

Supplementary Material

Age, petrochemistry, and origin of a REE-rich mineralization in the Longs Peak - St. Vrain pluton near Jamestown, Colorado (USA)

Julien Allaz^{1*}, Markus B. Raschke², Philip M. Persson³, and Charles R. Stern¹

Recalculation of H₂O, CO₂ and ferric-ferrous iron

Allanite-(Ce) is known for its variable ferric and ferrous iron. The recalculation of Fe²⁺ and Fe³⁺ and of weight-% H₂O was performed following recommendations in Ercit (2002), assuming a total of 6 cations in the T (Si, Al) and M (Al, Fe, Mn, Mg, Ti) sites, 12 oxygen atoms, and 1 OH group. After recalculation of atom per formula unit of Fe²⁺ and Fe³⁺ by charge balance, FeO and Fe₂O₃ weight-% were recalculated. Manganese in all analyses was assumed to be only Mn²⁺ [i.e., only Khristovite-(Ce) component; Table 1] as charge balance can be achieved by varying Fe²⁺ and Fe³⁺ contents only, and most analyses yield less than 0.10 apfu Mn. An exception to the latter is the inner rim composition (e.g., analysis domains #4 and 5 in Fig. 8b; crosses in Fig. 9), where Mn-content reaches in average 1.50 wt-% MnO (0.12 apfu). If manganese is considered as Mn³⁺ (i.e., only Piemontite component; Table 1), all points in Figure 9 shift to the right, and form a closer cluster of points for the inner rim compositions (Fig. DR1). The exact determination of Fe²⁺, Fe³⁺, Mn²⁺ and Mn³⁺ contents is beyond the scope of this paper, and the reality is probably between Figure 9 and Figure DR1.

Iron content in *törnebohmite-(Ce)*, *fluorbritholite-(Ce)* and *cerite-(Ce)* was assumed to be all ferric. The weight-% H₂O of these hydrous phases has been recalculated based on stoichiometry. We assumed a total of 1 OH group (= OH + F + Cl) and 12 oxygen atoms in

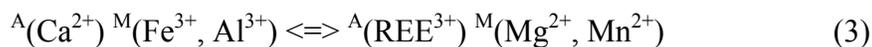
fluorbritholite-(Ce), 1 OH group and 8 oxygen atoms for törnebohmite-(Ce), and 4 OH groups and 17 cations (without H) for cerite-(Ce). The total amount of OH groups in cerite-(Ce) appears to be variable depending on the source; IMA and Pakhomovsky et al. (2002) recommend 7 OH groups, whereas Moore and Shen (1983), the Handbook of Mineralogy (RRUFF database: <http://rruff.info/doclib/hom/ceritece.pdf>), and webmineral.com website suggest 4 OH groups. Recalculation based on 7 OH groups yields totals above 102% with *ca.* 3 wt-% H₂O and 1 wt-% F, whereas recalculation based on 4 OH groups yields more acceptable totals with *ca.* 1.3 wt-% H₂O and 1 wt-% F. The charge balance indicates only a slight charge deficit on recalculation with 4 OH groups (in average -0.55 out of 58 negative charges), whereas the charge balance with 7 OH groups yields stronger charge excess (+2.45 out of 55 negative charges). Nonetheless, this uncertainty on OH groups does not affect the results discussed in this study. A more direct approach on the quantification of H-content and oxidation state for Fe and Mn in cerite would be desirable to resolve this issue, and remains out of the scope of this paper.

The weight-% of CO₂ and H₂O for *bastnäsite-(Ce)* were also recalculated by stoichiometry assuming 1 oxygen atom, 1 CO₂ group, 1 OH group (= OH + F). Despite this recalculation, totals remain low, around 95-96% for pure bastnäsite, most likely due to some inaccuracy in the water recalculation, possible beam damage during the analysis, and errors on F-analysis. However, we remain confident that the REE-analysis in this mineral is accurate, as the normalization yields close to a total of 1 cation.

