

# Hydrothermal alteration of chevkinite: insights from natural rocks and experiments

RAY MACDONALD<sup>1,2</sup> and BOGUSŁAW BAGIŃSKI<sup>1,\*</sup>

<sup>1</sup> University of Warsaw, Faculty of Geology, Department of Geochemistry, Mineralogy and Petrology,

Żwirki i Wigury 93, 02-089 Warszawa, Poland;

e-mails: raymacdonald186@gmail.com, b.baginski1@uw.edu.pl

<sup>2</sup> Environment Centre, Lancaster University, Lancaster LA1 4YQ, UK.

\* Corresponding author

## ABSTRACT:

Macdonald, R. and Bagiński, B. 2022. Hydrothermal alteration of chevkinite: insights from natural rocks and experiments. *Acta Geologica Polonica*, **72** (4), 413–421. Warszawa.

The contributions of the members of the Department of Geochemistry, Mineralogy and Petrology, University of Warsaw, to the study of the chevkinite-group of minerals (CGM) are described. The range of research topics includes: (i) geochemical and mineralogical studies of natural occurrences of the group, and attempts to relate their chemical composition to host lithology; (ii) detailed analysis of the hydrothermal alteration of CGM in various settings, with the aim of understanding element redistribution and the potential implications for ore formation. An ongoing series of high P-T experiments is providing quantitative information on the pressures, temperatures and melt water conditions under which the alteration assemblages have formed. Various spectroscopic techniques are being used to determine the structure of the CGM and to identify cation distribution in the structures.

**Key words:** Chevkinite group minerals; Compositional variations; REE mobility; Hydrothermal alteration experiments; Structural studies.

## INTRODUCTION

During research on the Olkaria Volcanic Complex, Kenya Rift Valley, one of us (RM) identified optically microphenocrysts in peralkaline rhyolites as the mineral aenigmatite ( $\text{Na}_4(\text{Fe}^{2+}_{10}\text{Ti}_2)\text{O}_4(\text{Si}_{12}\text{O}_{36})$ ). Later electron microprobe analyses (Macdonald *et al.* 2002) showed that the phase was in fact chevkinite-(Ce), generally thought at the time to be a rare accessory mineral in alkaline igneous rocks. A literature search strongly suggested that minerals of the CGM may actually be widespread, occurring in many different geological settings and lithologies. For the past 12 years, the CGM have been an important theme of research in the Department of Geochemistry, Mineralogy and Petrology, involving such aspects as occurrences, chemical composition, crystal chemistry, hydrothermal alteration and high

P-T experiments. This contribution focusses on our work on alteration.

The term hydrothermal alteration refers to any alteration of rocks and minerals by the reaction of hot (>50°C) aqueous fluids with pre-existing solid phases. Accessory minerals, which commonly contain the bulk of a rock's budget of rare metals such as the rare-earth elements (REE), Th, U, Zr, Hf, Nb and Ta, are particularly prone to the process. A common result is that these elements can be released into the fluids and lost from the immediate system. It is important to understand the nature of the mobility of these elements during the fluid-induced alteration of the accessory phases because the nature of the fluid-mineral chemical exchanges helps determine the availability of these elements to hydrothermal fluids and thus the mineralizing potential of the fluids (Salvi and Williams 1996; Smith *et al.* 2000). The

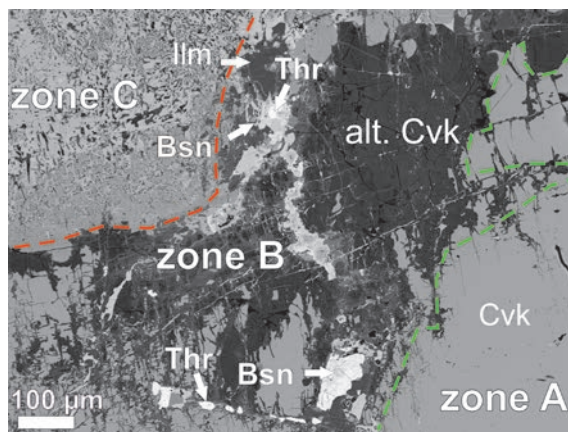
value of U/Pb and Th/Pb geochronological studies can also be constrained by late-stage remobilization of Th and U from accessory minerals (Harlov *et al.* 2011; Williams *et al.* 2011; Seydoux-Guillaume *et al.* 2012; Lewerentz *et al.* 2019).

The chevkinite group (CGM) currently includes twelve approved members, of which the two most abundant are chevkinite  $((\text{REE}, \text{Ca}, \text{Na}, \text{Th})_4(\text{Fe}^{2+}, \text{Mg})_2(\text{Ti}, \text{Fe}^{3+})_2\text{Si}_4\text{O}_{22})$ , and perrierite  $((\text{REE}, \text{Ca})_4\text{Fe}^{2+}(\text{Fe}^{2+}, \text{Fe}^{3+}, \text{Ti})_4(\text{Si}_4\text{O}_{22}))$ . The group is being increasingly recognised as widespread accessory phases in a very wide range of igneous, metamorphic and metasomatic rocks (see review by Macdonald *et al.* 2019). Hydrothermally altered CGM are common in all parageneses, providing ample scope for studying the mechanisms and products of alteration in a variety of situations. Their compositions, with up to 50 wt%  $\text{REE}_2\text{O}_3$  and significant concentrations of such rare-metals as Nb, Ta, Th and Zr, makes them of particular value in studies of ore genesis. At Warsaw, we have been using two approaches to determining the mechanisms and products of hydrothermal alteration of the CGM: natural rocks and high P-T experiments.

