences in range and mass of the materials in these scenarios has little effect. The energy deposition in these scenarios range from a factor of 20 less to almost 2000 times more than the 35,300 J/g predicted Wasson (1996). Of the scenarios presented in Table 6, a slight enhancement to the 50 keV, 2×10^{14} p/cm²-s, for 10 sec would be the monoenergetic conditions that best matches an enhanced SEP that could melt chondrules. These conditions favor lower-energy particles and have demonstrated melting, albeit for a longer exposure time, in the synthetic forsterite.

The possibility that SEP could melt early solar system condensates offers an intriguing mechanism for the formation of chondrules and some CAI textures. The predicted conditions for forming chondrules are well described in literature (Ciesla, 2005; Desch et al., 2012; Hewins, 1996). Rubin (2000) succinctly summarized chondrule forming conditions as the following:

- Operated over large regions of the inner solar nebula during a time period for which the nebula cooled from ~ 900 K to below ~ 600 K.
- The mechanism should be repeatable and be able to melt many objects more than once.

- The mechanism should be capable of raising the temperature very rapidly or “flash-heating” followed by rapid cooling.
- The mechanism should be capable of various degrees of heating which could range from partial to complete melting.
- Peak temperatures should result in temperature changes between 1750-2150 K.
- The total energy provided should be at least ~ 2200 J/g.
- Were heated on times scales of seconds to minutes.

A SEP melting mechanism satisfies these conditions exceedingly well. The most intriguing aspect of invoking such a mechanism is its ability to create the observed size distribution of chondrules. This is a critical requirement for any chondrule forming mechanism and its significance is often overlooked in the literature.

While chondrules are often referred to millimeter-sized silicate blebs, their actual average diameters are typically less than 0.5 mm. A comprehensive study on size distribution by Friedrich et al. (2015) details the average diameter of chondrules; this compilation is recreated in Fig. 24. The range of a 10 MeV proton is ~ 500 μm in most silicates, and thus correlates well to chondrule sizes. However, the number of these high-energy particles in a solar flare could be limited. This could be overcome by a larger-flux of lower energy particles accompanied by heat transport to reach observed sizes. Furthermore, if the chondrules/pre-cursor materials were rotating during irradiation, the effective volume exposed would be a factor of 2 greater. This is significant, as it shifts the energy requirements to lower-energy particles.

Lower-energy particles are also more efficient at depositing energy than higher-energy. This is due to decreased coulombic interactions at higher energies. When considering energy deposition in forsterite, 80 keV is the energy where coulombic interactions are greatest. This region is dominated by electronic stopping, with the maximum value being referred to as the Bragg Peak. The rate of energy loss at this peak is approximately 15x greater than for protons at 10 MeV.

Critical to proposing any chondrule formation mechanism is their creation and distribution throughout the solar system. Popular proposed mechanisms include impacts,

lighting, heating by the Sun, shock waves, impact jetting, and many others (Johnson et al., 2014; Johnson et al., 2015; McSween and Huss, 2010). The reader is referred to Boss (Boss, 1996) for a concise guide to chondrule formation mechanisms, and should note that a SEP irradiation mechanism flirts with several of these concepts. Similarities can be drawn from lighting discharges (Love et al., 1995; Whipple, 1966), interactions with a protostellar wind (Huss, 1988), ablation droplets formed by protostellar jets (Liffman and Brown, 1995), and through intense photon bombardment, or the X-wind model (Lee et al., 1998; Shu et al., 1997; Shu et al., 1996). Precursor chondrule material that exists as “dust balls” could be extremely sensitive to proton heating due to a high surface-to-volume ratio (Bischoff and Keil, 1984; Whipple, 1966). Invoking a SEP mechanism for melting would support the formation of secondary or recycled chondrules, as primary chondrules may form as condensates concurrently with CAIs in the solar nebula (Bollard et al., 2017).

In addition to melting chondrules, CAIs could have experienced secondary processing from SEP irradiation heating. Multiple CAI textures exist, including those which directly resemble the predicted condensate morphology, while others have more of an igneous texture, suggesting secondary processing (Brearley and Jones, 1998; MacPherson et al., 2005). SEP irradiation could result in secondary heating of CAIs, which would produce the variety of textures observed in primitive meteorites. Beryllium isotopic signatures in CAIs suggest that their formation occurred in the inner solar system. Based on calculations, the proximity to the protostar should readily supply the minimum flux to both melt and thermally alter CAIs.

To summarize, experimental conditions in this study are aligned with theoretical predictions for the particle environment in the early solar system. The length scale for which protons interact, as well as their ability to rapidly increase temperatures, makes enhanced SEP irradiation an attractive mechanism for melting early solar system materials. Furthermore, size distributions of chondrules in the meteorite record can be correlated to the implanted proton ranges when a distribution of energies are considered combined with minimal thermal transport. The size distribution could reflect heterogeneous SEP events, whose frequency and magnitude could vary over protostar

development. Secondary processing of CAIs is also supported by a large flux of particles in the innermost solar system.

4.2.3 Fluorescence

The emission of light at specific wavelengths is due to electronic transitions, which are common in most insulators during irradiation. Valence electrons move into the conduction band temporarily and then fall back to the original position, which is accompanied by photon emission. Forsterite has a history for use in scintillation detectors and lasers and strongly fluoresced during irradiation (Jia et al., 1994; Walker et al., 1994). The degree to which a target can continue to scintillate during irradiation is due to the radiation tolerance of the material. Ballistic collisions with incident and target ions can result in dislodging atoms from their normally occupied lattice positions. This along with damage resulting from ionization and bond breakage can result in a gradual transition from the crystalline to an amorphous state. Radiation-induced amorphization results in a decrease in scintillation; the reduction can be measured and quantified to track the degree of amorphization in crystalline materials (Crespillo et al., 2016; Gosnell et al., 2005; Townsend and Crespillo, 2015). Atomic structure changes, as measured by the optical properties, thus classifies these effects as physical.

Under certain high-flux conditions, some targets can transition from scintillation to thermal emission. While photon emission during scintillation represents transitions in the electronic structure, thermal emission is the result of atomic and electronic vibrations. Most of the irradiated materials behave as a black body under irradiation, which results in shorter wavelengths being emitted with increasing temperature.

4.2.3.1 Cosmochemical Significance of Decreased Luminescence

Tracking changes in luminescence during irradiation can be a direct link to understanding transitions from the crystalline to amorphous state. However, heat deposited during irradiation can anneal damage and prolong the transition. The results

discussed below do not directly measure radiation damage, rather they caution experimentalists on how heat deposited during irradiations can possibly anneal damage.

The results from these studies may address multiple references to radiation damage and surface modification in the planetary literature. For instance, there exist discrepancies in the crystallinity between dust surrounding protoplanetary disks and in the interstellar medium (ISM). Kemper et al. (2004) used infrared spectroscopy to study the ISM and found it to consist of amorphous pyroxene (~15%) and amorphous olivine (85%). This is in contrast to developing systems where dust is almost entirely crystalline (van Boekel et al., 2004). Understanding the dust structure transition between star birth and death is of considerable interest and can have implications for planet building processes (Glauser et al., 2009). Dust is exposed to extremes in radiation during the entire evolutionary cycle of a star system. This includes irradiation during protostar development from SEP, as well as end-stage explosive processes that could result in simultaneous production and irradiation.

Radiation damage in forsterite has been extensively researched to understand surface modification; this includes both early solar systems process, as well as a long-term surface modification such as on asteroids and planetary bodies. Glauser et al. (2009) determined that the fluence required to amorphize forsterite using 1.9 and 50 keV protons was 1.93×10^{17} and 7.06×10^{17} p/cm²-s, respectively. This is supported by multiple authors who conducted irradiations followed by Transmission Electron Microscopy (TEM) (Bringa et al., 2007; Carrez et al., 2002; Glauser et al., 2009; Jäger et al., 2003). The time required to reach this amorphization threshold by protons is entirely dependent on flux. A $\sim 10^{14}$ p/cm²-s flux would take on the order of 1,000 sec while a $\sim 10^8$ would take ~ 50 yr (Glauser et al., 2009). Fluxes on the order of 10^8 are equivalent to the solar wind and have been used to explain surface modification of the moon and asteroids (Bennett et al., 2013; Davoisne et al., 2008; Harries and Langenhorst, 2014; Loeffler et al., 2009). Additional effects of long-term exposure to these high-fluences can result in surface water deposits through the formation of hydroxide mineral species (Pieters et al., 2009).

Critical to experimental and theoretical understanding of radiation damage in early solar system and prolonged solar wind exposure experiments is the concept of displacement, or removal of atoms from their normal lattice positions through ballistic collisions. The common unit for addressing atom displacement during irradiation is the *dpa*, or displacements per atom. A numerical value of 1 dpa describes the displacement scenario where every target atom is knocked from its original lattice position on average one time. The software package SRIM (Ziegler et al., 2010) can aid in performing such calculations by correlating fluence to dpa. For forsterite, the $\sim 10^{17}$ p/cm² amorphization threshold is equivalent to 2.5 dpa (Glauser et al., 2009; Trappitsch and Ciesla, 2015). Critical to these calculations is to understand the software cannot predict how many atoms will return back to their displaced positions. If a significant number of atoms return, calculated dpa could be an underestimation of the threshold dpa to amorphize.

While radiation damage effects were not directly investigated in these studies, our melting observations have significant implications in understanding radiation tolerance. The significant rise in temperature during irradiation can effectively anneal, or counteract radiation-induced amorphization. The concept of dynamic annealing during irradiation is not novel for researchers investigating radiation damage for energy materials (Goldberg et al., 1995; Kuznetsov et al., 2003; Pelaz et al., 2004). However, the elevated temperatures that could result during experiments has not been thoroughly examined in planetary sciences. For instance, researchers performing experiments to investigate the effects of solar wind cannot use the actual 10^8 flux of protons. This rate would require decades of continuous radiation to reach the 10^{17} fluence associated with amorphization. As a result, fluxes far exceeding actual conditions are used to explore radiation response. For instance, Davoisne et al. (2008) used 4 keV He⁺ fluxes of $3 \times 10^{13-15}$ and 1 keV Ar⁺ and H⁺ ions of 3×10^{12} and 9×10^{12} ions/cm²-s to investigate amorphization thresholds.

It is critical that experiments investigating radiation damage and amorphization conditions not overlook the temperature effects associated with the flux of ions used in the experiments. Self-annealing well below the melting point may result in experiments indicating higher than necessary fluences are required to amorphize materials. Experimentalists should consider energy deposition in terms of dose (e.g. J/kg-s) rather

than just power (e.g. J or watts) to better understand the role of flux in irradiation experiments, as the mW or W values which are developed may seem innocuous. When the volume which the energy is deposited is considered, the value becomes much more significant.

4.3 Chemical Effects

4.3.1 Surface Darkening

Figures 5 and 7 represent two different examples of carbon deposition during irradiation. In Fig. 5, a glassy carbon layer is distributed across a region of the surface. The SEM images indicate that the carbon compound was liquid at some point and filled in portions of the porous microstructure. This texture and chemistry were unique to only the olivine-gabbro mixture; both the olivine-anorthosite, and olivine-corundum pellets were subjected to the same irradiation conditions. It is likely the carbon on this sample is a surface contaminant, possibly the cement that was used to adhere the sample to the screws for irradiation. Upon irradiation, the carbon chemically interacted with the surface to form a glassy carbon-oxygen compound which is variably distributed over the surface, as observed in Table 5. EDXS spot scans from 3 positions in Fig. 5 indicate that the bulk chemical composition outside the darkened region (area scan 1) is that expected for an olivine-gabbro silicate mixture. Inside the dark spot, the glassy carbon heterogeneously distributed as point scan 2 is representative of the silicate mixture with carbon, and point scan 3 is predominately carbon and oxygen.

The general surface darkening on all samples is due to the deposition of carbonaceous compounds assisted by ion irradiation. Figures 7 and 8 are examples of the darkening on an olivine-gabbro pellet, with the large swath on Fig. 7 due to the sample being moved through the beam. As can be seen in the figures, the area of deposition can be many times larger than a typical beam spot of 0.01 cm. The degree of darkening, or contrast between irradiated and unirradiated areas, is often most apparent with lower-fluence exposures. In higher-flux and longer-fluence irradiations, the visual effect is a darkening around the periphery of the beam, as can be seen between points *b* and *c* in

Fig. 3a. The inverse relationship between darkening and irradiation flux is due to surface temperature. Above a threshold temperature, carbon compounds are unable to stick directly at the beam-surface interface, and deposition occurs at some distance from the beam spot where the surface is cooler.

4.3.1.1 Cosmochemical Significance of Carbon Deposition

Results from these experiments and from Wetteland et al. (2018) support a proton irradiation mechanism for the formation of gaseous and solid organic material. The discussion below addresses the cosmochemical significance in the development of organic material found in the matrix of carbonaceous chondrites.

As in many early system phenomena, a singular mechanism for the formation of carbonaceous compounds has not been agreed upon. These synthesis mechanisms consider a wide range of processing conditions which include temperature, pressure, sources of energy, and timing in the chondrite evolutionary process. Proposed mechanisms include: formation through aqueous alteration on planetary bodies, Fisher-Tropsch (FTT) reactions, low-temperature gaseous reactions, and irradiation of ices containing H₂O, CO, CO₂, NH₃, and CH₃OH using UV photons (Alexander et al., 2007; Anders et al., 1973; Ciesla and Sandford, 2012). Critical to explaining organic content in chondrite meteorites, is the necessity to account for the high deuterium/hydrogen (D/H) ratios. It is suspected that compounds with high D/H ratios have an origin in the interstellar medium (ISM) due to correlations between the insoluble organic matter (IOM) in interplanetary dust particles (IDP) and comets (Alexander et al., 1998; Nittler, 2003; Robert and Epstein, 1982). Determining the role of proton irradiation on carbonaceous compound development, should begin with examining the most abundant source of carbon in meteorites, which is matrix

Matrix is a fine-grained (50-100 nm) mixture of silicates, oxides, sulfides, metals, phyllosilicates, and carbonaceous material which cements the larger constituents together in carbonaceous chondrites. The chemical composition of matrix resembles bulk chondrites, with the addition of more volatile components (McSween and Huss, 2010).

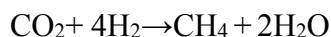
Carbon-bearing components in the matrix are ~ 2% by weight of carbonaceous chondrites. These components can be further resolved into soluble (~30%) and insoluble components (~70%) (Sephton, 2002). Soluble components are more easily extractable and characterized, while insoluble material requires aggressive chemical extraction procedures. Aliphatic compounds include alkanes and alkenes, while the most abundant aromatic compounds include the polycyclic aromatic hydrocarbons (PAHs) fluoranthene and pyrene (McSween and Huss, 2010).

It is interesting to speculate if the radiation produced solid carbon bearing compounds developed in our experiments share a similar chemistry to organic compounds found in the matrix component of carbonaceous chondrites (Alexander et al., 1998; Pizzarello et al., 2006; Sephton, 2002). Some correlation is supported by results from Wetteland et al. (2018) who found that during proton irradiation alkenes such as C_4H_8 and other hydrocarbons were formed as measured by mass spectrometry. It was suggested that the formation of the aliphatic hydrocarbon was due to the disassociation of the long-chained organic molecules in vacuum pump oil vapor which were present in the $\sim 10^{-6}$ Torr vacuum system. The solid dark coating was not directly measured in these experiments, but it is reported that carbon compounds are deposited in many surface characterization techniques that use ionizing radiation: this includes techniques such as SEM and X-ray Photoelectric Spectroscopy (XPS) (Barr and Seal, 1995; Mangolini et al., 2014). The sources of the solid carbon-containing compounds are from the breakdown of vacuum oil, cutting fluid, and skin oils, as these compounds persist even at low-pressures of 10^{-9} Torr and below. Carbon deposition on the surface is enhanced at the beam/surface interface due to ionization and heating of the substrate. Ionized particles can assemble into more coherent/stable structures on surfaces with increased temperatures.

It is predicted that proton irradiation of gases such as H_2 , CO, CO_2 , and H_2O at 10^{-1} - 10^{-3} torr (10^{-3} - 10^{-5} atm), the conditions of the nebula during chondrule formation, would result in considerably more organic matter generated. The ionized gasses would be subject to multiple formation and disassociation events resulting in the myriad of organic compounds found in carbonaceous chondrites. In an experimental setting, this

would include thicker coatings at the beam-surface interface, as well as on the internal surfaces of the chamber where gasses would condense. Furthermore, it is possible organic matter would form directly from the vapor and fall onto the bottom surfaces of the chamber. In a nebular environment, thicker coatings would be deposited on solid phases, and compounds formed directly from vapor could mix with other constituents during agglomeration.

Proton irradiation may play a role in both (i) creating organic matter, and (ii) breaking down large macromolecules into smaller compounds. For instance, the Sabatier reaction (Brooks et al., 2007), is a FTT process which has been proposed as a possible formation mechanism for methane production (Alexander et al., 2007; Kress and Tielens, 2001; Ziurys et al., 2016). The reaction considers carbon dioxide and hydrogen reacting in the presence of a catalyst to form methane and water:



Ionization could limit the requirement for a catalytic surface, such as iron or nickel, as proposed for many FTT reactions.

Breaking down larger macromolecules into smaller compounds could be accomplished by proton irradiation, and directly compare to suggestions which consider an enhanced flux of UV radiation (Boss et al., 2002). The authors cite photolysis, or photodissociation mechanisms in the solar nebula which consider the decomposition and breakdown of larger carbonaceous compounds via photons. The formation of alkenes and other hydrocarbons as measured by the mass spectrometer during irradiation is a direct analog for photolysis.

It is likely organic matter found in chondrites is a mixture of D-enriched material from the ISM as well as newly formed organic matter in the inner solar system (Alexander et al., 2007). Some of the material, such as IDPs, from the ISM avoided irradiation breakdown and survived retaining their high D/H ratio. Other organic material from the ISM may have been broken down and combined with inner solar system material which ultimately resulted in a diluted D/H ratio. Over chondrite accretion

time, the reservoir of high D/H material was depleted, which resulted in a lower D/H ratio in later-forming carbon compounds.

4.3.2 Volatilization

The volatilization of several elements and species were observed with the RGA; however, it is likely some of signals may be artifacts due to contamination. This is particularly true in the pressed pellets observed in Figs. 10 and 11. Indicators that the data are suspect includes: (i) the background partial pressure for the elements and compounds is not reflective of respective element volatilities, (ii) the shapes of the spectra follow nearly identical trends regardless of volatility, and (iii) in the case of the feldspar, elements that should not be present in the rock are being released during irradiation. The cause of (i) and (ii) is likely a result of the large water signal which evolved from the pressed targets and flooded the detector system. The porous nature of the pressed targets resulted in water absorption, which was released upon heating. The RGA loses sensitivity when the pressure exceeds 10^{-5} Torr, which led to the erroneous partial pressure measurements. The water release in the olivine-anorthosite was so large that Ca indicated a negative change in pressure, which is a further indicator of the detrimental effects of large amounts of water release.

Oils and other contaminants can additionally result in RGA artifacts; this can be observed in the measurement of both Mg and Fe and from the feldspar in Fig. 11; however, feldspar should not contain appreciable amounts of Mg and Fe. Based on the shapes of the spectra and previous literature (Wetteland et al., 2018), these signals are from contaminants in the vacuum system that have mass numbers equivalent to 24 and 56. Minus the Fe and Mg signals, the respective Na and S evolution from the respective feldspar and pyrite targets show trends which may be reasonable and warrant further discussion. The volatilization discussion will therefore be limited to the feldspar and pyrite.

The RGA signals from S and Na show variable sensitivity and dissimilar evolution over the course of the irradiation. Figure 13 indicates that a threshold flux was

required to elicit a S₂ signal from the sulfide target. A 6.2×10^{13} p/cm²-s flux yielded no change in the spectra, but a 50% increase resulted in significant and immediate volatilization of S₂. Similar to the sulfide, the feldspar required a threshold flux as can be observed in Fig. 25. A 1.2×10^{14} p/cm²-s (2 μ A) flux did not result in a significant change in the partial pressure; but a factor of two more beam current did result in a sharp change. Over the course of the sulfide irradiation, the partial pressure of S₂ grew over hundreds of seconds before reaching a steady state. Conversely, the feldspar experiment yielded a sharp increase in Na for ~60 sec before values fell to just above background.

The microstructures of the irradiated areas were considerably different when observed post irradiation. The feldspar formed a glassy bubble several mm high, while the sulfide exhibited a mottled texture. EDXS line scans indicated that the irradiated region in the sulfide was chemically reduced from the initial FeS₂ stoichiometry to FeS_{2-x}. The surface of the sulfide also had regions where sections had flaked off, exposing fresh material to the beam. The exposure of fresh material to the beam resulted in the spike of S₂ gas at ~ 1500 sec. The irradiation spot on the feldspar straddled an orthoclase/albite grain boundary, which did not allow for a comparison of Na loss before and after irradiation.

Even though melting temperatures are similar for both minerals, the chemical and morphological changes were significantly different. This suggests that multiple types of radiation response mechanisms are present. Wetteland et al. (2018) described two mechanisms for volatile formation; the first related to ionization, while the second is related to heating.

Ionization and dissociation may dominate in the two-element sulfide system. As bonding energies are on the order of tens of eV, the Fe and S can become dissociated over the entire ion range in the solid. Instead of returning to the original FeS₂ structure, some portion of the ionized S combines to form gas resulting in a residual sub-stoichiometric FeS_{2-x}. The generation of S₂ gas during irradiation is consistent with halide bubbles which form during alkali halide electron irradiations (Dubinko et al., 2000; Hobbs et al., 1973). The link between flux and S₂ generation could be additional heat deposited which releases gas bubbles trapped in the structure.

In contrast to the sulfide, the feldspar required a greater threshold flux to volatilize Na; this could be evidence for a heating mechanism rather than ionization. The multi-element feldspar can form glass and or a new compound, which retains elements and limits loss through gas formation. Both nuclear and ionic damage in silicates can result in the formation of amorphous compounds; this is supported by the glassy textures in Figs. 3, 8 and 12. Silicates and glasses have a long history of being examined for nuclear waste storage, which includes an extensive body of literature that describes how readily some silicates can be amorphized during radiation exposure (Eby et al., 1992; Trachenko, 2004; Wang et al., 1998).

4.3.2.1 Cosmochemical Significance of Volatilization

Results from these experiments begin to explore the volatility of certain elements during proton irradiation. Specifically, the results may aid in the understanding of whether chondrule formation occurred in an open or closed system.

The proton irradiation of the feldspar and sulfide was conducted to specifically explore radiation effects in minerals that form at the lower temperature limits of chondrule formation. These phases may have increased sensitivity to both heating and ionization effects. Studying the most volatile elements can address whether the chondrule formation environment can be considered open or closed (Alexander et al., 2008; Pringle et al., 2017; Sears et al., 1996; Wai and Wasson, 1977). In an open system, the most volatile elements can be lost. The resultant chemical composition of chondrules would then be a combination of the residual phases and new compounds formed from interactions with the ambient gasses. In a closed system, volatiles are not lost, nor do the components interact with ambient gases (Sears et al., 1996).

Understanding the volatility of some elements can place constraints on the processing conditions during chondrule formation. For instance, considerable literature has addressed the upper temperature limits for chondrule formation, the length of time during which chondrules were molten, and the pressures of the nebula by investigating

Na abundances (Hewins, 1991; Tsuchiyama et al., 1981; Yu and Hewins, 1998). The feldspar irradiations indicate that despite Na being moderately volatile, its loss during irradiation could be limited to the irradiation zone only. This, combined with the relatively high-threshold flux for volatilization, indicates that Na may be less volatile when contained in feldspars than the 50% condensation temperature, which is 970K (Lodders, 2003), may predict. This has implications for removing the elevated Na pressure conditions surrounding chondrules to suppress Na loss over the temperature and time scales performed in our experiments (Lewis et al., 1993; Rubin, 2000). However, this interpretation could be flawed, and considerable more Na loss could occur in a radiation environment where the material is closer to chondrule size versus the bulk targets irradiated in the above experiments.

It should be noted that sodium loss or migration in these experiments shares a relationship to the measurement of labile species using electron probe micro analysis (EPMA). Literature results have described intensity loss of characteristic K and Na X-ray lines using moderate EMPA conditions such as 15 kV, 0.01 μ A, in a 5 μ m spot size (Helz, 1976; Kushiro, 1972; Nielssen and Sigurdsson, 1981). Electron beams in microscopes can deposit significantly more energy than protons, as the current density and thus effected volume is considerably smaller.

