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Criteria for the occurrence of fission-fragment tracks in crystalline substances

Part 1 *Studies on fission-track dating*

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The tracks left in minerals by fission fragments arising from the spontaneous decay of uranium impurities serve as an important method for geological dating. If it is assumed that fission tracks in crystalline substances have a structure similar to that of an amorphous phase, then four criteria concerning whether such substances will be useful for dating can be made. These are the existence of amorphization following heavy-ion impact, the identification of an etchant, a high enough crystallization temperature, and the position of the substance on a scale of amorphizability. The criteria are illustrated by applying them to apatite, cobalt titanate, and columbite. Amorphization occurred with all three following bombardment with 10 to 35 keV Kr^+ ions. Amorphous apatite was more successfully etched with aqueous KOH than with the commonly used HNO_3, while amorphous columbite could be etched with an $HF-HNO_3$ mixture. The crystallization temperatures, which lay in the interval 810 to 905 K for experiments of short duration, were judged to be sufficiently high to insure track retention at the temperature of the surface of the earth over a geological time scale. The positions on a scale of amorphizability were established by noting the bombardment doses at which there was sufficient amorphization to cause the loss of one-half of an inert-gas marker when specimens were heated or etched. Considering all four criteria, it is concluded that apatite and columbite but not cobalt titanate should be useful for dating, with a similar conclusion holding for other substances which are structurally or chemically similar.

1. Introduction

Certain minerals with uranium impurities can be accurately dated by a procedure which involves cleaving to expose an interior surface, etching the surface, and counting the initial number of fission tracks per unit area, ρ_i, as revealed by the etching. Then, in independent experiments, the final number of tracks per unit area, ρ_f, which is present following a neutron irradiation of known fluence is determined. The age, A, follows from the ratio of track densities [1]:

$$\rho_i/(\rho_f - \rho_i) = [\exp(\lambda_D A) - 1]\,[\text{constants}]/[\text{neutron fluence}],$$

where λ_D, equal to 1.54×10^{-10} year^{-1}, is the total decay constant of uranium. The underlying principle in this method is that fission fragments, which have energies of 50 to 100 MeV, sometimes cause trails of radiation damage which have an enhanced chemical reactivity and which, provided a correct etchant can be found, can be dissolved at a much greater rate than the sub-

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This paper is dedicated to Professor C.A. Winkler of McGill University on the occasion of his sixty-fifth birthday by one of his former students (R.K.).

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strate and thereby be made visible to optical microscopy. Alternatively, if the specimen is thin enough, the radiation damage can be resolved by transmission electron microscopy. With crystalline substances, the tracks probably have a structure like that of an amorphous (i.e. metamict) phase:

(a) they do not contribute to electron diffraction [2];

(b) with mica they anneal to give a new crystalline phase [2];

(c) very high doses of fission fragments lead to overt amorphousness with corundum, zircon, and U_3O_8 [3];

(d) tracks in apatite, mica, quartz and zircon anneal at similar temperatures as do continuous amorphous layers [4].

With glassy substances one is probably dealing with the formation of a phase having a different degree of amorphousness than the original glass. Such phases are known with As_2Se_3 [5], $Pd_{20}Si_{80}$ [6], Se [5], SiO_2 [7], and possibly Ta_2O_5 [8]. With organic substances, fission tracks probably arise from chemical decomposition and are quite unrelated to amorphization.

The accuracy of the datings has normally been very satisfactory [9]. Nevertheless, current work is somewhat narrow in its scope, with most results continuing to be obtained with a limited group of minerals (mainly apatite, mica, sphene, tektite, and zircon [9]). The problem is particularly acute now that effort is being made to date lunar specimens.

One of the reasons why so few minerals are used probably lies in the somewhat empirical approach that has been taken. Thus specimens are chosen without regard to their sensitivity to fission-fragment induced damage and are exposed to etchants without prior knowledge of the selectivity of these etchants for the damage. Failure to observe tracks must be expected commonly in such a situation, even if the necessary uranium impurities are present.

The present work is intended as a contribution to the problem of fission-track dating in which the emphasis will be placed, not on the explicit observation of tracks, but on deciding whether a mineral or group of minerals is likely to be useful for dating. Only crystalline substances will be considered, for which there is evidence [2–4] that fission tracks have a structure similar to that of an amorphous phase. Provided the tracks are in fact amorphous, it follows that four criteria concerning whether a substance will be useful for dating can be made.

(a) Amorphization must be evident when specimens are subjected to bombardment with heavy ions at energies where nuclear collisions dominate over ionization (roughly < 100 keV). Amorphization will be here sought by means of reflection electron diffraction [10, 11].

(b) An etchant must be identified which is specific to the amorphous phase. The etchant will be sought by bombarding with a radioactive ion to induce an amorphous phase and then following the residual activity as a function of time of etchant exposure, i.e. obtaining "dissolution curves" [12, 13].

