# Arsenoflorencite-(Ce): a new arsenate mineral from Australia

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## Abstract

Arsenoflorencite-(Ce) has been found at three localities in Australia—two in South Australia, and one in Queensland. It occurs as colourless to light brown scalenohedral crystals and crystal fragments in stream sediments. Electron microprobe analysis gave $Ce_2O_3$ 12.97, $La_2O_3$ 8.62, $Pr_2O_3$ 3.35, $Nd_2O_3$ 2.40, $Gd_2O_3$ 1.38, $Sm_2O_3$ 0.38, SrO 1.99, $Al_2O_3$ 28.75, $As_2O_5$ 27.02, $P_2O_5$ 4.68, $SO_3$ 1.21%; calc, $H_2O$ 9.36%; total 102.11%. The simplified formula is $RE\mathrm{Al}_3(\mathrm{AsO}_4)_2(\mathrm{OH})_6$, with Ce as the dominant *RE* element. Arsenoflorencite-(Ce) is rhombohedral, has space group $R3m$ with $\alpha_{\mathrm{hex.}}$ 7.029 and $c_{\mathrm{hex.}}$ 16.517 Å, and $Z = 3$. Strongest X-ray powder diffraction lines are: 3.513(6)(110), 2.963(10)(113), 2.201(4)(107), 1.905(5)(303) and 1.753 Å(4)(220). Density is 4.096 (meas.) and 4.091 (calc.) g/cm$^3$. Hardness is $\mathrm{VHN}_{10}$ 170. Arsenoflorencite-(Ce) is brittle, breaks with a conchoidal fracture, and has no perceptible cleavage. The mineral is colourless in transmitted light, uniaxial positive, and has $\omega$ 1.739 and $\varepsilon$ 1.745 ($\lambda = 589$ nm). Arsenoflorencite-(Ce) is the arsenate analogue of florencite-(Ce), and the name was chosen to indicate this relationship.

KEYWORDS: arsenoflorencite-(Ce), arsenates, florencite-(Ce), new mineral, South Australia, Queensland, Australia.

## Introduction

DURING the microscopic examination of heavy-mineral concentrates from stream-sediment samples collected during mineral exploration, one of the authors (J.E.T.) found a colourless rhombohedral crystal similar to florencite-(Ce), but with appreciably higher refractive indices. When it was found to contain substantial amounts of As, in addition to Ce and Al, the crystal, and some others found later, were submitted to the CSIRO laboratories where the other author (EHN) determined the properties of the mineral, and established that it was a new mineral.

The new mineral was originally recovered from a stream-sediment sample taken on the Kimba 1:250 000 mapsheet on the Eyre Peninsula in South Australia; this locality will be referred to as Locality 1. The trap site from which the sample was taken is formed by units of the Lower Proterozoic Hutchinson Group which consists of quartzite, quartz–sericite schist and minor amphibolite and iron formation. The heavy-mineral concentrate in which the new mineral was found consisted of about 50% multimineralic rock fragments, 10–20% martite (altered magnetite), 3–10% tourmaline, 1–3% of each of amphibole, garnet and sillimanite, minor amounts of ilmenite and apatite, and a few grains of biotite, epidote, rutile, zircon, spinel, xenotime and arsenoflorencite-(Ce).

Arsenoflorencite-(Ce) was subsequently found at two other localities. One was from a stream-sediment sample taken on the diagonally adjacent Port August 1:250 000 mapsheet, also in South Australia (Locality 2). This second sample was derived from the Carpentarian Corunna Conglomerate, and consisted mainly of limonite and rock fragments, minor amounts of barite, ilmenite, rutile, tourmaline and arsenoflorencite-(Ce), and a few grains of epidote, garnet, kyanite and zircon.

