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Trapped-charge thermochronometry and thermometry: A status review

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ABSTRACT

Trapped-charge dating methods including luminescence and electron spin resonance dating have high potential as low temperature (<100 °C) thermochronometers. Despite an early proof of concept almost 60 years ago, it is only in the past two decades that thermoluminescence (TL), electron-spin-resonance (ESR), and optically stimulated luminescence (OSL), have begun to gain momentum in geological thermochronometry and thermometry applications. Here we review the physics of trapped-charge dating, the studies that led to its development and its first applications for deriving palaeo-temperatures and/or continuous cooling histories. Analytical protocols, which enable the derivation of sample specific kinetic parameters over laboratory timescales, are also described. The key limitation of trapped-charge thermochronometry is signal saturation, which sets an upper limit of its application to <1 Ma, thus restricting it to rapidly exhuming terrains (>200 °C Ma^{-1}), or elevated-temperature underground settings (>30 °C). Despite this limitation, trapped-charge thermochronometry comprises a diverse suite of versatile methods, and we explore potential future applications and research directions.

1. Introduction

The need to constrain the rate and timing of landscape evolution has led to a continuous growth of thermochronometric techniques, which quantify the thermal histories of rocks (Reiners and Ehlers, 2005). A suite of methods are applicable to different temporal and spatial scales, however constraining recent (<1 Ma) thermal histories at temperatures <100 °C remains challenging. Luminescence and electron-spin-resonance (ESR) dating are trapped-charge dating methods whose thermal sensitivities can span this temporal gap. They are based on the quantification of free electric charge (electrons and holes), which become trapped in the proximity of various defects and impurities in the crystalline lattice of minerals (e.g. quartz, feldspar) as a result of their exposure to environmental radiation (cf. Aitken, 1985). This charge can be evicted by exposure of the crystal to external energy such as heat, light and/or pressure, and hence its concentration can be related to the last exposure of natural materials to high temperature (Aitken et al., 1968; Brown et al., 2009). Therefore, trapped-charge techniques can be used to gain insights into the thermal histories of rocks.

Although the possibility of interpreting trapped charge within natural crystals as records of their thermal histories was initially demonstrated more than half a century ago (Houtermans et al., 1957), this technique received only marginal attention from the geological community, initially for surface palaeothermometry (e.g. Ronca and Zeller, 1965), and later for characterising lunar surface temperatures (e.g. Durrani et al., 1977). With an increasing interest for quantifying recent stages of rock thermal histories from the thermochronological community (Reiners and Ehlers, 2005) and the need to constrain the rate and timing of landscape evolution during the Quaternary, trapped-charge dating methods utilising ESR, thermoluminescence (TL), and optically stimulated luminescence (OSL) were (re)investigated in the context of low-temperature thermochronometry (Grün et al., 1999; Tsuchiya and Fujino, 2000; Herman et al., 2010; Guralnik et al., 2015a; King et al., 2016a). In particular, OSL-thermochronometry has been the focus of rapid development since its introduction in 2010, and has come to be recognized as a new developing field of luminescence dating (Duller, 2015a, 2015b; Roberts and Lian, 2015). In its simplest form, trapped-charge thermochronometry comprises constraining the interplay between (i) the rate of charge trapping, due to exposure to ionising radiation, and (ii) the rate of charge detrapping, due to temperature (Christodoulides et al., 1971). By constraining charge trapping and detrapping rates on a sample-specific basis, the natural concentrations of trapped charge can be translated into ages and their corresponding palaeotemperatures.

Here we aim to provide a brief overview of the underlying physics of trapped-charge dating, describe the common equipment and key measurements of each sub-technique, and trace the development of trapped-charge thermochronometry from early pioneering studies to the current state-of-the-art. At a time when a range of new low-temperature thermochronometric techniques are under development (e.g. Tremblay et al., 2014; Shuster and Cassata, 2015; Amidon et al., 2015),

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it is particularly interesting to review trapped-charge dating methods with comparable thermal stabilities, that could be used in conjunction with the above geochemical methods to obtain even higher-resolution palaeotemperature constraints, inaccessible when using each method independently.

2. Physical principles

2.1. Electron traps in a crystalline lattice

Both luminescence and ESR dating are based on the measurement of trapped electrons, which build up in crystal defects (Fig. 1A) due to naturally-occurring ionising radiation. Such defects or imperfections include atomic interstitials, atomic vacancies and elemental substitutions. Even the purest crystals contain defects, and even impurity concentrations of the order of 10^{-3} ppm can result in defect concentrations of ~10^{13} cm^{-3} (Preusser et al., 2009). When ionising radiation from alpha, beta or gamma decay, as well as from cosmic radiation, interacts with the crystalline lattice (Fig. 1B), sufficient energy may be transferred to some bonding electrons, causing them to detach from their sites; once mobile, free electrons diffuse towards positively-charged defects and impurities within the crystal. Conversely, each evicted electron leaves a 'hole' behind (a lack of an electron; a virtual particle with a charge of e^+) which experiences an analogous diffusion towards negatively-charged defects and impurities. Once in their traps, electrons and holes remain immobile until thermal lattice vibrations give electrons sufficient energy to escape, allowing them to diffuse again through the crystal (Fig. 1C) and to recombine with trapped holes. Upon electron-hole recombination, excess energy is released either in the form of measurable light (luminescence) or dissipated as heat in the crystal. For more in-depth descriptions of electron and hole trapping and detrapping in quartz and feldspar minerals, the reader is referred to e.g. Aitken (1985); Chen and Pagonis (2011), and Jain and Ankjærgaard (2011).