(c) The crystallization temperature, as measured at high temperatures in an experiment of short duration (1 to 10 min), must be sufficiently high to insure track retention at the temperature of the surface of the earth over a geological time scale. The crystallization temperatures will be here determined by marker-release measurements [11, 14] and compared empirically with track-annealing temperatures of minerals commonly used for dating.

(d) The mineral must lie sufficiently high on a scale of amorphizability as to suggest that amorphization could arise from individual fission fragments as distinct from the repeated passage of fragments. This will be explored by deducing amorphizabilities from the information of (b) and (c) and comparing them empirically with the values of substances known either to show or not to show tracks when explicitly exposed to fission fragments.

In so far as this approach is valid, it is hoped that it will provide a partial solution to the problem inherent when tracks in crystalline substances are sought directly, namely that finding them depends not only on points (a) to (d) above being satisfied, but also on the presence of uranium impurities. In effect, five conditions must be satisfied simultaneously.

The arguments will be illustrated in terms of cobalt titanate ($CoO.TiO_2$), as well as the two minerals, apatite ($CaF_2.3Ca_3(PO_4)_2$) and columnbite ($(MN, Fe)O.(Nb, Ta)_2O_5$). Cobalt titanate is here regarded as a representative of the following isostructural minerals [15]:

ilmenite	$(Mg, Fe)O.TiO_2$
pyrophanite	$MnO.TiO_2$,

while apatite is a member of a group in which F can be replaced to varying extents by OH, Cl or O. Columbite can be taken as representative of a particularly broad group of minerals which are either isostructural or closely related and of which a few of the members are the following [15]:

magnocolumbite	$MgO.(Nb,Ta)_2O_5$
tapiolite	$FeO.(Ta, Nb)_2O_5$
fergusonite	$(Ce, Y)_2O_3.(Nb,Ta)_2O_5$
stibiocolumbite	$Sb_2O_3.(Ta,Nb)_2O_5$
thoreaulite	$SnO_2.(Ta,Nb)_2O_5$

We will in a subsequent paper treat five additional substances: Nb_2O_5, Ta_2O_5, cassiterite (SnO_2), olivine ($2(Mg,Fe)O.SiO_2$), and wolframite ($(Mn, Fe)O.WO_3$) [16].

2. Experimental section

The apatite and columbite were natural specimens supplied by the Geological Survey of Canada. The apatite originated from Huddersfield Twp., Quebec. One group of columbites, originating from Iveland, Norway, had an Nb/Ta ratio which was determined by X-ray fluorescence* to be about 5.0. Another group of columbites, from Pennington Co., S.D., had Nb/Ta = 2.0, while a third group, from near Yellowknife, N.W.T., had Nb/Ta = 0.8. The surfaces were prepared by cutting with a diamond saw, polishing on a series of emery papers, followed by annealing in air at 1475 K. For re-use specimens were polished, etched, and annealed.

The cobalt titanate specimens consisted of sintered pellets 10 mm in diameter and 5 mm thick prepared from commercially obtained powder. They were fabricated by cold-pressing in a circular die without use of a binder. The pellets were then sintered in air at 1475 K, polished, and annealed.

The existence of amorphization was sought by bombarding specimens with 10 to 35 keV Kr^+ ions and then examining the surfaces with the reflection electron diffraction unit of a Philips EM-300 electron microscope operated at 60 to 100 kV [10, 11]. The mean projected ion ranges are as in Table I and are thus sufficient, assuming that the amorphization occurs to a depth of about twice the ion range [12, 13], to make reflection diffraction practical.

Etchants were tested by bombarding specimens with 35 keV $^{85}Kr^+$ ions at various doses and then following the residual activity as a function of time of etchant exposure. The appearance of well-defined, dose-dependent discontinuities in the resulting dissolution curves was taken as indicating that the etchant was specific to the amorphous phase.

TABLE I Mean projected ranges of Kr^+ ions*

Substance	$\langle x \rangle$ for 10 keV Kr^+ (nm)	$\langle x \rangle$ for 35 keV Kr^+ (nm)
Apatite	7.0–7.5	17–18
Cobalt titanate	5.0–5.5	12.5–13.0
Columbite	5.0–5.5	12.5–13.5

* Deduced from values for Al_2O_3, SiO_2, Nb_2O_5, WO_3, and Ta_2O_5 due to Schiøtt [17] by interpolating according to the mean target mass. Schiøtt based his work on standard "LSS" range theory [18].

Crystallization temperatures were determined by marker-release measurements [11, 14]. In most instances this involved placing specimens containing ^{85}Kr in a stream of O_2 or He while the temperature was raised linearly at 25 K min^{-1}. The O_2 or He flowed over the specimens at 110 cm^3 min^{-1} and through a counting chamber with a volume of 30 cm^3 which was positioned 10 mm beneath a G.M. counting tube. The result was that differential curves giving the rate of marker release (dF/dT, where F is the fractional marker release) were obtained and the temperature of the release process correlating with crystallization could be determined. Low-dose data for apatite were obtained using a somewhat different procedure. It involved alternate counting and heating so as to yield integral (rather than differential) marker-release data.

