The nature of radiohaloes in biotite: Experimental studies and modeling

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ABSTRACT

Several micro-techniques (confocal laser-Raman microprobe, optical absorption micro-spectroscopy, high-resolution transmission electron microscopy, electron microprobe analysis) were employed in the detailed characterization of radiohaloes in biotites from two Variscan rocks from Germany. The studied biotites are intermediate members of the phlogopite-annite series with Mg/ Fe²⁺ ratios in the range 1.6–1.0. Radiohaloes in biotite resulted from the impact of ⁴He cores (α particles) emitted from actinide-bearing inclusions. Monte Carlo simulations yielded α (²³⁸U, ²³⁵U, and 232 Th series) penetration ranges in biotite between 12.5 and 37.3 μ m, which are in reasonable agreement with the observed radii of radiohaloes in natural biotites. The coloration pattern of a radiohalo closely correlates with the calculated distribution pattern of point defects generated in displacive events. Calculated point defect densities in the range from $< 10^{-5}$ to at most 10^{-2} dpa (displacements per lattice atom) suggest that there are only scattered point defects in a mainly preserved biotite lattice. This is consistent with HRTEM studies that did not reveal any indication for initial volume amorphization in the haloes. However, general Raman band broadening and intensity loss suggest that the short-range order in radiohaloes is significantly disturbed. The darkened color of radiohaloes, when compared with the un-irradiated host biotite, is caused by increased light absorption over the complete visible range due to increased point defect density. No additional color centers were found, and the absorbances of the VIFe2+, Fe2+-Fe3+, and Fe2+-Ti4+centers seem hardly to be changed. Both Raman and optical absorption spectra obtained from radiohaloes retain a clear orientational dependence. The results suggest that the formation of point defects rather than ionization is the main process causing the coloration of radiohaloes in natural biotites. The haloes represent an early stage of structural radiation damage, characterized by significantly disturbed short-range order but still widely preserved long-range order of the structure.

INTRODUCTION

Self-irradiation damage of natural, actinide-bearing minerals, finally leading to the metamict state, has been investigated and discussed in numerous papers. Metamict minerals (such as zircon, titanite, monazite, pyrochlore, and fergusonite) can be transformed from an initially crystalline to an amorphous state by long-term accumulation of damage resulting from α -decay events (e.g., Chakoumakos et al. 1987; Murakami et al. 1991; Meldrum et al. 1998). Most of this damage is caused by the recoil of the heavy daughter nuclei upon emission of an α particle (⁴He core), whereas other related processes—such as α -radiation, spontaneous fission, etc.—make minor contributions to metamictization (e.g., Weber et al. 1994; Nasdala et al. 1996). Radiation-damage phenomena, however, are also observed in minerals that do not contain major amounts of radionuclides in their structures. Such minerals may have undergone radiation-induced alteration due to long-term irradiation originating from their neighboring phases. In these cases, radiation damage is mainly due to α -particles, penetrating some ten μ m into minerals (for comparison, recoil-nuclei ranges are on the order of hundreds of Å). Thus, strong α -emitters are typically surrounded by alteration haloes (usually called radiohaloes) with thicknesses corresponding to the travel distance of the α particles.

The appearance of radiohaloes may vary appreciably and depends on the strength of the irradiation and particularly on the radiation-damaged mineral itself. Among the most widespread mineral species containing radiohaloes is biotite, where haloes are easily recognized by their significantly darker colors ("pleochroic haloes"; e.g., Gentry 1974). Haloes with similar coloration are also found in minerals such as cordierite, amphibole, fluorite, and chlorite. Radiohaloes in quartz appear

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somewhat different. Here, α -radiation does not cause coloration but the damage is recognized from changes in cathodoluminescence (Owen 1988; Meunier et al. 1990).

The aim of the present study was to characterize the nature and degree of radiation-induced alteration in biotite radiohaloes. For this purpose, radiohaloes and unaltered biotites as well as their accompanying actinide-bearing inclusions were studied in detail by various micro-techniques; especially confocal laser-Raman micro-spectroscopy. This technique has already been used to investigate radiation-damage phenomena in other minerals such as halite (Groote et al. 1994), zircon (Nasdala et al. 1995; Wopenka et al. 1996), and quartz (Martin et al. 1996). However, no study that uses Raman spectroscopy to investigate α -damage in biotite has been published so far. This is probably due to the experimental difficulties connected with Raman analysis of Fe-bearing sheet silicates.

As early as 1981, Raman spectroscopy was successfully used by Nédélec and Paquet (1981) to identify glass-like biotite formed by partial melting of gneisses. These authors showed a biotite spectrum but provided no data (Fig. 6 in Nédélec and Paquet 1981). The "biotite" spectrum published by Herman et al. (1985; Fig. 11) showed strong bands at 265, 417, and 707 cm⁻¹ and therefore is most likely a muscovite spectrum (cf., Tlili et al. 1989). In more recent Raman spectroscopy studies, Fe-bearing micas seems to have been avoided. This was probably due to the relatively high sensitivity of such micas to light absorption phenomena, which is a particularly disturbing problem in the case of Raman microprobe analyses, due to the high light focussing. Raman spectra of nearly Fe-free micas (muscovite, phlogopite, lepidolite, and zinnwaldite) were, for example, described in detail by Loh (1973; see also Steger 1975), Tlili et al. (1989), and McKeown et al. (1999a, 1999b). In contrast, no adequate description of the biotite spectrum has been published so far.

We have, therefore, first recorded polarized Raman spectra of a macroscopic biotite crystal lacking noticeable radiation damage. The interpretation of these spectra is, however, very general and restricted to the main spectroscopic features for sound interpretation of the Raman microprobe analyses of radiohaloes. On the basis of these standard spectra, high-resolution Raman spectra of radiohaloes in the structural and hydroxyl stretching ranges were collected. The experimental analysis also included optical absorption micro-spectroscopy, HRTEM, and electron microprobe analysis. In addition, Monte Carlo simulations and calculation of point defect densities were completed based on chemical data.

SAMPLES AND PREPARATION

Radiohaloes in biotites from two Variscan rocks were investigated. Rock sample no. 30 is a staurolite gneiss from Aschaffenburg, Spessart (Germany) that consists mainly of muscovite, biotite, quartz, staurolite, and garnet. The biotite is greenish brown and partially replaced by pale-green chlorite. Accessory minerals include apatite, zircon, monazite, xenotime (rare), and magnetite. Rock sample no. 57 is a quartz diorite from an outcrop between the villages of Seussen and Grafenreuth in the Bavarian Fichtelgebirge (Germany). Its major constituents are quartz, plagioclase, K-feldspar, biotite, hornblende, and less abundant clinozoisite and garnet. Biotites are yellow-brown to orange-brown. The grains appear to be relatively fresh, and chloritization is less common than in gneiss sample 30. Several accessory minerals are present, including titanite, zircon, monazite, apatite, and magnetite.

In addition, a macroscopic biotite crystal from Horni Slavkov (formerly Schlaggenwald, Czech Republic) was analyzed. This crystal was $\approx 25 \times 12 \times 2$ mm in size and is dark brown. Under the optical microscope, manually separated tiny platelets with an approximate thickness of 20–30 µm appeared homogeneous and showed intermediate reddish-brown [E \perp c^{*}; with c^{*} being the direction normal to the a-b plane, i.e. normal to (001)] to pale yellowish (E // c^{*}) interference colors.

Rock samples were prepared as doubly polished, $\approx 25 \,\mu m$ thin-sections. A low-fluorescent, acetone-soluble epoxy was used to attach the sections to the glass slides. Biotite crystals with their cleavage plane almost perpendicular to the polished surface and rear side were selected for electronic absorption spectroscopy and detached from the glass slide. For HRTEM, detached biotite crystals were ion thinned and then carbon coated.

EXPERIMENTAL METHOD

Confocal laser-Raman microprobe analysis

In general, micas are relatively poor Raman scatterers. In addition, biotite is known to be much more light absorbing than Fe-free micas such as muscovite, phlogopite, or lepidolite. The need to use low-excitation energies and, with that, the great decrease of the already low-signal output, makes micro-Raman analysis of biotite a challenging task. The advent of new-generation, notch filter-based Raman systems has opened up new opportunities to analyze biotite in the micro-range. These systems have an excellent optical throughput, compared with triple monochromators (which are much more powerful in terms of spectral resolution). Thus, even the extremely low-signal intensity, scattered from a tiny volume range in biotite irradiated with a low-energy laser beam, can be detected.

