Stability constants of lanthanide(III)-EDTA complex formation and

Gd-break with tetrad effect in their series variation

Iwao Kawabe[*]

Department of Earth and Planetary Sciences, Graduate School of Environmental Studies,

Building-E of Faculty of Science, Nagoya University

Chikusa, Nagoya 464-8602, Japan

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* e-mail address, kawabe@eps.nagoya-u.ac.jp

Abstract

The logarithmic stability constants of (1:1) lanthanide(III)-EDTA complex formation, logK(Ln-EDTA), have been reported by polarography, radiotracer-cation exchange, and potentiomery with different ion-selective electrodes. The polarographic data (Schwarzenbach et al.,1954) with uncertainties less than 0.1 for all Ln but Ho are the experimental basis to put forward the Gd-break and convex tetrad effect of logK(Ln-EDTA). Nevertheless, the data for each logK(Ln-EDTA) by the different methods are variable in a range of ± 0.5 or more, although their series changes are fairly parallel. Apparently the polarographic data can never be assessed by the other methods, but we found that all the reported data except those by the radiotracer-cation exchange need further corrections when the standardized condition of T=298.15 K (25°C) and ionic strength μ=0.1 is chosen with assuming that logK(Cu-EDTA)=18.80 (20°C) and logK(Pb-EDTA)=18.04 (20°C). After the corrections and the subsequent normalization of logK(Y-EDTA)=17.62, all the five data sets of logK(Ln-EDTA) by the different methods converge within 2σ(mean) errors less than 0.9 % for all Ln. Here are accepted the converged values and their 2σ(mean) errors as the experimental logK(Ln-EDTA) ones and uncertainties. The Gd-break and convex tetrad effect certainly exist in logK(Ln-EDTA) beyond the experimental uncertainty, but the observed convex tetrad effect in the light Ln series appears less obvious than in the heavy Ln one. The slightly asymmetrical tetrad effect is possibly due to the hydration changes of Ln-EDTA and ligh Ln^{3+}(aq) series.

Introduction

It is well known that the trivalent lanthanide (Ln) ions in aqueous solution form stable (1:1) complexes with the chelating agent of ethylenediaminetetraacetic acid (EDTA).   The stability constants of Ln(III)-EDTA complex formation have been reported by several different methods including polarography, radiotracer-cation exchange, and potentiometry with various ion-selective electrodes (Wheelwright et al., 1953; Schwarzenbach et al., 1954; Betts and Dahlinger, 1959; and Suzuki et al., 1980), which are summarized in Table 1.   Gritmon et al. (1977) also reported their results of stability constants of Ln(III)-EDTA complex formation at μ=0.5 M (NaClO4) and 25°C, but the μ value of ionic strength is greater than μ=0.1 or 0.09 M (KNO$_3$ or KCl) in the other cases.   Therefore, the results by Gritmon et al. (1977) are not considered here. The reported results are plotted against the atomic number of Ln series in Fig. 1, together with their logK(Y-EDTA) data.   The break is observed at the position of Gd in the series change of logK(Ln-EDTA).   Wheelwright et al. (1953) interpreted that EDTA may act as a hexadentate group for Ln^{3+} from La to Eu but a pentadentate one from Gd to Lu, while Schwarzenbach and Gut (1956) emphasized that the Gd-break may be related to the half-filled effect at Gd^{3+} with the electronic configuration of [Xe](4f^7).

Fidelis and Siekierski (1966) reported that the separation factor for successive Ln members, β=K$_{(Z+1)}$/K$_{(Z)}$ in reversed phase partition chromatography show regular series variations in the Ln(III)-complex systems with the two phosphonic acid derivatives (HEHϕP and HDEHP).   Peppard et al. (1969 and 1970) demonstrated that the

regularity of β corresponds to the lanthanide tetrad effect in logK. Fidelis and Siekierski (1966) also mentioned that β's for K(Ln-EDTA) and other Ln(III) complex systems show such regularities. However, Rowlands (1967) re-examined the regularity using stability constant data for Ln(III) with fourteen complexing ligands including HEHϕP, HDEHP, and EDTA, and concluded that the proposal by Fidelis and Siekierski (1966) was based on insufficient data and left doubt as to the general validity, but he accepted that the regularity exists in the two Ln(III)-complex systems with HEHϕP and HDEHP.

