Rock-Forming Minerals Radiation-Induced Volumetric Expansion – Revisiting Literature Data
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Journal of Advanced Concrete Technology, volume 16 (2018), pp.191-209

Development of Soundness Assessment Procedure for Concrete Members Affected by Neutron and Gamma-irradiation
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Journal of Advanced Concrete Technology, volume 15 (2017), pp. 440–523.

Review of the Current State of Knowledge on the Effects of Radiation on Concrete
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Journal of Advanced Concrete Technology, volume 14 (2016), pp.368–383.

Change in Relative Density of Natural Rock Minerals Due to Electron Irradiation
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Journal of Advanced Concrete Technology, volume 14 (2016), pp.706-716
Abstract

Neutron radiation-induced volumetric expansion (RIVE) of concrete aggregate is recognized as a major degradation mechanism causing extensive damage to concrete constituents (Hilsdorf et al. 1978; Seeberger and Hilsdorf 1982; Field et al. 2015). Nearly 400 RIVE data obtained in test-reactors on varied rock-forming minerals were collected by Denisov et al. (2012). These data were input into the Oak Ridge National Laboratory (ORNL) irradiated minerals, aggregates and concrete (IMAC) database and were reanalyzed in order to develop a general empirical model for minerals RIVE and interpret the susceptibility of silicates toward expansion. The empirical models best regression coefficient ($r^2 = 0.95$) is obtained by combining two different modeling techniques: (1) an interpolation-like model based on the relative distance to existing data points, and, (2) a nonlinear regression model assuming varied mathematical forms to describe RIVE as a function of the neutron fluence $\phi$ and the average irradiation temperature. The susceptibility to develop irradiation-induced expansion greatly varies with the nature of minerals. Silicates, i.e., $[\text{SiO}_4]^{4-}$-bearing minerals show a wide range of maximum RIVEs, from a few percents to what appears as a bounding value of 17.8% for quartz. The maximum RIVE of varied silicates appears to be governed, macroscopically, by three parameters: (1) Primarily, the dimensionality of silicate networks. (2) The relative number of Si–O bond per unit cell, and, (3) the relative bonding energy (RBE) of the unit cell.

1. Introduction

1.1 Context

For nuclear applications, the study of irradiation effects on minerals and ceramics is motivated by two issues: (1) finding sustainable encapsulation matrix for radiological waste forms and Pu surplus, and, (2) assessing the long-term operation and the structural significance of exposing the concrete of nuclear power plant to high levels of neutron and gamma radiation, e.g., (Dubrovskii et al. 1967; Kontani et al. 2010; Rosseel et al. 2016).

Long-term operation of nuclear power plants (NPPs) resulting in prolonged neutron and gamma irradiation exposure of the concrete biological shield (CBS) exiting the reactor pressure vessel (RPV), the susceptibility of concrete against irradiation greatly varies as a function of its constituents, i.e., coarse aggregates, sand, and hardened cement paste (hcp). A literature review of publicly available data (Field et al. 2015) and modeling studies (Le Pape et al. 2015; Giorla et al. 2015; Le Pape et al. 2016; Giorla et al. 2017) confirmed anterior studies (Hilsdorf et al. 1978; Seeberger and Hilsdorf 1982) about the dominant role of radiation-induced volumetric expansion (RIVE) of aggregates in the development of damage in concrete subjected to neutron radiation. In particular, higher irradiation susceptibility was found as a direct function of aggregates, i.e., their propensity of swelling was found directly influenced by their minerals contents, structures and textures. Although silicate-bearing aggregates were found to be more RIVE-prone than carbonates, it appears that, for engineering applications, ASTM C294-12 classification of aggregates for concrete fails to characterize the susceptibility of aggregates against neutron irradiation: e.g., Kelly et al. (1969) reported limestone aggregates showing RIVE higher than most silicate-bearing aggregates (i.e., serpentine, flint, dolerite... See (Field et al. 2015, Fig. 8) for details. Hence, to develop a more rational classification of irradiation-sensitive aggregates for concrete, it is necessary to characterize the irradiation effects, and in particular, the radiation-induced swelling of aggregate-forming minerals, i.e., primarily silicates

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The neutron fluence characterizing the number of particles crossing a unit surface is generally given in $\text{n.cm}^{-2}$. Since irradiation exposure in light water reactors and test reactors of concrete constituents reach fluence levels of $10^{19} - 10^{20} \text{n.cm}^{-2}$, fluences are alternatively given in $\text{n.pm}^{-2}$, i.e., $1.0 \text{n.pm}^{-2} = 10^{20} \text{n.cm}^{-2}$ in this article. Also, it is convenient to express fluence for a given energy threshold, i.e., the neutron kinetic energy. In this article, both the usual notation and a specific compact notation are used, i.e., $1.0 \text{n.pm}^{-2} (E > 10 \text{keV})$ is equivalent to $1.0 \text{n}^{10 \text{keV}} \text{.pm}^{-2}$. 

and carbonates. The purpose of this research is to revisit the literature about the effects of irradiation on rock-forming minerals with the objective to derive empirical models to describe the RIVE of minerals commonly found in ordinary concretes used for the construction of CBSs in light water reactors (LWRs).

1.2 Brief review on minerals amorphization

Regarding radiological waste encapsulation, α-decay atom recoils induce the most structural damage, by creating several thousands of permanently displaced atoms, gradually percolating to form clusters of disordered zones. A number of other materials have been actively investigated as possible waste forms, including rutile TiO₂, perovskite CaTiO₃, zirconolite CaZrTi₂O₇, zirconia ZrO₂, zircon ZrSiO₄, pyrochlores GD₃Ti₂O₇ and GD₃Zr₂O₇, APO₄ monazites and other complex oxides, e.g., (Chakoumakos et al. 1987; Ewing et al. 1988, 2003; Weber et al. 1998b, a; Sickafus et al. 1999, 2000, 2007).

Naturally occurring amorphization (metamictization) ofsilicated minerals caused by α-decay of radionuclides (U and Th series) have been studied on titaniite mineral phases brannerite, perovskite, pyrochlore, zirconolite, (Lumpkin 2001) and zircon (Murakami et al. 1991; Nasdala et al. 2001). The amorphization transformation characterizes the evolution from a periodic crystalline state to an aperiodic, i.e., isotropically disordered, state. A number of other materials have been actively investigated as possible waste forms, including rutile TiO₂, perovskite CaTiO₃, zirconolite CaZrTi₂O₇, zirconia ZrO₂, zircon ZrSiO₄, pyrochlores GD₃Ti₂O₇ and GD₃Zr₂O₇, APO₄ monazites and other complex oxides, e.g., (Chakoumakos et al. 1987; Ewing et al. 1988, 2003; Weber et al. 1998b, a; Sickafus et al. 1999, 2000, 2007). Naturally occurring amorphization (metamictization) of silicated minerals caused by α-decay of radionuclides (U and Th series) have been studied on titaniite mineral phases brannerite, perovskite, pyrochlore, zirconolite, (Lumpkin 2001) and zircon (Murakami et al. 1991; Nasdala et al. 2001). The amorphization transformation characterizes the evolution from a periodic crystalline state to an aperiodic, i.e., isotropically disordered, state called metamict (Pabst 1952) in naturally irradiated minerals. The resistance, i.e., the critical amorphization dose (CAD), of natural rock-forming silicates was extensively studied by Wang et al. (1991); Eby et al. (1992) using ionic bombardment. Irradiation effects on zircon (Zr, nesosilicate) and quartz (Qz, tectosilicate) have been the subject of considerable research and, hence, can illustrate these effects. Radiation-induced crystalline-to-amorphous transition (CAT) affects the physical, chemical, optical and mechanical properties of silicates, including (The references are provided as examples since abundant literature is available elsewhere): (1) density decrease, dimensional change, unit cell expansion (Wittels and Sherrill 1954; Wittels 1957; Primak 1958; Lell et al. 1966; Zubov and Ivanov 1966; Bykov et al. 1981; Murakami et al. 1991; Weber et al. 1998b; Maruyama et al. 2016), (2) elastic and hardness properties (Bottom 1947; Mayer and Lecomte 1960; Zubov and Ivanov 1967; Weber et al. 1986; Chakoumakos et al. 1991; Bonnet et al. 1994; Gedeon et al. 2012; Wang et al. 2017), (3) susceptibility to dissolution (Weber et al. 1985; Pignatelli et al. 2016), (4) refractive indices and birefringence (Primak 1958; Wong 1974), (5) thermoluminescence (Frondel 1945), and, (6) color (Frondel 1945). While the CAD of varied silicates have been extensively studied using ion-implantation, the knowledge of the CAD is of limited practical use for the evaluation of the irradiation-induced mechanical damage in concrete-forming aggregates. In addition, while amorphization is the primary neutron-irradiation effect, it does not entirely govern the radiation-induced change of density:

(1) Continued irradiation beyond the CAD can result in continued change of density (Lumpkin and Ewing 1988);
(2) Fused silica, which could be considered as a pre-amorphized materials, exhibits contraction while remaining amorphized but gradually transforming to a different disordered state (Mayer and Lecomte 1960). While a mechanistic understanding of the relation between irradiation-induced amorphization and density change is certainly necessary, engineering-oriented applications require the development of empirical models of irradiation-induced volumetric expansion for a large set of rock-forming minerals.

