

New INAA analysis of a mantle-derived titanate mineral of the crichtonite series, with particular reference to the rare earth elements

A. P. JONES¹

*Division of Geological and Planetary Sciences
California Institute of Technology, Pasadena, California 91125*

AND V. EKAMBARAM

*Department of Geophysical Sciences
University of Chicago, Chicago, Illinois 60637*

Abstract

Titanate minerals of the crichtonite series ($AM_{21}O_{38}$, A = Sr in crichtonite; M = Ti, Fe, Cr) reported from mantle peridotite xenoliths associated with kimberlites appear to be solid solutions of several named end members (mostly Ba, Sr, K, Ca) that contain some rare earth elements (REE). Knowledge of the REE distribution in these titanates could be very important for geochemical modelling of the upper mantle. An instrumental neutron activation analysis (INAA) was obtained for a single titanate grain from a typical veined peridotite xenolith from kimberlite. The data support original electron probe REE analyses showing enrichment in the light REE. The absence of significant heavy REE disagrees with recent structural interpretation for the analogous Ba and K end members (lindsleyite, mathiasite respectively) based on a bimodal light and heavy REE distribution. Similar structural interpretation of bimodal REE in the Ca end member (loveringite) is reexamined and also considered doubtful.

Introduction

Two new members of the crichtonite group found in mantle peridotite xenoliths (Jones et al., 1982; Smyth et al., 1978) were recently named by Haggerty et al. (1983). These are lindsleyite and mathiasite, the Ba and K members of the $AM_{21}O_{38}$ series, where A is the name-specific large radius cation, and M = Ti, Fe, Cr (mostly). Both are potentially important reservoirs for REE and large ion lithophile (LIL) elements in the upper mantle and may also form rare discrete nodules in a few kimberlites (Haggerty, 1983). They appear to be related to metasomatic fluids of a kimberlitic nature (Jones et al., 1982) or to kimberlites themselves. The Ca end member, loveringite, occurs as an accessory phase in layered ultrabasic intrusions and was described by Campbell and Kelly (1978). They reported an apparently bimodal REE distribution, which was interpreted in terms of two distinct structural sites. Similarly, the Ba and K end members were reported to contain both light and heavy REE (Haggerty et al., 1983). By analogy with loveringite, the apparent bimodal REE in mathiasite and lindsleyite were interpreted to indicate partitioning of the REE between two distinct structural sites (Haggerty, 1983).

In this paper we show that a single grain of the Ba–Sr–Ca-titanate from Bultfontein is light REE-rich, and poor in

the heavy REE, with abundances very similar to electron probe analyses originally reported by Jones et al. (1982). Inspection of different electron probe data presented by Haggerty et al. (1983) for both mathiasite and lindsleyite, reveals inconsistencies in characteristic odd–even abundances of the REE, whether they are rationalized either in terms of chondritic or terrestrial values. Such electron probe errors in the heavy REE could have resulted both from interferences (eg: Exley, 1980) and from poorly constrained background contributions. Electron probe data for the heavy REE are also considered unreliable in the earlier descriptions of loveringite (Campbell and Kelly, 1978; Table IV). It appears that their interpretation may have been influenced by the previous spectrographic determination of bimodal REE in the related mineral davidite (Hayton, 1960).

In addition to providing new chemical data, we also tabulate additional X-ray lines for the titanate, which is compositionally closer to lindsleyite, the Ba end member (Haggerty et al., 1983). Lindsleyite has recently been synthesized under both dry and hydrothermal conditions at a temperature of 900°C and pressure of 22 kbar (Podpora and Lindsley, 1984).

Sample studied

The grain studied was obtained from a phlogopite-rich vein in a peridotite xenolith from Bultfontein Mine, S. Africa, originally collected by J. B. Dawson (sample

¹ Present address: School of Geology, Penrhyn Road Centre, Kingston Polytechnic, Kingston Upon Thames, England KT1 2EE.