The plot of all the reported experimental data of logK(Ln-EDTA) listed in Table 1 is obviously indicating a large variability of 0.5 or more for each Ln (Fig. 1). The reported experimental errors by Schawarzenbach et al. (1954) are not greater than 0.1, though logK(Ho-EDTA) is not reported, so that the Gd-break and small tetrad-like variation is plausible as long as the data set is accepted. However, if the large variability of Fig. 1 is regarded as the experimental uncertainty assigned to each logK(Ln-EDTA) from the different experimental methods, it is impossible to make significant discussion on the Gd-break and convex tetrad effect as argued by Rowlands (1967). The polarolgraphic data by Schwarzenbach et al. (1954) suggesting the Gd break and small tetrad effect, can never be crosschecked by the different methods.

Concerning the Gd-break and tetrad effect of Ln(III)-complexing behavior in natural water systems, REE geochemists are being split into the three: the first is accepting the discussion by Rowlands (1967) and addressing its unimportance (Wood, 1990; Byrne and Sholkovitz, 1996), the second is apparently uninterested in it, and the third is

putting forward the tetrad effect variations of $\log K(LnCO_3^+)$ and $\log K(Ln(CO_3)_2^-)$ and the importance in seawater solutions (Kawabe, 1999a; Ohta and Kawabe, 2000a, b). Hence we are concerned with the proposal by Fidelis and Siekierski (1966) and the conclusion by Rowlands (1967).

Apart from the variability of logK for each Ln-EDTA in Fig. 1, the parallelism of reported data appears fairly good. Hence it seems important to compare all the data in Table 1 at the standardized experimental condition, because the experimental temperatures are not exactly the same in Table 1. The reference values of logK(Cu-EDTA) at 20°C are also different between Schwarzenbach et al. (1954) and Wheelwright et al. (1953).

The purpose of this study is to show that the apparent variability of logK for each Ln in Fig. 1 is too large to be accepted as the uncertainty evaluated from the different experimental methods. Indeed, the most of the experimental data in Table 1 involve uncorrected differences from those at the standardized condition at 25°C and $\mu=0.1$. The acceptable values of logK(Ln-EDTA) and their experimental uncertainties will be evaluated by making the corrections for the standardized condition and the normalization with logK(Y-EDTA) values, and then the Gd-break and convex tetrad effect will be assessed solely on the basis of experimental data of logK(Ln-EDTA).

Results and Discussion

1) Necessary corrections for the standardized experimental condition

When the standardized experimental condition is chosen as T= 298.15 K (25°C) and

μ=0.1, all the reported data in Table 1 except those by Betts and Dahlinger (1959) are to be corrected with respect to the temperature difference between 20° and 25°C.   Suzuki et al. (1980) reported the experimental results at 25°C, but they used the reference values of logK(Cu-EDTA)=18.80 and logK(Pb-EDTA)=18.04 at 20°C without temperature corrections. Hence their data are not free from such corrections. Wheelwright et al. (1953) accepted logK(Cu-EDTA)=18.38 (20°C) in order to calculate their results from the potentiometric data with glass electrode at 20°C, whereas Schwarzenbach et al. (1954) reported their data at 20°C by using the revised value of logK(Cu-EDTA)=18.80 (20°C).

  The temperature correction for logK is based on the assumption as to approximate constant values of ΔH and ΔS in ΔG for a small temperature range:

$$\Delta G \approx -2.303 RT \log K(T) \approx \Delta \overline{H} - T \Delta \overline{S}, \tag{1}$$

where we neglect the subtle difference between ΔG and $-RT \ln K(T)$ at $\mu = 0.1$ as the first-order approximation.   For two slightly different temperatures of T_0 and T, it follows that

$$\log K(T) \approx (T_0/T) \cdot \log K(T_0) + (T - T_0) \cdot \Delta \overline{S}/(2.303 RT). \tag{2}$$

Note that the ΔS value is necessary for the temperature correction of (2), and that the ΔS value is usually calculated from experimental values of ΔH and ΔG=-2.303RTlogK. Hence, even when the experimental value of ΔH is known, the ΔS value cannot be calculated until logK(T) value is known.   Nevertheless, it is only necessary to use an approximate value of $\Delta \overline{S}$ in (2), because the second term of (2) is a small correction insensitive to the choice of logK(T) value.   The ΔS values for Ln-EDTA formation

have been reported by Mackey et al. (1962), in which logK(Ln-EDTA) at 25°C by Betts and Dahlinger (1959) and logK(Y-EDTA) by Wheelwright et al. (1953) were accepted, together with their experimental ΔH values. The ΔH values for Cu(II)- and Pb(II)-EDTA formation at 25°C and μ=0.1 (KNO₃) are -36.8 (kJ/mol) and -54.7 (kJ/mol), respectively (Handbook of Chemistry, 5th ed., 2004). The approximate values of $\Delta \bar{S}$ in (2) for Cu(II)- and Pb(II)-EDTA formation are +236 (J/mol/K) and +162 (J/mol/K), respectively.

