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Volcanic feldspars anomalous fading: Evidence for two different mechanisms☆

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HIGHLIGHTS

- Anomalous fading of TL of volcanic feldspars is drastic in a few weeks.
- Anomalous fading after two decades of storage is twice the fading after one decade.
- After storage for two decades at 77 K the fading is practically suppressed.
- Anomalous fading is due at least to two several different mechanisms.
- Volcanic feldspars have disordered lattice and electrons can hop from trap to trap.

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ABSTRACT

This study presents measurements of anomalous fading of feldspars extracted from volcanic units from the Auvergne (France) and Patmos Island (Greece). We measured the fading rate for samples stored at ambient temperature, and also at liquid nitrogen temperature. A strongly different behaviour is then observed, the fading is reduced to values usually obtained and explained by pure tunnelling recombination of charges to near enough luminescence centres, which is athermal. We suggest that the temperature dependent or "frozen" part of the fading is relevant to a different mechanism, which is "hopping", already proposed in the mid-sixties, which preserves the experimental logarithmic fading decreasing law.

1. Introduction

Feldspars display an anomalous fading that can lead with volcanic samples to a nearly complete loss of the stored thermoluminescence (TL), OSL or IRSL after a few years storage. Since the first observations (Wintle, 1973, 1977) many attempts have been made to evaluate this decay in contradiction with conventional kinetics of TL, in order to use feldspars in TL or OSL dating (Spooner, 1992, 1994; Lamothe and Auclair, 1999; Huntley and Lamothe, 2001; Lamothe et al., 2012) and this phenomenon has been well documented (Aitken, 1985, 1998). Among various possible mechanisms for the reported anomalous fading tunnelling recombination has been favoured as it accounts for its reported temperature independence and experimental logarithmic decay law (Visocekas, 1979, 1985, 1993).

This very strong anomalous fading present in most plagioclases or K-feldspars (sanidine or anorthose) extracted from volcanic

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rocks appears to us not to be quantitatively justifiable by a simple tunnelling mechanism. Tunnelling is a quantum effect, strictly temperature independent. By tunnelling, fixed ionised centres and trapped electrons recombine through the potential barrier separating them, with kinetics: exp($-\alpha t$) for a given distance, The life time ($1/\alpha$) is a function of the distance d between them from a fraction of a second to a near infinite time. Thus electrons trapped at greater distances will not actually recombine by simple tunnelling even for times of storage up to 1 Ma. They could be detrapped only thermally in TL or OSL. Examples are shown at scale on Fig. 1. The decay of tunnel luminescence at time t after excitation has been consistently observed down to 77 K to fit nearly a ($1/t$) law over many decades of time (Delbecq et al., 1974, Visocekas et al., 1976, Huntley, 2006). This observation is well accounted for by the addition of all tunnel recombinations of electron-centre pairs: $\int_0^\infty exp(-\alpha t)d\alpha = 1/t$

Simple is a purely quantum effect by which a trapped electron has some probability to be beyond the potential barrier trapping it. There it may recombine radiatively in a centre. This effect is temperature independent. It may be quantitatively justified (Visocekas, 1979 with calcite), there were similar observations of it in many materials (see Huntley, 2006 for a review). It is all the more expected to display similar intensities in all K-feldspars, volcanic or granitic, since they have quite similar composition and crystallography and display similar glow curves following similar irradiations. The odd thorough anomalous fading observed specifically in volcanic feldspars (at ambient temperature), typically such as sanidine, leads to propose another mechanism for electrons detrapping, namely “hopping” to account for it (Visocekas et al., 2014).

It is based on the oddity that in such feldspars the constitutive Al3+ ions are no more ordered in the lattice (Barth, 1934). This disorder generates a huge density of defects or “localised centres” acting as traps (Mott, 1968). Trapped electrons can enjoy some mobility by “hopping” from one trap to a next one, a short range tunnelling with weak thermal stimulation as sketched in Fig. 2 (Poolton et al., 2002). Finally, all of them end up by tunnelling into a luminescent centre when they get near enough to it, with a lifetime depending on the initial distance to reach this centre (Visocekas et al., 2014).

The possibility of such a mechanism of fading adding to tunnelling at ambient temperature will be further confirmed by the experimental results proposed hereafter. They will show drastic reduction of the anomalous fading by storage at liquid nitrogen temperature. This is totally at odds with tunnelling, basically an athermal quantum effect.