Two notch filter-based Raman systems equipped with an Si-based, Peltier-cooled charge-coupled device (CCD) detector were used for laser-Raman micro-spectroscopy. Most spectra were obtained with a Renishaw RM 1000 research-grade Raman microscope equipped with a Leica DMLM series microscope. Spectra were excited with the Ar⁺ 5145 Å line. A Leica $100 \times$ objective (numerical aperture = 0.95) was used. Confocal measurements were done with a lateral resolution of better than 2 µm and an estimated depth resolution of about 2-3 µm. Measurements in the hydroxyl stretching range (here, 3325–3975 cm⁻¹) were done with a static grating position whereas full spectra in the range 100-4000 cm⁻¹ were obtained in the so-called "continuous extended scan" data collection mode (Nasdala and Massonne 2000). In addition, a "line scan" (i.e., a number of Raman measurements placed along a line) was obtained using a Jobin Yvon Labram I system equipped with an Olympus BX 40 microscope. These spectra were excited with the 6328 Å line of a He-Ne laser and an Olympus $100 \times$ objective (numerical aperture = 0.95) was used. Confocal measurements were collected with a lateral resolution of

≈1.5 µm and a depth resolution better than 2 µm. Both Raman systems were equipped with gratings with 1800 grooves/mm. With both systems, the wavenumber accuracy was better than 1 cm⁻¹ and the spectral resolution was ≈2.5 cm⁻¹ (Ar⁺) and ≈2 cm⁻¹ (He-Ne excitation), respectively.

The small spot diameters of the highly focused laser beams (diameter $\approx 1 \ \mu m$) required that extremely low laser power be used to avoid laser damage. Preliminary tests showed that, using both red and green excitation, laser powers as low as 3 mW were too intense and caused significant local biotite heating, alteration, or disintegration. Therefore, laser powers were decreased to $\approx 30 \ \mu W$ and $\approx 80 \ \mu W$ for Ar⁺ and He-Ne excitation, respectively. The extremely low intensity of the scattered light made long acquisition times necessary. Depending on the signal intensity, overall counting times varied from 5–20 hours per single analysis in the case of extended scans to about 4 hours for spectra obtained at static grating positions.

Optical absorption spectroscopy

Polarized absorption measurements were obtained with a Bruker IFS 66v/S FTIR spectrometer equipped with a Bruker IRscope II microscope. The optical absorption spectra were recorded in the range 32000-5000 cm⁻¹, using different combinations of light sources (high-pressure Xe lamp, W lamp), beam splitters (quartz, KBr), and detectors (GaP diode, Si diode, and liquid nitrogen-cooled MCT) for different spectral regions. A Glan prism was used as a polarizer. Measurements were carried out with a spectral resolution of 25 cm⁻¹. An effective limiting aperture of 32 µm diameter in the sample plane was used. A total of 1024 scans were made for each measurement. The phase correction mode of the interferogram was performed following the procedure of Mertz (1965; see Griffiths and de Haseth 1986). The Norton-Beer-weak mode was chosen as the apodization function. Spectra were corrected for sample thickness and displayed as linear extinction coefficient vs. wavenumber.

Other micro-techniques

The chemical compositions of the biotites were determined by electron microprobe analysis on a JEOL JXA 8900 RL electron microprobe. The accelerating voltage was 15 kV and the beam current was 12 nA. The electron beam diameter was 2 μ m. Chemical compositions of monazite inclusions were measured at 15 kV and 50 nA.

Lattice images and electron diffraction patterns of radiohalo areas in biotite were obtained with a Philips CM 200 transmission electron microscope, at a voltage of 200 kV. The spot size of the focused electron beam was 200 nm and the beam current was 1 nA.

X-ray diffraction and Mössbauer spectroscopy

X-ray powder diffraction data for the Horni Slavkov biotite were obtained on a Seifert XRD 3000 TT diffractometer with graphite secondary monochromator, using CuK α radiation. The X-ray tube was operated at a voltage of 40 kV and the current was 30 mA. The scan was collected from 2–150 °2 Θ , with a step size of 0.02 °2 Θ and a scanning rate of 10 s per step.

A Mössbauer spectrum in the velocity range ±4 mm/s was

obtained with a constant-acceleration spectrometer. The spectrum was collected at room temperature using a ⁵⁷Co, singleline source in a Rh matrix (\approx 50 mCi). For analysis, an \approx 0.5 mm thick chip of the Horni Slavkov biotite crystal was irradiated parallel to **c***. The velocity scale was calibrated using a standard α -Fe absorber.

EXPERIMENTAL RESULTS AND DISCUSSION

General characterization of biotites

For this study, we have chosen a large, macroscopically homogeneous biotite crystal from Horni Slavkov as the "external standard" for the Raman spectroscopy. Its powder diffractogram is dominated by strong (00*l*) Bragg peaks that correspond to a layer thickness of 10.03 (2) Å. However, because the monoclinic polytype could not be determined unambiguously from the powder diffractogram, precise lattice constants are not be given. A detailed structural characterization including determination of the polytype would require single crystal analysis and is beyond the scope of the present study.

The Mössbauer spectrum of the Horni Slavkov biotite crystal showed strong orientation effects (different line intensities within doublets). Two intense, asymmetric lines at ≈ -0.1 and +2.3 mm/s (values relative to α -Fe) were fitted reasonably well by two Fe²⁺ doublets, interpreted as octahedral Fe²⁺ at the *trans* (M1: $\delta = 1.07$ mm/s; $\Delta = 2.25$ mm/s) and *cis* (M2: $\delta = 1.09$ mm/s; $\Delta = 2.50$ mm/s) positions (cf., Annersten 1974; Dyar 1987). The overall content of Fe³⁺ is estimated to be about 3% of total Fe. There was no indication for any potential influence of different, coexisting biotite polytypes (cf., Takeda and Ross 1975) on the Fe sites.

Results of electron microprobe analyses of the biotites are shown in Table 1 and calculated biotite formulae are presented in Table 2. Chemical formulae were calculated on a basis of 12 anions per formula unit, assuming complete occupancy of the OH site by hydroxyl groups and complete occupancy at the fourfold coordinated cation sites ($^{IV}Si + {}^{IV}Al = 4$). Iron was assumed to be completely divalent in all biotites, except for the Horni Slavkov sample where the Mössbauer result (Fe3+ 3% of total Fe) was considered. All three biotites investigated (the Horni Slavkov standard and the two biotites from rocks no. 30 and 57) are intermediate members of the phlogopite-annite series. Because F was not measured, potential variations of the OH/F ratio cannot be assessed. As indicated by uniform interference colors between crossed polarizers, the chemical composition of the Horni Slavkov biotite crystal is uniform. Although the three biotites show moderate differences in the occupancy of the octahedral cation positions (see calculated formulae in Table 2), the Horni Slavkov biotite may be used as a calibration standard for micro-Raman analysis and electronic absorption micro-spectroscopy.

Characterization of radiohaloes

Radiohaloes in biotites are small, localized areas around inclusions of actinide-bearing minerals, where the biotite shows significantly darker colors in plane-polarized transmitted light as compared to the unaffected host biotite. A variety of such

Analytical spot	Analyses	SiO ₂	Na ₂ O*	K ₂ O	TiO ₂	FeO	AI_2O_3	MgO	CaO*	Cr ₂ O ₃ *	MnO* Total
Standard biotite (Horni Slavkov)											
	10	37.70(75)	0.35(4)	8.69(14)	2.04(12)	14.85(26)	18.18(41)	13.67(42)	n.d.	0.03	0.06 95.56(72)
			Bioti	tes from roc	k sample 3	0 (staurolit	e gneiss, S	pessart)			
30-1, radiohal	o 6	35.51(51)	0.36(5)	9.07(34)	1.77(9)	18.60(60)	19.14(16)	10.69(18)	n.d.	0.06	0.22(2) 95.43(62)
30-1, unaltere	d 6	35.66(16)	0.32(6)	9.19(10)	1.83(3)	18.76(41)	19.16(21)	10.50(20)	0.01	0.05	0.21(2) 95.70(15)
30-3, radiohal	o 6	35.82(20)	0.32(3)	9,23(9)	1.92(2)	18.91(30)	18.97(21)	10.53(13)	n.d.	0.05	0.23(3) 95.97(39)
30-3, unaltere	d 6	35.73(34)	0.30(5)	9.31(19)	1.89(5)	18.94(41)	18.94(17)	10.60(14)	0.01	0.06	0.23(3) 96.00(42)
Biotites from rock sample 57 (quartz diorite, Fichtelgebirge)											
57-1, radiohal	o 6	37.76(48)	0.09	9.77(15)	3,57(19)	17.16(18)	15.38(27)	12.49(21)	0.01	0.10	0.25(1) 96.58(54)
57-1, unaltere	d 6	37.63(56)	0.10	9.81(23)	3.66(11)	16.85(24)	15.28(40)	12.54(37)	0.03	0.10	0.24(2) 96.25(71)
57-2, radiohal	o 6	37.68(19)	0.08	10.11(12)	2.43(73)	17.04(28)	15.87(55)	12.77(48)	0.02	0.03	0.24(6) 96.27(21)
57-2, unaltere	d 6	37.37(96)	0.07	9.42(89)	2.25(47)	17.34(75)	15.71(56)	13.41(50)	0.02	0.06	0.28(3) 95.93(85)
	.d		0.1 10/								

TABLE 1. Electron microprobe analyses of biotites (in wt% oxide)

n.d. = not detected or mean value < 0.01 wt%.

