ABC_2O_8 – a new look on the crystal chemistry and classification of samarskite group minerals

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Introduction

The purpose of this paper is to present, based on the collective database of Electron MicroProbe Analyses (EMPA) of Samarskite Group Minerals (SGM), crystal chemical evidence for an ordered formula – ABC_2O_8 – and the need for a redefinition of the mineral group.

SGM comprise a complex group of metamict Y-REE-U-Nb-Ta-oxides, characterized by a significant content of *iron*. The current general formula ACO_4, where A = Y, REE, U or Fe, and C = Nb *or* Ta, was first suggested by Komkov (1965). For easier comparison, the dominant Nb-Ta-site in all oxides is characterized as C, thus ACO_4 instead of ABO_4, etc. A survey performed on 19 "alteration-free samples" concluded that the ACO_4 model was "correct" and that "samarskite is a true complex oxide without a simple compositional analogue" having a mixed tri-valent A-site with large (Y, REE, Ca, U, Th) and small cations (Fe^{2+}, Fe^{3+}, Ti) in order to attain the required site radius for octahedral coordination, and a C-site with Nb, Ta and sometimes Ti (Warner & Ewing, 1993). IMA currently accepts five SGM: **samarskite-(Y)**, $(Y,Ce,U,Fe,Nb)(Nb,Ta,Ti)O_4$; **ishikawaite**, $(U,Fe,Y)NbO_4$; **calciosamarskite**, $(Ca,Fe,Y)(Nb,Ta,Ti)O_4$ (Hanson et al., 1999); **yttrotantalite-(Y)**, $(Y,U,Fe^{2+})(Ta,Nb)(O,OH)_4$ (shown by Ercit, 2005); and **samarskite-(Yb)**, $YbNbO_4$ (Simmons et al., 2006). Natural samarskite heated to 660° C produced an ixiolite- or wolframite-like unit cell (P2/c) with a = 4.82, b = 5.68, c = 5.15 Å (Komkov, 1965). A high-T cell with a doubled b-axis (Komkov's a-axis) appeared after heating natural material up to 1000° C and "some sort of ordering" was suggested to be the cause (Sugitani et al., 1984). Several complex formulas have been suggested (e.g. AC_2O_6, Nilssen, 1970; $A_3C_5O_8$, Sugitani, 1985) but ordering do not match observed x-ray data. The high-T cell has survived as an identifier (e.g. Simmons et al., 2006) but no one has systematically derived an ordered chemical formula typical for a doubled ACO_4-cell, i.e. ABC_2O_8, from extant chemical data, although occasionally SGM data have been presented on the similar $A(BC)_3O_8$ form (e.g. Feldman & Konopleva, 1969; Makarochkin, 1972). SGM are α-PbO_2 derivative structures, comprising basic layers of edge-sharing Nb-Ta octahedra and a metal:oxygen ratio of 1:2, of which Graham & Thornber (1974) recognized two types: *α-PbO₂ related structures*, to which they counted the samarskite, ixiolite, wolframite, columbite, and wodginite groups, which have small (0,60-0,83 Å) A-, B-, and C-cations in octahedral coordination and a structural tendency for cation disordering, and *α-PbO₂ structures with mixed coordination*, e.g. euxenite group and M'-fergusonite, which have layers with B-C-cations in octahedral coordination, alternating with layers of large A-cations (>0,86 Å) coordinated by a square antiprism. There are two problems with this classification: (i) SGM are clearly metamict; and (ii) the A-site components of each group – ($Mn,Fe^{2+},Fe^{3+},Sc^{3+}$) and ($U^{4+},Th^{4+},Y^{3+},REE^{3+},Ca^{2+}$) – are mutually exclusive, *except* for in the SGM! These problems are solved if the SGM are placed with the metamict mixed coordination structures, if it can be shown that the large cations in SGM comprise a separate site, and thus are more ordered than the present understanding supposes. Despite the existence of chemical and structural data suggestive of a more ordered structure the ACO_4 model has become more entrenched with each major publication on SGM (e.g. Warner & Ewing, 1993; Hanson et al., 1998, 1999; Simmons et al., 2006). The "CV_1-CV_2 three-group diagram" by Ercit (2005) seems also to have had an unintentional conserving effect on the "ACO_4 paradigm", even though obviously not a structural scheme. Any attempts to reform the SGM must find support in the accumulated chemical data and also be able to address crystallographic and structural features and observations.

