Applications of Natural Alpha-particle-induced Defects in Quartz to Exploration of Uranium Deposits

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Summary

Electron-paramagnetic resonance (EPR) spectroscopic studies of natural quartz crystals associated with high-grade uranium mineralization in the Athabasca Basin, together with EPR results from artificially-irradiated quartz, allow us to identify and characterize a suite of alpha-particle-induced defects. These alpha-particle-induced defects in quartz are diagnostic of radioactive decay of uranium (and thorium) and have been shown to be useful for the exploration of uranium deposits in the Athabasca Basin. For example, the presence and abundance of alpha-particle-induced defects in drusy quartz have been shown to be capable of distinguishing mineralized and barren hydrothermal alteration zones. Similarly, the distribution and abundance of alpha-particle-induced defects in detrital quartz appear to be useful for defining and tracing ancient pathways of uranium-bearing fluids.

Introduction

Radiation-induced defects in quartz have attracted intense scientific research for over five decades (e.g., McClelland and Donoghue, 1953; Weeks, 1956). Natural radiation-induced defects and related luminescence properties in quartz also have long been proposed to be useful for mineral exploration, particularly the search for uranium deposits, but their use has met with mixed results. The main pitfall is that natural quartz commonly contains a myriad of radiation-induced defects at extremely dilute concentrations, which therefore are difficult to detect and quantify. Moreover, these defects were usually poorly understood with respect to both their structures and origins (i.e., linkage to specific types of radiation). Consequently, most previous attempts to use radiation-induced defects in quartz as a mineral exploration tool were based on trial-and-error. We suggest that a better understanding of specific radiation-induced defects in quartz is the key to the successful application of this method for mineral exploration. For the exploration of uranium deposits, alpha-particle-induced defects should be the most diagnostic because alpha particles are produced only from decay of heavier elements (atomic number 52 and greater). Beta electrons and gamma ray, on the other hand, are known to be emitted from lighter elements as well.

Analytical Techniques

Radiation-induced damage in quartz can be investigated by a number of analytical techniques (e.g., cathodoluminescence (CL) imaging and spectroscopy, Raman spectroscopy, and EPR spectroscopy). Of these, EPR spectroscopy, which measures resonance absorption and emission of paramagnetic species (i.e., ions or molecules with at least one unpaired electron) in the presence of an external magnetic field, is by far the most sensitive and informative.

EPR measurements of the most characteristic alpha-particle-induced defects in quartz are best made at room temperature (Botis et al., 2005, 2006, 2008; Hu et al., 2008). Thermal annealing at below 200 °C as well as measurements done at high microwave powers are known to substantially enhance the detection of these defects (Botis et al., 2005, 2006).

Results

Detection and nature of alpha-particle-induced defects in quartz

The most common and best characterized radiation-induced defect in quartz is the so-called E_1' center (also known as the oxygen-vacancy electron center), which represents the trapping of an unpaired electron on a SiO_3 group after the removal of an oxygen atom (Silsbee,1966; Jani et al., 1983; Boero et al., 1997). Rink and Odom (1991) proposed that the E_1' center and its precursor oxygen vacancies are produced by alpha recoil nuclei emitted from uranium and thorium (and their radioactive daughter isotopes) in quartz. However, other studies on both natural and artificially irradiated quartz samples, including those from the Athabasca Basin, show that the formation of the E_1' center is more consistent with an origin related to beta electrons and gamma rays (Toyoda, 2005; Botis et al., 2005, 2006).

The most compelling evidence for alpha-particle-induced damage in quartz comes from haloes around uranium- and thorium-rich inclusions as revealed by CL imaging (Owen, 1988; Meunier et al., 1990; Komuro et al., 2002; Botis et al., 2005; Krickl et al., 2008). These haloes of bright CL colors have widths of ~35 to ~45 μm, consistent with the maximum penetration distances of alpha particles emitted from decay of uranium and thorium (Owen, 1988; Komuro et al., 2002). Botis et al. (2005, 2006) observed similar CL patches along the margins of quartz grains in contact with uranium-rich minerals. They also noted the presence of continuous CL rims along the margins and fractures of quartz grains, both associated with and without visible uranium-rich minerals (see also Meunier et al., 1990). Botis et al. (2006) interpreted these continuous CL rims to be produced by alpha particles emitted from uranium-bearing fluids.

Detailed single-crystal and powder EPR studies have established a suite of superoxide (O_2^-) and ozonide (O_3^-) radicals in quartz from the Athabasca Basin. These radicals also have been shown to be concentrated preferentially in the CL haloes, patches and continuous rims, suggesting their formation is related to alpha particles (Botis et al., 2008; Nilges et al., 2008, 2009; Pan et al., 2008, 2009). Available experimental data, supported by density functional theory (DFT) calculations, suggest that these superoxide and ozonide radicals are related to precursors next to silicon vacancies, which were probably produced by alpha recoil nuclei. Pan and Hu (2009) provided detailed information about the thermal properties and decay kinetics for several of these superoxide and ozonide radicals in quartz. These new results have made interpretation of natural radiation-induced defects in quartz from the Athabasca Basin possible.