1.3 Neutron-Irradiation data

Minerals-RIVE caused by neutron-irradiation were collected since the 50s and gathered, notably, in a recently published book (Denisov et al. 2012) (in Russian). As such, it constitutes the largest database ever assembled on this subject. Most data were obtained in Russian test reactors (Krivokoneva and Sidorenko 1971; Krivokoneva 1976; Krivokoneva et al. 1977; Denisov et al. 1979; Bykov et al. 1981; Denisov et al. 1981, 1984, in particular), but also include Western studies (Wittels and Sherrill 1954; Wittels 1957; Primak 1958; Groves and Kelly 1963; Hickman and Walker 1965). In an effort to make the presented data accessible to the public, the Light Water Reactor Sustainability Program of the U.S. Department of Energy has been developing a database, namely IMAC, for Irradiated Minerals, Aggregates and Concrete. Because neutron spectrums vary from one test reactor to another, fluences were pre-normalized by Denisov et al. based on the test reactor spectrums, for energies > 10 keV, to make the data cross-comparison possible. Recent irradiation simulations on silicates and carbonates suggest that 95% of the damage measured in displacements per atom (dpa) occurs at energy above (> 100 keV) for a typical 2-loop pressurized water reactor (PWR) spectrum (Remec et al. 2016); neutrons above 10 keV energy contributing to nearly 100% to the total dpa. Per se, the choice of 10 or 100 keV, as a damage threshold, is somewhat arbitrary as long as consistency is ensured across the data set and that neutrons spectrums are available for fluence conversions. Regarding the data used in this paper, corresponding spectrums of the Russian reactors can be found in Tab. 2.2. of Denisov et al. (2012).

The average irradiation temperature is also provided, which is critical for the determination of predictive RIVE models: higher irradiation temperatures cause the annealing of point-defects resulting in delayed and reduced volumetric expansion rates (Bykov et al. 1981). However, it must be recognized that the knowledge of the total fluence and average irradiation temperature are not sufficient to determine unambiguously the post-irradiation expansion. Test reactors are not operated at constant power because of refueling outages and specific operating cycles governed, for example, by the production of byproducts, such as isotopes. Power cycles cause impor-
tant variations of the neutron flux and temperature of the irradiated specimens during prolonged testing (e.g., Fig. 1 in [Dubrovskii et al. 1967]). In that regard, Le Pape et al. (2016)‘s proposed expansion model and showed that substantial post-irradiation expansion discrepancies can be found assuming either a realistic temperature and flux history, or constant irradiation temperature and flux (i.e., considering average values). In addition, temperature varies within the specimen (energy-deposition induced heating) and the location in the irradiation rig, causing further variations. Unfortunately, the irradiation temperature history could not be found in the publications about irradiated minerals and mineral analogues. Only the average irradiation temperature is provided.

Hence, the interpretation of Denisov et al.’s data requires to account for these inherent uncertainties using a probabilistic approach. The 32 different irradiated minerals studied by Denisov et al. (2012) belong to three general classes: (1) silicates, (2) carbonates, and, (3) oxides. All data were collected after irradiation in varied test reactors located for the most part in Russia. The neutron fluxes were not extensively reported but are estimated, by the authors, in the order of $10^{13}$–$10^{14}$ n.cm$^{-2}$s$^{-1}$ (integrated flux) based on the information provided by on similar reactors (Dubrovskii et al. 1967; Maruyama et al. 2017). The ranges of irradiation dose and temperature are $<10^{11}$ n.cm$^{-2}$, ($<10$ n.pm$^{-2}$) and $30^\circ$C – $300^\circ$C, respectively.

The next section details the proposed empirical models, solely based on phenomenological observations of the swelling curve trends, i.e., without attempting to construct a mechanistic-based model, to estimate minerals RIVE as a function of neutron fluence and irradiation temperature. In the subsequent sections, these models are applied to various mineral groups, and critically reviewed against open literature-based knowledge. In the discussion, the susceptibility, i.e., the lack of tolerance, of varied minerals against neutron irradiation is analyzed to derive an empirical relation between the maximum radiation-induced volumetric expansion and the structural and chemical properties of minerals.

2. RIVE modeling approach

The minerals RIVE database (currently $\approx400$ available data points) can be viewed as a cloud of points in the three-dimensional space of fluence, temperature and volumetric expansion: $\{\Phi, T, \Delta T, \varepsilon_2\}$, respectively. The objective is to develop an empirical model to estimate RIVE as a function of irradiation exposure, i.e., $\{\varepsilon_2^* \sim R(\Phi, T)\}$. Two limitations must be overcome: (1) The data points do not pave consistently the entire ($\Phi$–$T$) plane: Figure 1 provides an illustration for quartz, the mineral providing, by far, the highest number of data. Even, in that favorable case, data points form clusters (pink areas) leaving large unchartered portions (light blue areas). (2) The average irradiation temperature is subject to significant uncertainties (vertical ‘error’ bars in Fig. 1).

The proposed model is based on a combination of two approaches: (1) A nonlinear regression model, i.e., the determination of best-fit parameters, $\{\chi_{\text{data}}^{(k)}\}$ ($n$ is the total number of parameters of the model), is derived by nonlinear least squares minimization using Levenberg-Marquardt algorithm (Levenberg 1944; Marquardt 1963), i.e., finding $\{\chi^{(k)}\}$ to minimize $\left(\sum (\varepsilon_2 - \varepsilon_2^*)^2\right)$. The adopted RIVE mathematical models vary for each type of minerals, e.g., sigmoidal behavior for most silicates, threshold behavior for carbonates, among others. The irradiation temperature uncertainties were accounted for by using a probabilistic approach: the average irradiation temperature for each data point is modeled by a uniform distribution $\tilde{T}_i \sim U(T_i, \pm \Delta T_i)$, and, the output best-fit parameters correspond to the average value of $10,000$ regression analysis. (2) An interpolation model based on a weighted averaging of the neighboring data in the areas of sufficient data density. Note that the term density indicates here the number of data points available in the database within a given radius, $\delta$, in a normalized space of temperature and fluence.

2.1 Empirical equations

The nonlinear regression model assumes a set of empirical equations, which mathematical forms rely on previous studies from the literature, or ‘best-form’ assumptions made by the authors. The mechanistic understanding and quantification of the density change of
irradiated minerals is still a topic of ongoing research although recent progress was made thanks to atomistic modeling, e.g., such as molecular dynamics simulations of irradiated quartz, calcite, albite and almandine (Pingnatelli et al. 2016; Krishnan et al. 2017b; Hsiao et al. 2017, 2018). Hence, the development of RIVE models can only be constructed, at this stage, from the empirical observation of the general swelling curves trends with fluence and irradiation temperature. Several empirical equations have been used in an attempt to capture the change of volumetric expansion $\varepsilon^* (\Phi, T = T_{irr})$ as a function of the irradiation conditions. It must be recognized that these mathematical models only provide a macroscopic description of the RIVE, and by no means, can capture the relation between microscopic defects, the resulting disorders and the macroscopic dimensional changes. It is also important to emphasize that while some minerals RIVE (mostly silicates) clearly exhibits a sigmoidal behavior, other minerals RIVE is much harder to characterize by a definite mathematical form by lack of data. Hence, it is expected that given future research providing additional data, the proposed models will need to be revised. Figure 2 illustrates the different empirical models used in this research. Their description is provided in the next sections.

