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Revision 1

Dry annealing of metamict zircon: a differential scanning calorimetry study

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Abstract

We report the results of a Differential Scanning Calorimeter (DSC) study of the annealing of a metamict Sri Lankan zircon. Raman measurements on most chips of the powdered zircon starting material, Sri Lankan zircon (WZ19), showed no evidence of a crystalline structure whereas a few chips retained residual Raman bands typical of highly radiation damaged zircon. DSC runs on aliquots of the powdered sample were heated to 850°C and 1000°C at rates of 2°C and 10°C/minute and to 1500°C at a rate of 10°C/minute. Raman spectroscopy was used to investigate the crystallinity of grains at selected temperature stages. Exothermal peaks were observed at about 910 °C and 1260°C during the DSC run to 1500°C. The 910°C peak was demonstrated by Raman spectroscopy to mark the crystallization of tetragonal zirconia and the exothermic peak at about 1260°C was demonstrated to represent the reaction of zirconia and amorphous silica to form crystalline zircon. The degree of crystallinity of these grains was almost identical to that of highly crystalline zircons from recent gem gravels from New South Wales. A small number of experimental chips from DSC analyses under 1000°C were found to have zircon Raman bands that indicated they had undergone partial annealing.

Key words: radiation damage, metamict zircon, radiation damage annealing, Differential Scanning Calorimeter, zircon Raman spectra

Introduction

The breakdown of the zircon structure by the radioactive decay of minor components U and Th and their radioactive daughters has been the subject of research for over fifty years (e.g. Holland and Gottfried 1955; Pabst 1952; Weber 1990; Ewing et al. 2003; Zhang et al. 2000; Nasdala et al. 2001; Geisler et al. 2001, and others). Understanding the damage processes and the structural changes of zircon as it evolves to the metamict state is important in explaining discordant results in zircon U-Pb dating, anomalous zircon (U-Th)/He ages (e.g. Guenthner et al. 2013), and in estimating the integrity of zircon as a host for the disposal of actinide nuclear waste and predicting the properties of zircon in ceramic applications. The annealing of radiation damaged zircon is equally important in the above fields as well as fission track dating (e.g. Hasebe et al. 2003) and has applications in geochronology in its own right (e.g. Pidgeon 2014).

Early investigations of zircon radiation damage and annealing used optical (e.g. Vance and Anderson 1972), X-ray diffraction (XRD) techniques (e.g. Holland and Gottfried 1955) and various density and electron microscope (TEM) techniques (e.g. Weber 1990; McLaren et al. 1994; Capitani et al. 2000). Differential thermal analysis has also been applied (Lipova et al. 1965, Kulp et al. 1952) and more recently Raman spectroscopy has proved to be extremely effective in monitoring changes in radiation damage in zircons (Nasdala et al. 1995; Geisler et al. 2001, Zhang et al. 2000). A number of researchers concluded that annealing of metamict zircon takes place in two stages involving first, the formation of zirconia and second, full recrystallization back to the original zircon structure. Weber (1990) reported that annealing of a Pu doped amorphous zircon involved two steps, initial crystallization of pseudo-cubic zirconia at about 1050^{o}C and full density recovery at about 1450^{o}C where the zircons transforms back to its

original zircon structure. Colombo and Chrosch (1998) also reported that the recovery of thermally treated metamict Sri Lankan zircon involved two phases, zircon and pseudo-cubic ZrO_2. Váczi et al. (2009) reported that dry annealing of fully metamict zircon involved initial formation of ZrO_2, between 800°C and 1000°C prior to the formation of crystalline zircon above 1150°C. McLaren et al. (1994) also reported the formation of zirconia on dry heating a high U Sri Lankan zircon to 900°C. In the present research our objective was to investigate the progressive annealing and phase changes in metamict zircon during isochronal dry annealing, as determined by a Differential Scanning Calorimeter (DSC) study using Raman spectroscopy to monitor the evolving zircon crystal structure.

The zircon sample

The zircon sample used in the study, WZ19, was a black, translucent pebble from the Sri Lankan alluvial deposits. The U and Th concentrations of the pebble, determined on an aliquot of the powdered sample, are 9902 ppm and 2296 ppm respectively by isotope dilution ICP-MS. The α-dose experienced by the zircon was 13.2×10^{15} α/mg, determined from the U and Th concentrations and a "radiation damage age" for Sri Lankan zircons of 375 Ma (Palenik et al. 2003). The radiation damage age is defined as the time needed to generate the observed radiation damage and takes into account the realisation that the Sri Lankan zircons have been annealed since their formation (e.g. Nasdala et al. 2001, 2004; Garver 2002). The method for determination of radiation damage ages has been described by Pidgeon (2014). Previous reports where α-doses have been determined using the 560 Ma U-Pb age of Sri Lankan zircons (e.g. Zhang et al. 2000) give α-doses that are in excess of that needed to generate the observed damage. The α-doses in these reports need to be adjusted down by about 0.55 (Nasdala et al. 2004). For example the α-dose of 23.5×10^{15} α/mg for the most severely radiation damaged Sri Lankan zircon, sample 82988, reported in Table 1 of Zhang et al. (2000), would be reduced to 12.9×10^{15} α/mg. Rios et al. (2000) concluded that zircons with a dose higher than about 8×10^{15} α/mg (revised to 4.4×10^{15} α/mg) show no further changes in their metamict structure with further bombardment. Murakami et al. (1991)

also proposed an α-dose of 8 (4.4) x 10^{15} α/mg for their Stage III level of radiation damage where zircon appears to be entirely aperiodic as far as can be determined by X-Ray or electron diffraction. An α-dose of 12 (revised to 6.6) x 10^{15} α/mg was found by Holland and Gottfied (1955) to correspond with the disappearance of zircon XRD peaks. Weber (1990) noted that TEM studies of natural zircon confirm that an α-dose of 6.5.to 9.5 (revised to 3.6 to 5.2) x 10^{15} α/mg will result in complete amorphization of zircon. Zircon WZ19 used in the present study, with an effective α-dose of 13.2 x 10^{15} α/mg (from the time of zircon annealing), is far in excess of these values and of the same order as sample 82988 of Zhang et al. (2000), indicating it has a fully aperiodic structure. However, as rare chips of the powdered sample have residual "Raman" bands it is evident that the zircon is not homogeneous but has some lower U zones that are highly damaged but not entirely metamict.

