

Low-temperature hydrothermal interactions between granite and solutions containing Cs, Rb, and Sr: an experimental approach

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Abstract. This paper summarizes the results of low-temperature hydrothermal experiments in which solutions containing Cs, Rb, and Sr were allowed to react with medium-grained biotite granite from Podlesí (Krušné hory Mts., Czech Republic). The experiments were performed at 115 and 150 °C under < 0.5 kbar hydrostatic pressure, for durations of 1872–5562 hours. In these experiments, hydrothermal solutions containing Rb and Sr did not react with the rock-forming minerals in the granite. However, the Cs-containing solution did react with the rock-forming minerals, particularly the feldspars, to produce pollucite, a secondary Cs aluminosilicate. Pollucite could thus be used to delineate migration pathways of solutions through the granite samples. Three important migration pathways were distinguished: microcracks, grain boundaries, and cleavage planes. We also discuss the influence of sample processing on the observed permeability, and the effect of the crystallization of secondary phases on the disproportion between the sorption – desorption coefficients.

Key words: hydrothermal alteration, Cs, Rb, Sr, pollucite, rock-waste interaction, granite

Introduction

The current ideology concerning the disposal of toxic, radioactive, industrial waste (“radwaste”) is to use deep repositories with multi-barrier containment systems. The most important of these is the geological barrier. Therefore, any information concerning the permeability of this barrier, and all observations about the chemical interactions between the radwaste elements with the rocks of which this barrier is composed, is valuable for the assessment of its retardation parameters. If, for example, a solution containing some radionuclides migrates through the geological barrier, it will interact with the host rocks and significantly changing their chemistry. These reactions are quite complex and may include purely physical processes, as well as direct and indirect chemical reactions.

A number of authors have studied the migration of fluids of various compositions through igneous, metamorphic, and sedimentary rocks. A theoretical study of the migration of fluids through the geological barrier was presented by Chapman et al. (1987), while the other authors studied the problem experimentally. Static experiments and autoradiography were employed by Vandergraaf et al. (1982) to determine the relation between the spatial distribution of sorbed Cs and the accompanying mineralogy. The sorption of Sr and Cs was studied by Skagius et al. (1982), while the diffusion of Sr, I, and Cs through granitic rocks was investigated by Ittner et al. (1990). Tsukamoto and Ohe (1993) studied the effects of the presence of biotite on the cesium distribution in granite. Byegård et al. (1998) used radioactive tracers to quantify the depth of penetration of Ca, Cs, and Ba into a granite matrix. The ¹⁴C-PMMA method (in which rocks are impregnated with ¹⁴C-labelled methylmethacrylate) was used by Hellmuth et al. (1993, 1994) and Byegård et al. (1998) to map the spatial distribution of porosity in the rock matrix.

The present experiments were conducted to evaluate two important factors that control the retardation parameters: migration pathways, and rock/waste interactions.

Starting material and experimental conditions

The material used in this study was a medium-grained biotite granite from Podlesí, sampled from drill holes PTP2 and PTP3. The petrology of the granite from Podlesí has been described in detail by Breiter (2002). Samples were taken from cores drilled in fresh granite that did not exhibit any alteration or contain visible fissures. From such samples cubes with sides of 8–10 mm in length were cut with a diamond saw. Their surfaces were not polished.

Experiments were performed in steel Bernghof DAB–II vessels equipped with 25 ml PTFE fillers. The granite cubes were immersed in solutions containing 0.5 or 0.1 M Cs, Rb, or Sr. The solutions used were prepared from Cs₂CO₃ (Aldrich – 99%), Rb₂CO₃ (Aldrich – 99.8%), RbCl (Merck – 98%), and SrCl₂ · 6H₂O (Aldrich – 99%). Experimental temperatures were measured with Ni–NiCr thermocouples and are accurate to ± 3 °C. The pressure did not exceed 0.5 MPa.

The conditions of selected experiments are summarized in Table 1.

After the experiments, the rock cubes were split in half and the section surfaces were polished. These were then studied under an electron microprobe. The BSE and X-ray images gave information about the phase composition and the distribution of elements.

Experimental results

Solutions containing Sr and Rb did not react with any of the rock-forming minerals, and therefore there is no infor-

Table 1. Conditions of selected hydrothermal alteration experiments

Run No.	Solution	Rock sample	Time hours	T, °C
WR1	0.5M, Cs ₂ CO ₃	PTP2, 219 m	5542	150
WR2	0.5M, RbCl	PTP2, 219 m	5542	150
WR4	0.1M, Cs ₂ CO ₃	PTP3, 221 m	1939	150
WR5	0.1M, Cs ₂ CO ₃	PTP3, 221 m	1939	150
WR7	0.5 M, SrCl ₂	PTP3, 221 m	1867	150
WR8	0.1M, Cs ₂ CO ₃	PTP3, 32 m	1939	150
WR9	0.1M, Rb ₂ CO ₃	PTP3, 221 m	3200	115
WR10	0.1M, Cs ₂ CO ₃	PTP3, 221 m	3200	115

mation concerning their penetration into the sample.

