The compensation effect (Meyer–Neldel rule) on $[\text{AlO}_4/\text{h}^+]^\theta$ and $[\text{TiO}_4/\text{M}^+]^\theta$ paramagnetic centers in irradiated sedimentary quartz

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The compensation effect (Meyer–Neldel rule) on \([\text{AlO}_4/h^+]^0\) and \([\text{TiO}_4/M^+]^0\) paramagnetic centers in irradiated sedimentary quartz

I. INTRODUCTION

Signals from \([\text{AlO}_4/h^+]^0\) and \([\text{TiO}_4/M^+]^0\) paramagnetic centers are generally used to date sedimentary quartz by electron spin resonance (ESR) because of their easy identification and quantification as well as their response to irradiation (Toyoda and Ikeya, 1991a; Kink et al., 2007; and Tissoux et al., 2008). Another prerequisite for accurate dating is the use of a thermally stable signal. The two defects are considered to fulfill this requirement at ambient temperature (Toyoda and Ikeya, 1991a; 1991b; and Duval et al., 2017). Although a comprehensive understanding of the thermal decay kinetics of these defects is of utmost importance not only for dating but also for thermochronometry (Cirinnà et al., 1999; King et al., 2020), the majority of studies carried so far circumvented the time-consuming determination of laboratory kinetics by adherence to the standard literature values or performed investigations only for a single laboratory given dose under the assumption that the decay parameters do not depend on the given dose (see, e.g., Richter et al., 2019 and references therein).

For higher doses, a higher density of defects clearly exists, and very recent studies on irradiated ionic solids such as \(\text{Al}_2\text{O}_3\), MgO, and MgF\(_2\) showed that the defect recombination kinetics is not characterized uniquely by the activation energy with a constant pre-exponent, but, instead, these parameters depend on the radiation dose (Kotomin et al., 2018; Popov et al., 2018; and Baubekova et al., 2020). No studies have so far investigated such a possible effect in quartz.

The wide bandgap makes quartz an excellent insulator. However, the existence of cations allows the ionic conductivity to take place as a response to electromagnetic and/or thermal excitation. It is
generally accepted that the mobility of the ions in hexagonal quartz is mostly taking place through the open c-channel (Martin et al., 1983; Martini et al., 1995; and Campone et al., 1995). Aluminum centers in quartz are known to be compensated by monovalent cations M⁺ (where M⁺ is usually H⁺ or alkali ions such as Li⁺ or Na⁺) (Weil, 1975). Under gamma irradiation, [AlO₄/M⁺]⁰ interacts with holes, releasing the cation (M⁺) and producing [AlO₂/h⁺]⁰ centers (Haliburton et al., 1981). At the same time, [TiO₂/M⁺]⁰ is formed after an electron is trapped by a substitutional titanium ion, forming a [TiO₄]⁻ center that also traps a cation acquiring a paramagnetic stable state (Woda and Wagner, 2007). Consequently, the formation of [AlO₂/h⁺]⁰ and [TiO₂/M⁺]⁰ by gamma irradiation occurs by releasing and trapping, respectively, of a cation. The reverse mechanism is known to occur on heating. It was suggested that by heating at around 325°C, the release of cations from an unidentified defect (denoted as [XO₄/M⁺]⁰) and their trapping at uncompensated Al sites resulted in the emission of thermoluminescence at this temperature (Itoh et al., 2002).

In this study, we examine the dependence of thermal kinetic parameters as a function of the previously given dose for [AlO₂/h⁺]⁰ and [TiO₂/M⁺]⁰, showing that these parameters obey the Meyer–Neldel rule or, in other words, during thermal activation, the pre-exponential factor depends exponentially on the activation energy in respect of the given dose. Furthermore, our results support the hypothesis of the ionic exchange between [AlO₂/M⁺]⁰ and a second defect, which we hereby assign to [TiO₂/M⁺]⁰, thus extending the previous interpretive studies (Itoh et al., 2002; Williams and Spooner, 2018).