The maximum volumetric expansion, $\varepsilon^*_{max}$, varies with the mineralogy contents and the nature of the bonds (ionic or covalent). This specific question is the subject of the discussion.

(1) Quartz-Like sigmoidal expansion

At a given average irradiation temperature, post-neutron irradiation dimensional changes of $\alpha$-quartz exhibit a sigmoidal behavior when plotted against the neutron fluence (Bykov et al. 1981) – See Fig. 3. Post-irradiation swelling of irradiated quartz (Zubov and Ivanov 1966) exhibits typical S-shaped curves. The sigmoidal nature of this curve is observed independently of the irradiation temperature (Bykov et al. 1981). Increasing the irradiation temperature reduces the expansion rates as a result of point defect annealing, but the final expansion remains unchanged in the range of $\approx 40{^\circ}\text{C}$ to $< 300{^\circ}\text{C}$.

**Zubov’s model (Z).**

Zubov and Ivanov’s model (Zubov and Ivanov 1966), referred to as (Z) in the following, is based on two main assumptions: (1) The relative change of volume of quartz is proportional to the volume fraction of amorphized materials and to the neutron flux; (2) The rate of creation of the relative change of volume is also a function of the volume fraction of amorphized materials, and, as crude approximation, a linear function was proposed. The integration leads to the so-called Zubov’s equation, presented here in its modified form (Le Pape et al. 2016):

![Diagram](image-url)
\begin{equation}
\varepsilon^*(\Phi, T = T_{\text{ref}}) = \varepsilon_{\text{max}} \frac{1 - e^{-\Phi}}{1 + e^{-\Phi}}
\end{equation}

With \( \Phi \) the characteristic fluence that primarily governs the rate of expansion at the inflexion point of the sigmoid, and \( \Phi_i \) the latency fluence, i.e., the fluence at the inflexion point, which is located at about half of the total expansion. Note that when \( \Phi_i \rightarrow -\infty \), the expansion becomes: \( \varepsilon^*(\Phi, T = T_{\text{ref}}) = \varepsilon_{\text{max}} (1 - e^{-\Phi}) \). Only the temperature dependence of the latency fluence and the characteristic fluence, separately, need to be addressed. Two options are considered in term of temperature dependence: (L) linear (Le Pape et al. 2016) and (A) Arrhenius-like activation (Arrhenius 1889).

**Temperature dependence.**

\( \Phi_i \) and \( \Phi_L \) depend on the irradiation temperature (So does \( \Phi_0 \) for the (N) model presented in the next section). The choice of the reference temperature, \( T_{\text{ref}} \), is rather arbitrary. Since the temperature of the CBS in LWRs is limited to 65°C by design, this value is chosen as the reference temperature. Hence, the minerals RIVE parameters provided in this document are directly applicable to LWRs conditions. Based on the interpretation of Bykov et al.’s data (Bykov et al. 1981; Le Pape et al. 2016) found a quasi-linear relation. It can also be assumed that the temperature effects could be derived through an activation-energy-type relation (Arrhenius 1889).

**Linear model (L) (Le Pape et al. 2016):**

\begin{equation}
\Phi_i(T) = a_i T + b_i \quad \text{or} \quad \Phi_i(T) = a_i (T - T_{\text{ref}}) + \Phi_i(T_{\text{ref}})
\end{equation}

where \( i = c, L \).

Energy activation (A):

\begin{equation}
\Phi_i(T) = \Phi_i(T_{\text{ref}}) e^{\frac{E_{\text{a,j}}}{R} \left( \frac{1}{T} - \frac{1}{T_{\text{ref}}} \right)}
\end{equation}

where \( i = c, L, 0 \) and \( E_{\text{a,j}} \) is the activation energy and \( R \) is the universal gas constant.

**Nucleation-growth model (N).**

Field et al. (2015) showed that a nucleation-growth model, also known as Kolmogorov-Johnson-Mehl-Avrami (KJMA) model (Kolmogorov 1937; Johnson and Meh 1939; Avrami 1939, 1940, 1941), can also correctly reproduce the sigmoidal nature of the expansion curve obtained by gathering literature data on quartz (Wittels and Sherrill 1954; Primak 1958; Mayer and Lecomte 1960; Weissmann and Nakajima 1963; Grasse et al. 1981; de Goer 1986; Bonnet et al. 1994)

\begin{equation}
\varepsilon^*(\Phi, T = T_{\text{ref}}) = \varepsilon_{\text{max}} \left( 1 - e^{-\frac{\Phi - \Phi_i}{\Phi_{\text{ref}}}} \right)
\end{equation}

With \( d \) the characteristic rate and \( \Phi_0 \) the KJMA characteristic fluence. When \( d = 1 \), similar equation has been used by Weber (1981, 1984) and Murakami et al. (1991) to describe the damage ingrowth, i.e., the variation of the lattice parameter \( \Delta a/a_0 \) as a function the alpha dose in CeO₂, UO₂, PuO₂, zircon of PU-doped zircon.

This model is referred to as (N) in the following, and is combined only with Arrhenius-like activation model to account for the effects of irradiation temperature.

**RIVE data collected by Denisov et al. (2012)** suggest that some other silicates, i.e., feldspars, pyroxenes exhibit a similar sigmoidal behavior, although the determination of an exact value for \( \varepsilon_{\text{max}} \) is more uncertain. For hornblends and olivines, the expansion curves do not show a sigmoidal behavior, but rather, a fast expansion rate, gradually decreasing until reaching the maximum expansion plateau. From a mathematical perspective, this behavior corresponds to a degenerated sigmoid, and thus, is derived by the same equations with \( \Phi_i \rightarrow -\infty \) for Zubov’s model, and \( d < 1 \) for the nucleation-growth model. Hence, three different models are tested for most silicates, i.e., (ZA), (ZL) and (NA). Sigmoidal models – (Z) or (N) – appear to successfully apply to the following minerals: alkali feldspars, bromellite, corundum, hornblends, olivines, periclase, plagioclases, pyroxenes and quartz.

(2) Non-Sigmoidal expansions

**Threshold model (T).**

Some minerals expansion do not seem to obey to a well-defined function of fluence and temperature. Such is the case of irradiated carbonates – See Fig. 4. Instead, it appears that beyond a certain fluence, the expansion rapidly reaches a “plateau”. Given the data uncertainties
and the lack of data showing the actual increase of expansion with increasing fluence, the “threshold” model is used as a crude empirical model for minerals generally exhibiting low expansion levels compared to most silicates. This model is simply defined by:

$$\varepsilon^*(\Phi) = \begin{cases} 0, & \forall \Phi \leq \Phi_0 \\ \varepsilon_{\text{max}}, & \forall \Phi > \Phi_0 \end{cases}$$

(5)

This model was applied to the following minerals: ankerite, calcite, dolomite, hematite, magnesite, ankerite, nepheline, rutile, siderite and spinel.

**Caped-exponential model (X).**

Analcime (usually classified as a zeolite mineral, but structurally and chemically, more similar to the feldspatooids (Anthony et al. 2003)) data could not be modeled using regular sigmoidal expansion curves. Data are scarce but suggest a rapid exponential increase in the fluence range of $0 - 2 \times 10^{10} \text{keV}\cdot\text{pm}^{-2}$ at temperatures of about 75 - 95°C. Hence, an exponential growth model is proposed. It maximum value is capped by the maximum expansion value, $\varepsilon_{\text{max}}$.

$$\varepsilon^*(\Phi, T = T_{\text{off}}) = \min\left(\varepsilon_{\text{max}}, \varepsilon^*_{\text{max}} e^{\frac{\Phi - \Phi_0}{T_{\text{off}}}} - 1\right)$$

(6)

It is expected that given future RIVE data available for analcime, this model will also need revision.