Conversely, the Cs-containing solutions reacted readily with the rock-forming minerals in the granite. These minerals are encountered by hydrothermal solutions along grain boundaries and microfissures. The alumina and silica thus released react immediately to form the Cs aluminosilicate, pollucite (CsAlSi₂O₆). The dissolution and metasomatic replacement of rock forming minerals are very noticeable. At 150 °C and in more concentrated solutions (0.5 M) these reactions proceed quite quickly, and the run products consist of strongly altered rock-forming minerals (Fig. 1). At 115 °C the samples were distinctly less altered, though at this temperature the solutions must have entirely penetrated the samples.

Pollucite crystallized on the surfaces of the samples as spherical aggregates (Plate Ie). The degree of alteration near the surface of the samples is generally more extensive than inside, as shown in Plate Ia. In all experiments pollucite filled microfissures and grain boundaries (Plate Ia, b), and metasomatically replaced plagioclase (Plate Ia). Incipient metasomatic replacement of plagioclase along cleavage planes at low temperature is shown in Plate Ii, j. K-feldspar also reacted with Cs-containing solutions (Plate Ig, h). Though biotite reacted only weakly, the replacement of biotite by pollucite along cleavage is documented in Plate Ic, d. In samples treated in Cs-containing solutions for longer times at 150 °C, the quartz grains became strongly corroded (Plate Ia).

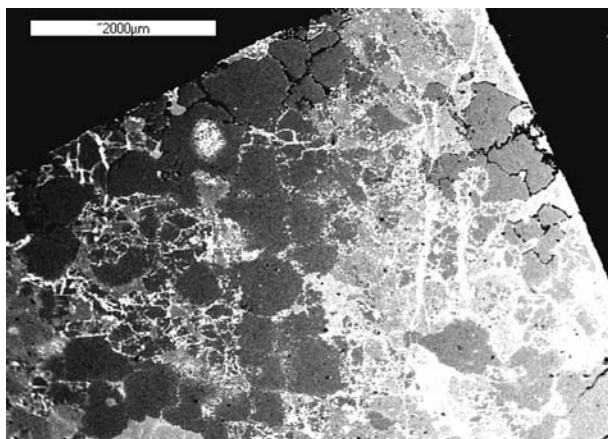


Figure 1. WR 1, BSE image of pollucite distribution. Pollucite is coloured white. Analyst: R. Skála.

The diffusion of Cs through mineral masses free of microfissures or cleavage appears to be negligible under the conditions used in this study.

Discussion and conclusions

1. Solutions containing Rb and Sr do not appear to react with the rock samples used in this study. On the contrary, cesium-containing hydrothermal solutions react readily with rock-forming minerals of these samples, producing the Cs aluminosilicate, pollucite, which is deposited along the migration pathways (grain boundaries, microfractures, and cleavage planes) that form an interconnected network. Thus, hydrothermal alteration experiments without radionuclides provide results comparable to those obtained by Hellmuth et al. (1993, 1994), Byegård et al. (1998), and Vandergraaf et al. (1982), all of whom used the technique of radioactive tracers.
2. The observed formation of secondary aluminosilicate from the interaction between hydrothermal solutions and granite could be a reason for the disproportion between the sorption and desorption coefficients, discussed by Byegård et al. (1998). Thus not only the sorption alone but also the crystallization of secondary phases may affect the retarding capability of rocks in the geological barrier. In some cases, the secondary phases might constitute a significant component of the entire retardation in the barrier. The experiments reported in this article show that low-temperature hydrothermal alteration experiments could supplement the data obtained by sorption experiments.
3. The present experiments also indicate that the matrix of the studied biotite granite is permeable to hydrothermal solutions. However, it is possible that microfractures form essentially as a consequence of the drilling and sawing processes (sample preparation). In order to evaluate all possible causes, a systematic study of a full range of preparation and experimental techniques ought to be carried out.

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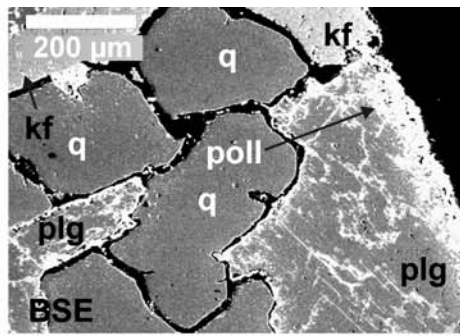
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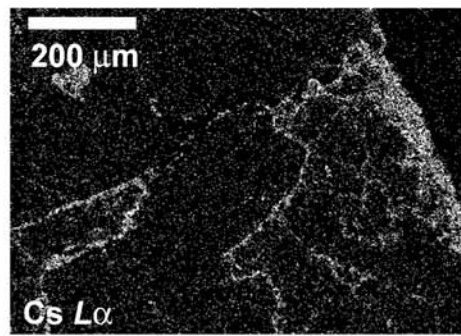
Plate I

Distribution of Cs on the cut surfaces in BSE and Cs $L\alpha$ images. White areas in the BSE images and in the Cs $L\alpha$ images indicate where the formation of Cs aluminosilicate has occurred. Run WR1 a, b, c, d; WR5 e, f, g, h; WR10 i, j.