II. MATERIALS AND METHODS

Sedimentary quartz of size between 63 μm and 90 μm extracted from Holocene soil at loess–paleosol sequence in Enders, NE, Great Plains (USA), was used. The treatment and extraction procedures were presented in detail in Tecsa et al. (2020). ESR investigations were carried out using an X band Bruker EMX plus spectrometer. Room temperature irradiations were performed at the Centre for Nuclear Technologies, Technical University of Denmark (DTU NUTECH), using a calibrated ⁶⁰Co-60 gamma cell with a dose rate of about 2 Gy/s. The defect effective concentration was quantified by measuring the peak-to-peak amplitude (App) of their ESR signals (Toyoda, 2015). The ESR linewidth was verified to have no-slight variation with the dose, which makes the ESR-App variation equivalent to the effective concentration variation (Chesnul, 1977). The [AlO₂/h⁺]⁰ variation is then considered to be similar to that of the difference between the top of the first hyperfine line of the electronic transition due to g₂ and the bottom of the sixth hyperfine line of the electronic transition due to g₁, whereas that of [TiO₂/M⁺]⁰, where M⁺ is mainly Li⁺, was taken as the difference between the top of the electronic transition corresponding to g₁ and the bottom of the electronic transition corresponding to g₂, knowing that both centers possess an anisotropic g-tensor (see Toyoda, 2015). The pulse annealing experiment is characterized by a linear dependence between temperature and time. The temporal variation in temperature can be written as \( T = T_0 + Q \cdot t \), where \( T_0 \) is the room temperature (\(~294\) K) and \( Q \) is the heating rate, which can be expressed as \( Q = q/t_0 \), where \( t_0 \) is the annealing duration equal to 600 s and \( q \) is the temperature increment from pulse to pulse, which in our case equals to 50 K.

III. RESULTS AND DISCUSSIONS

A. Investigated signals

Figure 1 shows the ESR spectra of [AlO₂/h⁺]⁰ and [TiO₂/M⁺]⁰ centers recorded at 90 K for samples irradiated with gamma doses of 94 Gy and 9.4 kGy. It can be noted that the signal of [TiO₂/M⁺]⁰ we are quantifying herein corresponds mainly to [TiO₂/Li⁺]⁰ because of the observable four hyperfine transitions at the central transition,
corresponding to the electronic spin interaction with the 3/2 nuclear spin of "Li" [Fig. 1(a)]. However, the last transition toward the high magnetic field is known to be overlapped by that of [TiO\textsubscript{2}/M\textsuperscript{+}]\textsuperscript{0} (Tissoux et al., 2008; Toyoda, 2015; and Duval et al., 2015). In the following, we are considering that the variation in [TiO\textsubscript{2}/M\textsuperscript{+}]\textsuperscript{0} is mainly that of [TiO\textsubscript{2}/Li\textsuperscript{+}]\textsuperscript{0}.

**B. Thermal decay for different doses**

Figure 2 exhibits the dose–response curves for [AlO\textsubscript{4}/h\textsuperscript{+}]\textsuperscript{0} and [TiO\textsubscript{2}/M\textsuperscript{+}]\textsuperscript{0} before and after annealing pulses. For the unheated sample, the [AlO\textsubscript{4}/h\textsuperscript{+}]\textsuperscript{0} dose–response is growing with the dose until close to saturation, while the [TiO\textsubscript{2}/M\textsuperscript{+}]\textsuperscript{0} signals exhibit a growth with the dose, followed by a pronounced decrease after a certain threshold value (around 10 kGy here). The [AlO\textsubscript{4}/h\textsuperscript{+}]\textsuperscript{0} signal variation with the dose is fitted by the model recently proposed by Benzid and Timar-Gabor (2020) for annealing treatments at a temperature up to 300 °C [Fig. 2(a)]. The variation in the [TiO\textsubscript{2}/M\textsuperscript{+}]\textsuperscript{0} signal was fitted following the model presented by Woda and Wagner (2007) up to full annealing around 350 °C [Fig. 2(b)].