Sulfur has been the subject of similar investigations as Na to understand heating and cooling rates in chondrules (Yu et al., 1996). Results from the irradiations indicate that sulfides and organic compounds have similar radiation sensitivity from both ionization and heating effects. It is likely that that volatilization via ionization is largely energy independent down to hundreds of keV. This could allow the lower-energy, higher-flux protons from an enhanced solar wind to have a prolonged influence on microstructure and chemistry of the low-temperature compounds. This is in contrast to other processing effects such as melting, which require greater fluxes generated from the enhanced SEP. Prolonged irradiation could result in the complete reduction to metal, which could limit the stability of sulfides in a radiation environment. This will be explored further in the subsequent section.

4.3.3 Metal Formation

The formation of metal droplets occurred in both low and high-energy irradiations, as can be seen in Figs. 6 and 9. The droplets in Fig. 6 were found on the surface of the olivine-corundum mixture in the low-energy irradiations, while the olivine-gabbro exhibited the droplets in greater abundance below the surface for the high-energy irradiation. The formation of Fe-Ni droplets should be independent of the chemistry of the pellets, as they all contain roughly the same amount of Fe and Ni. This of course excludes the synthetic pellets, which are Fe- and Ni-free. San Carlos olivine is a well-studied Mg-rich, ~Fo₉₀ (Frey and Prinz, 1978) olivine and can have up to 0.44 wt% NiO (Galoisy et al., 1995). All of the silicate mixtures likely underwent similar processes which resulted in the formation of the droplets; however, surface temperatures may have vaporized the metallic components.

4.3.3.1 Cosmochemical Significance of Metal Droplet Formation

Results from these experiments offer two novel alternatives for metal formation in chondrites. The mechanisms could also explain the distribution of metals in chondrules.

Any mechanism proposed for forming the predominantly silicate chondrules must explain their metal content. Furthermore, the occurrence of metal on the rims of chondrules and in the matrix of chondrites may or may not require alternative formation mechanisms. Chondrules can be classified as Type I having FeO-poor silicates, and Type II, having FeO-rich silicates (McSween 1977). Opaque phases primarily occur as Fe-Ni metal in Type I, and in sulfides such as troilite and pentlandite, in Type II. Several sources have been cited as the origin of Fe-metal in Type I chondrules: (i) direct condensation from the solar nebula, (ii) conversion from Fe-O in the presence of a reducing agent, and (iii) re-condensation of vaporized pure metal lost during a previous melting event (Cohen and Hewins, 2004; Connolly et al., 2001; Krot et al., 2000).

Connolly et al. (2001) described several scenarios for which Fe-O could be reduced, including reaction with solid C in precursor materials or in the nebular gas.

Sources of solid carbon could be in the matrix, and as a thin layer on some metal grains (Kong et al., 1999). Melting experiments have shown that when solid C is added to silicate mixtures above the melting temperature, metal forms which is both compositionally and texturally similar to that which is found in chondrules. In contrast, experiments which investigated metal formation by exposing analog synthetic melts to gaseous mixtures of CO, CO₂, and H₂ have been unsuccessful in the development of expected silicate and metal textures (Cohen et al., 2000a; Cohen et al., 2000b; Connolly et al., 2001; Tsuchiyama and Miyamoto, 1984).

Three proton irradiation mechanisms may support the reduction of Fe-O to metal. The first is the formation of carbonaceous compounds via irradiation, followed by heating and melting from enhanced SEP. This would satisfy the solid C reduction process as suggested by Connolly et al. (2001). The second considers direct implantation of a reducing agent, and the third considers enhanced SEP induced evaporation and re-condensation. While metal formation from oxide interaction with a nebular gas is not supported, implantation of a reducing agent such as H could be an alternative scenario. The reduction of the oxide and metal droplet formation in Figs. 6 and 9 could be explained by the following chemical reaction:



In this reaction, the excess SiO₂ could result in the formation of pyroxene. The formation of silica-rich pyroxene was proposed by Connolly et al. when considering the carbon reduction reaction (Connolly et al., 2001). It was further postulated that reduction may be one of several process which results in the overall modal pyroxene abundance in Type-1 chondrules from primitive chondrites. Other processes include thermal metamorphism in the presence of an oxidizing vapor on parent bodies (McSween and Labotka, 1993).

Figure 26 outlines the process for droplet formation in an experimental and cosmochemical context: a mono-energetic laboratory experiment and a multi-energy SEP event. In the mono-energetic 2 MeV irradiation (Fig. 26a), the hydrogen ions would

come to rest $\sim 30 \mu\text{m}$ inside the silicate target. The reaction area would be limited to this region, minus the migration of small amounts of metal along grain boundaries and pores to the surface. The 50 keV irradiations would be similar to those at 2 MeV; however, the ion implantation range is significantly reduced ($0.4 \mu\text{m}$) which is shallow enough for droplets to form at the surface. Figure 26b outlines the process for actual solar irradiation conditions, which would include a distribution of energies at various fluxes. The figure here limits the upper range to 10 MeV, thus the $500 \mu\text{m}$ maximum depth. Droplets could be formed from the surface to the end of proton range, resulting in a distribution of metal. As lower-energy ions are favored, it is likely more metals droplets would form towards the surface in an actual solar environment. This could potentially explain the formation of metal-rich rims observed on some chondrules (Chaumard et al., 2018; Connolly et al., 2001; Kong et al., 1999; Kong and Palme, 1999). Migration of dense metal blobs to the rims of chondrules could be aided centrifugal forces (Grossman and Wasson, 1985; Tsuchiyama, 2000). Prolonged heating would allow droplets to coalesce and form larger metal particles. Both low- and high-energy irradiations show metal formation without the need for melting, which is unique compared to other metal formation mechanisms.

The formation of metals by direct ion implantation is supported in literature on space weathering. Surfaces of asteroids and planets exhibit spectral darkening or reddening as measured using visible and near-infrared spectrometry. This effect is the result of ferrous iron reduction from either micrometeorite impact volatilization or solar wind hydrogen implantation, producing nanophase Fe particles (Bennett et al., 2013; Hapke, 2001; Loeffler et al., 2009). Considerable research has been conducted by irradiating Fe-bearing silicates using a variety of ions (e.g. H, He, Ar, N) typically at energies of 10 keV and less (Dukes et al., 1999; Hapke, 1965; Yin et al., 1976). The literature provides mixed results on how effective ion implantation can be in reducing Fe-O to form metal. However, the experiments described in this work do support the formation of metal at the μm scale. The difference is the additional heat energy, which allows for the growth of metal droplets beyond nanoparticle size.

The final metal formation mechanism considers the temperatures conditions responsible for chondrule formation. As chondrule formation mechanisms exceeded

1600 K, some volatilization of metals and silicates during melting must have occurred (Hashimoto, 1990; Johnson et al., 2014; Miller et al., 2017; Wasson, 1996). The 50% condensation temperature for Fe and Ni are 1137 K and 1353 K respectively (Lodders, 2003), which based on melting results above (Figs. 3 and 8) are far exceeded.

Therefore, a plausible formation mechanism for the droplet formation could then be evaporation followed by condensation of metals during irradiation melting. The 2 MeV irradiation which showed abundant metal droplets was from the subsurface, as the surface spalled off during post irradiation handling. Evaporated metal from the subsurface would be trapped and eventually condense when the irradiation is stopped. Low-energy irradiations could also result in metal formation; however, energy deposition is confined to the near surface, which would result in metal being completely evaporated and lost to the chamber and vacuum system. In a chondrule formation scenario, the evaporated metal could re-condense on another chondrule, which would be supported by metal rimmed chondrules (Kong et al., 1999; Kong and Palme, 1999).

4.4 Nuclear Transmutations

The sequence of radiation detection experiments was designed with previous experimental knowledge that silicates becomes activated, or emit short-term radiation for minutes to hours when irradiated with >2 MeV protons. The experimental sequence is detailed schematically in Fig. 27. Multiple detection systems were implemented in order to progressively rule out elements and then identify isotopes responsible for decay. The ultimate goal of the sequence is to identify isotopes that can undergo nuclear reactions below 10 MeV, as this is the threshold energy typically investigated in SLR production (Gounelle et al., 2013; Herzog et al., 2011; Leya et al., 2003). Experiments investigating spallation effects at <10 MeV are absent from the literature.

The peaks from the spectra in Fig. 15 are largely the result of nuclear transitions that release quantized photons (γ -rays) upon absorption of energy. The transitions occur over femto-nanosecond time scales and can be used to identify specific isotopes. For instance, ^{28}Si has a first excited state of 1.77903 MeV. If a nucleus absorbs energy

greater than ~ 1.8 MeV, it will transition to an elevated state. In the process of returning to the ground state, a quantized photon will be released equal to the difference between the elevated and ground state. The additional peaks in the Si spectrum are the result of transitions in all three stable isotopes and can be identified via energy level diagrams such as in Fig. 28 (IAEA); identifying all the transitions is not required, as will be explained below. The data in Fig. 15 would be similar to satellite-based γ -ray spectroscopy data obtained from many NASA planetary missions (Boynton et al., 2004). However, these studies make use primarily of energetic neutrons from galactic cosmic rays striking the planetary surfaces to generate γ -rays.

An expanded comparison of all four materials for the 3.8 MeV irradiation can be observed in Fig. 29. The remarkable aspect of these data is that the bulk of γ -rays measured are directly related to silicon isotopes. Over the energy range studied, the Si and SiO₂ spectra closely follow each other. This implies that oxygen isotopic transitions resulting in measured γ -ray emission are limited. When compared to the olivine-gabbro mixture and the meteorite over a limited energy range, only three new γ -rays can be observed as indicated in the circles; these peaks could be from transitions in Na, Fe, Al or Ca. The suite of materials irradiated over the three energies indicated that Si isotopes were responsible for the bulk of the reactions, and would be the most logical element to study in future experiments.

The data from Fig. 16 were designed to explore the nature of residual radioactivity present in the 2 MeV irradiated silicon; specifically, to determine if there is a measureable decay rate from isotopes emitting γ -rays. The Geiger-Mueller tube is unable to discriminate individual γ -rays, but rather the total radiation yield. The detector is capable of detecting α , β , and γ -rays, but with the detector outside the vacuum chamber, only γ -rays are measureable. The prompt radiation measured in Fig. 16 represents the integrated and non-discriminated γ -rays generated in Fig. 15 for an equivalent 2 MeV irradiation. Of interest in Fig. 16, is the radiation generated when the target is removed from the chamber and directly placed under the detector (340-500 seconds). The data from 340 to 500 sec is further expanded in Fig. 17 to detail the total decay radiation measured. Outside of the chamber, α , β , and γ -radiation can be measured

and the decay curve is a measure of all three. Curve fitting the data to determine the exponential can ultimately be used to identify a decay rate using the familiar equation:

$$A(t) = A_0 e^{-\lambda_d t} \quad \text{Eq. 8}$$

where $A(t)$ is the activity as a function of time, λ_d is the disintegration constant, and t is time. The half-life, $t_{1/2}$, can then be determined by:

$$t_{1/2} = \frac{\ln(2)}{\lambda_d} \approx \frac{0.693}{\lambda_d} \quad \text{Eq. 9}$$

The exponential value generated in Fig. 17 (-0.0080) can be inserted into Eq. 9 to determine a half-life of 1 minute and 26 seconds. The half-life can be used to identify possible short-term (unstable) and daughter nuclides that can be formed through proton reactions. Possible isotopes should be located adjacent to Si, as the target is pure.

Figure 30 is a selected area of the chart of the nuclides centered around the stable Si isotopes. Proton capture and (p,n) reactions for irradiated Si would result in the formation of phosphorus isotopes; proton capture would result in the Si isotope moving directly up on the chart, while a (p,n) reaction results in a diagonal move up and to the left. A (p,n) reaction preserves the mass of the original isotope, while capture reactions result in both mass and atomic number change. Figure 31 schematically shows decay schemes and the formation of isotopes through H and He capture. Low-atomic number radionuclides generally decay to form stable isotopes within the figure. Table 7 details the possible proton capture and (p,n) reactions possible, with decay, and half-lives for proton reactions in Si. The table indicates that there are no P isotopes which have a half-life of 1 min 26 sec. The closest decay would be from ^{30}P , which β^+ decays with a 2.498 min half-life.

Further examination of Fig. 17, shows that the exponential fits well between 500-850 sec, but deviates towards the beginning of the decay curve. This could indicate that multiple radionuclides are responsible for the decay shape. The steepness of the curve

indicates elements may exist which have shorter half-lives, such as ^{29}P with 4.140 seconds. The removal of the decay contribution of ^{29}P from the decay curve could support ^{30}P as the primary radionuclide, as it would shift the calculated half-life to longer values. However, due the relatively short half-live of ^{29}P , large quantities would have to be produced to alter the curve substantially. An alternative to the P isotopes could be radionuclides formed from multiple proton captures and subsequent decays, or decay schemes such as α -particle emission. However, limited multiple capture and α -particle emission in the lower atomic number isotopes is expected during proton irradiation, except for in higher-energy irradiations (>10 MeV).

To further elucidate the nature of observed short-term decay, additional experiments were performed using a more sensitive radioactive counting station. Counting stations are typically lead-shielded systems, for which the sample to be measured is directly placed on the detector to increase the sensitivity. The output of the counting station is an energy-resolved spectrum, similar to Fig. 15 and can be observed in Fig. 18. Of primary interest is the annihilation peak at 0.511 MeV, but other decays can additionally be observed. Figure 19 displays the 0.511 MeV annihilation peak integrated at 10-sec intervals with an exponential fit. Good agreement exists between the data and fit, with the λ_d of -0.0045 resulting in a $t_{1/2}$ of 2.56 min. This value agrees well with the previously mentioned ^{30}P , which β^+ decays to ^{30}Si with a 2.498 min. half-life. If the formation of ^{30}P is the result of a ^{29}Si isotope capturing a proton, the net result would alter the natural solar abundance to ^{30}Si rich signature. If a (p,n) reaction is responsible, ^{30}P would decay back to ^{30}Si with no effect on the Si isotopic ratios.

A final source of radiation present during the LANL multi-energy experiments was neutrons. While not quantitatively measured, neutron generation directly followed increases in beam energy. Spallation events with protons can result in neutron emission, or (p,n) reactions. Furthermore, neutron generation is directly related to flux and energy. These factors limit both the energy and flux of incident protons that can be investigated, as neutron shielding for radiation safety becomes a factor. The 3.8 MeV proton irradiations operated at the facilities safety limit for neutron production for the flux used.

4.4.1 Cosmochemical Significance

A large body of meteoritics literature examines subtle isotopic deviations from normal solar abundances. These differences are often correlated to secondary processing such as temperature. The discussion below addresses an alternative to traditional isotope fractionation effects through proton irradiation.

The formation of isotopes that could alter the normal solar elemental abundances has implications for interpreting isotopic fractionations. This includes spallation events in the solar system, as well as phases formed during explosive nuclear synthesis (Dauphas et al., 2015; Poitrasson, 2017; Russell et al., 1978; Thiemens and Heidenreich, 1983). Understanding the transmutation effects from the silicon irradiations above, may have implications for interpreting isotope fractionations in various meteorite phases; this includes SiC (Zinner et al., 1989), graphite (Hoppe et al., 1995), CAIs (Shahar and Young, 2007), and bulk chondrite values (Fitoussi et al., 2009). Example data from Fitoussi et al. can be observed in Fig. 32 to understand the implications of any changes to normal solar isotopic ratios. While detailed discussion of the data is not warranted, the plot indicates that enstatite, ordinary, and carbonaceous chondrites have different ^{30}Si signatures. These differences are often attributed to mass-dependent fractionation processes which favor loss of light isotopes through kinetic processes. Irradiation transmutation may negate discussion of such fraction processes. While discussion has focused on Si isotopes, there may be a suite of other low-atomic number isotopes that have similar or more sensitive response to radiation.

The development of non-solar isotopic ratios through proton irradiation could have implications in other studies examining fractionation effects (Hulston and Thode, 1965; Lee and Papanastassiou, 1974; Thiemens and Heidenreich, 1983). It is well-known in the accelerator community that when accelerating >2 MeV protons that if the beam impacts stainless steel beam components, then considerable amounts of prompt radiation are generated. The radiation is the result of nuclear reactions with one of the steel alloying elements, such as Cr. Several studies have examined Cr isotopic signature in

meteorites to understand fractionation effects during core formation (Bonnand et al., 2016; Schoenberg et al., 2016). If Cr isotopes can be transmuted as suggested above for Si, a reconsideration of data which examine fractionation effects in the isotopic system would be required.

4.5 Experimental and Astrophysical Constraints and Uncertainties

The above experiments suggest that energetic protons can process early solar analog materials and that the resultant chemistry and texture share some similarities to those observed in primitive chondritic meteorites. The similarities may indicate that irradiation does have a role in processing early solar material. However, interpretations of the observed effects should consider any experimental error as well as constraints and uncertainties in the astrophysical environment where processing would occur.

4.5.1 Experimental Constraints

The primary constraint in interpreting the experimental results is the measurement of flux during irradiations. The measurement of flux, or beam current, has a long history of being investigated as a source of error in ion beam analysis and ion implantation experiments (Chu et al., 1978; Pászti et al., 1990; Sosolik et al., 2000). Many factors go into accurate beam current measurement, such as the energy and types of ions, the materials being irradiated, and the experimental equipment being used. It is easy to have current measurement errors of a factor of 10 or greater if careful measurement techniques are not considered.

On top of this error, the distribution of particles within the beam area may not be uniform. During our un-scanned low-energy experiments, the beam was observed to be non-uniform. The most uniform irradiation experiments are conducted when the beam can be scanned or defocused so that hot spots are eliminated. Hot spots are fractional areas of the beam that have increased flux; this results in a non-uniform flux distribution and resultant fluence over the irradiated area.

In a worst-case scenario, experimental error could result in a factor-of-100 underestimation in the applied flux over limited regions of the irradiated target; this is especially important for melting, as it requires the highest flux and fluences. For instance, if melting in the pure forsterite experiments (the phase with the highest melting temperature in chondrules) was actually the result of a $\sim 10^{16}$ flux rather than the measured $\sim 10^{14}$, this value may be pushing the limit of predicted enhanced SEP integrated fluxes. However, the constant in Eq. 5 used to generate Fig. 20 is conservative and could be a factor of 10 greater. This would move predicted integrated fluxes into the 10^{16} range. Furthermore, the value of flux required for melting is predicted to approach theoretical as the fragments get smaller. Smaller fragments have a reduced capacity for transferring and storing heat outside the irradiation area. This would allow for lower fluxes of particles to have greater effects in the case of melting. Additional heat from photons could also provide extra energy needed for melting. The advantage of including photons in the heat budget is they would heat the inside of grains, while particles acted on grain surfaces.

Overall, the experimental observation that melting occurred in bulk targets at fluxes within several orders of magnitude of predicted values is more than sufficient for actively pursuing irradiation melting in early solar materials. Processing mechanisms, other than melting which occur below 10^{14} p/cm²-s, are less vulnerable to experimental error in flux measurement as their values fall within predicted theoretical values.

4.5.2 Astrophysical Constraints and Uncertainties

To properly ascertain the role energetic protons can have in processing early solar material, the astrophysical environment needs to be considered; this includes the stage of protostellar evolution, ambient temperature, radial distance, and gas pressure, all as a function of time. This is an extremely complicated problem which would require extensive modeling and is outside the scope of this work. However, discussions of two of the most crucial constraints, flux and pressure, are presented below.

As the above experimental work indicates, flux, rather than energy or fluence, is the most influential irradiation parameter. It is therefore important to first develop an understanding of the relationship of flux with distance, pressure, and time; these general relationships are suggested in Fig. 33. Fig. 33a considers the relationship of flux versus distance, which follows a typical inverse square law, or $1/x^2$ where x is distance; e.g. a flux of 10^{14} at 0.1 AU would be 10^{12} at 1 AU. Fig. 33b is the general relationship predicted for flux as a function of pressure. The dust and gaseous atmosphere of the disk can attenuate particles and limit the flux for a given distance; this relationship is developed in more detail below. Fig. 33c is a hypothetical flux that considers both pressure and time. It is expected that the relationship between flux and time would normally resemble a similar inverse square law as in Fig. 33a for a fixed distance, because developing stars have diminished particle outputs over time (Feigelson et al., 2002). However, as pressure in the disk drops, there may actually be an increase of flux for a fixed distance over a narrow window of time. This is due to the addition of lower-energy particles that had been previously attenuated by gas and dust.

Gas and dust in the disk will ultimately limit irradiation processing, as the distance a proton can travel is inversely related to the respective concentration and density. To further complicate the issue, the concentration and pressure of dust and gas can change rapidly in the early solar nebula as a function of time and radial distance (Birnstiel et al., 2010). Using the software package SRIM (Ziegler et al., 2010), calculations were performed to investigate the range of energetic protons in H_2 at 1000 K. The values in Table 8 indicate that 500 keV, 5 MeV, and 50 MeV protons have respective ranges of 0.1, 6, and 412 km at 10^{-3} atm. At 10^{-5} atm the respective ranges are 10, 600, and 4×10^4 km. 50 MeV particles first reach 10^6 km distances at a pressure of 10^{-6} atm, while 500 keV particles require pressures to drop to 10^{-10} atm. The 10^6 km value represents a proposed CAI formation distance of 0.06 AU as predicted in the X-wind model (Lee et al., 1998; Shu et al., 1997; Shu et al., 1996). The above calculations would seemingly limit irradiation processing to only the highest-energy protons or until the pressure in the disk dropped. However, such low gas pressures have not been investigated using SRIM, and results are subject to significant correction factors (Ziegler

et al., 2010). Furthermore, the data exhibit a trend which shows a limiting behavior for the relationship between pressure and range; this is not expected and thus makes the low-pressure calculations suspect.

Contrary to the SRIM calculations, isotopic evidence supports irradiation processing at high gas pressures. High-energy spallation effects in CAIs are supported by the measurement of extinct ^{10}Be , and other isotopes such as ^{41}Ca , ^{53}Mn , and possibly ^{26}Al (MacPherson and Huss, 2001; MacPherson et al., 2003; McKeegan et al., 2000; Sugiura et al., 2001). McKeegan et al. (2000) suggested a flux of $2 \times 10^9 \text{ p/cm}^2\text{-s}$ at 0.1 AU of $> 20 \text{ MeV}$ protons which operated over decades to hundreds of years would produce the measured ^{10}Be values. It should be noted that previous studies investigating particle irradiation scenarios for anomalous isotopes and SLRs fail to mention any attenuation by gas or have ignored its effect on flux (Goswami et al., 2005; Goswami et al., 2001; Leya et al., 2003; McKeegan et al., 2000).

These measurements contradict the results predicted by SRIM, as some flux of high-energy particles must reach CAI distances, or else major changes in the CAI formation model must be examined. Collateral irradiation processing would include the $2 \times 10^9 \text{ p/cm}^2\text{-s}$ flux of $> 20 \text{ MeV}$ protons, plus a lower-energy unknown component that was not completely attenuated by the gas. If this unknown contribution resulted in a minimum of a 10^{11-12} flux of protons and operated over decades to hundreds of years, irradiation processing is expected to play a role in additional processing of early nebula material.

CHAPTER 5: CONCLUSIONS

To explore the effects of exposure to an enhanced flux of energetic protons, a series of experiments using particle accelerators to irradiate early Solar System analog materials was performed. The experiments represent some of the first high-energy investigations designed to specifically explore irradiation processing in a nebular environment. Both synthetic and natural analog materials associated with carbonaceous chondrites were irradiated using keV-MeV protons. It was discovered that conditional exposure to protons resulted in physical, chemical, and nuclear effects:

- Physical effects specifically refer to mechanical fracture, melting, and radiation damage.
- Identified chemical effects include the formation of carbonaceous compounds, volatilization of certain elements and compounds, and the reduction of iron oxide to metal droplets.
- Radiation effects include the formation of radioactive isotopes below energies typically investigated in transmutation studies.

Collectively, enhanced SEP processing could potentially have had a role in comminuting larger material to sub-mm sized fragments; melting fragments, chondrule precursors, and chondrules; developing the textures associated with some refractory calcium aluminum inclusions (CAIs); annealing radiation damage; forming or modifying of some carbonaceous compounds found in the matrix of meteorites; volatilizing labile elements such as sodium and sulfur; reducing iron oxides to develop metals outside of the expected condensation sequence; and isotopic transmutations which result in nonstandard solar abundances.

Combining physical, chemical, and nuclear effects may offer additional support for considering irradiation processing in the early Solar System; three examples of combinatorial processing are considered below.

The first is a novel two-step transmutation-volatilization fractionation process. Transmutations from H and He particles in Si can result in the formation of P and S; see

Figs. 30 and 31. After irradiation, the new isotopes have both different volatilities and chemical affinities, with the 50% condensation temperatures for Si, P, and S being 1340 K, 1151 K, and 648 K, respectively (Lodders, 2003). In the case of Si isotopes, regardless of a capture or p,n reaction, the formation of P could be followed by some immediate vaporization due to the ~200 K difference in condensation temperature. The result is a deficiency in the transmuted Si isotope, which would be reflected in the measurement of Si isotopic ratios. The ΔT that drives vaporization could be from ambient conditions, heat deposited during the irradiation, or both.