Analytical methods

In the present study samples were analysed with a TA Instruments SDT Q600 simultaneous DSC-TGA in a nitrogen atmosphere flowing at 100 ml/minute. The heat flow between the sample and reference crucibles was calibrated using a sapphire disc provided by the instrument manufacturer. This allows the differential temperatures to be converted into heat flow. The sample aliquot and reference (an empty alumina pan) are heated at the same rate and the temperature difference between them is recorded. Powdered ~50 mg aliquots of zircon pebble WZ19 were placed in a 90 µL alumina crucible and annealing experiments were run over (1) a temperature range of 25°C to 850°C and (2) a temperature range of 25°C to 1000°C with heating rates of 10°C/minute and 2°C/minute (these runs were made on a different instrument: see accompanying material) and a temperature range of 25°C to 1500°C, with a heating rate of 10°C/minute (Fig.1). Raman spectra were determined on ten individual grains of the powdered Sri Lankan zircon (WZ19) starting material and sample chips from the DSC runs. Typical Raman Spectra are shown on Figs 2, and 3.

Raman spectra were collected at room temperature with an ISA LabRam dispersive Raman spectrometer at the Department of Chemistry at Curtin University

using the 632.817 nm line of a HeNe laser and a beam power of 2 mW at the sample. The scattered Raman light was analysed with a charge coupled device (CCD) detector after being dispersed by a grating of 1800 grooves per mm. A 50x objective was used on a BX-40 microscope. The spectral resolution of ~1.9 cm^{-1} was determined from FWHM measurements of the Neon Raman bands. The Raman shift positions were calibrated against the 520.7 cm^{-1} Silicon Raman band. Counting times were between 15 and 200 seconds depending on the structural state of the sample.

One Raman analysis was made on each of twenty selected zircon fragments (chips) from the reacted powdered sample after each DSC run.

Results

The unheated zircon.

Raman analyses were made on twenty chips of the powdered zircon sample WZ19. Five representative Raman spectra are shown on Fig. 2A. Most analyses (e.g. 4, 5, and 2) form irregular traces with no zircon Raman bands and are consistent with an amorphous structure. The spectra show broad mounds at 450 to 650 cm^{-1} and 850 to 1050 cm^{-1} suggesting some structural memory survives. Zhang et al. (2000) suggest such mounds indicate coexistence of an amorphous structure with embedded damaged crystalline material. The analysis on chip 3 shows residual zircon Raman peaks which indicate that this chip is highly radiation-damaged but not to the extent of the other chips. The analysis on chip 1 also shows small residual zircon Raman peaks which indicates a residual crystallinity. This demonstrates that zircon sample WZ19 is not homogeneous, but has minor domains with residual crystal structure within the main metamict body of the crystal. The measured U and Th contents of aliquots of the powered sample therefore represent average values.

DSC analyses

The trace of heat flow versus temperature for the DSC analysis on a 60 mg aliquot of the WZ19 zircon powder heated to 1500°C at 10°C/minute is shown on Fig. 1. The trace shows two exothermic peaks at 910°C and 1260°C. The first sharp peak shows a rapid rise from 897 °C to 910°C and a tail to ~920°C. The recorded heat release is 41 J/g. The second broader and flatter peak shows a rise from about 1185°C to 1260°C and a tail to about 1350°C. The recorded heat release of this peak is 49 J/g. Further DSC runs to 850°C and 1000°C were made at a heating rate of 2°C/minute (see accompanying material)

Representative Raman spectra of chips (20 measured) from runs to 850°C and 1000°C are shown on Fig. 2. Four of the five spectra on Fig. 3A, (to 850°C) show no zircon or other Raman bands but resemble the irregular spectra of unheated metamict zircon on Fig. 1, except that the broad mounds from 450-650 cm^{-1} and 850-1050 cm^{-1} are more defined than comparative structures on the Raman spectra in Fig. 1. This clearly demonstrates that the metamict structure has undergone additional ordering as the temperature has risen to 850°C. There is no evidence of any thermal peaks that might suggest a phase change or reaction in the sample below 850°C.

One Raman analysis (WZ19b-2)(Fig. 2B) from the 850°C run shows definite zircon (and some anomalous) bands. In this spectrum the zircon $\nu_3(SiO_4)$ stretching vibration has a peak position of 1003.7 cm^{-1} and a FWHM of 12.5 cm^{-1} (Fig. 5). We interpret this as a partial recovery of a highly damaged, but not completely metamict, domain in the WZ19 zircon, such as shown by the spectrum for unheated chip WZ19A-3 in Fig. 2A.

Six Raman spectra of chips heated to 1000°C are presented on Fig. 2C. Also shown on this figure is a representative Raman spectrum of a highly crystalline “Mud Tank” zircon. It is most striking that all Raman spectra contain numerous peaks that are not characteristic of zircon. These peaks are interpreted as indicating a new mineral phase that formed between the temperatures 850°C and 1000°C, clearly coinciding with the exothermal peak at about 910°C. A representative Raman spectrum, WZ19C-3 from Fig. 2B, and the Raman spectrum of tetragonal zirconia (from Mercer et al. 2007) are shown on Fig. 3. The two spectra are similar, and include lines at 148 cm^{-1} and 263 cm^{-1} that are not present in the monoclinic zirconia spectrum and do not have a line at 348cm^{-1} that is

peculiar to the monoclinic phase. The cubic zirconia spectrum has far fewer lines than the zirconia spectra shown on Fig. 3 (Phillippi and Mazdiyasni 1971). We conclude from the Raman spectra that the exothermic peak observed at about 910^{o}C represents the rapid crystallization of tetragonal zirconia. Definite zircon peaks are present in the spectra of WZ19C-1 and C-6. These data are shown on Fig. 5 to fall well away from those of the recystallised grains (see following) and off the trend through the Permian rhyolite – River gem-gravel zircons. This is interpreted as indicating a recovery rather than a recrystallisation of highly radiation damaged zircon.

Also striking are the Raman spectra (Fig. 4) of sample chips after heating to 1500^{o}C. Six of the seven representative Raman spectra shown on Fig. 4 have strongly crystalline zircon Raman spectra together with remnants of the previously dominant zirconia peaks. This demonstrates that zirconia and amorphous silica have recrystallised to form zircon between 1000^{o}C and 1500^{o}C and it is evident that this reaction coincides with the exothermic phase change observed in the DSC analysis at about 1260^{o}C (Fig. 1). The Raman shift positions and FWHM of ten of the spectra are shown on Fig. 5. Also shown on this figure are Raman data from unannealed, Permian rhyolite zircons from Nasdala et al. (1998) and highly crystalline zircon pebbles from river gem gravels from the slopes of Tertiary volcanoes in New South Wales. These are the most crystalline zircons known to the present authors. The recrystallised WZ19 zircon grains form a tight group on Fig. 5 demonstrating that metamict WZ19 zircon grains have undergone uniform recrystallization during the DSC run and the degree of crystallinity of the grains is only slightly less than the highly crystalline river gravel zircons.