The decay rate of the signal as a function of temperature in the pulse annealing procedure, considering the first and second order kinetics, can be written as

\[
R_{1H} = \frac{dN_H(t)}{dt} = -\lambda(T)N_H
\]

and

\[
R_{2H} = \frac{dN_H(t)}{dt} = -\lambda'(T)N_H^2 = -\lambda(T)\frac{N_H^2}{(N_D - N_0)},
\]

respectively, where \(\lambda(T) = \lambda_0 e^{-\left(E_0 / k_B T\right)}\) is the Arrhenius law, \(\lambda_0\) (Hz) is the frequency factor, \(E\) (eV) is the activation energy, \(K_B\) (8.615 \times 10^{-5} eV K\textsuperscript{-1}) is the Boltzmann constant, \((N_D - N_0)\) is the initial effective concentration in respect of the accumulated gamma dose, and \(\lambda'(T) = \frac{\lambda(T)}{\Delta N - N_0}\). The subscripts D and H indicate that the parameter is taken in respect of dose and of temperature for a fixed gamma dose, respectively.

Equations (1a) and (1b) can be solved by replacing the time variation (dt) with the temperature variation (dT) via the heating rate \(Q = dT/dt\) (see Sec. II) and integrating from \((N_D - N_0)\) to \(N_H\) and from \(T_0\) to \(T_0\). The exact solution involves the exponential integral function. However, by asymptotically approximating the function in the second order (Bleistein and Handelsman, 1986), one obtains the first and second order kinetics effective concentration variation (see the supplementary material) as

\[N_{1H}^0 = (N_D - N_0)e^{-\lambda_0K_B\left(T_0e\left(-\frac{E}{k_BT_0}\right) - T_0e\left(-\frac{E}{k_BT}\right)\right)}\]

and

\[N_{2H}^0 = (N_D - N_0)^2\left(1 + \frac{\lambda_0K_B\left(T_0e\left(-\frac{E}{k_BT_0}\right) - T_0e\left(-\frac{E}{k_BT}\right)\right)}{Q}\right)^{-1}.\]

Figure 3 presents the evolution of the effective concentration of [AlO\textsubscript{4}/h\textsuperscript{+}]\textsuperscript{0} and [TiO\textsubscript{2}/M\textsuperscript{+}]\textsuperscript{0} after accumulating various gamma doses as a function of annealing temperature. One can observe that the effective concentration of both defects remains constant up to annealing temperatures of about 200 °C–250 °C. Beyond this temperature range, the concentrations decrease with temperature and the signals eventually disappear around 350 °C and 450 °C for [TiO\textsubscript{2}/M\textsuperscript{+}]\textsuperscript{0} and [AlO\textsubscript{4}/h\textsuperscript{+}]\textsuperscript{0}, respectively.

The datasets in Figs. 3(a) and 3(b) have been fitted by Eqs. (2a) and (2b). It was observed that the second order kinetics characterizes better the decay, as previously reported by others (Toyoda and Ikeya, 1991b). The use of both equations gives similar kinetic parameters (E and \(\lambda_0\)). In the following, we consider the second order kinetic model \(N_{2H}^0 = N_H^0\).

By examining Figs. 3(a) and 3(b), one can see that the high dose signals drop faster than the low dose signals on heating, inferring that the kinetic parameters are dose dependent. As such, one expects the temperature, where the defect concentration \(R_H(T)\) is minimal, to be dose dependent too. For visualization, we show the absolute variation with temperature \([|R_H(T)|]\) in Figs. 3(c) and 3(d). The variation with temperature [Eq. (1b)] gives dose-dependent peaks as a function of the given dose at about 280 °C–440 °C for [AlO\textsubscript{4}/h\textsuperscript{+}]\textsuperscript{0} and at about 260 °C–370 °C for [TiO\textsubscript{2}/M\textsuperscript{+}]\textsuperscript{0}.

