

Team 3 Geochronometer

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The age of a zircon can be estimated using the principle of a U-Pb geochronometer. This system works because of the reluctance of $ZrSiO_4$ to incorporate Pb atoms into its structure, while it is easier to substitute Zirconium atoms for Uranium. This is illustrated in the paper using DFT calculations to determine formation energies and by creating supercells to simulate impurities of U and Pb in a zircon. It is also remarked upon how diffusion of Pb and radiation damage are detrimental to the accuracy of the geochronometer.

Keywords: : DFT, Geochronometer, Zirconium silicate, Uranium, Lead, diffusion

I. INTRODUCTION

Not much is known about the early stages of the Earth's history. The only experimental evidence comes from zircon minerals ($ZrSiO_4$).[1] To fix certain events, e.g. moon formation or first habitable conditions, in time it is necessary to determine the age of these minerals. The technique to determine this age is called a geochronometer.

The principle of this geochronometer technique is straightforward. In nature, the zircon mineral contains a small concentration of uranium impurities, because uranium can easily be incorporated in the zircon lattice. Over time, uranium decays to lead. Any lead impurity inside the mineral can then reasonably be assumed to be due to this radioactive decay. Therefore, the age of a mineral can be linked to the ratio of Pb and U concentrations inside zircon. For uranium-lead decay, there are two different decay chains possible:

$$^{238}U \rightarrow ^{206}Pb \text{ decay of 4.5 billion years,} \quad (1)$$

$$^{235}U \rightarrow ^{207}Pb \text{ decay of 713 million years.} \quad (2)$$

As can be seen in equation (1) and (2), the decay of uranium takes an extremely long time. Using a superposition of the two different decay paths, it is possible to make a good estimation of the age of the Zircon crystal.

The accuracy of this geochronometer is subject to the diffusion of lead in the zircon crystal, since any lead that gets out of the crystal by diffusion will influence the ratio and thus the accuracy of this aging technique. Measuring a lower lead concentration leads to an underestimation of the age. In this short paper, DFT calculations were

performed to examine the zircon geochronometer concept. Multiple positions of uranium and lead impurity atoms inside the zircon crystal are studied. Afterwards calculations are performed to investigate the influence of radiation damage on these impurities.

II. METHODS

The DFT calculations in this paper were performed with the QUANTUM ESPRESSO code and the PBE exchange-correlation functional. The first step is the execution of convergence tests (details in section V Appendix), where the calculation parameters are chosen to get sufficient precision in the calculated properties in a reasonable amount of time and with the available computing resources. Examples of these parameters are the k-mesh/number of k-points, which is a grid in three dimensions of the first Brillouin zone; *ecutwfc*, which determines the basis set size for describing the wave functions; *ecutrho* is usually taken 4 or 8 to 12 times the *ecutwfc* value. For the $ZrSiO_4$, $PbSiO_4$ and $USiO_4$ crystals, the found convergence parameters are a $4 \times 4 \times 4$ k-mesh, an *ecutwfc* of 105 Ry and an *ecutrho/ecutwfc* ratio of 4. These parameters have been used for all performed calculations.

The next section summarizes the calculated results. These results are geometry optimization calculations of the $ZrSiO_4$ crystal with three different concentrations of substitutional uranium and lead impurities and of a 25% impurity concentration for two interstitial positions. For one of these interstitial positions, the calculations are repeated with additional radiation damage added to the crystal. All calculations are based on the $ZrSiO_4$ crystal structure, shown in FIG. 1. The conventional unit cell is pictured with 100% uranium and lead substitutional concentrations.

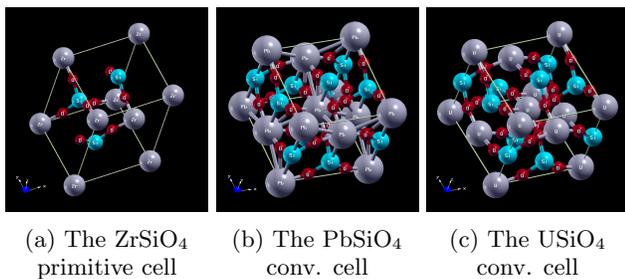


FIG. 1: Representation of the ZrSiO_4 primitive (a) and conventional (b,c) unit cell. The conventional unit cell is shown with a 100% substitutional concentration of lead (b) and uranium (c).