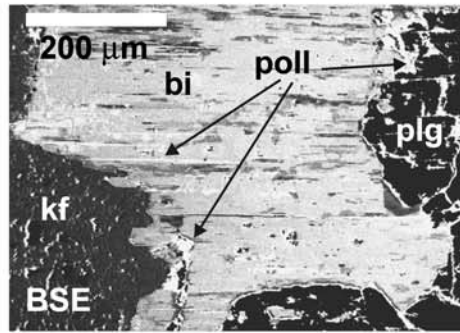
BSE – back scattered electrons; poll – pollucite; plg – plagioclase; kf – K-feldspar, q – quartz; bi – biotite. For experimental conditions see Table 1. Analysts: A. Gabašová and R. Skála.



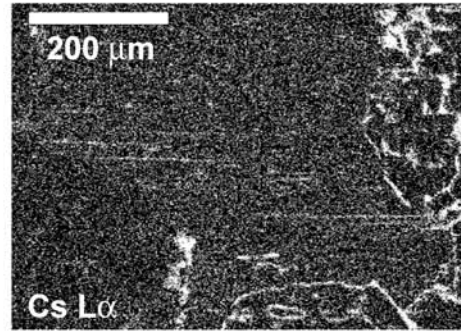
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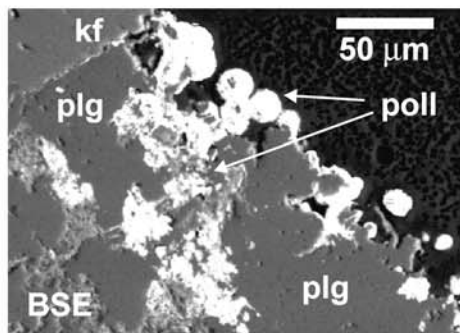
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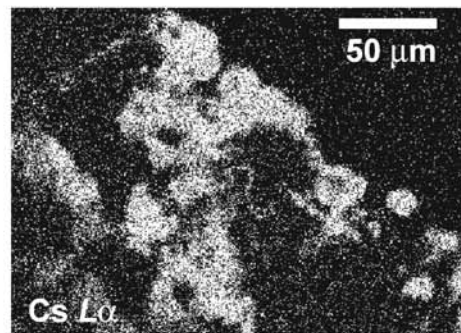
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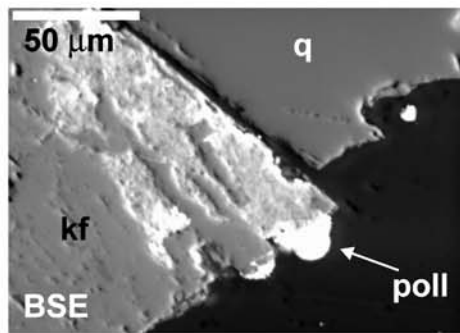
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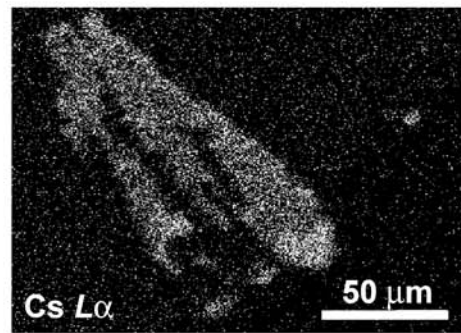
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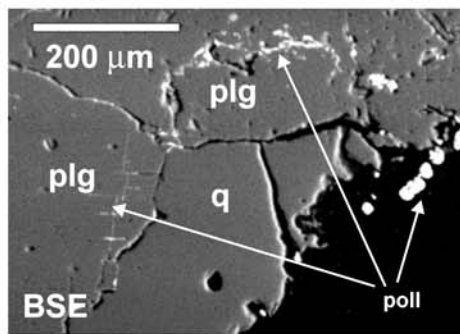
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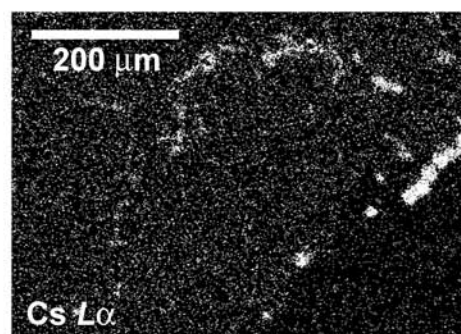
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