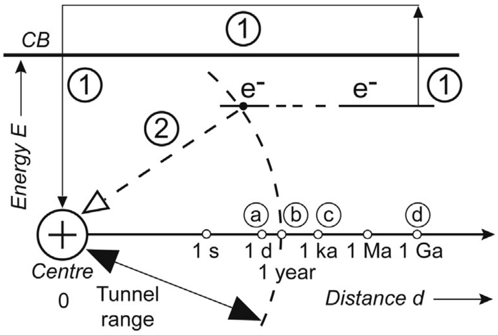

Fig. 1. Sketch of the structure and relation of distance from centre to electron with the half-life of tunnelling.

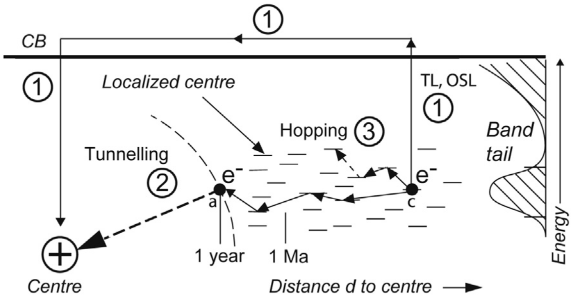

Fig. 2. The three routes for luminescent electron-centre recombination. (1) After strong thermal or optical stimulation: from trap to conduction band (CB), independent from the distance, the route of TL and OSL. (2) By tunnelling: without any stimulation, temperature independent, very strongly dependent on the electron-centre distance (distances are shown for lifetimes 1 year and 1 Ma). (3) By hopping from trap to trap with weak thermal stimulation: the flow is greatly increased by a high density of defects and all trapped electrons may eventually detrap in a few decades.

2. Samples and experimental settings

2.1. Sample preparations

Three K-feldspars and a plagioclase have been studied. One sanidine comes from Patmos Island (Greece). It is a new sample preparation different from those studied by some authors (Spooner, 1992). We named it Patmos-B to prevent any confusion with other samples coming from the same Island. We selected a single and large (ca 1 cm) phenocryst from a late tertiary trachytic formation at the base of the island. Its age can be attributed from 5 Ma to 5.5 Ma (Barton and Wyers, 1991). Others two K-feldspars are phenocrysts coming from two different outcrops in the Puy de Sancy stratovolcano (France): Roc de Courlande and Puy de la Tache. Based on geological evidence, they are dated between 500 ka and 350 ka (Nomade et al., 2012). For these three samples a crystal the size of a centimetre is crushed and sieved. The 80–160 μm fraction is then cleaned in an ultrasonic bath. Ferromagnetic grains (due to small magnetite inclusions within the crystal) are removed using a permanent magnet.

The last sample is a plagioclase extracted from a basaltic lava flow outcrop at Olby in the Chaîne des Puys (France) volcanic province. It is a well-known lava flow because it evidences the last Earth magnetic field excursion (Laschamp Event) and is dated about 41.5 ka (Laj et al., 2014). This sample is made of the plagioclase microliths of the basalt. The rock is crushed, sieved and the fraction 80–125 μm cleaned in distilled water and ethanol in an ultrasonic bath. Then, the fraction of density less than 2.8 is separated using tribromomethane and ethanol. Once dried at 40 °C, the ferromagnetic grains are removed.

2.2. Experimental settings

TL measurements were carried out with a laboratory made TL-OSL reader holding 36 disks (Guérin and Lefèvre, 2014). A near UV glass filter (Sagem DH 380c′) is used, with a band from 320 nm to 430 nm (Supp. Figure 1), almost equivalent to a Schott BG 39 associated to a Corning 7–59.

The protocol of measurements starts by a thermal bleaching of a batch about 300 mg of each sample. Using an open-air furnace, sanidine samples (Courlande, la Tache and Patmos-B) are heated up to 650 °C (at an approximate rate of 15 °C/s) and then left to cool slowly for 1 h to ambient temperature. The plagioclase sample (Olby) is bleached in the same way but heated up to 750 °C in order to empty the very high temperature traps (revealed by TL experiments in the 325 nm UV domain).