A second example of combinatorial processing considers both nuclear and physical effects in CAIs. Approximately a third of CAIs exhibit textures that indicate direct condensation from a gas phase, while the remainder have textures resembling igneous crystallization; this includes melting with some expected evaporation (McSween and Huss, 2010). The igneous textures could be developed through melting from the same energetic protons responsible for nuclear transmutations. Protons are considerably more efficient at heating and melting as compared to photons; this is due to the limited range of particles in solids. However, the totality of secondary heating would be from a combination of both photons and protons, with the flux requirements greatly reduced due to the elevated temperature of the CAI-forming region.

A final example considers the physical and chemical effects proton irradiation processing may have in developing chondrules, metals, and matrix components in chondrite meteorites. The development of chondrite texture and mineralogy may include:

- Irradiation comminution (physical) of agglomerated bodies to produce sub-mm fragments of precursor chondrule material.
- Irradiation melting (physical) of chondrule precursor material, comminuted material, and chondrules.
- Irradiation reduction (chemical) of Fe-O to metal droplets.
 - Direct reduction from implanted species
 - Reduction during melting in the presence of C
- Irradiation reduction (chemical) of sulfides to metal
- Formation of carbonaceous compounds (chemical)

- Irradiation amorphization of silicates found in matrix (physical)

It should be noted that a comminution step is not necessary to develop chondrule precursor material, and that melting can occur in nebular dust balls or condensates. A unique aspect of considering SEP as a chondrule formation mechanism is that melting can occur over a wide range of energies. This is confirmed by experimental data which indicated that melting occurred at both 50 keV and 2 MeV for a respective fluxes of 6.24×10^{14} p/cm²-s and 2×10^{14} p/cm²-s

Final interpretation of the experiments identified a wide array of possible irradiation processing mechanisms existing at the extremes of the developing Sun's radiation environment. These range from high-temperature processing during CAI and chondrule formation, to low-temperature effects in sulfides and carbonaceous compounds. While combinatorial effects are an attractive mechanism to explain observed chemistry and textures in primitive chondrites, the applications should be tempered by considering stellar particle output (flux), temperature, and pressure – all as a function of time and radial distance from the developing star. There is no doubt this work is far from complete and would benefit from additional investigations (see Appendix 1), but it does suggest that proton irradiation may have played a significant role in the early solar nebula.

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APPENDIX

Appendix 1: Future Work

The above experimental work represents some of the first high-energy (> 50 keV) irradiations conducted on meteorite materials. As in any first-time experiments, much can be improved and proposed for future work, with some suggestions given below.

Mechanical Fracture

Future work could consider comparing different chondrule and CAI components under irradiation. This could include a detailed understanding of the various minerals associated with CAIs such as corundum, hibonite, perovskite, spinel, and melilite. Of interest, could be the preferential destruction or comminution of some CAI phases over others during irradiation.

Performing irradiations of chondrules and CAIs at elevated temperatures could help to understand the role of the nebular environment. Heating the samples to temperatures up to 1000 K could determine

Fluorescence/Radiation Damage

All planetary radiation studies would benefit from a systematic radiation damage study on the role of flux in identifying the critical amorphization fluence for key mineral phases. In addition to luminescence studies, techniques such as TEM (Sickafus et al., 1999), IR and X-ray photoelectric spectroscopy (Loeffler et al., 2009), grazing angle X-ray diffraction (Shen et al., 2007), and Rutherford Backscattering (channeling) (Wetteland et al., 1997) could be used to understand the role of ion flux. For instance, observations from this study and experiments performed by Brucato et al. (2004) would suggest that a flux less than 10^{12} ions/cm²-s could be a reasonable value to perform radiation damage experiments on bulk targets. These experiments would further benefit from mounting schemes that were capable of cooling the targets to minimize temperature increases. The effectiveness of cooling targets would benefit from computer simulations similar to those addressed below in the Melting Section.

A series of fluxes from 10^{11} through 10^{14} could be used to assess a wide range of possible heating effects associated with flux in a variety of chondrite constituents. Suggested fluxes could include: 5×10^{11} , 1×10^{12} , 5×10^{12} , 1×10^{13} , and 5×10^{14} ions/cm²-s; time for the experiments would range from 23 days to less than an hour. Low-energy ion guns exist which can operate continuously with energies between 1-50 keV. These guns can irradiate 10 cm² plus areas, which would allow a series of minerals to be examined simultaneously. The irradiations would be evaluated using TEM to track transitions from the crystalline to amorphous phase. These studies would have applicable results to radiation studies in ceramic materials outside of planetary science.

Organic Compound Formation

Future experiments could directly examine the formation of organic compounds from a representative solar nebular gas. Gasses could be mixed in multiple ratios and pressures followed by irradiation in a closed system. A proton beam would be passed through a thin ceramic or metal window into an isolated vacuum chamber. The vacuum chamber could regulate total pressure via a turbo pump system with gasses mixed using a mass flow controller to adjust the respective ratios and pressures. A baffle valve would be placed in front of the turbo pump to reduce the pressure load during irradiation. This experimental configuration is analogous to many thin-film deposition systems such as those used for sputtering metallic films (Kern, 2012; Seshan, 2012).

Experimental results would include the formation and characterization of both solid and gaseous components. It is hypothesized that at elevated pressures proton radiation can transform gaseous mixtures of H₂, CO, CO₂, and H₂O to methane and other more complex hydrocarbons that could be measured using a RGA. Under the elevated pressure conditions, it is additionally expected that solids would form directly from the gas phase and result in a thick coating on surfaces and loose organic debris in the chamber. The formation of these solids could be investigated both *in* and *ex situ* using Fourier-transform infrared spectroscopy (FTIR), and visible/UV techniques (Hesse et al., 2008; Pretsch et al., 2000). As many of the compounds could react with air, direct

measurement in the vacuum chamber or measurement through an IR transparent window would be preferred. The measurement of any organic compound *in situ* would be aided by a “cold finger” which would increase the probability that radiation generated compounds would stick to a region that could later be observed.

Melting

Future experimental work should consider irradiating volumes of material which directly resemble chondrule size distributions (0.5-1 mm). Materials should include both chondrule analogs and CAI minerals. Irradiating materials of this size requires special consideration for mounting. Furthermore, developing a mounting scheme that could suspend the oxides to minimize thermal transport, and recreating the gas pressures of the nebula should be considered. Another benefit of irradiating small particles is that the possibility of explosion should decrease as the irradiated volume approaches the fragment size. If a bulk of the volume is irradiated, thermal gradients would not be present to cause fracture.

A novel idea to perform such experiments would be to develop a clamping system that resembles a jewelry mount, such as in a necklace as seen in Fig. A1. A small chip of forsterite, alumina, hibonite, and other natural and synthetic minerals could be mounted in a platinum setting to investigate melting at this scale. Platinum is malleable and a common gemstone mount with a high melting temperature (~2000 K) should the beam come into direct contact with the metal. A minimal amount of Pt wire would be necessary, and it could hang freely in the vacuum chamber to reduce thermal contact to a stage or platform in contrast to the above experiments.

To more accurately replicate irradiations conditions in the inner and early solar system, the irradiation chamber could be differentially pumped so that the experiments could be conducted in pressure conditions resembling the nebula. It is predicted that additional energy would be required to heat and melt under the low-vacuum conditions rather than the 10^{-6} Torr (10^{-9} atm) pressure used in the above experiments.

Irradiations could be performed in an H_2/CO_2 atmosphere to examine combination heating and reduction processing.

It may be that chondrule sized fragments are too difficult to irradiate, and accounting for heat loss to mounting systems may be difficult to minimize. Furthermore, performing irradiations on multiple materials under a variety of conditions can be time intensive and costly. Developing theoretical models and solving using computer simulations can greatly supplement experimental work when considering heat loss. Modeling the irradiation conditions could allow for treatment of: (i) multiple irradiation conditions including a distribution of energies, (ii) a variety of sizes and compositions, (iii) thermal conductivity outside of the irradiation area, (iv) changing ambient pressure conditions to replicate conditions in the nebula, and (v) some volatilization of the surfaces.

Preliminary work has begun to formulate models to understand how heat loss from the irradiation zone can limit the maximum temperature developed during irradiation. Several experiments from above considered a pellet which was 13 mm in diameter and 0.5mm thick. A typical irradiation volume was 0.01 cm^2 with an ion range of $\sim 25 \text{ }\mu\text{m}$; this irradiation volume represents less than 1% of the total volume. It is unknown how much heat is lost to the bulk over the course of the irradiation.

To address thermal transport, a finite difference algorithm was developed to solve a combination of materials and energy balances using similar conditions investigated in the low-energy synthetic forsterite irradiations. Preliminary work has been conducted, with examples of data generated presented in Fig. A2. The experimental conditions simulated were a 1 cm^2 beam depositing 100 J/s for 3 seconds into forsterite. Figure A2 indicates that surface and subsurface temperatures can reach a relatively uniform temperature over the course of a 3-second irradiation, while 36b indicates the melt fraction developed over the entire surface over the course of the irradiation. In both cases, the area outside of the irradiation volume experiences significant temperature increases to the point that melting occurred. These two examples just scratch the surface for the many conditions which can be modeled using computer simulations.

The most significant role modeling can have, is to determine the minimum flux required to melt actual chondrule sized material in a nebular environment. Identifying the minimum flux capable of melting chondrule components which is at or below the predicted value for early solar flares will lend credence to adding irradiation melting to the long list of possible chondrule forming mechanisms. It is predicted that a proton flux on the order of 10^{12-13} p/cm²-s may supply the minimum energy to melt isolated chondrule sized precursor material. An integrated value of flux on this scale should be readily achievable from an enhanced SEP, thus strengthening the concept of an irradiation melting/thermal alteration mechanism. As mentioned previously, an enhanced SEP would also be accompanied by a flux of photons and electrons. This along with the contribution from an enhanced static solar wind could further contribute to the energy input for melting and heating early solar materials.

Metal Formation

Reduction effects could be further investigated by other characterization techniques such as cross-sectional SEM and TEM, as well as X-ray Photoelectron Spectroscopy (XPS). Cross-sectional microscopy may give further information on metal formation as a function of energy/flux and depth in targets. XPS could be critical to observing subtle oxidation changes, such as the transition from olivine to pyroxene.

Investigating metal formation through carbon deposition in a gaseous atmosphere followed by high-flux heating could be accomplished with an experimental configuration as suggested from the future work of the Organic Compound Formation section. This could entail experiments which deliberately deposit various amounts of carbonaceous material, followed by heating and surface analysis. Conversely, using a cold finger to remove carbon compounds from the vacuum system could offer complementary information. It is expected that if carbonaceous compounds are reduced in the vacuum system, it would suppress metal droplet formation.

Additional radiation experiments could investigate alternative materials and different implantation species. For instance, examining a more fayalitic olivine may offer

additional insight into metal formation. It is expected that olivine with higher iron content should generate more droplets. Furthermore, irradiation experiments using alternative ions such as He or Ar could rule H as a reducing agent. In addition to implanting H, C could also be implanted to further test ion reduction scenarios. If carbon is significantly more effective at reducing oxides as compared to hydrogen, it may be worth considering the fractions of a percent it occupies in the solar wind and flares (Bennett et al., 2013). Over large fluences, the concentrations of carbon could be a significant reduction mechanism to consider

Developing models to examine the efficiency of ion implantation reduction would additionally be beneficial. In the proposed chemical reaction that reduces FeO, a 1:1 H to Fe⁰ conversion ratio is considered. Calculations can approximate if the 1×10^{17} p/cm² fluence is producing equivalent amounts of metal. From Fig. 9a, it can be observed that the metal droplets have a radius of ~ 0.5 μm and over a $10 \mu\text{m} \times 10 \mu\text{m}$ region there are approximately 100 droplets. Using an atomic density of 8.48 Fe atoms/cm³, it can be determined there are approximately 4.5×10^{10} atoms in each droplet. If the $100 \mu\text{m}^2$ area was extrapolated to 1 cm², there would be $\sim 10^6$ droplets. The 10^6 droplets per cm² multiplied by the 4.5×10^{10} atoms per droplet comes close to the 1×10^{17} fluence; this would indicate a 1:1 conversion ratio. If the total amount of metal is greater than what is predicted in this estimate, additional mechanisms to recycle H would have to be considered if it were to be invoked as reduction/metal formation mechanism.

Volatilization

Considerable work could be conducted to further investigate volatilization effects. Volatilization effects during irradiation would benefit by selecting a larger group of minerals which are water-free. The pressed silicate minerals that were the subject of much of this report could not be examined due to absorbed water content; preheating the pellets in a furnace above 100 °C could allow these samples to be revisited. Examining natural mineral fragments at lower-fluxes, or bringing up the beam current slowly to eliminate fracture could allow the investigation of more elements and species.

Furthermore, irradiating a suite of alternative minerals under a variety of irradiation conditions could help separate heating versus ionization effects. This would be especially applicable in monitoring Na loss, which was performed using a feldspar containing both large grains of albite and orthoclase. Volatile monitoring of an albite target followed by EDXS of the surface could yield additional information on Na loss from the surface. This would be analogous to other volatilization experiments which investigated Na loss by EPMA (Tsuchiyama et al., 1981; Yu and Hewins, 1998). Volatiles such as K have similar cosmochemical interests as Na, but were not measured in these experiments. (Alexander et al., 2000; Humayun and Clayton, 1995; Young, 2000). So long as there are no or minimal mass interferences, K can be measured similarly to Na with the RGA. Improving the sensitivity of the detection system, as well as reducing overlapping contaminants would be required for investigating all species and elements. Suggestions for such improvements were given in Wetteland et al. (2018).

Transmutation

The transmutation experiments would benefit from characterization techniques which could measure transmuted or daughter products produced in the irradiated area. This could include techniques such as SIMS (Secondary Ion Mass Spectrometry) and laser ablation multi-collector inductively coupled mass spectrometry (LA-MC-ICPMS). Si isotopes could be measured at the beam spot and directly compared to unirradiated material on the same crystal.

As many other low-atomic isotopes that could be transmuted below 10 MeV, a series of radiations specifically to look for isotopic deviations other than in Si could be examined. Transmutations could be tracked directly through count rate experiments to determine decay rates for those elements that decay slow enough to measure. These experiments would benefit from a counting station mounted within or immediately adjacent to the vacuum system with a fast load lock. This would allow for rapid removal of the sample so as not to miss any isotopes which decay rapidly. Both pure elemental and isotopic substances could be irradiated followed by measurement using SIMS or LA-

MC-ICPMS. As suggested for the Si irradiation above, each target would have a built-in standard to act as a reference. Performing these measurements is critical for determining nuclear cross sections, which allow for direct calculation of nuclear reaction products as a function of energy and fluence. Extending the irradiation energy beyond 2 MeV would likely identify additional transmutations. Many accelerators could produce protons up to 6 MeV; however, significant shielding of the beam line components and chamber would be required as prompt radiation including neutron and γ -ray would be considerable. Furthermore, the sample may need several weeks to radioactively “cool off” before handling, as other isotopic systems could have longer decay half-lives. Performing similar count rate experiments from above could directly identify radioactive isotopes.

Appendix 2: List of Irradiation Experiments with Descriptions

Exper. Block	Samp. #	Material	Energy	Flux (p/cm ² -s)	Fluence (p/cm ²)
A	1	Synthetic Forsterite	50 keV	6.24x10 ¹³	1.1x10 ¹⁶
	2	Synthetic Forsterite	50 keV	6.24x10 ¹³	1.1x10 ¹⁷
	3	Synthetic Forsterite	50 keV	6.24x10 ¹⁴	1.1x10 ¹⁶
	4	Synthetic Forsterite	50 keV	6.24x10 ¹⁴	1.1x10 ¹⁷
B	5	San Carlos Olivine/Nain Gabbro Mixture	1.8 MeV	9x10 ¹³	2x10 ¹⁶
	6	Fused SiO ₂	1.8 MeV	9x10 ¹³	2x10 ¹⁶
	7	Chondrite	1.8 MeV	9x10 ¹³	2x10 ¹⁶
	8	Undoped Si	1.8 MeV	9x10 ¹³	2x10 ¹⁶
	9	San Carlos Olivine/Nain Gabbro Mixture	2.8 MeV	9x10 ¹³	2x10 ¹⁶
	10	Fused SiO ₂	2.8 MeV	9x10 ¹³	2x10 ¹⁶
	11	Chondrite	2.8 MeV	9x10 ¹³	2x10 ¹⁶
	12	Undoped Si	2.8 MeV	9x10 ¹³	2x10 ¹⁶
	13	San Carlos Olivine/Nain Gabbro Mixture	3.8 MeV	9x10 ¹³	2x10 ¹⁶
	14	Fused SiO ₂	3.8 MeV	9x10 ¹³	2x10 ¹⁶
	15	Chondrite	3.8 MeV	9x10 ¹³	2x10 ¹⁶
	16	Undoped Si	3.8 MeV	9x10 ¹³	2x10 ¹⁶
C	17	San Carlos Olivine	2 MeV	6.24x10 ¹²	1x10 ¹⁴
	18	San Carlos Olivine	2 MeV	6.24x10 ¹²	2x10 ¹⁴
	19	San Carlos Olivine	2 MeV	6.24x10 ¹²	1x10 ¹⁵
	20	San Carlos Olivine	2 MeV	6.24x10 ¹²	2x10 ¹⁵
	21	San Carlos Olivine	2 MeV	1.87x10 ¹³	1x10 ¹⁴
	22	San Carlos Olivine	2 MeV	1.87x10 ¹³	2x10 ¹⁴
	23	San Carlos Olivine	2 MeV	1.87x10 ¹³	1x10 ¹⁵
	24	San Carlos Olivine	2 MeV	1.87x10 ¹³	2x10 ¹⁵
	25	San Carlos Olivine	2 MeV	6.24x10 ¹³	1x10 ¹⁴
	26	San Carlos Olivine	2 MeV	6.24x10 ¹³	2x10 ¹⁴
	27	San Carlos Olivine	2 MeV	6.24x10 ¹³	1x10 ¹⁵
	28	San Carlos Olivine	2 MeV	6.24x10 ¹³	2x10 ¹⁵
	29	San Carlos Olivine	2 MeV	1.87x10 ¹⁴	1x10 ¹⁴
	30	San Carlos Olivine	2 MeV	1.87x10 ¹⁴	2x10 ¹⁴
	31	San Carlos Olivine	2 MeV	1.87x10 ¹⁴	1x10 ¹⁵
	32	San Carlos Olivine	2 MeV	1.87x10 ¹⁴	2x10 ¹⁵
	33	San Carlos Olivine/Nain Gabbro Mixture	2 MeV	6.24x10 ¹²	1x10 ¹⁴
	34	San Carlos Olivine/Nain Gabbro Mixture	2 MeV	6.24x10 ¹²	2x10 ¹⁴
	35	San Carlos Olivine/Nain Gabbro Mixture	2 MeV	6.24x10 ¹²	1x10 ¹⁵
	36	San Carlos Olivine/Nain Gabbro Mixture	2 MeV	6.24x10 ¹²	2x10 ¹⁵
	37	San Carlos Olivine/Nain Gabbro Mixture	2 MeV	1.87x10 ¹³	1x10 ¹⁴
	38	San Carlos Olivine/Nain Gabbro Mixture	2 MeV	1.87x10 ¹³	2x10 ¹⁴
	39	San Carlos Olivine/Nain Gabbro Mixture	2 MeV	1.87x10 ¹³	1x10 ¹⁵
	40	San Carlos Olivine/Nain Gabbro Mixture	2 MeV	1.87x10 ¹³	2x10 ¹⁵
	41	San Carlos Olivine/Nain Gabbro Mixture	2 MeV	6.24x10 ¹³	1x10 ¹⁴

	42	San Carlos Olivine/Nain Gabbro Mixture	2 MeV	6.24×10^{13}	2×10^{14}
	43	San Carlos Olivine/Nain Gabbro Mixture	2 MeV	6.24×10^{13}	1×10^{15}
	44	San Carlos Olivine/Nain Gabbro Mixture	2 MeV	6.24×10^{13}	2×10^{15}
	45	San Carlos Olivine/Nain Gabbro Mixture	2 MeV	1.87×10^{14}	1×10^{14}
	46	San Carlos Olivine/Nain Gabbro Mixture	2 MeV	1.87×10^{14}	2×10^{14}
	47	San Carlos Olivine/Nain Gabbro Mixture	2 MeV	1.87×10^{14}	1×10^{15}
	48	San Carlos Olivine/Nain Gabbro Mixture	2 MeV	1.87×10^{14}	2×10^{15}
D	49	San Carlos Olivine/Nain Gabbro Mixture	80 keV	5×10^{13}	2.3×10^{16}
	50	San Carlos Olivine/Anorthosite Mixture	80 keV	5×10^{13}	2.3×10^{16}
	51	San Carlos/ Corundum Mixture	80 keV	5×10^{13}	2.3×10^{16}
	52	San Carlos Olivine/Nain Gabbro Mixture	80 keV	5×10^{13}	2.3×10^{17}
	53	San Carlos Olivine/Anorthosite Mixture	80 keV	5×10^{13}	2.3×10^{17}
	54	San Carlos/ Corundum Mixture	80 keV	5×10^{13}	2.3×10^{17}
	55	San Carlos Olivine/Nain Gabbro Mixture	80 keV	1×10^{14}	2.3×10^{16}
	56	San Carlos Olivine/Anorthosite Mixture	80 keV	1×10^{14}	2.3×10^{16}
	57	San Carlos/ Corundum Mixture	80 keV	1.0×10^{14}	2.3×10^{16}
	58	San Carlos Olivine/Nain Gabbro Mixture	80 keV	1.25×10^{14}	2.3×10^{16}
	59	San Carlos Olivine/Anorthosite Mixture	80 keV	1.25×10^{14}	2.3×10^{16}
	60	San Carlos/ Corundum Mixture	80 keV	1.25×10^{14}	2.3×10^{16}
E	61	San Carlos Olivine/Nain Gabbro Mixture	2 MeV	2×10^{14}	5×10^{15}
	62	San Carlos Olivine/Anorthosite Mixture	2 MeV	2×10^{14}	5×10^{15}
	63	San Carlos Olivine/Nain Gabbro Mixture	2 MeV	2×10^{14}	1×10^{16}
	64	San Carlos Olivine/Anorthosite Mixture	2 MeV	2×10^{14}	1×10^{16}
	65	San Carlos Olivine/Nain Gabbro Mixture	2 MeV	2×10^{14}	2×10^{16}
	66	San Carlos Olivine/Anorthosite Mixture	2 MeV	2×10^{14}	2×10^{16}
	67	San Carlos Olivine/Anorthosite Mixture	2 MeV	2×10^{14}	1×10^{17}
F	68	San Carlos Olivine/Nain Gabbro Mixture	2 MeV	6.2×10^{13}	Variable
	69	San Carlos Olivine/Anorthosite Mixture	2 MeV	6.2×10^{13}	Variable
	70	K-Feldspar	2 MeV	6.2×10^{13}	Variable
	71	San Carlos Olivine/Nain Gabbro Mixture	2 MeV	1.2×10^{14}	Variable
	72	San Carlos Olivine/Anorthosite Mixture	2 MeV	1.2×10^{14}	Variable
	73	K-Feldspar	2 MeV	1.2×10^{14}	Variable
	74	San Carlos Olivine/Nain Gabbro Mixture	2 MeV	2.5×10^{14}	Variable
	75	San Carlos Olivine/Anorthosite Mixture	2 MeV	2.5×10^{14}	Variable
	76	K-Feldspar	2 MeV	2.5×10^{14}	Variable
	77	Pyrite	2 MeV	6.2×10^{13}	Variable
	78	Pyrite	2 MeV	9.5×10^{13}	Variable
G	79	Undoped Si	2 MeV	4×10^{14}	1×10^{17}
	80	San Carlos Olivine/Nain Gabbro Mixture	2 MeV	4×10^{14}	1×10^{17}
	81	Undoped Si	2 MeV	4×10^{14}	1×10^{17}
	82	San Carlos Olivine/Nain Gabbro Mixture	2 MeV	4×10^{14}	1×10^{17}

Exper. Block	Accelerators Used	Description
A	LANL Varian Ion Implanter	Preliminary experiments designed to investigate melting in synthetic forsterite. Forsterite is the most refractory and abundant silicate in chondrules and chondrites; it requires the greatest energy input to melt. Characterization was conducted post irradiations with optical and electron microscopy
B	LANL Tandem Accelerator	Irradiation of a series of silicate materials to understand the threshold energy and compositions which result in the formation of short-lived radioactive isotopes. Nuclear reactions which result in γ -ray emission are measured during irradiation with a liquid cooled scintillation detector.
C	UW-Madison Tandem Accelerator	Irradiation of sintered mixtures of San Carlos Olivine (80 wt.%) and a Gabbro (20 wt.%) to determine threshold fluxes and fluences for fracture and melting. Post irradiation examination conducted by optical and electron microscopy.
D	LANL Varian Ion Implanter	Series of irradiations in sintered mixtures of minerals including San Carlos Olivine (80 wt.%) and a Nain Gabbro (20 wt.%), San Carlos Olivine and Stillwater Anorthosite (20%), and San Carlos Olivine (50%) and synthetic corundum (50%). Post irradiation examination to determine conditions required to melt conducted by optical and electron microscopy.
E	UW-Madison Tandem Accelerator	Series of irradiations in a mixture of minerals including San Carlos Olivine (80 wt.%) and a Nain Gabbro (20 wt.%), San Carlos Olivine and Stillwater Anorthosite (20%) for a comparative study to determine conditions required to melt. Post irradiation examination conducted by optical and electron microscopy.
F	UW-Madison Tandem Accelerator	Experiments designed to explore volatility in materials with variable condensation/evaporation temperatures. Sample were measured <i>insitu</i> with a mass spectrometer to track changes in partial pressure of specific molecular species and elements as a function of flux and time.