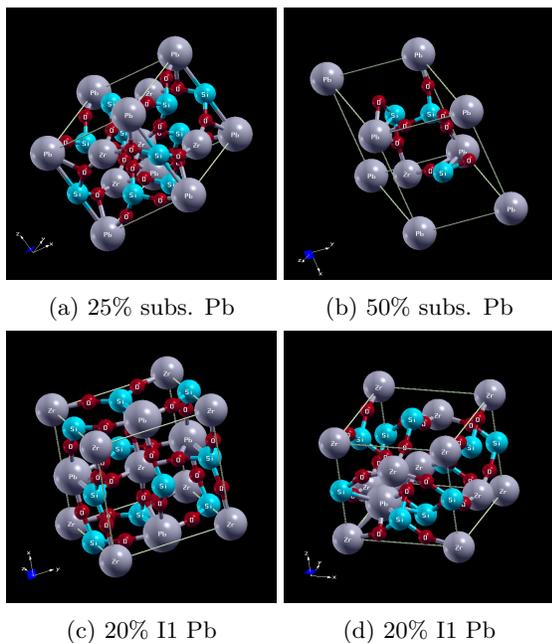


FIG. 2: Representation of the four different lead impurity unit cells. Two different substitutional concentrations (25% and 50%) and lead in two interstitial positions I1 and I2.

III. DFT RESULTS

A. Appearance in nature

In the Crystallography Open Database, there are no files about PbSiO_4 and only one about USiO_4 , dating all the way back to 1958, and also concerning ZrSiO_4 . One can thus assume that these two crystals have not been studied extensively and they might not exist in nature. For each of these three crystals, the formation energy (per atom) with respect to the elemental ground state crystals was calculated (with unit cells in FIG. 1). For ZrSiO_4 for example, this is the energy difference (per atom) if Zr, Si and O from their elemental crystals react to form

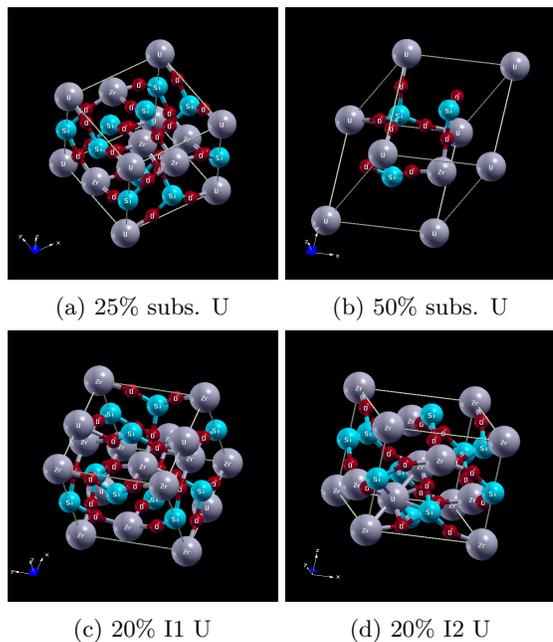


FIG. 3: Representation of the four different uranium impurity unit cells. Two different substitutional concentrations (25% and 50%) and uranium in two interstitial positions I1 and I2.

a ZrSiO_4 crystal. The results can be found in TABLE I. The ZrSiO_4 and USiO_4 crystals have a formation energy lower than -3 eV/atom. Thus, there is a significant energy gain in forming ZrSiO_4 and USiO_4 . According to the Open Quantum Materials Database, these formations are on the convex hull. Therefore, these crystals energetically favoured to exist in nature. The PbSiO_4 crystal has a higher formation energy and lies energetically above the convex hull. As a result PbSiO_4 is not found in nature.

	$E_{\text{formation}}$ (eV/atom)
ZrSiO_4	-3.1602
USiO_4	-3.1356
PbSiO_4	-1.4608

TABLE I: Formation energies with respect to the elemental ground state crystals

B. Impurities

To study uranium and lead impurities in ZrSiO_4 these atoms are treated as both substitutional and interstitial impurities. For the substitutional impurities the unit cells are constructed with 100%, 50% and 25% of the zirconium atoms replaced by U or Pb. Lower concentrations could not be reached due to computational restrictions. Aside from the substitutional calculations

the impurity atoms are also added to the conventional unit cell in two different interstitial positions (I1 and I2), leading to a 20% impurity concentration. All unit cells used for the equations can be seen in FIG. 2 and 3.

The unit cells with impurities are geometrically optimized to find the ground state energy configurations. The total energies of these unit cells are scaled to the size of a conventional unit cell. For the substitutional impurities these total energies are subtracted with the total energy of the ZrSiO_4 conventional unit cell. The corrected energies, called E_Δ , can be found in TABLE II. This table shows that the E_Δ for uranium is already converging with a substitutional concentration diluted to 25%. The energy of the lead unit cells is however not yet converging. The energy could still further increase by diluting the impurity concentration more. Therefore, because the E_Δ of the 25% uranium is lower than the 25% lead, it is reasonable to assume that a substitutional uranium impurity will be more energetically favourable than a lead one.

% U atoms	E_Δ (Ry)	% Pb atoms	E_Δ (Ry)
25%	-721	25%	-563
50%	-728	50%	-1125
100%	-2885	100%	-2251

TABLE II: E_Δ depending on the concentration of substitutional impurities.