The spectra on Fig. 4 are arranged to show the increasing presence of unassigned peaks. The peak at about 300 cm^{-1} on spectra WZ19-10 could be remnant zirconia peak. However, the large peak at about 680 cm^{-1} and other minor anomalous peaks in the WZ19-6 spectrum have not been identified. This peak is not cubic zirconia which would show as a broad peak at about 625 cm^{-1} (Phillippi and Mazdiyasni 1971). We tentatively interpret these as anomalous luminescence bands.

Discussion

Our DSC and Raman analyses demonstrate that the annealing path of metamict zircon is marked by two phase changes, first the crystallization of metastable tetragonal zirconia at a temperature of about 897°C to 920°C and second the recrystallization of nearly undamaged zircon at 1185°C to 1260°C. It is interesting to note that in an early Differential Thermal Analysis (DTA) study of metamict zircons Kulp et al. (1952) identified an exothermic "doublet" reaction at about 900°C but were unable to explain the cause. Our results confirm previous reports of a two-stage process in the crystallization of metamict zircon involving initial stages of zirconia formation followed by a second stage of formation of crystalline zircon (e.g. Weber 1990; Weber et al. 1994; Capitani et al. 2000). Capitani et al. (2000) reported that, on dry heating highly amorphosed zircons, ZrO_2 grains were detected at 930°C and small zircon grains were observed after 16 hours at 1330°C. Capitani et al. (2000) and McLaren (1994) also reported zirconia formation in less radiation damaged zircon after dry heating to about 900°C although in detail zirconia formation may relate to amorphous domains in these grains.

Of these reports the two isochronal annealing studies most closely related to our DSC study are those of (1) Vance and Anderson (1972), who reported crystallization of tetragonal zirconia during isochronal annealing experiments on metamict zircon where the grain size was recorded as 100 Å after heating for one hour at 850-950°C and 500 Å after heating for 1 hour at 1100°C; and (2) Weber (1990, 1991) who reported XRD and density data for an isochronal annealing study of an amorphous Pu-doped zircon with anneals carried out for 12 hrs at 100°C intervals from 200-900°C, 50°C intervals from 900°C to 1250°C and 100°C intervals to 1600°C. The first recovery stage was a density increase coincident with XRD evidence for the presence of pseudo-cubic zirconia. The second stage of recovery is associated with transformation back to the original zircon structure as measured by the density before or at the 1450°C temperature step. McLaren et al. (1994) and Capitani et al. (2000) also observed growth of zirconia grains from metamict zircon at about 900°C and Vance (1975) reported full recovery of the infrared spectrum of a metamict zircon at 1450°C.

In our results the broad exothermic peak from about 1185°C to 1350°C (Fig. 1) marks the reaction between zirconia and amorphous silica to form crystalline zircon (Figs. 2 and 5). It can be seen from Fig. 5 that the crystallised zircon is not quite

248 complete, as compared to the data points of the gem gravel zircons, but extends along the
249 trend of slightly radiation damaged zircon indicated by the distribution of data points
250 from unannealed zircon from a Permian rhyolite (Nasdala et al. 1998). We attribute this
251 to the incorporation of defects into the rapidly crystallising zircon lattice during the DSC
252 run with a temperature increase of 10^{o}C/ minute. The extended temperature range of the
253 exothermic peak from about 1185^{o}C to 1350^{o}C (Fig. 1) contrasts with the sharp
254 exothermic peak of the first annealing stage (Fig.1). This could be due to kinetic factors
255 such as diffusion rates of ions moving from defect to lattice positions or as a consequence
256 of the heterogeneity of disorder in the amorphous zircon, where energy required for
257 zircon crystallization is lower in relatively less disordered domains than that in more
258 highly disordered domains.
259 The enthalpy of reaction of the formation of zircon from its constituent oxides has
260 been determined by Ellison and Navrotsky (1992) as -27.9 kJ/mol. However, given the
261 starting material of quartz and spectroscopic grade ZrO_2 used in this determination the
262 results may have little relevance to the reconstitution of zircon from the amorphous silica-
263 zirconium mixture present in metamict zircon. More relevant is the enthalpy
264 determinations of zircon formation from radiation damaged zircon by Ellsworth et al.
265 (1994) who reported enthalpy determinations of zircon annealing using drop calorimetry
266 at a temperature of 1000^{o}C, for a number of radiation damaged zircons including
267 metamict Sri Lankan zircon 6500 which contains about 7600 ppm of equivalent U and
268 has an α-dose of 11.7 (corrected to 6.4) x 10^{15} α/mg. After heating to 1000^{o}C an aliquot
269 of zircon 6500 showed only zirconia XRD peaks, which is in accord with the present and
270 previous studies that show a higher temperature is required for zircon recrystallization.
271 The measured enthalpy of this reaction was -55 kJ/mol. Ellsworth et al. (1994) comment
272 that if sample 6500 had annealed to only ZrO_2 (tetragonal) and SiO_2 (glass) "the
273 measured enthalpy should be -16.6 kJ/mol, suggesting that most of sample 6500 must
274 have annealed to a state energetically similar to crystalline zircon". Whereas this is
275 difficult to reconcile with our DSC results, which show stage 2 recrystallization to zircon
276 above 1100^{o}C, the heat emission for our stage 1 crystallization of zirconia of 40 J/g (Fig.
277 1), equated to an enthalpy of -5 kJ/mol, is far lower than the enthalpy values reported by
278 Ellsworth et al. (1994). The interpretation of our thermal data as an enthalpy value

assumes that all zirconium has taken part in the reaction which is probably not correct as we know zircon WZ19 has domains with residual crystallinity. Even with as much as 20% of the zirconium unavailable our estimate of the enthalpy of the reaction of up to -6 kJ/mol is significantly lower than the Ellsworth et al. (1994) estimate. This discrepancy is at present unexplained. Our estimate for the enthalpy of stage 2, the crystallization of zircon, is similar to stage 1 but will require further confirmation as areal integration of this broad, flat exothermal peak (Fig. 1) is susceptible to uncertainty in the choice of the baseline.

