RADIATION STABILITY OF AMPHIBOLES

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ABSTRACT: The kinetics of radiation iron oxidation for four amphiboles of different composition has been investigated by nuclear gamma resonance (NGR) and electron probe microanalysis (EPMA). The results show that taramite has the best stability against radiation. The method of radiation stability assessment of iron-containing minerals can be used for geologycal massifs to be selected for construction of radioactive waste storage.

Key words: amphibole, radiation oxidation, nuclear gamma resonance, electron probe microanalysis, kinetic parameters

The problem of long-lived radioactive waste disposal in geological formations sets requirements to composition and properties of rocks to be used as engineering barriers. Feasibility of radioactive waste disposal is estimated by simulation of processes taking place in the system of radioactive waste-disposal medium. Prediction of long term reliability of safety structures is estimated by rock (and its mineral components) stability against irradiation. In the presented work, γ-irradiation effect on stability of several iron- and hydroxyl-containing amphiboles that are components of many rocks, has been investigated.

It is shown [1,2,5,6] that the most sensitive to γ-irradiation structure element is bivalent iron ions able to be oxidised to trivalent state. That is why, changing content of iron oxidised by radiation with time, is considered as an indicator of amphibole structure stability against irradiation, and investigation of the process kinetics was the aim of the presented work. Magnesia and chermacite hornblendes, as well as riebeckite and taramite have been chosen for investigation. These minerals have the following formulas:

1. $(\mathrm{Na0}_{0,11}\mathrm{K}_{0,04})_{0,15}(\mathrm{Ca}_{1,82}\mathrm{Na}_{0,15}\mathrm{Mn}_{0,03})_{2,00}(\mathrm{Mg}_{3,36}\mathrm{Fe}^{2+}_{1,00}\mathrm{Fe}^{3+}_{0,38}\mathrm{Al}_{0,21}\mathrm{Ti}_{0,05})_{5,00}(\mathrm{Si}_{6,89}\times$
$\times\mathrm{Al}_{1,11})_{8,00}(\mathrm{O}_{21,60}\mathrm{OH}_{0,40})_{22,00}(\mathrm{OH})_{2,00}$

2. $(\mathrm{Na}_{0,19}\mathrm{K}_{0,23})_{0,42}(\mathrm{Ca}_{1,40}\mathrm{Na}_{0,60})_{2,00}(\mathrm{Mg}_{2,19}\mathrm{Fe}^{2+}_{1,75}\mathrm{Fe}^{3+}_{0,63}\mathrm{Al}_{0,34}\mathrm{Mn}_{0,05}\mathrm{Ti}_{0,04})_{5,00}(\mathrm{Si}_{6,47}\times$
$\times\mathrm{Al}_{1,53})_{8,00}(\mathrm{O}_{21,34}\mathrm{OH}_{0,66})_{22,00}(\mathrm{OH}_{1,88}\ \mathrm{F}_{0,10}\mathrm{Cl}_{0,02})_{2,00}$

3. $(\mathrm{Ca}_{0,37}\mathrm{Na}_{1,14}\mathrm{K}_{0,04}\mathrm{Mn}_{0,03})_{1,58}(\mathrm{Mg}_{2,33}\mathrm{Fe}^{2+}_{1,00}\mathrm{Fe}^{3+}_{1,62}\mathrm{Al}_{0,05})_{5,00}(\mathrm{Si}_{7,40}\mathrm{Al}_{0,41}\mathrm{Ti}_{0,19})_{8,00}\times$
$\times\mathrm{O}_{22,00}(\mathrm{OH}_{1,32}\mathrm{O}_{0,68})_{2,00}$

4. $(\mathrm{Na}_{0,47}\mathrm{K}_{0,38})_{0,85}\ (\mathrm{Ca}_{1,39}\mathrm{Na}_{0,61})_{2,00}\ (\mathrm{Mg}_{0,23}\mathrm{Mn}_{0,21}\mathrm{Fe}^{2+}{}_{3,48}\mathrm{Fe}^{3+}{}_{0,86}\ \mathrm{Al}_{0,14}\ \mathrm{Ti}_{0,08})_{5,00}$ x

$\mathrm{x}(\mathrm{Si}_{6,30}\mathrm{Al}_{1,70})_{8,00}(\mathrm{O}_{20.73}\mathrm{OH}_{1.27})_{22,00}(\mathrm{OH})_{2,00}$

Samples were exposed to certain γ-irradiation doses (D), maximum dose being $6.8 \cdot 10^8$ Gy. The iron valent state was determined using NGR and EPMA. EPMA determination of aliovalent iron ions content have been done with specially developed methods [3]. Results of the investigation are interpreted on the basis of amphibole structural data [4].

