American Mineralogist, Volume 70, pages 1224–1231, 1985

An experimental study of hydroxyl groups and water in synthetic and natural zircons: a model of the metamict state

RAOUL CARUBA, ALAIN BAUMER

Laboratoire de Géologie-Géochimie, UA 725 .CNRS
Université de Nice, Parc Valrose 06 034 Nice Cedex, France

MAX GANTEAUME

Centre de Thermodynamique et de Microcalorimétrie
26 Rue du 141° R.I.A. 13 003 Marseille, France

AND PHILIBERT IACCONI

Laboratoire de Physique Expérimentale, Université de Nice
Parc Valrose 06 034 Nice Cedex, France

Abstract

Synthesis of zircon has been attempted between 200 and 800°C at 1 kbar in a fluorinated environment. Zircon is obtained between 400 and 800°C. It is a solid solution of the type $Zr(SiO_4)_{1-x}(OH,F)_{4x}$ with $0.2 < x < 0.8$ and where the $(OH,F)_4$ group takes the place of a SiO_4 tetrahedron.

The Si/(OH, F) atomic ratio increases with the crystallization temperature. The stability of these hydroxylated zircons depends on the concentration of dissolved OH,F. The lattice of hydroxylated and fluorinated zircons is clearly less stable than that of normal zircons. However, even after annealing at 950°C, there are still traces of $(OH,F)_4$ groups in the lattice. The cell parameters of hydroxylated-fluorinated zircon are smaller to those of normal zircon: $6.581 < a < 6.663$Å and $5.949 < c < 5.978$Å.

The reason for this substitution is suggested to be the presence of fluorine in the $(OH)_4$ tetrahedra. These zircons are compared to natural metamict zircons. We conclude that natural metamict zircons are formed at low temperature in a hydrous and fluorinated environment which is enriched in heavy rare earth and radioactive elements. The particles emitted by the radioactive atoms readily destroy the hydroxylated lattice of such zircons.

Introduction

Zircons are minerals which have the general formula: $ZrSiO_4$. Often their structure is damaged as a result of the decay of dissolved radioactive isotopes. Those zircons are known as metamict. They are found in rocks enriched in volatile substances like water, fluorine, CO_2 and elements such as U, Th and REE. They are formed at low temperature, usually towards the end of crystallization or in hydrothermal veins (Speer, 1980). Various studies indicate that these zircons show larger than normal cell parameters, and contain structural water (Frondel, 1953; Krstanovic, 1964). Usually the entry of water is considered to occur after crystal formation because it is assumed that hydration is accomplished easily when the crystalline lattice was damaged during metamictization (Mumpton and Roy, 1961). But the metamictization phenomenon in natural crystals is not uniform, and often the intensity of metamictization is zoned (Sahama, 1981) or is higher in specific parts of the crystal.

For some years, experimental work has shown that synthetic zircon may contain OH groups (Frondel and Collette, 1957; Caruba et al., 1975b). This kind of zircon has a general formula $Zr(SiO_4)_{1-x}(OH)_{4x}$, where $(OH)_4$ tetrahedrons take the place of SiO_4 groups. Some of its properties are similar to those of natural metamict zircons. Therefore, it is interesting to study the similarities between synthetic zircons and natural metamict zircons. The aims of this study are:

(a) To define at $P = 1$ kbar, the chemical and temperature conditions needed to form hydroxylated zircon, synthesized by the hydrothermal method, to determine the role of fluorine during their crystallization, to show with infra-red spectrometry the presence of $(OH)_4$ groups, and to measure thermogravimetrically the concentration of $(OH)_4$ as a function of temperature of formation.

(b) To determine at $P = 1$ atm the decomposition temperature of these hydroxylated zircons, to analyse the emitted gases and to verify with thermoluminescence the presence of (OH,F) groups on the lattice before and after these minerals have been fired at 950°C.

0003–004X/85/1112–1224$02.00

(c) To compare the properties of these synthetic zircons to the properties of natural metamict zircons.

(d) To propose a model for natural metamict zircon genesis.

Experimental conditions

Zircons were hydrothermaly synthesized in PER 41 alloy autoclaves (Imphy, France). The pressure is measured to ±50 bars and the temperature to ±5°C. The reactants were put into gold capsules. The purity of the synthetized zircons was checked with X-Ray diffractometry (Co anode) and the cell parameters were measured with a Guinier-Seeman-Bohling RX camera with CaF_2 as internal standard.

A modified Setaram G.70 thermoanalyzer was used for thermogravimetric analysis. The temperature of the linear furnace was increased at a constant rate of 58°C/hr until the desired temperature was reached. The zircon samples (0.1 g for natural minerals and 0.04 g for synthetic crystals) were put in a boat which was swept by a constant flow (4.7 l/hr) of nitrogen.

The gases emitted during the heating of the different samples were analyzed with a method (Thevand et al., 1982) which combines the advantages of controlled decomposition rate thermal analysis (Rouquerol, 1969; Rouquerol and Ganteaume, 1977) with those of an analysis of the evolving gas with a quadrupole mass analyzer.