For the interstitial impurities E_Δ is defined as the energy difference between the conventional unit cell with and without the interstitial impurity. These results are found in TABLE III. Thus this is the binding energy that the crystal gains when an interstitial impurity is added. Both uranium and lead interstitials lower the energy of the unit cell more than the substitutional impurities. Since the energy of the lead substitutional impurity is expected to further increase, the energy difference between a substitutional and an interstitial lead atom is larger than the energy difference between a substitutional and interstitial uranium atom. Therefore more lead than uranium atoms might be in interstitial positions. An important remark is that the interstitial calculations are also performed with a 20% lead concentration (with respect to zirconium) and that these results can still significantly change in the more diluted case.

U atoms	E_Δ (Ry)	Pb atoms	E_Δ (Ry)
I1	-1021	I1	-869
I2	-1027	I2	-870

TABLE III: E_Δ depending on the interstitial position of uranium and lead.

C. Radiation Damage and Diffusion

The previous section showed that the lead atoms prefer interstitial positions. There is however an extra aspect: radiation damage. This is induced mainly by the alpha-decays in the decay chain. The alpha particles have a few MeV of energy and also the daughter nuclei gain a kinetic energy of around 100 keV. Particles with such energies can cause vacancies and maybe even more extended damage to the crystal. Relative unit cells under investigation are unit cells with an I1 lead impurity and a missing atom next to the impurity (FIG. 4). TABLE IV shows the energy difference between such a unit cell and the same unit cell without the interstitial impurity. Thus this is the energy to add an interstitial lead atom next to a vacancy (zirconium, oxygen or silicon). Again, a conventional unit cell is used so that the impurity concentration is 20%. Surprisingly, adding an interstitial next to a vacancy lowers the unit cell energy by approximately the same energy as in the case of adding an interstitial without a vacancy (TABLE III). However, the energy is still one or two Ry lower, indicating that the lead atoms are more likely to be in the presence of vacancies that can be caused by radiation damage. The total energy per atom is lower in the radiation damage case because the unit cells contain 24 atoms and not 25 as in TABLE III.

Removed atom	E_Δ (Ry)
Zr	-871
Si	-871
O	-870

TABLE IV: E_Δ for an I1 lead impurity in a conventional unit cell with a vacancy to simulate radiation damage.

Studying the lead diffusion quantitatively is beyond the scope of this paper, but we can propose a qualitative model. The lead atoms preferably sit at interstitial positions close to vacancies. The decay chain of uranium to lead will introduce more radiation damage, vacancies, to the crystal. The lead diffusion process can then be seen as a discontinuous process where the lead atom jumps between interstitial positions. A following quantitative approach would be to monitor the energies of a certain unit cell or supercell, where the lead atom is slowly moved from one interstitial position to the other. A static DFT calculation at each point of the path will provide an energy barrier of the jumping process. With this energy barrier the diffusion process can be defined quantitatively and connected to experimental parameters, such as the temperature.

The amount of radiation damage will depend on the local U concentration. A region of high concentration will be exposed to more radioactive decays and accumulate more damage. Between regions with a big difference in U concentration, fission tracks can be

formed, which can further influence the diffusion of Pb. [2]

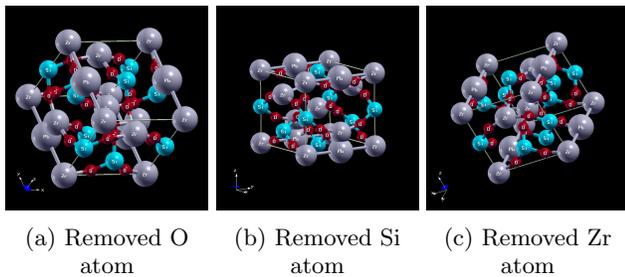


FIG. 4: Representation of a ZrSiO_4 conventional unit cell with an I1 lead impurity and a this lead impurity has one of its neighbouring atoms (Zr, Si or O) removed.

D. Pressure

Beneath the Earth's crust the pressure can be significantly higher (up to 50 GPa). The increase in pressure (which was not calculated) would mainly have its effect on the formation energies of vacancies and interstitials. Intuitively, compressing the crystal brings the

atoms closer together, therefore, reducing the impact of vacancies and leaving less space for interstitials. As a result the interstitial energy might increase pushing more lead atoms into substitutional positions. Following this reasoning, the diffusion rate of Pb would be lowered.

IV. CONCLUSION

The zircon geochronometer is a powerful method to determine the age of very old minerals. But, one has to take into account the loss of lead because of diffusion processes. In this paper, it was calculated that the lead atoms lower the energy of the zircon crystal the most when they are in interstitial positions close to vacancies. These vacancies can be caused by radiation damage following the decay chain of uranium. A possible model for the lead diffusion is for the atom to jump from one of these interstitial positions to the next. To accurately date a zircon mineral, its history must be taken into account. This is because it has probably been in environments of elevated temperature and pressure. Important is that regions with a high concentration of substitutional lead impurities will never exist, because the formation energy of PbSiO_4 is too high to let the crystal exist in nature. Regions of high lead concentration will decompose into binaries or unaries.