Calculation, site assignment and data sorting

More than 1100 EMPA performed between 1991 and 2017 was surveyed in the frame of this study (Warner, 1991 and Warner & Ewing, 1993: 417 analyses; Kjellman: unpubl. yttrotantalite, 76;

Muftakov, 1999: 15; Hanson et al. 1998, 1999, and 2003: 84; Ercit, 2005: 25; Ercit: unpubl. Grenville data, 228; Simmons et al., 2006: 11; Davis & Nicolescu, 2012: 14; Pieczka et al., 2014: 200; Capitani et al., 2016: 13). All averaged published data were replaced by original data sets kindly provided by the authors, but for samples YL, S1Q1 and SPH1 in Hanson et al. (1998), which could not be found.

The complete data set, 1102 analyses, was recalculated so that all elements with an octahedral cation radius between 0.60 and 1.03 Å, and Pb^{2+} (1.12 Å) were included in the SGM formula calculations. These were based on 8 oxygens and the expected cation:anion ratio of 1:2 was calculated by charge balance of the Fe^{2+}/Fe^{3+}. Uranium was calculated as UO_2. The amounts of Al^{3+} (0.54 Å), Si^{4+} (0.40 Å) or K^+ (1.39 Å), were assessed relative to, but not included in, the SGM formula calculations as these elements were observed associated with general weight loss and considered to be present only as impurities.

All "large" cations (0.86-1.02 Å) like $U^{4+} + Th^{4+}$ (U*) and $Y^{3+} + REE^{3+}$ (Y*), Ca^{2+} and Na^+, were provisionally assigned to the A-site by analogy to the mixed coordination structures of Graham & Thornber (1974). The high charge small cations (0.60-0.64 Å) Nb^{5+}, Ta^5, and $(\pm W^{6+})_B$. were attributed to the C-site. The remaining elements with intermediate cation radii (0.65-0.83 Å) $(\pm Mn^{2+})_A$, Fe^{2+}, Mg^{2+}, $(\pm Sc^{3+})_A$, Fe^{3+}, Sn^{4+}, Zr^{4+} $(\pm Ti^{4+})_C$ were assigned to the B-site (Cations in brackets with lettered subscripts signify elements that may substitute at neighbouring sites.).

A provisional plot of the $\Sigma A:\Sigma ABC$-cations ratio (A/ABC) vs. total-wt.% revealed a clustering around 0.25 – the expected ratio for ABC_2O_8-structures (A/ABC will provisionally identify α-PbO_2 related structures, A/ABC = 0.5 for ACO_4; 0.33 for $A(BC)_2O_6$; and 0.25 for ABC_2O_8. Primary/secondary alteration will increase/decrease A/ABC, and hamper identification). The cluster is characterized by *high analytical totals* (>95 oxide wt.% excl. SiO_2, Al_2O_3 and K_2O), *"high"content of FeO* (4-14 %), *"low" CaO* (<2 %) and *a metal:oxygen ratio of 1:2*, i.e. suggesting no hydroxyl or water molecules. These features were used to sort the data into five qualitative groups, Q_4-Q_0, where Q_4 satisfies all four criteria and Q_0 none. Fig. 1a illustrates that the SGM data comprise a broad range of individual analyses and series of different qualities: near fresh-slightly altered SGM (Q_4); altered (Q_3-Q_2) with increased A/ABC and totals above 90 % overlap with highly-severely altered material (Q_1-Q_0) with totals below 90 wt.% and/or falling A/ABC, i.e. intense effects of primary and secondary alteration. Fig. 1b illustrates that A/ABC also is positively correlated with Ca increase, and that the primary Ca at the A-site may be as low as 0.1 a.p.f.u. Figs. 2a, 2b and 2c, which are major substitution plots of the A-, B-, and C-site elements, attest to the validity of the ABC_2O_8 formula and the ordered character of SGM-Q_4 data as it aligns along the 1:1 substitution lines. These plots were highlighted with Q_4-data from three recent papers that were adjusted for minor substitutions.

From the data pattern of Fig. 1b it can be concluded that the expected contribution of Ca at the A-site in the primary SGM is quite low (max 0.1-0.2 a.p.f.u.) and that increased Ca-values induce disorder. But what does Ca do specifically? Fig. 3 illustrates how and if increase of Ca [a.p.f.u.] affects the A-, B-, or C-sites: (i) it is clear from the y-axis intersections – A=0.95, B=1.06 and C=1.98 – that the low-Ca SGM-Q_4 data are ordered; (ii) the slopes of the regression lines – A=-0.003, B=-0.816 and C=-0.027 – indicate that the secondary Ca in the SGM-EMPA is present due to metasomatism only of the Fe-rich B-site, which have a strong negative (near 1:1) correlation with the Ca increase. Thus, this "mechanism" is the cause behind the highly varied Ca- and Fe-content observed in SGM throughout history. The C-site, and surprisingly the Y*-U*-dominated A-site, are largely "unaffected" and retain their site totals.