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The third occurrence of arsenoflorencite-(Ce) was in a sample taken in the area of the Northern Territory/Queensland border, on the edge of the Westmoreland 1:250 000 mapsheet near the Gulf of Carpentaria (Locality 3). This sample consisted mainly of rock fragments and leucoxene, 3–10% each of hematite and limonite, minor amounts of cassiterite, martite, rutile and zircon, and a few grains of anatase, ilmenite, monazite and arsenoflorencite-(Ce).

The name arsenoflorencite-(Ce) was given to the mineral because it is the arsenic analogue of florencite and because Ce is the predominant rare-earth element. Both the mineral and the name have been approved by the I.M.A. Commission on New Minerals and Mineral Names. Specimens have been deposited with the Museum of Victoria in Melbourne, the Smithsonian Institution in Washington, and the British Museum (Natural History) in London.

## General description

The grains of arsenoflorencite-(Ce) occur as euhedral to subhedral crystals and crystals fragments from 0.2 to 0.5 mm in diameter. The crystals are scalenohedral (Fig. 1*a*) and exhibit {102} and {101} forms. Most of the grains are creamy-white to tan in colour, with a cloudy, translucent appearance, but some are clear and colourless, including the crystal shown in Fig. 1*a*.

Many of the grains of arsenoflorencite-(Ce), particularly those from Locality 2, are partially to completely covered by a thin coating of one or more other minerals, of which alunite (Fig. 1*b*) appears to be the most common one. Others include quartz, florencite-(Ce) (Fig. 1*c*) and what appears to be the La-rich analogue of arsenoflorencite-(Ce). Some of the grains of arsenoflorencite-(Ce) also contain inclusions, mainly of quartz (Fig. 1*c*) and alunite (Fig. 1*d*). One composite grain was found to consist partly of arsenoflorencite-(Ce) with alunite inclusions, and partly of an intimate intergrowth of alunite and the La-rich analogue of arsenoflorencite-(Ce) (Fig. 1*d*).

## Chemical composition

A fragment of a crystal from Locality 1 was mounted in plastic, sectioned and polished. The polished section was then analysed by electron microprobe using a defocused beam, since it was evident that the mineral decomposes under a sharply focused beam. The analytical procedure involved the use of crystal spectrometers and the following standards: synthetic GaAs (As) synthetic glasses (La, Pr, Nd, Sm and Gd), synthetic Ce oxide (Ce), synthetic alumina (Al), strontianite (Sr), apatite (P) and pyrite (S). Corrections were made by means of the MIDAS computer program (Colby, 1971). Because the Pr-$L\alpha_1$ emission peak is overlapped by that of La-$L\beta_1$, the Pr counts were corrected according to the procedure recommended by Roedder (1985). Water content was calculated from the amount of OH necessary to maintain charge neutrality. The analytical results are shown in Table 1, together with the atomic proportions calculated on the basis of $Al + As + P + S = 5$.

Table 1 shows that the total number of Al atoms is 3.2, and the sum of $As + P + S$ is 1.8, rather than 3.0 and 2.0, respectively, as would be expected from a mineral related to florencite-(Ce). Assuming that the microprobe analysis is correct, it is necessary to shift 0.2 atoms Al to the anionic group if full site occupancies are to be maintained. This suggests partial substitution of tetrahedral $(AlO_4)$ for $(AsO_4)$. Although this type of substitution has apparently not been reported heretofore, the ionic radii of tetrahedral $Al^{3+}$ and $As^{5+}$ are sufficiently close (0.51 Å and 0.46 Å, respectively) to make this type of substitution plausible. The empirical formula derived from the analytical results of Table 1 can therefore be written as follows:

$$(Ce,La,Pr,Sr,Nd,Gd,Sm)_{1.115}Al_{3.000}(As,P,Al,S)_{2.000}O_{8.000}(OH)_{5.908}.$$

The simplified formula is $(Ce,La)Al_3(AsO_4)_2(OH)_6$ which (with $Ce:La = 0.6:0.4$) requires $Ce_2O_3$ 16.40, $La_2O_3$ 10.85, $Al_2O_3$ 25.47, $As_2O_5$ 38.28, $H_2O$ 9.00%.