No exothermal peaks were observed in the DSC run up to 850^{o}C suggesting that the recovery process up to this point does not involve phase changes or specific reaction. This is also shown in Raman measurements on most chips heated to 850^{o}C which retain amorphous Raman spectra however, strong zircon Raman peaks have been identified in one chip, WZ19B-2 in the run to 850^{o}C (Fig. 2B) and Raman peaks have been identified in the zirconia dominated spectra of chips WZ19C-1, 5 and 6 in the run to 1000^{o}C (Fig. 5). Raman data of these grains are included in a table in the accompanying material. On Fig. 5 it can be seen that data points fall well away from the cluster of annealed zircon points and away from the trend through the points and the unannealed Permian rhyolite zircon data points of Nasdala et al. (1998). This demonstrates a process of annealing very different from that observed in the other grains and is interpreted to represent partial recovery of less damaged, possibly lower U, domains in the parent zircon crystal, such as illustrated by the Raman spectrum of unheated chip WZ19A-3 on Fig. 2A. These results demonstrate that recovery of partially metamict zircon, that has a remnant crystalline structure, is active by 850^{o}C.

These observations are in accord with the results of experiments at lower temperatures (e.g. Geisler et al. 2001), where annealing of highly radiation damaged zircon occurs by progressive removal of defects. Geisler et al. (2001) reported the results of a series of dry heating experiments on two partially metamict Sri Lankan zircons that consist of misoriented disordered crystalline domains within an amorphous matrix as revealed by TEM studies (e.g. Bursill and Mc Laren, 1966; Murakami et al. 1991; Weber et al. 1994; Capitani et al. 2000). At temperatures from 600^{o}C to 900^{o}C and durations from 1 minute to 200 hours, recovery of the zircon structure measured, by the Raman

peak position and line width (FWHM) of the $\nu_3(SiO_4)$ stretching vibration did not follow the initial correlation trend observed during the accumulation of radiation damage, where line-width increased systematically with decreasing phonon frequency (Geisler et al. 2001) (see Fig. 5). Instead, heating experiments showed that the $\nu_3(SiO_4)$ Raman peak increased in intensity and showed a rapid initial recovery of the phonon frequency compared to a slower recovery of the line width. Geisler et al. (2001) interpreted this as evidence that the first stage in the recovery of the radiation-damaged zircon structure is the recovery of the short-range order by the removal of point defects in the crystalline domains and at this stage recrystallization of amorphous zircon is limited or not activated at all (Geisler et al. 2001). The anomalous positions of Raman shift and FWHM data of grains from DSC runs up to 1000^{o}C on Fig. 5 can be readily explained by a rapid recovery of the Raman shift but slower recovery of the Raman peak as demonstrated experimentally by Geisler et al. (2001). These results support our and previous conclusions that annealing of amorphous zircon and the recovery of partially radiation damaged zircon are two separate processes. These observations also confirm reports that propose two stages in the annealing process involving firstly the recovery of heavily disturbed but still crystalline domains and secondly the recrystallization of amorphous regions (Colombo and Chrosch, 1998).

Implications

Results of our DSC study of the annealing of a metamict zircon provide enthalpy and reaction-temperature information for phase changes at 900-915^{o}C and 1185-1350^{o}C, that have been identified from Raman measurements to represent initial crystallization of tetragonal zirconia followed by recrystallization of zirconia and amorphous silica to form undamaged zircon. This confirms previous reports of two-stage annealing of metamict zircon involving the formation of zirconia followed at higher temperature by recrystallization to undamaged zircon. This annealing process can be distinguished from the recovery of partially metamict zircon described by Geisler et al. (2001) and could form the basis for a definition of “amorphous” zircon as “zircon that has such a high

degree of radiation damage that recrystallization involves initial formation of metastable zirconia followed at a higher temperature by crystallization of zirconia and amorphous silica to form undamaged zircon". This is not to imply that structural differences within an amorphous region do not exist (Rios et al. 2000). Our results and previous studies are important for nuclear waste applications where zircon has been proposed as a host mineral for long-term storage of actinides. If, in such a facility zircon broke down to an amorphous state, as shown by Weber (1991) can happen in a few years to a Pu-doped zircon, its resistance to water penetration and possible actinide loss is greatly reduced (Geisler et al. 2003). Our results show that it would be impractical to recrystallise the amorphous zircon back to its undamaged crystalline form. Amorphous zircon is highly susceptible to loss of Pb and He severely limiting its usefulness in geochronology. Recrystallization of amorphous zircon on the other hand would most likely reset the geochronological systems as well as the crystal structure establishing a time zero point for geochronological measurements, including zircon fission track, radiation damage and (U-Th)/He dating. However, as far as the authors are aware there have been no reports of evidence such as multiple zirconia inclusions in zircon from natural settings that could indicate that annealing of "amorphous" zircon has taken place. This suggests that annealing of amorphous zircon is rare in dry geological environments which is in accord with our result as even in granulite to eclogite facies metamorphism temperatures rarely rise to 900^{o}C.

However, a factor that can seriously affect the annealing behaviour of radiation damaged zircon is the presence of water (Geisler et al. 2004). Geisler et al. (2004) reported the formation of monoclinic zirconia in hydrothermally treated metamict Sri Lankan zircon at a temperature of 400^{o}C demonstrating the profound influence of water in lowering the activation energy for zirconia formation. The formation of zirconia in these hydrothermal experiments also demonstrates that the annealing of amorphous zircon takes place as a two stage process whether under dry or hydrothermal conditions. These results indicate that annealing of amorphous zircon to zirconia and then crystalline zircon is possible under natural metamorphic conditions where water is present.

Our DSC experiment provides a means for investigating the annealing and recovery of radiation damaged materials. The DSC runs can be stopped at any

372 temperature providing a continuous record of the stages of annealing of a metamict zircon
373 or other radiation damaged mineral. This provides an opportunity to study reactions and
374 configurations of zirconium, silicon, oxygen and trace elements at the atomic scale at
375 selected stages in the annealing process. It also provides an opportunity to measure the
376 electrical and other properties of the amorphous zircon as it progressively anneals.
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Figure Captions

Figure 1. DSC profile of 60 mg of powder of zircon WZ19 heated to 1500°C at 10°C/minute.

Figure 2. (A) Stacked Raman spectra made on individual chips of the unheated powdered sample of zircon WZ19. (B) Stacked Raman spectra of chips of the sample after heating to 850°C at 2°C/minute. (C) Stacked Raman spectra of chips of the sample after heating to 1000°C at 2°C/minute.

Figure 3. (A) Raman spectrum of chip WZ19C-3 heated to 1000°C at 2°C/minute. (B) Raman Spectrum of tetragonal zirconia from Mercer et al. (2007).

Figure 4. Stacked spectra of Raman analyses on individual chips of the sample after heating to 1500°C at 10°C/min.