Figure 4 presents the dose-dependency of the kinetic parameters (E and \(\lambda_0\)) along the investigated dose scale besides the ESR amplitudes.

As the thermal decay was not found to follow simple first order kinetics, lifetimes cannot be computed, strictly speaking (Prokein and Wagner, 1994). However, as an approximation, by using the values of the activation energy and the frequency factors for [TiO\textsubscript{2}/M\textsuperscript{+}]\textsuperscript{0} and [AlO\textsubscript{4}/h\textsuperscript{+}]\textsuperscript{0} and their change with dose [Figs. 4(c) and 4(d)] lifetimes, \(\tau = 1/\lambda\) at an estimated average temperature of 10 °C range from 10\textsuperscript{10} years for doses about 100 Gy to only a couple of years for doses in the kGy range. A recent study on sedimentary quartz extracted from Chinese loess (Tsukamoto et al., 2018) suggested that [TiO\textsubscript{2}/M\textsuperscript{+}]\textsuperscript{0} could be less stable than...
FIG. 3. Second order kinetic evolution as a function of annealing temperature of the effective concentration of (a) \([\text{AlO}_4^{-}/h^+0]\) and (b) \([\text{TiO}_4^{2+}/M^0]\) after accumulating various doses [data were fitted by Eq. (2b)]. The insets in (a) and (b) show this evolution after accumulating 9.4 kGy fitted by the first and second order kinetics according to Eqs. (2a) and (2b). Panels (c) and (d) show the rate variation in the effective concentrations [Eq. (1b)] for various accumulated gamma doses using the kinetic parameters given by the fitting in (a) and (b).

previously believed. Moreover, the same study presented a concerning discrepancy between the natural and the laboratory generated dose–response curves. By investigating quartz samples from the Luochuan loess–paleosol sequence where age control is available based on the well-known stratigraphy, signals for both \([\text{AlO}_4^{-}/h^+0]\) and \([\text{TiO}_4^{2+}/M^0]\) centers recorded for natural samples older than about 300 ka–600 ka (corresponding to doses in the 1 kGy–2 kGy range) were recorded in field saturation or, in other words, no longer increasing with age (and hence the dose). This indicates that a steady state has been reached. On the other hand, laboratory signals generated by the same doses, however, given in a time order of magnitude shorter than in nature and measured immediately after irradiation displayed no such signs of early saturation. Moreover, in the above-mentioned study, the application of a preheat treatment before the measurement of the laboratory dose–response curve was shown to change not only the amplitude of the signals but also the saturation characteristics \((D_0 \text{ value}) or, in other words, the shape of the dose–response curve. This suggests that thermal treatments might have different effects on the signals recorded after laboratory irradiations at higher doses than for low doses.

Our results clearly indicate that both \([\text{AlO}_4^{-}/h^+0]\) and \([\text{TiO}_4^{2+}/M^0]\) defects are less thermally stable above 1 kGy–2 kGy than below this dose range. This is in good agreement with the observations of Tsukamoto et al. (2018) on natural dose–response curves constructed on quartz from Chinese loess, described above.

By further analyzing the values obtained for the frequency factor and activation energy, we show (Fig. 5) a very important feature of these defects under thermal activation, namely, the fact that the frequency factor depends exponentially on the activation energy or, in other words, that the kinetic parameters satisfy the Meyer–Neldel rule.

The variation in the activation energy as a function of the frequency factor can be written from Eq. (2b) as

\[
E = (K_B T \ln \left( \frac{N_D - N_0}{N_H} \right) + (K_B T \ln (\lambda_0)).
\]

This equation has been used as the fit to the dataset in Fig. 5.

The Meyer–Neldel rule is well known in different processes although the basis of this empirical rule is not fully understood yet. However, it is known to accompany the rise of macroscopic disordering in materials under irradiation, which is not necessarily accompanied by amorphization (Kotomin et al., 2018; Baubekova et al., 2020).