The change of relative content of oxidised iron in the amphibole structure ($\alpha= [\mathrm{Fe}^{3+}]/\mathrm{Fe}_{\mathrm{total}}$) under radiation is considered as a result of two oppositely directed oxidation and reduction processes competing with time. The input of each process is changing with time. The change in relative content of Fe^{3+} ions during irradiation can be described by the equation:

$$\alpha = \alpha_\infty - [\alpha_\infty - \alpha_0] \exp [- (k_1 + k_2)t], \qquad (1)$$

where $\alpha_\infty = [\mathrm{Fe}^{3+}]_\infty/\mathrm{Fe}_{\mathrm{total}}$ - relative content of Fe^{3+} ions at $t \to \infty$; $\alpha_0 = [\mathrm{Fe}^{3+}]_0/\mathrm{Fe}_{\text{общ}}$ - relative content of Fe^{3+} ions before irradiation; k_1 and k_2– constants of oxidation and reduction rate respectively; t – irradiation time, (t=D/P). Table 1 shows data of α_∞ and $k_1 + k_2$, such that equation (1) describes the received experimental data in the best way, as well as the calculation results for k_1 and k_2 according to

$$\alpha_\infty = [\mathrm{Fe}^{3+}]/\mathrm{Fe}_{\mathrm{total}}= k_1/(k_1+ k_2) \qquad (2)$$

Table. 1. Rate constants of iron oxidation and reduction in amphiboles

Sample №	α_∞	$(k_1 + k_2)$, 10^{-7} s^{-1}	k_1, 10^{-7} s^{-1}	k_2, 10^{-7} s^{-1}
1	0,660	2,020	1,320	0,698
2	0,448	1,476	0,661	0,815
3	0,784	1,922	1,066	0,856
4	0,451	0,290	0,131	0,152

Experimental and calculated with equation (1) data α for taramite at the certain irradiation doses (time), are given in Table 2 and shown in Fig.1. Good agreement between theory and experiment for α indicates validity of the kinetic consideration.

Table 2. Reaction kinetic parameters of radiation oxidation of iron in amphibole structure on irradiation dose

D, 10^8 Gy	Sample №	α_{exp}	α_{theor}	V, 10^{-8} c^{-1}	G, 10^{14} ion/Dg	E, 10^3 eV/ion
0*	1	0,303	0,303	7,23	30,05	2,07
- "-	2	0,279	0,279	4,49	17,25	3,62
- "-	3	0,618	0,618	3,19	25,40	2,96
- "-	4	0,245	0,245	0,597	12.09	5.172
1,2	1	0,564	0,532	2,51	10,48	5,96
- "-	2	0,377	0,367	1,16	7,99	7,82
- "-	3	0,721	0,723	1,17	9,32	6,71
1,62	4	0,312	0,304	0,43	8,64	7,23
2,8	1	0,629	0,625	0,62	2,57	24,37
- "-	2	0,420	0,420	0,41	2,86	21,85
- "-	3	0,768	0,768	0,31	2,45	25,55
3,64	4	0,365	0,354	0,28	5,69	10,99
4,7	1	0,641	0,649	0,12	0,48	129,66
- "-	2	0,432	0,439	0,12	0,85	73,95
- "-	3	0,770	0,780	0,06	0,50	125,00
5,7	1	0,650	0,652	0,05	0,20	312,54
- "-	2	0,444	0,444	0,06	0,45	140,48
- "-	3	0,778	0,782	0,03	0,22	288,30
6,4	1	0,654	0,654	0,03	0,10	625,00
- "-	2	0,445	0,445	0,04	0,28	220,14
- "-	3	0,782	0,783	0,02	0,13	489,60
6,8	4	0,399	0,401	0,15	2,956	21,142

NOTE. * - relates to the calculation when all data make sense at negligibly small radiation dose and time, i.e. when D and $t \to 0$, α_{exp} shows ratio of aliovalent iron ions, related to the structure of unexposed minerals.

Other parameters of iron oxidation process were calculated using mathematical approach described in [1]. These parameters allow comprehensive estimation of sensitivity to irradiation of the amphibole structures. Namely: V – rate of Fe^{3+} relative content change on irradiation time, G - Fe^{3+} ions, formed under irradiation energy unit, E - field energy required to increase Fe^{3+} ions by one (Table 2). G – one of the basic parameters of radiation field interaction with crystal lattice, characterising the lattice stability against irradiation. The dependence of logarithm G on radiation dose (time) allows using its graphic representation (Fig. 2) for radiation control of natural radiation fields effect by associating amphiboles close by their composition to standard experimentally irradiated ones. Dependencies of $ln\ G=f(D)$ are described by linear regression equation:

$$ln\ G=a+bD, \qquad (3)$$

where constants for magnesia and chermacite hornblendes, as well as riebeckite and taramite are equal to respectively: a – 35.652, 35.086, 35.460 and 34.714, b - 0.887, -0.642, - 0.828• and – 0.197•10^{-8} Gy^{-1} when R-factor is not less than 0.999. Comparison of these dependencies, in particular, slope ratios of lines characterising rates of oxidised iron accumulation processes, as well as k_1 and k_2 data, allows resistance estimation of the investigated amphiboles crystal structure against radiation fields.