## NATURAL ROCKS

Material for these studies comes mainly from two sources. First, as part of our own field and petrological studies, e.g., UK Palaeogene granites (Macdonald *et al.* 2013), high-K trachyandesites from Moravia (Macdonald *et al.* 2017), the Kłodzko-Złoty Stok intrusion, Sudetes (Nejbert *et al.* 2020), the Joe Lott Tuff, Utah (Galanciak *et al.* 2020), the Gold Flat Tuff, Nevada (Macdonald *et al.* 2021) and the Krasnopol intrusion, Mazury Complex (Domańska-Siuda *et al.* 2022). Second, through ongoing collaborations with other organizations, e.g., the U.S. Geological Survey, GFZ Potsdam, the Russian Academy of Sciences (Moscow and Apatity), the Polish Academy of Sciences (Kraków), and the Universities of Edinburgh and Milan. A particular advantage of the Russian Academy of Science (Apatity) connection is that it has allowed us to work on the mineralogically diverse alkaline suites of the Kola Peninsula, Russia.

Samples are first examined by optical microscopy, with preliminary identification of minerals; the identification may then be confirmed, if necessary, by scanning electron microscopy (SEM) and electron back-scattered diffraction (EBSD). Textural relationships between the phases, critical to our understanding of the alteration process, are documented. Mineral compositions are then determined by electron micro-

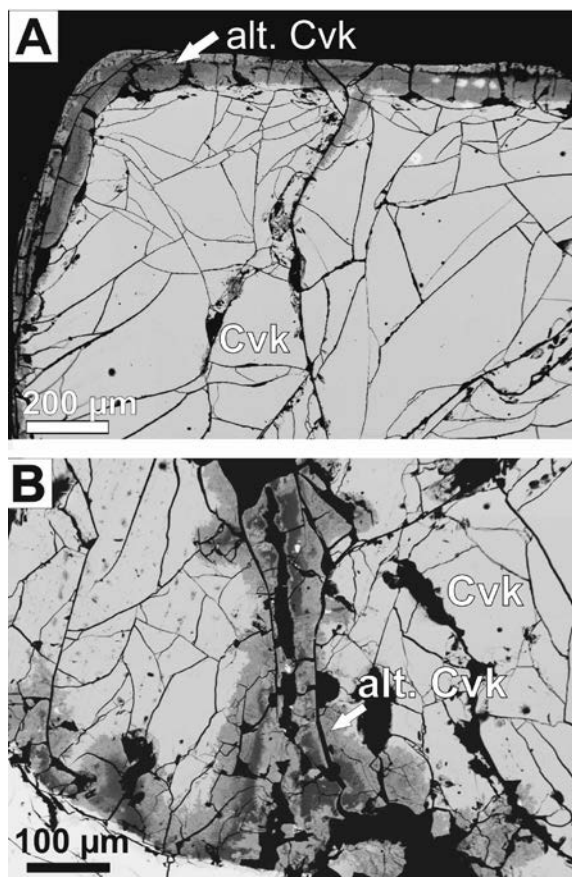


Text-fig. 1. BSE image of a cross-section through the alteration crust of chevkinite-(Ce) (Cvk) from the Vishneve Mountains, Urals Region, Russia (Macdonald *et al.* 2015a). Zones A to C represent the progressive alteration of the mineral. alt. Cvk, altered chevkinite; Bst, bastnäsite; Ilm, ilmenite, Thr,  $\text{ThSiO}_4$ .

probe analysis (EPMA), using microprobes housed in the Faculty of Geology.

Perhaps the most common alteration type in our experience is that the chevkinite breaks down to a REE-bearing phase (e.g., monazite, britholite, REE-epidote) and a Ti-bearing phase (titanite, pyroxene, rutile, ferriallanite). In detail, however, the product assemblage and the sequence of formation of the phases vary widely, the variation being related to the nature of the host rock (and the pre-alteration mineralogy) and, importantly, the composition of the hydrothermal fluids. Qualitatively we could show from our natural samples that fluids containing significant F and  $\text{CO}_2$  were particularly efficient at promoting breakdown of the chevkinite.

An example of the roles of F and  $\text{CO}_2$  is given by a syenitic pegmatite from the Vishneve Mountains, Urals Region, Russia (Macdonald *et al.* 2015a). The alteration of the chevkinite-(Ce) to a bastnäsite-(Ce)–ilmenite–columbite-(Fe) assemblage progressed through a series of texturally complex intermediate stages (Text-fig. 1). Zone A is unaltered chevkinite-(Ce). B is a thin, heterogeneous, partly stringy zone mainly of altered chevkinite but with patches and veins of ilmenite, bastnäsite and  $\text{ThSiO}_4$  (huttonite or thorite). The main part of Zone C comprises an interlocking mosaic of ilmenite, bastnäsite-(Ce), columbite-(Fe) and quartz. From the nature of the alteration products the hydrothermal fluids were inferred to have been F- and  $\text{CO}_2$ -rich, with variable levels of Ca activity, and with  $f\text{O}_2$  mainly between the nickel-nickel oxide and magnetite-hematite buffers.



Text-fig. 2. BSE images of chevkinite-(Ce) from the Rova occurrence, West Keivy massif, hydrothermally altered (A) along the rim, and (B) along cracks. From Bagiński *et al.* (2015).

In contrast, chevkinite-(Ce) crystals in a quartzolite from the Rova occurrence, West Keivy massif, are patchily mantled by a thin zone of altered chevkinite (Text-fig. 2a), which also occurs along fractures in the crystals (Text-fig. 2b). The absence of secondary alteration phases led Bagiński *et al.* (2015) to suggest that the fluid was dominantly hydrous.

An aim of such studies is that they can be more widely applicable. Given, however, the complex interplay of factors at an occurrence (P, T, fluid composition(s), host lithology), all occurrences are to some degree different and application of the results from one example to another must be done with caution. Nevertheless, we are beginning to see relationships between the nature of the product assemblages and inferred ligands in the fluids, such as some insights into element mobility, the efficiency of various ligands, and the occurrence of incompatible minerals, e.g., titanite and narsarsukite.