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- [1] W. J. Valley. *Nature Geoscience*, 7:219–223, 2014.
 [2] R. L. Romer. *Contributions to Mineralogy and Petrology*, 145:481–491, 2003.

V. APENDIX

k-mesh	Pressure (kPa)	Time (s)
1x1x1	465.6	50
2x2x2	478.24	60
3x3x3	483.05	80
4x4x4	482.73	119
5x5x5	482.49	151
6x6x6	482.53	222
7x7x7	482.53	285
8x8x8	482.57	402
9x9x9	482.53	494
10x10x10	482.54	660
11x11x11	482.54	808
12x12x12	482.54	1026

TABLE V: Hydrostatic pressure as a function of the k-mesh, with $ecutrho=683$ and $ecutwfc=93$

<i>ecutwfc</i>	<i>ecutrho</i>	Pressure (kPa)	Time (s)
63	504	352.53	166
73	584	447.53	226
83	664	477.82	273
93	744	482.55	290
103	824	481.5	383
113	904	480.91	429
123	984	481.23	490
133	1064	482.02	575
143	1144	482.83	604
153	1224	483.24	727
163	1304	483.11	857
173	1384	482.53	908
183	1464	481.83	968
193	1544	481.39	1155
203	1624	481.4	1181
213	1704	481.83	1328
223	1784	482.45	1648
233	1864	482.97	2017
243	1944	483.18	2086
253	2024	483.07	2110

TABLE VI: Hydrostatic pressure as a function of *ecutwfc* for k-mesh 7 x 7 x 7 while the *ecutrho/ecutwfc* ratio is kept constant at 8 and the *ecutwfc* is varying.

<i>ecutrho/ecutwfc</i>	Pressure (kPa)	Time (s)
5	482.85	552
6	482.82	603
7	482.82	651
8	482.83	603
9	482.82	752
10	482.82	791
11	482.83	853
12	482.82	943
13	482.83	970
14	482.82	1014
15	482.82	1081

TABLE VII: Hydrostatic pressure as a function of *ecutrho/ecutwfc* ratio for k-mesh 7 x 7 x 7 while the *ecutwfc* = 143.

k-mesh	Pressure (kPa)	Time (s)
1x1x1	134.44	198
2x2x2	83.82	473
3x3x3	83.46	816
4x4x4	83.16	1990
5x5x5	83.33	2693
6x6x6	83.37	7080
7x7x7	83.30	7980
8x8x8	83.38	11880
9x9x9	83.12	22260
10x10x10	83.28	31440
11x11x11	83.24	9960
12x12x12	83.39	15720

TABLE VIII: Hydrostatic pressure as a function of the k-mesh, with *ecutrho*=323 and *ecutwfc*=47

$ecutwfc$	Pressure (kPa)	Time (s)
17	-4988.95	196
27	-2162.15	320

TABLE IX: 2 calculations with different $ecutwfc$ values

k-mesh	Pressure (kPa)	Time (s)
1x1x1	229.64	230
2x2x2	221.81	483
3x3x3	225.72	755
4x4x4	226.72	1788
5x5x5	226.82	2560
6x6x6	226.74	4800
7x7x7	226.95	7020
8x8x8	227.11	12840
9x9x9	226.89	21960
10x10x10	227.00	32040
11x11x11	226.72	23700
12x12x12	226.80	30000

TABLE X: Hydrostatic pressure as a function of the k-mesh, with $ecutrho=323$ and $ecutwfc=47$

$ecutwfc$	Pressure (kPa)	Time (s)
17	/	471
27	-3945.31	830
37	-58.97	1697
47	226.83	2447
57	217.19	3900
67	220.07	4080
77	226.52	4620
87	227.72	9120
97	226.85	7140
107	226.91	8100
117	227.72	9120
127	227.69	10620

TABLE XI: Hydrostatic pressure as a function of $ecutwfc$ for k-mesh 5 x 5 x 5 while the $ecutrho/ecutwfc$ ratio is kept constant at 7 and the $ecutwfc$ is varying.

$ecutrho/ecutwfc$	Pressure (kPa)	Time (s)
2	227.73	2428
3	227.71	2640
4	227.71	3600
5	227.70	3660
6	227.72	4020
7	227.72	4200
8	227.71	3960
9	227.70	4020
10	227.71	4140

TABLE XII: Hydrostatic pressure as a function of $ecutrho/ecutwfc$ ratio for k-mesh 5 x 5 x 5 while the $ecutwfc = 117$.