**Linear-growth-and-jump (LJ).**

This empirical model has been introduced in an attempt to capture the irradiated expansion of micas. While increasing fluence level causes increasing RIVE, the trend is unclear and was found to be best modeled by a linear relation. The irradiation temperature in the range 45 - 100°C does not seem to have a significant influence on the observed expansion below fluences of $2 \times 10^{10} \text{keV}\cdot\text{pm}^{-2}$. However, at high fluences, some micas display RIVE levels, much higher than a monotonic linear increase could reach. The corresponding data (Crawford and Wittels 1958) are discussed in the text.

$$\varepsilon^*(\Phi, T) = \begin{cases} 1 - \frac{\Phi}{\Phi_0}, & \forall \Phi \leq \Phi_0 \\ \varepsilon_{\text{max}}, & \forall \Phi > \Phi_0 \end{cases}$$

(7)

It is expected that given future RIVE data on micas, this model will need to be revised.

### 2.2 Interpolation model

As illustrated in **Fig. 1**, the post-irradiation expansion data are inhomogeneously distributed in the fluence temperature ($\Phi - T$) plane, typically because higher irradiation flux involve higher temperature, and cooling specimens during irradiation is difficult. In addition, because of mineral sourcing variabilities and measurement uncertainties, expansion data in the ($\Phi - T$) plane are not monotonically distributed with increasing fluence or temperature: i.e., iso-thermal irradiation-induced expansion is expected to increase with the neutron fluence due to amorphization, and, RIVE at a given fluence is expected to decrease with increasing temperature due to annealing effects. Noticeably, for the same exposure ($\Phi_0$, $T_0$), different experimental expansions may be reported. Hence, the proposed “interpolation” approach needs to account for the irregularity, uncertainty and scatter of the data in the ($\Phi - T$) space.

The estimated expansion is solely based on the proximity of data points, $\{\varepsilon_j\} \in N_j$, near a given state ($\Phi_0$, $T_0$) for which a RIVE estimate, $\varepsilon^*_j$, is sought. $N_j$ is the domain defining the vicinity region in the normalized space ($\phi - t$):

$$\text{All } \{\varepsilon_j\} \in N_j, \text{ such that } d_{ij} = \sqrt{(\phi_i - \phi_j)^2 + (t_i - t_j)^2} < \delta$$

(8)

with $\phi = (\Phi - \Phi_{\text{min}}) / (\Phi_{\text{max}} - \Phi_{\text{min}})$ and $t = (T - T_{\text{min}}) / (T_{\text{max}} - T_{\text{min}})$. A value for $\delta$ of 0.15 was arbitrarily chosen. The RIVE estimate (smearred) is calculated as an average of the neighboring data weighted by their respective “distances”:

$$\varepsilon^*_{\text{interpolated}}(\Phi, T) = \frac{\sum_{\varepsilon_j} (1 - d_{ij}) \varepsilon_j}{\sum_{\varepsilon_j} (1 - d_{ij})}$$

(9)

### 2.3 Combined Empirical Model

Finally, the nonlinear regression model and the interpolation model are combined based on a rule that, in higher data density, the interpolation model is more likely to provide accurate predictions, while, in lower data density...
with density of data points above which the interpolation model is considered fully valid. For the proposed calculations, the number in parenthesis corresponds to the variation of the best-fit parameters obtained for the 10,000 simulations run for each mineral or minerals group.

### Table 1 Silicates exhibiting (quasi-)sigmoidal RIVE. Best-fit parameters, regression coefficients and errors.

| Model | Parameters | Quartz, $e_{max} = 17.8\%$ | $\Phi$ | $a_l^{(1)}$ | $b_l^{(1)}$ | $E_{a,L}$ | $\Phi$ | $a_l^{(1)}$ | $b_l^{(1)}$ | $E_{a,L}$ | $\Phi$ | $a_l^{(1)}$ | $b_l^{(1)}$ | $E_{a,L}$ | $\Phi$ | $a_l^{(1)}$ | $b_l^{(1)}$ | $E_{a,L}$ | $\Phi$ | $a_l^{(1)}$ | $b_l^{(1)}$ | $E_{a,L}$ | $\Phi$ | $a_l^{(1)}$ | $b_l^{(1)}$ | $E_{a,L}$ |
|-------|------------|---------------------------|-------|-------------|-------------|---------|-------|-------------|-------------|---------|-------|-------------|-------------|---------|-------|-------------|-------------|---------|-------|-------------|-------------|---------|-------|-------------|-------------|---------|
| (ZL)  | $a_l^{(1)}$ | $b_l^{(1)}$ | $E_{a,L}$ | $\Phi$ | $a_l^{(1)}$ | $b_l^{(1)}$ | $E_{a,L}$ | $\Phi$ | $a_l^{(1)}$ | $b_l^{(1)}$ | $E_{a,L}$ | $\Phi$ | $a_l^{(1)}$ | $b_l^{(1)}$ | $E_{a,L}$ | $\Phi$ | $a_l^{(1)}$ | $b_l^{(1)}$ | $E_{a,L}$ | $\Phi$ | $a_l^{(1)}$ | $b_l^{(1)}$ | $E_{a,L}$ | $\Phi$ | $a_l^{(1)}$ | $b_l^{(1)}$ | $E_{a,L}$ |
| (ZA)  | $a_l^{(1)}$ | $b_l^{(1)}$ | $E_{a,L}$ | $\Phi$ | $a_l^{(1)}$ | $b_l^{(1)}$ | $E_{a,L}$ | $\Phi$ | $a_l^{(1)}$ | $b_l^{(1)}$ | $E_{a,L}$ | $\Phi$ | $a_l^{(1)}$ | $b_l^{(1)}$ | $E_{a,L}$ | $\Phi$ | $a_l^{(1)}$ | $b_l^{(1)}$ | $E_{a,L}$ | $\Phi$ | $a_l^{(1)}$ | $b_l^{(1)}$ | $E_{a,L}$ | $\Phi$ | $a_l^{(1)}$ | $b_l^{(1)}$ | $E_{a,L}$ | $\Phi$ | $a_l^{(1)}$ | $b_l^{(1)}$ | $E_{a,L}$ |
| (NA)  | $a_l^{(1)}$ | $b_l^{(1)}$ | $E_{a,L}$ | $\Phi$ | $a_l^{(1)}$ | $b_l^{(1)}$ | $E_{a,L}$ | $\Phi$ | $a_l^{(1)}$ | $b_l^{(1)}$ | $E_{a,L}$ | $\Phi$ | $a_l^{(1)}$ | $b_l^{(1)}$ | $E_{a,L}$ | $\Phi$ | $a_l^{(1)}$ | $b_l^{(1)}$ | $E_{a,L}$ | $\Phi$ | $a_l^{(1)}$ | $b_l^{(1)}$ | $E_{a,L}$ | $\Phi$ | $a_l^{(1)}$ | $b_l^{(1)}$ | $E_{a,L}$ | $\Phi$ | $a_l^{(1)}$ | $b_l^{(1)}$ | $E_{a,L}$ |

The number in parenthesis corresponds to the variation of the best-fit parameters obtained for the 10,000 simulations run for each mineral or minerals group.

### 3. Results

The parameters obtained by the nonlinear regression analysis for the silicates exhibiting a sigmoidal, or quasi-sigmoidal, RIVE behavior are detailed in Table 1. Additional plots are provided in Appendix - Data analysis. These minerals are quartz, feldspars (plagioclase and potassium feldspar series), pyroxenes and hornblendes. The (ZL) model always leads to lower RIVEs and the RIVE estimates obtained by the combined model. These results indicate that Arrhenius-like activation model accounting for the effects of average irradiation temperature is a more effective approach to derive the RIVE of the studied minerals.