Allanite-(Ce) compositional zoning

Allanite-(Ce) is the only REE-mineral showing a large intra-grain compositional variation, and it is also the first REE-mineral to crystallize either as isolated crystals in the aplite, as veinlets, or

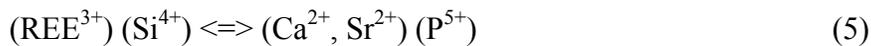
as the rim of the larger REE veins and pods. Allanite-(Ce) is part of the epidote group, with a general formula of $A_2M_3(Si_2O_7)(SiO_4)O(OH)$ ($A = Ca, REE, Sr, Na, U, Th$; $M = Al, Fe, Mg, Mn, Ti$; Table 1). Since all REE in allanite-(Ce) are trivalent cations and Ca is a divalent one, the incorporation of REE in allanite-(Ce) must involve a coupled substitution to balance the charges. With increasing REE content, Fe^{3+} , Mg, Mn, and Na increase, whereas Ca, Al, and Fe^{2+} decrease. Substitution involving reduction of Fe^{3+} to Fe^{2+} is likely, but remains hard to ascertain, as oxidation state for Fe cannot accurately be determined through mineral formula recalculation; nonetheless a positive correlation between Fe^{2+} calculated by charge balance and REE is observed. Increase in Mg (0.08-0.16 apfu) and Mn (0.07-0.12 apfu) is positively correlated with the increase in REE and a decrease in Al^{VI} (2.04-1.86 apfu). A slight increase in Na (up to 0.03 apfu) is also observed with increasing REE content. Vacancies in the A-site can also balance the increasing concentration of REE, and both are indeed positively correlated. Thus, the incorporation of REE is achieved by at least four coupled substitutions (in order of importance):



The increasing component of ferriallanite-(Ce) associated to the increase in REE as found, is due to the simple substitution $Al^{3+} \rightleftharpoons Fe^{3+}$ on the M-site. The evolution of allanite-(Ce) composition is consistent in the two studied samples. From core to rim, the REE-content increases, which likely reflect a progressive saturation of the REE in the fluid associated to the mineralization (see §5.4.2).

Fluorbritholite-(Ce) compositional variation

Fluorbritholite-(Ce) shows discrete variation of composition, essentially among P, Si, Ca, and REE content. However, such chemical variation appears chiefly between grains or between samples, and is not clearly observed within each grain. The P and Si substitution reflecting britholite-(Ce)-apatite solid solution must be coupled with another substitution to balance the charge (see Pan and Fleet 2002). A strong anti-correlation between 5+ and 2+ cations (P, Ca, Sr) and 4+ and 3+ cations (Si, REE, U, Th, Fe, Mn) is observed. As mentioned in Pan and Fleet (2002) and Liferovich and Mitchell (2006), this implies the following simplified coupled substitution:



Whereas Liferovich and Mitchell (2006) observe an additional high Si-content and attribute this discrepancy to either preferential leaching in the A-site or an undermined element in the A-site, our measurements do show a value approaching 3.00 ($Si+P = 2.90$ to 3.14 ; average 3.01) with few but not all analyses above the $\Sigma = 3.00$ apfu line (Fig. 10d). Variation of Si not correlated with P is possibly due to micro-inclusion of quartz. The A-site appears to be slightly deficient, with a total of 4.64 to 5.00 apfu for the sum of 2+ and 3+ cations (chiefly Ca, Fe, Mg, Y and REE), and all analyses fall slightly below or close to the mixing line Ca_5-REE_5 (Fig. 10e). This deficiency in the A-site remains unexplained. It could be due to the presence of vacancies, or analytical artifacts of minor beam damage during the analysis, yet with missing element unlikely with analysis totals between 98.7 and 102.2% , except for one set of data around $96.3-98.4\%$. Qualitative EDS analysis does not reveal other elements. An increase in vacancies is possibly correlated with an increase in REE-content and a decrease in Ca-content, suggesting that some

REE might enter the britholite-(Ce) structure through the following substitution, as suggested by Pan and Fleet (2002):



However, Holtstam and Andersson (2007) pointed out that no physical evidence exists for cation vacancies in fluorbritholite-(Ce), leaving this point unresolved.

