# Plumbopyrochlore, ceriopyrochlore-(Ce), wulfenite and andradite from the Gjerdingen ekerite

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### Introduction

A complete list of minerals from miarolitic cavities in ekerite from Gjerdingselva, Lunner, Oppland, was published by Raade (2005). The purpose of the present note is to update the list with four additional minerals: plumbopyrochlore, ceriopyrochlore-(Ce), wulfenite and Mn-rich andradite.

A list of Gjerdingen minerals on the mindat.org website also includes 'apatite' and cerianite-(Ce). It is not known to me who has identified these minerals and by which methods.

# Plumbopyrochlore and ceriopyrochlore-(Ce)

A reconnaissance study of pyrochlore crystals (*in situ* in micromount samples) from the Gjerdingen ekerite was performed in April 2005 by SEM-EDS. Three samples from the Gjerdingen collection of Haug & Raade in the Geological Museum were examined (nos. 52, 146 and 258). Interference from the surrounding minerals makes the interpretation of the spectra problematic. Overlapping peaks of Ta and Si make it difficult to distinguish these two elements. The major elements are Pb and Nb with minor Ti and Ce. Sample 52 has an appreciable amount of F.

A pyrochlore crystal group from Gjerdingselva was analysed with a Cameca SX100 electron probe in May 2006. Wavelength-dispersive (WDS) analyses were performed at 15 kV operating voltage and 15 nA probe current with a focused electron beam. The probe standards and measured peaks were: wollastonite (Ca  $K\alpha$  and Si  $K\alpha$ ), pyrophanite (Mn  $K\alpha$  and Ti  $K\alpha$ ), galena (Pb  $M\alpha$ ), REEPO<sub>4</sub> ( $L\alpha$  lines for La and Ce;  $L\beta$  lines for Pr and Nd), a synthetic glass for U ( $M\alpha$ ) and pure metals for Nb ( $L\alpha$ ) and Ta ( $M\alpha$ ). A small amount of Sm could not be analysed because of interference with Ce. No other elements (in particular not F) were detected in the WDS scans.

The back-scattered electron (BSE) images of two intergrown pyrochlore crystals in Figs. 1 to 3 display a high degree of inhomogeneity. The various shades of grey correspond to variations in chemical composition, the lighter shades indicating higher atomic numbers (i.e. the presence of heavier elements). The electron-microprobe (EMP) analytical work was concentrated on the smaller, lower right crystal which seems to have suffered some sort of secondary alteration along the rim. The analytical results on the medium grey central part and the lighter rim are shown in Table 1 (columns 1 and 2, respectively).

Pyrochlore minerals are extremely diverse in composition and have the general formula  $A_{2-m}B_2X_{6-w}Y_{1-n}$ 

where **A** is typically a large eight-coordinated cation (Na, Ca, Pb, Y, Ce, U, etc.),

B is a smaller six-coordinated cation (Nb, Ta, Ti, etc.),

X is mainly O and Y is typically OH, F or O.

 $H_2O$  can be incorporated at the A and Y sites, and the formula indicates the possibility of incomplete occupancy of the A, X and Y sites. Consequently, the empirical formulae of pyrochlore minerals should be calculated on the basis of  $\mathbf{B} = 2$ .

Such a calculation of the analytical data for the central part of the crystal results in the empirical cation composition

 $(Ce_{0.25}La_{0.09}Nd_{0.07}Pr_{0.02}Ca_{0.14}Mn_{0.06}U_{0.05})_{\Sigma 0.68}(Nb_{1.41}Ti_{0.55}Ta_{0.04})_{\Sigma 2.00}$  [Pb and Si < 0.01]. According to the current IMA classification of pyrochlore minerals (Hogarth 1977), this is a ceriopyrochlore-(Ce).<sup>1</sup>

The rim of the crystal has the empirical cation composition

 $(Pb_{0.42}REE_{0.12}Ca_{0.06}U_{0.05}Mn_{0.02})_{\Sigma0.67}(Nb_{1.08}Si_{0.57}Ti_{0.29}Ta_{0.06})_{\Sigma2.00}.$ 

This is classified as a plumbopyrochlore.