* standard deviations are only given for means > 0.10 wt%.

Biotite	Formula
Horni Slavkov standard	(K _{0.82} Na _{0.05}) (Mg _{1.50} Fe ²⁺ _{0.89} Fe ³⁺ _{0.03} Al _{0.35} Ti _{0.11} □ _{0.12}) [Al _{1.23} Si _{2.77} O ₁₀ / (OH) ₂]
30-1, radiohalo	(K _{0.88} Na _{0.05}) (Mg _{1.21} Fe _{1.18} Al _{0.39} Ti _{0.10} Mn _{0.01} □ _{0.11}) [Al _{1.31} Si _{2.69} O ₁₀ / (OH) ₂]
30-1, unaltered	(K _{0.89} Na _{0.05}) (Mg _{1.18} Fe _{1.18} Al _{0.40} Ti _{0.10} Mn _{0.01} □ _{0.13}) [Al _{1.31} Si _{2.69} O ₁₀ / (OH) ₂]
30-3, radiohalo	(K _{0.89} Na _{0.05}) (Mg _{1.18} Fe _{1.19} Al _{0.38} Ti _{0.11} Mn _{0.01} □ _{0.13}) [Al _{1.30} Si _{2.70} O ₁₀ / (OH) ₂]
30-3, unaltered	(K _{0.90} Na _{0.04}) (Mg _{1.19} Fe _{1.19} Al _{0.38} Ti _{0.11} Mn _{0.01} □ _{0.12}) [Al _{1.31} Si _{2.69} O ₁₀ / (OH) ₂]
57-1, radiohalo	(K _{0.93} Na _{0.01}) (Mg _{1.39} Fe _{1.07} Al _{0.16} Ti _{0.20} Mn _{0.02} □ _{0.16}) [Al _{1.19} Si _{2.81} O ₁₀ / (OH) ₂]
57-1, unaltered	(K _{0.94} Na _{0.01}) (Mg _{1.40} Fe _{1.05} Al _{0.15} Ti _{0.21} Mn _{0.02} □ _{0.17}) [Al _{1.19} Si _{2.81} O ₁₀ / (OH) ₂]
57-2, radiohalo	(K _{0.96} Na _{0.01}) (Mg _{1.42} Fe _{1.07} Al _{0.22} Ti _{0.14} Mn _{0.02} □ _{0.13}) [Al _{1.18} Si _{2.82} O ₁₀ / (OH) ₂]
57-2, unaltered	(K _{0.90} Na _{0.01}) (Mg _{1.50} Fe _{1.09} Al _{0.19} Ti _{0.13} Mn _{0.02} □ _{0.07}) [Al _{1.20} Si _{2.80} O ₁₀ / (OH) ₂]

haloes is shown in Figure 1. Similar to unaltered biotite, colors of radiohaloes show a strong dependence on orientation. The color of a halo is always more intense with $\mathbf{E} \perp \mathbf{c}^*$. Radiohaloes with reversed coloration (Moazed et al. 1977) were not observed in the present study.

In transmitted light, the radiohaloes typically have radii of 37-40 µm. Radiohaloes around small (<10 µm) inclusions are generally less intensely colored and consist of a relatively dark circle in the center (radius $\approx 26-29 \,\mu\text{m}$) surrounded by a weakly colored, circular area, the latter showing a narrow coloration "ring" (radius ≈ 36–39 µm; Figs. 1D and 1E). However, more than two concentric rings or circles, as were, for example, documented by Gentry (1974; see in particular his Fig. 1i), were not observed. This difference is most probably due to the relatively large thickness of the thin-sections investigated (25 μ m). The observed radii of 37-40 µm are generally on the order of the penetration ranges of α -particles in biotite (e.g., Rankama 1954), with the outer radius assigned to the α -particle with the highest energy (8.376 MeV; ²¹²Po \rightarrow ²⁰⁸Pb decay in the ²³²Th series). Direct comparison of the observed radii with literature data is limited because most α -ranges were reported for biotites containing U-dominant inclusions (e.g., Moazed et al. 1973; Gentry 1974) whereas most of our radiahaloes are caused by Th-dominant monazites. However, there is no indication for unusually large radii of radiohalos in the investigated samples, which would have suggested processes such as Rn diffusion.

Estimation of the birefringence of intensely colored radiohaloes in biotite is difficult or even impossible, as the dark color of the halo generally masks the observed interference color. To compare the birefringence of radiohaloes and their neighboring host biotite, we have chosen haloes in biotites cut almost perpendicular to the cleavage (which is roughly perpendicular to the circular section of the indicatrix). In the case of weakly colored radiohaloes (Fig. 1F, left picture), notably higher interference colors (Fig. 1F, right picture), indicating enhanced birefringence, were usually observed in cross-polarized light. In contrast, some of the more intensely colored radiohaloes appeared to show slightly diminished interference colors. Because electron microprobe analyses did not reveal significant chemical differences between haloes and their surrounding biotites (Tables 1 and 2), variations in the chemical compositions can be excluded as potential causes of the changed interference colors. Another possible explanation for these color differences is that the volume expansion of a metamict inclusion might cause local stress and, with that, enhanced birefringence in the surrounding biotite. However, enhanced birefringence was observed both around zircon and monazite inclusions, although no evidence of monazite metamictization was observed. Moreover, it would be remarkable that such local stress in biotite always extended over the same distance as the α -irradiation. We explain the changed birefringence to indicate a slight disturbance of the structure resulting from aradiation: this disturbance results first, at low degrees of radiation damage, in slightly enhanced and, at advanced radiation damage, in slightly decreased anisotropy. However, high degrees of radiation-induced disorder, which would cause the material to become isotropic and, with that, yield greatly diminished interference colors (see Chakoumakos et al. 1987; Nasdala et al. 1998), were not found. These observations suggest that radiohaloes generally represent a relatively early stage of radiation damage accumulation.

Characterization of actinide-bearing inclusions

Actinide-bearing minerals, which cause radiohaloes due to α -irradiation of the biotite, were identified as monazite, zircon, and rare xenotime in sample 30. Large crystals (>30 µm) of these minerals are generally surrounded by darker radiohaloes than are small inclusions. Furthermore, haloes



FIGURE 1. Photomicrographs of typical radiohaloes in biotites (A, C, and D, sample no. 57; B, E, and F, sample no. 30). Images A to E were obtained in plane-polarized transmitted light. The light was polarized with the **E** vector parallel to the horizontal direction of the pictures. (**A**) Intensely colored, with $\mathbf{E} \perp \mathbf{c}^*$ almost black appearing haloes around large, prismatic zircon crystals. (**B**) Uniformly colored haloes (center: halo 30-1) surrounding round monazite grains. (**C**) Halo 57-2: This monazite inclusion, approximately 22 µm in diameter, is surrounded by an extremely intense halo, which is due to its high actinide content (\approx 83 000 ppm Th; Table 3). (**D**) A weakly zoned radiohalo (57-4) surrounding a small (\approx 5.5 µm) monazite grain. (**E**) A zoned radiohalo (30-7) surrounding an 8 µm monazite grain. Note the distinct "outer ring" with a radius of 37.1 µm, the generation of which is due to 8.376 MeV α -particles (²¹²Po decay). (**F**) A weakly colored radiohalo around a zircon inclusion. Left image (obtained in plane-polarized transmitted light): in this position, with an angle of 45° between the cleavage plane and the **E** vector of the light, both the halo and the surrounding biotite appear pale brownish. Right picture (obtained in cross-polarized transmitted light): note that the radiohalo shows enhanced birefringence (blue-red in the halo in contrast to orange-yellowish color in the unaltered biotite).

around monazite and xenotime usually appear more intense than haloes around zircon (which have generally lower U and Th) of similar size. The apparent coloration intensity is generally proportional to the total α -dose (cf., Hradetzky et al. 1990).