## EXPERIMENTS

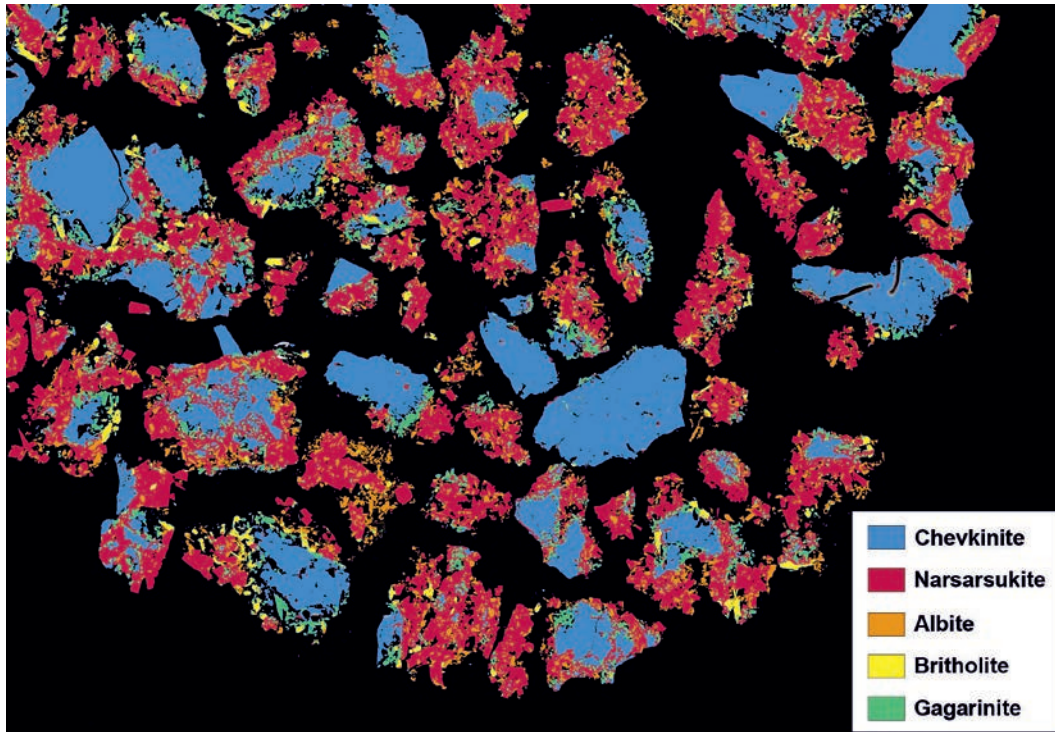
Ongoing experiments are undertaken at the Deutsches GeoForschungsZentrum Potsdam in collaboration with Professor D.E. Harlov. Chips of a natural chevkinite-(Ce) (from the Diamer district, Pakistan) are loaded into sealed platinum capsules, 15 mm long and 3 mm in diameter. All charges contain 5–6 mg H<sub>2</sub>O, along with a range of other components added in varying combinations: CaCl<sub>2</sub>, CaCO<sub>3</sub>, CaF<sub>2</sub>, Ca(OH)<sub>2</sub>, Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>, FeS, NaF, fluorapatite, bytownite, anorthite glass, and Al<sub>2</sub>O<sub>3</sub>. The components are chosen to vary such parameters as the alkalinity of, and H<sub>2</sub>O/F ratio in, the fluids. The choice of P-T conditions must be made from experience with natural sequences or from previous experimental studies.

The capsules are then placed into a standard cold seal autoclave in conjunction with a hydrothermal high-pressure line. An internal thermocouple is placed such that its tip is located half-way up along the capsule placed at the end of the autoclave. Experiments are then run at temperatures of either 500, 550 or 600°C, at pressures of either 200 or 400 MPa, for periods of 21, 42 or 63 days. After the run, the autoclave is quenched using compressed air. Temperatures of 100°C are generally reached within 1 minute. The charge is then lightly fragmented to ≤1mm and embedded in epoxy (Text-fig. 3). The charges are first evaluated using high contrast back-scattered electron (BSE) at the GFZ and, where satisfactory, are sent to the Department of Geochemistry, Mineralogy and Petrology, Warsaw for further SEM and EMP analysis.

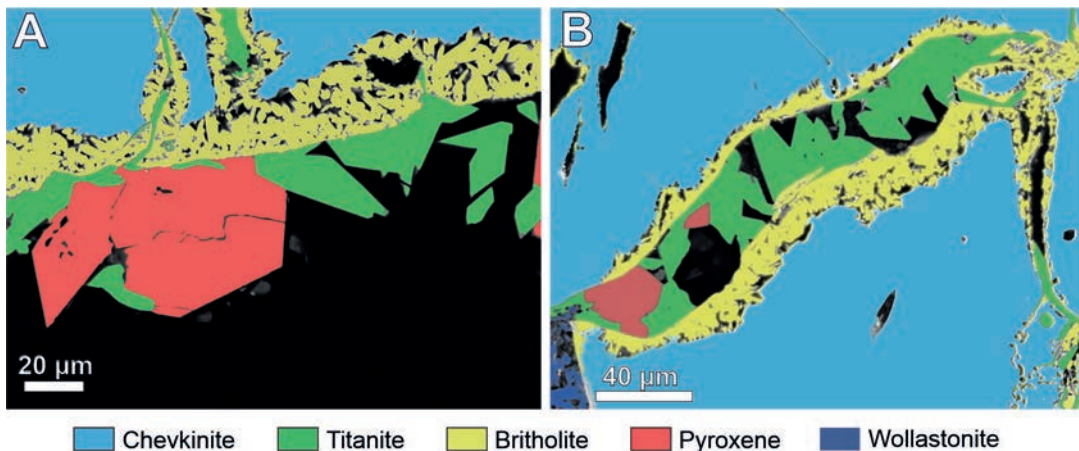
A strength of the experimental approach is that it allows us to determine in quantitative terms the P-T-fluid composition conditions in which certain reactions take place, and, by changing the parameters, how the reactions vary in P-T-time space. It provides information on the efficacy of various ligands in promoting reaction. For example, CaCl<sub>2</sub> and S (added as FeS) produced no significant alteration effects in our experiments. In natural rocks, the nature of the ligands has to be inferred from the product assemblage, e.g., the presence of carbonates, sulphides or fluorides.