The experiments as described were sufficient to determine the amorphizabilities.

3. Results

3.1. Existence of amorphization

The existence of bombardment-induced amorphization was confirmed for all three substances by using reflection electron diffraction. Fig. 1a and b, for example, show how the initially single-crystal pattern of apatite is replaced by diffuse haloes, conventionally taken as characteristic of an amorphous state, after bombardment with 35 keV Kr^+ to a dose of 9×10^{15} ions cm^{-2}. Fig. 1c and d show corresponding results for co-

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* The analyses were carried out at the E.M. & R. Laboratories in Ottawa by S. Courville.

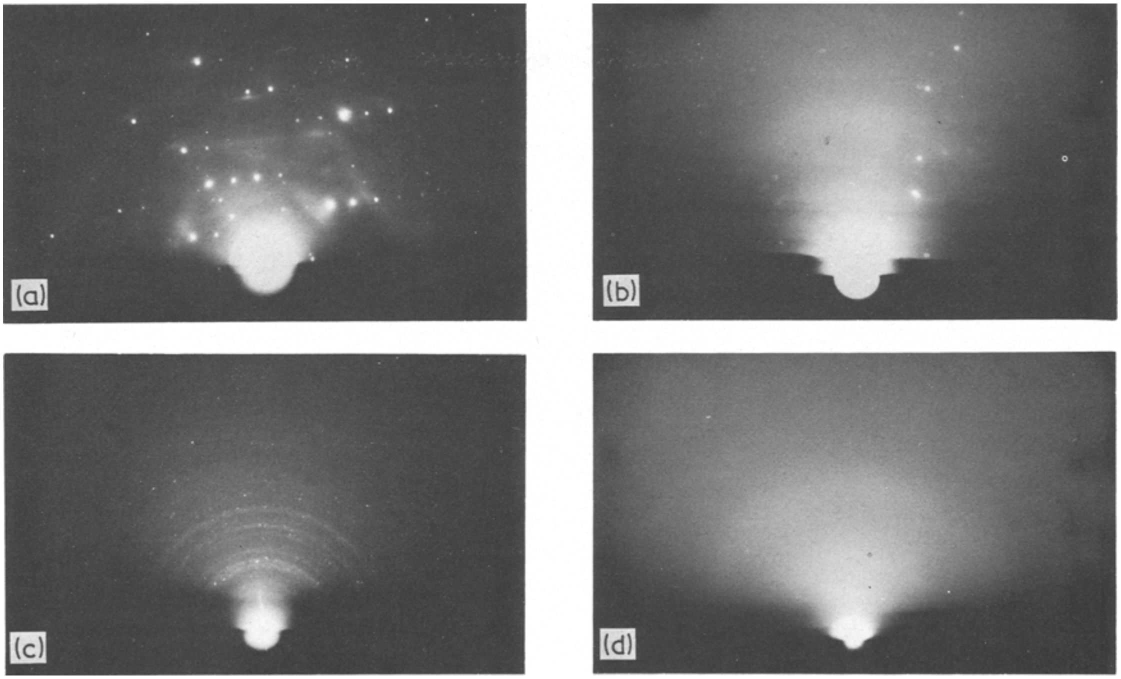

Figure 1 Reflection electron-diffraction patterns at 60–100 kV. (a) Apatite, before bombardment. (b) Apatite, after 9×10^{15} ions cm^{-2} of 35 keV Kr$^+$. (c) Cobalt titanate, before bombardment. (d) Cobalt titanate, after 9×10^{15} ions cm^{-2} of 20 keV Kr$^+$. With each substance an initially crystalline pattern is replaced by diffuse haloes, conventionally taken as characteristic of an amorphous state, as a result of the bombardment.

balt titanate, with overall results as summarized in Table II.

Columbite showed an important effect which can in some respects be regarded as a new category of bombardment-induced structural change and which will be discussed in greater detail elsewhere [19]. As summarized in Table II, columbite with Nb/Ta = 5.0 evolved through an amorphous state to polycrystalline phases consisting, with increasing dose, of NbO plus first one and then another still unidentified substance designated A and B. Columbite with Nb/Ta = 0.8 evolved through an amorphous state to a polycrystalline phase distinct from those occurring with the other specimens and here designated C. The occurrence of NbO shows that a stoichiometry change has occurred which is at first sight much like those known with a number of simple oxides (MoO_3, V_2O_5, TiO_2, Nb_2O_5 [20-22]). What is different here is that the substance is complex and the Nb and O which constitute the NbO have, therefore, had to migrate over a distance similar to the

TABLE II Summary of reflection electron-diffraction data

Bombardment dose (ions cm^{-2})	Apatite*	Cobalt titanate†	Columbite‡ (Nb/Ta = 5.0)	Columbite‡ (Nb/Ta = 0.8)
0	single crystal	polycrystal	single crystal	single or polycrystal
9.0×10^{15}	amorphous	amorphous	amorphous or amorphous + NbO	amorph. + original or amorphous + C
1.9×10^{16}	–	amorphous	NbO + A	C
3.8×10^{16}	–	–	–	C
4.7×10^{16}	–	–	NbO + B	–

* Bombarded with 35 keV Kr$^+$.