Figure 5 presents the comparison of the experimental RIVEs and the RIVE estimates obtained by the combined model. Similar analysis, not presented here for the sake of conciseness, were performed separately on the nonlinear regression model and the interpolation models. Both approaches lead to coefficients of determination, $R^2$, of ≈ 0.9, while the combined model resulted in an im-

areas, the nonlinear regression model is likely to be more reliable. The weighting factor is governed linearly by the density of data point, $p$, in a given radius.

$$e_i^c (\Phi_i, T) = p \Phi_i (\Phi_i, T) + (1 - p) \Phi_i (\Phi_i, T)$$

With $p = \min(n / n_{max}, 1)$ where $n$ is the number of data points found inside $N_i$ and $n_{max}$ a threshold number of data points above which the interpolation model is considered fully valid. For the proposed calculations, $n_{max}$ is set to 5.

### 3. Results

The parameters obtained by the nonlinear regression analysis for the silicates exhibiting a sigmoidal, or quasi-sigmoidal, RIVE behavior are detailed in Table 1.
proved coefficient of determination of $r^2 \approx 0.95$. Some scatter is still observed at higher expansion levels for some data relative, in particular, to quartz and micas. The observed scatter for some quartz data is likely to be explained by the uncertainties on the irradiation temperature, and, the likely multiplication of quartz sourcing leading to variation of purity of the tested minerals.

4. Discussions

4.1 RIVE Susceptibility of Silicates

More than 90% on the crust is composed of silicate minerals. Most abundant silicates are feldspars – plagioclase ($\approx 40\%$) and alkali feldspar ($\approx 10\%$). Other common silicate minerals are quartz ($\approx 10\%$) pyroxenes ($\approx 10\%$), amphiboles ($\approx 5\%$), micas ($\approx 5\%$), and clay minerals ($\approx 5\%$) (Wedepohl 1971). The remaining silicates comprise 3% of the crust. Only 8% of the crust is composed of non-silicates, i.e., carbonates, oxides, sulfides, etc. Rock-forming silicates are complex minerals. Their specific topology is primarily governed by the degree of polymerization of the $[\text{SiO}_4]^{4-}$ tetrahedra, also, referred to as the dimensionality of silicate polymerization (DOSP) by Eby et al. (1992). Detailed description of the structure of silicates can be found in, e.g., (Eby et al. 1992; Deer et al. 1963, 1997b, c, a, 2001, 2003, 2004, 2009).

The five main classes of silicate structure are: (1) Orthosilicates (island-silicates: isolated (insular) $[\text{SiO}_4]^{4-}$ tetrahedra connected only by interstitial, DOSP = 0) include several groups: phenakite, olivine, garnet, zircon, titanite in particular; (2) Inosilicates or chain silicates – polymerized single or double chains of $[\text{SiO}_4]^{4-}$ tetrahedral extending infinitely in one dimension (DOSP = 1) – include pyroxenes and pyroxenoids (single chain group) and amphiboles (e.g., hornblende, double chain group); (3) Cyclosilicates or ring silicates – chains of tetrahedra joined end-to-end into rings (DOSP = 1.5, intermediate between chains and sheets); (4) Phyllosilicates or sheet silicates – polymerized sheets of tetrahedra extending infinitely in two dimensions (DOSP = 2) – include notably micas, chlorites, clays and serpentines; (5) Tectosilicates or framework silicates – fully interconnected tetrahedra that forms a three-dimensional framework (DOSP = 3); The tectosilicates include various forms of crystalline silica (e.g., quartz, cristobalite), feldspars (plagioclase and alkali-feldspars), feldspathoids and zeolites. (Eby et al. 1992).

Denisov et al.’s RIVE data covers quite extensively the varied silicates classes (the number in parenthesis indicates the number of available data points): Orthosilicates class – olivine group: forsterite (12); Inosilicates class – pyroxene group: single-chain (35); double-chain: hornblende (8); Cyclosilicates class – no data; Phyllosilicates class – mica group (25); cserpentine group (24); Tectosilicates class – quartz (124); feldspar group (65); zeolite/feldspathoid group (11).

![Fig. 5 Combined model. Scatter plot of experimental and empirical model-based RIVEs of minerals. Red marks: silicates; blue marks: carbonates; green marks: oxides. (○) quartz; (▼) plagioclase; (▲) potassium felspar; (■) pyroxene; (●) mica; (★) olivine; (♦) forsterite; (▲) other silicates; (○) calcite; (▼) dolomite; (●) siderite; (▲) magnesite; (▼) hematite; (★) bromellite; (▲) periclase. (a)/(b) $\delta' = \varepsilon' \pm 0.5\%$.](image-url)
(1) Maximum RIVEs of Varied Tectosilicates
Quartz. ($\alpha$-SiO$_2$) is a simple binary oxide and predominantly a covalent-bond material. As such, its simple structure, unique within the silicates family, has led to an abundant literature on the effects of varied irradiation, e.g., (Frodl 1945; Wittels and Sherrill 1954; Primak 1958; Mayer and Lecomte 1960; Weissmann and Nakajima 1963; Grasse et al. 1981; de Goer 1986; Inui et al. 1990; Bonnet et al. 1994; Harbsmeier and Boie 1998; Lebedev et al. 2007; Ibragimova et al. 2014; Krishnan et al. 2017a). “The displacement of atoms in quartz causes a reduction of long-range periodicity at the expense of forming rearranged and distorted polyhedra in order to maintain the short-range bonding requirements.” (Hobbs 1987; Eby 1992) While the maximum RIVE of quartz is well established 17.8% (Zubov and Ivanov 1966), i.e., 15% relative loss of density (Primak 1958; Bonnet et al. 1994) – similar to irradiated silica (Mayer and Lecomte 1960) – by numerous sources under varied temperature and irradiation conditions, the actual maximum RIVE of other silicates is more difficult to determine precisely by lack of sufficient data.

(2) Feldspars
Feldspars (KAlSi$_3$O$_8$ - NaAlSi$_3$O$_8$ - CaAl$_2$Si$_2$O$_8$) crystallize in both intrusive and extrusive igneous rocks, are also present in many types of metamorphic rock, and are also found in many types of sedimentary rocks.

Feldspars can be found in high or low structural state depending on if they retain the high-temperature formation structure, or if they result from slow cooling or crystallization at lower temperatures. Calcic and potassic feldspars are generally considered separately as plagioclases (series ranging from albite, Ab: NaAlSi$_3$O$_8$, to anorthite, An: Ca$_2$Al$_2$Si$_2$O$_8$ end-members along the substitution of Na$^+$ by Ca$^{2+}$ to include oligoclase: $[\text{Ab}_{0.7-0.9}\text{An}_{0.3-0.1}]$, andesine: $[\text{Ab}_{0.5-0.7}\text{An}_{0.5-0.3}]$, labradorite: $[\text{Ab}_{0.3-0.5}\text{An}_{0.7-0.5}]$, bytownite: $[\text{Ab}_{0.1-0.3}\text{An}_{0.9-0.7}]$) and potassium feldspars (potassium-bearing mineral of general formula, $\text{Na}_x\text{K}_{1-x}\text{AlSi}_3\text{O}_8$, such as orthoclase (Or, end-member formula KAlSi$_3$O$_8$), microcline, sanidine, adularia and amazontite, respectively). The two groups meet at the high-sodium end-members, i.e., albite (Ab), oligoclase (Olg) and anorthoclase (Ano).

Feldspar RIVEs are provided by Krivokoneva (1976); Denisov et al. (1979, 1981); Denisov (1986); Denisov et al. (2012) for plagioclases: albite (8), oligoclase (17) and labradorite (4), and for alkali-feldspars: sanidine (7) and microcline (29) (dimorphous with orthoclase). Hence, a large proportion (≈ 85%) of plagioclases RIVE data points corresponds to high-sodium plagioclases (albite content: Ab > 70%). Expansions above ≈ 5% only correspond to oligoclase samples of different origins and tested in different reactors. The apparent maximum RIVE for oligoclase at fluence ranging from $\approx 3.5 - 6\ \text{n}^{\text{E}>10\ \text{keV}}\cdot\text{pm}^2$ and temperature of $< 90 - 130^\circ\text{C}$ can be estimated at about 7%. All other data points fall under ≈ 1.5% regardless of the irradiation temperature ranging from 45°C to 270°C. Without data obtained at high-fluence, i.e., $> 0.5\ \text{n}^{\text{E}>10\ \text{keV}}\cdot\text{pm}^2$, and low-temperature, i.e., $<\approx 80^\circ\text{C}$, it is difficult to conclude whether full-saturation expansions were reached for albite and labradorite. Alkali-felspar RIVEs above 5% are also limited in number but comprise both intermediate and high-potassium members, which interestingly, appear to reach similar levels 8% at fluence $> 4\ \text{n}^{\text{E}>10\ \text{keV}}\cdot\text{pm}^2$ and temperature $< 140^\circ\text{C}$. While the currently available data are lacking to assess the effects of the Na–Ca–K substitution on feldspars RIVE, it seems reasonable as a first approximation to assume that their maximum RIVE is similar, i.e., 7% - 8%, independently of the chemical composition.

