

Zoned hibonites from Punalur, South India

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Abstract

Zoned hibonites from a kalsilite, leucite, spinel, corundum, perovskite gneiss from the southern Indian granulite terrain near Punalur, Kerala, have rims that are the most Ti-rich yet recorded (0.83–0.87 Ti atoms per 19 O) and are essentially free of REE elements ($\Sigma REE < 0.01$ atoms per 19 O) while the cores are the most REE-rich compositions yet recorded ($\Sigma REE = 0.55$ – 0.65 atoms per 19 O). Within the limits of analytical uncertainty, the compositions of the hibonite can be related to the theoretical end-member $\text{CaAl}_{12}\text{O}_{19}$ by the substitutions $REE R^{2+} \rightleftharpoons \text{CaAl}$ and $R^{2+}R^{4+} \rightleftharpoons \text{Al}_2$ with the REE-rich cores containing in excess of 50% of the REE $R^{2+}\text{Al}_{11}\text{O}_{19}$ end member. Minor substitution of Na for Ca occurs in the rims, while non-stoichiometry in both the cores and rims is indicated by partial 12-fold site occupancy. Ion-microprobe analysis of the REE-rich hibonites reveals strong enrichment in LREE with La/Lu *c.* 250 000.

KEYWORDS: hibonite, rare earth elements, titanium, zoning, ion-microprobe analysis, India.

Introduction

HIBONITE ($\text{CaAl}_{12}\text{O}_{19}$) is a rare mineral of the magnetoplumbite group, found principally in carbonaceous chondrites (e.g. Burns and Burns, 1984). Terrestrial occurrences are restricted to four localities in metamorphosed calcareous rocks (Curien *et al.*, 1956; Kuzmin, 1960; Yakovlevskaya, 1961; Maaskant *et al.*, 1980). Reported analyses show that terrestrial, unlike meteoritic hibonites, contain appreciable rare earth element (REE) concentrations, with the REE replacing Ca on the 12-fold coordination site. Both terrestrial and meteoritic forms contain appreciable Ti, Fe and Mg. In this contribution we report a new terrestrial occurrence from the southern Indian granulite terrain near Punalur, Kerala. This includes strongly zoned hibonites that greatly extend the known compositional range of terrestrial hibonites. In particular they include a new REE-rich end-member. The origin and petrogenesis of this unique rock are discussed

in greater detail elsewhere (Sandiford and Santosh, 1990).

The hibonite occurs as brown prisms up to 3 mm long in aggregates with spinel and corundum in an exceptionally aluminous gneiss (>50% Al_2O_3 by weight, Sandiford and Santosh, 1990), forming part of a sequence of supracrustal gneisses (khondalites and leptynites) interlayered with charnockites. Other phases in the rock include kalsilite, leucite, K-feldspar, perovskite, sphene, apatite, and phlogopite (Sandiford and Santosh, 1990). Most hibonite is optically homogeneous with compositions essentially free of REE (see below); however abrupt zoning is preserved in the cores of some grains and in rims developed around inclusions of apatite (Fig. 1).

Analytical data

Electron microprobe data for the zoned hibonites are presented in Table 1, while an ion

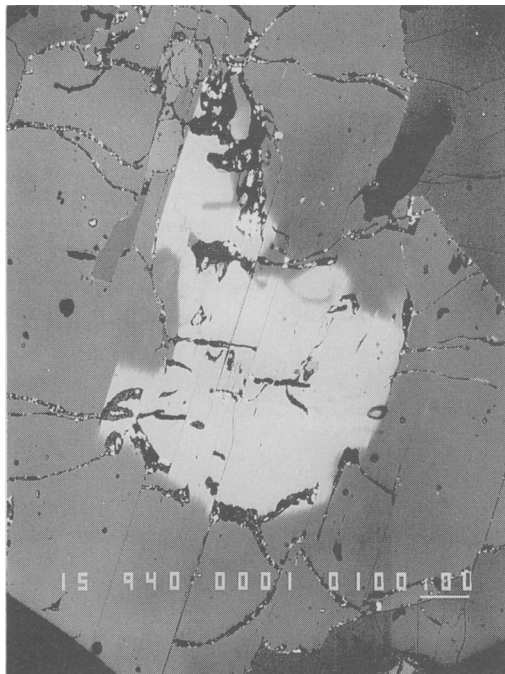


Fig. 1. Backscattered electron image of the zoned Punalur hibonite, showing a central *REE*-rich core surrounded by a *REE*-free rim. Bar scale is 100 μm .

