ESR Dating - No. 2

ESR Dating Measurement Using Quartz

Quartz is a mineral which occurs globally and can be used for ESR dating and gives good information on geological events shown in Table 1. Different types of paramagnetic centers existing in quartz have been reported (1), mainly using the signals from the Al and Ti-Li centers.

Table 1. Quartz sample and corresponding event

Sample	Event
Volcanic products	Volcanic Eruptions
Granite	Cooling of Rock
Sediment	Sedimentation
Flint	Human Activity
Gypsum	Environmental Changes
Fault Clay	Fault Movements

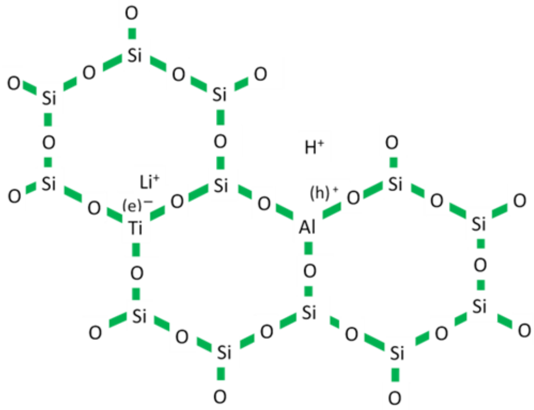

Fig 1. Example of Lattice Defect in Quartz

(1) Al Center Signal

This impurity in quartz has Al^{3+}substituted at one of the Si^{4+} positions. Normally, a monovalent cation ($M^{+} = H^{+}$, Li^{+}, Na^{+}) is located between the lattices near the Al^{3+} to form $[AlO4^{-}/M^{+}]$ so compensating for the charge difference. By irradiation, a hole is generated. Then Al^{3+} captures the hole (h) to make $[AlO_4/h]^{0}$ and, at the same time, the cation diffuses between the lattices. The hole is captured by the non-bonding 2p orbital of oxygen near the substituted Al (2)(3). This gives rise to the Al (I＝5/2) center signal which, at 77K shows hyperfine coupling. (Fig. 2)

(2) Ti Center Signal

This impurity in quartz has Ti^{4+} substituted at one of the Si^{4+} positions. The Ti captures electrons generated by irradiation ($[TiO^{4+}e^{-}]^{-}$) and a monovalent cation ($M^{+} = H^{+}$, Li^{+}, Na^{+}) to compensate for the charge difference. When the counter-cation is Li^{+}, this was named the Ti center, but other centres, e.g. Ti-H and Ti-Na centers, have also been found in natural quartz (5).

ESR Measurement

For ESR measurement, it is preferable to monitor a standard signal, e.g. Mn^{2+} marker, to correct the magnetic field and sensitivity, after proper selection of the measurement conditions. (e.g. micro wave power; 5mW; magnetic field modulation: 0.1mT; magnetic field sweep time: 30sec; time constant: 0.03sec). The measurement, based on the Al, Ti-Li center signals, is made at a sample temperature of 77K (6).

Measurement methods for ESR dating require reagents which have known spin concentrations such as Mn^{2+} and DPPH (diphenylpicrylhydrazyl). For Al & Ti-Li centers, the signal intensity, i.e. the peak height (Fig 2), is measured and corrected by the gain, divided by the weight, and normalized by the signal intensity of the Mn marker. In order to reduce the angular dependency for micro crystalline substances, it is recommended to make several measurements rotating the tube ~30^{O} each time. The mean or average value is used for the signal intensity.

For the calculation method, please refer to "Application Note ER-080001".

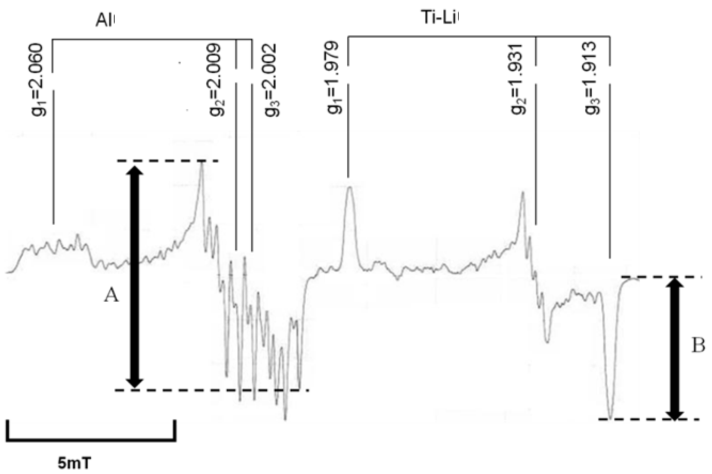

Fig. 2. ESR signal of Al, Ti-Li centers in quartz at 77K[6].
A: Al center signal intensity B: Ti-Li center signal intensity.

References

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(6) Shimada, A. and Toyoda, S. (2004): The temperature and microwave condition suitable for ESR measurement of impurity center in quartz, *Advances in ESR Applications*,21,13-16.