Because monazite is the most abundant mineral causing intense radiohaloes in biotite, several inclusions of this mineral were selected for chemical analysis. These analyses were completed to determine concentrations of actinide element contents and to calculate the total α -fluence emitted by these inclusions, which enables us to estimate the α -dose experienced by the surrounding biotite. Monazite analyses, presented in Table 3, show this mineral to be homogeneous in composition in both rock samples. Note that monazites from sample no. 57 are particularly high in radionuclides, with ThO₂ reaching up to 19.38 wt% (~170 000 ppm Th).

Optical absorption spectroscopy

Micas are often spectroscopically treated as uniaxial minerals, which is possible because the polarization behavior in the cleavage plane is almost negligible (Rossman 1988). Then, only the spectrum with the **E** vector parallel ($\mathbf{E} \perp \mathbf{c}^*$) and perpendicular to the cleavage plane ($\mathbf{E} // \mathbf{c}^*$) needs to be measured, respectively. This orientational approximation had no influence on the interpretation of the resultant pairs of optical absorption spectra, because the spectra of the radiohaloes and their unaltered biotite host always were measured along the same crystallographic orientations.

The polarized spectra obtained from several pairs of microareas (radiohalo and neighboring, unirradiated host biotite) generally showed a similar pattern. Figure 2 shows a representative set of spectra and the spectra obtained from the Horni Slavkov standard biotite. All optical absorption spectra show strong anisotropy in the case of biotites sectioned normal to the cleavage.

The spectra are dominated by a strong tail with increasing intensity toward higher wavenumbers, resulting from strong oxygen-metal charge transfer (OMCT). This broad band has its maximum intensity well in the ultraviolet region. Since OMCT transitions are allowed according to both Laporte and spin-multiplicity selection rules, their absorption intensities are about 10^3 – 10^4 times higher than those caused by crystal-field transitions. Correspondingly, their low-energy "wing" extends into the visible spectral region (Lever 1984; Burns 1993).

Prominent absorption bands were observed at about 8700 (band I in Fig. 2), 11 000 (band II), 13 500 (band III), and 22 000

cm-1(band IV). These bands, which are relatively low in intensity, are caused by absorption phenomena involving transition metals. According to electron microprobe data (Table 1), Fe and Ti are the only major transition metals that can result in detectable optical absorption. The bands at 8700 and 11 000 cm-1 are generally assigned to components of the Fe2+ dd spinallowed transition ${}^{5}T_{2} \rightarrow {}^{5}E$ in octahedral coordination (Faye 1968; Robbins and Strens 1972; Smith and Strens 1976). In addition, Smith (1978) and Smith et al. (1980) concluded from their redox investigations on biotites that, with E in the cleavage plane, much of the absorption in the spectral range 12000-8000 cm⁻¹ is due to exchange coupling of Fe²⁺-Fe³⁺ pairs that intensify the Fe2+ spin-allowed dd bands. Polarized measurements obtained by Smith and Strens (1976) revealed that the absorption band at 13 500 cm⁻¹ is largely absent in the direction perpendicular to (001). Considering the structure of biotite and the strong pleochroism, these authors attributed this band to Fe²⁺-Fe³⁺ intervalence charge transfer (IVCT). Faye (1968) discussed that the absorption band at $\approx 22\ 000\ \text{cm}^{-1}$ is most probably caused by Fe2+-Ti4+ IVCT rather than by a Ti3+ spin-allowed dd transition. However, the details have not yet been clarified in this system. Due to the strongly anisotropic behavior of the absorption edge, the 22 000 cm⁻¹ band is only observed perpendicular to the cleavage plane whereas it might be obscured with $\mathbf{E} \perp \mathbf{c}^*$. These absorption patterns (Fig. 2) generally concur with previously published biotite spectra (e.g., Rossman 1988).

To the best of our knowledge, only one optical absorption spectrum obtained from a radiohalo in biotite has been reported previously (Seal et al. 1981). That sample was from Madagascar and exhibited bleached haloes. Unfortunately, neither the orientation of the sample was described nor any information about polarization was given. The spectra in the present study obtained from dark-colored radiohaloes in biotite are typically distinguished from those obtained from neighboring, unaltered biotite by having higher absorption intensities over the full spectral range. This difference is mainly due to a remarkable shift of the absorption edge into the visible range, i.e. by roughly 10 000 cm⁻¹ toward lower wavenumbers. This energy shift is interpreted as being due to a new component of a broad chargetransfer band caused by radiation-induced defects in the biotite lattice, superimposed on the "original" OMCT absorption edge.

According to Sherman (1985a, 1985b), calculated energies of OMCT for sixfold coordinated $[Fe^{3+}O_6]^{-9}$ clusters are shifted

TABLE 3. Electron microprobe analyses of monazite inclusions (in wt% oxide)

Radiohalo	Ce ₂ O ₃	CaO	Gd_2O_3	Nd_2O_3	Dy_2O_3	Y_2O_3	Sm ₂ O ₃	La ₂ O ₃	Pr_2O_3	Ho ₂ O ₃	FeO	SiO ₂	ThO ₂	UO ₂	PbO	P_2O_5	Total
Monazites from rock sample 30 (staurolite gneiss, Spessart)																	
30-1	27.34	0.81	1.45	12.17	0.77	2.07	2.01	13.10	2.91	0.25	0.10	0.13	3.13	0.54	0.04	29.61	96.45
30-2	26.91	0.89	1.53	11.89	0.78	2.10	1.97	13.17	2.84	0.11	0.14	0.13	3.43	0.60	0.06	29.60	96.17
30-3	25.99	1.20	1.54	12.09	0.55	1.42	2.40	12.63	2.89	0.29	0.05	0.14	4.01	0.85	0.05	29.96	96.07
30-4	26.92	1.12	1.98	12.10	0.68	1.89	2.32	12.94	2.85	0.03	0.14	0.19	4.01	0.74	0.06	29.92	97.87
30-5	27.52	0.88	2.04	12.98	0.46	1.39	2.49	13.14	3.08	n.d.	0.04	0.16	3.06	0.63	0.05	29.98	97.90
Monazites from rock sample 57 (quartz diorite, Fichtelgebirge)																	
57-1	23.64	0.26	n.d.	8.13	0.05	0.24	0.67	13.91	1.74	0.29	0.77	5.33	19.38	1.19	0.15	22.19	97.96
57-2	28.41	0.47	0.47	8.85	0.04	0.29	0.71	17.56	2.36	n.d.	0.36	2.12	9.44	0.30	0.06	27.76	99.20
57-3	30.09	0.43	0.27	9.48	n.d.	0.28	0.69	17.42	2.55	0.04	0.54	1.79	7.74	0.25	0.05	27.87	99.51
nd = not c	hotoctod	or ovide		t bolow	0.01.w/	0/.											

n.d. = not detected or oxide content below 0.01 wt%



FIGURE 2. Optical absorption spectra of biotites. (**A**) Spectra obtained from the Horni Slavkov standard. (**B**) Four spectra obtained from a biotite from sample no. 30. In the latter plot, the upper two spectra were measured in the radiohalo and the lower two spectra (marked "Host") in the neighboring, un-irradiated host biotite. Solid lines, $\mathbf{E} \perp \mathbf{c}^*$; dotted lines, $\mathbf{E} // \mathbf{c}^*$. I and II, Fe²⁺ spin-allowed dd bands; III, Fe²⁺-Fe³⁺ IVCT band; IV, Fe²⁺-Ti⁴⁺ IVCT band.

by only ≤3000 cm⁻¹ to lower wavenumbers when compared to those of $[Fe^{2+}O_6]^{-10}$ clusters. This effect has been experimentally verified in absorption spectra of synthetic fayalites with defined concentrations of Fe³⁺ (Cemič et al. 1986). Consequently, the observed shift of the low-energy "wing" of the absorption edge by ≈10 000 cm⁻¹ in our spectra cannot be simply due to an increased concentration of Fe³⁺ generated by the ionization of Fe²⁺.