† Bombarded with 20 keV Kr$^+$. Amorphous also at 6×10^{15} ions cm^{-2}.

‡ Bombarded with 35 keV Kr$^+$. "A", "B", and "C" stand for unidentified phases. Specimens with Nb/Ta = 2.0 were not examined by diffraction.

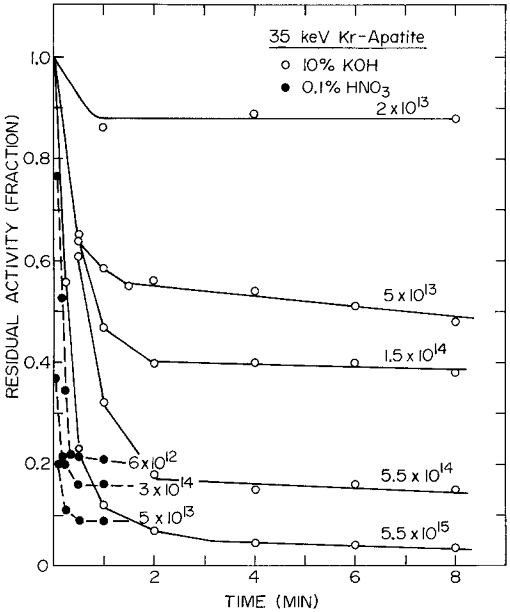

Figure 2 Residual activity versus time of etchant exposure for apatite which has been bombarded with 35 keV $^{85}Kr^+$ ions to doses as indicated (in units of ions cm^{-2}) and then exposed to 10% KOH or 0.1% HNO_3.

crystallite size. In effect, bombardment-induced segregation has occurred along with the stoichiometry change.

3.2. Etchants

As already indicated, etchants were sought in experiments in which specimens were first bombarded with 35 keV $^{85}Kr^+$ ions and then alternately counted and exposed to various etchants. Fleischer and Price [23] have suggested the use of HNO_3 with apatite. The resulting etched tracks were, however, nearly triangular in appearance and, in the opinion of the present authors, were probably overetched. This supposition was supported in that the final residual activities obtained using 0.1% HNO_3 (Fig. 2, dashed) were low and independent of dose, as would be expected if HNO_3 were a solvent for the surface layer containing the stopped ions rather than for amorphousness. (Pringle [8] has found a related effect with Ta_2O_5 bombarded with Ar, Kr, Xe, or Cu). The use of 10% aqueous KOH gave excellent results, however, with well-defined, dose-dependent discontinuities appearing within 120 to 240 sec (Fig. 2, solid). It will be interesting to see how this etchant works with fission tracks.

In the case of columbite with Nb/Ta = 2.0 we have examined two etchants, fluoboric acid saturated with NH_4Cl and an $HF–HNO_3$ mixture consisting of 15 ml HF, 10 ml HNO_3 and 50 ml H_2O (the so-called "P etch" used in semiconductor technology). It is clear from Fig. 3 that the $HF–HNO_3$ mixture meets the requirements rather well. The present authors [16] have shown that "P etch" can be used also with Nb_2O_5 and Ta_2O_5, thence by implication with columbite having any value of Nb/Ta, while Haack [24] has found that a similar, although not identical, mixture is effective with stibiocolumbite.

An etchant for cobalt tianate has not yet been determined.

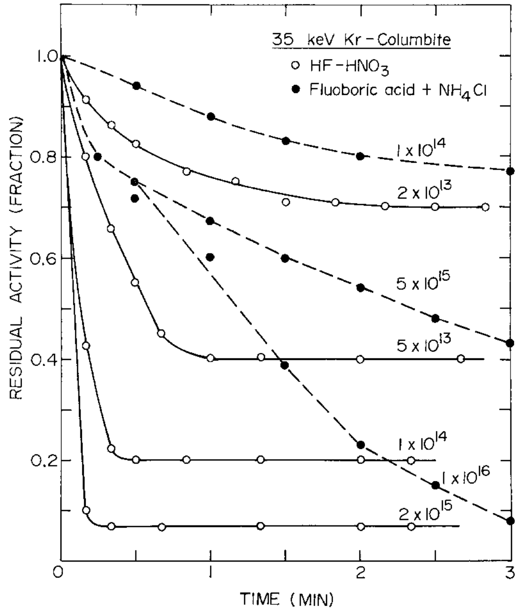

Figure 3 Residual activity versus time of etchant exposure for columbite (Nb/Ta = 2.0) which has been bombarded with 35 keV $^{85}Kr^+$ ions to doses as indicated (in units of ions cm^{-2}) and then exposed to an $HF–HNO_3$ mixture or fluoboric acid + NH_4Cl.