microprobe analysis of *REE* concentrations of the hibonite core shown in Fig. 1 is presented in Table 2. Because of the possibility of non-stoichiometry in the Punalur hibonites (see below) we have made no attempt to estimate Fe^{3+} . The electron microprobe analyses were performed at the Australian National University, Dept of Geology, using a Cameca instrument. The ion microprobe analyses were performed at the University of Cambridge (Department of Earth Sciences) using an AEI 1M-20 instrument. The method of analysis was similar to that used for apatite as described elsewhere (Reed, 1986). The intensities of selected isotopic peaks of La, Pr, Nd, Sm and Eu were measured relative to Ce, and oxide peaks of Gd, Tb, Dy and Ho were measured relative to CeO. The intensity ratios (after correction for isotopic abundance) were converted to concentration ratios using relative yield factors derived from measurements made on synthetic silicate glass standards. The Ce/Ca ratio was measured on rim and core areas, with a beam diameter of about 15 μm , enabling the Ce concentration in the *REE*-poor rim to be estimated, the Ca concentration of the rim having been determined by electron probe analysis.

The analyses show a dramatic change in the *REE* content from rim to core, corresponding to the optical zoning. The *REE* content in the rims is beneath the detection limit of the electron microprobe. Ion microprobe analysis showed $(\text{Ce}/\text{Ca}_{\text{core}})/(\text{Ce}/\text{Ca}_{\text{rim}})$ *c.* 800 corresponding to *c.* 0.001 Ce atoms per 19 oxygens. Such low concentrations of *REE* distinguish the Punalur hibonite rims from other terrestrial occurrences (e.g. Maaskant *et al.*, 1980), which all contain significant *REE*. In contrast, the concentration of *REE* in the cores of the Punalur hibonites ($\Sigma\text{REE}^{\text{xii}} = 0.55\text{--}0.65$) greatly exceeds previously analysed terrestrial hibonites, with the cores containing in excess of 50% of the *REE* end-member (see below). The ion microprobe data show that the hibonite cores are strongly enriched in *LREE* with La/Dy *c.* 682 and La/Lu *c.* 250 000 (where the concentration of Dy is the actual measured value and that of Lu has been extrapolated; see Table 2).

The Punalur hibonite rims are further distinguished from previously analysed hibonites by the presence of minor Na (Table 1) which is assumed to occupy the 12-fold coordination site. In both cores and rims the 12-fold coordination site appears to be only partially filled ($\text{xii-occupancy} = 0.89\text{--}0.95$).

Substitution mechanisms

The chemistry of Punalur hibonite is dictated by the substitutions (Fig. 2): $\text{REE } R^{2+} \rightleftharpoons \text{Ca Al}$ and $R^{4+}R^{2+} \rightleftharpoons \text{Al}_2$, where R^{2+} includes Mg^{2+} and Fe^{2+} , and R^{4+} includes Ti^{4+} and Si^{4+} . Thus, in accord with previous studies (Maaskant *et al.*, 1980) the analyses presented here allow that *REE* substitution for Ca on the 12-fold site is coupled with the substitution of Al by Mg and possibly Fe on one or more of the (five) tetrahedral, five-fold and octahedral coordination sites. The theoretical *REE* end-member composition is therefore $\text{REE } R^{2+} \text{Al}_{11}\text{O}_{19}$.

The site preferences for Mg and Fe^{2+} (as well as Fe^{3+}) in natural hibonites are only poorly understood. Previous studies of *REE*-bearing hibonites (e.g. Burns and Burns, 1984) suggest that Mg, Fe^{2+} and Fe^{3+} are preferentially accommodated on tetrahedral and five-fold coordination sites. However the data on the Punalur hibonites do not allow unequivocal assessment of such details, particularly since the possibility of non-stoichiometry precludes the determination of ferric/ferrous ratios.

Table 1

Electron microprobe analyses of Punalur hibonite cores and rims. Structural formulae have been recalculated on the basis of 19 oxygens.