G	UW-Madison Tandem Accelerator	High-flux/fluence irradiations followed by count rate experiments in order to determine the half-life of short-lived radioactive species. Samples were immediately removed from the vacuum and measured with either a Geiger-Mueller Tube or a Na-I detection system.
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Appendix 3: Monitoring Volatilization Products Using Residual Gas Analyzers During MeV Ion Beam Irradiations

This chapter is a reformatted version of a manuscript published in *Nuclear Instruments and Methods B* (NIMB) in January of 2018 by C.J. Wetteland, K. Kriewaldt, L.A. Taylor, H.Y. McSween Jr., and K.E. Sickafus

Monitoring Volatilization Products Using Residual Gas Analyzers During MeV Ion Beam Irradiations

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ABSTRACT

The use of Residual Gas Analyzers (RGAs) during irradiation experiments can provide valuable information when incorporated into experimental end-stations. The instruments can track the volatilization products of beam-sensitive materials, which may ultimately aid researchers in selecting appropriate flux values for conducting experiments. Furthermore, the type of gaseous species released during an irradiation can be monitored directly, which may lead to new insights into the radiolysis and/or heating mechanisms responsible for gas evolution. A survey of several classes of materials exposed to extremes in particle flux is presented to show how RGA instrumentation can be incorporated to qualitatively assess ion-solid interactions in a variety of fields.

I. INTRODUCTION

Common to many modern vacuum and accelerator systems are Residual Gas Analyzers (RGAs). RGAs are mass spectrometers used for monitoring vacuum conditions and are especially useful for identifying leaks. For instance, in a typical vacuum system operating in the 10^{-8} Torr range, an RGA readily measures the $\sim 10^{-9}$ partial pressures of air, water, and oils, and is readily configured into a leak detection mode for helium measurement. However, if an RGA is appropriately designed into experimental end-stations, it can become a useful instrument for measuring gaseous species that may become volatilized due to ionization and beam heating during irradiation experiments. Two possible applications for RGAs in irradiation experiments include determining the proper beam flux for conducting accelerated irradiation experiments, and direct measurement of radiolysis (ionization) effects in materials.

Accelerated irradiation studies are experimental irradiations performed at dose rates in excess of the dose rates associated with the physical phenomena they are meant to simulate: such as in nuclear reactors, radioactive waste storage, and space weathering (Bennett et al., 2013; Mazey, 1990; Weber et al., 1991). Whereas the energy and fluence in irradiation experiments are typically predetermined, the flux is often not. Many experimentalists overlook this crucial variable, as the flux, or beam current, is oftentimes determined by what the equipment is capable of outputting on any given day. Researchers benefit from stable, high-current irradiations as they can save valuable time over the course of a long irradiation campaign, particularly when considering experiments lasting days and weeks. Furthermore, it is easy to reconcile the economics of an irradiation that could be performed over the course of eighty hours, or *tweaking* a couple of knobs in order to complete the experiment in one long working day.

Most ion irradiation experiments typically use keV or MeV beams with nanoamp to microamp beam currents, resulting in fractions of a watt-like energy deposition. Even these seemingly innocuous wattages can elevate the temperature in the irradiated region, as the volume of energy deposition is small; ion ranges are typically on the order of nanometers to tens of microns in depth for most materials. Limiting the temperature gain

in the target is critical, as elevated temperatures may result in deleterious effects such as volatilization and undesired defect recombination or dynamic annealing (Goldberg et al., 1995; Kuznetsov et al., 2003; Pelaz et al., 2004). This limits the flux of particles which can be used without considering extensive mechanisms for heat removal such as liquid interfaces and other cooling schemes during irradiation (Naab et al., 2011).

In addition to tracking the role of beam flux during an irradiation, the RGA can be used to understand radiation degradation and radiolysis in materials. For instance, the technique has been used to simulate α -particle exposure in polymers that come into close contact with actinides (Fisher et al., 2006; Pugmire et al., 2009; Wetteland et al., 2006). A novel analogous example is understanding the effects of high-energy protons from solar flares on precursor planetary material. Stars such as our Sun were far more active proton emitters during their early evolution. It is possible that chemical alteration of primitive solar material could be simulated in experiments similar to those above, with chemicals released from the target material being tracked with the RGA.

In this report, we present several examples of ion irradiation experiments wherein we used an RGA to monitor radiolysis effects and target volatilization. Our examples involve multiple classes of materials.

II. EXPERIMENTAL

A series of ion beam irradiations were performed using 2 MeV H^+ ions (University of Wisconsin-UW) and 5.5 MeV He^{++} ions (Los Alamos National Laboratory-LANL). Figure 1 shows a typical experimental setup. A Stanford Research Systems (SRS) 300 amu (atomic mass unit) RGA was connected in series with the end-station and the accelerator beam line for the LANL experiments. Twin 70 l/s turbo pumps are adjacent to the ionizing filament as can be observed in detail 10 of the figure. For the experiments conducted at UW, the RGA was mounted on the side of the end-station using a single 70 l/s pump adjacent to the filament. In both configurations, some portion of the volatilized products are pulled past the RGA filament due to the local pressure gradient created by the turbo pumps. The SRS RGA has manufacturer detection limits of

5×10^{-11} Torr using the instrument's Faraday cup, and 5×10^{-14} when the optional electron multiplier is used. The maximum operating pressures for the Faraday cup and electron multiplier are 10^{-4} and 10^{-6} Torr respectively. The instrument is capable of monitoring up to 10 different amu species simultaneously, with the data being output in multiple pressure-versus-time configurations. The data presented in this report typically entails only one or two of the volatilized products for a given sample, and is displayed with the partial pressure (Torr) on the ordinate, with time on the abscissa. It should be noted that the mass filter selects species based on their mass over charge ratio (m/q), and that data displayed represents a major element in the target. The targets were mechanically mounted on an electrically isolated, un-biased stainless steel stage, with charge collected using a Brookhaven Instruments Corporation (BIC) current integrator. The current measured on the isolated stage agreed well with a pre-chamber Faraday cup.

Materials examined include: (1) a polished slab of Portland cement and (2) a zone refined nickel slab, each irradiated with un-scanned 2 MeV H^+ ions to simulate neutron exposure in a reactor environment; (3) a Kapton[®] (polyimide) film irradiated with scanned 5.5 MeV He^{++} ions to simulate α -particle exposure from an actinide; and (4) a sulfide mineral irradiated with un-scanned 2 MeV H^+ ions to simulate meteorite precursor material exposed to solar flare particles during stellar evolution. Post irradiation analysis techniques employed in this study include scanning electron microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDXS) on the sulfide mineral using a Phenom Pro-X SEM, and Thermal Gravimetric Analysis (TGA) on the cement using a TA Instruments Q500. Experimental irradiation conditions are summarized in Table 1.

III. RESULTS and DISCUSSION

III.a Cement Example

Figure 2 shows an RGA mass scan for microcrystalline cement irradiated with 2 MeV protons using two different ion fluxes. The initial background pressure of water for the cement is over two orders of magnitude higher than the other materials used in this study.

Figure 2 shows that a flux of $4.7 \times 10^{12} \text{ H}^+/\text{cm}^2\text{-s}$ was applied at an elapsed time of 15 seconds and stopped after a minute of irradiation. A second irradiation was performed using a flux of $9.4 \times 10^{12} \text{ H}^+/\text{cm}^2\text{-s}$ and started at an elapsed time of 120 seconds, and stopped 140 seconds later. The irradiation was performed over a 0.04 cm^2 area with respective beam currents of 30 and 60 nA.

A considerable difference in water loss is evident between the two flux values. Understanding and limiting water loss should be critical in performing accelerated aging studies in cement. Both radiolysis and heating effects during irradiation may result in water loss and subsequent mechanical property degradation of concrete structures (Field et al., 2015; Le Pape et al., 2015).

Gas generation in the case of cement via radiolysis is accomplished by the dissociation of water and the subsequent formation of liberated molecular species. Limited literature exists which describes the radiolysis of cement. However, a specific concern in these scenarios is the buildup and explosion hazard of H_2 gas generated from radioactive materials sealed in cement casks. Siskind (1992) determined that H_2 and H_2O are generated by the radiolysis of trapped pore water in the cement structure. Bibler and Orebaugh (1976) examined beta particle irradiation in concrete from tritiated water and found that a steady state H_2 production was reached which is directly related to the intensity of irradiation.

Common to these studies is the quantification of gas generation through use of the *G value*. The *G value* is defined as the number of molecules generated when a substance absorbs 100 eV of energy. In the above studies, the gasses were confined and measured from a closed system. As only a portion of gasses generated in this study were measured by the RGA, it is not possible to report actual *G* values.

Water loss can additionally occur during radiation induced heating of the cement. TGA was used to establish how weight loss in cement varies with increasing temperature. Figure 3 shows weight loss in Portland cement between 24 and 950 °C as measured with TGA. Data shows a relatively small decrease in weight occurs between room temperature and 105 °C, which correlates to the loss of adsorbed water. Beyond 105 °C, weight loss is from the decomposition of chemically bound water from the main

hydration product of Portland cement: calcium-silicate-hydrate or C-S-H (Bazant and Kaplan, 1996).

It is likely that both ionization and thermal mechanisms may be responsible for water loss in cement/concrete systems. Discerning the relevant contribution of each mechanism is beyond the scope of this work. However, limited heating and ionization is expected in the case of neutron radiation damage in a reactor environment. Therefore, selecting a beam current that minimizes water loss as identified by the RGA may result in data that best reflects conditions required to perform accurate accelerated aging studies in concrete systems.

III.b Metal Example

In contrast to cement, metals can be exposed to significantly higher fluxes of protons before measureable effects can be observed with the RGA. Figure 4 shows the partial pressures of masses (q equal to 1) 58 and 56 for a zone purified nickel target irradiated with 2 MeV H^+ ions. The target was sequentially subjected to fluxes of 6.2×10^{13} , 3.7×10^{14} , 5.0×10^{14} , and $6.2 \times 10^{14} H^+/cm^2-s$ at elapsed times of 360, 660, 920, 1030 seconds. Figure 4 shows distinct changes in the mass 56 signal with changing flux, while minimal changes were detected from mass 58. The fluxes applied are equivalent to a 1, 6, 8, and 10 μA beam over a $0.1 cm^2$ area. The series of irradiations resulted in over an order of magnitude change in vapor pressure in the mass 56 signal during the course of the experiment. It should be noted that during the irradiation, the target transitioned from spectral emission in the orange to emission in the white. Visible emission in the orange of metals is associated with temperatures of approximately $900^\circ C$, while the white is approximately $1200^\circ C$.

Thin film techniques for vapor deposition of metallic elements use temperature-pressure curves (Honig and Kramer, 1969) to determine optimal conditions for vaporizing metallic targets. From such curves, it can be determined that the temperature predicted by the color change in nickel would result in a pressure change from $\sim 7 \times 10^{-8}$ to $\sim 7 \times 10^{-5}$ Torr for conditions similar to Honig and Kramer (1969). However, the data from

Fig. 4 indicates that minimal detection of evolved nickel vapor ($m/q=58$) was observed over the course of the irradiation. What is directly correlated, is a regular change in the m/q equal to 56. It is plausible that the rise in 56 signal is from iron in the stainless steel holder that the nickel target was mounted on. Per the vapor curves, iron does exhibit a greater degree of volatility as compared to nickel. However, it is more likely that this experiment demonstrates the dangers of contamination and mass interferences in identifying liberated species during the irradiation event.

Several prominent hydrocarbon species exist in the ~ 50 amu range, one type being alkenes. Alkenes can be formed from the cracking of long-chained oil compounds ubiquitous in vacuum systems, with possible direct mass interference coming from the hydrocarbon C_4H_8 . It is probable that the signal generated for mass 56 represents the fragmentation of oils on the target, target holder, and end-station as the temperature substantially increases over the irradiation. This particular mass interference would make it exceedingly difficult to measure iron volatilization in a similar measurement as performed here for nickel. Overall, the results indicate that the sensitivity of the instrument is unable to detect gaseous nickel over the range of experimental conditions investigated.

III.c Polymer Example

Kapton[®] is an aromatic polyimide film with a long history of use in radiation and vacuum environments due to its thermal stability and radiation tolerance (Hanks and Hamman, 1971; Megusar, 1997). A Kapton[®] film was exposed to three successive 2.7×10^{13} He⁺⁺/cm² irradiations (~ 5 MGy) using 5.5 MeV particles. Figure 5 shows that over the elapsed time of the irradiation, a reduction in evolved CO₂ gas as a function of dose is observed. The oscillatory pattern of evolved CO₂ gas is due to scanning the 25 nA, 0.09 cm² beam, over a 1 cm² area in order to achieve a uniform irradiation and to minimize target heating. The dip in the pattern represents a period during the scan where the beam was not hitting the polymer target, while the peak represents the entire beam on the film. Figure 5 indicates that during the first seconds of the irradiation, an

approximate 40x increase in the partial pressure of mass 44 (CO₂) was detected by the RGA. Over the course of the first irradiation, the partial pressure of CO₂ was observed to decrease. This trend continues for the second dose, while the pressure during the third remains relatively unchanged over the course of the irradiation. The data also indicates that only ~2 minutes were required between each irradiation for the system to return to the background partial pressure of CO₂.

The rapid detection of CO₂, direct correlation between CO₂ generation and scan pattern, and relatively low beam current scanned over a wide area, are all indicators that gas generation in the polymer is related to ionization effects rather than thermal heating. Literature results for the gaseous species generated in KAPTON[®] support this, and vary for the type of incident radiation. Hegazy et al. (1992) found that when using gamma-rays the dominant evolved species in decreasing order were CO₂, CO, H₂, and CH₄. Lewis and Lee (1991) found that CO, H₂, and CO₂ were the dominant species when using 200 keV Si ions. In the case of the Si irradiation, the authors developed separate mechanisms for the formation of CO and CO₂. Double scission of a carbonyl-amidic bonds results in the spontaneous formation of CO, while the formation of CO₂ is more complex. Ionization results in the formation of an O-C=N radical; this is followed by double scission which leads to decarboxylation forming the CO₂ molecule. The decrease of CO₂ generated over the course of the irradiation described by Lewis and Lee is similar to the trend observed in Fig. 5. Overall, the results indicate that the RGA is sensitive to volatilization products formed during scenarios which simulate α -particle radiolysis in polymers.

III.d Sulfide Example

Understanding mechanisms responsible for the formation of planets and the distribution of elements in the solar system can be investigated by studying meteorites. Meteorites can contain primitive assemblages of minerals, metals and amorphous phases, which represent various stages of cooling and condensation from a hot nebular gas. These may include high-temperature refractory minerals such as corundum (Al₂O₃) and

forsterite (Mg_2SiO_4), coexisting with a suite of medium and low-temperature condensation minerals including iron/nickel metal and sulfides (FeS , and Fe_{1-x}S). It may be that protons discharged in exaggerated solar flare events during stellar evolution could chemically alter these phases. Whereas the above experiments on nickel may be relevant to investigating some metallic phases in meteorites, additional 2 MeV proton irradiations were conducted on an FeS analog, pyrite (FeS_2).

Figure 6 shows an RGA scan of mass 64, S_2 , from an irradiated polished slab of FeS_2 . At an elapsed time of 360 seconds, a flux $6.2 \times 10^{13} \text{ H}^+/\text{cm}^2\text{-s}$ ($1 \mu\text{A}$ over 0.1 cm^2) was applied to the target; no change in the RGA spectrum was observed. However, at 720 seconds the flux was increased to $9.5 \times 10^{13} \text{ H}^+/\text{cm}^2\text{-s}$, and a significant change in the S_2 signal was detected. The scan in Fig. 6 shows a steady increase in the S_2 signal for approximately 720 seconds before it begins to level out. At approximately 1500 seconds, the signal exhibited a drastic increase again; in this case, there was no change in the beam current. At approximately 1600 seconds, the beam was turned off and the S_2 signal decreased rapidly, then slowly decayed toward background over 1000 seconds before the measurement was stopped.

The sulfide example has similar behavior to the cement, as a threshold flux was required to generate volatilization products. Furthermore, the rapid approximately two order of magnitude change in S_2 could be another indicator ionization is the dominant mechanism for gas generation. The sharp increase at 1500 seconds was the exposure of fresh FeS_2 material to the beam due to a small portion of the surface spalling off. This was observed post irradiation with optical and backscattered electron SEM images as shown in Figs. 7a and 7b. An EDS line scan in Fig. 7c across the surface shows the relative concentrations of Fe and S. The irradiated area indicates sulfur loss, while the inner region reveals the FeS_2 stoichiometry. It is expected that S_2 generation would have reached a steady value and eventually fallen off, had the surface remained intact.

The integrated flux between 1 keV and 2 MeV in solar flares should be greater than the flux of 2 MeV protons used in this experiment. This is due to a predicted 10^5 increase in proton flux from developing stars (Feigelson et al., 2002), as compared to present day values. However, the distribution of particles in a solar flare would favor a

lower-energy distribution of protons, as an exponential relationship between energy and flux exists (Reedy and Arnold, 1972). Based on these results, sulfides in the early solar system may have limited stability in an irradiation environment. Over the course of a prolonged irradiation, it may be possible to completely reduce a sulfide to a metal.

III.d Lessons Learned and Recommendations

The results presented here are strictly qualitative, but steps could be taken to both quantitatively determine volatilization products and increase the overall sensitivity. For best results, the end-station should be completely isolated from the beamline; this would involve passing the beam through a thin-window such as Havar[®] or Si₃N₄. In this experimental configuration, all pumping would be accomplished through a high-vacuum pump in series with the RGA, where all evolved gasses would pass by the filament of the RGA. While this configuration may be the simplest, there exists a limitation for the total beam current which can pass through the thin film. Thin film windows could degrade and fail under the presence of prolonged high-current beams.

A second option for quantifying the technique and increasing the sensitivity, could be the combination of a differentially pumped end-station and a calibrated leak. A differentially pumped vacuum system, where the end-station pressure was below that of the beamline, would favor the collection of the majority of volatilized species. This could be accomplished by increasing the pumping speed in the end-station and installing a restrictive orifice before the chamber. A calibrated leak could additionally be used to determine what percentage of the gas is lost to the beam-line vacuum system. A correction factor based on the gas lost could then be used to quantify the data.

To best eliminate mass inferences due to contaminants, dedicated small irradiation chambers which have been sufficiently cleaned and baked should be used. Furthermore, irradiating a standard target which is unlikely to evolve any gasses over a range of temperatures could be used to set background values of contaminants in the system prior to actual irradiations. The RGA in this experiment came with a channel electron multiplier which can increase the sensitivity of the instrument, but its functionality was

not examined here. However, it has a maximum operating pressure that depending on the volatility of the target, may limit its usage.

The degree of volatilization in any target is determined by the compounds present, beam current used, and the ability of the target to conduct heat from the near surface. Heat removal is dependent on the electronic properties of the material, size of the target, mounting mechanisms, beam size, and additional steps taken to remove heat (air, chilled water, etc.). Materials possessing metallic bonding resist volatilization from ionization, and can conduct heat away from the beam spot to limit local temperature increases. However, metals with lower vapor pressure, poor thermal conductivity, or those which have dramatic changes in the conductivity as the temperature increases may begin to exhibit volatilization. Non-metallic materials are more difficult to determine the nature of volatile product formation, as gasses can evolve from both ionization and heating. Separating these effects is difficult, but could be resolved by cooling the target and using a sequence of low-flux irradiations with a more sensitive experimental geometry.

The cement and metal examples share a similar experimental context, as both materials are the subject of accelerated aging studies associated with neutron damage in nuclear reactors. The flux of these two H^+ ion irradiation experiments represent two extreme values. The relatively lengthy time (1 hour) required for the initial pump down of the cement target to 1×10^{-5} Torr, as compared to the nickel (20 minutes) can be a pre-irradiation indicator of the relative sensitivity of the targets to flux.

In the case of the sulfide experiments, currents above 3 μA resulted in pressures in the 10^{-4} range at the RGA. These high pressures are beyond the upper operating limit of the RGA, and care should be taken during testing to determine maximum beam currents to be investigated. Precautions should also be taken to isolate the RGA from the end-station during sample exchange in order to avoid filament exposure to low-vacuum or atmospheric conditions. The filaments are extremely sensitive and costly to replace if damaged.

IV. CONCLUSIONS

Ion irradiation experiments were conducted to demonstrate how a Residual Gas Analyzer (RGA) can be used to monitor the evolution of volatilization products as a function of irradiation conditions. In many cases, volatilization of primary elemental or molecular constituents can be directly identified by the corresponding atomic mass as measured by the RGA. However, care should be taken to account for compounds that may mass interfere; this includes diatomic molecules, multiple charge state ions, and other vacuum contaminants such as hydrocarbons. While a major use for collecting RGA spectra during an irradiation could be to limit deleterious heating and ionization effects from high-beam currents, it is also ideal for tracking volatilization products from radiolysis and in scenarios that may mimic early solar system processes.