3.3. Crystallization temperatures

The marker-release measurements were most straightforward with apatite. As seen in Fig. 4 and Table III, a narrow peak occurs characterized by a maximum temperature (T_{max}) of 865 ± 20 K and a width at half height ($\Delta T_{1/2}$) given by

$$\Delta T_{1/2}/T_{max} = 0.085 \pm 0.025 \text{ K/K}.$$

This peak accounted for an increasing fraction of the marker-release as the dose increased and both this and the fact that $\Delta T_{1/2}/T_{max}$ lay in the

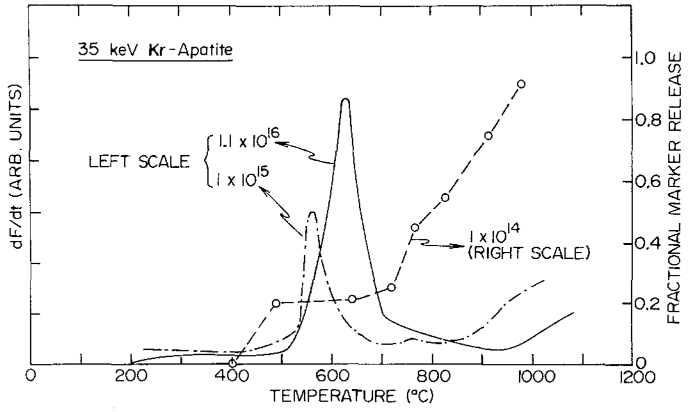

Figure 4 Typical marker-release spectra for apatite specimens which have been bombarded with 35 keV $^{85}Kr^+$ ions to doses as indicated (in units of ions cm^{-2}) and then heated at 25 K min^{-1} in flowing He. Two processes are resolved, of which that maximizing near 600° C has the characteristics (see text) of being due to epitaxial crystallization. The left scale applies to differential data and the right scale to integral data.

interval 0.056 to 0.096 may be taken [11] as indicating that the peak arises from marker which is swept out during the epitaxial crystallization of an amorphous surface layer.

Results for cobalt titanate were similar to apatite (Fig. 5 and Table III) except that the width of the peak at 850 ± 20 K was greater than would be expected for epitaxial crystallization. To determine if the peak could nevertheless be attributed to crystallization, a supplementary experiment was done in which a bombarded specimen was heated for 5 min at 875 K and then examined by reflection electron diffraction. Inner rings were found to be developed, showing that crystallization had begun (Fig. 6).

Results for columbite with Nb/Ta = 5.0 (Fig. 7 and Table III), which revealed the presence of two processes, were more difficult to interpret. The process maximizing at 810 to 905 K is the one most reasonably attributed to crystallization; the width was, however, too large for epitaxial crystallization (Table III) and the dose dependence was not well defined (Fig. 7). Very similar results have been obtained with single-crystal cassiterite (SnO_2), where the crystallization process proceeds in two steps involving first a polycrystalline product and only then epitaxy [16]. A comparison can also be made with thorite ($ThO_2 . SiO_2$) and zircon ($ZrO_2 . SiO_2$). When the amorphous forms of these are crystallized thermally,

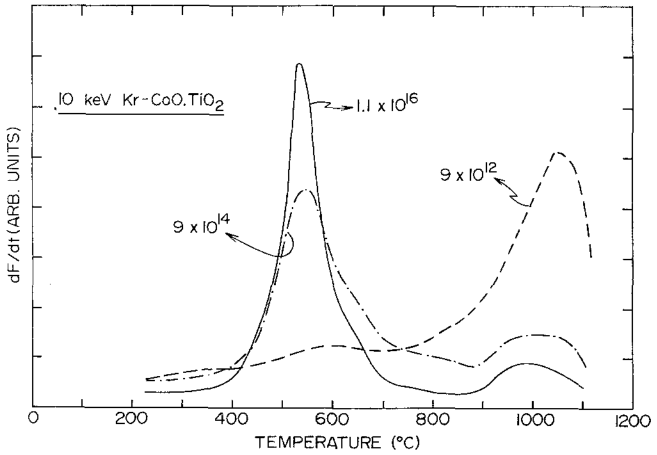

Figure 5 Typical differential marker-release spectra for cobalt titanate specimens which have been bombarded with 10 keV$^{85}Kr^+$ ions. Two processes are resolved, of which that maximizing near 550° C could be identified (see text) as being due to imperfect crystallization.