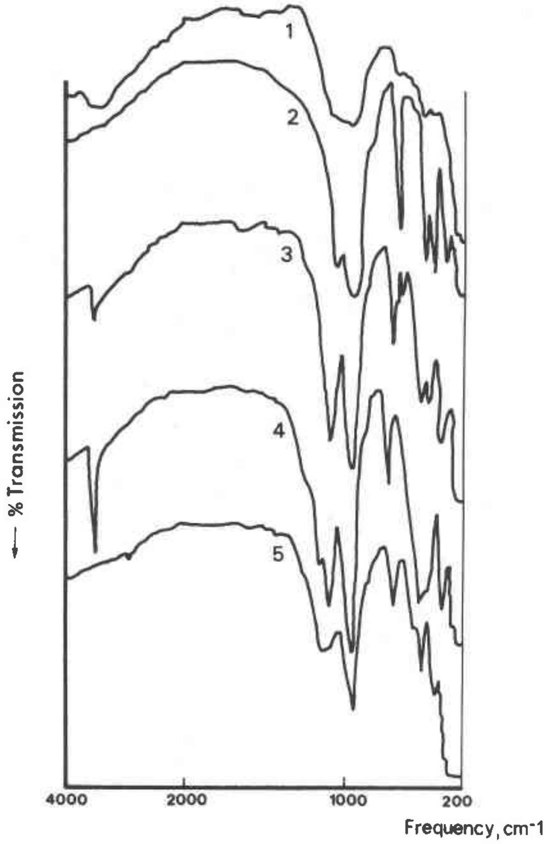

Fig. 1. Infrared spectra of natural metamict (1) (Ampassipoana); and synthetic zircons: (2) $ZrSiO_4$; (3) $Zr(SiO_4)_{0.88}(OH)_{0.46}$ (800°C–1 kbar); (4) $Zr(SiO_4)_{0.54}(OH)_{1.86}$ (500°C–1 kbar); (5) Zircon number 4 reheated at 950°C under 1 atm.

The IR instrument is a 225 Perkin-Elmer spectrometer. The sample of zircon was diluted with KBr (1 mg of zircon per 300 mg of KBr) and pressed to form a 13 mm diameter pellet.

The thermoluminescence method (TL) and experimental details have been described by Iacconi (1979). A sample of 4 mg is X-ray irradiated (W target, 2 mA and 45 kV) at 77 K for 10 min in a secondary vacuum with a heating rate of 0.5°C/sec. The TL signal is detected with two photomultipliers with S13 an S20R response (2018 B and XP 1017 of Radiotechnique) through a filter centered on 285 nm. The spectral analysis of the TL peaks is carried out between 250 nm and 800 nm with 10 to 20 nm bandwidth interference filters.

Fluorine was analyzed by the "Service Central d'Analyses" of the CNRS and at the "CRPG" in Nançy.

Basic products

To prepare synthetic hydrothermal zircons we used two methods (Caruba et al., 1975). One, for hydroxylated zircons, based on the reaction between crystalline zirconium fluoride monohydrate and amorphous silica (Koch Light products): $ZrF_4 \cdot H_2O + 2\ SiO_2$. The other, for normal zircon, by means of the reaction $ZrO_2 + SiO_2$.

The selection of natural zircons from different collections depended on their metamict characteristics. They are from various regions: Ampassipoana, Betafo and Berere (Madagascar), Ontario (Canada), Tarraouadji (Niger). Dr. T. Sahama supplied us with zircons from Ceylon and A. Carion with those from Arabia. Only the zircon samples from Ampassipoana, Arabia and Ontario were large enough for a chemical analysis preceding our experiments; they contained 0.21, 0.10 and 0.16 wt.% of fluorine respectively.

Experimental results

Synthesis of hydroxylated zircon

The synthesis experiments were done at a constant pressure (1000 bars) every 100°C from 200 to 800°C for 96 hours. Between 400 and 800°C zircon was synthesized, but at 200 and 300°C we did not obtain any zircon and only newly formed quartz was detected. The pH of the aqueous solution in the capsules was about one. The synthesized zircons have different colors, varying from grey or black for the low temperature zircons to white for those formed at high temperature.

Infrared properties

The IR spectra of synthetic zircon prepared in a fluorine-rich environment show an absorption band at 3515 cm^{-1} which is 80 cm^{-1} wide at half height, and whose intensity falls as the synthesis temperature rises (Fig. 1). The band at 3515 cm^{-1} is specific to the O–H and H–O–H vibrations in these zircons and is well defined. It actually is broader than observed for OH peaks for other minerals, such as apatite (Reisner and Klee, 1982) so we may assume that the $(OH,F)_4$ tetrahedra are not exactly identical nor symmetrical. The spectra also show a band at about 1100 cm^{-1}

Table 1. Properties of hydroxylated zircons synthetized at a pressure of 1 kbar

SAMPLE	COMPOSITION			a	c	LOSS	COLOR	TL PEAKS
	Zr	(SiO4)	(OH)	+0.005Å	+0.005Å	% WEIGHT		°K
400°	1	0.19	3.25	6.581	5.949	17.9	BLACK	153
500°	1	0.54	1.86	6.592	5.966	9.7	BLACK	143
600°	1	0.75	0.98	6.595	5.969	5.0	GREY	128
700°	1	0.84	0.66	6.599	5.972	3.1	WHITE	118-163
800°	1	0.89	0.46	6.599	5.976	2.3	WHITE	118-163

which is absent in normal zircon because its amplitude depends on the OH concentration in the crystal.

We also noticed some shifts in the position of some specific peaks when these spectra are compared to those for non-hydroxylated zircons. The characteristic SiO_4 peaks shift from 1020 to 1045 cm^{-1} and from 615 to 635 cm^{-1}, while those at 900 cm^{-1} do not show any variations. These shifts are probably due to a weight loss resulting from the replacement of SiO_4 by $(OH,F)_4$ (density change in the tetrahedra).

