

## AUTHOR'S REPLY

### Ultimate removal mechanisms of elements from the ocean (reply to a comment by M. Whitfield and D. R. Turner)

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FOR ease of discussion, I have replotted the  $\log C_{op}/C_{sw}$  (concentration ratio of element in oceanic pelagic clays and seawater) vs  $\log *K_1$  (the first hydrolysis constant) and  $\log K_1$  or  $K_2$  (first and second dissociation constants of acids) in Fig. 1a, and  $\log C_{op}/C_{sw}$  ( $= -\log K_p$ ) vs  $Q_{MO}$  ( $= [\chi_M - \chi_O]^2$ ) in Fig. 1b. The  $\log C_{op}/C_{sw}$  values for various elements are summarized by Li (1982b) but seasalt components in pelagic clays were subtracted for Na and  $SO_4$  (Cl, I, and Br in pelagic clays are entirely seasalt components). The  $*K_1$  values recently summarized by Baes and Mesmer (1976, 1981) are adopted here. The exceptions are Au and Be, which are predicted from the linear relationship between  $\log *K_1$  and the ionization potential (Li, 1981). The electronegativity values ( $\chi_M$ 's) are obtained from Pauling (1960) and Gordy and Thomas (1956). The  $K_1$  and  $K_2$  are given by Dean (1979).

Our argument centers on whether the observed correlation between  $\log C_{op}/C_{sw}$  and  $\log *K_1$  for mono- and divalent cations (dashed lines in Fig. 1a) as predicted from the surface complex formation model is real or not. I have argued that a few exceptions to the correlation can be explained. For example, the adsorption of Cs and Rb (and to some extent K) on aluminosilicates is not due to the formation of M-O bond ( $*K_1$ 's for Cs and Rb are too small to be measured) but rather due to the electrostatic attraction between cations and negatively charged aluminosilicate particles. Ba in pelagic clays exists mainly as  $BaSO_4$  (Dehairs *et al.*, 1980, and references therein) and Mn as  $MnO_2$ , not as adsorbed species. Tl may exist as  $Tl_2O_3$  in pelagic clays or be adsorbed as  $Tl^{+3}$ . The low  $\log C_{op}/C_{sw}$  for  $UO_2^{+2}$  is due to the formation of strong complex of  $UO_2(CO_3)_2^{-2}$  in seawater. For a reminder, Ca in pelagic clays is associated mainly with  $MnO_2$  phases in addition to aluminosilicates and apatite phases, not with  $CaCO_3$  (Li, 1982a). In the microcosm tanks (MERL) simulating Narragansett Bay, the spiked radioactive Hg behaves like Fe(III), Th, Cr(III), Pb, Pa, Pu, Am and Be (Santschi *et al.*, 1981). These elements all give high distribution coefficients in the microcosm tanks ( $10^5$ - $10^6$  cm<sup>3</sup>/g) as would be expected from their high  $*K_1$  values. But in a MANOP benthic chamber on the deep sea floor, the spiked Hg behaves more like relatively mobile Cs and Ba with distribution coefficients of only about  $10^3$  cm<sup>3</sup>/g (Santschi *et al.*, 1982). Since both MERL tanks and MANOP chamber were filled with seawater, the higher mobility of Hg in the deep sea than in the near shore environment should not be caused by the formation of chloride complexes as I originally thought. Further studies are needed to explain the high mobility of Hg in the deep ocean.

The tri-valent cations such as rare earths and Y also fall on the top end of the main correlation line for mono- and di-valent cations. But  $\log C_{op}/C_{sw}$  does not increase linearly with  $\log *K_1$  for other tri- and tetra-valent cations, instead  $\log C_{op}/C_{sw}$  reaches a maximum around Al and Th; then

decreases again. The decrease may indicate the weakening of the M-O bond due to the existence of OH groups on the fully hydrolyzed tri- and tetra-valent cations, but we need to improve  $C_{sw}$  data for In, Ga, Hf, Zr and Bi to substantiate this hypothesis. Though certain cations are enriched preferentially in certain major phase(s) of pelagic clays (e.g. aluminosilicates,  $MnO_2$  or  $FeOOH$  phases), the concentration of any cation in pelagic clays is a weighted average of major phases. Therefore it is unwarranted to chop up my Fig. 1a into pieces as shown in Fig. 2 of the comment by Whitfield and Turner.