Dating of uranium mineralization and remobilization

Toyoda et al. (1998) reported an attempt at EPR dating of the Permian, sandstone-hosted Kanyemba uranium deposit (Zimbabwe) by use of the E_1' center in quartz. Their plot of gamma-ray dose rates versus the amount of oxygen vacancies in quartz yielded two distinct isochrones. Toyoda et al. (1998) interpreted these two isochrones to record two uranium-related processes and noted that they have an age ratio of 50 on the basis of the slopes of the two isochrones. However, they were unable to calculate the absolute ages from these isochrones because of uncertainties about the formation processes of the oxygen vacancies in quartz.

Okumura et al. (2008) also evaluated alpha-particle-induced CL haloes in quartz for geochronological applications. Pan and Hu (2009) noted that the alpha-particle-induced defects and their precursors in quartz have comparable thermal stabilities and similar orders of characteristic decay time to the E_1' center. Hence, these alpha-particle-induced defects and their precursors in quartz are potentially useful for dating of uranium mineralization or remobilization. Presently, however, the sensitivity of and relationships between specific alpha-particle-induced defects in quartz and radiation dose rates remain unknown.

Discrimination of barren and mineralized alteration zones

One of the most characteristic features of all major uranium deposits in the Athabasca Basin is their association with intensive and extensive hydrothermal alteration haloes/envelopes. Recognition of these is the cornerstone of most exploration programs. However, there are also many examples of well-developed alteration zones without any evidence of uranium mineralization known in the Athabasca Basin. Hence, definitive discrimination between barren and mineralized alteration zones would be useful for the exploration of uranium deposits. Various techniques (e.g., mineral assemblages, trace element compositions, fluid inclusion characteristics, paleomagnetic directions, and isotope signatures) to do this have been attempted in previous studies.

EPR spectra from drusy quartz from several alteration zones in the Athabasca Basin contain the same suite of alpha-particle-induced defects but differ significantly in their abundance (Hu et al., 2008). Drusy quartz is complex in paragenesis but is undoubtedly an integral part of hydrothermal processes that formed the host alteration zones. Therefore, alpha-particle-induced defects in drusy quartz can be used to evaluate hydrothermal fluids responsible for the formation of alteration zones. Particularly, drusy quartz in alteration zones associated with uranium mineralization is characterized by elevated levels of alpha-particle-induced defects, but such defects are generally at or below detection limits in drusy quartz from barren alteration zones. These results suggest that alpha-particle-induced defects in drusy quartz are useful for distinguishing barren and mineralized alteration zones. Moreover, Hu et al. (2008) noted that drusy quartz at or near the present-day surface (i.e., hundreds of meters above mineralization) at the McArthur River deposit contains abundant alpha-particle-induced defects, suggesting that blind uranium deposits can be detected from quartz defects in overlying sandstones.

Detecting and tracing of ancient pathways of uranium-bearing fluids

Alpha-particle-induced defects in detrital quartz are more complicated in origin than those in drusy quartz, mainly because of the common presence of U- and Th-bearing mineral inclusions of complex origins in the former (Botis et al., 2005, 2006). The key to exploration using alpha-particle-induced defects in detrital quartz is to distinguish between defects associated with the U- and Th-bearing mineral inclusions and those produced by exposure to U-bearing fluids. Preliminary results from several occurrences in the Athabasca Basin suggest that the levels of alpha-particle-induced defects in detrital quartz from “less-altered sandstones” are broadly comparable and can be interpreted to represent “background values”. Consequently, the abundance of alpha-particle-induced defects in detrital quartz from potentially altered sandstones, particularly those just above the sandstone-basement unconformity, can be compared with the “background values” to determine whether they recorded additional contributions from U-bearing fluids (and U-bearing minerals in matrices) or not. For example, the abundance of alpha-particle induced defects in detrital quartz from altered sandstones near the sandstone-basement unconformity at the McArthur River and Key Lake deposits is two orders of magnitude or more greater than the background abundance. These results support the hypothesis that U-bearing fluids were channelized along the unconformity surface. Moreover, these results suggest that quantitative analyses of alpha-particle-induced defects in detrital quartz can be used to define and trace ancient pathways of uranium-bearing fluids.

Conclusions

EPR studies have revealed that quartz in the Athabasca Basin contains a suite of superoxide and ozonide radicals related to alpha particles emitted from uranium. These alpha-particle-induced defects are shown to be a powerful new aid for the exploration of uranium deposits.

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