However, while most minerals exhibit anisotropic lattice parameter expansion after irradiation, albite lattice constants show either extension or contraction depending on the crystal axis (Seeberger and Hilsdorf 1982; Denisov et al. 2012). Data on irradiated anorthite are scarce but seem to indicate that (1) Anorthite appears more radiation-resistant than albite: The Kr$^+$-ion-induced CAD – i.e., the dose at which an initially-crystallin material becomes fully disordered – for anorthite is nearly 75% higher than the CAD for albite, which is qualitatively consistent with the evolutions of the melting temperature, the elastic properties and the Si–O bond contents (Eby et al. 1992). (2) The amplitude of irradiated-anorthite lattice parameter change appear to be lower than that of albite (Seeberger and Hilsdorf 1982). Except for the end-members, compositional twinning prevents testing mono-crystalline samples (Eby et al. 1992). Perthitic forms, i.e., exsolved lamellae or irregular inter-growths of sodic-alkali-feldspar in a potassium-rich alkali feldspar, can occur leading to heterogenous forms. Hence, pure crystalline form may not provide a complete understanding of natural minerals. As observed by Krivokoneva (1976): “When feldspars are irradiated with neutrons, they also crack and partially disperse, even more so under higher flux intensity: under the microscope, irradiated feldspars appear as if they are intensively pelletized.” As a result, the proposed maximum RIVE value of 7% - 8% is likely to incorporate the volumetric effects of internal cracking, which could govern the expansion behavior more significantly than the radiation-induced crystal lattice parameter changes.

Finally, for the other tectosilicates for which RIVE data are also available, i.e., nepheline and analcime, the exposure range is not sufficient to conclude about their respective maximum RIVE as the reported RIVE values do not exceed 1% for fluorines under $2\ \text{n}^{\text{E}>10\ \text{keV}}\cdot\text{pm}^2$ at $T < 95$ celsius, or at $\approx 4.5\ \text{n}^{\text{E}>10\ \text{keV}}\cdot\text{pm}^2$ at 240°C. These values are, however, comparable to feldspars RIVEs under similar irradiation conditions.

(3) Maximum RIVEs of Varied Micas
Phyllosilicates, or sheet-silicates, refer to layered-structure silicates, such as micas, chlorites, serpentine, and clay minerals. The determination of the maximum
expansion of sheet-silicates is even more difficult, vary considerably in terms of chemical composition, but are all characterized by a platy morphology and perfect basal cleavage, consequence of the layered atomic structure (Deer et al. 2003). The general formula of common micas is (KNaCa)3(AlMgFe)6Si3O10(OHF)4. The most common form is muscovite (di-octahedral, K2Al3[SiAl]6O20(OHF)4 although numerous atoms substitutions are observed) occurring in a wide variety of geological environments. Biotites (end-members: annite, siderophyllite and lepidomelane) denote iron-rich tri-octahedral micas with Mg : Fe < 2 : 1, as an arbitrary differentiation with phlogopites. Micas (phyllo-silicates) are experimentally difficult to work with due to their nearly perfect basal cleavage. In addition, the couple of data on muscovite exhibiting high volumetric expansions > 15% at fluence of 1.5 nE>10 keV·pm^-2 were both obtained at the Material Testing Reactor (MTR) (Crawford and Wittels 1958), while all other data obtained either in Russian reactors, or at Oak Ridge Graphite Reactor, show no expansion higher than < 5% for fluences up to 1.25 nE>10 keV·pm^-2. Hence, it is difficult to assess whether this apparent sudden increase of RIVE around 1.5 nE>10 keV·pm^-2 is caused by abnormal data or by an actual physical mechanism to be determined. However, it should be noted that large expansion variations have already been encountered: (1) Large variation of high thermal expansion perpendicular to the basal plane of phlogopites ranging from 1% to 300% at 600 °C thermal expansion. (2) Premature severe cracking of some irradiated granites was attributed to the presence of micas (Seeberger and Hilsdorf 1982), although it is unclear whether intrinsic irradiation effects or temperature gradient within the specimens are the main cause. In addition, the irradiation-induced damage and expansion in such minerals can result from (1) the localized amorphization and shallow etch pit formation in the crystalline sheets (Fukuda et al. 1989; Singh et al. 2010), and, (2) the formation of gaz bubbles by heating of interlayer water or the implantation of rare gas (Hishmeh et al. 1993; Templier et al. 1996).

(4) Maximum RIVEs of Varied Inosilicates

Pyroxenes. Pyroxenes are a group of important rock-forming inosilicate minerals found in many igneous and meta-morphic rocks. The general pyroxene formula is XY(SiAl)2O6 where X and Y are cations of various nature due to the incorporation flexibility in the chain silicate structure: Ca, Na, Fe2+ and Mg and more rarely Zn, Mn and Li. Typical pyroxenes are augite (monoclinic, (CaNa)(MgFeAlTi)(SiAl)2O6), diopside or diopside-hedenbergite (monoclinic, CaMgSi2O6 to CaFe2+Si2O6), enstatite (orthorhombic, Mg2Si2O6). Irradiated diopside and diopside-hedenbergite samples in the temperature range of ≈75 °C to 130 °C at relatively high fluence levels, i.e., 2 to 6 nE>10 keV·pm^-2, exhibit similar volumetric expansion ≈ 2.5% – 3%, although some significant scatter at the highest fluences ≈ 6 nE>10 keV·pm^-2 is observed. No data above ≈ 2 nE>10 keV·pm^-2 is available for irradiated enstatite. However, diopside and enstatite data appear consistent at similar irradiation exposure suggesting that both mineral could exhibit similar RIVEs.

Regarding hornblendes, data are limited to the volumetric expansions derived from the changes in crystal lattice parameters, which can largely underestimate the actual dimensional change on irradiated samples, e.g., (Seeberger and Hilsdorf 1982). Except a single data point, all fluences are < 2 nE>10 keV·pm^-2 for rather cold temperatures 45 – 95 °C. Hence, it is difficult to assert what the maximum RIVE value for hornblende actually is. The proposed value of ≈ 1.5% should be considered only as a mere approximation based on the limited available data.

(5) Maximum RIVEs of Varied Orthosilicates

Orthosilicates (island-silicates: isolated (insular) [SiO4]4- tetrahedra connected only by interstitial) includes several groups: phenakite, olivine, garnet, zircon, titanite, in particular. Olivines are magnesium-iron silicates (end-members: forsterite Mg2SiO4, fayalite Fe2SiO4) often incorporating other elements such as manganese, calcium or nickel (Eby et al. 1992). Denisov et al. provide data on forsterite (9), and magnesian olivine (2), i.e., presumably close to forsterite. Crawford and Wittels (1958)’s data also refers to forsterite. Hence, the provided dataset seems only relevant for magnesian olivines, and not for all types of olivines. In particular, it should be noted that ion-beam irradiation data indicate that the irradiation resistance of forsterite (Wang et al. 1998; Carrez et al. 2002; Christoffersen and Keller 2012) is much higher than that of fayalite (Eby et al. 1992). Neutron-irradiation-induced volumetric expansions of olivines gathered by Denisov et al. (2012); Crawford and Wittels (1958) are limited in number (12 data points) and exhibit important scatter at similar irradiation temperature: e.g., at 65 °C, olivine RIVEs range from 0.3% to 0.9%. The RIVE variation range appears to narrow to [0.3%, 0.9%] at higher temperatures and fluences. Hence, a tentative best-fit analysis led to extremely poor regression coefficients and large errors. Consequently, no attempt to use Zubov’s equation on the olivines dataset could be justified without additional confirmatory data. Eq. (11) provides RIVE estimates using the bounding values found by Denisov et al. (2012); Crawford and Wittels (1958)

\[
\varepsilon(\Phi > 0.1 \text{n pm}^{-2}, T > 85^\circ \text{C}) \approx 0.5\% - 0.9\%
\]