Experiment CF1 was conducted at 600°C and 400 MPa, and with *f*O<sub>2</sub> buffered at Ni-NiO. Ca(OH)<sub>2</sub> was added to the fluid. The main reaction products (Text-fig. 4a) were, first, britholite-(Ce) ((Ce,Ca)<sub>5</sub>(SiO<sub>4</sub>)<sub>3</sub>OH) which formed a rim to the chevkinite-(Ce). This was followed by titanite and hedenbergite. The dark areas in the britholite-(Ce) are pore spaces, evidence that the alteration proceeded by the migration of fluid into the chevkinite-(Ce). Alteration also took place along





Text-fig. 3. Fragmented charge from experiment CF13 embedded in epoxy resin, prepared for use in EPMA and EBSD studies. Note the variable degree of alteration of the fragments and the alteration proceeding along fragment rims and along cracks.

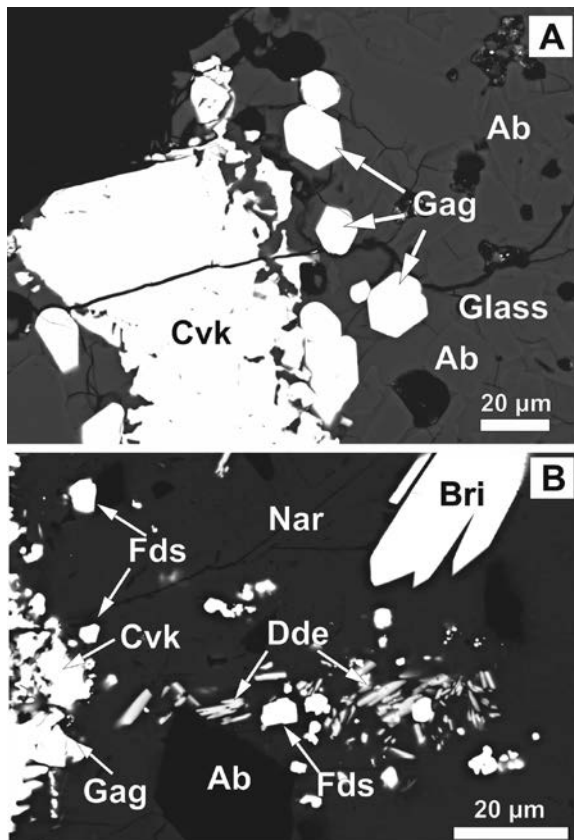


Text-fig. 4. False colour images showing fluid-induced alteration of chevkinite-(Ce), experiment CF1. (A) Alteration along the rim of the fragment. (B) The same assemblage formed along cracks in the fragment.

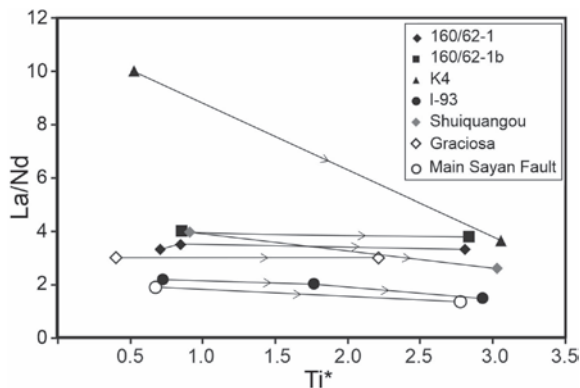
cracks penetrating into the chevkinite-(Ce), generating the same assemblage as on the rims (Text-fig. 4b).

On one occasion the experiments produced totally unexpected results. In an experiment run at 600°C, 400 MPa with added NaF for 21 days, the mineral gagarinite-(Ce) ( $\text{Na}(\text{REE}_x\text{Ca}_{1-x})(\text{REE}_y\text{Ca}_{1-y})\text{F}_6$ ) was synthesized. This mineral was known from only one locality, Strange Lake, Canada (Jambor *et*

*al.* 1996). A further experiment was run at 550°C, 200 MPa with added NaF for 84 days, where gagarinite-(Ce) formed again, associated with narsarsukite ( $\text{Na}_4(\text{Ti,Fe})_2(\text{Si}_8\text{O}_{20})(\text{O,OH,F})_2$ ), frankdicksonite ( $\text{BaF}_2$ ), and delindeite, a mineral of the lamprophyllite group ( $\text{Na}_2\text{Ba}_2\text{Ti}_3(\text{Si}_2\text{O}_7)_2\text{O}_2(\text{OH})_2(\text{H}_2\text{O})_2$ ) (Text-fig. 5). This exotic assemblage is unlike any reported in nature and presumably records experimental pa-



Text-fig. 5. (A) Euhedral crystals of gagarinite-(Ce) (Gag) in matrix of anhydrous, largely glassy, material with pools of albite (Ab). The subrounded dark areas are voids. Experiment CF4. (B) Gagarinite-(Ce) formed along rim of chevkinite-(Ce) (not seen). The enclosing phase is narsarsukite (Nar), with inclusions of albite and a large crystal of fluorbritholite-(Ce) (Bri). A vein-like group of small crystals includes frankdicksonite (Fds) and delindeite (Dde). Experiment CF13.



Text-fig. 6. La/Nd (atomic) ratio plotted against  $Ti^*$  to show variable fractionation of La from Nd during progressive alteration of chevkinite-(Ce).  $Ti^*$  is (total Ti apfu - 2). Data for 160/62-1, 1b and I-93 – Bagiński *et al.* (2015); K4 – Macdonald *et al.* (2015a); Shuiquangou – Jiang (2006); Graciosa – Vlach and Gualda (2007); Main Sayan Fault – Savel'eva and Karmanov (2008). Modified from Bagiński *et al.* (2015).

rameters not found in nature. It remains a mineralogical curiosity. It did, however, allow us to explore various crystal-chemical features of gagarinite-(Ce) and frankdicksonite (in preparation).