After heating to 950°C under 1 atm for one hour, the zircons synthesized at 400, 500 or 600°C lose their absorption peak at 3515 cm^{-1}, while the peak of zircons synthesized at 700 and 800°C and reheated to 950°C decreases but does not disappear completely. Even in this last case, the dehydroxylation is not complete.

The IR spectra of dehydroxylated zircon are different from those of normal zircon. The peak at 1100 cm^{-1} does not disappear. The one at 900 cm^{-1} shifts to 880 cm^{-1} and the one at 635 cm^{-1} does not change. For normal zircon it is the peak located at 615 cm^{-1} which does not vary (Hubin and Tarte, 1971).

The IR spectra of natural hydrous zircons and of hydroxylated metamict zircons have wider absorption bands between 3700 and 3000 cm^{-1} due to presence of OH, than those of synthetic zircons. After heating the sample with KBr at 300°C under vacuum, we notice the presence of a large absorption band caused by OH. This indicates a large variation in the energy of the OH bands (Deliens et al., 1977). But there is no characteristic peak for H_2O at 1600 cm^{-1}.

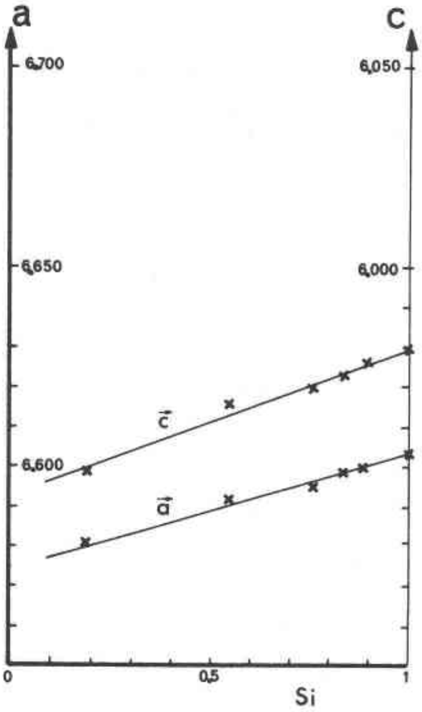

Fig. 2. *a* and *c* lattice parameters of synthetic hydroxylated zircons, depending on the number of silicon atoms on the lattice. The numbers 1, 2, 3, 4 and 5 correspond to the zircons synthetized at 400, 500, 600, 700 and 800°C at 1 kbar respectively. Number 6 corresponds to the theoretical case of pure zircon.

Unit cell parameters

Hydroxylated synthetic zircons have very small but measurable variations in their lattice parameters (Table 1). The measurements indicate that the lattice parameters vary with the amount of substitution of SiO_4 by $(OH,F)_4$ (Figs. 2 and 3). After being fired at 950°C, the lattice parameter of these zircons become close to normal.

Natural metamict zircons have characteristically wide absorption bands and increased lattice parameters. Annealing of natural zircon leads to the restructuring of the lattice and thus to a decrease of the lattice parameters, which tend to approach the theoretical values of the pure zircon without ever reaching them.

Thermal analysis

The thermogravimetric graphs indicate the thermal decomposition of hydroxylated zircons synthesized between 400 and 800°C and at 1 kbar pressure. Samples synthetized at higher temperature are also stable to higher temperatures and show less weight loss (at 950°C) (Fig. 5).

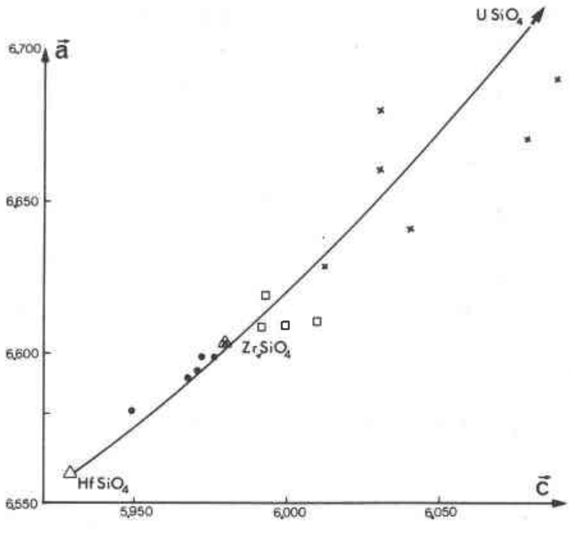

Fig. 3. Comparison between the unit cell parameters of synthetic hydroxylated zircon (point), natural metamict zircon, hydrous or hydroxylated (cross) and reheated zircon (square).