Here is accept logK(Cu-EDTA)=18.80 (20°C) as in Schwarzenbach et al. (1954), and then the data by Wheelwright et al. (1953) are corrected for the difference between logK(Cu-EDTA)=18.38 and 18.80 at 20°C. The corrected data of Wheelwright et al. (1953) are further adjusted to the condition of 25°C using eq. (2), along with the reported data by Schwarzenbach et al. (1954). The corrected values to 25°C are listed in Table 2.

In the case of the two data sets with Pb- and Cu electrodes of Suzuki et al. (1980), the temperature corrections were applied to their reference values of logK(Cu-EDTA)=18.80 and logK(Pb-EDTA)=18.04 at 20°C by using eq. (2). They are reduced to logK(Cu-EDTA)=18.69 and logK(Pb-EDTA)=17.88 at 25°C. The respective differences between the two temperatures are the corrections to the two data sets with Pb- and Cu electrodes. The resultant values are listed in Table 2. All the values of Table 2 are for the standardized experimental condition of T= 298.15 K (25°C) and μ=0.1 with assuming that logK(Cu-EDTA)=18.80 and logK(Pb-EDTA)=18.04 at 20°C. They are plotted against the atomic number of Ln in

Fig. 2-A.

It is apparent in Table 2 and Fig. 2-A that the polarograhic data by Schwarzenbach et al. (1954) are almost in accordance with the data with Cu-electrode by Suzuki et al. (1980), while the potentiometric ones by Wheelwright et al. (1953) are close to the data with Pb-electrode by Suzuki et al. (1980). The reported data by the radiotracer-cation exchange technique (Betts and Dahlinger, 1959) at 25°C and μ=0.1(KCl) in Table 1, which are free from the assumptions as to logK(Cu-EDTA) and logK(Pb-EDTA), are closer to the data sets by potentiometry with Pb-electrode (Suzuki et al., 1980) and glass electrode (Wheelwright et al., 1953).

2) Acceptable values of logK(Ln-EDTA) and their uncertainties

The corrected data in Table 2 and those by Betts and Dahlinger (1959) in Table 1 reveal that the experimental data for logK(Ln-EDTA) by five different methods are fairly consistent, but there still remain some discrepancies possibly due to systematic experimental differences (Fig. 2-A). In order to find the acceptable data set and their uncertainties we have normalized the corrected data in Table 2 to logK(Y-EDTA)=17.62. The normalizing value of logK(Y-EDTA) is that by Pb-electrode method of Suzuki et al. (1980), which is closer to the corrected potentiometric value of 17.37±0.15 by Wheelwright et al. (1953). In addition, although Betts and Dahlinger (1959) did not report the logK(Y-EDTA) value, their data for logK(Ln-EDTA) are closer to those by Pb-electrode method of Suzuki et al. (1980) and by the glass electrode of Wheelwright et al. (1953). If we normalize the data to

logK(Y-EDTA)=18.09±0.04 of the corrected polarograhic value by Schwarzenbach et al. (1954) or 18.12 by Cu-electrode method of Suzuki et al. (1980), the systematic discrepancy of about 0.5 is left between those by Betts and Dahlinger (1959) and the others.   This is the reason why we prefer the normalization by logK(Y-EDTA)=17.62 to those by other values.

The normalized values plotted in Fig. 2-B are listed in Table 3.   The comparison of Fig. 1 with Fig.2-B is illustrating the importance not only of the corrections for the standardized experimental condition but also of the subsequent normalization by logK(Y-EDTA)=17.62.   The mean value for each logK(Ln-EDTA) and the two-sigma error for the mean have been calculated from the four data sets by potentiometry and polarography and from the five data sets including those by the radiotracer-cation exchange (Betts and Dahlinger, 1959).   The means and the two-σ(mean) errors for the experimental data with and without those by the radiotracer-cation exchange are listed in the last two columns of Table 3.   There are no significant differences between the means and the two-σ(mean) errors for n=4 and 5, suggesting that the reported values by the radiotracer-cation exchange (Betts and Dahlinger, 1959) are consistent with those by potentiometry and polarography corrected to the standardized condition and then normalized to logK(Y-EDTA)=17.62.