## BEHAVIOUR OF REE DURING ALTERATION

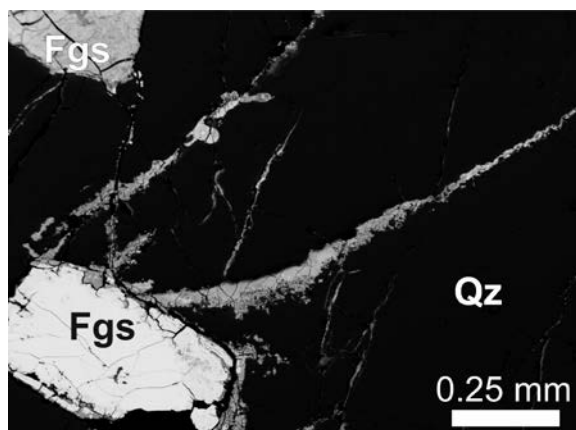
With the rapidly increasing use of REE in modern technology, current REE deposit exploration is exploring all potential sources. An important input to this will be an understanding of how the REE are concentrated into ore deposits by late-stage magmatic processes, hydrothermal alteration, and supergene processes. A focus of our CGM studies has been, therefore, the behaviour of the REE during hydrothermal alteration.

HREE are present in the great majority of CGM in very small amounts, often at levels below the detection levels of EPMA. We are collaborating, therefore, with Professor R. Anczkiewicz (Polish Academy of Sciences, Kraków) who in determining REE in our experimental products by ICP-MS.

Some preliminary results are: (1) The LREE are easily removed from chevkinite and rapidly fixed in such minerals as britholite and monazite. (2) The LREE are variably fractionated from each other (Text-fig. 6). (3) It appears that F- and  $CO_2$ -rich fluids promote the largest degrees of LREE fractionation.

## ELEMENT MOBILITY DURING ALTERATION

An issue associated with alteration is the mobility of the elements released from the chevkinite. Can they be transported far from the alteration site, or are they trapped close to it? One approach to this issue is to use mass balance calculations. Jiang (2006) used such calculations involving the original chevkinite-(Ce) and the reaction products in a syenite from the Shuiquangou intrusion, China, to show that during alteration no element left the alteration zone in significant amounts. In a study of chevkinite-(Ce) from the Sin Quyen Fe-Cu-LREE-Au deposit, Vietnam, Li and Zhou (2017) used mass balance calculations to show that some elements, such as Ti, La and Ce, were removed from the system during alteration, whereas others, such as Ca, Al, Nb, U and REE were supplied by the metasomatic fluids. They further suggested that REE and HFSE had been mobilized on a scale of at least hundreds of micrometres, ascribing the variable degrees of mobility in different systems to a high flux and strong chemical reactivity of the metasomatic fluids.



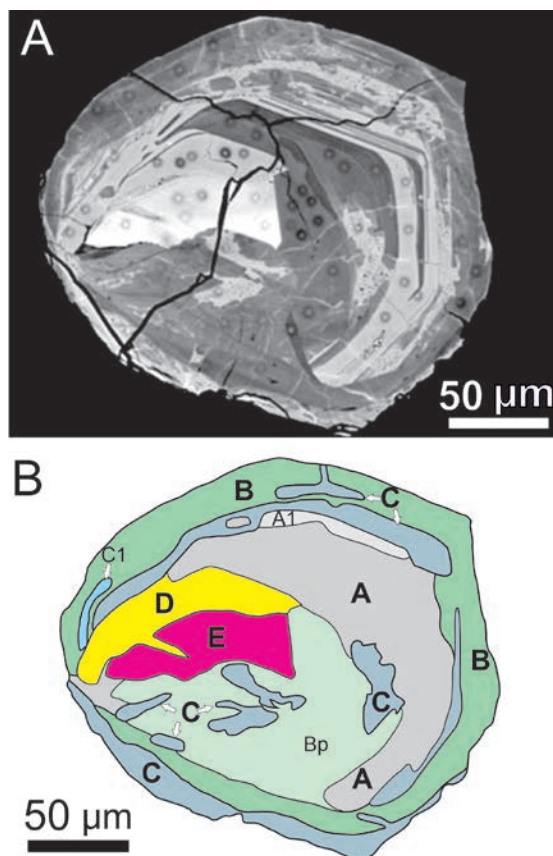
Text-fig. 7. BSE image of expansion cracks radiating from fergusonite-(Y) (Fgs) in quartzolite from the Rova occurrence (Macdonald *et al.* 2017b). The veins show variable thickness, intensity and form along their length and are compositionally different (see text). Qz, quartz.

More direct evidence of mobility was provided by a quartzolite from the Rova occurrence, Keivy alkaline province (Macdonald *et al.* 2017b). A series of expansion cracks in quartz originated in hydrothermally altered fergusonite-(Y) (tetragonal  $\text{YNbO}_4$ ) crystals (Text-fig. 7). All are dominated by Nb, U, Pb and the REE, with lesser amounts of Th, Si and Fe. There are two main types: the first is rich in U (up to 35 wt%  $\text{UO}_2$ ), the second in REE ( $\leq 25$  wt%  $\text{REE}_2\text{O}_3$ ). Abundances of PbO are up to 27 wt%. Fluorine levels are below detection and Cl levels are low ( $\leq 0.18$  wt%). The nature of the vein-filling material is unknown but it may not be crystalline. The veins do, however, provide evidence of fluid mobility during or after the alteration of the fergusonite-(Y), albeit of limited extent in this case. This is consistent with the results of a study of the alteration of  $\text{ThSiO}_4$  included in chevkinite-(Ce) from the Rova occurrence, Keivy, which showed that Th appears to have shown limited mobility, having been retained locally in the system (Macdonald *et al.* 2017a). It is also consistent with the small  $\text{ThSiO}_4$  veins in the Vishnevye Mountains described above (Text-fig. 1).