Figure 5. Shows Raman shift and width data-points of twenty zircon chips after the DSC run to 1500°C together with points for partially annealed zircon chips after DSC runs to 850°C and 1000°C. Error bars are 1σ. Also shown for reference are Raman data-points of zircons from gem gravels from New South Wales and unannealed zircons from a Permian rhyolite from Saxony, Germany (Nasdala et al. 1998). The approximately linear trend of these data-points, which includes the crystalline zircons from the 1500°C DSC run, defines the "Radiation Damage Trend" described by Geisler et al. (2001).

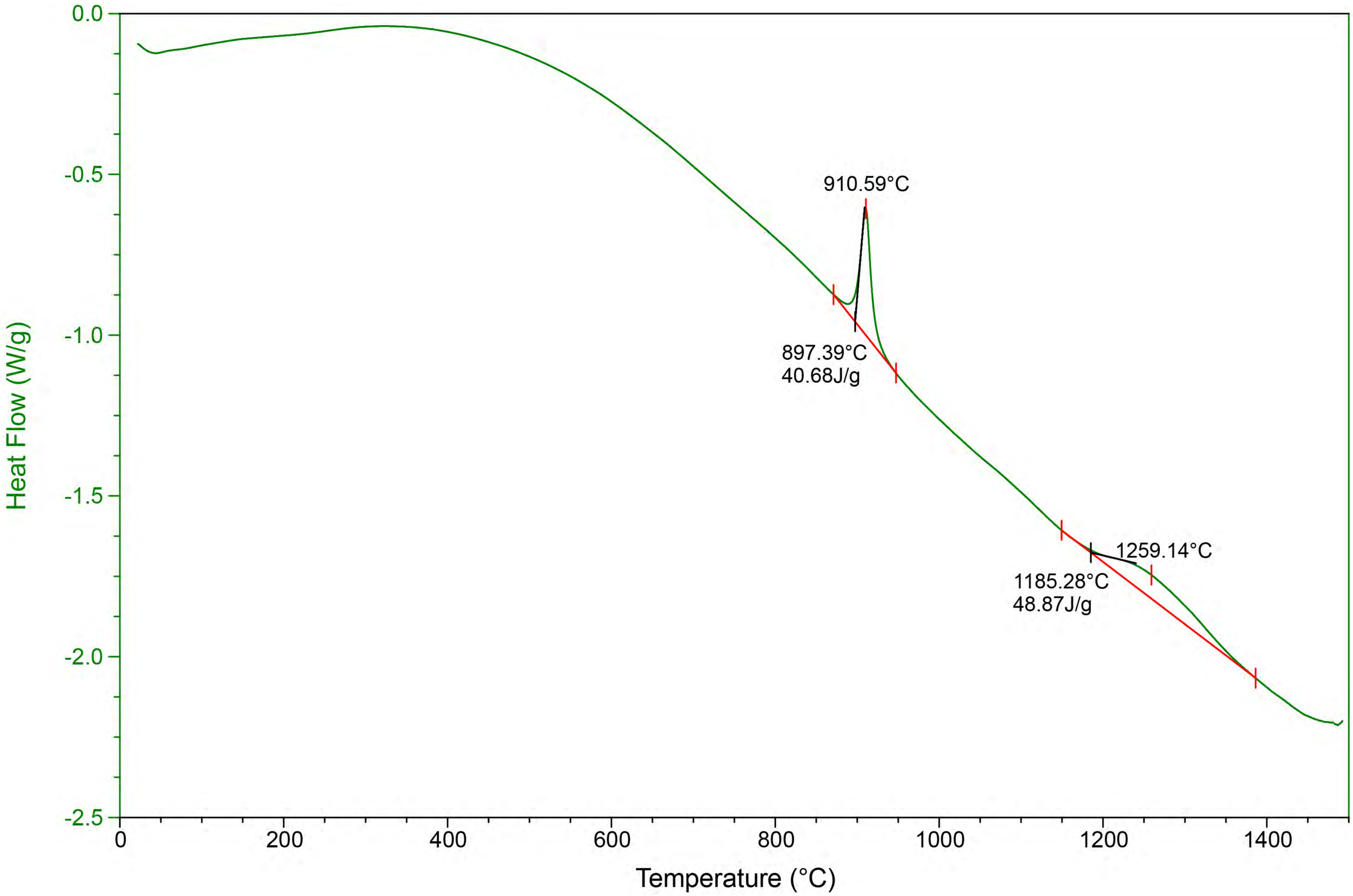

Figure 1

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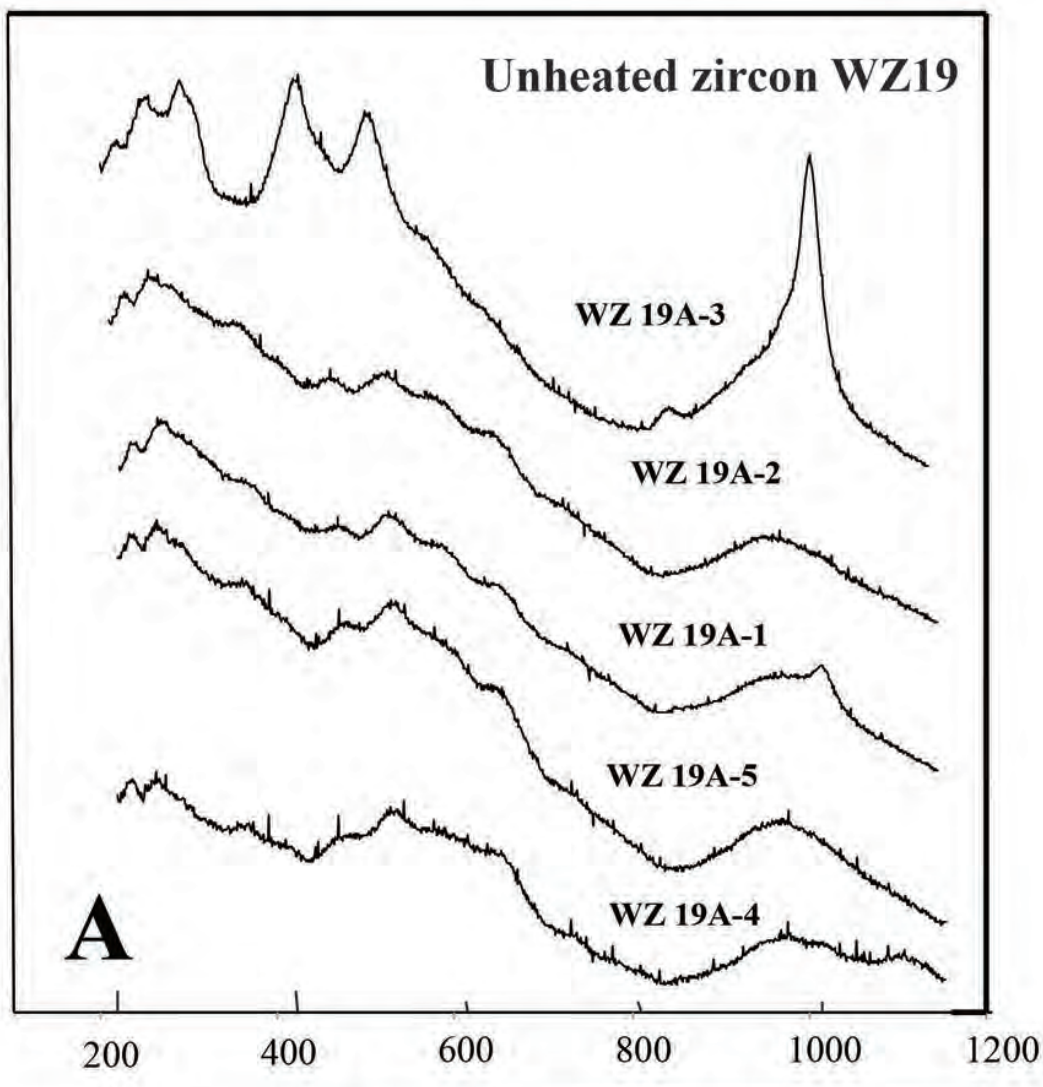