The two-σ(mean) errors for the respective means of logK(Ln-EDTA) for the five data sets are less than 0.9 % for all Ln.   Although two-σ(mean) errors for the logK(Ln-EDTA) values with Ln=La, Ho, and Er are equal to 0.1 or slightly beyond 0.1, those errors for the others are less than 0.1.   We have accepted the means and

two-σ(mean) errors in the last column of Table 3 as the most probable values of logK(Ln-EDTA) and their experimental uncertainties. They are based on the results by five different methods for the standardized condition that T=298.15 K (25°C), μ=0.1, logK(Cu-EDTA)=18.80(20°C), and logK(Pb-EDTA)=18.04 (20°C), together with the normalization condition of logK(Y-EDTA)=17.62(25°C).

3) Gd-break and tetrad effect existing in the series change of logK(Ln-EDTA)

  The logK(Ln-EDTA) values accepted by us give a smooth curve for each tetrad of Ln similar to Peppard et al. (1969), which is shown in Fig. 3.   The smooth tetrad curves have been determined by the least-squares method assuming second-order polynomials of the atomic number of Ln for the respective tetrads, in which the following constraints were imposed: the cusps between the first and second tetrad curves and between the third and fourth ones are located at the mid-points between Nd and Pm and between Ho and Er, respectively.   The least-squares method with such constraints has applied to the problem of lanthanide tetrad effect by Minami and Masuda (1997), in which the details of the fitting method are described. The second-order polyniomials was used to describe the smooth tetrad curves from experimental data by Masuda et al. (1994).   The characteristic variations exhibit the Gd-break and the tetrad effect beyond the experimental errors of two-σ(mean).   For most of the accepted values of log logK(Ln-EDTA), their two-σ(mean) errors are less than 0.1.

  The Gd-break and convex tetrad effect of logK(Ln-EDTA) have confirmed solely on the basis of experimental data.   It seems interesting that the tetrad effect variation of

Fig. 3 is not quite symmetrical between the light and heavy Ln series: The convex tetrad effect in the light Ln series appears less obvious than in the heavy Ln one. The slightly asymmetrical tetrad effect as the series change property of logK(Ln-EDTA) is possibly related to the hydration changes of light Ln^{3+}(aq) and Ln-EDTA$^-$(aq) series (Rizkalla and Choppin, 1991; Kawabe, 1999a and b). This invites further studies of the Ln-EDTA formation and the other (1:1) Ln-chelate complex formation from the viewpoints of thermodynamics, spectroscopy, and the improved refined spin-pairing energy theory for thermodynamic data (Kawabe, 1992 and 1999a, b; Kawabe and Masuda, 2001). They will be presented elsewhere, together with further implications to REE geochemistry.

Conclusions

The polarographic data of logK(Ln-EDTA) with uncertainties less than 0.1 for all Ln but Ho (Schwarzenbach et al., 1954) have been the experimental basis to put forward the Gd-break and convex tetrad effect of logK(Ln-EDTA). Nevertheless, logK(Ln-EDTA) data by polarography, radiotracer-cation exchange, and potentiomery with various ion-selective electrodes, exhibit a large variability of ±0.5 or more for each Ln, although their series changes appear to be fairly parallel. Apparently it is impossible to assess the polarographic data from those by the other methods, but we found that the reported data, except those by the radiotracer-cation exchange, need further corrections for the standardized condition of 25°C and μ=0.1 with assuming logK(Cu-EDTA)=18.80 (20°C) and logK(Pb-EDTA)=18.04 (20°C). The large

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variability of ±0.5 or more is too large to be accepted as the experimental uncertainty for logK(Ln-EDTA).   The conclusions in this study are as follows:

1) All the four data sets of logK(Ln-EDTA) by polarography and potentiometry, when corrected properly to the standardized condition and normalized to logK(Y-EDTA)=17.62, are combined with the data by the radiotracer-cation exchange which are not reporting the logK(Y-EDTA) value.   The five data sets converge within 2σ(mean) errors less than 0.9 % for all Ln.

2) The means of five experimental values and 2σ(mean) errors for logK(Ln-EDTA) have been accepted.   The polarographic data by Schwarzenbach et al. (1954) are justified by the potentiomeric data with different ion-selective electrodes and those by the radiotracer-cation exchange.