BD3094). The rounded grain measured approximately 50 by 100 μm and was selected as the largest of several similar grains released from crushing approximately 1 cm^3 of sample 3094. A preliminary analysis of the same mineral from a probe section from elsewhere in the same xenolith gave Ce as undetected (Jones et al., 1982). Repeated probe analyses of additional grains using higher energy conditions (see footnote to Table 2) gave La, Ce, Nd and Y within the ranges for the same minerals associated with several veined peridotites from Bultfontein (Jones et al., 1982). The grain was cleaned in double distilled water, acetone and ethanol. It was black in color with a uniform luster, and was optically free from its original phlogopite host. Physical and optical properties for the grain are as described by Haggerty et al. (1983). It is a typical sample of the titanate minerals which characterize seven of the fourteen veined peridotite xenoliths from the Bultfontein kimberlite studied by Jones et al. (1982).

Analytical procedure

X-Ray

For the purposes of X-ray determination the grain was mounted in a Gandolfi camera and X-ray powder diffraction patterns obtained with Ni-filtered $\text{CuK}\alpha$ radiation, where quartz was used as an internal standard. Contrary to data for crichtonite (Grey et al., 1976), the patterns are inconsistent with a space group of $R\bar{3}$ or $R\bar{3}$. Refinement of our data (D. H. Lindsley, personal communication 1984) suggests a hexagonal unit cell similar to that recently obtained for synthetic lindsleyite (Podpora and Lindsley, 1984) and such indices are given in Table 1.

INAA

The titanate mineral was analyzed by instrumental neutron activation analysis (INAA) following a procedure similar to that of Davis et al. (1978). The first radiation was designed to determine Mg, Al, Ca, Ti, Mn, V and Dy. Johnson-Matthey Specpure MgO , Al_2O_3 , CaCO_3 and TiO_2 , Standard Pottery SP (Perlman and Asaro, 1969), BCR-1, Suprasil SiO_2 and the sample were each weighed at least ten times with a Perkin-Elmer AD-2Z electronic microbalance, and sealed in pouches weighing 0.73–2.1 mg made from HNO_3 -washed, Dow-530 polyethylene film. They were individually irradiated at the University of Missouri Research Reactor (MURR) for 5 minutes at a flux of 1.0×10^{14} $\text{n}\cdot\text{cm}^{-2}\cdot\text{sec}^{-1}$, using a pneumatic transfer system. After a 10 minute cooling period, each was counted for 500 seconds for ^{27}Mg , ^{28}Al , ^{49}Ca , ^{51}Ti and ^{52}V using a high efficiency Ge(Li) detector, coupled to a 8192 channel pulse-height analyzer. After 2.5–7.1 hours they were counted again for 10^3 seconds for ^{56}Mn and ^{163}Dy . Neutron flux variations were monitored by periodically irradiating Co-doped aluminum wires and counting ^{60}Co several days later, but corrections were not necessary since the maximum deviation in thermal flux was only 2.5%. The counting data for Specpure Al_2O_3 and Suprasil SiO_2 were used to correct for the following interfering fast neutron reactions: $^{27}\text{Al}(\text{n,p})^{27}\text{Mg}$, and $^{28}\text{Si}(\text{n,p})^{28}\text{Al}$.

The second irradiation was for longer-lived activation products. The sample was reweighed and sealed into a Suprasil vial weighing 12.1 mg. New samples of SP and BCR-1 were prepared in the same manner. A standard solution of each REE was prepared as outlined by Davis et al. (1982) and were then combined into two separate standard solutions; one for La, Eu, Tb, Ho, Tm and Yb,

Table 1. X-ray diffraction patterns for titanate 3094 compared with lindsleyite

titanate 3094			lindsleyite	
hkl	d	I	d	I
(113), (005)	4.13			
(105)	3.75			
(204)	3.37	m	3.37	30
(205)	3.03	s	3.04	40
(300)	2.993			
(302), (116)	2.877	s	2.87	70
(214)	2.840	m	2.83	70
(303)	2.743		2.73	20
(215)	2.618		2.61	10
(108)	2.478		2.47	30
(223)	2.426			
			2.39	30
(400), (314)	2.243	ms	2.24	40
(315)	2.134	ms	2.13	100
(410)	1.960			
(324)	1.917		1.91	20
(325)	1.844		1.85	10
(500), (318)	1.794	s	1.80	100
(415)	1.770			
(332)	1.705		1.70	40
(423), (505)	1.649			
(328)	1.609			
(506)	1.591	s	1.59	100
(513?)	1.574			
(336)	1.549		1.55	20
(515)	1.502		1.50	50
(432)	1.461			
(433)	1.441	v	1.44	100
(604)	1.436			
(525)	1.359			
(5111)	1.221			
+ 14 lines				