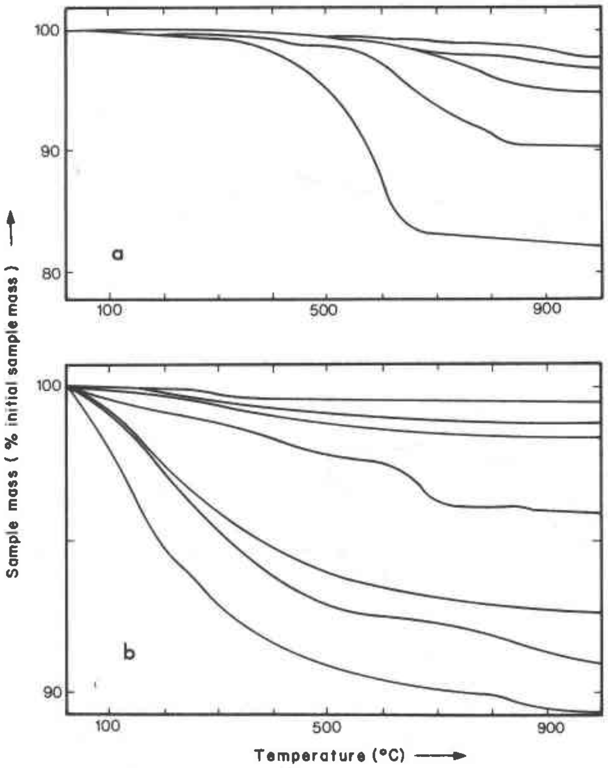

Fig. 4. Thermal decomposition of synthetic and natural zircons. (a) Hydroxylated synthetic zircons: from top to bottom, the curves correspond to zircons synthesized at 800, 700, 600, 500 and 400°C. (b) hydroxylated and hydrated natural zircons: from top to bottom, the curves correspond to natural zircons from Ceylan, Arabia, Tarraouadji, Ontario, Berere, Betafo and Ampassipoana. Sample mass curves vs. temperature.

The analysis of gases released during heating shows first a release of water, and second a release of hydrofluoric acid, sometimes accompanied by some water. An example is given in Figure 6 for the thermal decomposition of zircon synthesized at 400°C. Measurement of these losses leads to the establishment of the composition of these zircons (Table 1).

The thermogravimetric graph for natural zircons (Fig. 4b) shows a loss of water at the onset of heating, for all the samples except for the ones from Ceylon. The water concentration of these zircons can exceed 10%. Coleman and Erd (1961) have described zircons containing up to 16.6% of water. Therefore we compare these zircons to synthesized zircons which were crystallized at 400°C. This water is only weakly bonded to the lattice and escapes in a similar way to that observed for gels (Caruba et al., 1975). Some of the natural zircons (from Ampassipoana, Betafo, and Ontario) have in common with hydroxylated synthetic zircons a high temperature loss of OH groups in the form of water which is seen thermogravimetrically, hence these natural zircons release water at low temperature and OH groups at higher temperatures. From other natural zircons (Arabia, Berere, Ceylon, and Tarraouadji) all the water escapes at the same temperature.

Thermoluminescent properties

The general characteristics of the TL graph of a synthetic zircon include a very high peak at about 115 K followed by a smaller one at 160 K.

The spectra of these peaks show an emission band at 285 nm which is specific for OH groups (Iacconi and Caruba, 1977; Iacconi et al., 1980).

The zircons formed at temperatures below or equal to 500°C have a wide peak at 150 K. The zircons formed at higher temperatures have their peak split into two different high peaks at 115 K and 160 K. At still higher synthesis

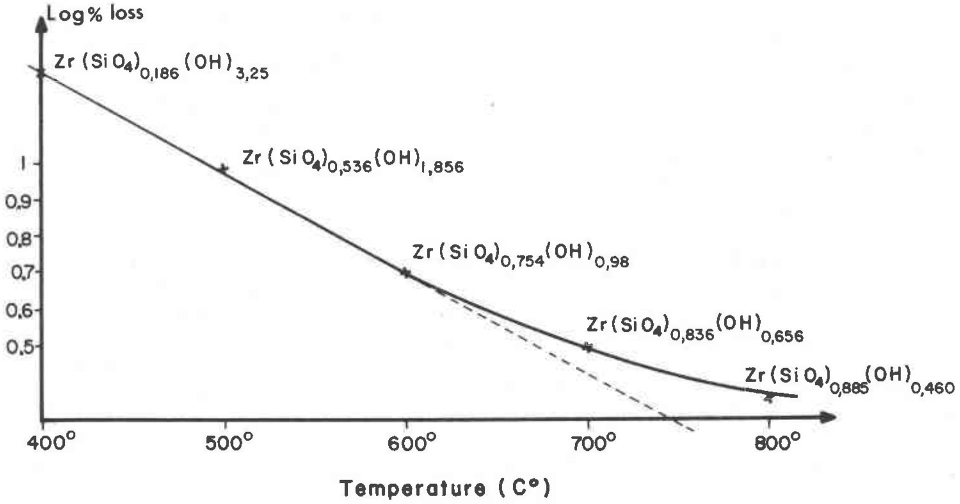

Fig. 5. Weight loss of hydroxylated zircons reheated to 950°C at 1 atm pressure plotted against their temperature of synthesis at uniform pressure (1 kbar).

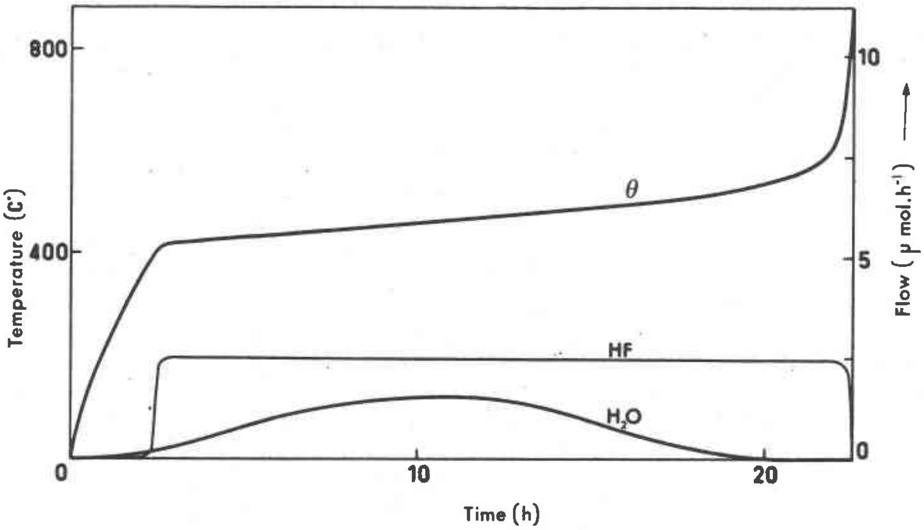

Fig. 6. Controlled decomposition rate EGA of the 400°C-1 kbar sample: temperature (θ), hydrogen fluoride flow (HF) and water flow (H_2O) curves vs. time.