3) The Gd-break and convex tetrad effect certainly exist in the series change of logK(Ln-EDTA) beyond the experimental uncertainty.   The convex tetrad effect in the light Ln series appears less obvious than in the heavy Ln one. The faintly asymmetrical tetrad effect is possibly related to the hydration changes of light Ln^{3+}(aq) and Ln-EDTA series.

References

Betts, R. H. and Dahlinger, O. F. (1959) The heat and entropy of association of the complex ions fromed by EDTA with the lanthanide elements in aqueous solution. *Can. J. Chem.*, **37**, 91-100.

Byrne, R. H. and Sholkovitz, E. R. (1996) Marine chemistry and geochemistry of the lanthanides. *Handbook on the Physics and Chemistry of Rare Earths (Eds. Gschneider, K. A. Jr. and Eyring, L.),* **23**, 497-593, Elsevier, Amsterdam.

Chemical Society of Japan (2004) *Handbood of Chemistry (5th ed.) Basic Chemistry*, Part, 2, Chapter 11, p.367.

Fidelis, I. and Siekierski, S. (1966) The regularities in stability constants of some rare earth complexes. *J. inorg. nucl. Chem.*, **28**, 185-188.

Gritmon, T. F., Goedken, M. P., and Choppn, G. R. (1977) The complexation of lanthanides by aminocarboxylate ligands-I. *J. inorg. nucl. Chem.*, **39**, 20021-2023.

Kawabe, I. (1992) Lanthanide tetrad effect in the Ln^{3+} ionic radii and refined spin-pairing energy theory. *Geochem. J.*, **26**, 309-335.

Kawabe, I. (1999a) Hydration change of aqueous lanthanide ions and tetrad effects in lanthanide(III)-carbonate complexation. *Geochem. J.*, **33**, 267-275.

Kawabe, I. (1999b) Thermochemical parameters for solution of lanthande (III) ethylsulphase and trichrolide hydrate series: Tetrad effects and hydration change in aqua Ln^{3+} ion series. *Geochem. J.*, **33**, 249-265.

Kawabe, I. and Masuda, A. (2001) The original examples of lanthanide tetrad effect in solvent extraction: A new interpretation compatible with recent progress in REE

geochemistry. *Geochem. J.*, **35**, 215-224.

Mackey, J. L., Powell, J. E., and Spedding, F. H. (1962) A calorimetric study of the reaction of rare-earth ions with EDTA in aqueous solution. *J. Am. Chem. Soc.*, **84**, 2047-2050.

Masuda, A., Matsuda, N., Minami, M., and Yamamoto, H. (1994) Approximate estimation of the degree of lanthanide tetrad effect from precise but partially void data measured by isotope dilution and an electron configuration model to explain the tetrad phenomenon. *Proc. Japan Acad.*, **70B**, 169-174.

Minami, M. and Masuda, A. (1997) Approximate estimation of the degree of lanthanide tetrad effect from the data potentially involving all lanthanides. *Geochem. J.*, **31**, 125-133.

Ohta, A. and Kawabe, I. (2000a) Rare arth element partitioning between Fe oxyhydroxide precipitate and aqueous NaCl solutions doped with $NaHCO_3$: Determinations of rare earth element complexation constant with carbonate ions. *Geochem. J.*, **34**, 439-454.

Ohta, A. and Kawabe, I. (2000b) Theoretical study of tetrad effects observed in REE distribution coefficients between marine Fe-Mn deposit and deep seawater, and in REE(III)-carbonate complexation constants. *Geochem. J.*, **34**, 455-473.

Peppard, D. F., Mason, G. W., and Lewey, S. (1969) A tetrad effect in the liquid-liquid extraction ordering of lanthanides(III). *J. inorg. nucl. Chem.*, **31**, 2271-2272.

Peppard, D. F., Bloomquist, C. A. A., Horwitz, E. P., Lewey, S., and Mason, G. W.

(1970)   Analogous actinide(III) and lanthanide(III) tetrad effects.   *J. inorg. nucl. Chem*., **31**, 2271-2272.

Rizkalla, E. N. and Choppin, G. R. (1991) Hydration and hydrolysis of lanthanides. In: *Handbook on the Physics and Chemistry of Rare Earths (Eds. Gschneidner, K. A. Jr. and Eyring, L.),* **15**, 393-442, Elsevier, Amsterdam.