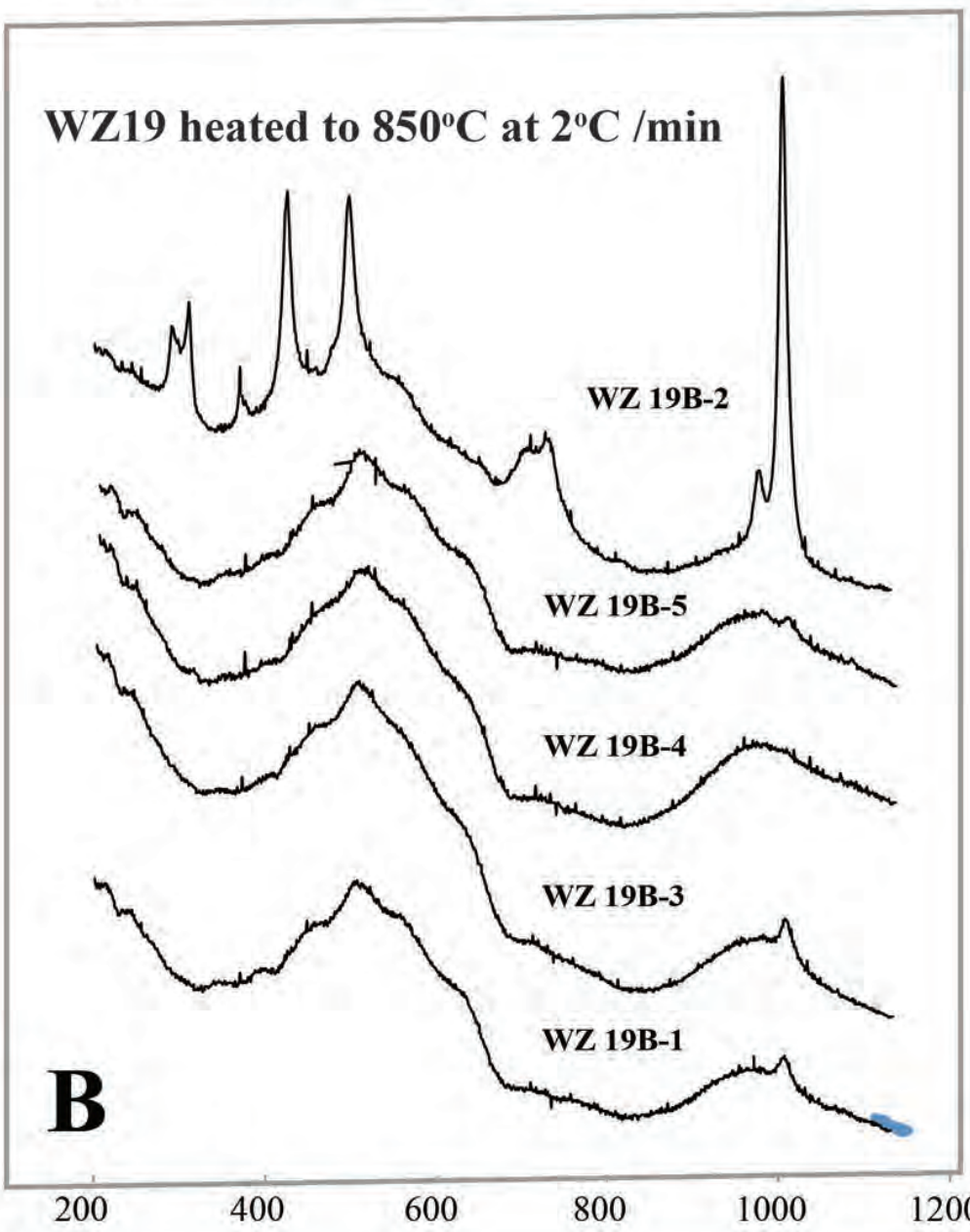

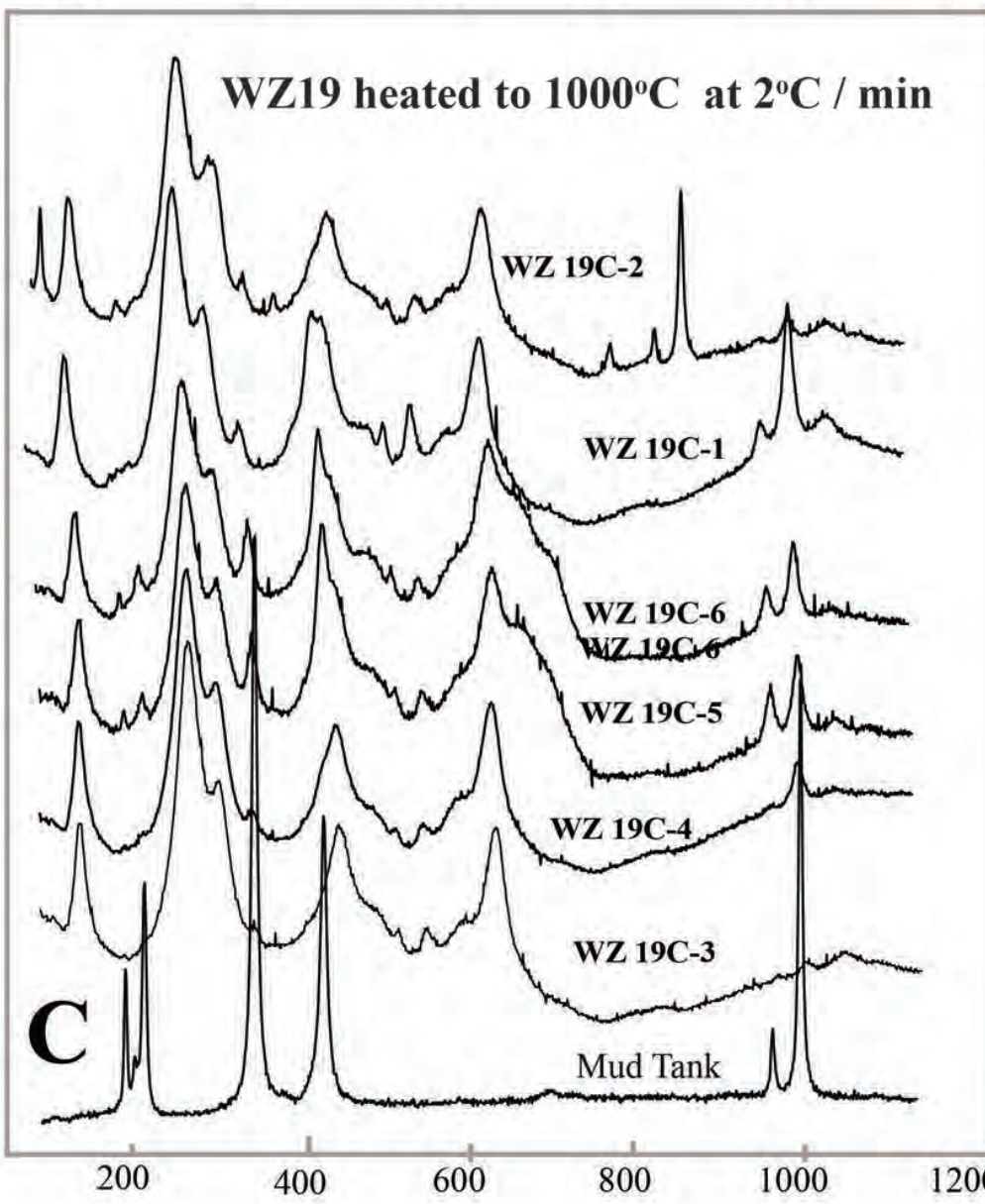

Figure 2