## RELATED PROJECTS

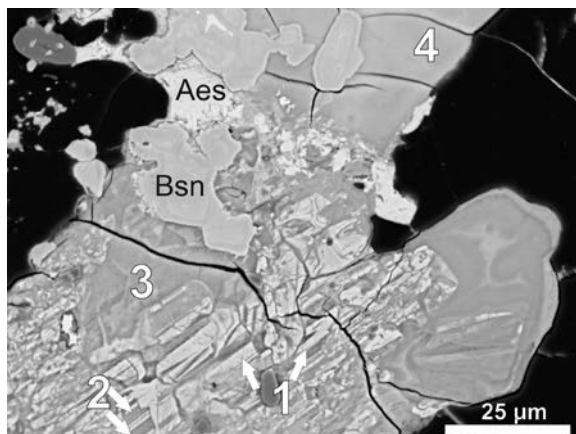
Our natural samples and experimental products are an excellent laboratory in which to study crystallographic and structural aspects. Two examples are discussed here. Our studies of a natural Nb-rich chevkinite-(Ce) from the Biraya rare-metal deposit,

Russia, revealed a very complex hydrothermal alteration history, with major compositional changes (Text-fig. 8). Stachowicz *et al.* (2019a, b) conducted X-ray diffraction and photon spectroscopy studies of the mineral in the Department of Chemistry, producing results which provided new insights into the group. Among them were: (1) regions crystallizing in both the  $C2/m$  and  $P2_1/a$  space groups are present in the crystal; (2) Ti is present as  $\text{Ti}^{4+}$  and  $\text{Ti}^{3+}$ , and possibly  $\text{Ti}^{2+}$ ; (3) cation distribution between the various structural sites is considerably more complex than in standard models of the chevkinite group; for example, Mg may enter the  $D$  site in the  $C2/m$  structure, whereas in the  $P2_1/a$  structure  $\text{Mg}^{2+}$  and  $\text{Ti}^{2+}$  tend to enter the  $B$  site; (4) Nb may enter into the chevkinite structure by the substitutions  ${}^C\text{Fe}^{3+} + {}^D\text{Ti}^{4+} \leftrightarrow {}^C\text{Fe}^{2+} + {}^D\text{Nb}^{5+}$  and  $2{}^D\text{Ti}^{4+} \leftrightarrow {}^D\text{Nb}^{5+} + {}^D\text{Ti}^{3+}$ , the latter leading to significant Nb enrichment. It is suggested that the techniques employed in the study to represent cation distribution can profitably be used to examine similar complexity in other mineral groups.



Text-fig. 8. (A) BSE image of a crystal of Nb-rich chevkinite-(Ce) from the Biraya deposit, Russia. The complex internal zonation is shown by the variations in intensity. (B) Simplified interpretation of the textural variations: the original crystal (zones A and D) was progressively replaced by hydrothermal fluids.





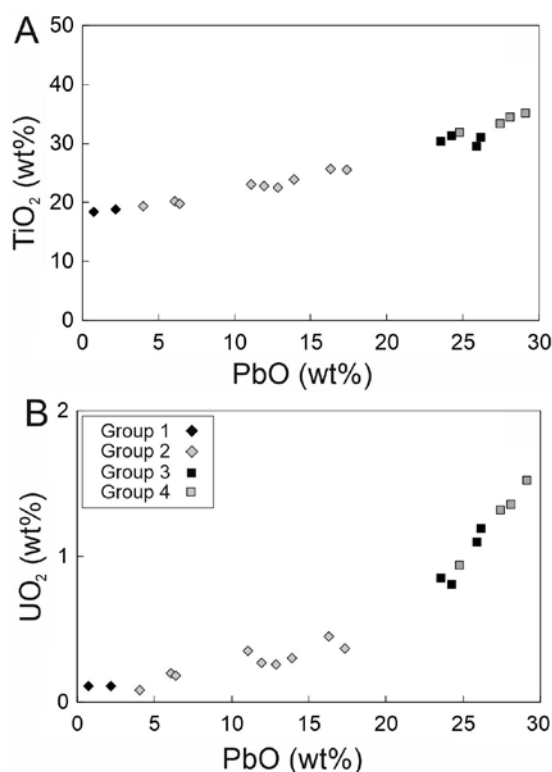
Text fig. 9. BSE image of the progressive breakdown of chevkinite-(Ce) (Group 1) to a partially altered chevkinite (Group 2) and then through a mixed type (Group 3) to a pseudo-homogeneous area (Group 4). Examples of each group are shown by arrows. Aes, aeschynite-(Y), Bsn, bastnäsite-(Ce). White Tundra pegmatite, Keivy alkaline province.

We noted above the synthesis of the rare mineral gagarinite-(Ce) in an experiment aimed at documenting the hydrothermal alteration of chevkinite. In common with all minerals containing significant amounts of Na, F and REE, gagarinite-(Ce) presents severe challenges for electron microprobe analysis, due to element losses under the electron beam and complex peak overlaps. Through a painstaking series of tests, Petras Jokubauskas has developed a technique to produce high-quality analyses of such minerals (extended abstract by Jokubauskas *et al.* 2021) which will undoubtedly be of great value to researchers elsewhere. The new analyses complemented by the results of an EBSD study, provided new information on cation distribution and substitution mechanisms in gagarinite-(Ce). The overall substitution mechanism for the REE-rich varieties is:  $(2x-y)\text{REE}^{3+} \rightarrow y\text{BNa}^+ + (x-y)\text{ANa}^+ + y\text{ACa}^{2+} + (x-y)/3\text{A}\square$ , where  $\square$  stands for vacancy and  $x > y$ .