Rowlands, D. L. G. (1967)   Observations of the separation factors of the rare earths with various lingads.   *J. inorg. nucl. Chem.,* **29**, 809-814.

Schwarzenbach, G., Gut, R., and Anderegg, G. (1954) Komplexone XXV. Die polarographische Untersuchung von Austauschgleichgewichten. Neue Daten der Bildungskonstanten von Melallkomplexen der Äthylendiamin-tetraessigsäure und der 1,2-Diaminocyclohexan-tetraessigsäure.   *Helv. Chim. Acta*, **37**, 937-957.

Schwarzenbach, G. and Gut, R. (1956) Die Komplexe der Seltenen Erdkationen und die Gadoliniumecke.   *Helv. Chim. Acta*, **39**, 1589-1599.

Suzuki, Y., Yokoi, S., Katoh, M., Minato, M., and Takizawa, N. (1980) Stability constants of rare-earth complexes with some organic ligands. In: *The Rare Earths in Modern Science and Technology* (eds. G. J. McCarthy et al.), vol. 2, 121-126, Plenum, New York.

Wheelwright, E. J., Spedding, F. H., and Schwarzenbach, G. (1953)   The stability of the rare earth cpmplexs with ethlendiaminetetraacetic acid. *J. Am. Chem. Soc*., **75**, 4196-4201.

Wood, S. A. (1990)   The aqueous geochemistry of the rare-earth elements and yttrium 1. Review of available low-temperature data for inorganic complexes and the

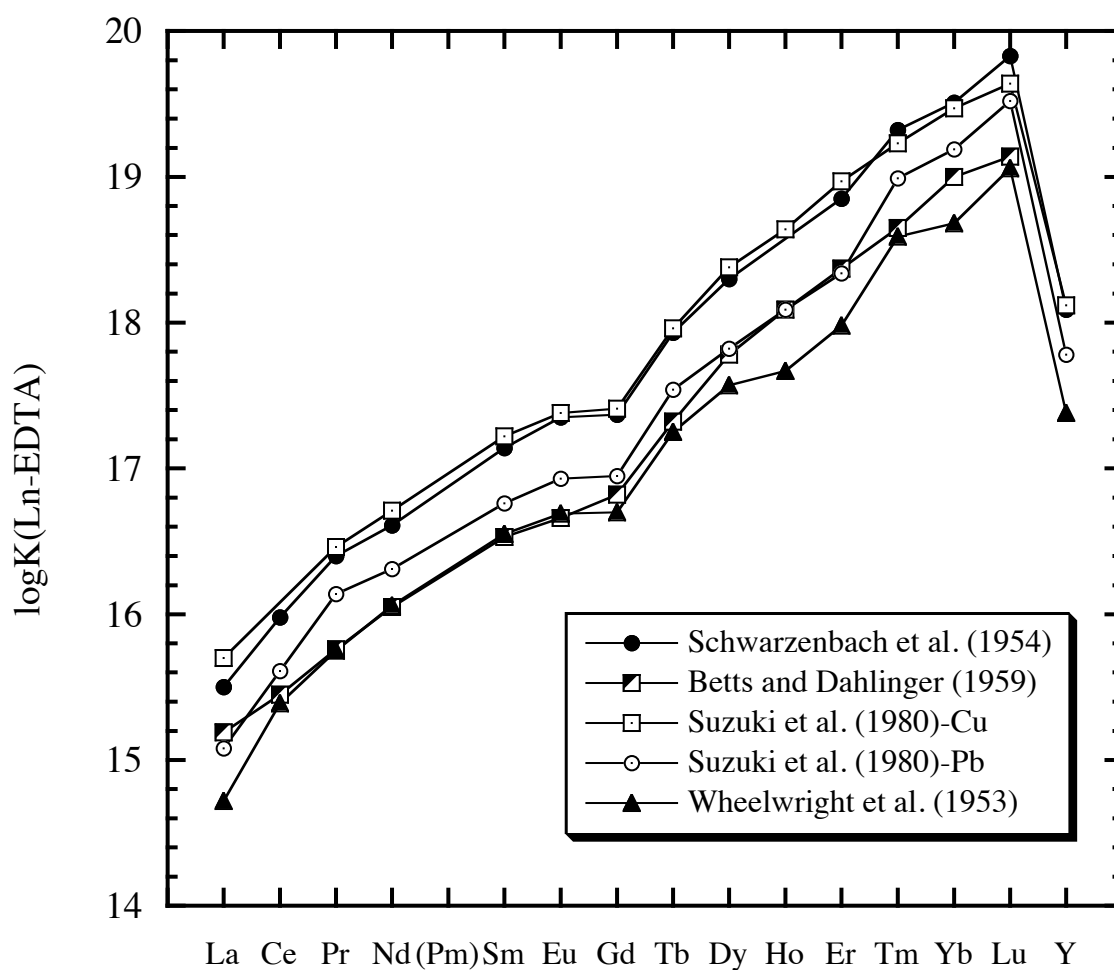inorganic REE speciation of natural waters. *Chem. Geol.,* **82**, 159-186.