Note:—titanate intensities are visual estimates, quantitative measurements were hampered by fogging of the film—presumably due to the high U content of the mineral. Abbreviations as follows, m = medium, s = strong, v = very strong. Lindsleyite data from Haggerty et al. (1983). hkl indices provided by D.H. Lindsley, State University of New York, Stony Brook.

the other for Ce, Nd, Sm, Gd, Dy and Lu. This separation has been shown to be more reliable than theoretical calculations for interferences of neighbouring REE (Ekambaram et al., 1984). Three other group standard solutions, Os–Ru, Au–Ir–Re and Ag–Ni–Pd–Pt–Se–Zn, were also weighed into small silica tubes. The vials containing the sample or standards, together with an empty vial for blank correction, were separated into five groups, each of which was sealed into a large 3-inch long Suprasil vial. Included in each group was a small vial with Co-doped aluminum wire. Sample, standards, blank and flux monitors were irradiated in the flux trap of the MURR at a flux of 6.0×10^{14} $\text{n}\cdot\text{cm}^{-2}\cdot\text{sec}^{-1}$ for 68.57 hours. The largest deviation of the thermal neutron flux from the mean was 0.62%, as determined from the measured specific activities of ^{60}Co in the aluminum wires. Corrections based on these variations were applied to all nuclides used in this study, including ^{58}Co , which is produced by fast neutrons via $^{58}\text{Ni}(\text{n,p})^{58}\text{Co}$ (see Grossman et al., 1981). Flux corrections for ^{152}Eu and ^{166}Dy were applied as in Davis et al. (1982). After irradiation, the small vials were washed in aqua regia, nitric acid, distilled water, double distilled water, acetone and ethanol to remove surface contamination. They were then counted with high-resolution Ge(Li) detectors four times: (1) for 0.3 to 15.9 hours each, 3.3 to 6.2 days after irradiation (AI); (2) for 0.39 to 69.7 hours each, 9.4 to 19 days AI; (3) for 0.20 to 3.8 days each, 19 to 75 days AI; (4) for 0.25 to 7.0 days each, 19 to 75 days AI.

Data reduction. Calculated corrections for ^{24}Na produced by fast neutron reactions on $^{27}\text{Al}(\text{n,\alpha})^{24}\text{Na}$ and $^{24}\text{Mg}(\text{n,p})^{24}\text{Na}$ ac-

count for less than 1% of the ^{24}Na counts. Fast neutron reactions with ^{27}Al produce ^{27}Mg and with ^{28}Si produce ^{28}Al which interfere with Mg and Al determinations. Corrections for the first interference, made by counting pure Al_2O_3 amounted to 6.7% of total Mg counts. Since Si of the titanate is negligible (Jones et al., 1982) corrections to ^{28}Al counts due to ^{28}Si were not made. Determination of Zr is complicated by the production of ^{95}Zr by neutron-induced fission of ^{238}U and a ^{154}Eu peak at almost the same energy as ^{95}Zr . Corrections for the former effect, amounted to 4.5% of the ^{95}Zr activity; the latter was <0.6% since the sample has a very high Zr/Eu ratio. Production of ^{141}Ce by double neutron capture on ^{139}La and overlap of a ^{175}Yb peak are potential interferences with determination of Ce via ^{141}Ce . The magnitude of the former effect was determined to be 1.6% total counts, by counting ^{141}Ce in the Ce-free La standard. The ^{175}Yb interference was negligible because of the high Ce/Yb ratio in the sample. Overlap of X-rays from ^{239}Pu interferences with the 103.2 keV peak of ^{153}Sm was corrected as in Grossman et al. (1979). Determination of Sm via ^{153}Sm can also be complicated by the reaction: $^{151}\text{Eu}(n,\gamma)^{152\text{m}}\text{Eu}(\text{EC})^{152}\text{Sm}(n,\gamma)^{153}\text{Sm}$. This correction amounted to <1% of the total ^{153}Sm counts, as determined from the number of ^{153}Sm counts in the Sm-free Eu standard. Using the ratio of ^{182}Ta counts at 84.7 keV to those at 1221.4 keV in a sample of pure Ta and the counts at 1221.4 keV in the sample, we corrected for the overlapping ^{182}Ta at the 84.3 keV peak of ^{170}Tm . After this correction, we could only determine an upper limit for Tm. In order to circumvent the potential interferences of 208.2 keV ^{199}Au produced by double neutron capture on ^{197}Au and from decay following neutron capture on ^{198}Pt and 209.7 keV ^{239}Np , Lu was determined from the third and fourth counts, after the decay of ^{199}Au and ^{239}Np . Correction to Lu for ^{177}Lu produced from Yb was achieved by counting ^{177}Lu in the Lu-free Yb standard.