## Physical and optical properties

The density of arsenoflorencite-(Ce) determined by suspension in Clerici Solution, is 4.096 g/cm$^3$. Its indentation hardness, using a 10-gram load, is VHN 170. The mineral is brittle, and breaks with a conchoidal fracture; no cleavage was observed.

Arsenoflorencite-(Ce) varies from colourless to light brown, and from transparent to translucent. It does not exhibit appreciable fluorescence in ultraviolet light, nor cathodoluminescence under an electron beam. In transmitted light the mineral is uniaxial positive, with $\omega$ 1.739 and $\varepsilon$ 1.745 in monochromatic light with $\lambda = 589$ nm. The compatibility between measured and calculated refractive indices, derived by means of the

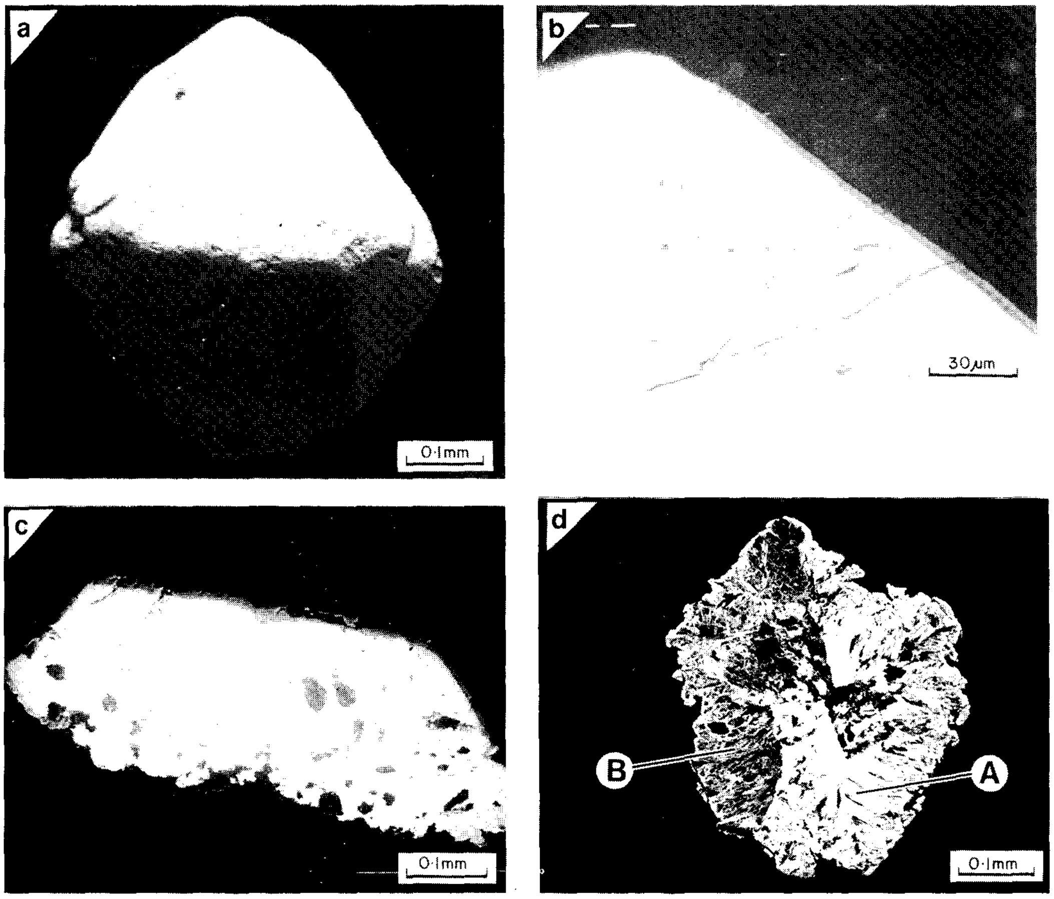

FIG. 1. SEM micrographs. (*a*) Euhedral crystal of arsenoflorencite-(Ce) from Locality 1. (*b*) Polished section of arsenoflorencite-(Ce) (light grey) with a thin coating of alunite (medium grey) from Locality 2. (*c*) Polished section of arsenoflorencite-(Ce) crystal (white) with abundant quartz inclusions (dark grey), and rimmed on the upper surface by florencite-(Ce) (light grey), from Locality 2. (*d*) Polished section of a complex grain consisting partly of arsenoflorencite-(Ce) (marked 'A') with linear inclusions of alunite (dark grey) and partly of an intimate intergrowth of alunite and the La analogue of arsenoflorencite-(Ce) (marked 'B'), from Locality 2.

Gladstone–Dale calculation (Mandarino, 1976), is 0.016, which is regarded as superior (Mandarino, 1979).