Fig.1. Reported data of log K for Ln-EDTA complex formation (Table 1) are plotted against the atomic number of Ln. The apparent variability of logK for each Ln exceeds ±0.5, though the series changes are fairly parallel among the five data sets. The data of log(Y-EDTA) are plotted on the right of Lu.
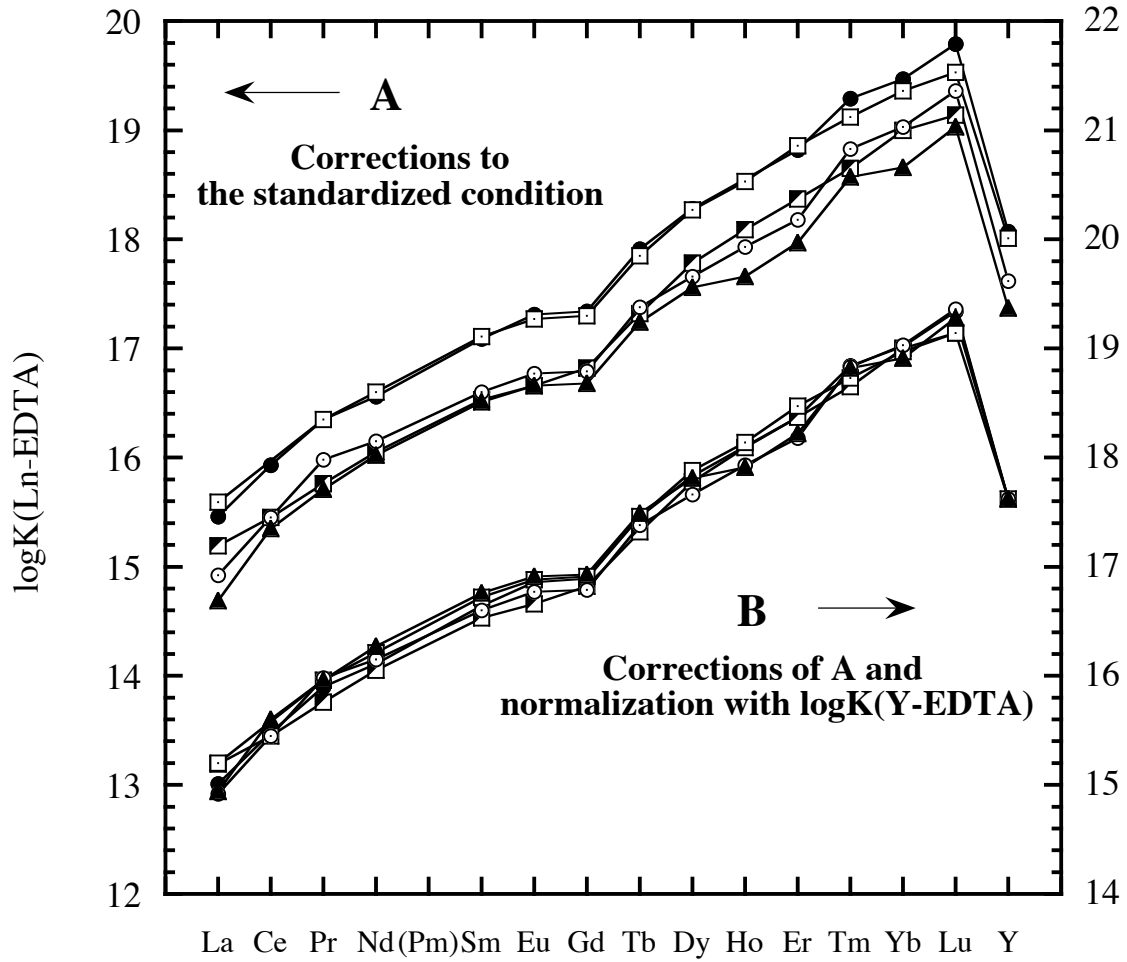
Fig. 2. A: Corrected data of logK(Ln-EDTA) and logK(Y-EDTA) by polarography (Schwarzenbach et al., 1954) and potentiometry (Suzuki et al., 1980; Wheelwright et al., 1953) to the standardized condition listed in Table 2. B: The corrected data of A are further normalized to logK(Y-EDTA)=17.62 (Table 3). Symbols are the same