(11)

(6) Summary

Table 2 summarizes the main results of the best-fitting analysis of the empirical models along with other physical characteristics and critical amorphization doses (ion-irradiation, (Eby et al. 1992)). Although the number
of data is insufficient to attempt a regression analysis, it appears quite clearly that the DOSP of silicate minerals is a major factor influencing the expansion susceptibility. Higher DOSPs appear to result in higher radiation-induced expansions. The Si–O covalent bond (bond dislocation energy: \( BDE = 800 \text{kJ mol}^{-1} \)) is stronger and more directional than other, mostly ionic, bonds in silicates (e.g., Na–O: 270 kJ mol\(^{-1} \); K–O: 275 kJ mol\(^{-1} \); Ca–O: 383 kJ mol\(^{-1} \), Al–O: 502 kJ mol\(^{-1} \)) (Luo 2007). Under irradiation excitation, the lower energy bonds are more likely to reorganize and maintain atomic topological constraints (Pignatelli et al. 2016). In other words, more coordinated [SiO\(_4\)]\(^4-\) tetrahedron results in higher long-range disordering under irradiation, e.g., > 3 Å in quartz (Krishnan et al. 2017a). The RIVE susceptibility is therefore increased for higher cell bond energy and higher number of Si–O bonds. As a first-order approximation attempt, the RIVE susceptibility, defined empirically in terms of propensity to exhibit volumetric expansion, has been developed by the authors by an index, \( I \in [0;1] \), function of the dimensionality of SiO\(_4\) polymerization (DOSP), the relative number of Si–O bond per unit cell (#Si–O), and the relative bonding energy (RBE), i.e., the bonding energy normalized by that of quartz on (24–O) unit cells (Keller 1954) – See corresponding data in Table 2:

\[
I = \frac{1}{4} \#\text{Si}–\text{O} \times \text{RBE}(1 + \text{DOSP})
\]

Table 2 Summary of irradiated silicates RIVE best-fit models (ZA) and physical characteristics.

| Silicate Family     | Sample          | \( I_{\text{max}} \) | \( \Phi_r \) | \( \Phi_l \) | \( r^2 \) | \( crr \) | \#Si–O | RBE | CAD |
|---------------------|-----------------|----------------------|-------------|-------------|---------|----------|--------|-----|-----|
| Tectosilicate       | quartz          | 17.8%                | 0.38        | 1.00        | 0.85    | 4.5%     | 3      | 1.00| 1.00| 1.4 |
|                    | plagioclase     | 7.0%                 | 0.15        | 1.61        | 0.96    | 0.8%     | 3      | 0.50| 0.86-0.92| 1.6-2.7 |
|                    | K-spar          | 7.7%                 | 0.19        | 1.56        | 0.94    | 1.2%     | 3      | 0.50| 0.91-0.92 | 1.6- |
| Feldspar            | nepheline       | <0.7%*               | n.a.        |              |         |          | 0.2%   | 3   | 0.85 |
| Phyllosilicate      | mica            | <5.0%†               | n.a.        |              |         |          |        |     |     |
| Cyclosilicate       | no irradiation data available | 1\(^{12}\) | | | | | | |
| Inosilicate         | single chain    | pyroxene             | 2.8%        | 0.28        | 0.62    | 0.81     | 0.4%   | 1   | 0.364| 0.86 | 2.1-2.6 |
|                    | double chain    | hornblende           | 1.5%‡      | 0.57        | –∞      | 0.80     | 0.2%   | 1   | 0.400| 0.85 |        |
| Ortho/Sorosilicate  | Mg-olivine      | = 0.8%               | 0.56        | –∞          | low     | 0.3%     | 0     | 0.250| 0.80 | 1.6  |

\( a \): Eby et al. (1992), \( b \): Keller (1954). \( \dagger \): Denisov et al.’s data excluding Crawford and Wittels’s data. \( \approx \): no RIVE data above 1.7 \( \text{nE}\text{keV}\text{pm}^{-2} \). DOSP: dimensionality of SiO\(_4\) polymerization. \#Si–O: relative number of Si–O bond per unit cell. RBE: bonding energy relative to quartz bonding energy (24–O) unit cells. CAD: critical amorphization dose under 1.5 MeV Kr\(^+\)-irradiation. 

\( I_{\text{max}} \approx 15\% \), \( I_{\text{max}} \approx 15\% \).

\( : \) crystal lattice volumetric change. \( : \) no RIVE data above 1.7 \( \text{nE}\text{keV}\text{pm}^{-2} \).

DOSP: dimensionality of SiO\(_4\) polymerization. \#Si–O: relative number of Si–O bond per unit cell. RBE: bonding energy relative to quartz bonding energy (RBE, i.e. the bonding energy normalized by that of quartz on (24–O) unit cells (Keller 1954)) – See corresponding data in Table 2:

\[
I = \frac{1}{4} \#\text{Si}–\text{O} \times \text{RBE}(1 + \text{DOSP})
\]

**Figure 6** shows the correlation between the RIVE susceptibility index, \( I \), and the maximum RIVE expansion normalized by that of quartz, i.e., \( \frac{I_{\text{max}}}{I_{\text{max}}(\text{qz})} \) (Left figure) and puts it in perspective with the weathering tolerance of silicates against weathering.
tolerance (Goldich 1938) of the same silicates also know as the Goldich series (Right figure). As a general trend, increasing silica content, number of covalent bonds and degree of silicate polymerization (DOSP) result in both higher weathering resistance and higher RIVE. However, noticeable difference needs to be emphasized: (1) The left branch of the Goldich series shows a gradual increase of resistance comparable to the gradual increase of radiation-induced expansion branch, i.e., from olivine to quartz, with the notable difference that, in terms of weathering resistance, micas do not seem to exhibit similar behaviors: Muscovite shows a higher resistance to weathering than alkali-feldspars, themselves showing better resistance than biotites. Interestingly, the two RIVE data points collected by Denisov (corresponding to Crawford and Wittels’s data) show quite high expansion, ≈ 15% (hence the vertical dashed line in the RIVE figure) while the biotite. Interestingly, Seegerberger and Hilsdorf (1982) state that “The elongation of the muscovite is hindered during the irradiation so that micro-fractures form due to the tensile stresses developing in granite. With neutron fluence of 2.5 - 5 x 10^{18} n\cdot cm^{-2} (fast flux), the fracture formation leads to a complete destruction of the granite.” (origin: Schwartzwald). Hence, further research is needed to determine whether muscovite exhibits higher RIVE-sensitivity than other micas. (2) Calcium-sodium substitution results in variation of the plagioclase stability (right branch of the Goldich’s diagram). In the Denisov’s data, the high RIVE values (similar to the alkali-feldspar values) corresponds to oligoclase samples only by lack of data on other plagioclases at high fluence/low temperature. Hence, the collection of additional data on various plagioclases appears necessary.

No apparent correlation could be found between the characteristic and latency fluences, \( \Phi_1 \) and \( \Phi_2 \) considered independently or combined – (\( \Phi_1 + 2 \Phi_2 \)) provides an approximation of the fluence level near maximum RIVE – and the critical amorphization dose derived by selected area electron diffusion (SAED) pattern analysis of mineral samples irradiated at 1.5 MeV Kr\(^+\)-irradiation (Eby et al. 1992).