TABLE III Summary of marker-release data

Substance	Carrier gas	Number of spectra obtained	T_{max} for low-temperature process (K)	$\Delta T_{1/2}/T_{max}$ for low-temperature process (K/K)	T_{max} for high-temperature process (K)
Apatite	He	7	865 ± 20	0.085 ± 0.025	> 1273
Cobalt titanate	O_2 or He	13	850 ± 20	0.140 ± 0.015	> 1273
Columbite	O_2	15	905 ± 20	0.125 ± 0.020	1245
Columbite	He	18	810 ± 25	0.105 ± 0.025	1105–1250*

* This temperature is dose-dependent.

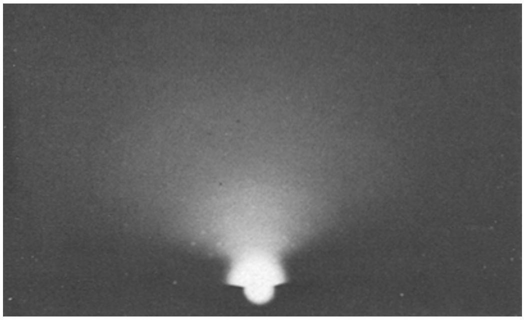

Figure 6 Reflection electron-diffraction pattern at 60 kV of cobalt titanate which has been bombarded with 1.5×10^{16} ions cm^{-2} of 20 keV Kr^+ and then heated for 5 min at 875 K. Crystallization is seen to have begun.

the first phases to appear are, respectively, ThO_2 and ZrO_2, with the original compound appearing in a second step [25, 26]. We will take the stand that the process maximizing at 810 to 905 K represents the first stage of crystallization, even if the details of the crystallization are unclear.

3.4. Amorphizability

Both the marker-release measurements and the dissolution curves make possible an empirical measure of amorphizability. This follows from either of two points of view. If an amorphous layer is assumed to develop in a more or less continuous fashion, such that it is bounded by a well-defined interface, then an increasing dose will lead to a deeper interface and the fraction of marker (F) which escapes either thermally or by etching will be a true measure of this depth (Fig. 8a; also [12, 13]). Alternatively, the amorphization can be envisaged as developing as discrete "zones" which are distributed in depth. F will again increase with the extent of amorphization, although not in as simple a manner as in the first case (Fig. 8b; also [27]). In either case, the escaping marker serves as a measure of the extent of amorphization and a characteristic dose can be deduced to serve as a measure of the amorphizability.

Curves of F versus dose are shown in Fig. 9,

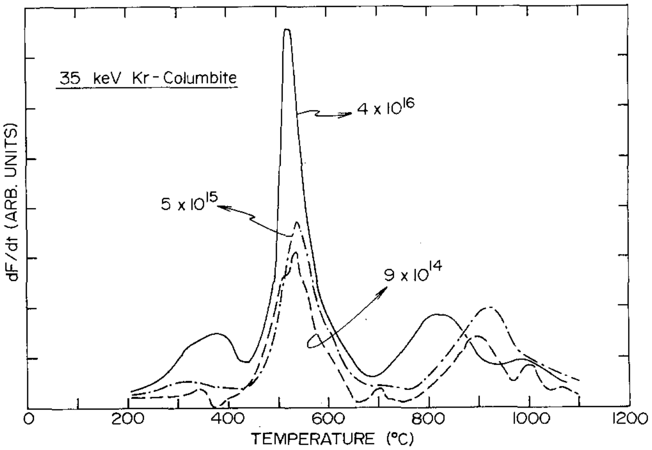

Figure 7 Typical differential marker-release spectra for columbite specimens (Nb/Ta = 5.0) which have been bombarded with 35 keV $^{85}Kr^+$ ions. Two processes are resolved of which that maximizing near 525° C has been taken tentatively (see text) as signaling the first stage of crystallization.

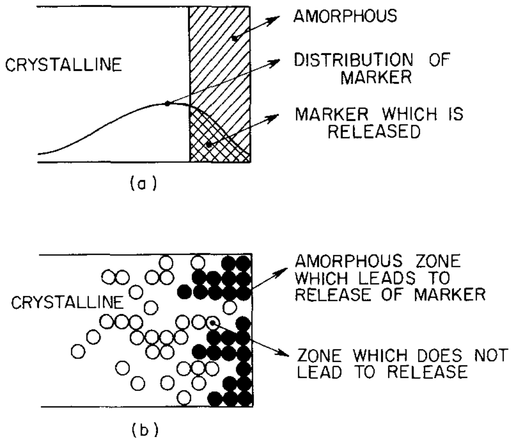

Figure 8 Schematic view of the near-surface regions of a solid, showing the formation of bombardment-induced amorphousness. In (a) the amorphousness is shown as developing in a more or less continuous fashion, such that it is bounded by a well-defined interface. In (b) the amorphousness is envisaged as developing as discrete "zones" which are distributed in depth. The black zones, which are those forming a continuous path normal to the surface, would lead to marker-release according to the model of [27]; release is assumed by the same model not to occur from the white zones.

based on etching in the case of apatite and columbite and on thermal release at 1025 K in the case of cobalt titanate. The corresponding half-doses, i.e. the doses for which $F = 0.5$, are included in Table IV.