Furthermore, a notably increased presence of Fe³⁺ in the radiohaloes would imply that a major portion of the initial Fe²⁺ is oxidized. In this case, the Fe²⁺ dd-bands (bands I and II in Fig. 2) would have diminished and, simultaneously, the Fe²⁺-Fe³⁺ IVCT band (band III) would have increased in intensity, which is not observed. Effects of Fe²⁺ \rightarrow Fe³⁺ ionization would particularly affect an increasing intensity of the IVCT band (band III), as these kinds of transitions are allowed according to both Laporte and spin-multiplicity selection rules. IVCT bands are generally characterized by absorption intensities that are on the order of 10–100 times stronger than those of crystal field dd-transitions (Lever 1984).

In contrast, intensity changes that extend the experimental error of the absorption bands caused by dd transitions, IVCT, and exchange-coupled Fe^{2+} - Fe^{3+} pairs were not detected. Additional bands in the spectra of radiohaloes, as compared with spectra from unaltered biotites, were not observed. Thus, our observations contradict the hypothesis that the generally darkened colors of radiohaloes, as compared with their unaltered host biotite, are mainly due to ionization processes, as such processes would also affect the valence of Fe. Instead, optical absorption spectra indicate that the dark coloration of radiohaloes is due to absorption phenomena related to point defects.

HRTEM

TEM analysis has been applied successfully to the study of radiation damage phenomena in natural minerals (Murakami et al. 1991; Weber et al. 1994; Meldrum et al. 1998), synthetic Cm- and Pu-doped samples (Weber et al. 1986), and minerals irradiated with electron and heavy-ion beams (Wirth 1985; Wang et al. 1998, 1999; Wang and Weber 1999; Wang et al. 2000). Radiation damage can be particularly well recognized in lattice images, ranging from slight disorder phenomena up to the entire loss of periodicity (occurrence of amorphous regions).

Our HRTEM studies did not show significant differences between haloes and their surrounding, unaltered biotite. All samples studied were found to be crystalline with well-ordered structures (Fig. 3). The preserved lattice symmetry and order can be particularly recognized in the Fourier-filtered images (see Fig. 3B). Slightly blurred areas (several nanometers in size) in these images may indicate a low-degree of local lattice distortion. This distortion is, however, probably not due to α -damage, because such blurred nano-areas were also observed in the unaltered, host biotite.

Although direct correlation of images obtained from different mineral species has to be done with appropriate care, a comparison of the observed regularity of the lattice fringes with HRTEM images of other minerals (e.g., Weber et al. 1994) suggests that the radiohaloes cannot have accumulated a radiation damage dose exceeding ≈ 0.05 dpa. Correspondingly, electron diffraction patterns showed sharp reflections. Therefore, the HRTEM results suggest that even intensely colored radiohaloes in biotite are characterized by a relatively low degree of structural radiation damage.

Confocal laser-Raman microprobe analysis

As with optical absorption spectroscopy, the biotites were treated as uniaxial minerals in terms of their Raman spectra (cf., Rossman 1988). Spectra of micas published recently by McKeown et al. (1999a, 1999b) demonstrate that the orientational dependence of Raman bands within the cleavage plane is almost negligible: mica platelets irradiated perpendicular to their cleavage (i.e., along c^*) gave generally similar spectra, independent of the polarization (parallel to [100] or [010], both of which are $\perp c^*$) of the scattered light. Therefore, only two general orientations of Raman spectra ($\mathbf{E} // \mathbf{c}^*$ and $\mathbf{E} \perp \mathbf{c}^*$) will be discussed in the following.

Polarized Raman spectra of the Horni Slavkov biotite are shown in Figure 4. The spectra are dominated by anisotropic bands in the lattice (200–1200 cm⁻¹) and hydroxyl stretching



FIGURE 3. Results of HRTEM investigations of an intensely colored radiohalo in a biotite from sample 57, cut parallel to the cleavage plane (001). (A) Lattice image of the radiohalo. (B) Detail enlargement of the Fourier-filtered version of the same image, showing the regularity of the lattice. (C) Corresponding electron diffraction pattern, exhibiting sharp reflections.

regions. The lattice region shows, as expected, some similarity with the Raman spectra of phlogopite (Clemens et al. 1987; Tlili et al. 1989; McKeown et al. 1999a). Apart from moderate band shifts, a conspicuous difference between the phlogopite and biotite spectra is an apparent band splitting in the biotite: the main phlogopite band at $\approx 680-690$ cm⁻¹ seems to correspond with a group of at least three biotite bands (see spectrum with $\mathbf{E} \perp \mathbf{c}^*$ in Fig. 4). Although the apparent band splitting certainly needs further confirmation, we interpret it as the result of diverse occupation of octahedral sites (mainly by Mg²⁺ and Fe²⁺), causing different vibrational modes involving movements of atoms of the tetrahedral and octahedral sheets. Sound, detailed assignment of these bands would require much more extensive experimental work and factor group analysis (cf., McKeown et al. 1999a, 1999b), which was beyond the scope



FIGURE 4. Polarized Raman spectra (stacked) of the Horni Slavkov biotite. Ar⁺ 5145 Å excitation. The y-axis is the intensity scale in arbitrary units. Note the slightly increased background at $E \perp c^*$ which is due to weak, laser-induced luminescence.

of the present study.

There are two main bands observed in the hydroxyl stretching region. The band at 3675 cm⁻¹ is particularly strong with E // c* (Fig. 4). The direction of this hydroxyl O–H bond direction must be oriented nearly normal to the cleavage plane (001). We assign this band to hydroxyl groups coordinated by three occupied octahedra. However, considering the chemical composition of the Horni Slavkov biotite (Table 3), it is likely that the 3675 cm⁻¹ band consists of a close overlap of several hydroxyl bands with different cation configurations, for example [Mg, Mg, Fe²⁺], [Mg, Fe²⁺, Fe²⁺], other configurations involving trivalent cations, etc. (cf., the infrared results of Redhammer et al. 2000). This conclusion is supported by the slightly asymmetric shape of the band. In addition, the relatively large full width at half-maximum (FWHM) of 65-70 cm⁻¹ points to several simultaneous cation configurations: Robert et al. (1989) demonstrated that the Raman band of hydroxyl groups in a synthetic phlogopite, exclusively coordinated by [Mg²⁺, Mg²⁺, Mg²⁺], has a FWHM of only ≈30 cm⁻¹, whereas micas with uneven cation occupation always show much broader OH stretching bands. A second hydroxyl stretching band at ≈ 3600 cm⁻¹ (Fig. 4) has much lower intensity and is only observed with $\mathbf{E} \perp \mathbf{c}^*$ whereas with $\mathbf{E} // \mathbf{c}^*$, this band is superimposed on the low-frequency slope of the intense 3675 cm⁻¹ band. The corresponding O-H dipole, which is greatly tilted toward the cleavage plane, is assigned to hydroxyl groups coordinated by one vacant and two occupied octahedra. Analogous to the above, the band at \approx 3600 cm⁻¹ probably exhibits contributions from stretching vibrations of hydroxyl groups with different cation configurations, for example $[Ti^{4+}, Al^{3+}, \Box]$, $[Al^{3+}, Mg^{2+}, \Box]$, etc.

Representative Raman spectra of biotites from rock samples 30 and 57 are presented in Figure 5. Spectra obtained from biotites outside the radiohaloes are similar to the Horni Slavkov spectra. There are only minor effects caused by the small differences in the chemical compositions of the three biotites (Table 2). In contrast, clear changes are observed when comparing the spectra obtained from radiohaloes. These spectra are characterized by general loss of intensity and broadening of bands, accompanied by band shifts (Fig. 5). As chemical compositions of radiohaloes and their neighboring host biotites are broadly similar, changes in the Raman spectra cannot be explained by chemical differences. We assign the Raman spectral changes to the radiation-induced structural damage in the haloes. This interpretation is supported by the similar broadening, weakening, and frequency shifts of Raman bands in zircon with increasing structural radiation damage (Nasdala et al. 1995).