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Appendix 4: Tables

Table 1. Materials Processing Conditions for Irradiated Targets

Material	Source	Processing Conditions	Surface Preparation
San Carlos Olivine Pyrite Alkali Feldspar Weathered Chondritic Meteorite	Arizona, USA Unknown Madawaska, Can. Unknown	None	Ground slabs (800 grit SiC) between ~0.5-2 mm thick
Synthetic Olivine	MgO and Al ₂ O ₃ Fisher Scientific	Sintered in air at 1550°C for 12 hours	Pellets sliced and ground (800grit SiC) between 0.5-2 mm thick
San Carlos Olivine (80 wt.%) Nain Diorite Gabbro (20 wt.%)	Arizona, USA and Labrador, Can.	Ball milled and mixed in a zirconia canister. 13mm pellets sintered in a vacuum furnace at 1150°C for 12 hours	Pellets sliced and ground (800 grit SiC) ~0.5 mm thick
San Carlos Olivine (80 wt.%) Still Water Anorthosite (20 wt.%)	Arizona & Montana USA	Ball milled and mixed in a zirconia canister. 13mm pellets sintered in a vacuum furnace at 1150°C for 12 hours	Pellets sliced and ground (800 grit SiC) ~0.5 mm thick
San Carlos Olivine (50 wt.%) Synthetic Al ₂ O ₃ (50 wt.%)	Arizona, USA & Fisher Scientific	Ball milled and mixed in a zirconia canister. 13mm pellets sintered in a vacuum furnace at 1150°C for 12 hours	Pellets sliced and ground (800 grit SiC) ~0.5 mm thick
Fused Silica	MTI Corporation	None	None
Undoped Silicon Single Crystal	University Crystal	None	None

Table 2. Characterization and Irradiation Conditions

Characterization Technique	Facility	Energy	Compositions Studied	Flux (p/cm ² -s)	Fluence (p/cm ²)
<i>In situ</i> Monitoring (Digital Camera), Optical, and SEM	UW	2 MeV	San Carlos Slab	10 ¹²⁻¹⁴	10 ¹⁴⁻¹⁷
	LANL	2 MeV	Pyrite Slab		
		2 MeV	K-Feldspar Slab		
		50 keV	Synthetic Olivine Pellet		
		2 MeV & 80 keV	Olivine-Gabbro Pellet		
		2 MeV & 80 keV	Olivine-Anorthosite Pellet		
Residual Gas Analysis SRS RGA 300	UW	2 MeV	San Carlos Slab	10 ¹²⁻¹⁴	10 ¹⁵
			Pyrite Slab		
			K-Feldspar Slab		
			Olivine-Gabbro Pellet		
			Olivine-Anorthosite Pellet		
			Olivine-Corundum Pellet		
<i>In situ</i> Radiation Detection PGT Germanium Detector	LANL	1.8 MeV	Fused Silica	9x10 ¹³	2x10 ¹⁶
		2.8 MeV	Single Crystal Si		
		3.8 MeV	Olivine-Gabbro Pellet		
			Ordinary Chondrite		
<i>In situ</i> Radiation Detection Vernier VRM-BTD Geiger-Mueller	UW	2 MeV	Single Crystal Si Olivine-Gabbro Pellet	4x10 ¹⁴	1x10 ¹⁷
Post Experiment Radiation Decay Measurements	UW	2 MeV	Single Crystal Si Olivine-Gabbro Pellet	4x10 ¹⁴	1x10 ¹⁷

Table 3. Area and Elemental Concentrations as Measured with EDXS of the Synthetic Forsterite Sample

Element	Native Area Scan Atomic%	Melt Reg. Area Scan Atomic%	Spot Scan Point 1 Atomic%	Spot Scan Point 2 Atomic%
Oxygen	61.0	62.2	59.5	64.6
Magnesium	25.2	11.4	26.5	11.0
Aluminum	0.0	1.8	0.0	1.9
Silicon	13.0	18.9	13.5	18.1
Yttrium	0.0	0.7	0.0	0.6
Calcium	0.2	2.0	0.2	1.7
Zirconium	0.6	3.0	0.2	2.1

Table 4. General Results from the 80 keV/amu Irradiations of the Silicate Mixtures

Flux p/cm ² -s	Fluence p/cm ²	Result
5.0x10 ¹³	2.3x10 ¹⁶	No remarkable changes from the original microstructure
5.0x10 ¹³	2.3x10 ¹⁷	The anorthosite and corundum mixtures had no remarkable changes from the original microstructure; the gabbro mixture exhibited an oval deposition of a glassy carbon compound
1.0x10 ¹⁴	2.3x10 ¹⁶	No remarkable changes from the original microstructure
1.25x10 ¹⁴	2.3x10 ¹⁶	The anorthosite and gabbro mixtures had no remarkable changes from the original microstructure; the corundum mixture had a distribution of micron sized droplets of Fe-Ni metal on the surface

Table 5. Spot Elemental Analysis of the San Carlos-Gabbro Pellet as Measured by EDXS

Element	Area Scan 1 Atomic%	Point Scan 2 Atomic%	Point Scan 3 Atomic%
Carbon	0	31	80.25
Oxygen	62.2	46.2	17.7
Sodium	2.1	1.3	0
Magnesium	8.1	5.3	1.1
Aluminum	6.8	4.7	0.18
Silicon	16.9	9.4	0.77
Calcium	2.2	1.3	0
Iron	1.7	0.8	0

Table 6. Energy Deposition for Multiple Irradiation Conditions

Energy eV	Flux p/cm ² -s	Time Sec.	J/g
2x10 ⁶	2x10 ¹⁴	10	6.4x10 ⁴
2x10 ⁶	2x10 ¹⁴	100	6.4x10 ⁵
2x10 ⁶	2x10 ¹⁴	1000	6.4x10 ⁶
2x10 ⁶	2x10 ¹²	1000	6.4x10 ⁴
2x10 ⁶	2x10 ¹³	10	6.4x10 ³
2x10 ⁶	2x10 ¹⁵	1000	6.4x10 ⁷
5x10 ⁴	2x10 ¹⁴	10	1.6x10 ³
5x10 ⁴	2x10 ¹⁴	100	6.4x10 ⁴
5x10 ⁴	2x10 ¹⁴	1000	6.4x10 ⁵
5x10 ⁴	2x10 ¹²	1000	1.6x10 ³
5x10 ⁴	2x10 ¹³	1000	6.4x10 ⁴
5x10 ⁴	2x10 ¹⁵	1000	1.6x10 ⁶

Table 7. Silicon Isotopes and Nuclear Reactions

Isotope	Abundance %	Reaction	New Isotope	Decay Mode	Time	Decay Product
^{28}Si	92.23	p Capture p,n	^{29}P ^{28}P	β^+, γ $\beta^+, \text{p}, \alpha, \gamma$	4.14 s 0.20 s	^{29}Si ^{28}Si
^{29}Si	4.67	p Capture p,n	^{30}P ^{29}P	β^+, γ β^+, γ	2.5 m 4.14 s	^{30}Si ^{29}Si
^{30}Si	3.10	p Capture p,n	^{31}P ^{30}P	Stable β^+, γ	Stable 2.5 m	Stable ^{30}Si

Table 8. Proton Range as a Function of Pressure and Energy

Pressure atm	500 keV Range (km)	5 MeV Range (km)	50 MeV Range (km)
1.0E-03	1.1E-01	6.0E+00	4.1E+02
1.0E-04	1.0E+00	6.0E+01	4.1E+03
1.0E-05	1.1E+01	6.0E+02	4.1E+04
1.0E-06	1.1E+02	6.0E+03	4.1E+05
1.0E-07	1.1E+03	6.0E+04	4.1E+06
1.0E-08	1.1E+04	6.0E+05	4.1E+07
1.0E-09	1.1E+05	6.0E+06	4.1E+07
1.0E-10	1.1E+06	6.0E+06	4.1E+07

Table 9. Materials and Irradiation Conditions

Material	Target Geometry	Ion & Energy	Facility	Irradiation Area	Beam Current	Flux/Fluence
Portland Cement	Polished Slab 48 mm ² x 4 mm thick	2 MeV H ⁺	UW	0.04 cm ²	30 nA 60 nA	4.7x10 ¹² H ⁺ /cm ² -s 9.4x10 ¹² H ⁺ /cm ² -s
Nickel	Zone Refined Boule 150 mm ² x 0.7 mm thick	2 MeV H ⁺	UW	0.1 cm ²	1 μA 6 μA 8 μA 10 μA	6.2x10 ¹³ H ⁺ /cm ² -s 3.7x10 ¹⁴ H ⁺ /cm ² -s 5.0x10 ¹⁴ H ⁺ /cm ² -s 6.2x10 ¹⁴ H ⁺ /cm ² -s
Kapton [®] HN	Film 100 mm ² x 0.13 mm thick	5.5 MeV He ⁺⁺	LANL	1 cm ² (0.09 cm ² Beam Spot)	25 nA	(3) 2.7x10 ¹³ He ⁺⁺ /cm ²
FeS ₂	Irregular Mineral Slab ~ 64 mm ² x 2 mm thick	2 MeV H ⁺	UW	0.1 cm ²	1 μA 1.5 μA	6.2x10 ¹³ H ⁺ /cm ² -s 9.5x10 ¹³ H ⁺ /cm ² -s

Appendix 5: Figures

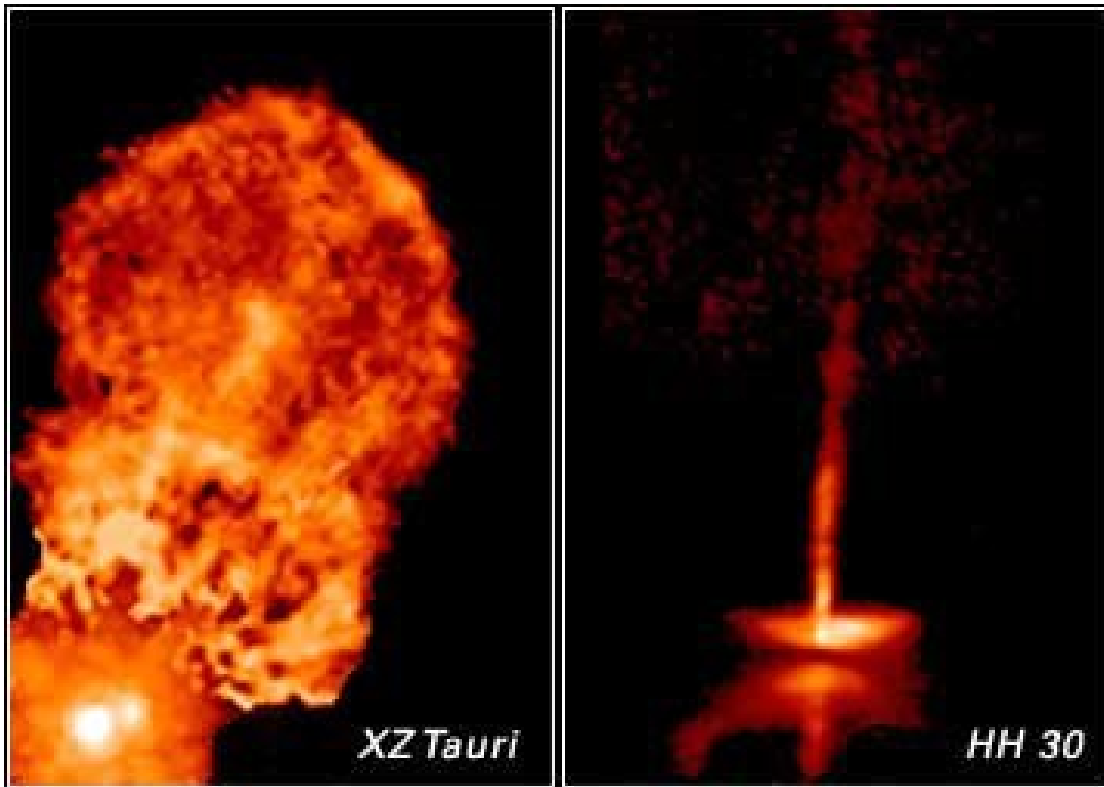


Figure 1. Hubble Space Telescope images of developing stars showing instabilities and mass loss.

The images indicate mass loss which extends outwards to hundreds of AU. The image on the left is a gaseous discharge from the XZ T Tauri star, while on the right, HH30 is a classic bi-polar outflow of gaseous and ionized particles. These stars are from the Taurus-Auriga molecular cloud and are less than 1 million years old.

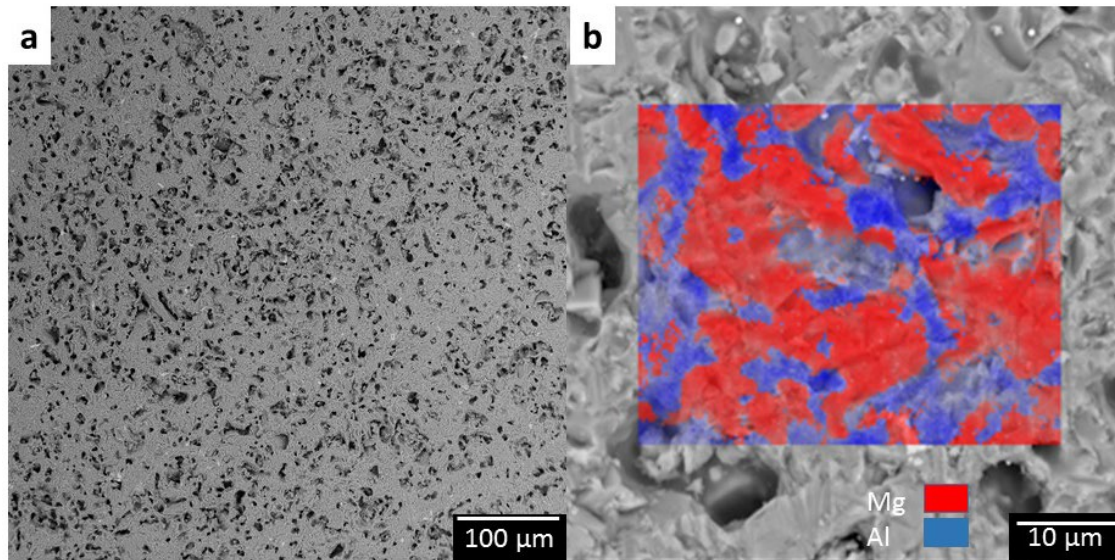


Figure 2. Characteristic microstructure of a sintered pellet.

The pellet microstructure in (a) shows considerable porosity, indicating incomplete sintering and densification; b) Energy Dispersive X-Ray Spectroscopy (EDXS) map indicating relative distributions of olivine (Mg) and plagioclase (Al) mineral components for a mixture of 80 wt.% San Carlos olivine and 20 wt.% Nain gabbro.

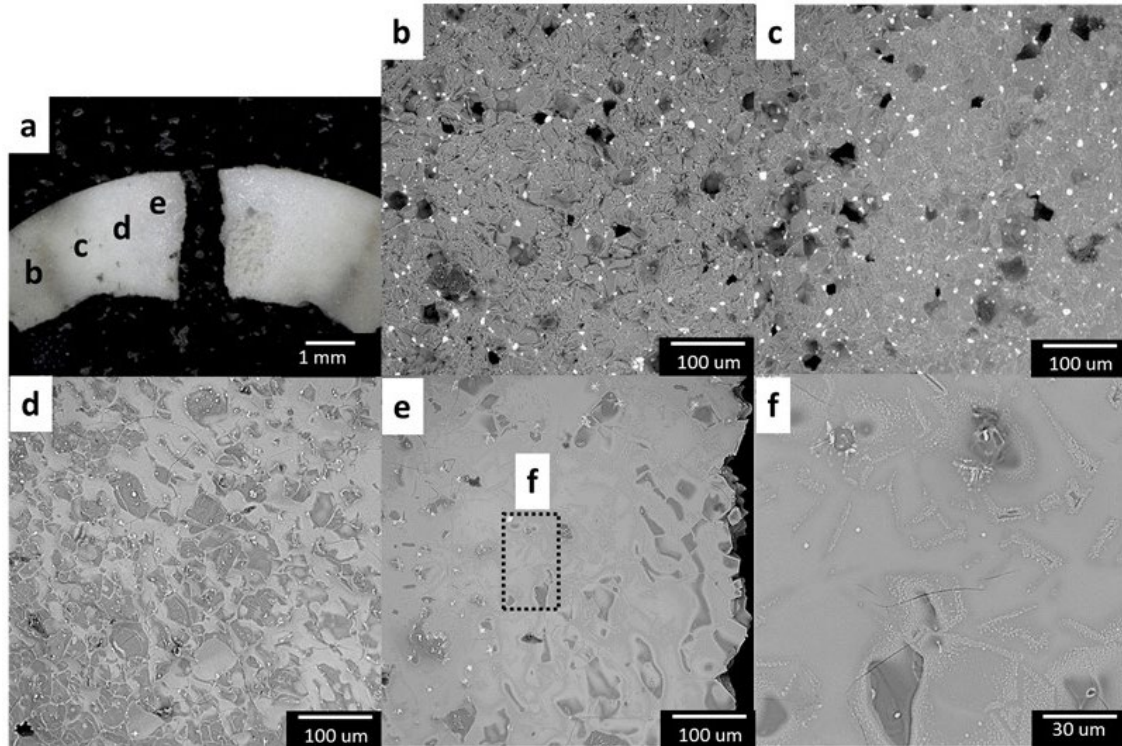


Figure 3. Optical and SEM BSE images of the irradiated microstructure over a distance of 5 mm from the center of the beam.

Optical (a) and SEM (b, c, d, e, f) images of: a) image of a fragment from the synthetic forsterite pellet irradiated with a 6.24×10^{14} p/cm²-s flux of 50 keV protons to a fluence of 1.1×10^{17} p/cm²; b) native microstructure at position (b) indicating abundant porosity with a distribution of bright zirconia particles from ball milling; c) transition zone at point (c), ~3 mm from beam center showing a reduction in porosity with the surface taking on a glassy texture; d) approximately 2 mm from the center, point (d) shows limited porosity as the microstructure continues to transition to an apparent glassy texture; e) the glassy texture at point (e) is split at the beam center, with the target fracturing with a nearly symmetrical microstructure on the opposite fragment; f) a higher- magnification image of the beam epicenter at position (e). The bright phases are zirconia particles from the ball milling process, which generally outline surface and subsurface forsterite grains.

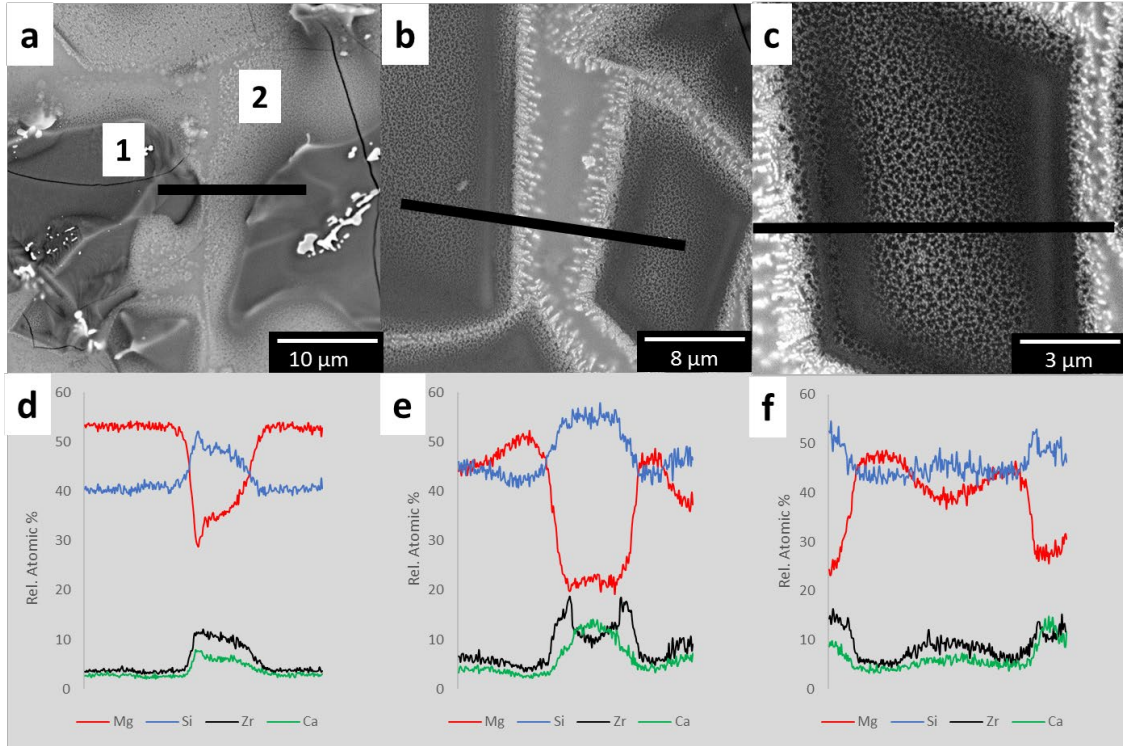


Figure 4. Higher-magnification SEM images of the melt zone from Fig. 3
 Figure (a) indicates positions of EDXS point and line scans which detail chemical compositions on a grain (spot 1 Table 3), the glassy matrix (spot 2 Table 3), and between two grains in (d). Images (b) and (c) are scan locations which detail relative atomic concentrations of Mg, Si, Zr, and Ca in (e) and (f) respectively.

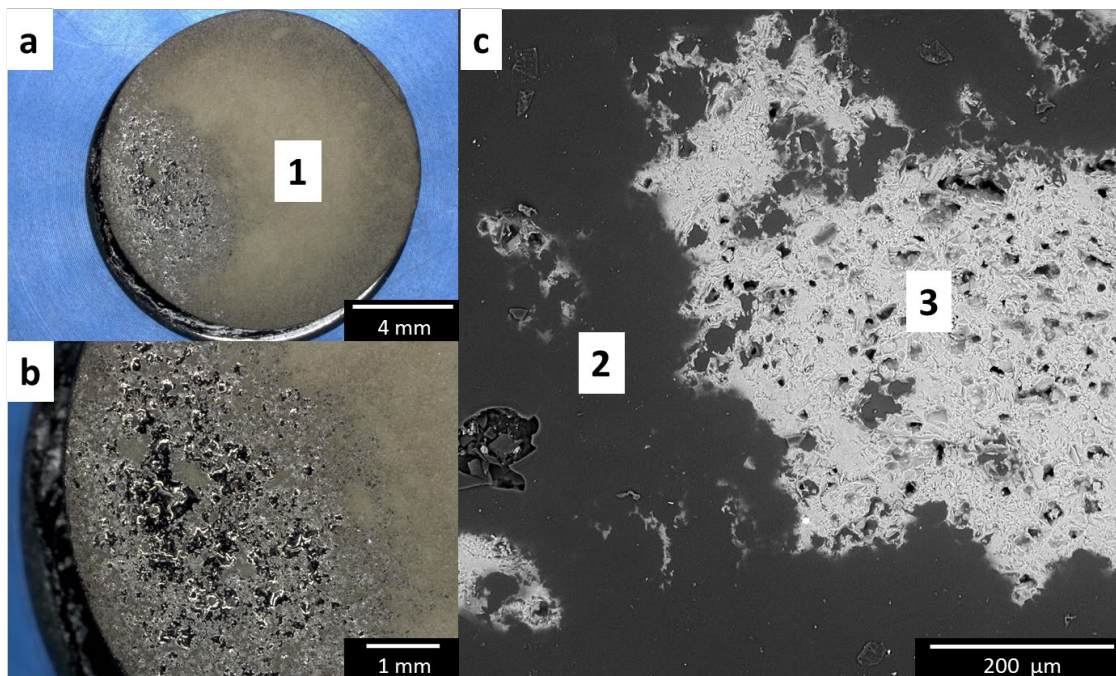


Figure 5. The San Carlos-gabbro pellet irradiated with 80 keV/amu protons to $2 \times 10^{17} \text{ p/cm}^2$ using a flux of $5.0 \times 10^{13} \text{ p/cm}^2\text{-s}$.

Optical microscope images in (a) and (b) indicate the location and size of the carbonaceous compound, while (c) is a low-magnification SEM image from (b). EDXS spot scans taken at positions 1, 2, and 3 indicate considerable differences in the surface chemistry which is detailed in Table 5.

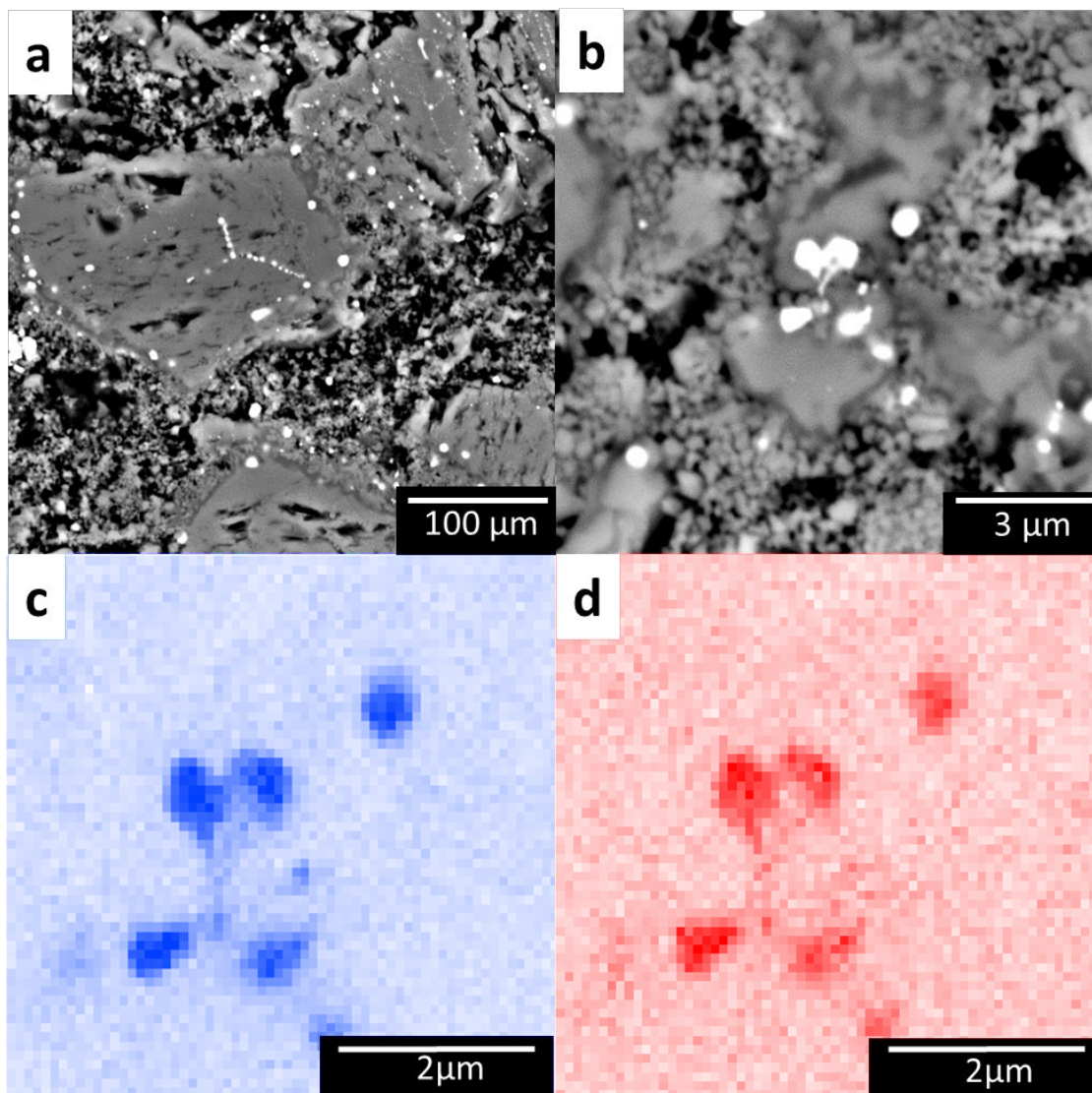


Figure 6. Distribution of metallic droplets on the surface of the San Carlos olivine-corundum mixture .