Both minerals have a very low cation occupancy of the A site, where also  $H_2O$  and/or vacancies may be present. Ceriopyrochlore-(Ce) has a higher Ti content than plumbopyrochlore but the most conspicuous difference is in the high Si content of plumbopyrochlore.

Pyrochlore-group minerals with high contents of SiO<sub>2</sub> (up to 16.8 wt.%) are guite common (e.g. Johan & Johan 1994, Uher et al. 1998, Chakhmouradian & Mitchell 2002, Wang et al. 2003, Bonazzi et al. 2006). With few exceptions, Si is fourcoordinated in minerals; it is six-coordinated in stishovite (high-pressure SiO<sub>2</sub>) and in thaumasite (a low-pressure and low-temperature mineral in which Si is surrounded by six OH groups). Incorporation of Si in pyrochlore minerals is problematic since it can only occupy the six-coordinated B site. The problem of Si in pyrochlore structures is not completely resolved; the presence of Si in an amorphous or dispersed state has been suggested. Bonazzi et al. (2006) found, by single-crystal diffraction and transmission electron microscopy, that 30-50% of the Si detected by EMP analysis of pyrochlore from Narssârssuk, Greenland, occupies the octahedral site of the structure of non-metamict material, the remaining major part of the Si being concentrated in radiation-damaged portions. In the calculation above, Si is assumed to substitute at the B site, in accordance with the negative correlation between Si and the sum of the other B cations found by Johan & Johan (1994) and Chakhmouradian & Mitchell (2002). Such a correlation is evident in the analytical data of plumbopyrochlore and ceriopyrochlore-(Ce) in Table 1.

Analytical sums around 89-90 wt.% (Table 1) are quite normal in EMP analysis of pyrochlore minerals. Two analyses (not displayed here) of the darkest regions of Fig. 1 have even lower sums of 82.74 and 80.31 wt.% and  $SiO_2$  contents of 3.30 and 2.18 wt.%. The low summations are apparently due to a pronounced deficiency of REEs compared to the ceriopyrochlore-(Ce) analytical data in Table 1, the PbO contents ranging from 0.23 to 0.45 wt.%. An increased  $H_2O$  content may be assumed for these regions, probably caused by a metamictization process. It should be noted that the Ca and Mn contents in ceriopyrochlore-(Ce) display a large variation as indicated by the high standard deviations (Table 1), and they show a noticeable negative correlation.

## Wulfenite

A micromount sample supplied by Astrid Haugen and Hans Vidar Ellingsen contained a very small, steeply pointed prism of yellow colour, looking suspiciously like wulfenite. An SEM-EDS examination performed in April 2005 indicated the presence of major Mo and Pb in roughly equal atomic proportions, thus confirming the visual

<sup>&</sup>lt;sup>1</sup> A subcommittee of the Commission on New Minerals, Nomenclature and Classification (CNMNC) of the International Mineralogical Association (IMA) has in March 2009 presented a draft of a new pyrochlore-group classification and nomenclature. As a first step, the CNMNC members are invited to comment on the proposal. If necessary, the proposal is redrafted and then sent to the CNMNC members for a final vote. Pyrochlore mineral names are expected to change according to the new nomenclature.

identification as wulfenite. The specimen is now in the collection of the Geological Museum, University of Oslo, donated by the finders.

### Mn-rich andradite

Rhodonite and two associated, unidentified Mn minerals from the Gjerdingen ekerite were reported by Raade & Haug in *Interne Notater, Geologisk Museum* (1983, pp. 116-117). The analyses were performed in November 1982 with an ARL-EMX electron probe equipped with a Link EDS detector. The program ZAF4/FLS was used for data reduction and the calibration element was Co (peak at 6.9242 keV).

It was not always easy to obtain analyses with totals close to 100% with the ARL instrument. For a massive, yellow to brown mineral intergrown with rhodonite, an analysis with sum 99.33 and all iron as FeO was chosen (*loc. cit.*). A recent reassessment of the analytical data with iron as  $Fe_2O_3$  resulted in a close match with a garnet formula.