Results

The X-ray diffraction pattern for the titanate (3094) is directly comparable to data given by Haggerty et al (1983) for mathiasite and lindsleyite, and also to loweringite (Gatehouse et al., 1978). The titanate is compositionally closer to Lindsleyite (Ba) and for this reason, the X-ray data are tabulated in Table 1, since these augment the data of Haggerty et al. (1983).

The full INAA analysis for the titanate is given in Table 2, and is compared to ranges for those elements analyzed by electron probe. The latter are taken directly from Jones et al. (1982, Table 7; "H1" excluding analysis 4(b)). The only element which lies outside of the range determined by electron probe, is Mg. We have checked our data and feel confident in the precision of the INAA results. Therefore, we assume that this represents a genuine value for Fe/Mg for the particular grain selected and increases the range of Mg values to slightly lower levels than previously reported. The titanate can be recast into major components of at least six end members using the existing nomenclature (summarized by Gatehouse et al., 1978). Using the cation proportions of the A-site normalised to 1 (from the generalized formula $\text{AM}_{21}\text{O}_{38}$), this would be $\text{Ba}_{0.41}\text{Sr}_{0.23}\text{K}_{0.22}\text{Ca}_{0.08}\text{RE}_{0.03}\text{Na}_{0.02}$. The combined INAA and electron probe data provide values and limits for a total of 40 analyzed elements in the titanate grain.

Table 2. Chemical composition of titanate 3094 (INAA) compared with electron probe analyses

Oxide wt. %	3094	3094 ^a	H1 ^b	
Nb ₂ O ₅		0.11		
V ₂ O ₅	0.501 ± 0.006	0.72		
TiO ₂	62.41 ± 0.32	58.4	57.2	63.0
ZrO ₂	3.20 ± 0.15	2.41	2.32	4.93
SiO ₂		0.00	0.00	0.04
Al ₂ O ₃	0.80 ± 0.025	0.11	0.11	1.22
Cr ₂ O ₃	14.16 ± 0.04	15.1	14.2	17.5
FeO _T	12.10 ± 0.05	12.2	7.37	13.4
MnO	0.103 ± 0.004	0.10	0.00	0.12
MgO	0.91 ± 0.17	3.41	2.88	3.88
NiO	0.025 ± 0.002	0.07		
CaO	<0.25 ±	0.47	0.22	1.69
BaO	3.32 ± 0.11	3.57	0.35	5.39
SrO	1.28 ± 0.04	1.60	0.47	1.60
Na ₂ O	0.026 ± 0.001	0.08	0.04	0.15
K ₂ O	0.56 ± 0.11	0.43	0.17	0.81
RE ₂ O ₃		0.07		
Additional trace elements and lanthanides in ppm ^c for grain 3094				
La	2279.0 ± 19.0	Sc	168.4 ± 0.10	
Ce	2550.0 ± 4.7	Co	63.86 ± 0.27	
Nd	404.0 ± 42.0	Cs	<0.37	
Sm	30.44 ± 0.09	Ta	204.9 ± 1.3	
Eu	8.01 ± 0.12	Os	<0.001	
Tb	4.24 ± 0.13	Ir	<0.007	
Dy	24.4 ± 2.8	Au	0.875 ± 0.022	
Tm	<2.2	Th	14.68 ± 0.26	
Yb	13.10 ± 0.81	U	98.0 ± 3.9	
Lu	1.96 ± 0.24	Hf	691.5 ± 3.3	