as in Fig. 1. The half-filled squares (Betts and Dahlinger, 1959) are the reported ones free from the corrections and normalization here.
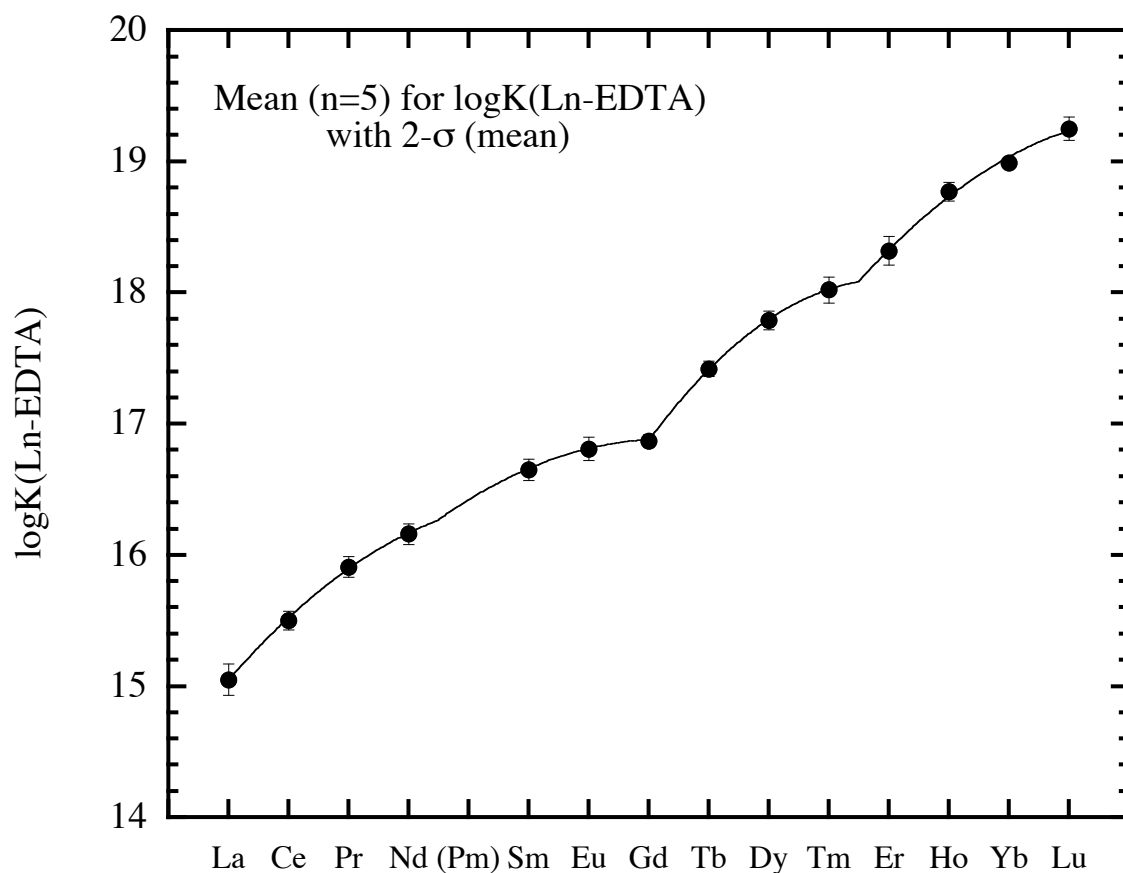
Fig. 3. The series change of the accepted means with 2-σ(mean) errors for logK(Ln-EDTA) from the five data sets (the last column of Table 3). Smooth curves for the respective tetrads are the least-squares fittings with second-order polynomials of the atomic number of Ln with the following constraint: the cusps between the first and second tetrad curves and between the third and fourth ones are located at the mid-points between Nd and Pm and between Ho and Er, respectively (see text).