SEM images of the 80 keV/amu irradiation using a flux of 1.25×10^{14} and a fluence of 2.5×10^{16} . Images (a) and (b) show the distribution and size of the metallic droplets, while (c) and (d) are EDXS K_{α} X-ray maps of figure (b) which show the distribution of Fe (blue) and Ni (red).

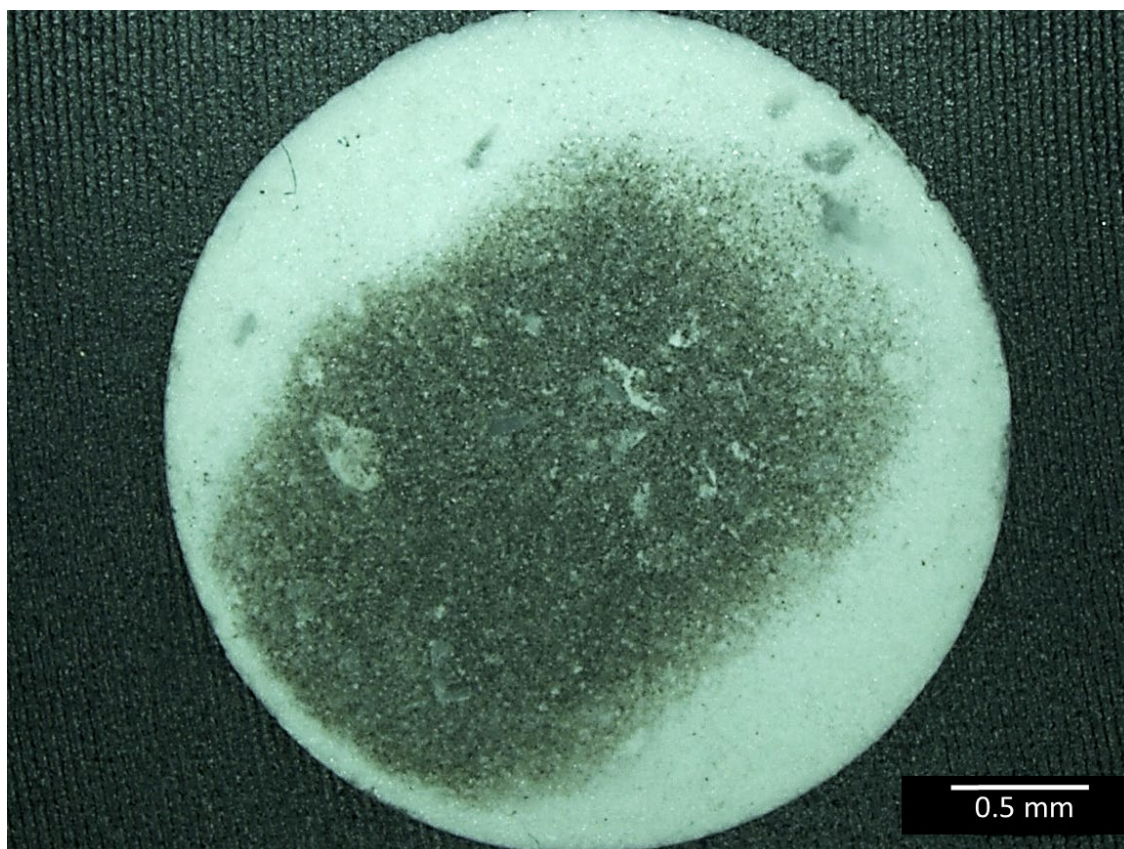


Figure 7. Dark coating deposited on a pellet surface during irradiation.
An optical microscope image of an irradiated pellet showing the dark coating that developed as the beam was moved across the sample.

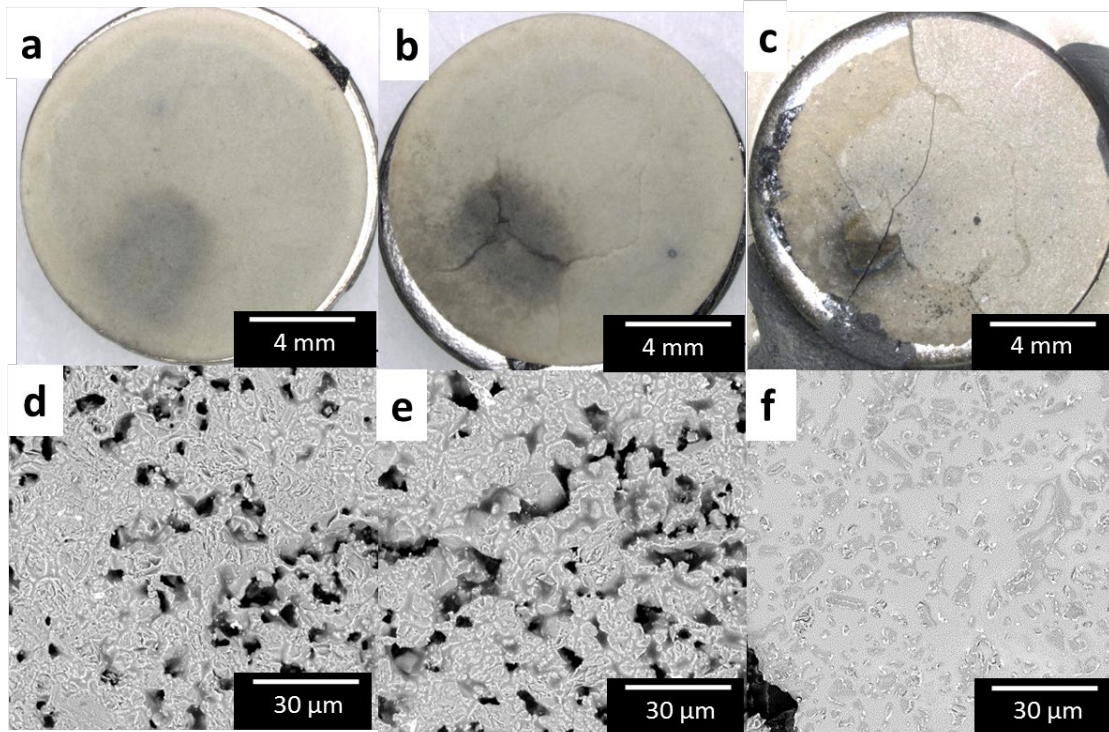


Figure 8. Optical and SEM images of irradiated olivine-gabbro pellets.

Using a constant flux of 2×10^{14} p/cm²-s. olivine and gabbro pellets were irradiated to a progressively greater fluences of 2 MeV protons. The respective optical (upper) and SEM (lower) images and fluences are: (a, d) 5×10^{15} , (b, e) 1×10^{16} , and (c, f) 2×10^{16} p/cm². The optical images show increased macroscopic fracture while the SEM details transitions to the glassy texture developed in the highest-fluence irradiation.

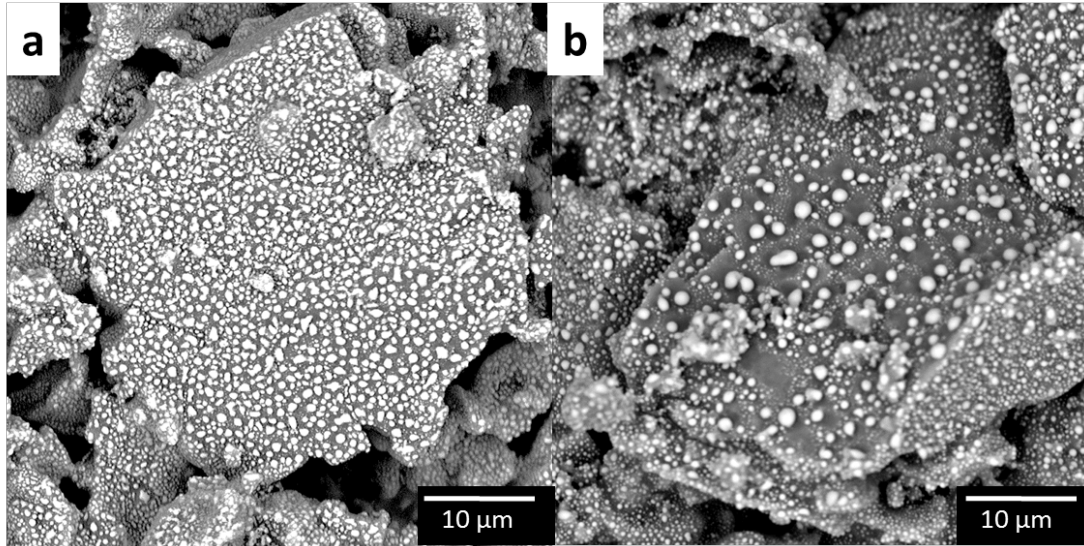


Figure 9. SEM images detailing droplet morphologies from the highest-fluence 2 MeV irradiation.

The sub-surface of the pellet was exposed when the top of the pellet flaked off after removal from the irradiation sample holder. EDXS measurements indicate the droplets have an approximate Fe/Ni ratio of 4/1.

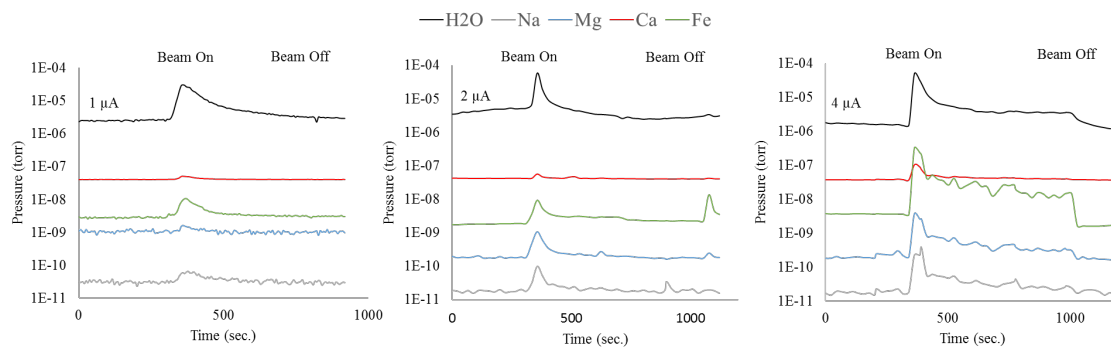


Figure 10. Mass spectrometer data from the olivine-gabbro pellet detailing volatile formation as a function of beam current

The series of RGA spectra show that as beam current is increased, the respective amounts of volatilized components increases as well. Additionally, with increased current, the response time between the beam being applied and the volatilized species being detected decreases as can be seen in the slope of the respective signals.

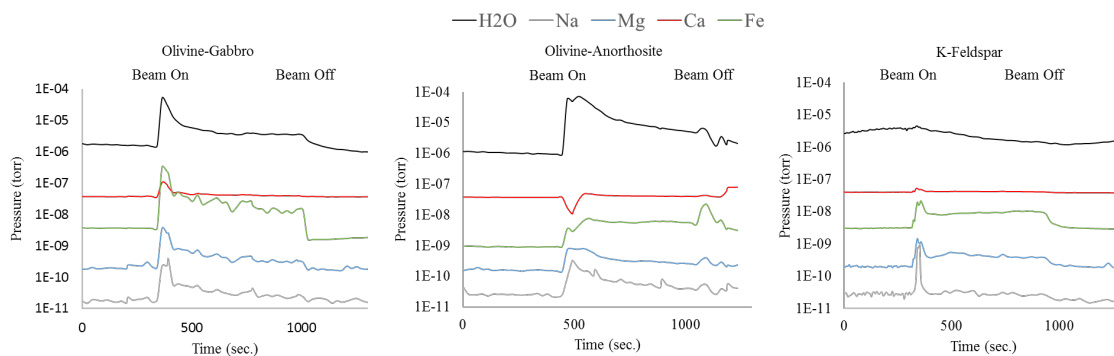


Figure 11. Mass spectrometer data from olivine-gabbro, olivine-anorthosite, K-feldspar, and olivine-gabbro using a 4 μ A beam current.

The two pellets show considerable more water evolution over the course of the irradiation as compared to the K-feldspar. The other species measured in the olivine-anorthosite closely follow the trend of the water signal over the course of the irradiation. The K-feldspar shows a distinctive change in the Na signal, with lesser changes in the Fe and Mg.

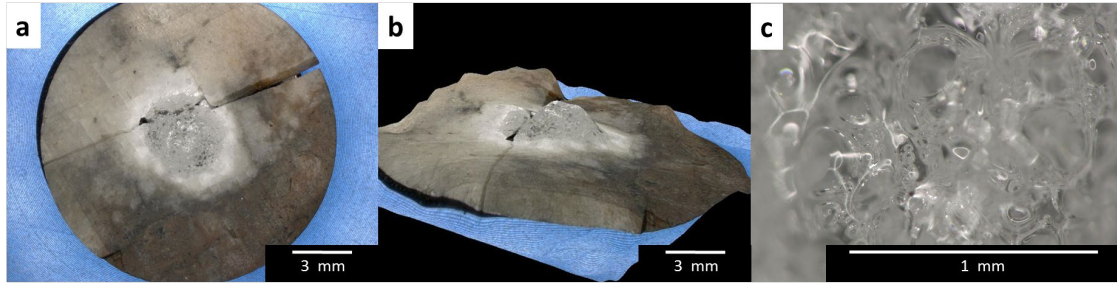


Figure 12. Optical microscope images of the K-feldspar target irradiated with 2 MeV protons to a flux of 2.5×10^{14} p/cm²-s

The series of images show: (a) the irradiated pellet formed a bubble and fractured along a cleavage plane; b) 3-D rendering of irradiated pellet showing relative degree of bubble growth; c) glassy texture of the bubble surface.

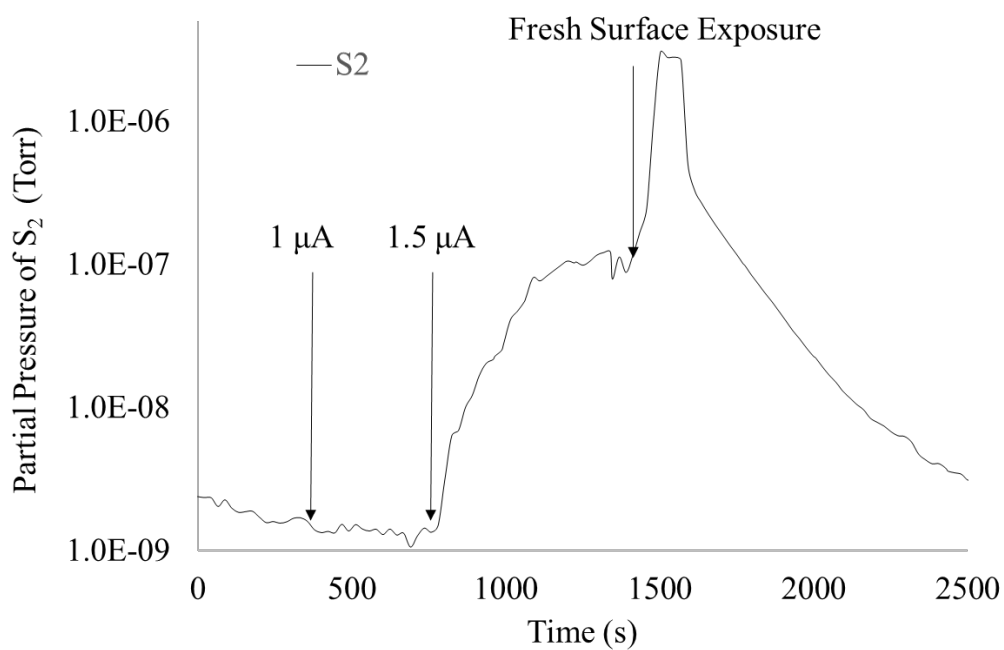


Figure 13. RGA spectrum of 2 MeV proton irradiated FeS₂ using two different beam currents.

A 1 μA beam was applied after 360 seconds with no measurable effect in the mass 64 signal (S₂). However, at 720 seconds the current was increased by 50% and a significant evolution of S₂ is observed. At approximately 1500 seconds an additional increase in the signal was measured. The beam was turned off at ~1600 seconds.

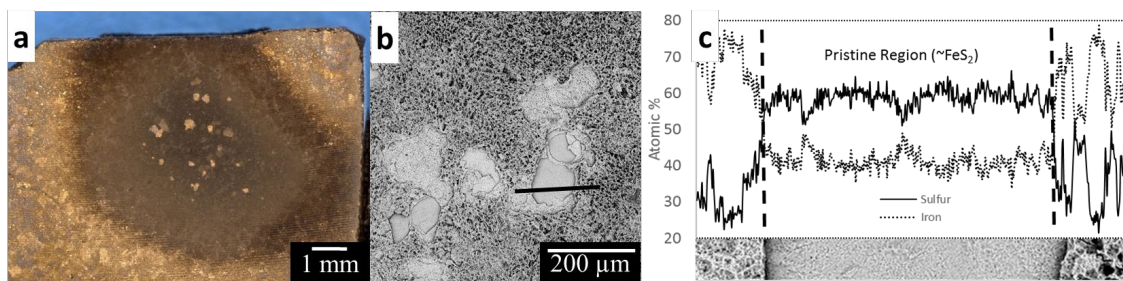


Figure 14. Optical and SEM images of irradiated FeS₂ with EDXS analysis. The optical image of the FeS₂ target in (a) shows the darkened area of the beam spot with bright regions located at the beam center; b) SEM image showing texture of the bright flecks and location of an EDXS line scan; c) EDXS line scan indicating the change in Fe:S ratio over the analyzed region. The scan indicates that the darker irradiated region is sulfur deficient as compared to the brighter features.

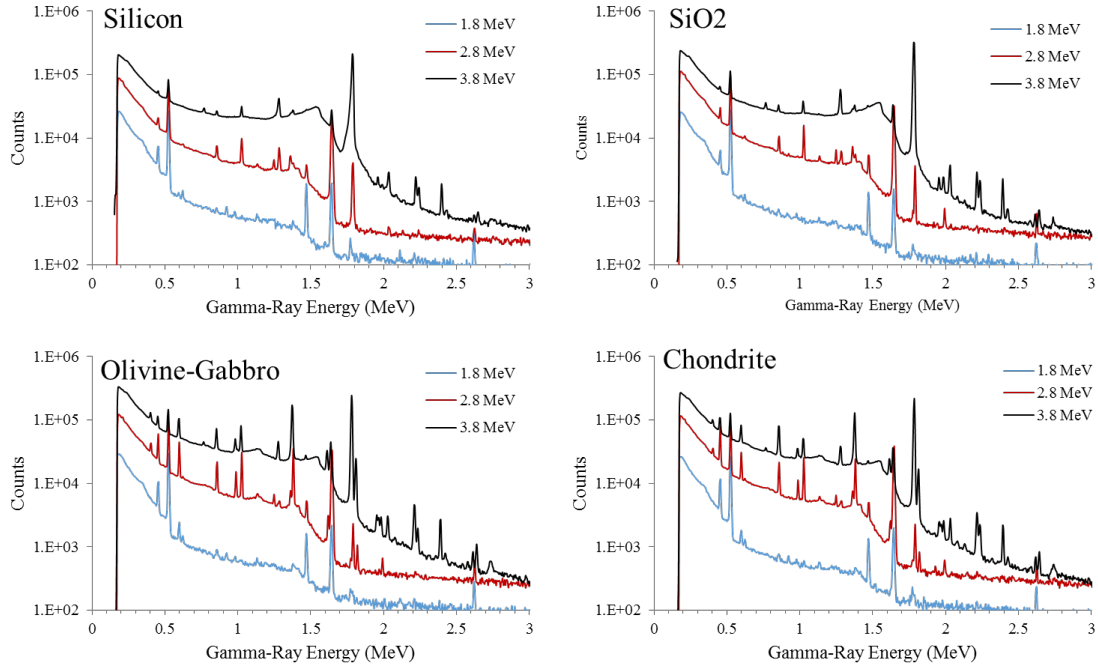


Figure 15. Instantaneous γ -ray yields in Si, SiO₂, olivine-gabbro mixture, and an ordinary chondrite during proton irradiation for three different energies. Gamma-ray spectra from 1.8, 2.8, and 3.8 MeV irradiations using a flux of 9×10^{13} p/cm²-s to a fluence of 2×10^{16} p/cm². The spectra show that numerous (p, γ) reactions exist with all energies, and that with increasing energy both the number and quantity of reactions increase.

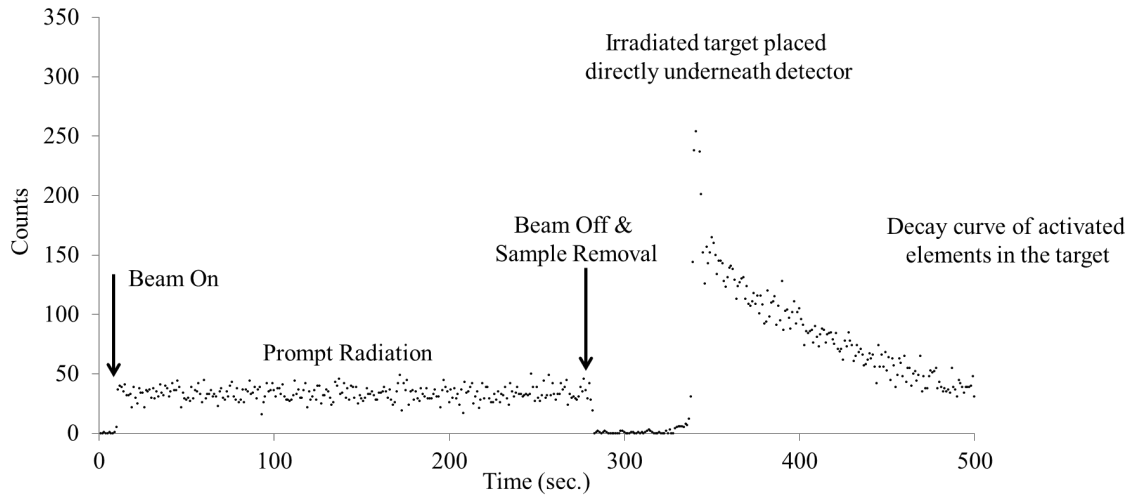


Figure 16. GM tube radiation measurement during a 2 MeV, 4×10^{14} p/cm²-s irradiation.

The Si target was irradiated for 265 seconds (1×10^{17} p/cm²) then removed from the chamber and placed 2 cm below the detector; between 330 and 500 seconds the detector measures the decay of any activated species in the target.

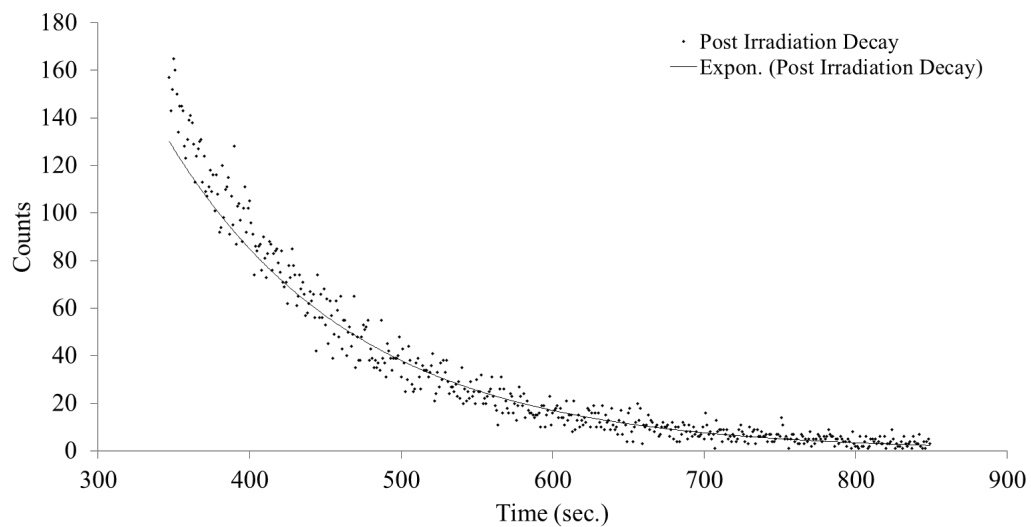


Figure 17. Plot of decay region from Fig. 16 between 350-850 sec.
Decay curve and exponential fit which yielded an exponential of -0.008 s^{-1} . The fit indicates good agreement at longer times, but deviates during the initial decay.