temperatures, the two peaks become distinguishable indicating two distinct types of lattice imperfections. The distinction between the two peaks is due to different ways in which the OH groups can be excited. When non-metamict hydroxylated zircons are irradiated at 77 K, one may observe either a rupture of the OH groups and formation of negatively charged oxygen ions (O^-) and neutral hydrogen atoms (H°), or the loss of an electron and formation of OH° and e^-. Some of the H° and e^- diffuse away and can recombine with O^- or OH, but most of them are trapped in the lattice positions. The probability of recombination at 77 K, increases with the OH concentration. At 115 K the trapped H° are free to recombine with O^- while emitting radiation at 285 nm. At 160 K, the electron joins an OH° group, and emits a de-excitation radiation at 285 nm (Iacconi et al., 1980).

Hence with increasing synthesis temperature, the number of OH groups on the lattice diminishes, and H° and e^- get more easily trapped, as shown by the rise of the intensity of the TL signal (Table 1).

After annealing at 1000°C, the characteristic radiation of OH is noticeable in the thermoluminescence signal of natural zircons. This proves that the OH groups are well integrated to the lattice.

Interpretation

Fluorine is required to synthesize hydroxylated zircons. In these zircons, fluorine has an essential stabilizing role, it causes the transformation of $(OH)_4$ to $(OH,F)_4$. This stabilization does not occur in garnet, which has a structure similar to zircon (Robinson et al., 1971; Novak and Gibbs, 1971; Speer and Cooper, 1982), but where the replacement of SiO_4 by $(OH)_4$ is accomplished without the presence of fluorine (Cohen-Addad et al., 1964).

The decrease of the *a* and *c* lattice parameters for hydroxylated zircons proves the presence and the important role of fluorine. As a matter of fact, the OH groups should increase the size of the unit cell, as is the case for garnet (Cohen-Addad, 1970; Table II). This is not true for zircon. Garnet can easily accomodate an increase in the distance between the oxygens, which are simultaneously an edge of the tetrahedron and the dodecahedreon. Such an expansion is not possible in the zircon unit cell. Fluorine is essential for the stability of hydroxylated zircons because it reduces the size of a $(OH,F)_4$ tetrahedron, making it compatible with the size requirements of the zircon's structure.

The annealing of hydroxylated zircons at 950°C causes the formation of $ZrSiO_4$ and ZrO_2. This shows that there was initially a shortage of silicon atoms compared to zirconium atoms. In the solid solution $Zr\,(SiO_4)_{1-x}(OH,F)_{4x}$, the tetrahedra contain on the average more OH^- than F^- ions. The simultaneous release of H_2O and HF leads to the decomposition of low temperature zircon

$$((OH)_3,F)_x] \rightarrow xH_2O + xHF + 2xO \ldots Zr.$$

(The O … Zr symbol stands for oxygens of the OH groups bonded to the lattice after the zircon has been strongly

Table 2. Comparison of the length of O–O bonds in the SiO_4 or $(OH)_4$ tetrahedra of garnets, normal zircon, and hydroxylated zircon. The A–A′ length corresponds to the distance between two oxygen atoms which are common to a SiO_4 tetrahedron and a XO_8 dodecaedron. The C–C′ length is a distance between two oxygen atoms in a SiO_4 tetrahedron, which also belongs to two successive XO_8 dodecaedrons (Robinson et al., 1971).

	LENGHT A-A'	LENGHT C-C'	REFERENCE
GARNET	2.56 Å	2.74 Å	ROBINSON et al.(1971)
SYNTHET.OH-GARNET	3.18 Å	3.30 Å	COHEN-ADDAD et al.(1964)
ZIRCON	2.43 Å	2.75 Å	ROBINSON et al.(1971)
NATURAL OH-ZIRCON	2.47 Å	2.73 Å	PAVLOVIĆ et al.(1965)