As for apatite structure, two different A-sites hosting Ca and REE are distinguished in britholite-(Ce) structure: two 9-fold coordinated Ca(1) sites, and three slightly smaller 7-fold coordinated Ca(2) sites. REE preferentially enter first the smaller Ca(2) site (Carpéna et al. 2001), and most Ca(1) sites are usually filled with Ca, making an ideal formula close to $\text{Ca}_2\text{REE}_3(\text{SiO}_4, \text{P}_2\text{O}_5)_3(\text{OH})$. Most analyses yield slightly higher REE content (2.99 to 3.32) and lower Ca content (1.46-1.67; Table DR2), with only minor Fe, Mg, and Sr. Such high REE content is also reported by Holtstam and Andersson (2007) and Liferovich and Mitchell (2006). Therefore, we suggest that REE can partially fill the Ca(1)-site after filling entirely the preferred Ca(2) site. Minor Sr is also present in fluorbritholite-(Ce), and occupies the same site as Ca (Pan and Fleet 2002; Liferovich and Mitchell 2006). Sr is positively correlated with Ca and LREE, and anti-correlated with Fe, HREE, and total REE in general, suggesting that Sr-rich britholite-(Ce) tend to prefer REE-poor britholite-(Ce). No correlation is found for F and other cation, suggesting that F enter the britholite-(Ce) structure through a simple $\text{OH} \Rightarrow \text{F}$ substitution.

Bibliography

Carpéna, J., Boyer, L., Fialin, M., Kiénast, J.-R., Lacout, J. (2001) $\text{Ca}^{2+}, \text{PO}_4^{3-} \rightleftharpoons \text{Ln}^{3+}, \text{SiO}_4^{4-}$ coupled substitution in the apatitic structure: stability of the mono-silicated. *Comptes*

Rendus de l'Académie des Sciences de la Terre et des planètes / Earth and Planetary Sciences, 333, 373–379.

Ercit, T.S. (2002) The mess that is “allanite.” *Canadian Mineralogist*, 40, 1411–1419.

DOI:10.2113/gscanmin.40.5.1411

Holtstam, D. and Andersson, U.B. (2007) The REE minerals of the Bastnäs-type deposits, South-Central Sweden. *The Canadian Mineralogist*, 45(5), 1073-1114. DOI:

10.2113/gscanmin.45.5.1073

Liferovich, R.P. and Mitchell, R.H. (2006) Apatite-group minerals from nepheline syenite, Pilansberg alkaline complex, South Africa. *Mineralogical Magazine*, 70(5), 463-484. DOI:

10.1180/0026461067050346

Moore, P.B., and Shen, J. (1983) Cerite, $RE_9(Fe^{3+}, Mg)(SiO_4)_6(SiO_3OH)(OH)_3$: its crystal structure and relation to whitlockite. *American Mineralogist*, 68, 996–1003.

Pakhomovsky, Y.A., Men'shikov, Y.P., Yakovenchuk, V.N., Ivanyuk, G.Y., Krivovichev, S., Burns, P.C. (2002) Cerite-(La), $(La, Ce, Ca)_9(Fe, Ca, Mg)(SiO_4)[SiO_3(OH)]_4(OH)_3$, a new mineral species from the Khibina Alkaline Massif: Occurrence and crystal structure. *The Canadian Mineralogist*, 40, 1177–1184. DOI:10.2113/gscanmin.40.4.1177

Pan, Y. and Fleet, M.E. (2002) Compositions of the apatite-group minerals: substitution mechanisms and controlling factors. In M. J. Kohn, J. Rakovan, and J. M. Hughes, Eds., *Reviews in Mineralogy*, vol. 48: Phosphates - geochemical, geobiological, and materials importance, p. 13-49. Washington, D.C., Mineralogical Society of America.