### Crystallography

Attempts were made by Dr P. G. Slade of the CSIRO Division of Soils in Adelaide, South Australia, to obtain a usable single-crystal diffraction pattern to determine the space group and, hopefully, the crystal structure. Unfortunately, none of the crystals examined was suitable because they consist of numerous mis-oriented crystal domains. However, the powder diffraction pattern (Table 2) is very similar to that of minerals of the florencite group, and it is therefore reasonable to conclude that arsenoflorencite-(Ce), like other minerals in the group, crystallizes in space group $R\bar{3}m$. The unit-cell parameters, obtained by least-squares calculation from the powder pattern, are *a* 7.029 and *c* 16.517 Å (hexagonal cell), which gives a unit-cell volume of 706.8 Å$^3$. With Z = 3, and a composition as given in Table 1, the calculated density is 4.091 g/cm$^3$, which is in very close agreement with the measured density. Both the *a* and *c* unit-cell dimensions are slightly larger than that of florencite-(Ce) (Table 3), which can

Table 1. Electron microprobe analysis of arsenoflorencite-(Ce) (average of 3 analyses)

| | Weight % | Standard Deviation | | Atomic Proportions |
|---|---|---|---|---|
| $Ce_2O_3$ | 12.97 | 0.29 | Ce | 0.449 |
| $La_2O_3$ | 8.62 | 1.37 | La | 0.301 |
| $Pr_2O_3$* | 3.35 | 0.86 | Pr | 0.115 |
| $Nd_2O_3$ | 2.40 | 0.24 | Nd | 0.081 |
| $Gd_2O_3$ | 1.38 | 0.13 | Gd | 0.043 |
| $Sm_2O_3$ | 0.38 | 0.11 | Sm | 0.012 |
| SrO | 1.99 | 0.59 | Sr | 0.114 |
| $Al_2O_3$ | 28.75 | 0.35 | Al | 3.204 |
| $As_2O_5$ | 27.02 | 1.15 | As | 1.337 |
| $P_2O_5$ | 4.68 | 0.53 | P | 0.374 |
| $SO_3$ | 1.21 | 0.05 | S | 0.085 |
| $H_2O$ (calc.) | 9.36 | | OH | 5.908 |
| | 102.11 | | | |

* Corrected for 12.4% overlap between the $Pr_{L\alpha 1}$ and $La_{L\beta 1}$ peaks. (Roedder, 1985)

Table 2.