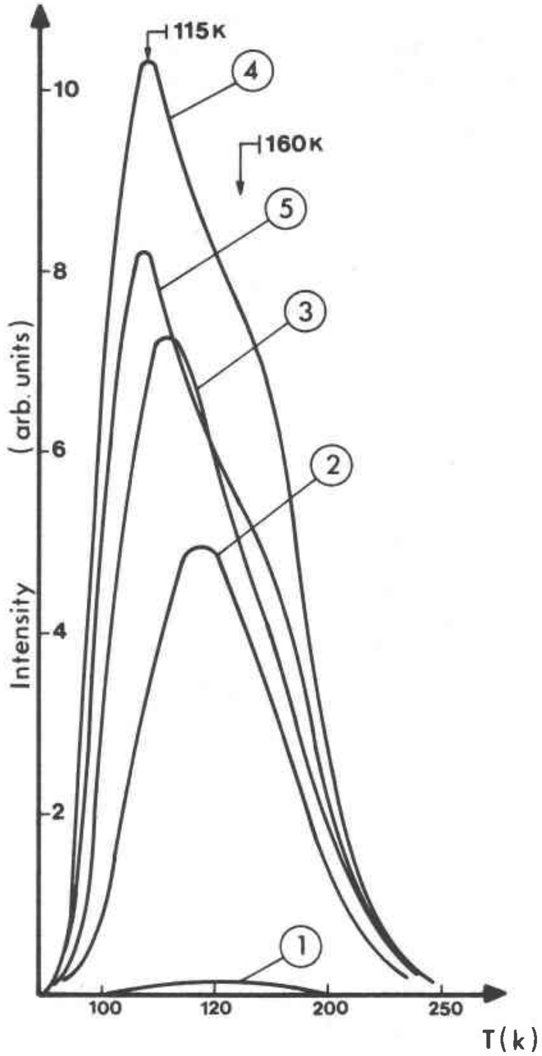

Fig. 7. Thermoluminescence curves of hydroxylated zircon synthetized at 400 (1), 500 (2), 600 (3), 700 (4) and 800°C (5) synthesized at 1 kbar pressure.

heated). In the last stage of the decompostion, HF is the only released gas (Fig. 6). Hence, these tetrahedra contain at least as much fluorine as OH. The composition should be:

$$((OH)_2,F)_x \rightarrow 2xHF + 2xO \ldots Zr.$$

A release of fluorine only has never been observed; it would correspond to tetrahedra of the type $(OH,F_3)_x$ or $(F)_{4x}$.

These hydroxylated zircons contain both types of tetrahedra, and that could be the reason for the OH absorption band width in the infrared spectrum. The decomposition temperature of these zircons depends on the OH concentration. Moreover, when there are only few OH groups they are more strongly attached to the lattice (they exist in the crystal at least to 950°C). Natural zircons show similar relationships (Fig. 1 and 4).

The heating of metamict zircons at low temperature causes an escape of water, which was only weakly bonded, and no recrystallization of the lattice. Water release at higher temperature leads to the formation of ZrO_2 and the recrystallization of the mineral. The relative amounts of H_2O and OH are different for each sample. Natural hydroxylated zircons have as general formula:

$$Zr(SiO_4)_{1-x}(OH,F)_{4x} \cdot zH_2O.$$

(The charge balance schemes will be discussed later). The simultaneous presence of H_2O and OH in natural metamict zircons confirm the results of the chemical analysis (Caruba and Iacconi, 1983) and of the thermolyses (Pavlovic and Krstanovic, 1965) for such zircons.

After annealing at 950°C, traces of OH have been found by thermoluminescence in metamict minerals just as in synthetic zircons. These residual groups are also strongly bonded to the lattice.

The substitution of SiO_4 by $(OH,F)_4$ causes a decrease in the density of these natural and synthetic crystals (Fig. 8). Density of the natural metamict zircons could have been plotted on such a diagram. Some of these crystals (Holland and Gottfried, 1955; Vance and Anderson, 1972; Sahama, 1981; Ewing et al., 1982) have a very low density, in some less than 4, which is less than the value for total replacement of the SiO_4 by $(OH, F)_4$. The cause of this could be the lattice parameter increase due to radioactive decay. The density difference between a natural metamict zircon and a synthetic hydroxylated zircon could be used as a measure of the intensity of metamictization, to a first approximation.

Model for the genesis of metamict zircons

The remarkable similarities between synthetic hydroxylated and natural metamict zircons, suggest the following model of formation for these minerals.

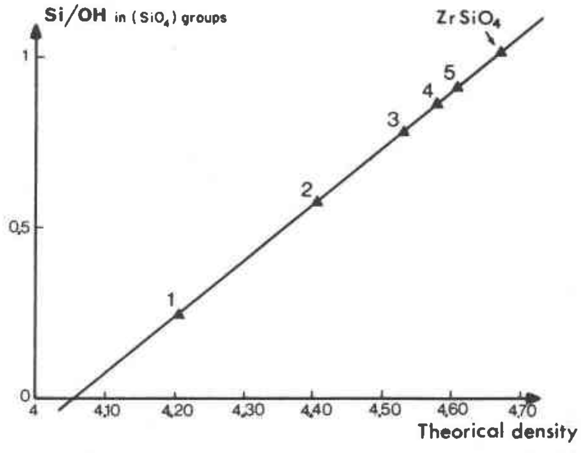

Fig. 8. Variation of the theoretical density of hydroxylated zircon depending on the degree of the Si/OH replacement in (SiO_4) groups. The numbers 1, 2, 3, 4 and 5 correspond to zircons synthetized at 1 kbar and 400, 500, 600, 700 and 800°C respectively.

The metamict zircons

Because of the presence of H_2O and OH, metamict zircons must have crystallized in a hydrous fluorinated environment, enriched in radioactive elements and REE at low temperatures. The 400°C temperature suggested by our experiments could be a lower temperature limit for the formation of metamict zircons. Initially, the general formula of metamict zircons would be:

$$(Zr,U,Th,REE\ldots)(SiO_4)_{1-x}(OH,F)_{4x}.$$

The amount of replacement of the SiO_4 tetrahedra by $(OH,F)_4$ depends on the crystallization temperature. The general formula does not correspond to a defined stoichiometry. The relatively low temperatures facilitate hydroxylation and thus eventual metamictization. This is the reason why metamict zircons are usually found in low temperature hydrous rocks formed close to the end of a crystallization sequence. The zirconium lattice site is occupied by heavy atoms, such as uranium, thorium and REE (Watson, 1980), while radicals such as OH^- or F^- are surrounding the silicon positions.