My original impression was that Whitfield and Turner mean  $Q_{MO}$  to proportion to the total M-O bond energy, since they mentioned Schindler's work in their original work (Whitfield and Turner, 1979), then stated ". . . the elements attach themselves to the mineral surfaces through the deprotonated surface hydroxyl group. This is essentially an ionic interaction, the strength of which can be related to the electronegativity of the element in question." I found that  $\log *K_1$  (a measure of M-O bond strength) is inversely correlated with  $Q_{MO}$  for each charge type except soft b-metals (Fig. 3 of Li 1981), therefore, I stated that their interpretation is erroneous (Li, 1981). Now they have clarified that  $Q_{MO}$  represents only the electrostatic contribution to the total M-O bond energy. It is, however, very hard to envision that the electrostatic contribution to M-O bond energy alone can control the partition of element between liquid and solid phases, especially as we already know that  $Q_{MO}$  is inversely related to  $\log *K_1$  or the total M-O bond energy. The specific association of various cations with aluminosilicate,  $MnO_2$ , and  $FeOOH$  phases of pelagic clays (Li, 1981, 1982a) also can be explained by James and Healy's (1972) adsorption model, which emphasizes the total bond energy between the adsorbed cation and solid ( $\Delta G_{ads.} = \Delta G_{cool} + \Delta G_{solv} + \Delta G_{chem}$ ), not just the electrostatic contribution ( $\Delta G_{cool}$ ).

Since  $\log *K_1$  and  $\log K_1$  is inversely correlated with  $Q_{MO}$  (see Fig. 3 of Li, 1981) it is not surprising to find the similarity between Fig. 1a and 1b. One can see a negative correlation between  $\log C_{op}/C_{sw}$  vs  $Q_{MO}$  for mono- and divalent cations, excluding Cs, Rb, Ba and soft b-metals for the reasons mentioned earlier, instead of a positive one. There is no *a priori* reason(s) to exclude Li, Na, K, Mg, Ca and Sr from the correlation test that they did (Whitfield and Turner, 1979). Even excluding alkali and alkaline earth elements and allowing  $\log C_{op}/C_{sw}$  to be positively correlated with  $Q_{MO}$ , it is still very hard to envision a physical reason for the increase in  $Q_{MO}$  to increase the  $\log C_{op}/C_{sw}$  for cations. Their only argument is "Kp should decrease with increasing  $Q_{MO}$ " with no further mechanistic explanation. For oxyanions we both agree that "the stronger the M-O bond, the stronger the acid and the weaker the bond between the Fe on the iron oxide surface and the O on the oxyanion". But it is not consistent to invoke the concept of