To document radiation-induced changes in the Raman spectra in more detailed, a series of spectra in the lattice and hydroxyl stretching regions were obtained from two radiohaloes. Measurements were made inside and outside the haloes at different distances from the inclusion-biotite boundary. Figure 6 shows that the band broadening and intensity loss in the lattice



Raman shift [cm⁻¹]

FIGURE 5. Polarized, confocal Raman spectra of radiohaloes (Ar⁺ 5145 Å excitation). (A) Halo 57-4 (cf. Fig. 1D). (B) Halo 30-1 (Fig. 1B). Quadruplets of spectra were obtained with $\mathbf{E} \perp \mathbf{c}^*$ (dotted lines) and $\mathbf{E} // \mathbf{c}^*$ (solid lines), respectively. Measurements were made in the radiohalo about 5 µm away from the central inclusion and in the neighboring host biotite, about 50 µm from the inclusion (which is more than 10 µm away from the outermost rim of the radiohalo).

increases gradually with decreasing distance from the monazite inclusion. Note that the intensity loss is not uniform but varies among bands. However, an explanation for this feature cannot be given at present. In general, Raman spectra suggest that the dark "inner circle" of that halo (similar to the halo in Fig. 1E) has experienced more damage than the light brown "outer ring," which correlates with the observed coloration intensity.

Similar trends were found for bands in the hydroxyl stretching region (Fig. 7). The OH-bands show rapid intensity loss and broadening with decreasing distance from the inclusion. In addition, there is a general shift of bands by about 30 cm⁻¹ toward lower wavenumbers. At the highest damage level, the equivalent of the 3675 cm⁻¹ band (E // c*) of the biotite host has shifted to ≈ 3654 cm⁻¹ and shows a clear shoulder at ≈3696 cm⁻¹. As the observed band actually consists of an overlap of several bands, this observation, as already mentioned for the lattice range, could simply be due to various degrees of intensity loss of different bands. An alternative interpretation is that the band broadening and appearance of a high-frequency shoulder is due to local charge imbalance among the atoms next to the H atom of the hydroxyl group, caused by displacive or ionization events. For example, Robert et al. (1989) proved a strong dependence of hydroxyl stretching frequencies on the valences of the three six-fold coordinating cations. The clear frequency shifts and broadening of the hydroxyl stretching



FIGURE 6. A series of confocal Raman spectra in the range 250 to 1100 cm⁻¹ (He-Ne 6320 Å excitation), obtained from halo 30-7 (not shown). This biotite is cut almost parallel to the cleavage plane, therefore, all spectra were obtained with $\mathbf{E} \perp \mathbf{c}^*$. The distance of the analytical spots from the inclusion-biotite boundary is given in micrometers. Note the resultant broadening and intensity loss of Raman bands toward the center of the halo.



FIGURE 7. Series of confocal Raman spectra in the hydroxyl stretching range (Ar^+ 5145 Å excitation), obtained from halo 30-4 (not shown). Note the gradually increasing broadening, shift, and intensity loss of bands toward the inclusion.

bands may be explained by considering that charge imbalance would affect the relatively weakly bonded H atoms more than the other more strongly bonded atoms.

The observed general dependence of the broadening of Raman bands on the *a*-irradiation, indicating increasingly irregular vibrational frequencies of atoms, points to a notably decreased short-range order in the radiohaloes. This decrease in order most probably is caused by local structural defects. However, irregular changes in the electronic configurations of the atoms due to ionization may also cause slightly irregular bond lengths and angles that enhance the broadening of vibrational bands. Although detailed explanations for the observed spectral changes cannot be given at present, the Raman data have revealed that biotite undergoes gradually increasing structural changes with increasing irradiation dose. Although the lattice symmetry is relatively little disturbed (as revealed by HRTEM), indicating low defect concentrations in the radiohaloes, the short-range order in radiohaloes seems to be significantly disturbed.

CALCULATIONS AND DISCUSSION

Monte Carlo simulations

Zircon, monazite, or xenotime normally contain three major radionuclides: ²³⁸U, ²³⁵U, and ²³²Th. Each α -decay event in the respective decay series causes emission of a ⁴He core having a distinct energy. Monte Carlo simulations were done for each of these α -energies (Table 4) to calculate: (1) α penetration ranges in biotite; (2) the number of atomic vacancies

TABLE 4. Results of Monte Carlo calculations

Nr.	α -decay	α -energy A	verage ran	ge Average
	event	[MeV]*	[µm]	vacancies/α
²³⁸ U →	206Pb series:			
1	²³⁸ U → ²³⁴ Th	4.198	13.5	234
2	²³⁴ U → ²³⁰ Th	4.775	16.2	235
3	²³⁰ Th → ²²⁶ Ra	4.688	15.7	236
4	²²⁶ Ra → ²²² Rn	4.784	16.2	235
5	222 Rn $\rightarrow ^{218}$ Po	5.489	19.7	243
6	$^{218}Po \rightarrow ^{214}Pb$	6.002	22.5	243
7	$^{214}Po \rightarrow ^{210}Pb$	7.687	32.7	255
8	$^{210}Po \rightarrow ^{206}Pb$	5.304	18.8	242
²³⁵ U →	²⁰⁷ Pb series:			
1	$^{235}U \rightarrow ^{231}Th$	4.596	15.3	235
2	²³¹ Pa → ²²⁷ Ac	5.059	17.5	238
3	²²⁹ Th → ²²³ Ra	6.038	22.7	242
4	²²³ Ra → ²¹⁹ Rn	5.871	21.8	242
5	$^{219}Rn \rightarrow ^{215}Po$	6.819	27.2	251
6	$^{215}Po \rightarrow ^{211}Pb$	7.386	30.7	256
7	²¹¹ Bi → ²⁰⁷ TI	6.623	26.1	246
²³² Th →	²⁰⁸ Pb series:			
4	232Th 228Da	4.013 (77.9 %)	† 12.7	(228)
I	Ra	3.954 (22.1 %)	† 12.5	228 (228)
2	²²⁸ Th → ²²⁴ Ra	5.423	19.3	237
3	²²⁴ Ra → ²²⁰ Rn	5.685	20.8	237
4	220 Rn $\rightarrow ^{216}$ Po	6.288	24.1	243
5	$^{216}Po \rightarrow ^{212}Pb$	6.778	27.0	253
c ²¹	² Bi → ²⁰⁸ Tl (36.2 °	%)† 6.207	23.6	244)
ю ₂₁₂	$Po \rightarrow {}^{208}Pb$ (63.8)	%)† 8.376	37.3	²⁰⁰ (261)
* α-ene	ergies according to	Firestone and	Shirley (199	6).
Deere				- /

† Branching ratios of possible decay paths.

(Frenkel defect pairs) produced by elastic collisions; and (3) the lateral distribution patterns of the resulting damage. These data were then used to estimate defect densities in the observed radiohaloes.

Monte Carlo simulations were done using SRIM (version 2000), a group of computer programs of which the most comprehensive is TRIM (the Transport of Ions in Matter). SRIM 2000 calculates the stopping and range of ions irradiated into a target using a full quantum-mechanical treatment of ion-atom collisions. The program calculates the final three-dimensional distribution of ions and all kinetic phenomena associated with the energy loss of the ion, including target damage, sputtering, ionization, and phonon generation, and provides detailed information about damage cascades in the target. For detailed descriptions of the theory see, for example, Biersack and Haggmark (1980) and Ziegler et al. (1985). Although Monte Carlo simulations using SRIM/TRIM have been used to estimate radiation damage phenomena in zircon and related structures (e.g., Weber et al. 1994; Wang and Weber 1999), such calculations, to the best of our knowledge, have not been done for biotite.

Calculations were done assuming a simplified target composition of $K_2Mg_3Fe_3Al_2Si_6O_{24}H_2$ and a target density of 8.84×10^{22} atoms/cm³ ($\rho = 3.1$ g/cm³). Default values were accepted for binding (≈ 3 eV) and displacement energies (between 10 eV for hydrogen atoms and 28 eV for oxygen atoms). The incoming ion (mass 4.003 amu) was assumed to be irradiated perpendicular to the surface of the target. Its energy corresponded in our case to the different energies of α -particles produced in the radioactive decay series of 238 U (eight α -decay events), 235 U (seven α -decay events), and 232 Th (six α -decay events). Altogether, calculations were done for 23 different α -energies. Consideration of further minor energies in the multiple α branches was beyond the needs of the present study. Two thousand incoming ions each were calculated to reach reliable mean values.

The results of the Monte Carlo calculations show that α particles penetrate between 12.5 and 37.3 µm into the biotite target, depending on their initial energies (Table 4). Simulations revealed that most of the initial α -energy is lost by ionization of lattice atoms (about 99.8%) and the generation of phonons. Only a tiny fraction ($\approx 0.01\%$) of the α -energy results in structural damage by creating vacancies (Frenkel defect pairs). This is because only at the end of its path is the α -particle sufficiently slowed down—by ionization losses—to interact with target atoms in elastic collisions and, thus, to displace these atoms. Consequently, most vacancies are created at the end of the α path. For example, the lateral distribution of ionization losses, the α penetration depth, and the distribution of vacancies in the biotite target calculated for the ²¹²Po \rightarrow ²⁰⁸Pb decay are compared in Figure 8.