4. Discussion

4.1. The likelihood of fission tracks in apatite, cobalt titanate, and columbite

If it is assumed that fission tracks in crystalline substances have an amorphous structure, then four criteria concerning whether such substances will show tracks and, therefore, be useful for geological dating, can be made. As discussed in Section 1, they concern the existence of bombardment-induced amorphization, the etchant, the crystallization temperature, and the amorphizability.

The three substances being studied all meet the first criterion: they are rendered amorphous by heavy-ion bombardment (Table II). The second criterion also present no difficulty: amorphous apatite is readily etched with aqueous KOH and amorphous columbite with an HF–HNO_3 mixture (Figs. 2 and 3).

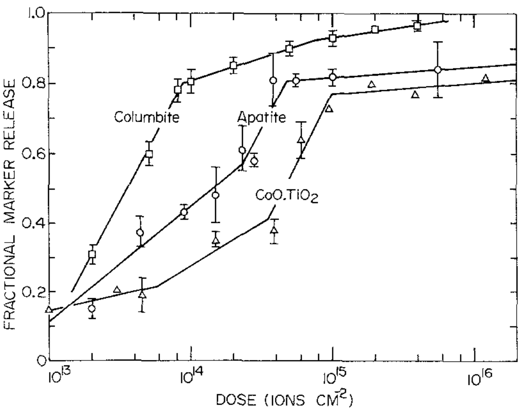

Figure 9 Fractional marker-release versus dose. The cobalt titanate was bombarded with 10 keV $^{85}Kr^+$ ions and the release brought about thermally by heating in air for 5 min at 1025 K. The apatite and columbite were bombarded with 35 keV $^{85}Kr^+$ ions and the release brought about by etching.

The third criterion concerns the numerical value of the crystallization temperature. It can be discussed only if information is available on track-annealing temperatures, as measured at high temperatures in experiments of short duration (1 to 10 min), which are sufficient to ensure track retention at the temperature of the surface of the earth over a geological time scale. This can be done empirically by noting that tracks in the commonly used dating minerals apatite, mica, sphene, tektite and zircon anneal only at temperatures greater than 775 K [9]. One infers that the three substances being studied, which have crystallization temperatures lying in the interval 810 to 905 K, will all be able to retain tracks.

The fourth criterion, about the position of the substance on a scale of amorphizability, again requires an empirical comparison. Table IV includes the half-doses for amorphization for fifteen substances which are known either to show or not to show fission tracks when explicitly exposed to fission fragments. We exclude in this connection instances where tracks appear due to surface alteration (e.g. furrowing) of a thin film [43], to small grain size [39, 40], or to a strain field [42]. The correlation between track occurrence and half-dose is rather marked and suggests that one can make the following generalization: if a substance amorphizes on heavy-ion impact such

TABLE IV Comparison of half-doses for amorphization with the occurrence of fission tracks

Substance	Dose for fractional marker release of 0.50 (ions cm^{-2})	Energy and ion applicable in column 2	Fission tracks by etching?	Fission tracks by electron microscopy?
V_2O_5	2×10^{13} [11]	10 keV Kr^+	yes [34] *	–
SiO_2	$< 4 \times 10^{13}$ [28]	40 keV Xe^+	yes [23]	yes [35]
MoO_3	4×10^{13} [11]	10 keV Kr^+	–	yes [36]
Columbite, (Mn, Fe)O·(Nb, Ta)$_2$O$_5$	4×10^{13} (this work)	35 keV Kr^+	–	–
Zircon, $ZrO_2 \cdot SiO_2$	1.3×10^{14} [29]	10 keV Kr^+	yes [37]	yes [38]
Apatite, $CaF_2 \cdot 3Ca_3(PO_4)_2$	1.4×10^{14} (this work)	10 keV Kr^+	yes [23]	–
Ge	$< 3 \times 10^{14}$ [30]	10 keV Kr^+	no [34]	no [39] ‡
Si	$\sim 3 \times 10^{14}$ [30]	10 keV Kr^+	no [34]	no [39]
Corundum, Al_2O_3	4×10^{14} [29]	10 keV Kr^+	–	no [40]
Cobalt titanate, $CoO \cdot TiO_2$	5×10^{14} (this work)	10 keV Kr^+	–	–
Diamond, C	8×10^{14} [29]	10 keV Kr^+	no [41]	–
BeO	none†	–	–	no [40] ‡
MgO	none [10]	40 keV Xe^+	–	no [39] ‡
ThO_2	none [32]	40 keV Xe^+	–	no [40] ‡
UO_2	none [32]	40 keV Xe^+	–	no §
Al	none [33]	9 keV Ne^+	–	no [44]
Pt	none [33]	9 keV Kr^+	–	no [45]

* Glass with composition $5V_2O_5 \cdot P_2O_5$.