A second analysis of the mineral with an apparently too low sum of 98.03% was initially rejected. However, converting FeO to  $Fe_2O_3$ , the analytical result is: MgO 0.09, CaO 19.29, MnO 16.81,  $Fe_2O_3$  27.16,  $Al_2O_3$  2.68,  $SiO_2$  34.71, sum 100.74 wt.%.

On the basis of O = 12, the empirical formula is in excellent agreement with that of a garnet:  $(Ca_{1.77}Mn_{1.22}Mg_{0.01})_{\Sigma 3.00}(Fe^{3+}_{1.75}Al_{0.27})_{\Sigma 2.02}Si_{2.98}O_{12}$ .

Consequently, the mineral is a Mn-rich andradite. Disregarding the minor amount of Mg, the composition corresponds to the following mole percentages of end-member garnets: 59% andradite  $[Ca_3Fe^{3+}_2(SiO_4)_3]$ , 29% calderite  $[Mn_3Fe^{3+}_2(SiO_4)_3]$  and 12% spessartine  $[Mn_3Al_2(SiO_4)_3]$ .

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**Table 1**. Electron-microprobe analyses of pyrochlore from the Gjerdingen ekerite (wt.%).

Oxide	1 (n = 5)	St. dev.	<b>2</b> (n = 8)	St. dev.
CaO	2.16	1.03	0.90	0.07
MnO	1.09	1.06	0.30	0.13
PbO	0.11	0.04	24.40	2.66
La <sub>2</sub> O <sub>3</sub>	4.07	0.07	0.72	0.20
Ce <sub>2</sub> O <sub>3</sub>	10.81	0.24	3.65	0.77
Pr <sub>2</sub> O <sub>3</sub>	1.05	0.14	0.28	0.15
$Nd_2O_3$	2.99	0.25	0.51	0.18
UO <sub>2</sub>	3.38	0.57	3.21	0.99
SiO <sub>2</sub>	0.06	0.02	8.75	0.65
TiO <sub>2</sub>	11.68	0.27	6.02	0.64
Nb <sub>2</sub> O <sub>5</sub>	50.36	1.35	37.13	1.47
Ta <sub>2</sub> O <sub>5</sub>	2.11	0.19	3.45	0.34
Sum	89.87	1.27	89.32	1.88

<sup>1 –</sup> Ceriopyrochlore-(Ce)

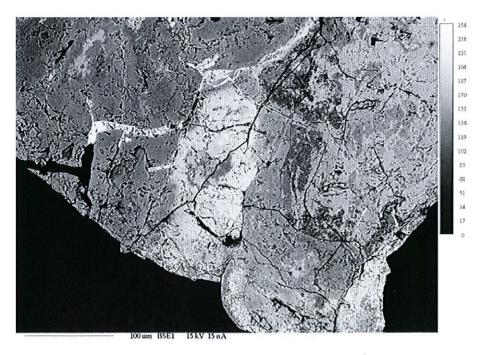
<sup>2 –</sup> Plumbopyrochlore

n – Number of single analyses

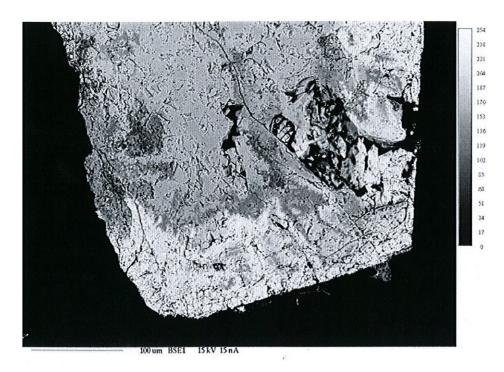
St. dev. - Standard deviation



**Fig. 1**. Back-scattered electron (BSE) image of two intergrown pyrochlore crystals from the Gjerdingen ekerite. Details of the lower parts are shown in Figs. 2 and 3.



**Fig. 2**. BSE image of pyrochlore from the Gjerdingen ekerite. Detail of the lower left part of Fig. 1.



**Fig. 3**. BSE image of pyrochlore from the Gjerdingen ekerite. Detail of the lower right part of Fig. 1.