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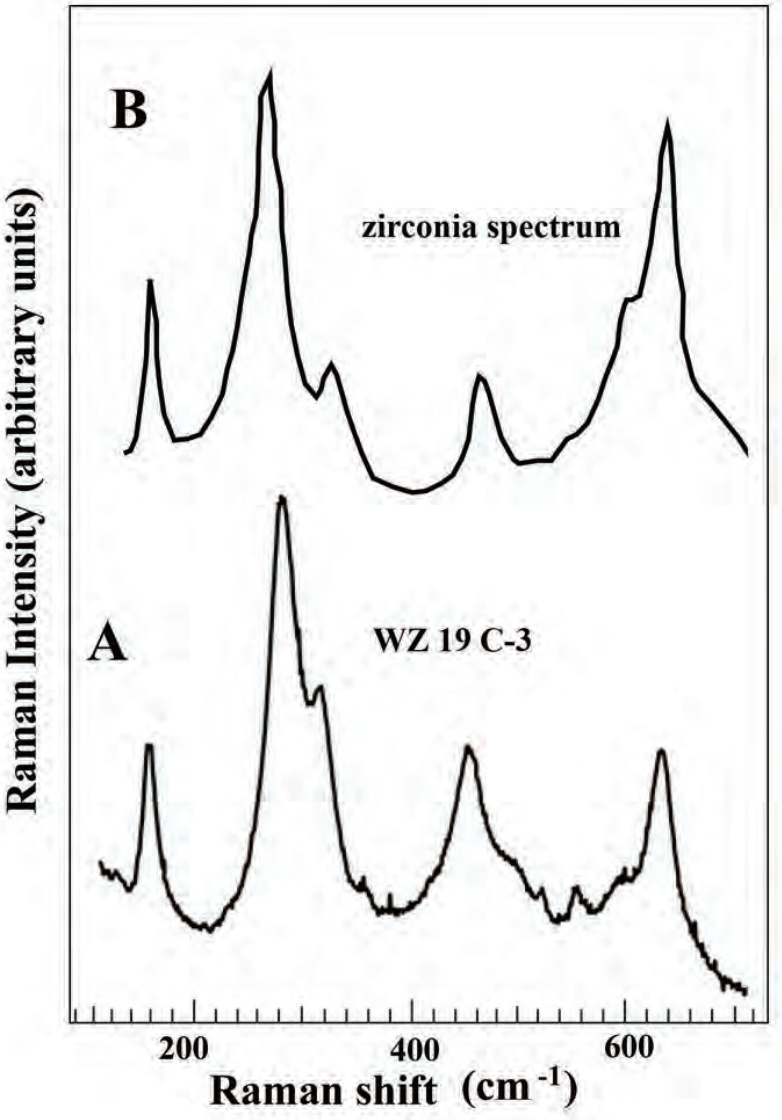