Conclusions – food for thought and discussion

The results of this preliminary paper can be summarized as follows: (a) Primary SGM (Q_4) ought to be described by an ordered formula, $(Y^*,U^*,Ca)(Fe^{3+},Fe^{2+},Ti)(Nb,Ta,W)_2O_8$, with an A-site occupied by large cations analogous to those in M'-fergusonite and euxenite. (b) Q_3-compositions, possibly even Q_2, may be written on the same formula but with secondary Ca at the B-site, e.g. $(Y^*,U^*)(Fe^{3+},Fe^{2+}Ca_{[alt]})(Nb,Ta)_2O_8$. (c) The practice of averaging SGM data should be abandoned, if it cannot be proven that the data is qualitatively constrained. (d) Some observed/possible primary substitutions include: $Y_A=REE_A=Sc_A$; $Nb_C=Ta_C$; $Ti_C+W_C=2(Nb,Ta)_C$; $Fe_B+2Nb_C=Ti_B+2Ti_C$; $Y^*_A+Fe^{3+}_B=U^*_A+Fe^{2+}_B$. (e) The ABC_2O_8-formula offer a new perspective for the study of stability reactions, e.g. $UO_2+FeNb_2O_6 = UFeNb_2O_8$; $YTaO_4+FeTaO_4 = YFeTa_2O_8$; $CaNb_2O_8+TiO_2 =$

$CaTiNb_2O_8$; $UO_2+3TiO_2 = UTi_3O_8$. (f) The data suggests that several species are questionable, e.g. calciosamarskite and samarskite-(Yb), of which the quality is too low (Q_2-Q_0) and does not fit the ABC_2O_8-formula. The results rise also some other questions. For example, Fig. 4a suggests that Q_4 data plot in an elliptic region in the SGM-field of the CV_1-CV_2 three-group diagram (Ercit, 2005), but the data are partially obscured/covered by Q_3-Q_0 data; and Fig. 4b shows well separated Q_4 data of yttrotantalite, samarskite and ishikawaite in the same diagram. Is there a possibility that something can be elaborated? The described formula calculations and interpretations will hopefully provoke discussions and renew ideas on the crystal chemistry and classification of samarskite group minerals.

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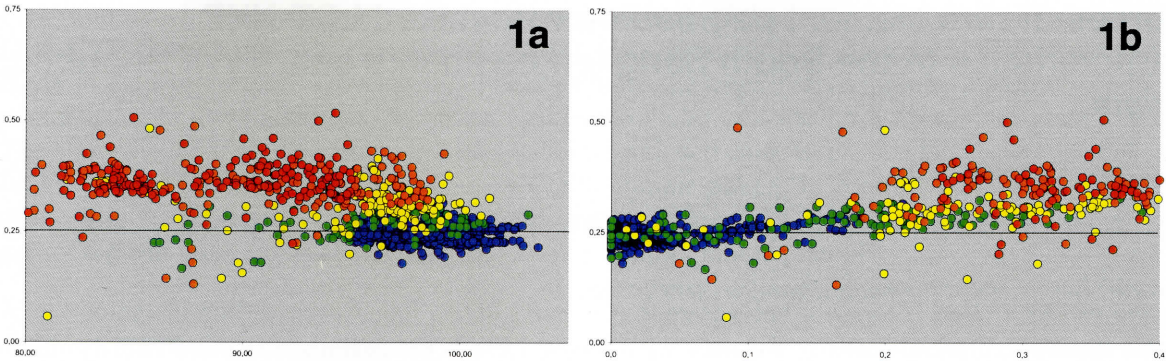Warner, J.K. & Ewing, R.C. 1993: Crystal chemistry of samarskite. *American Mineralogist 78*, 419-424.