X-ray powder diffraction data for arsenoflorencite-(Ce) (Analyst Dr P.G. Slade)

| $d_{obs}$ | $d_{calc.}$ | hkℓ | I/Io |
|---|---|---|---|
| 5.715 | 5.712 | 101 | 1 |
| 5.489 | 5.506 | 003 | 2 |
| 4.901 | 4.900 | 012 | 1 |
| 3.513 | 3.515 | 110 | 6 |
| 2.963 | 2.963 | 113 | 10 |
| 2.857 | 2.856 | 202 | 1 |
| 2.752 | 2.752 | 006 | 3 |
| 2.451 | 2.450 | 024 | 2 |
| 2.201 | 2.200 | 107 | 4 |
| 2.169 | 2.167 | 116 | 2 |
| 2.006 | 2.010 | 214 | 2 |
| 1.905 | 1.904 | 303 | 5 |
| 1.753 | 1.757 | 220 | 4 |
| 1.676 | 1.680 | 131 | 2 |
| 1.651 | 1.654 | 312 | 1 |
| 1.627 | 1.633 | 306 | 3 |
| 1.594 | 1.594 | 10.1.0 | 1 |
| 1.539 | 1.538 | 307 | 1 |
| 1.482 | 1.481 | 226 | 3 |
| 1.452 | 1.452 | 20.1.0 | 3 |
| 1.431 | 1.428 | 404 | 1 |
| 1.375 | 1.373 | 137 | 2 |
| 1.361 | 1.361 | 309 | 2 |
| 1.330 | 1.328 | 140 | 2 |
| 1.293 | 1.291 | 143 | 3 |

Pattern obtained by an 11.46 cm Gandolfi camera using $CuK_{\alpha}$ radiation.

be attributed to the replacement of $P^{5+}$ in florencite-(Ce) by the larger $As^{5+}$ ion in arsenoflorencite-(Ce). In comparison with related arsenates, such as arsenogoyazite and arsenocrandallite, in which one of the arsenate ions is protonated, the *c*-parameter of arsenoflorencite-(Ce) is appreciably less.

## Discussion

Minerals of the florencite and crandallite groups are closely related because they have rhombohedral or pseudo-rhombohedral symmetry (Radoslovich and Slade, 1980) and similar unit-cell dimensions. However, minerals in these two groups are distinguished by the valency of the cation in the large 8-coordinated site and the related protonation, or lack of it, of one of the anions. If florencite-(Ce) is taken as the prototype, charge balance in the formula $CeAl_3(PO_4)_2(OH)_6$ is maintained without protonation. However, if $Ce^{3+}$ is replaced by $Ca^{2+}$, as in crandallite, $CaAl_3H(PO_4)_2(OH)_6$, then a hydrogen ion (proton) is required to restore charge balance. Since the 8-coordinated site in arsenoflorencite-(Ce) is occupied largely by trivalent rare-earth elements, this mineral is evidently a member of the florencite group. Arsenoflorencite-(Ce) appears to be the first example of an arsenate-dominant member of the group.

A few of the crystals also contain what appears to be the La-dominant member of the group, but this supposition cannot be confirmed because the particles of this mineral are too small for X-ray diffraction analysis.

Since arsenoflorencite-(Ce) has so far been found only in detrital grains, its petrogenetic significance cannot be assessed with confidence, but the presence of quartz inclusions suggests that the mineral crystallized in a silicic environment. However, its occurrence in complex grains like the one shown in Fig. 1*d* indicates that some grains, at least, have had a complex history.

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Table 3. The unit-cell parameters of arsenoflorencite-(Ce) and some related minerals.

| Name | Formula | $a$(Å) | $c$(Å) | Reference |
|---|---|---|---|---|
| Florencite-(Ce) | $CeAl_3(PO_4)_2(OH)_6$ | 6.979 | 16.25 | Lefebvre & Gasparrini, 1980 |
| Arsenoflorencite-(Ce) | $CeAl_3(AsO_4)_2(OH)_6$ | 7.029 | 16.517 | this paper |
| Arsenogoyazite | $SrAl_3H(AsO_4)_2(OH)_6$ | 7.10 | 17.16 | Walenta & Dunn, 1984 |
| Arsenocrandallite | $CaAl_3H(AsO_4)_2(OH)_6$ | 7.08 | 17.27 | Walenta, 1981 |

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