C. Correlation between \([\text{AlO}_4^{-}/h^+0]\) and \([\text{TiO}_4^{2+}/M^0]\)

Benzid and Timar-Gabor (2020) presented a phenomenological model for the formation of \([\text{AlO}_4^{-}/h^+0]\) based on the dissociation of \([\text{AlO}_4^{2+}/M^0]\) that allowed explaining the shape (sum of two saturating exponential functions) of the empirical dose–response curve
by considering the different nature of the cation denoted by $M^+$ (hydrogen or alkali). Regardless of the cation nature, the formation of $[\text{AlO}_4/h^+]$ can be simplified as

$$[\text{AlO}_4/h^+M]^0 \rightarrow [\text{AlO}_4/h^+] + M^+.$$ (r1)

For the $[\text{TiO}_4/M^+]$ center, Woda and Wagner (2007) proposed the following mechanisms to occur under gamma irradiation: (i) irradiation-induced formation up to a certain dose by trapping one electron followed by (ii) irradiation-induced annihilation by trapping a second electron,

$$[\text{TiO}_4/M^+]^0 \rightarrow [\text{TiO}_4/M^+] e^- \rightarrow \text{[TiO}_4/M^+] e^- + M^+.$$ (r2)

According to mechanisms (r1) and (r2)-(i), the growth of $[\text{AlO}_4/h^+]$ and $[\text{TiO}_4/M^+]$ occurs by releasing and trapping cations, respectively. Thus, there is a reasonable possibility that the cations released from $[\text{AlO}_4/M^+]$ are being trapped by $[\text{TiO}_4/M^+]$. In addition, it is likely that defect annealing is the reverse of its formation.

If one considers that the formation mechanism of both defects under gamma irradiation follows the first order kinetics, hence the
production rate is proportional to the defect concentration, the ratio of the production rates of the two defects, defined as \( R_{Al}^{Al-h} / R_{D}^{Ti-M} \), can be expressed as

\[
\frac{R_{Al}^{Al-h}}{R_{D}^{Ti-M}} = \frac{\Gamma_{Al-h}}{\Gamma_{Ti-M}} \left( \frac{N_{D}^{Al-h} - N_{D}^{Al-h}}{N_{D}^{Ti-M} - N_{D}^{Ti-M}} \right),
\]  

(4)

where \( \Gamma_{Al-h} \) and \( \Gamma_{Ti-M} \) (Gy\(^{-1}\)) are the effective rate constants of mechanisms (r1) and (r2)–(i), respectively; \( N_{D}^{Al-h} \) and \( N_{D}^{Ti-M} \) (a.u) are the effective concentrations, taken here conventionally as the ESR-App; and \( N_{0}^{Al-h} \) and \( N_{0}^{Ti-M} \) (a.u) are the initial concentrations. The subscript D indicates that the parameter is taken in respect of the dose for a fixed temperature. Equation (4) can be rearranged as

\[
N_{D}^{Al-h} = N_{0}^{Al-h} + B(N_{D}^{Ti-M} - N_{0}^{Ti-M}),
\]

where \( B = \frac{R_{Al}^{Al-h} / \Gamma_{Ti-M}}{R_{D}^{Ti-M} / \Gamma_{Al-h}} \).

(5)

Figure 6 presents the evolution of the effective concentration of \([AlO_{4}/h^{+}]^{0}\) as a function of that of \([TiO_{4}/M^{+}]^{0}\) in respect of the accumulated dose, up to 10 kGy, after 10 min annealing at various temperatures.

One can see that the paramagnetic defects show a temperature-independent correlation. Equation (5) was used to fit the dataset. The temperature-independent proportionality constant B is found to be \(~5.2\). The weak value of \( N_{0}^{Ti-M} \) (~0.1) makes the intercept about the initial concentration of \([AlO_{4}/h^{+}]^{0}\) (~1.6 a.u). This relatively initial concentration is due to the significant values of the residual of this defect (see further details in Timar-Gabor et al., 2020). Above 10 kGy, after \([TiO_{4}/M^{+}]^{0}\) experienced radiation bleaching, the correlation does not hold longer. However, the decrease in \([TiO_{4}/M^{+}]^{0}\) by annealing correlates with that of \([AlO_{4}/h^{+}]^{0}\).