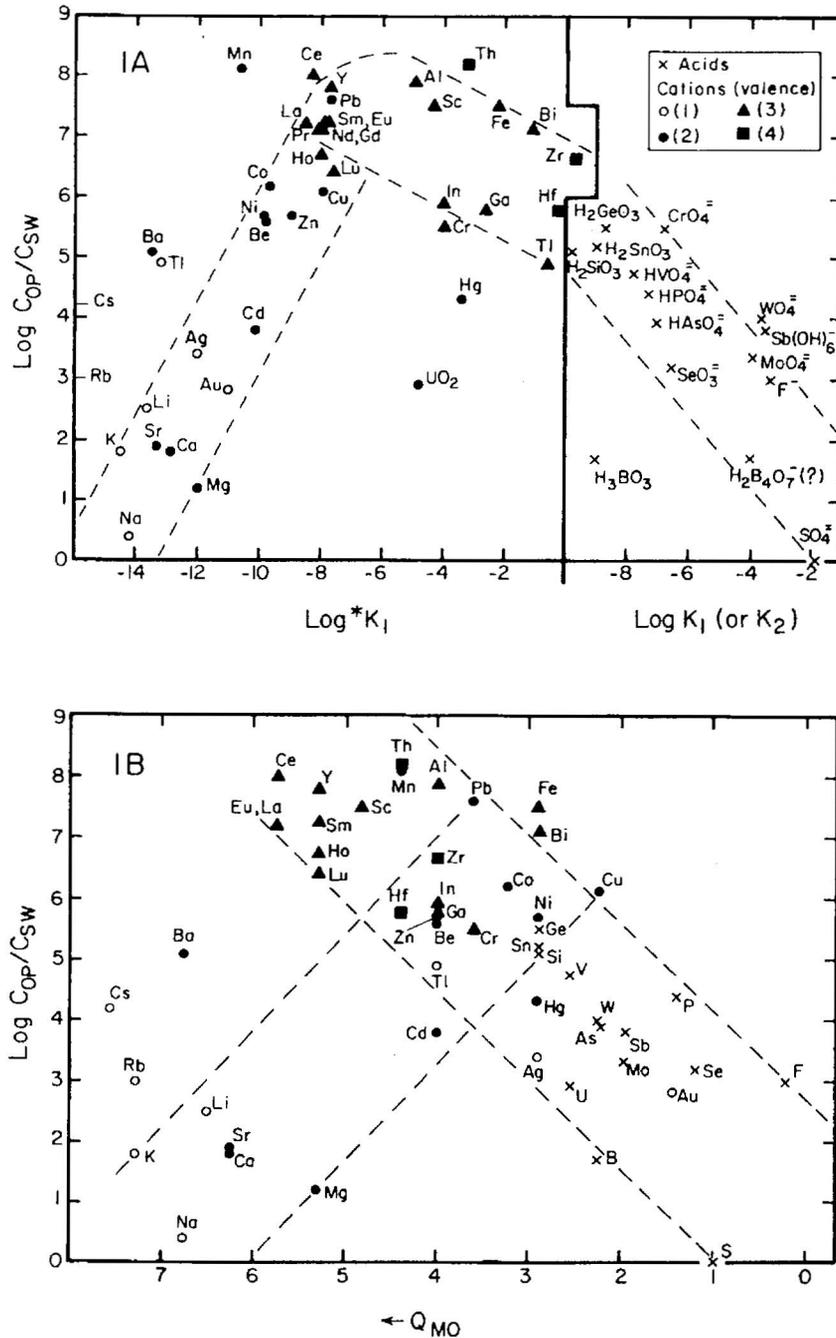


FIG. 1. The plots of  $\log C_{op}/C_{sw}$  vs 1a)  $\log *K_1$  and  $\log K_1$  (or  $K_2$ ) and vs 1b)  $Q_{MO}$ .

the bond strength between solid and adsorbed oxyanion here, while for cations they would rather use  $Q_{MO}$  instead of the total M-O bond strength as I did throughout my original paper. Various surface complex formation models have been successfully applied to the adsorption of both cations and anions onto different solid phases (e.g. Davis and Leckie 1978, 1979; Sigg and Stumm 1981; Balistreri and Murray 1981, 1982). There is no compelling reason to postulate two different ways to explain separately the adsorption of cations and anions.

The linear correlation between  $\log C_{op}/C_{sw}$  and  $Q_{MO}$  for tri-, tetra-valent cations and oxyanions (Fig. 1b) is nothing unusual. For example, the plots of  $\log C_{op}/C_{sw}$  vs ionization

potential (Fig. 2) or vs  $Z/\gamma$  (not shown here, since it is similar to Fig. 2) also give nice linear correlation for these elements. What is unusual about Fig. 1b is that mono- and di-valent cations (excluding IA and IIA group elements) fall on the middle of the correlation line. While in Fig. 2 as well as in Fig. 1a, mono- and di-valent cations are separated from the correlation line for higher valent cations and oxyanions and the values of  $I$  or  $Z/\gamma$  increase systematically from low to high valent cations and to oxyanions. It is not the case for  $Q_{MO}$  (Fig. 1b). My explanation for the anomaly is the following: Since the  $Q_{MO}$  values for di-, tri-, and tetra-valent cations very much overlap one another even when  $*K_1$  (therefore also for  $I$  and  $Z/\gamma$ ) are

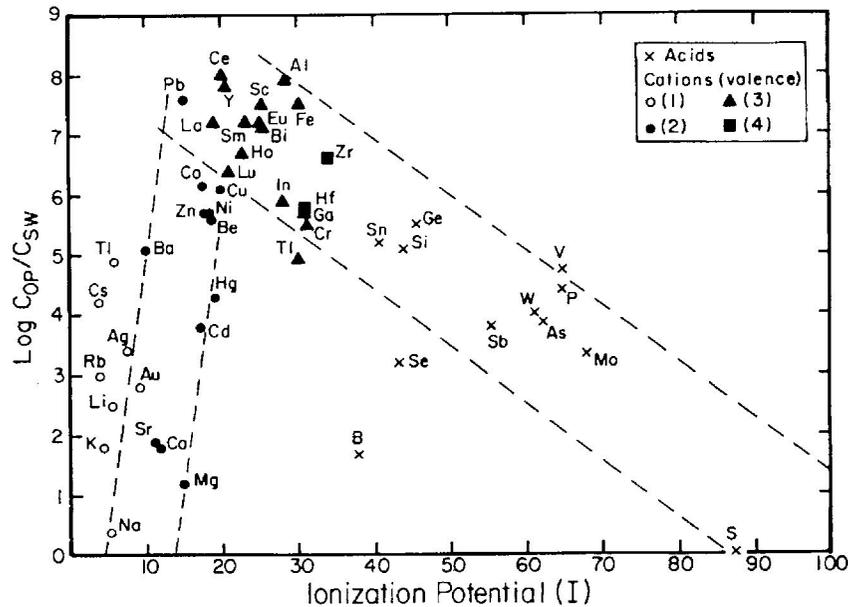


FIG. 2. The plot of  $\log C_{op}/C_{sw}$  vs ionization potential.

quite different (Fig. 3 of Li, 1981). Therefore, by excluding IA and IIA group elements, mono- and di-valent cations appear to fall at the middle of the correlation line for higher valent cations and oxyanions in Fig. 1b, and cause a pseudo-correlation between  $\log C_{op}/C_{sw}$  and  $Q_{MO}$  for all elements except IA and IIA group elements.

In summation, the surface complex formation model provides a consistent mechanistic explanation to the observed partitioning of elements between solid and liquid phases in the ocean, while the  $Q_{MO}$  parameter with the present form provides no insight with regard to the mechanisms of adsorption of dissolved elements onto particles in the ocean. The results from laboratory determination of distribution coefficients in seawater-sediments systems for large numbers of radioactive cations and anions hopefully will solve our argument.

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