† BeO does not amorphize when bombarded with moderate doses of fission fragments [31], whereas similar or smaller doses readily amorphize corundum, zircon, and U_3O_8 [3].

‡ These results are for thick films and/or large grains.

§ Tracks are in fact observed with UO_2 under special conditions. In [42] they were imaged by diffraction contrast from slightly deformed regions and thus appeared only for particular specimen orientations. In [43], where the UO_2 films were very thin, they were imaged due to furrowing at the surface.

that the half-dose for amorphization is < 1.5 to 3×10^{14} ions cm^{-2}, then it will probably show fission tracks provided uranium impurities are present. In the contrary case, when the half-dose is > 1.5 to 3×10^{14} ions cm^{-2}, tracks will probably not appear even if a source is present. Considering the half-doses for the three substances being studied (included in Table IV), we find that apatite and columbite meet the fourth criterion, although cobalt titanate does not.

The overall conclusion is that apatite and columbite, but not cobalt titanate, should be useful for dating. Apatite is, of course, an already well-established source of tracks and its consideration here serves mainly to show the self-consistency of the approach. Nevertheless, a new etchant is proposed. Columbite and columbite-like minerals are relatively unexplored except for work on tracks in stibiocolumbite [24].

A further important conclusion follows from the rather marked correlation between track occurrence and half-dose revealed in Table IV. It is that the assumption used throughout this work, that fission tracks in crystalline substances have an amorphous structure, is correct.

4.2. Other criteria for fission-track occurrence

The present work has been concerned with criteria for the occurrence of fission tracks in crystalline substances. Fleischer *et al.* [34] have, on the other hand, given a set of criteria for what might at first sight appear to be the same problem, while two of the present authors [4] have given criteria for the existence of bombardment-induced amorphization. We will therefore conclude with a brief discussion of what was intended in each case.

The criteria presented here concern amorphization as induced by heavy-ion bombardment. The assumption was made that fission tracks in crystalline substances have a structure similar to that of an amorphous phase and the work was on this basis argued to be relevant to the formation of fission tracks. The advantage gained is the comparative simplicity of heavy-ion experiments, especially when the ion is radioactive.

Fleischer *et al.* [34] were concerned with whether the trail of ionization left by a fission fragment will give rise to atomic displacements. They propose a group of criteria the most fundamental of which is that the force per unit area between lattice atoms ionized to have charges ze and separated by the mean atomic spacing λ should exceed about 1/10 of Young's modulus E:

$$z^2 e^2/4\pi\epsilon_0\epsilon\lambda^4 > E/10. \qquad (1)$$

If this condition is met the ions will fly apart, i.e. atomic displacements will occur.

We do not regard the criteria of Fleischer *et al.*, especially Equation 1, as being in conflict with the present work; in fact, we would suggest that with crystalline substances both sets of criteria must be met. The one determines whether atomic displacements occur along the trail of a fission fragment, while the other determines whether the displacements, whatever their origin, leave permanent radiation damage. It is only with organic materials and possibly (although not necessarily) glasses that the present work is not applicable and the criteria of Fleischer *et al.* remain the only ones relevant for establishing whether or not tracks occur.

The work of Naguib and Kelly [4] concerned giving a physical explanation for why amorphization occurs, whether due to ion or fission-fragment impact. It is therefore useful for predicting amorphization in the absence of experimental work, with its application to multiple oxides to be considered in a subsequent paper [16].

5. Conclusion

(1) If it is assumed that fission tracks in crystalline substances have an amorphous structure, it follows that four criteria concerning whether such substances will show tracks and therefore be useful for geological dating can be made. They concern the existence of bombardment-induced amorphization, the etchant, the crystallization temperature, and the amorphizability.

(2) The criteria are discussed with reference to apatite, cobalt titanate, and columbite. Heavy-ion impact causes amorphization in all three and the amorphous phase is shown to be etched by aqueous KOH (in the case of apatite) and by an $HF-HNO_3$ mixture (in the case of columbite). An etchant for cobalt titanate was not determined. The crystallization temperatures lie, in all three cases, in the interval 810 to 905 K and are thus comparable to the track-annealing temperatures of substances used for fission-track dating.

(3) The fourth criterion, concerning the amorphizability, is met by apatite and columbite but not cobalt titanate. It is concluded that only the first two of these substances will be useful for dating.

(4) As seen from Table IV, there is a marked correlation between track occurrence in crystalline substances and amorphizability. This suggests that the assumption referred to in (1) was correct.

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