Although the precise defects that give rise to OSL and TL from quartz are still the subject of investigation (e.g. Yang and McKeever, 1990; McKeever, 1991; Martini et al., 2009; Preusser et al., 2009), the UV-blue emissions which are typically measured from quartz have been associated with the substitution of Si^{4+} with Al^{3+}, this charge deficit being compensated by Li^+, Na^+ (Perny et al., 1992), H^+ (Itoh et al., 2002; Luff and Townsend, 1990) or a trapped hole (h^+) (Martini et al., 1995, 2009). Quartz also contains many paramagnetic centres that can be exploited in ESR dating, although usually only the Al and Ti centres are targeted (cf. Skinner, 2011; Blackwell et al., 2016). Finally, the source of the blue emission of feldspar in response to infra-red stimulation (termed IRSL, but broadly falling within the OSL category) remains understudied but has been associated with Al–O–Al centres (Finch and Klein, 1999). The reader is referred to Krbetschek et al. (1997) for a detailed review of luminescence emissions from quartz and feldspar minerals.

An electron-hole pair may be produced by any naturally occurring alpha, beta, gamma or cosmic radiation. The sample's natural radioactivity from all accountable sources is usually expressed as the natural dose rate ($\dot{D}$), with unit of Gray per unit time (e.g. Gy s^{-1} or Gy ka^{-1}). Conversely, the product n is the number of trapped electrons at any given time (see Table 1 for a short nomenclature guide). Since the number of crystal defects/impurities is finite, the amount of electrons that can become trapped is also limited. Consequently, out of N electron traps of a certain kind with $n \leq N$ electrons in them, only the empty sites ($N - n$) can attract newly produced charge (Klasens and Wise, 1946). This 'space limitation' is a key phenomenon in trapped-charge geo- and thermochronometry (cf. Li and Li, 2012; Guralnik et al., 2013) which generally results in signal saturation over timescales exceeding 10^5 years (Wintle, 2008). While some ESR centres or OSL traps may exhibit significantly later saturation (i.e. up to 10^6 years; Rink, 1997; Ankjærgaard et al., 2015), all trapped-charge systems seem to eventually be affected by the saturation phenomenon (Grün, 2001).

Various minerals, mineral defects and impurities have different trapping capacities and thermal stabilities (see Table 2 for some representative values). Therefore, trapped-charge thermochronometry comprises a versatile suite of different stability systems, with thermal sensitivity in the ~40–100 °C range (e.g. Grün et al., 1999; Wu et al., 2015; Guralnik et al., 2015a; Ankjærgaard et al., 2015; King et al., 2016a). Furthermore, these systems can be used in combination to provide multi-thermochronometric constraints (Qin et al., 2015; King et al., 2016a), enabling the derivation of continuous cooling histories. Trapped-charge techniques therefore lend themselves to a diverse range of applications including thermometry (Christodoulides et al., 1971), thermochronometry (Toyoda and Ikeya, 1991), and constraint of instantaneous cooling or reheating events (see reviews by Fleming, 1979; Bailiff, 2015; Tsukamoto, 2015).

2.2. Mathematical description

The most basic mathematical description of the simultaneous electron trapping and detrapping, which occurs in a crystal exposed to environmental radiation and heat, is given by:

$$\frac{dn}{dt} = p_{trapping}\,(N-n) - p_{detrapping}\,n \qquad (1)$$

in which t (s) is time, ($N - n$) and n the unitless number of empty and occupied electron traps respectively, and $p_{trapping}$ and $p_{detrapping}$ the probabilities of an electron occupying and vacating a trap per unit

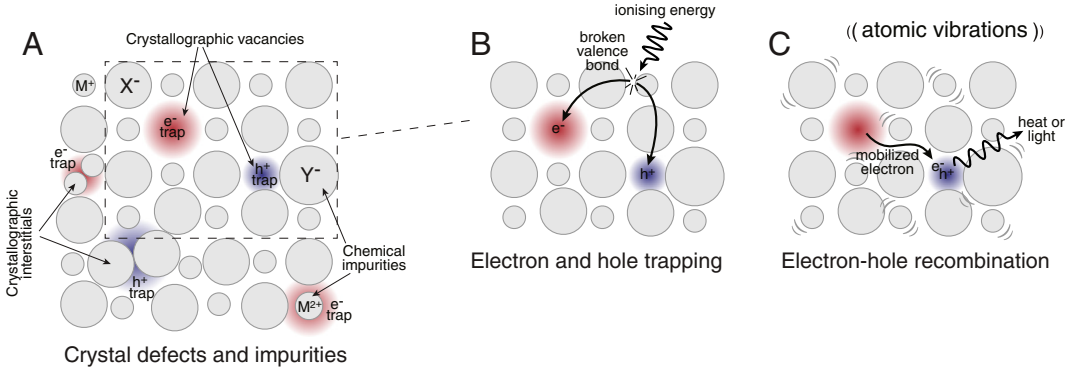

Fig. 1. Schematic diagram of charge trapping and release. (A) A crystalline alkali-halide lattice, depicting common lattice imperfections such as vacancies, interstitials, and impurities. (B) Trapping and (C) detrapping of an electron-hole pair (e^- and h^+ respectively) in the crystal due to the effects of radiation and temperature, respectively. In (B) ionization of an electron results in diffusion of e^- to an electron trapping site, and of h^+ to a luminescence recombination centre. Exposure of the mineral to heat (C) enables the electron to escape the trapping site and to recombine with a hole, leading to a release of excess energy either in the form of measurable light (luminescence signal), or via dissipation by heat.

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