By calculating the rate ratio \( R_{Al}^{Al-h} / R_{D}^{Ti-M} \) of the trapping/releasing cations by \([AlO_{4}/h^{+}]^{0}\) and \([TiO_{4}/M^{+}]^{0}\), one can write

\[
\Delta E = E_{Ti-M} - E_{Al-h} = -(K_{B}T) \ln \left( \frac{N_{0}^{Al-h}}{N_{D}^{Al-h}} \right) + (K_{B}T) \ln \left( \frac{N_{D}^{Ti-M}}{N_{0}^{Ti-M}} \right)
\]

(6)

This is shown in Fig. 7.

From the fitting of the datasets by Eq. (6) in Fig. 7 and by Eq. (5) in Fig. 6, one can get the following proportionality between the effective concentrations of the two defects under both gamma irradiation and thermal pulse annealing processes:

\[
\frac{R_{D}^{Ti-M}(N_{D}^{Al-h})}{R_{D}^{Al-h}(N_{H}^{Ti-M})} = \frac{N_{D}^{Al-h} - N_{0}^{Al-h}}{N_{D}^{Ti-M} - N_{0}^{Ti-M}}
\]

(7)

According to Eq. (6) used to fit the data presented in Fig. 7, the compensation energy for cations to migrate from \([TiO_{4}/M^{+}]^{0}\) to \([AlO_{4}/h^{+}]^{0}\) and vice versa was found to be 51.3 ± 4 meV. The corresponding Meyer–Neldel temperature is found to be about 325 °C in good agreement with the thermoluminescence band previously proposed by (Itoh et al. 2002) to originate from the migration of \(M^{+}\) to an Al site from then unidentified defect.

![FIG. 6. Evolution of the effective concentration of \([AlO_{4}/h^{+}]^{0}\) as a function of that of \([TiO_{4}/M^{+}]^{0}\) in the respect of the gamma dose, up to 10 kGy and above 10 kGy (inset), for 10 min annealing at various temperatures. The red dashed line indicates the correlation line [Eq. (5)].](image)

![FIG. 7. Evolution of the cation activation energy difference during the releasing/trapping process from \([TiO_{4}/M^{+}]^{0}\) to \([AlO_{4}/h^{+}]^{0}\). The inset represents a possible schematic of the energy diagram.](image)
IV. SUMMARY

Due to the neutrality principle, substitutional Al in quartz is compensated by monovalent cations (hydrogen and/or alkali ions) forming $[AlO_4/M\db]_\circ$ centers. Under gamma irradiation, the cations are replaced by holes producing paramagnetic $[AlO_4/h^+]_\circ$. At the same time, the diamagnetic $[TiO_4\db]$ traps the cations, forming the paramagnetic $[TiO_4/M\db]_\circ$. Under thermal excitation, the reverse process occurs, namely, the cations displace from $[TiO_4/M\db]_\circ$ to $[TiO_4/h^+]_\circ$ and $[AlO_4/M\db]_\circ$, respectively. This process is governed by the activation energies of cations and the effective lattice vibration frequencies of the medium. These parameters were found to be dose dependent. This finding clearly calls for future investigations when it comes to using electron spin resonance for dating in the high dose range or for thermochronometry applications. By analyzing the samples exposed to different radiation doses, the process was found to obey the Meyer–Neldel rule. A compensation energy of the samples exposed to different radiation doses, the process was dose range or for thermochronometry applications. By analyzing it comes to using electron spin resonance for dating in the high

SUPPLEMENTARY MATERIAL

See the supplementary material for the derivation of Eqs (2a) and (2b).

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DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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