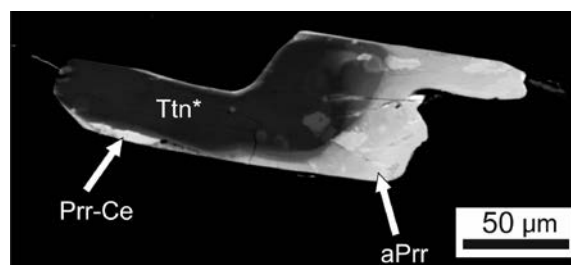
In a study of the White Tundra pegmatite, Keivy alkaline province, an unusual hydrothermal alteration scheme for a CGM was found. *viz.* progressive alteration by a Pb-CO<sub>2</sub>-bearing fluid converted a pristine phase (Group 1) through a partially altered phase (with up to 17.3 wt% PbO; Group 2), to a clearly mixed phase (Group 3) to a pseudo-homogeneous material containing Pb, Ti, Fe and Si (Group 4) (Text-fig. 9). Selected compositional changes are shown on Text-fig. 10. An EBSD study was aimed at tracing the structural changes during alteration. Groups 3 and 4 proved to be amorphous. The partially altered Group 2

mineral is shown by EBSD to have retained its crystallinity and chevkinitic nature despite a non-stoichiometric nature (e.g., A-site occupancy <4 and C-site occupancy >2) and low analytical totals (95.38–99.18 wt%). This raises the question, When does a hydrothermally altered mineral stop being that mineral? Is it as long as it maintains its structural integrity despite major compositional changes?

A related issue arose during our studies of the Mesoproterozoic Krasnopol intrusion, Mazury Complex (Domańska-Siuda *et al.* 2022). Hydrothermal alteration of perrierite-(Ce) resulted in a phase compositionally identical to titanite (Text-fig. 11). However,



Text-fig. 10. PbO-TiO<sub>2</sub> and PbO-U plots exemplifying the progressive compositional changes from Groups 1 to 4 shown in Text-fig. 9.



Text-fig. 11. BSE image of a perrierite-(Ce) crystal (brightest intensity; Prr) which has been progressively altered (aPrr) to a phase with titanite composition (black; Ttn\*). Krasnopol intrusion, Mazury Complex (Domańska-Siuda *et al.* 2022).

an EBSD analysis showed it to be amorphous and therefore not strictly titanite. It was noted earlier that titanite is a common alteration product of CGM (Jiang 2006; Prol-Ledemsa *et al.* 2012; Macdonald *et al.* 2015 b, c; Bągiński *et al.* 2016). As far as we are aware, none of the published descriptions included a structural study of the phase. Are they genuinely titanite?

## AND THE FUTURE?

Ongoing projects in the department cover several fields. (1) Studies of natural occurrences, including the Questa province, New Mexico (with the U.S. Geological Survey), and the alkaline intrusions of the Alto Paraguay Province, Brazil/Paraguay (University of Milan). (2) The search for hitherto unreported mechanisms of CGM alteration by hydrothermal alteration. (3) The progressive breakdown of the crystal structure during hydrothermal alteration. (4) Experimental studies of pressure-induced structural changes.

## Acknowledgements

Departmental colleagues Petras Jokubauskas, Jakub Kotowski, Witold Matyszczyk, Marcin Stachowicz and Harvey Belkin (U.S. Geological Survey), have been indefatigable contributors to our CGM studies. We gratefully acknowledge partial funding by NCN Harmonia grant no. 2017/26/M/ST10/00407. We thank Monika Kusiak and Łukasz Kruszewski for helpful comments on the text.

## REFERENCES

- Bągiński, B., Macdonald, R., Dzierżanowski, P., Zozulya, D. and Kartashov, P.M. (2015). Hydrothermal alteration of chevkinite-group minerals: products and mechanisms. Part 1. Hydration of chevkinite-(Ce). *Mineralogical Magazine*, **79**, 1019–1037.
- Bągiński, B., Zozulya, D., Macdonald, R., Kartashov, P.M. and Dzierżanowski, P. 2016. Low-temperature hydrothermal alteration of a rare-metal rich quartz-epidote-metasomatite from the El'ozero deposit, Kola Peninsula, Russia. *European Journal of Mineralogy*, **28**, 789–810.
- Domańska-Siuda, J., Nejbort, K., Bągiński, B., Katowski, J., Stachowicz, M. and Macdonald, R. 2022. Chevkinite-group minerals in selected intrusions of the Mazury Complex, NE Poland: insights into the formation of titanite by hydrothermal alteration. *Mineralogy and Petrology*, **116**, 105–119.
- Galanciak, J., Bągiński, B., Macdonald, R., Belkin, H.E., Kotowski, J. and Jokubauskas, P. 2020. Relationships between monazite, apatite and chevkinite-group minerals in the rhyolitic Joe Lott Tuff, Utah, USA. *Lithos*, **354–355**, 105349.
- Harlov, D.E., Wirth, R. and Hetherington, C.J. 2011. Fluid-mediated partial alteration in monazite: the role of coupled dissolution-reprecipitation in element redistribution and mass transfer. *Contributions to Mineralogy and Petrology*, **162**, 329–348.
- Jambor, J., Roberts, A.C., Owens, D.R. and Grice, J.D. 1996. Zajacite-(Ce), a new rare-earth fluoride from the Strange Lake deposit, Quebec-Labrador. *Canadian Mineralogist*, **34**, 1299–1304.
- Jiang N. 2006. Hydrothermal alteration of chevkinite-(Ce) in the Shuiquangou syenitic intrusion, northern China. *Chemical Geology*, **227**, 100–112.
- Jokubauskas, P., Macdonald, R., Bągiński, B. and Harlov, D.E. 2021. The advantages of EDS over WDS for beam-sensitive mineral analysis. Book of abstracts emc2020.pdf. <http://ptmin.pl/Book%20of%20abstracts%20emc2020.pdf> (extended abstract).
- Lewerentz, A., Harlov, D.E., Scherstén, A. and Whitehouse, M.J. 2019. Baddeleyite formation in zircon by Ca-bearing fluids in silica-saturated systems in nature and experiment: resetting of the U-Pb geochronometer. *Contributions to Mineralogy and Petrology*, **174**, 64.
- Li, X.-C. and Zhou, M.-F. 2017. Hydrothermal alteration of monazite-(Ce) and chevkinite-(Ce) from the Sin Quyen Fe-Cu-LREE-Au deposit, northwestern Vietnam. *American Mineralogist*, **102**, 1525–1541.
- Macdonald, R., Bągiński, B., Belkin, H.E. and Stachowicz, M. 2019. Composition, paragenesis, and alteration of the chevkinite group of minerals. *American Mineralogist*, **104**, 348–369.
- Macdonald, R., Bągiński, B., Dzierżanowski, P., Fettes, D.J. and Upton, B.G.J. 2013. Chevkinite-group minerals in UK Palaeogene granites: underestimated REE-bearing accessory phases. *Canadian Mineralogist*, **51**, 333–347.
- Macdonald, R., Bągiński, B., Kartashov, P. and Zozulya, D. 2017a. Behaviour of ThSiO<sub>4</sub> during hydrothermal alteration of rare-metal rich lithologies from peralkaline rocks. *Mineralogical Magazine*, **81**, 873–893.
- Macdonald, R., Bągiński, B. and Zozulya, D. 2017b. Differing responses of zircon, chevkinite-(Ce) and fergusonite-(Y) to hydrothermal alteration: Evidence from the Keivy alkaline province, Kola Peninsula, Russia. *Mineralogy and Petrology*, **111**, 523–545.
- Macdonald, R., Bągiński, B., Kartashov, P.M., Zozulya, D., Dzierżanowski, P. and Jokubauskas, P. 2015a. Hydrothermal alteration of a chevkinite-group mineral to a bastnäsite-(Ce)-ilmenite-columbite-(Fe) assemblage: interaction with a F-, CO<sub>2</sub>-rich fluid. *Mineralogy and Petrology*, **109**, 659–678.
- Macdonald, R., Bągiński, B., Stachowicz, M., Belkin, H.E., Pawłowski, J. and Kotowski, J. 2021. Magma mixing and