Figure 1. *A/ABC plots, where A=(Y*+U*+Ca+Na)* **a -** *A/ABC=f(total-wt.%)* **b -** *A/ABC=f(Ca2+) [a.p.f.u.]. Q_4 (blue-506 samples), Q_3 (green-114), Q_2 (yellow-150), Q_1 (orange-184), Q_0 (red-148).*
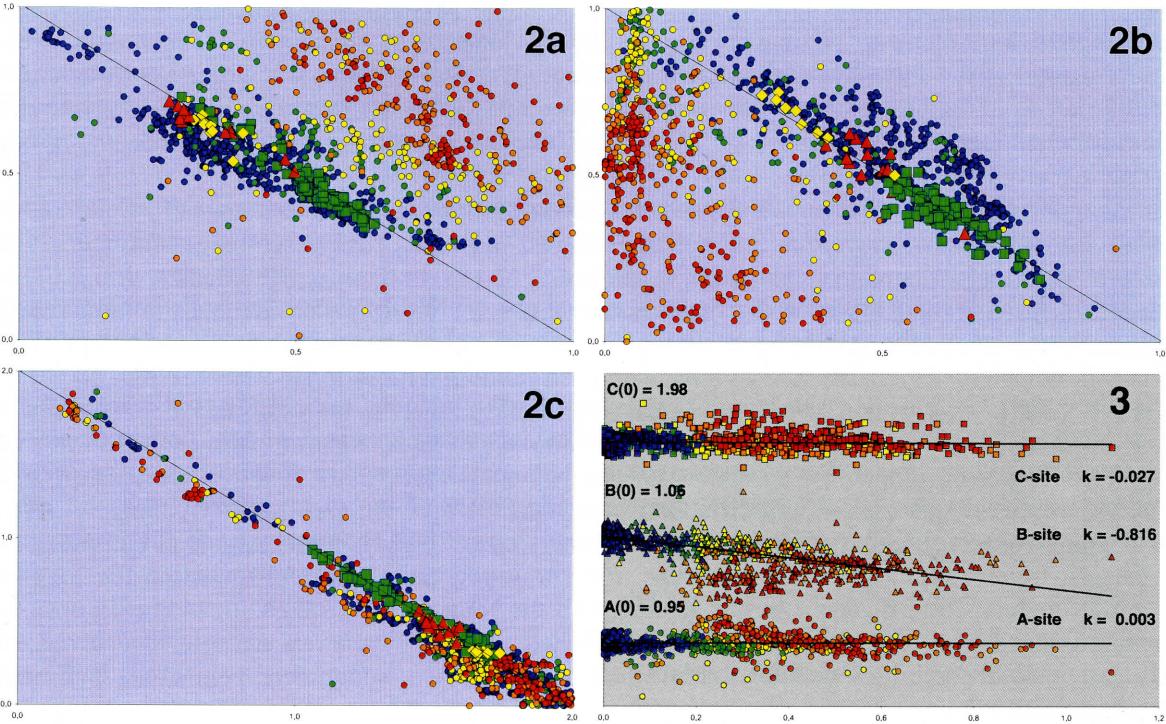

Figure 2. *Primary 1:1 substitutions in SGM:* **a -** *A-site,* **U^*+Ca** *vs.* **Y^***; **b -** *B-site,* **$Fe^{2+}+Mg+Mn+Sc$** *vs.* **$Fe^{3+}+Sn+Zr+Ti$**; **c -** *C-site,* **Nb** *vs.* **$Ta+W$**.; Q_4-Q_0 as in Fiure 1. Higlighted Q_4 data: yellow diamonds, Spinelli Prosp., CT, USA (Davis & Nicolescu, 2011); green squares, Juliana pegm. syst., Poland (Pieczka et al., 2014); red triangles, Garnet Codera Dike, Italy (Capitani et al., 2016).* **Figure 3.** *Ca [a.p.f.u.] vs. A-, B-, and C-site content. Q_4-Q_0 as in Figure 1.*
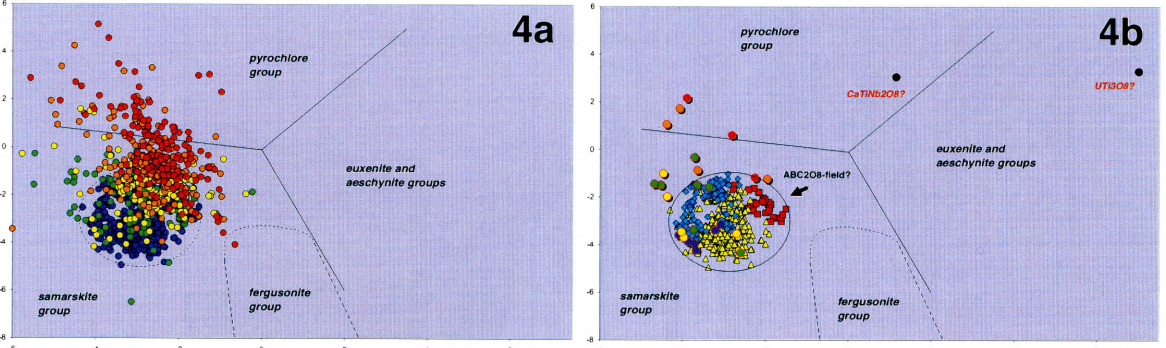

Figure 4. *SGM shown in CV_1-CV_2 three-group diagram of Ercit (2005):* **a -** *Disordering of Q_4-Q_0 (colours as in Figure 1).* **B -** *Species ordering of Q4 samples. red squares, yttrotantalite (30 samples/6 localities); yellow triangles, samarskite (325/20); blue diamonds, ishikawaite (151/10). For comparison/discussion: circles, original "samarskite" samples from Appendix III in Ercit (2005), sorted Q_4-Q_0 (colours as in Figure 1); black filled circles, hypothetic ABC_2O_8-ordered "endmembers".*