	core			rim		
SiO ₂	0.15	0.14	0.09	0.24	0.25	0.28
TiO ₂	2.05	1.99	1.36	9.89	9.49	9.76
Al ₂ O ₃	77.32	76.78	76.28	74.43	74.87	74.62
FeO	1.98	1.98	1.96	2.72	2.62	2.69
MnO	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03
MgO	3.34	3.24	3.32	2.72	2.62	2.69
CaO	2.53	2.59	2.14	6.53	7.11	6.77
Na ₂ O	0.08	0.08	0.03	0.32	0.24	0.30
Y ₂ O ₃	<0.03	<0.03	<0.03	<0.02	<0.02	<0.02
Ce ₂ O ₃	7.34	7.44	8.21	<0.01	<0.01	<0.01
La ₂ O ₃	4.64	4.68	5.48	<0.01	<0.01	<0.01
Nd ₂ O ₃	<0.06	<0.06	<0.06	<0.02	<0.02	<0.02
Yb ₂ O ₃	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Sm ₂ O ₃	0.11	0.13	0.10	<0.02	<0.02	<0.02
Total	99.54	99.06	98.99	98.07	98.23	98.20
Si	0.018	0.017	0.012	0.028	0.029	0.032
Ti	0.188	0.184	0.127	0.871	0.827	0.858
Al	11.088	11.085	11.120	10.269	10.312	10.280
Fe	0.202	0.203	0.203	0.266	0.256	0.263
Mn	0.000	0.0000	0.001	0.003	0.003	0.003
Mg	0.606	0.593	0.613	0.661	0.644	0.650
Ca	0.330	0.340	0.283	0.832	0.890	0.849
Na	0.020	0.018	0.007	0.072	0.055	0.068
Ce	0.327	0.334	0.372	0.000	0.000	0.000
La	0.208	0.212	0.250	0.000	0.000	0.000
Sm	0.004	0.006	0.004	0.001	0.000	0.000
Σ Ca site	0.889	0.910	0.916	0.905	0.945	0.917
Total	12.990	12.990	12.992	13.002	13.015	13.003

Table 2

Atomic concentrations of REE in Punalur hibonite core measured relative to Ce. Concentrations from Er to Lu have been extrapolated.

La	0.75
Ce	1.0
Pr	0.06
Nd	0.17
Sm	0.014
Eu	0.00063
Gd	0.0034
Tb	0.0032
Dy	0.0011
Ho	0.00011
Er	0.000016
Tm	0.000011
Yb	0.000039
Lu	0.000003

Discussion

The Punalur hibonite provides the first terrestrial occurrence of REE-free hibonite and implies the existence of a REE-free hibonite stability field in the metamorphic environment. REE-free hibonite is similar in composition to spinel–corundum–titanite, an assemblage that occurs in the metamorphic environment over a range of P – T conditions. Pelitic gneisses from Punalur record metamorphic temperatures of 700–800 °C and pressures of 3.5–6.5 kbar, estimates which are consistent with the occurrence of leucite with the hibonite (Sandiford and Santosh, 1990), implying that the breakdown of the spinel–corundum–titanite association by divariant reaction to form hibonite (Sandiford and Santosh, 1990) may be a feature of the low-pressure granulite-facies environments.

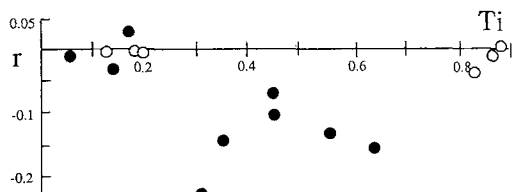


FIG. 2. Ti vs. r where r is the deviation from compositions defined by $\text{CaAl}_{12}\text{O}_{19}$ combined with the substitutions $\text{REE R}^{2+}\text{R}^{4+}\text{Al}_2$:

$$r = \text{Al} - [12 - 2(\text{Ti} + \text{Si}) - \Sigma\text{REE}].$$

The deviation of the Punalur hibonites (shown by open circles) lies within the analytical uncertainty of the theoretical composition. Closed circles are meteoritic hibonites from Burns and Burns (1984).

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References

- Burns, R. G. and Burns, V. M. (1984) Crystal chemistry of meteoritic hibonites, *Proc 15th Lunar Planet. Sci. Conf., J. Geophys. Res. supplement*, **89**, C313–21.
- Curien, H., Guillemin, C., Orceel, J., and Sternberg, M. (1956) La hibonite, nouvelle espece minerale. *C.R. Acad. Sci. Paris*, **242**, 2845–7.
- Kuzmin, A. M. (1960) Hogbomite from Gornaya Shoriya. *Geol. Geof.* **4**, 63–75.
- Maaskant, P., Coolen, J. J. M. M. M., and Burke, E. A. J. (1980) Hibonite and coexisting zoisite in a calcisilicate granulite from southern Tanzania. *Min. Mag.* **43**, 995–1003.
- Reed, S. J. B. (1986) Ion microprobe determination of rare earth elements in accessory minerals. *Mineral. Mag.* **50**, 3–15.
- Sandiford, M. and Santosh, M. (1990) A granulite facies kalsilite–leucite–hibonite association from Punalur, southern India. *Min. Petrol.* (in press).
- Yakovlevskaya, T. A. (1961) Hibonite from Gornaya Shoriya. *Zap. Vses. Min. Obshch.* **90**, 458–61.

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