Note:— ^aelectron probe analysis of different grain from same veined peridotite sample (Jones et al., 1982; Table 7, analysis #2); ^brange of similar mantle titanates in veined peridotites from Bultfontein Mine kimberlite (Jones et al., 1982; Table 7, "H1" except analysis 4(b)). ^c± 1 sigma from counting statistics. Additional element limits (weight %) deduced from electron probe analyses include P₂O₅ < 0.04, PbO₂ < 0.06, Y₂O₃ 0.01–0.02. Also REE ranges from Jones et al. (1982); La₂O₃ 0.17–0.05, Ce₂O₃ 0.23–0.06, Nd₂O₃ 0.05–0.02.

Analyzed REE are normalized to chondrite abundances (Nakamura, 1974) and plotted in Figure 1. Of key interest is the close agreement between our new INAA data for titanate 3094 and the range of electron probe analyses reported for the same mineral from several metasomatized xenoliths by Jones et al. (1982, Fig. 8). The titanate is clearly light REE-enriched, and although the INAA results show a shallower slope in the heavier REE (Tb to Lu), the mineral contains no unusual enrichment in the heavy REE. In detail, La and Ce are slightly higher than the electron probe values (Fig. 1). These data for the light REE (essentially La, Ce and Nd) are not significantly different from the electron probe ranges determined independently by both Jones et al. (1982) and Haggerty et al. (1983). The heavy REE that are present would be below typical detection limits with an electron microprobe, even when operated at extreme conditions. They are consistent with the Y values obtained by Jones et al. (1982), which has the same ionic radius as Ho (Whittaker and Muntus, 1970), a heavy REE (not Tm, as transcribed by Haggerty, 1983). The electron probe data for the heavy REE in related "LIMA" minerals reported by Haggerty (1983; Table 1) and Haggerty et al (1983; Table 2) have large anomalous abundances in disagreement with the low Y values. Thus, for example, they give $\text{Yb}_2\text{O}_3 = 0.01$, $\text{Lu}_2\text{O}_3 = 1.34$ and

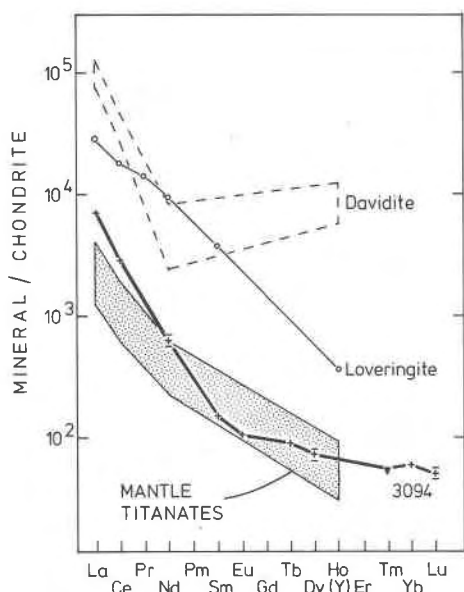


Fig. 1. REE distributions in titanate minerals of the crichtonite series normalized to chondrite abundances (Nakamura, 1974). Note close agreement between INAA data for titanate 3094 (this paper) and range of mantle titanates ("H1" from Jones *et al.*, 1982), Loveringite taken directly from Campbell and Kelly (1978), and Davidite from Gatehouse *et al.*, (1979). See text for details.

$Y_2O_3 = <0.03$ (all wt.%), when chondrite abundances for these same elements (ppm, Nakamura, 1974) are 0.22, 0.039 and 1.96 respectively. Their heavy REE are therefore judged to be incorrect. This emphasizes the caution which must be exercised with uncorrected electron probe data and casts doubt on peak-stripping methods for resolving interferences at low REE levels (see discussion in Jones and Wyllie, 1984). In general, Y serves as a good indicator for the heavy REE (when chondrite-normalized), and is readily measured by electron probe, as demonstrated successfully for the mantle titanates and davidite, in Figure 1.