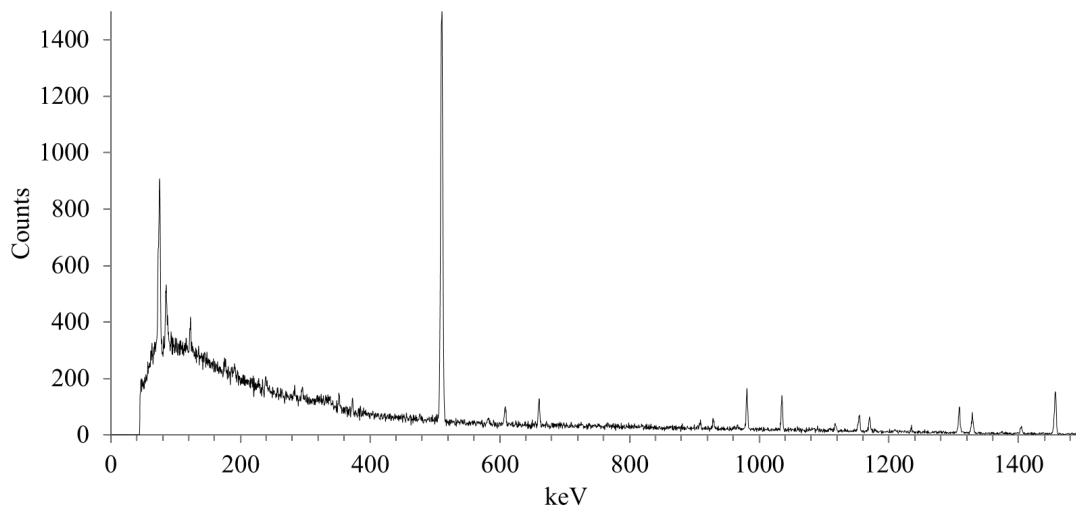


Figure 18. NaI counting station γ -ray spectrum.

The largest peak from the γ -ray decay spectrum of the olivine-gabbro pellet is the 0.511 MeV positron-electron annihilation γ -ray; the peak decreases exponentially over time. Other peaks represent additional decays from Co and Sc, but are difficult to quantify due to poor statistics.

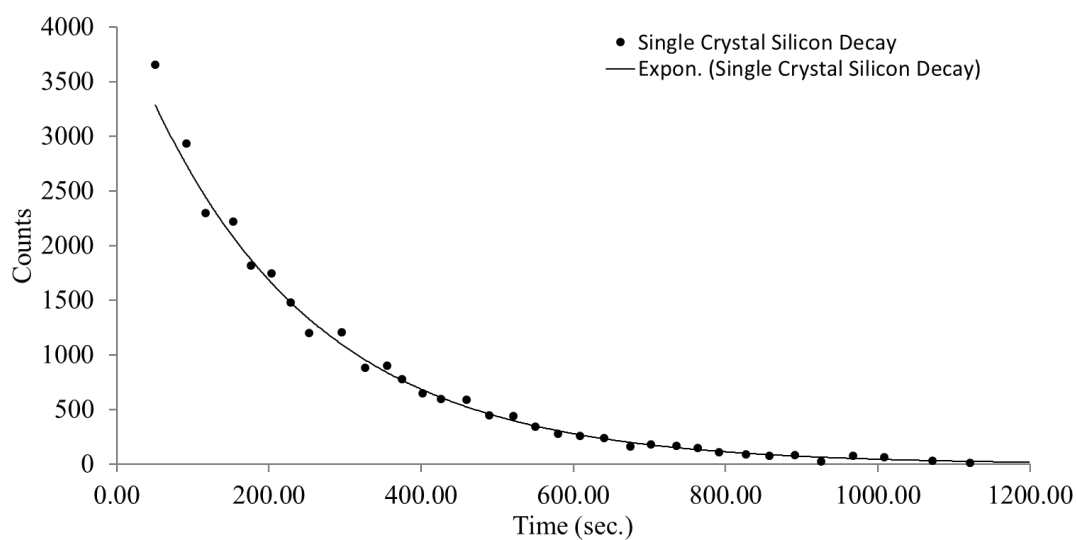


Figure 19. Data with exponential fit from the 0.511 MeV γ -ray of the irradiated Si target at 10 second intervals.

Integrating the peak at 10 sec intervals resulted in a decay curve which when curve fit with an exponential function yielded an exponent of -0.0045 s^{-1} .

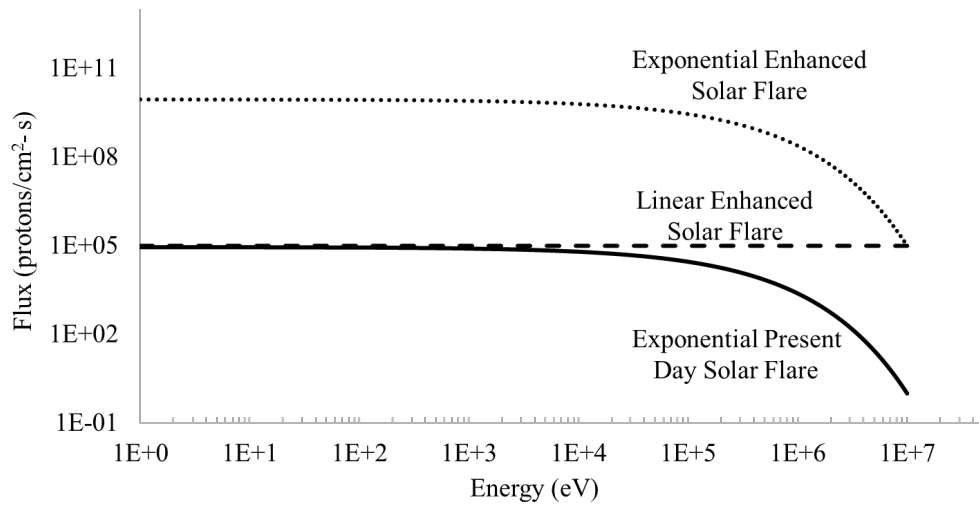


Figure 20. Predicted flux as a function of energy for solar flare protons at 1 AU. Flux as a function of energy for a present day solar flare, an enhanced solar flare with a linear relationship between flux and energy, and an enhanced solar flare with the predicted exponential flux/energy relationship. When the integrated from 0-10⁷ eV, the respective values for flux are 10¹⁰, 10¹², and 10¹⁵ p/cm²-s

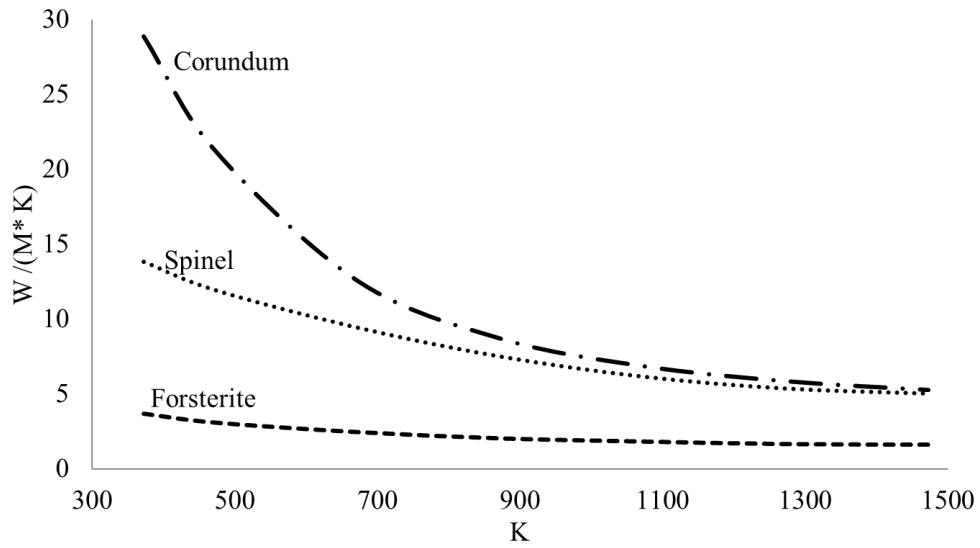


Figure 21. Compiled thermal conductivity values for corundum, spinel, and forsterite as a function of temperature.

Large discrepancies in thermal conductivities exist at low-temperatures, but values converge within a factor of three as the temperature increases.

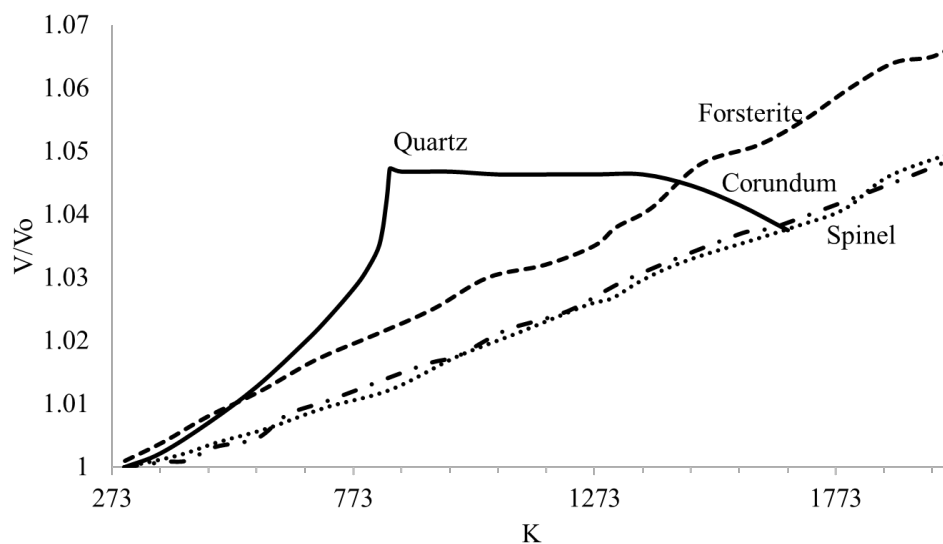


Figure 22. Compiled thermal expansion values for quartz, forsterite, corundum, and spinel as a function of temperature.

Corundum and spinel exhibit similar thermal expansion properties, while forsterite consistently shows ~25% more expansion for similar temperatures. Quartz undergoes a displacive phase transformation at 846 K, resulting in the drastic volume change.

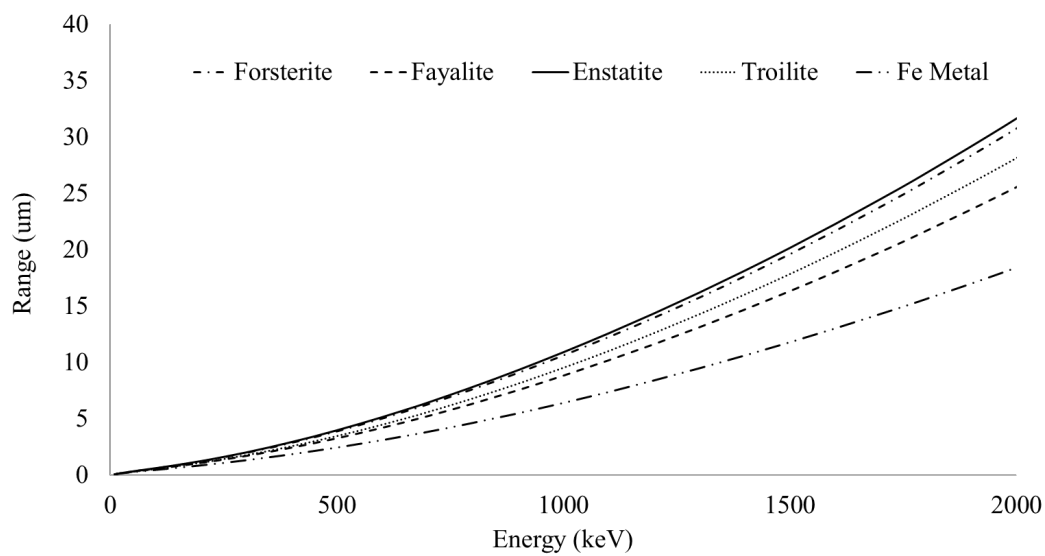


Figure 23. Range or depth a proton travels into chondrite constituents as a function of energy as calculated by SRIM.

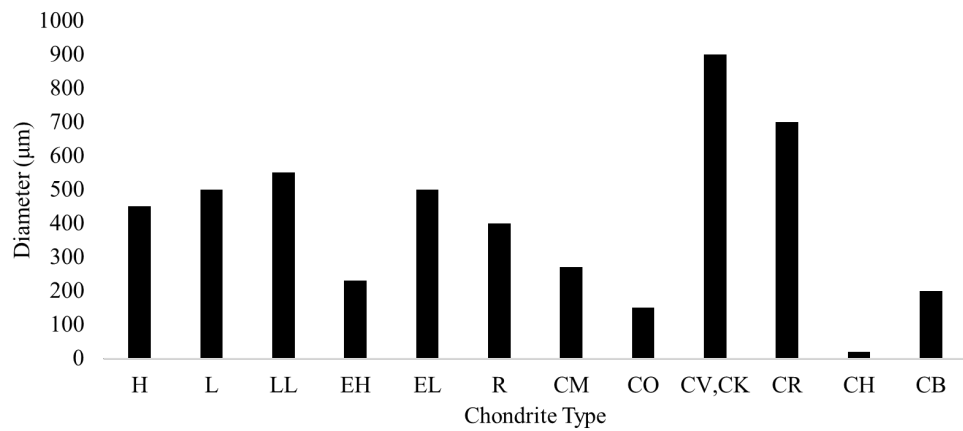


Figure 24. Compiled average size distribution of chondrules in the various classes of chondritic meteorites.

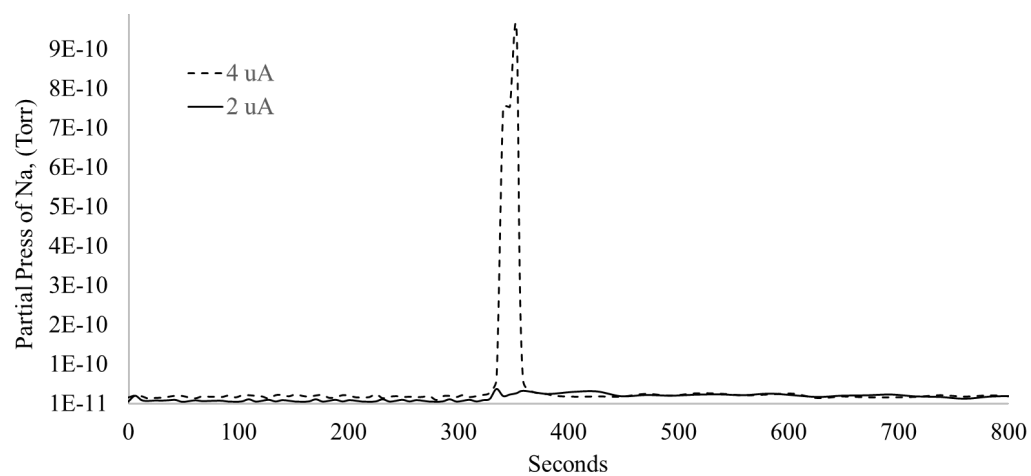


Figure 25. RGA spectrum from the alkali feldspar detailing Na evolution at two different beam current conditions.

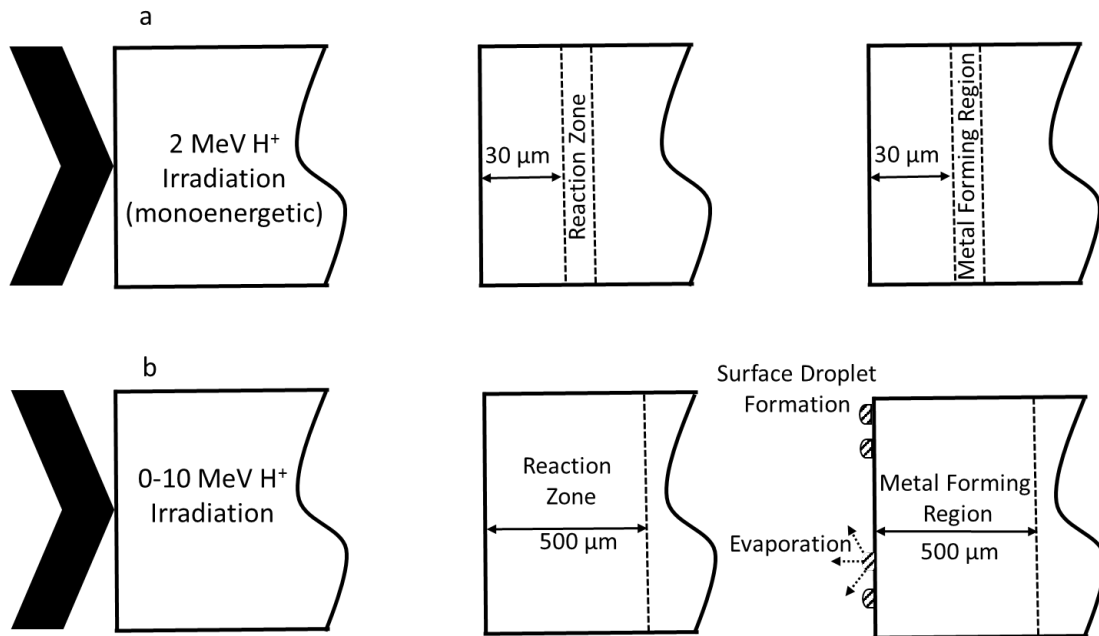


Figure 26. Radiation scenarios responsible for metal distribution from oxide reduction.

Two scenarios for metal formation and distribution: a) monoenergetic reaction where metal formation is limited to the end of range with limited migration of metal to the surface; b) a distribution of energies which results in metal formation over the entire proton range.

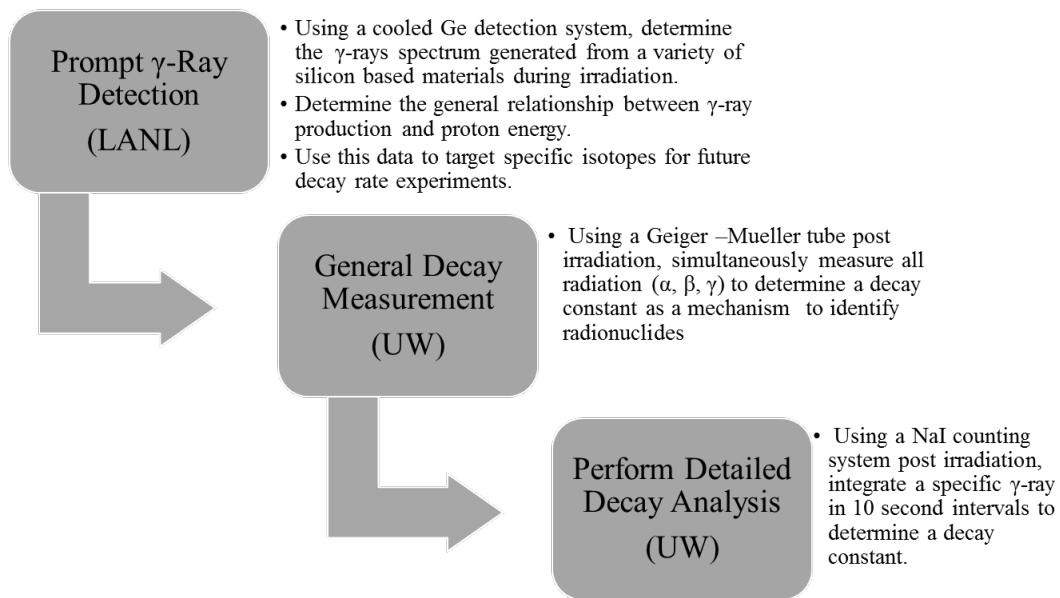


Figure 27. Sequence of radiation measurement experiments performed in this study.

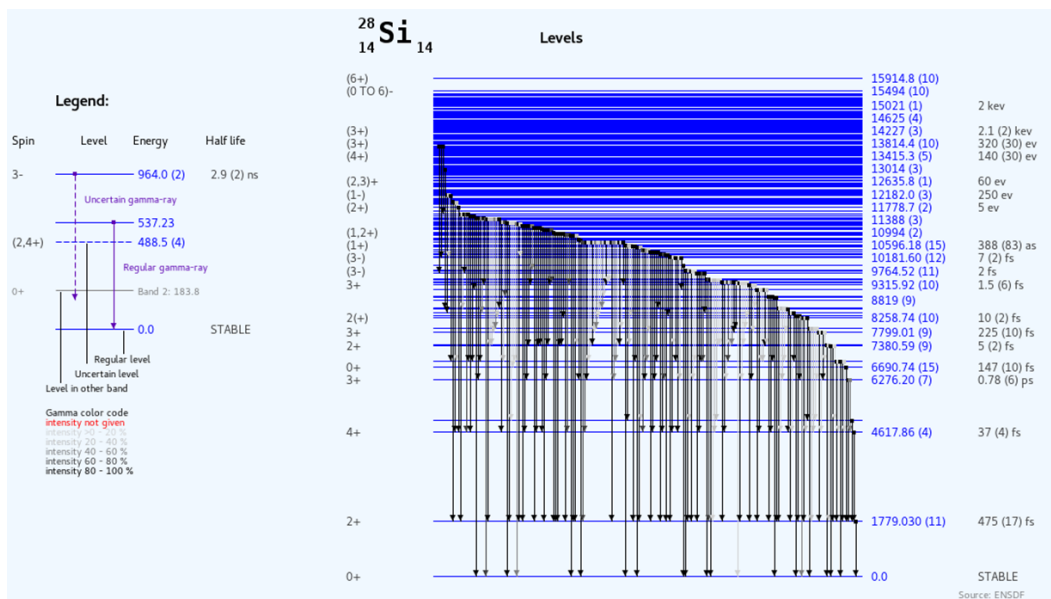


Figure 28. Nuclear transitions in ^{28}Si which can result in the emission of γ -rays.

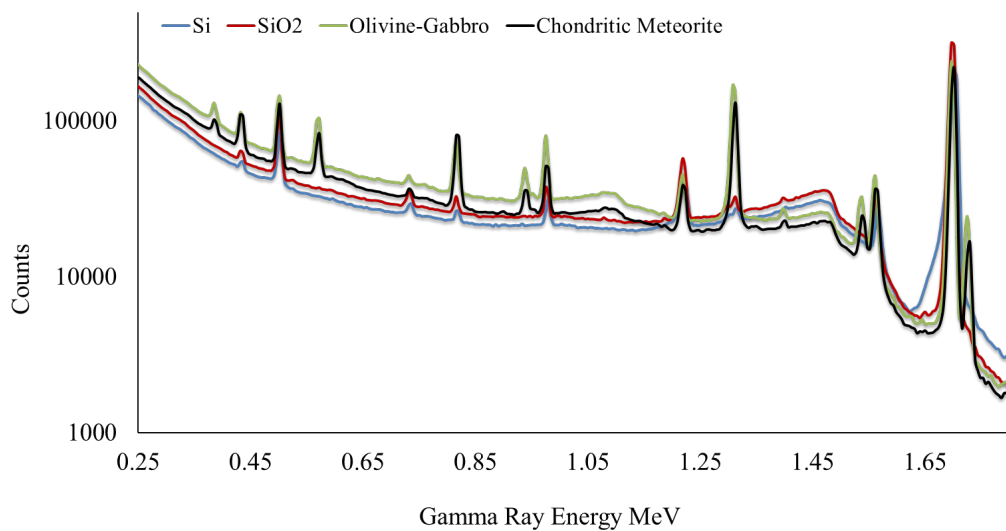


Figure 29. Comparison of Si, SiO₂, olivine-gabbro pellet, and the ordinary chondrite at 3.8 MeV.

Differences in the spectra are indicated in the circles.