Results suggest that if radiohaloes in biotite were caused by ionization, haloes should consist of concentric coloration spheres, with each sphere corresponding to a certain α -energy. This seems to be applicable to artificially α -irradiated biotites, which show lateral dependencies of the optical absorption coefficient (Moazet et al. 1975, 1977) that is reminiscent to the ionization curve in Figure 8. Even in thin-sections, such haloes would always appear as concentric full circles. In contrast, if radiohaloes were caused by point defects, narrow spherical damage shells should be formed. Such spheres would (in sufficiently thin samples) appear as concentric "rings." Observations on natural biotites prove that the second of the above two possibilities is applicable: it has been well documented that actinide-bearing inclusions with sizes of a few micrometers and smaller are commonly surrounded by several concentric, narrow ($\approx 1 \mu m$) spherical shells of dark color (see Fig. 1 in Gentry 1971; Fig. 1 in Gentry 1974). This finding clearly suggests that atomic displacements generating Frenkel defect pairs, but not ionization, is the major process causing the formation of dark-colored haloes in natural biotites.

Monte Carlo simulations also revealed that the depth with the maximum vacancy formation is indistinguishable on a micrometer-scale from the final travel distance of the ⁴He core (Fig. 8). Therefore, the α-particle penetration range values presented in Table 4 may be regarded as representing the distances from the α -emitter at which the host biotite experiences the most radiation damage. The α -particle travel distances strongly depend on the α -energy (Fig. 9). Calculated values correspond reasonably well with radii of haloes observed in the present study (cf., Figs. 1A-1F) and reported in the literature (Table 5). Nevertheless, calculated α -ranges have several uncertainties. First, SRIM 2000 treats the target material as amorphous and does not consider any crystallographic anisotropy. Second, natural radiohaloes may have slightly different radii due to variations of the composition of the host biotite (Mg/Fe ratio, OH/F ratio, etc.). For example, the α -ranges calculated for the Mg and Fe end-members gave radii variations exceeding 10% (Table 5). Default settings for binding and displacement energies of target atoms may not be perfectly applicable (different energies would, however, hardly change the α -ranges but mainly result in different vacancy numbers). Finally, the overall α -range decreases if the ⁴He core is emitted from a nucleus



FIGURE 8. Results of Monte Carlo simulations, given for the example of 8.376 MeV α -particles. Solid line, ionization losses; broken line, α -travel distances; dotted line, created vacancies. Note the corresponding maximums of α -ranges and created vacancies. The vacancy distribution curve is only shown here to provide a direct comparison, with arbitrary units at the y-scale.



FIGURE 9. Travel distances of α -particles in biotite as calculated by Monte Carlo simulation (Table 4). Note that the initial α -energy strongly determines the α penetration depth.

TABLE 5. Comparison of calculated and observed ranges

8.376 MeV α particle (²³² Th series; ²¹² Po \rightarrow ²⁰⁸ Pl	o decay):	
Average α penetration (in biotite, Mg ₃ Fe ₃)*	37.3 μm	(C)
Maximum of vacancies (Mg ₃ Fe ₃)	37.4 μm	(C)
Maximum of ionization (Mg ₃ Fe ₃)	35.4 μm	(C)
Average α penetration (in annite, Mg ₀ Fe ₆)	39.3 μm	(C)
Average α penetration (in biotite, Mg ₄ Fe ₂)	36.6 µm	(C)
Average α penetration (in phlogopite, Mg ₆ Fe ₀)	35.2 μm	(C)
Coloration (halo 57-4; Fig. 1D)	37.4 ± 0.8 μm	(0)
Coloration (halo 30-7; Fig. 1E)	37.1 ± 0.3 μm	(0)
Coloration (Rankama 1954)	41.8 μm	(0)
7.687 MeV α particle (²³⁸ U series; ²¹⁴ Po \rightarrow ²¹⁰ Pb	decay):	
Average α penetration (in biotite, Mg ₃ Fe ₃)*	32.7 μm	(C)
Maximum of vacancies (Mg ₃ Fe ₃)	32.8 µm	(C)
Maximum of ionization (Mg ₃ Fe ₃)	30.8 μm	(C)
Coloration (Rankama 1954)	33.5 μm	(0)
Coloration (Moazed et al. 1973) 35.5 ± 0.3	$\mu m; 34.8 \pm 0.3 \ \mu m$	(0)
Coloration (artificially induced; Gentry 1974)	33.1-34.4 mm	(0)
Coloration (natural radiohaloes; Gentry 1974)	30.8-34.0 mm	(0)
Extrapolated ionization (Moazed et al. 1975)	35.1 ± 0.2 mm	(C)
Coloration (Moazed et al. 1975)	32.2 ± 0.2 mm	(0)
Notes: c = calculated values. o = observed value * cf. Table 4.	S.	

inside the inclusion because α -ranges in zircon and monazite are somewhat shorter than those in biotite. Calculated ranges (Table 4) should, therefore, be regarded as estimates only.

Point defect density

An important result of the Monte Carlo simulations are data tables for the lateral distribution of point defects (about 240 Frenkel defect pairs generated per α -decay event; see Table 4 and Fig. 10A). These data enabled us to estimate roughly the defect density in radiohaloes. As an example, we have chosen halo 57-4 (Fig. 1D) that shows a spherically varying coloration surrounding a 5.5 µm isometric monazite, identified by confocal Raman analysis. Because this monazite grain is located in the middle of the 25 µm thick section, its composition could not be determined by electron microprobe analysis. However, other monazites from rock sample no. 57 were found to be Th-rich with ThO₂ ranging from 7.7 to 19.4 wt%. In the calculation, we assumed that the monazite in halo 57-4 has the same composition as the monazite in halo 57-1 (17.031 wt% Th and 1.049 wt% U; Table 3).

The shape of monazite 57-4 was assumed to be spherical to simplify the calculation. Assuming a density $\rho = 5$ g/cm³, the mass of the monazite is on the order of 435 pg. From these values, the total number of emitted α -particles (n_{α}) was calculated separately for each α -energy according to

$$n_{\alpha} = \frac{c \cdot N_A \cdot a \cdot m_i}{M \cdot 10^6} \cdot \left(e^{\lambda t} - 1\right) \cdot p \tag{1}$$

with *c* = present concentration of the respective parent actinide (in ppm), N_A = Avogadro's number (6.022 × 10²³ atoms/mol), *a* = relative natural abundance of the parent isotope (99.28% for ²³⁸U; 0.72% for ²³⁵U; 100% for ²³²Th), m_i = mass of the inclusion (435 × 10⁻¹² g), M = molecular weight of the parent isotope, λ = decay constant of the parent isotope, *t* = decay time (assumed 300 Ma according to the Variscan rock age), and *p* = relative portion of the respective α -energy in the decay event (100% except for the first and sixth decay in the ²³²Th chain;



FIGURE 10. Calculation of the defect density in halo 57-4 (Fig. 1D). (A) Lateral distribution of vacancies in the biotite structure created by an 8.376 MeV α -particle generated in the ²¹²Po \rightarrow ²⁰⁸Pb decay (see Fig. 8). (B) Lateral distribution of vacancies created by the number of α -particles corresponding to the α -decay events that have occurred in the monazite inclusion of halo 57-4 over the past 300 Ma. (C) Plot of the point defect density (in displacements per atom) vs. penetration depth. Solid line, same data set as in Figure B (i.e., still assuming a point source). Dotted line, laterally spread curve considering the 5.5 µm extension of the source. (D) Final calculated distribution of the point defect density for halo 57-4. Same graph as the dotted line in Figure C with intensities on a logarithmic scale.

see Table 4). The results are 5.46×10^8 , 2.9×10^7 , and 2.88×10^9 for each of the α -decay events in the ²³⁸U, ²³⁵U, and ²³²Th series, respectively. These values add up to a total of 2.18×10^{10} α -particles emitted by the 435 pg monazite, which corresponds to a fluence of $5 \times 10^{16} \alpha$ /mg.