Figure 3

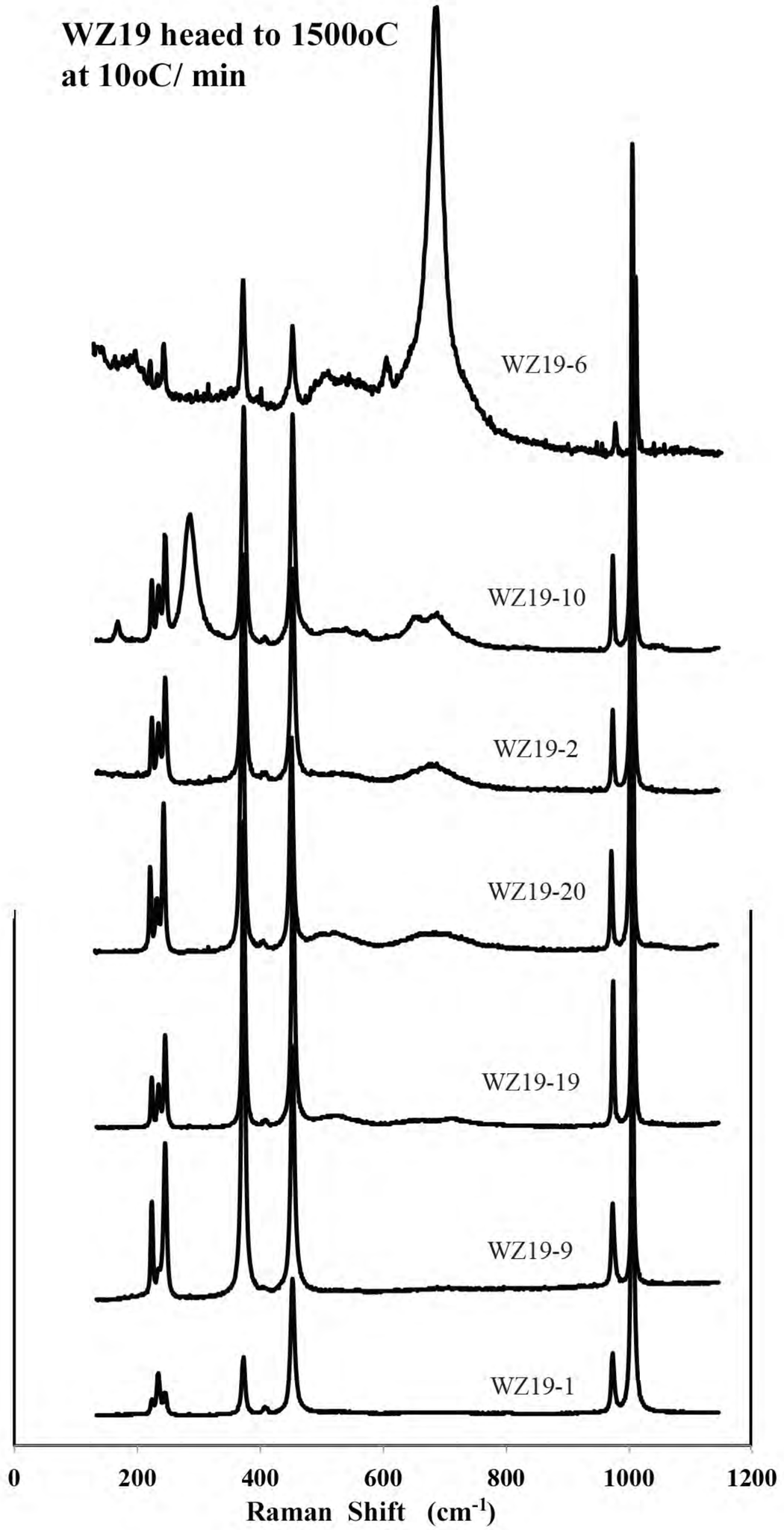

Figure 4

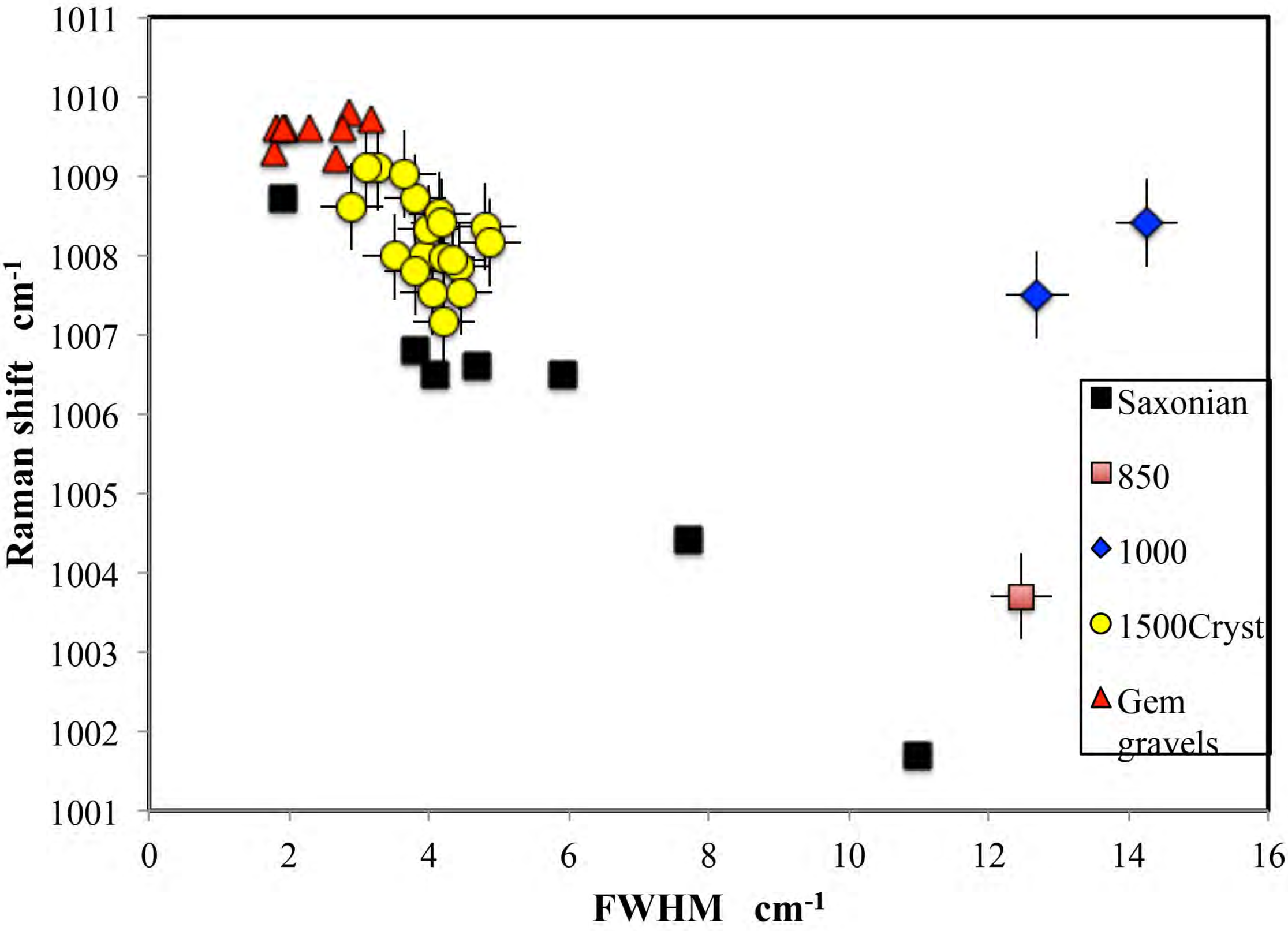

Figure 5