Discussion

The interpretation of a bimodal REE distribution in the mantle titanate minerals of the crichtonite series was rationalized by comparison with other members of the crichtonite series, namely loveringite and davidite (Haggerty, 1983; Fig. 5). Davidite has been shown to be enriched in both light and heavy REE (Hayton, 1960). Electron probe analyses of davidite have high Y values (Gatehouse *et al.* 1979) confirming the presence of heavy REE (see Fig. 1). Electron probe analyses of loveringite by Campbell and Kelly (1978) reportedly show a similar bimodal light and heavy REE enrichment. However, this is not rigorously supported by their own data, which shows Y at levels too low for heavy REE enriched patterns. All of their findings are based on the electron probe analysis of a single grain, which is replotted in Figure 1. We consider their data for the heavy REE to be close to expected detection

limits and since no special justification was mentioned, these we have ignored. Campbell and Kelly also gave an ion probe determination of the light REE normalized relative to Ce, but unfortunately gave no comparable data for the heavy REE (except for admittedly anomalous "?Gd"). Taken together, their Y data fall at the predicted values for simple light REE enrichment in loveringite, as extrapolated from their tabulated light REE data. This is surely more than coincidence. If our reinterpretation is proved correct, then their discussion of bimodal REE in terms of two distinct structural sites was almost certainly unwarranted. This certainly applies to the recent interpretation of lindsleyite (Haggerty, 1983; Haggerty *et al.* 1983) which we have shown to be only light REE-rich. Anomalous heavy REE data were tabulated for mathiasite as well as lindsleyite (Haggerty *et al.* 1983). Furthermore, the similar ranges in compositions of mantle titanates determined by both Jones *et al.* (1982) and Haggerty *et al.*, (1983) hint at considerable solid solution between Ba-, K- and Ca-crichtonites. Therefore, if our titanate sample from Bultfontein (~lindsleyite) is indeed representative of the mantle crichtonites, and these have compositions intermediate between multiple end members, it still remains to be shown that mathiasite, or any other of the crichtonite minerals apart from davidite, is also heavy REE-enriched.

Conclusions

We have presented new chemical data for a single grain of a mantle-derived titanate mineral belonging to the crichtonite mineral series. The INAA-obtained REE data reinforce earlier electron probe determinations of neighboring and associated grains (Jones *et al.*, 1982) of which the single grain from sample BD3094 was selected to be typical. We conclude that the electron probe-derived heavy REE data reported for the same recently named minerals (Haggerty, 1983; Haggerty *et al.*, 1983) are probably incorrect, in which case structural models used to interpret this artificial bimodal distribution are unwarranted. Reevaluation of electron probe data given by Campbell and Kelly (1978) for loveringite, suggests that the same applies to this Ca end member. Both sets of authors appear to have been drawn to the analogy with the related mineral davidite, which by contrast, does apparently show both light and heavy REE enrichment (Hayton, 1960; Gatehouse *et al.*, 1979).

Lastly, the mantle titanates of the crichtonite series are compositionally complex. Thus, on a ternary diagram (Ca + REE) + (Ba + Sr) - (K + Na), the mantle titanates occupy a broad band from intermediate compositions between loveringite/davidite (Ca + REE) and landauite/mathiasite (Na + K) towards the lindsleyite/crichtonite (Ba + Sr) apex (see Jones *et al.*, 1982, Fig. 2; and Haggerty, 1983, Fig. 2). Haggerty (1983) proposed the general word "LIMA" based on the Ba and K end members lindsleyite and mathiasite respectively, but this excludes for example the considerable crichtonite (Sr) and loveringite (Ca) components in these mantle titanates. Given the established crichtonite group name for these titanates, our current tita-

nate (3094) is closest to Ba-crichtonite (lindsleyite), and is more completely described as $(\text{Ba}_{0.41}\text{Sr}_{0.23}\text{K}_{0.22}\text{Ca}_{0.08}\text{RE}_{0.03}\text{Na}_{0.02})$ -crichtonite. The true extent of solid solution between the various end members at different pressures and temperatures remains to be defined and could be an important step in our further understanding of this complex mineral group.

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