The investigation results can be used for radiation control and long-term forecast of amphibole behaviour in radiation fields, that is important for rock selection as engineering barriers when construction of safety installations.

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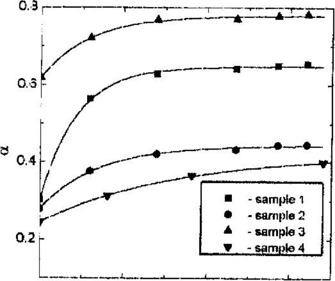
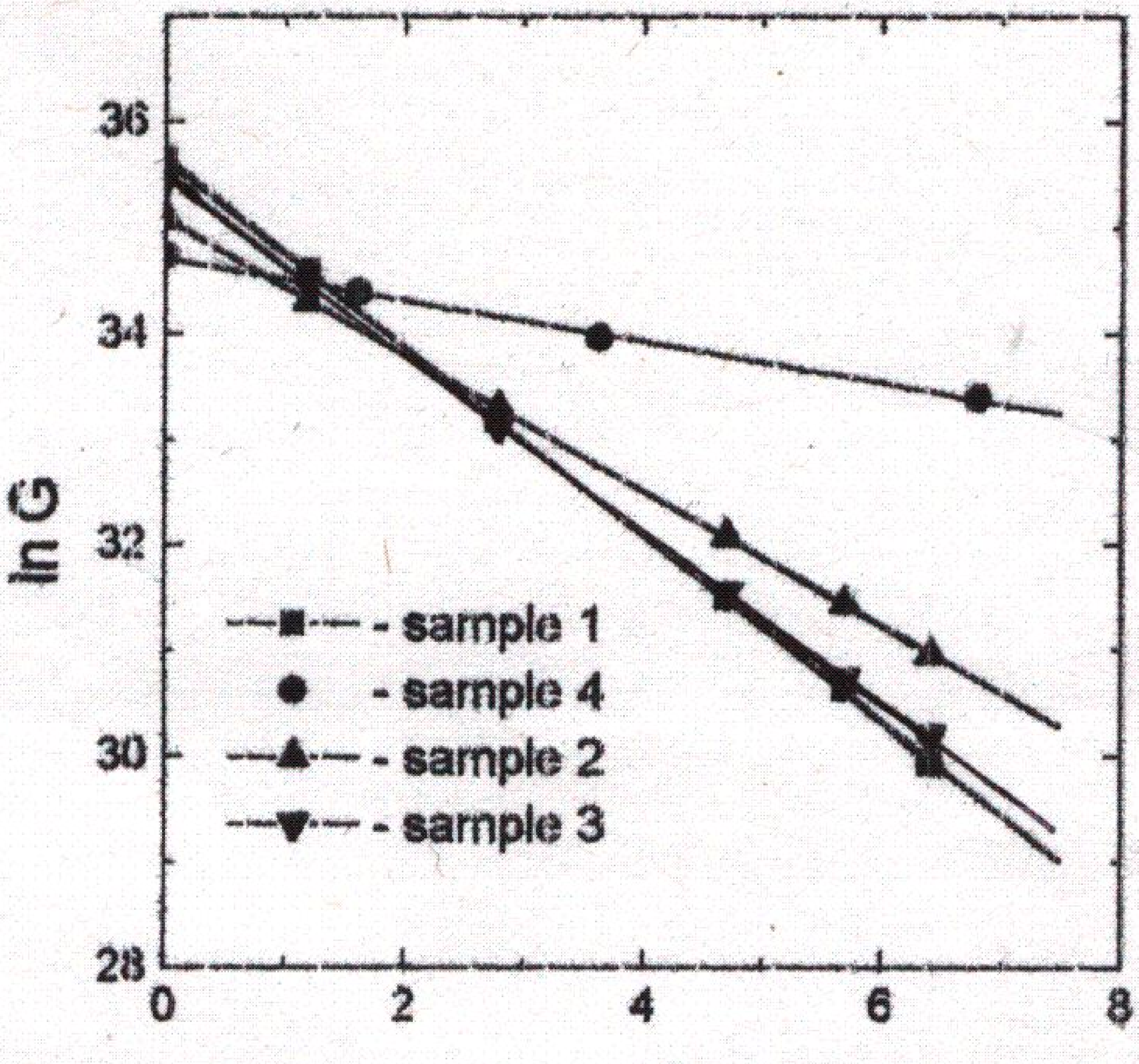
Fig.1. Fe^{3+} relative content in amphibole structure on irradiation dose: dots – experimental data, solid lines – theoretical calculation using equation (1).

Fig.2. ln G on irradiation dose for amphiboles of different composition


0.8
0.6
0.4
0.2
α
■ - sample 1
● - sample 2
▲ - sample 3
▼ - sample 4


lnG
36
34
32
30
28
0
2
4
6
8
D x 10^8, Гр
- sample 1
- sample 4
- sample 2
- sample 3