- exsolution phenomena in peralkaline rhyolites: insights from the Gold Flat Tuff, Nevada. *Comptes Rendus Géoscience*, <https://doi.org/10.5802/crgeos.45>
- Macdonald, R., Bagiński, B., Kartashov, P.M., Zozulya, D. and Dzierżanowski P. 2015b. Hydrothermal alteration of chevkinite-group minerals. Part 2. Metasomatite from the Keivy Mssif, Kola Peninsula, Russia. *Mineralogical Magazine*, **79**, 1039–1059.
- Macdonald, R., Bagiński, B., Kartashov, P.M., Zozulya, D. and Dzierżanowski, P. 2015c. Interaction of rare-metal minerals with hydrothermal fluids: evidence from quartz-epidote metasomatites of the Haldzan Buragtag massif, Mongolian Altai. *Canadian Mineralogist*, **55**, 1015–1034.
- Macdonald, R., Marshall, A.S., Dawson, J.B., Hinton, R.W. and Hill, P.G. 2002. Chevkinite-group minerals from salic volcanic rocks of the East African Rift. *Mineralogical Magazine*, **66**, 287–299.
- Macdonald, R., Nejbort, K., Bagiński, B. and Jurewicz, E. 2017. Ti-Zr-Nb-bearing accessory minerals in high-K trachyan-desitic rocks from the Western Outer Carpathians, Moravia, Czech Republic. *European Journal of Mineralogy*, **30**, 135–147.
- Nejbort, K., Bagiński, B., Kotowski, J., Jokubauskas, P., Jurewicz, E. and Macdonald, R. 2020. Chevkinite-group minerals in Poland. *Acta Geologica Polonica*, 2020, **70**, 97–106.
- Prol-Ledemsa, R.-M., Melgarejo, J.C., Martin, R.F. 2012. The El Muerto “NYF” granitic pegmatite, Oaxaca, Mexico, and its striking enrichment in allanite-(Ce) and monazite-(Ce). *Canadian Mineralogist*, **50**, 1055–1076.
- Salvi, S. and Williams-Jones, A.E. 1996. The role of hydrothermal processes in concentrating high-field strength elements in the Strange Lake peralkaline complex, northeastern Canada. *Geochimica Cosmochimica Acta*, **60**, 1917–1932.
- Savel’eva, V.B. and Karmanov, N.S. 2008. REE minerals of alkaline metasomatic rocks in the Main Sayan Fault. *Geology of Ore Deposits*, **50**, 681–696.
- Seydoux-Guillaume, A.-M., Montel, J.-M., Bingen, B., Bosse, V., de Parseval, P., Paquette, J.-L., Janots, E. and Wirth, R. 2012. Low-temperature alteration of monazite: Fluid mediated coupled dissolution – precipitation, irradiation damage, and disturbance of the U-Pb and Th-Pb chronometers. *Chemical Geology*, **330–331**, 140–158.
- Smith, M.P., Henderson, P. and Campbell, L.S. 2000. Fractionation of the REE during hydrothermal processes: Constraints from the Bayan Obo Fe-REE-Nb deposit, Inner Mongolia, China. *Geochimica Cosmochimica Acta*, **64**, 3141–3160.
- Stachowicz, M., Bagiński, B., Welch, M. D., Kartashov, P., Macdonald, R., Balcerzak, J., Tyczkowski, J. and Woźniak, K. 2019a. Cation ordering, valence states, and symmetry breaking in the crystal-chemically complex mineral chevkinite-(Ce): X-ray diffraction and photoelectron spectroscopy studies, and mechanisms of Nb enrichment. *American Mineralogist*, **104**, 595–602.
- Stachowicz, M., Welch, M.D., Bagiński, B., Kartashov, P., Macdonald, R. and Woźniak, K. 2019b. Cation ordering, valence states and symmetry breaking in the crystal-chemically complex mineral chevkinite-(Ce): Recrystallization, transformation and metamict states in chevkinite. *American Mineralogist*, **104**, 1481–1486.
- Vlach, S.R.F. and Gualda, G.A.R. 2007. Allanite and chevkinite in A-type granites and syenites of the Graciosa Province, southern Brazil. *Lithos*, **97**, 98–121.
- Williams, M.I., Jercinovic, M.J., Harlov, D.E., Budzyń, B. and Hetherington, C.J. 2011. Resetting monazite ages during fluid-related alteration. *Chemical Geology*, **283**, 218–225.

Manuscript submitted: 27<sup>th</sup> April 2022

Revised version accepted: 11<sup>th</sup> July 2022