These OH groups may contribute to the hydration of the zircon crystal in two possible ways:

(1) By donating a proton to $(OH,F)_4$ groups by means of the charge compensation reaction suggested by Caruba and Iacconi (1983):

$$\begin{array}{c} Zr^{4+} = M^{x+} + (4-x)H^+ \\ SiO_4 = (OH)_4 \\ \hline Zr^{4+} + SiO_4 = M^{x+} + (OH)_x + (4-x)H_2O \end{array}$$

where M stands for REE, trivalent elements, and vacancies.

(2) By a recombination of OH–H where the hydrogen was originally produced by the decomposition of other OH groups as a result of interaction with radioactive elements.

In both cases, the water molecule is only weakly bonded and can leave the lattice at lower temperature than $(OH,F)_4$ groups. At any time in the crystal's history, the water concentration depends on numerous factors, such as the initial OH^- and F^- concentrations, the radioactivity of the mineral which causes the destruction of the lattice already weakened by the presence of (OH,F) groups, the concentration of lower valency elements on zirconium's lattice site such as REE, Y, Fe ..., and on possible episodic or continuous reheating which would lead to the early escape of water.

Stability and decomposition

On heating, the lattice of hydroxylated and metamict zircon disintegrates at lower temperatures than that of normal zircon, i.e., at less than 1683°C (Butterman et al., 1967). This decrease in upper stability limit may be about 1000°C and depends on the degree of hydroxylation. The presence of $(OH,F)_4$ tetrahedra weakens the crystalline lattice considerably. Hence it can be destroyed easily as a result of radioactive disintegration. This is the reason that metamict zircons are hydroxylated, and that other minerals with highly radioactive element concentrations are not hydroxylated, e.g., uraninite UO_2, autunite $Ca(UO_2)_2(PO_4)_2$, 10 to 12 H_2O, thorianite ThO_2 are little or not all metamicticized. Finally, it should be pointed out that a great number of crystals show zonation in their degree of metamicticization (Burshill and McLaren, 1966; Headley et al., 1982; Schärer and Allègre, 1982). This may reflect an initial zoning of the water and radioactive element concentration of the zircon (Sahama, 1981). It should be observed that metamict zircons are more soluble in acid solutions (Caruba et al., 1975; Ewing et al., 1982). This promotes the escape of radioactive elements.

Conclusions

Zircon solid solution with a general formula $Zr(SiO_4)_{1-x}(OH,F)_{4x}$ with x varying from 0.2 to 0.8 can be synthetized hydrothermally in a fluorinated and hydrated medium.

The stability of the hydroxylated zircon depends directly on the $(OH,F)_4$ concentration and on the temperature. The experimental results (X-ray, IR, TL) obtained for synthetic hydroxylated zircons make it possible to compare these zircons with natural metamict zircons, and to propose a genesis for these minerals. The metamict zircons are hydroxylated, fluorinated and enriched in radioactive elements. This will lead to the destruction of the zircon's lattice because the replacement of a SiO_4 tetrahedron by a $(OH,F)_4$ group has a destabilizing effect.

However, there are still some unresolved problems concerning natural zircons such as the REE-OH interaction, the expansion of crystalline lattice, and the role of fluorine in SiO_4-$(OH,F)_4$ substitution.

Knowing how to synthesize hydroxylated zircons, it would be interesting:

(1) To vary fluorine concentration in the reaction mixture and measure how the OH concentration in the zircons will be affected quantitatively;

(2) To dope hydroxylated and normal zircons with REE in order to see if the presence of $(OH,F)_4$ groups influences the uptake of REE on the lattice, as a result of charge compensation;

(3) To irradiate hydroxylated and normal synthetic zircons (with different OH,F concentrations) artificially in order to observe and to compare the destruction of the lattices of these two types of zircon.

Acknowledgments

This work was supported in large measure by CNRS. Dr. G. R. Rossman is gratefully acknowledged for his suggestions. The authors acknowledge Dr. Gérard Thevand for his precious aid in CDRTA-EGA and Robert Morin for his technical assistance.

References

Bursill, L. A. and McLaren, A. C. (1966) Transmission Electron Microscope Study of Natural Radiation Damage in Zircon ($ZrSiO_4$). Physic Status Solidi, 13, 331–343.

Butterman, W. C. and Forster, W. R. (1967) Zircon stability and the ZrO_2–SiO_2 phases diagram. American Mineralogist, 52, 880–885.

Caruba, Raoul and Iacconi, P. (1983) Les zircons de Narssärssuk

(Groenland). L'eau et les groupements OH dans les zircons métamictes. Geochimica et Cosmochimica Acta, 39, 11–26.

Caruba, Raoul, Baumer, A., and Turco, G. (1975a) Nouvelles synthèses du zircon $ZrSiO_4$. Remplacements isomorphiques. Geochimica et Cosmochimica Acta, 39, 11–26.

Caruba, Raoul, Baumer, A., Mano, J., and Turco, G. (1975b) Etude comparative des propriétés respectives de zircons hydroxylés synthétiques et de zircons métamictes naturels; hypothèse de genèse. Pétrologie, I, 1, 57–70.

Cohen-Addad, Claudine (1970) Etude du composé $Ca_3Fe_2(SiO_4)1.15$ (OH)7.4 par absorption infrarouge et diffraction des rayons X et des neutrons. Acta Crystallographica, A26, 68–70.