Cl28	Cl29	Cl30	Cl31 150 ms ECp	Cl32 298 ms 1+ ECp,ECα,...	Cl33 2.511 s 3/2+ EC	Cl34 1.5264 s 0+ *	Cl35 3/2+ 75.77	Cl36 3.01E+5 y 2+ EC,β-
S27 21 ms ECp,EC2p,..	S28 125 ms 0+ ECp	S29 187 ms 5/2+ ECp	S30 1.178 s 0+ EC	S31 2.572 s 1/2+ EC	S32 0+ 95.02	S33 3/2+ 0.75	S34 0+ 4.21	S35 87.51 d 3/2+ β-
P26 20 ms (3+) ECp	P27 260 ms 1/2+ ECp	P28 270.3 ms 3+ ECp,ECα,...	P29 4.140 s 1/2+ EC	P30 2.498 m 1+ EC	P31 1/2+ 100	P32 14.262 d 1+ β-	P33 25.34 d 1/2+ β-	P34 12.43 s 1+ β-
Si25 220 ms 5/2+ ECp	Si26 2.234 s 0+ EC	Si27 4.16 s 5/2+ EC	Si28 0+ 92.23	Si29 1/2+ 4.67	Si30 0+ 3.10	Si31 157.3 m 3/2+ β-	Si32 172 y 0+ β-	Si33 6.18 s β-
Al24 2.053 s 4+ ECα *	Al25 7.183 s 5/2+ EC	Al26 7.4E+5 y 5+ *	Al27 5/2+ 100	Al28 2.2414 m 3+ β-	Al29 6.56 m 5/2+ β-	Al30 3.60 s 3+ β-	Al31 644 ms (3/2,5/2)+ β-	Al32 33 ms 1+ β-
Mg23 11.317 s 3/2+ EC	Mg24 0+ 78.99	Mg25 5/2+ 10.00	Mg26 0+ 11.01	Mg27 9.458 m 1/2+ β-	Mg28 20.91 h 0+ β-	Mg29 1.30 s 3/2+ β-	Mg30 335 ms 0+ β-	Mg31 230 ms β-n
Na22 2.6019 y 3+ EC	Na23 3/2+ 100	Na24 14.9590 h 4+ *	Na25 59.1 s 5/2+ β-	Na26 1.072 s 3+ β-	Na27 301 ms 5/2+ β-n	Na28 30.5 ms 1+ β-n	Na29 44.9 ms 3/2 β-n	Na30 48 ms 2+ β-n,β-2n,...

Figure 30. Selected area of the chart of the nuclides centered on the Si isotopes.

The black region represents stable isotopes.

			${}^3\text{He}$ in	α in
	β^- out	p in	d in	t in
	n out	Original Nucleus	n in	
t out	d out	p out	β^+ out ϵ	
α out	${}^3\text{He}$ out			

Figure 31. Relative locations of the products of various nucleation reactions.

Possible nuclear reactions relative to an arbitrary “original nucleus” from a proton (p), deuteron (d), triton (t), and helium nuclei (${}^3\text{He}$, α).

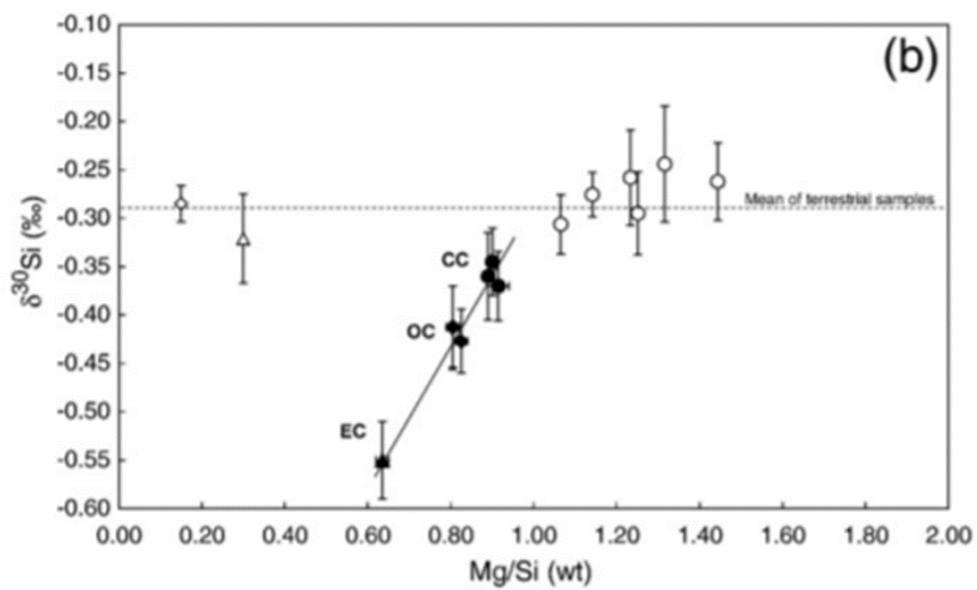


Figure 32. Example data referencing ^{30}Si concentrations as a fractionation effect to separate enstatite, ordinary, and carbonaceous chondrites.

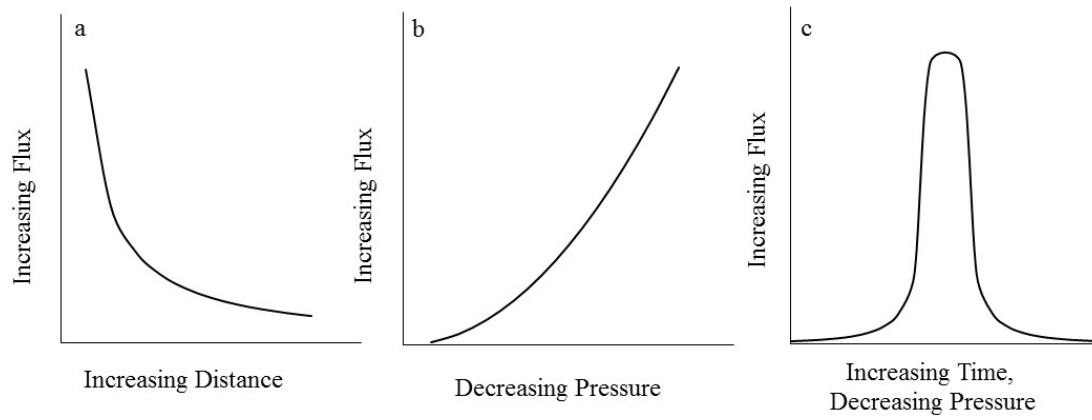


Figure 33. Predicted relationship between flux and (a) distance, (b) pressure, and (c) time and pressure.



Figure 34. Typical jewelry mount which could be used for suspending an olivine or other mineral fragment in a vacuum chamber for irradiation.

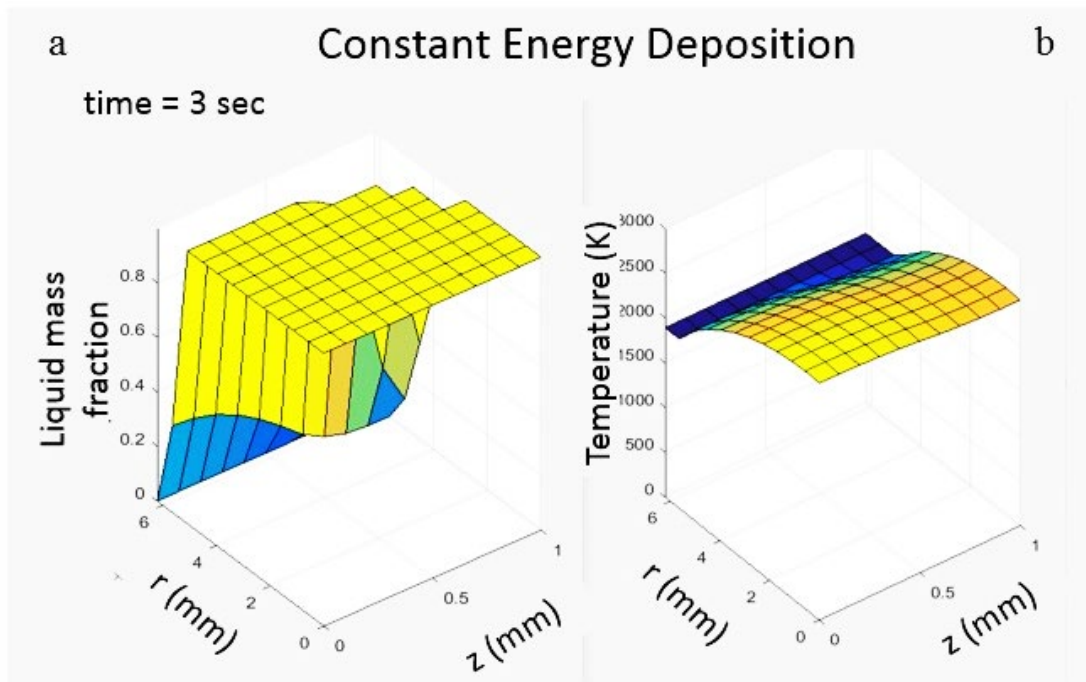


Figure 35. Proton irradiation simulations in synthetic forsterite considering a 100 J/s proton irradiation for 3 seconds.

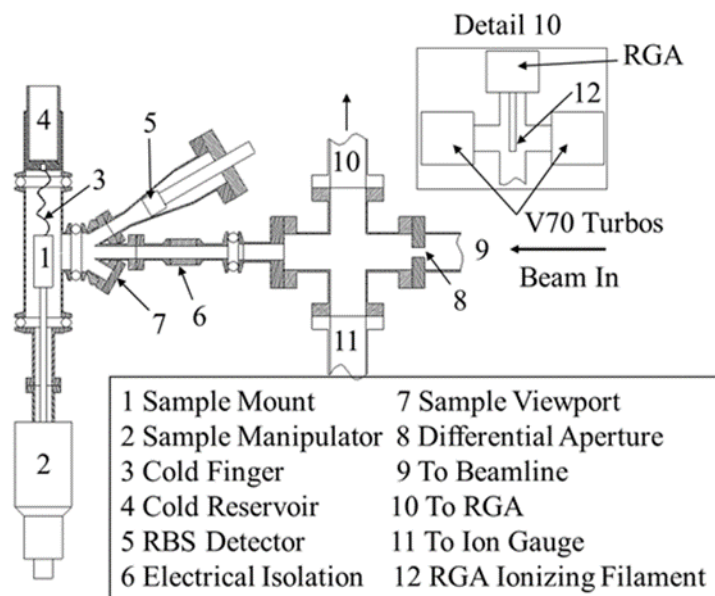


Figure 36. Experimental end-station capable of performing both traditional ion beam analysis and RGA studies.

Volatile products generated on the target located at (1) are pulled in an opposite direction to the beam towards the turbo pumps for the RGA and beamline; the aperture at (8) can be used to restrict loss to the beamline. To assure all gasses generated from exposure were measured by the RGA, a beam transparent window could be inserted at (8) to isolate the chamber completely from the remainder of the accelerator, increasing the sensitivity on the spectrometer.

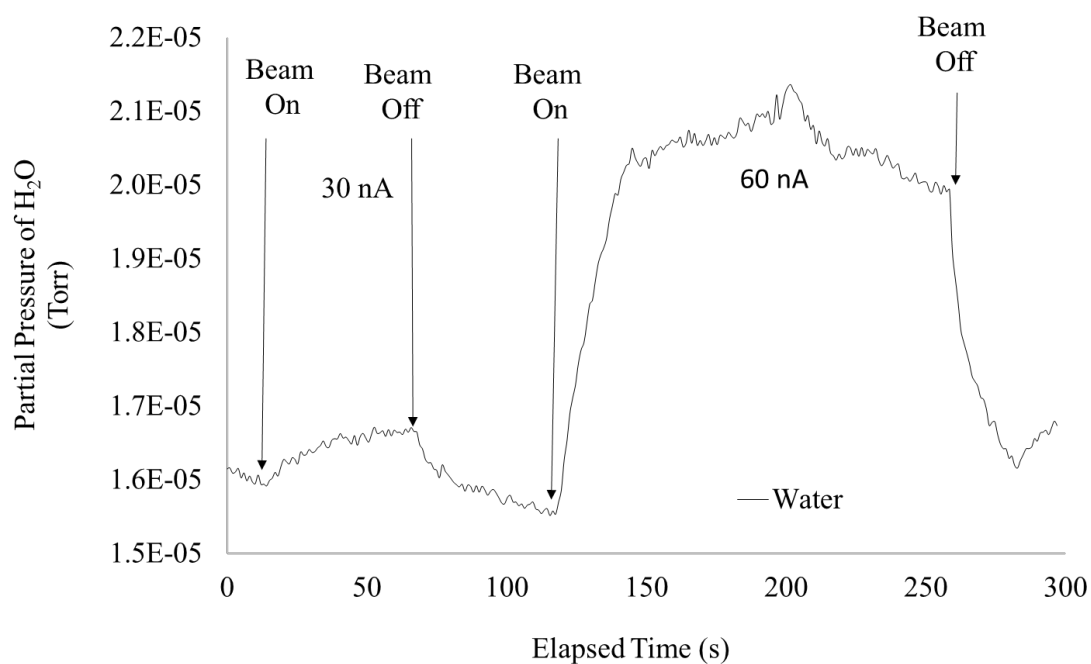


Figure 37. Water release from microcrystalline Portland cement detailing the effect of beam current on the overall change in partial pressure.
 An approximate 5% change in water vapor is detected by the RGA when the slab is irradiated using 30 nA, while a ~70% increase is detected when twice the beam current is used.

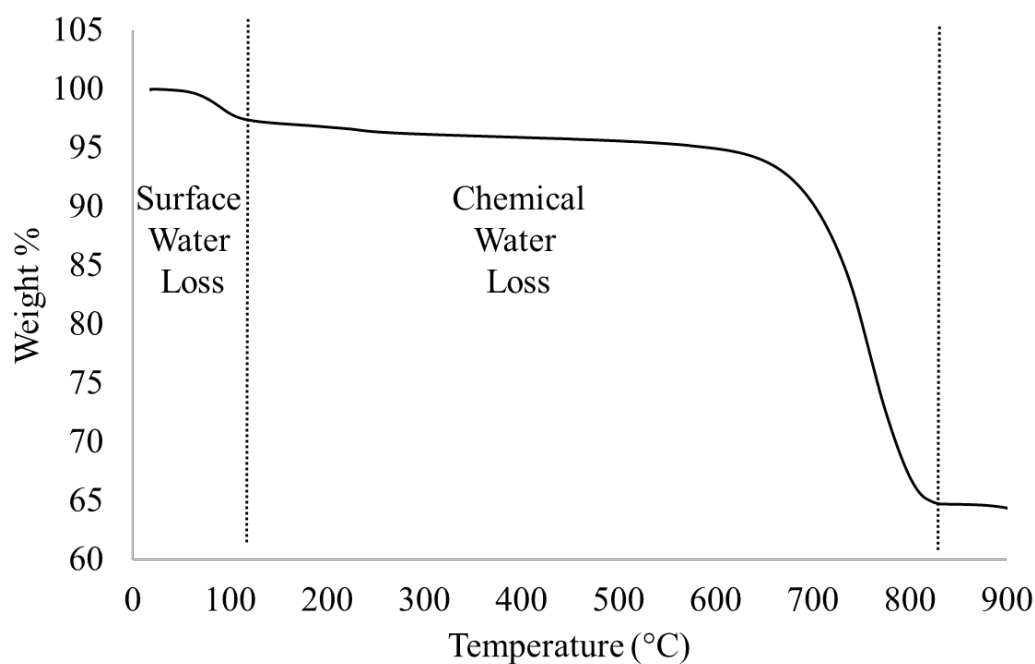


Figure 38. TGA of Portland cement showing mass loss as a function of temperature.

Between 25 and ~105°C the change in weight is from surface water loss. Beyond 105°C, but primarily between ~650°C and ~800°C, weight loss is due to chemical water bound in the C-S-H structure. It is unknown if the water signal measured by the RGA during the irradiation is due to thermal effects from surface and chemical water loss, ionization, or some combination of all three.

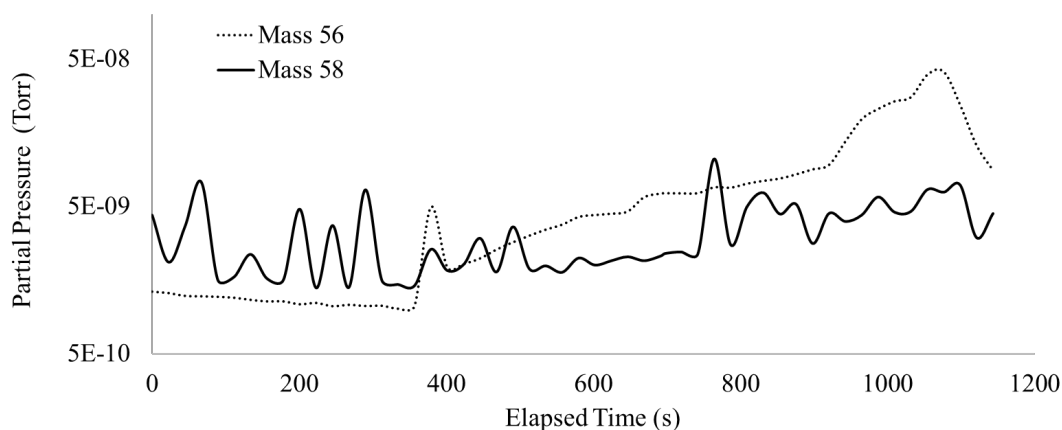


Figure 39. RGA Spectrum from the proton irradiation of a zone purified nickel slab.

The vapor pressures of mass 58 and mass 56 were monitored over time and variable flux conditions. The mass 58 signal showed half order of magnitude changes in the vapor pressure over the course of the irradiation, with only minor correlation to the changes in beam current. However, the mass 56 signal showed regular increases in the partial pressure as the flux conditions changed. Over the course of the irradiation, the visible emission transitioned from the orange to the white, which corresponds to a change in temperature from 900-1200°C. The data indicates that minimal, if any, volatilization from nickel was measured. The mass 56 signal likely correlates to the contaminate hydrocarbon C₄H₈, which is evolved from the target and chamber components as the nickel slab is heated, and this heat is transferred and radiated to the surroundings.

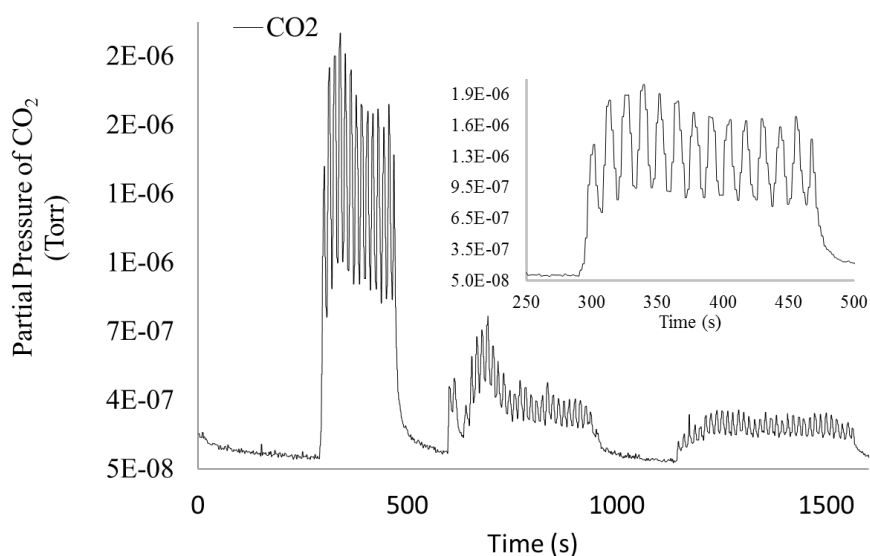


Figure 40. A Kapton® film exposed to three successive 5.5 MeV fluences of $2.7 \times 10^{13} \text{ He}^{++}/\text{cm}^2$.

Beam on and beam off conditions are evident in the sharp increase in the CO₂ signal over background. The beam was rastered (inset) over a 1 cm² area in order to obtain a uniform irradiation and minimize heating; the sharp oscillatory release of CO₂ is the result of the beam hitting the slits and target. A significant reduction in the release of gas is observed over the course of the three irradiations.

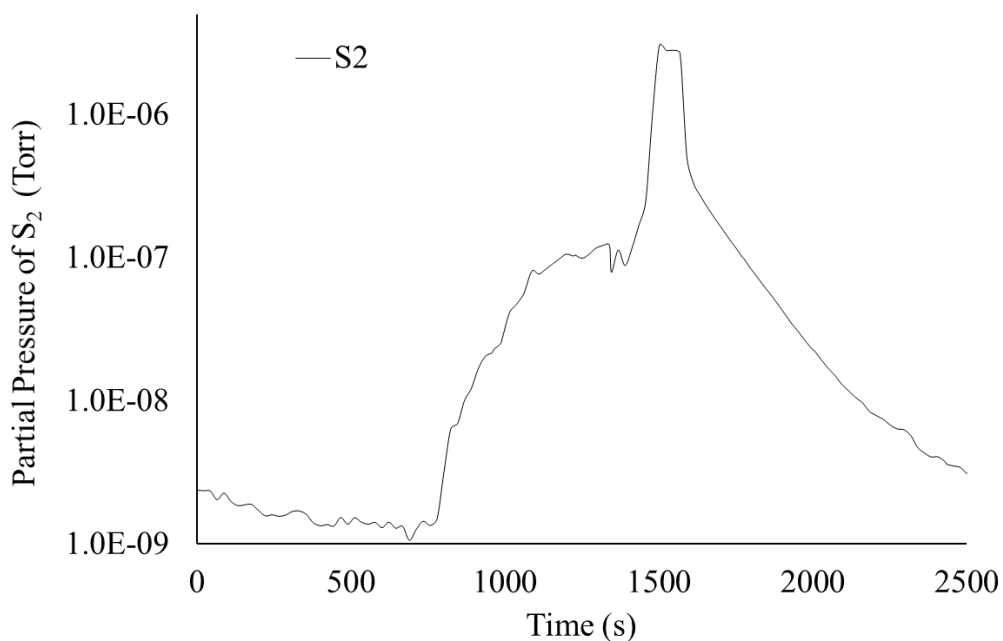


Figure 41. Irradiation of FeS₂ using 2 MeV protons.

A 1 μ A beam was applied after 360 seconds with no measurable effect in the mass 64 signal (S₂). However, at 720 seconds the current was increased by 50% and a significant evolution of S₂ is observed. At approximately 1400 seconds an additional increase in the signal was measured. This is due to the irradiated surface flaking off and exposing a fresh surface of FeS₂ to the beam. The beam was turned off after approximately 1600 seconds.

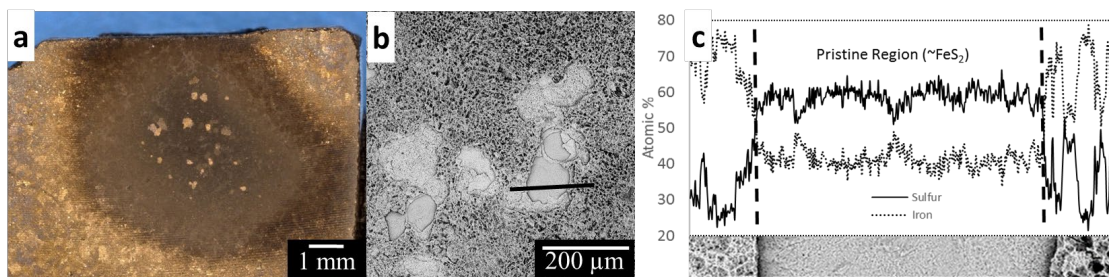


Figure 42. Optical and SEM Images with EDXS analysis.

a) Optical image of the irradiated FeS₂ target showing the darkened area of the beam spot with bright regions located at the beam center; b) BSE SEM image showing texture of the bright flecks and location of an EDS line scan; c) EDS line scan indicating the change in Fe:S ratio over the analyzed region.

VITA

Chris Wetteland is originally from the suburbs of Chicago, where he attended and graduated from Northeastern Illinois University (NEIU) with a BS in Geology. While at NEIU, he participated in a Department of Energy sponsored undergraduate program at Los Alamos National Laboratory (LANL) working with Dr. Kurt Sickafus on radiation damage in ceramics. Upon graduation (1998), he accepted a graduate assistantship at Rutgers University in Materials Science and Engineering. At Rutgers, he conducted research in 3D printing and ion beam analysis of ceramics, while still spending summers at LANL working in radiation effects. He graduated from Rutgers in 2000 with a MS and took a full time staff position at LANL. He later moved back to the Midwest, where he became a Research Fellow at the University of Wisconsin-Madison working on particle accelerators and accelerated aging of nuclear reactor components. Chris came to the University of Tennessee, to work in the Ion Beam Materials Laboratory in 2013. He then moved into a teaching faculty position in the department of Materials Science and Engineering, and began working part-time on his doctorate in Earth and Planetary Sciences. He is presently a Senior Lecturer in the department and teaches three required laboratory courses for undergraduates, supervises senior design projects, and serves on multiple committees in the department and college.