### 4.2 RIVE susceptibility of carbonates

A total of 20 post-irradiation expansions on carbonates including the end-members, i.e., calcite – (Cal), CaCO\(_3\), 9 data –, siderite – (Sd), FeCO\(_3\), 2 data –, and, magnesite – (Mgs, MgCO\(_3\), 5 data –, and intermediate members, i.e., dolomite – (Dol), CaMg(CO\(_3\))\(_2\), 2 data –, and ankerite – (Ank), Ca(Fe\(^{2+}\)MgMn\(^{2+}\))(CO\(_3\))\(_2\), 2 data), “brown spar” – were collected by Denisov et al. (2012); Wong (1974). To the exception of ankerite showing a volumetric expansion of \( \approx 1.3% \) at 0.1 n\(^{E=10\text{keV}}\)\cdot pm\(^{-2}\) (80°C) and \( \approx 3.3% \) at 0.57 n\(^{E=10\text{keV}}\)\cdot pm\(^{-2}\) (1400°C), all measured expansions at fluences above 0.051 n\(^{E=10\text{keV}}\)\cdot pm\(^{-2}\) and temperatures ranging from 60°C to 240°C fall between \( \approx 0.3% \) and 0.8%. The absence of specific information about the actual mineralogy and texture of the “brown spar” and the “abnormal” radiation-induced expansion, possibly resulting from the presence of impurities or more expansive phases, leads to discard these two data points. On natural calcite crystals (Mexico), Dran et al. (1992) estimated post-ion-irradiation step-height contraction of 3.5% and 5%, respectively at 10\(^{14}\) He\cdot cm\(^{-2}\) and at 10\(^{15}\) He\cdot cm\(^{-2}\) (1.8 MeV, T < 100°C). No contraction nor swelling was observed on similar samples under 200 keV Pb-ion bombardment at doses up to 6\( \times 10^{16}\) He\cdot cm\(^{-2}\). Using Raiteri’s potential (Raiteri et al. 2015), Krishnan et al.’s molecular dynamics (MD) simulations [UCLA, private communication] estimate the contraction of dolomite around 1% at 10\(^{18}\) keV cm\(^{-2}\) deposited energy.

Calcite expansions appear to be lower than dolomite and magnesite expansions at comparable doses. Consistently, after neutron irradiation at fluences up to 0.05 n\(^{E=10\text{keV}}\)\cdot pm\(^{-2}\) (Tab. 5 of (Seeberger and Hilsdorf 1982)) found elementary cells volumetric variations (X-ray diffraction (XRD) analysis) of -0.5% to 2.0% for calcite and 2.8% for dolomite. Krivokoneva et al. (1977) observed that the increase of Mg–Ca substitution (calcite, magnesian calcite (apopericlase marble, 1.7% – 3.1% MgCO\(_3\) molar content), dolomite) reduces the radiation resistance of carbonates. At similar neutron fluences, i.e., \( \approx 0.6 - 0.7 n^{E=10\text{keV}}\cdot pm^{-2}\), anisotropic lattice expansion of 0.5% along c-axis is observed on dolomite, 0.16% of the magnesian calcite, and no change of pure calcite (Krivokoneva et al. 1977). This effect is attributed, by Krivokoneva, to the loss of ionicity resulting by the higher electronegativity of Mg in regard to Ca, resp. 1.31 and 1.00 by Pauling’s scale (Pauling 1932). It must be clarified, here, that electronegativity only provides a crude approximation of the sensitivity of materials to irradiation (Eby et al. 1992; Trachtenko 2004). Neutron-irradiated siderite (Fe Pauling’s scale: 1.83) expansion appears to be close to dolomite (Krivokoneva et al. 1977).

The literature data on neutron irradiated carbonates do not allow to delineate a clear trend in terms of swelling rate, as it appears that an expansion plateau is rapidly reached above fluence of 0.05 n\(^{E=10\text{keV}}\)\cdot pm\(^{-2}\). Hence, no attempt to use Zubov’s equation on the carbonate dataset could be justified. Eq. (13) provides RIVE estimates using the bounding values found by Denisov et al. (2012); Wong (1974).

\[
\varepsilon(\Phi > 0.05 n^{E=10\text{keV}}\cdot \text{pm}^{-2}, \forall T) \approx \cdots
\]

\[
0.3% \text{ - } 0.5% \quad \text{for calcite}
\]

\[
0.4% \text{ - } 0.8% \quad \text{for dolomite}
\]

\[
0.55% \text{ - } 0.7% \quad \text{for siderite}
\]

\[
0.3% \text{ - } 0.45% \quad \text{for magnesite}
\]

### 5. Conclusions

The extensive set of neutron-radiation-induced volu-
metric expansion of rock-forming minerals collected by Denisov et al. (2012) (≈400 data points) was re-analyzed in order to develop an empirical RIVE model applicable to promote further research on the effects of irradiation on aggregate and concrete in LWRs. The best regression coefficient, \( r^2 \approx 0.95 \), was obtained by combining two different modeling techniques: (1) an interpolation-like model based on the relative distance to existing data, and, (2) a nonlinear regression model assuming varied mathematical forms to describe RIVE as a function of the neutron fluence and the average irradiation temperature. Despite the important uncertainties on the collected data, the proposed model estimates the empirical RIVE within \( \varepsilon^2 \pm 1.5\% \) with a 90% confidence when the whole dataset is considered.

The susceptibility to develop an irradiation-induced expansion greatly varies with the nature of minerals. Carbonates, i.e., \( \text{CO}_2^2 \) ion bearing minerals, mainly forming limestones and dolostone, exhibit relatively low RIVEs < 1%. The substitution of Ca by Mg leads to higher RIVEs. Silicates, i.e., \( [\text{SiO}_2]^m \) bearing minerals show a wide range of maximum RIVE, from a few percents to what appears as the bounding value of 17.8% for quartz. The maximum RIVE of silicate appears to be governed, macroscopically, by three parameters: 1. Prioritization of SiO polymerization (DOSP), then, 2. the relative number of Si–O bond per unit cell, and, 3. the relative bonding energy (RBE) of the unit cell. The maximum RIVEs of silicates are ranked in the following decreasing order: quartz, feldspars, pyroxenes and amphiboles. The determination of the maximum RIVE for micas and other tectosilicates, such as nesophile or homblende, requires additional irradiated data. Importantly, the macroscopic RIVE appears, in many cases, to result from internal cracking or “pelletization” of the irradiated minerals, due to impurities or structural heterogeneities (twinnings, perthitic forms, irregular intergrowth forms) possibly causing differential strains.

Acknowledgement
This material is based upon work supported by the U.S. Department of Energy, Office of Nuclear Energy, Light Water Reactor Sustainability Program, under contract number DE-AC05-00OR22725.

This manuscript has been authored by UT-Battelle, LLC under Contract No. DE-AC05-00OR22725 with the U.S. Department of Energy. The United States Government retains and the publisher, by accepting the article for publication acknowledges that the United States Government retains a non-exclusive, paid-up, irrevocable, worldwide license to publish or reproduce the published form of this manuscript, or allow others to do so, for United States Government purposes. The Department of Energy will provide public access to these results of federally sponsored research in accordance with the DOE Public Access Plan (http://energy.gov/downloads/doe-public-access-plan).

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Appendix - Data analysis
The data set used for this study is too large to be reproduced in this article. In the following, only the principal plots showing the data set and the result of the nonlinear regression are presented (See Fig. A7 – Fig. A14). The corresponding modeling parameters can be found in Table 1.
Fig. A11 RIVE. (◇): experimental data. ▼: sanidine; ▪: microcline expansions derived with the mean values of the parameters obtained from the 10,000 nonlinear regression analysis. Solid lines: corresponding isothermal RIVE curves. Vertical bars: min./max. values (theoretical model).

Fig. A12 Scatter plot. ▼: sanidine; ▪: microcline expansions derived with the mean values of the parameters obtained from the 10,000 nonlinear regression analysis. (○): mean expansion values from the 10,000 simulations results. Vertical bars: min./max. values.

Fig. A13 RIVE. (◇): experimental data. ▼: augite; ▪: diopside; ▪: enstatite expansions derived with the mean values of the parameters obtained from the 10,000 nonlinear regression analysis. Solid lines: corresponding isothermal RIVE curves. Vertical bars: min./max. values (theoretical model).

Fig. A14 Scatter plot. ▼: augite; ▪: diopside; ▪: enstatite expansions derived with the mean values of the parameters obtained from the 10,000 nonlinear regression analysis. (○): mean expansion values from the 10,000 simulations results. Vertical bars: min./max. values.