Cohen-Addad, Claudine, Ducros, P., Durif, A., Bertaut, R. and Delapalme, A. (1964) Détermination de la position des atomes d'hydrogène dans l'hydrogrenat Al_2, O_3CaO, $6H_2O$ par résonance magnétique nucléaire et diffraction neutronique. Journal de Physique, 25, 478–483.

Coleman, R. G. and Erd, R. C. (1961) Hydrozircon from the Wind River formation, Wyoming. Geological Survey Research, 256, 297–300.

Deliens, M., Delhal, J., and Tarte, P. (1977) Metamictization and U-Pb systematics—A study by absorption spectrometry of Precambrian zircons. Earth and Planetary Sciences Lettres, 33, 331–344.

Ewing, R. C., Haaker, R. F., and Lutze, W. (1982) Leachability of zircon as a function of alpha dose. In Werner, Lutze, Ed., Scientific Basis for Radioactive Waste Management-V, p. 389–397. Elsevier Science Publishing Co.

Frondel, Clifford (1953) Hydroxyl substitution in thorite and zircon. American Mineralogist, 38, 1007–1018.

Frondel, Clifford, and Collette, R. (1957) Hydrothermal synthesis of zircon, thorite and huttonite. American Mineralogist, 42, 759–765.

Headley, T. J., Ewing, R. C., and Haaker, R. F. (1982) TEM study of the metamict state. 13th General Meeting of the International Mineralogical Association at Varna, Bulgaria, Sept. 19–25.

Holland, H. D. and Gottfried, D. (1955) The effect of nuclear radiation on the structure of zircon. Acta Crystallographica, 8, 291–300.

Hubin, René and Tarte, P. (1971) Etude infrarouge des orthosilicates et des orthogermanates-IV. Structure scheelite et zircon. Spectrochimica Acta, 27A, 683–690.

Iacconi, Philibert (1979) Etude et interprétation des propriétés thermoluminescentes des zircons $ZrSiO_4$ et $Zr(SiO_4)_{1-x}(OH)_{4x}$ dopés par des éléments trivalents de al série des lanthanides. Thèse d'Etat, Université de Nice, France.

Iacconi, Philibert and Caruba, R. (1977) Sur le rôle des OH dans l'émission de thermoluminescence du zircon $Zr(SiO_4)_{1-x}(OH)_{4x}$ synthétique. Comptes Rendus de l'Académie des Sciences, Paris, 285, B, 227–229.

Iacconi, Philibert, Deville, A., and Gaillard, B. (1980) Trapping and Emission Centres in X-Irradiated Zircon I. Contribution of the OH Ion. Physic Status Solidi, a, 59, 139–146.

Krstanovic, Ilija (1964) X-Ray investigation of zircon crystals contening (OH) groups. American Mineralogist, 49, 1146–1148.

Mumpton, F. A. and Roy, R. (1961) Hydrothermal stability studies of the zircon-thorite group. Geochimica et Cosmochimica Acta, 21, 217–238.

Novak, G. A. and Gibbs, G. V. (1971) The crystal chemistry of the silicate garnets. American Mineralogist, 56, 791–825.

Pavlovic, S. and Krstanovic, I. (1965) Sur les possibilités de détermination d'âge absolu d'après les mesures cristallographiques du zircon. Colloque International de Géochronologie Absolue. Nanÿ, 3–8 Mai 1985. Sciences de la Terre, 10, (3–4), 285–290.

Reisner, I. and Klee, W. E. (1982) Temperature dependence of the (OH) bands of hydroxylapatite. Spectrochimica Acta, 38A, 8, 899–902.

Robinson, Keith, Gibbs, G. V. and Ribbe, P. H. (1971) The structure of zircon: a comparison with garnet. American Mineralogist, 56, 782–790.

Rouquerol, Jean (1969) Vacuum thermal analysis apparatus, with controlled residual pressure and with constant decomposition rate. In R. F. Schwenker Jr. and P. D. Garn, Ed., Thermal Analysis, p. 281. Academic Press, New York.

Rouquerol, Jean, and Ganteaume, M. (1977) Thermolysis under vacuum: essential influence of the residual pressure on thermoanalytical curves and reaction products. Journal of Thermal Analysis, 11, 201–210.

Sahama, T. (1981) Growth structure in Ceylon zircon. Bulletin de Minéralogie, 104, 89–94.

Schärer, Urs. and Allègre, C. J. (1982) Uranium–lead system in fragments of single zircon grain. Nature, 295, 5850, 585–587.

Speer, J. A. (1980) Zircon. In P. H. Ribbe, Ed., Orthosilicates, p. 67–112. Reviews in Mineralogy, Vol. 5, Mineralogical Society of America, Washington, D.C.

Speer, J. A. and Cooper, B. J. (1982) Crystal structure of synthétic hafnon, $HfSiO_4$, comparison with zircon and the actinide orthosilicates. American Mineralogist, 67, 804–808.

Thevand, Gérard, Rouquerol, F., adn Rouquerol, J. (1982) A new EGA approach for the kinetical study of a complex thermolysis (kerogens). In B. Miller, Ed., Thermal Analysis, Vol. 2, p. 1524–1529. John Wiley and Sons, New York.

Vance, E. R. and Anderson, B. W. (1972) Study of metamict Ceylon zircons. Mineralogical Magazine, 38, 605–613.

Watson, E. B. (1980) Some experimentally determined zircon/liquid partition coefficients for the rare earth elements. Geochimica et Cosmochimica Acta, 44, 895–897.

Manuscript received, November 19, 1984;
accepted for publication, June 18, 1985.