These values enable us to explain why no reversed coloration was observed in the investigated biotites. Moazed et al. (1977) found that biotite darkened by α -irradiation may lighten at doses that are at least one order of magnitude above the saturation level of darkening. These authors irradiated biotite with a 7.39 MeV α -beam and observed the onset of a coloration reversal at 5.4 × 10¹⁴ α /cm². In natural radiohaloes, 7.39 MeV α -particles form a narrow coloration shell with a radius of 32.7 µm (Table 4). Considering the surface area of this hollow sphere (1.34 × 10⁻⁴ cm²), the above calculated number of 5.46 × 10⁸ 7.39 MeV α -particles (seventh α -decay in the ²³⁸U chain) would correspond to an irradiation dose of 4 × 10¹² α /cm², which is well below the onset of reversal coloration effects.

The 23 lateral point defect distribution curves (vacancies per angstrom created by one α -particle) calculated from the Monte Carlo simulations (Fig. 10A) were then multiplied by the corresponding total number of α -particles (n_{α}) and added up. The resulting curve $n_V(r)$ (Fig. 10B), however, represents only the lateral vacancy distribution in halo 57-4 (i.e., the damage distribution if all α -particles were emitted from their source in the same direction). Point defect densities were calculated by including random, three-dimensional α -particle trajectories. For this, length-scale sections of the lateral vacancy distribution curve (Fig. 10B) were treated as thin hollow spheres. The ratio between the number of vacancies and the total number of atoms in such hollow spheres yields the point defect density according to

$$D(r) = n_v(r) \cdot \frac{M_B}{\frac{4}{3}\pi \left[\left(r + \Delta r \right)^3 - r^3 \right] \cdot \rho \cdot N_A \cdot 44}$$
(2)

where M_B is the molecular weight of K₂Mg₃Fe₃Al₂Si₆O₂₂(OH)₂ (929.1 g/mol), *r* and Δr are the inner radius and the thickness of the hollow sphere, respectively, ρ is the biotite density (3.1 g/cm³), and N_A is Avogadro's number (here multiplied by 44 because of 44 atoms per formula unit). The calculated function D(r), representing the point defect density as function of the penetration depth, is shown in Figure 10C (solid line). It is, however, still affected by the incorrect assumption that all α particles were emitted from a point source. Estimates of point defect densities were improved by considering the volume of the α -emitter (in this case a sphere 5.5 µm in diameter). The resulting spread curve is shown in Figures 10C (dotted line) and 10D where the point defect density is given in displacements per atoms (dpa).

Modeling a radiohalo

Point defect densities in radiohaloes vary as a function of the size of the α -source, the radionuclide contents in these sources, and the irradiation period (which is determined not only by the age of the biotite but also by its low-*T* history). However, a main result of the calculation presented in Figure 10 is that in the case of halo 57-4, the point defect density is between 10⁻⁵ and approximately 10⁻³ dpa (Fig. 10D). Because our example calculation was performed based on the composition of the inclusion with the highest observed radionuclide content (about 1/5 of the monazite's weight), the calculated defect density may be close to maximum values reached in Variscan biotites. This possibility was confirmed by similar calculations for larger monazite inclusions having the same age and chemical composition, which showed that even in such "maximum cases," the defect density barely exceeds the 10⁻² dpa level. In other words, calculations suggest that even in intensely colored haloes, at most some hundredth and normally a much smaller number of atoms in the biotite lattice are displaced. This agrees very well with the HRTEM observations showing that even intense radiohaloes in natural biotites still have a well-preserved crystal structure.

The calculated point defect distribution curve, shown in Figures 10C and 10D as a defect density vs. distance plot, was plotted again in a two-dimensional grayscale picture using the MATLAB (version 5.3) computer program. To construct this picture, the function D(r) was rotated in 3-D around x; y; z = 0. As the origin of halo 57-4 (i.e., the monazite inclusion) is located in the middle of the 25 µm thin-section, all resulting data points with $z > 12.5 \mu m$ and $z < -12.5 \mu m$ were cut-off (i.e., set to zero). The dpa values were then integrated in the zdirection, and resulting data are shown in an x-y-plot on a grayscale. Zero dpa was set to pale gray to consider the initial biotite color without any irradiation. The resulting plot (Fig. 11) simulates the view through the 25 µm section containing the radiohalo 57-4. Note that both the coloration pattern and the halo size in this plot show remarkable similarity with the photograph of that halo in Figure 1D. Because the MATLAB plot was derived from point defect distribution curves, this resemblance supports the conclusion drawn above that formation of point defects is the main process causing the coloration of radiohaloes.



FIGURE 11. Grayscale plot of the distribution pattern of the point defect density calculated for halo 57-4 pictured in Figure 1D, generated from the damage distribution curve shown in Figure 10D using the MATLAB program. A view perpendicular to a 25 μ m thick biotite platelet was modeled, assuming a 5.5 μ m α -source located in the middle between front and rear surfaces.

DISCUSSION

The variety of experimental observations on natural biotites and calculations presented in this study suggest that the formation of point defects due to the impact of α -radiation is the main process causing the dark coloration of natural radiohaloes, with ionization effects probably being only an enhancing factor. The point defects, especially the emplacement of "interstitial" atoms (displaced from their original lattice sites by elastic collisions), give rise to a locally decreased order of the crystal structure. The decreased order is observed from noticeably changed birefringence (interference colors), broadening of vibrational frequencies (Raman), and generally enhanced light absorption over the near ultraviolet and the full visible range (electronic absorption spectroscopy). The degree of structural radiation damage is, however, relatively low, which was observed from well-ordered lattice fringes (HRTEM). There is no formation of nanometer-sized, amorphous regions, as would occur in highly radiation-damaged structures.

The observation of narrow coloration shells in natural biotites (Gentry 1971, 1974), which correspond with the calculated point defect distribution curves (Figs. 8 and 10A), seems to be in apparent contradiction to the coloration patterns in artificially α -irradiated biotites (Moazed et al. 1975), which correspond with the calculated ionization curves (Fig. 8). This contrast suggests that light absorption in natural radiohaloes and experimentally α -irradiated biotite is different. The difference may be explained by the observation that ionization effects, which predominate the radiation damage in α -irradiated biotites, probably recombine with relative ease over geologic periods of time. In contrast, the structural damage caused by displacive events (i.e., elastic collisions) creating Frenkel defect pairs in the biotite structure, has a much greater long-term stability, thus becoming a dominant feature in natural radiohaloes.

For the discussion of the calculated point defect densities, it should be noted that the age of a radiohalo (i.e., the effective damage accumulation period) is not necessarily identical to that of its host biotite. It is well known that structural radiation damage phenomena in zircon may be annealed over geologic periods of time at ≈200-250 °C (e.g., Tagami and Shimada 1996; Meldrum et al. 1998), which is considerably below the closure temperature of the U-Pb isotopic system in zircon (generally assumed to be 700-900 °C in magmatic and on the order of 600 °C in metamorphic conditions; Mezger and Krogstad 1997). The clear temperature difference raises the possibility that structural radiation damage in biotite may be annealed at temperatures considerably below the closure temperature of the K-Ar isotopic system (around 300-350 °C; Berger and York 1981; Harrison et al. 1985). These doubts were confirmed by a study of Hradetsky et al. (1990) who demonstrated that the radiation damage in radiohaloes in biotite may be annealed at temperatures as low as 90-140 °C. At such low temperatures, isotopic systems of inclusions and micas would hardly be affected. Therefore, the Variscan mineral ages determined from isotope ratios should be cautiously treated only as maximum values for the duration of damage accumulation. More precise estimates of the ages of radiohaloes may be possible by the use of more closely related techniques such as α -recoil-track dating of biotite (cf., Gögen and Wagner 2000). However, this technique is still being developed and is currently not applicable to fine-grained biotites in metamorphic rock samples such as investigated in the present study.

Comparison of the coloration pattern of radiohalo 57-4 (Fig. 1D) with the calculated damage distribution curve (Fig. 9D) suggests that relatively low defect densities (on the order of 10^{-5} dpa) cause noticeable coloration of biotite, and defect densities between 10^{-4} and 10^{-2} dpa are sufficient to make a 25 µm thick biotite appear almost "black" in plane-polarized light with $\mathbf{E} \perp \mathbf{c}^*$. Considering that these point defect densities were calculated assuming an irradiation period of 300 Ma, significant coloration of natural biotite may perhaps occur at even lower levels of α -induced defect accumulation. Due to the generally low degree of radiation damage, radiohaloes in biotite are considered as representing a very early stage of metamictization.

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