Comment and Reply on "Sodium-calcium ion exchange in the weathering of shales: Implications for global weathering budgets"

COMMENT

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Cerling et al. (1989) discussed an important, largely neglected process governing the chemical composition of stream and ground waters. They emphasized the previously expressed idea (e.g., see Lee, 1981; Mermut and Arshad, 1987) that during the weathering of shales the liberation of sodium to solution takes place via cation exchange of dissolved Ca with Na on detrital clay minerals. On this basis, they stated that "up to 34% of the sodium in the (worldwide) dissolved stream load may be due to cation exchange rather than sodium production via silicate weathering reactions." This contradicts the conclusions of several previous workers (Garrels and Mackenzie, 1971; Holland, 1978; Meybeck, 1987; Berner and Berner, 1987). Herein we show that the exchange process, although of geochemical interest, may not be as important on a worldwide basis as envisaged by Cerling et al.

Shales do not consist only of clay minerals. Sodium-rich plagioclase feldspar is a common constituent of shales as well as other sedimentary rocks (see Table 1). During the weathering of shales, sodic plagioclase may be broken down to clay minerals and sodium plus silica in solution. Table 1 shows that in shales there is about the same amount of plagioclase sodium as that present as exchangeable ions on clays. In addition, Na-rich clay minerals such as smectite, under the proper conditions, also can weather to more aluminous clays such as kaolinite with the release of silica and sodium to solution (e.g., Altschuler et al., 1963). In both plagioclase and smectite dissolution, the weathering acid can be either sulfuric acid from pyrite oxidation or carbonic and organic acids from soil biological activity, and the resulting water chemical composition will be similar to that cited by Cerling et al. (1989) for a cation-exchange origin. An important test of whether dissolved sodium in waters draining shales comes from these dissolution reactions or from cation exchange lies in how much silica

is associated with the excess sodium. (Excess sodium refers to that in excess of chloride molar equivalent.) Unfortunately, no data on silica were given by Cerling et al. In fact, several of the waters they used from the work of Meybeck (1986) show sufficient silica that could be attributed to the dissolution of sodium-containing silicate minerals.

Acknowledging that the cation-exchange hypothesis may be correct for some rivers, we are still confronted with the question of its quantitative importance on a worldwide basis. Cerling et al. maximized the effect by ignoring plagioclase in shales and assuming that all clay carried by rivers represents recycled old shale whose cation-exchange capacity is dominated by smectite. However, it is well known that river-borne smectite is also derived from modern-day weathering and, as noted by Cerling et al., this material would not be expected to be enriched in Na in its exchange positions. In addition, smectite is transformed to illite during burial diagenesis (e.g., Hower et al., 1976) and, as a result, it is much less abundant in older shales (e.g., Garrels and Mackenzie, 1971; Weaver, 1967). If diagenetic loss of smectite is important, then, on the basis of the results of Hower et al. (1976), the sodium is lost from the clays.

We feel that several important questions must be answered before the Cerling et al. hypothesis can be assumed to be important globally. First, how much dissolved Na is contributed by the dissolution of Na-silicate minerals in shales, notably sodic plagioclase and smectite? Second, what percentage of shales actually contain high concentrations of clay minerals with abundant exchangeable Na? i.e., are the Na-rich clays largely lost during diagenesis? Third, does the ratio of silica to sodium in waters draining shales approximate that expected mainly for silicate dissolution or for ion exchange? Fourth, does the ubiquity of sodic plagioclase in sedimentary rocks, as well as in igneous and metamorphic rocks, overshadow the clay ion-exchange mechanism on a global scale? (We suspect this to be true.) Finally, what proportion of clays with high exchange capacity (i.e., smectite) carried by rivers are newly formed by silicate weathering as opposed to recycled clays from shales? (An answer to the last question is of significance not only to the origin of riverine sodium but also to the whole problem of geochemical recycling over geologic time.) Until these questions are addressed, the statement that clay cation exchange is a major control on worldwide river chemistry is premature.

TABLE 1. APPORTIONMENT OF AVERAGE Na₂O COMPOSITION IN SHALES

Lithology, age, no. of analyses	Na₂O in whole rock		Reference
	as plagioclase* (wt%)	as illite/smectite† (wt%)	
Subsurface Gulf of Mexico, Tertiary, 5	0.6	0.5	Hower et al. (1976)
Pierre Shale, Cretaceous, 226	0.5	0.6	Schultz (1964, 1978, 1980)
North American shales, Paleozoic-Tertiary, 400	0.6#	0.7	Shaw and Weaver (1965)
Average sedimentary rock (including sandstones)	0.7	0.1	Garrels and Mackenzie (1971)

* Determined from quantitative X-ray diffraction mineralogy and percent Na₂O in plagioclase. If the anorthite content was undetermined, then plagioclase was assumed to be albite.
† Determined either by quantitative X-ray diffraction mineralogy and detailed chemical analysis of the clay fraction or by difference of plagioclase Na₂O content from total whole-rock Na₂O.
# Reported as Na₂O in nonclay components (i.e., feldspars).

REPLY

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Berner et al. raise several points about the possible importance of cation exchange and the global weathering budget of sodium. These include (1) the observation that other workers have not previously come to the same conclusions; (2) that silicate dissolution reactions, such as weathering of plagioclase, producing sodium also produce silica; and (3) that river-borne smectite can be "recycled" or produced in the modern weathering cycle. They then raise five questions to be addressed before our "hypothesis can be assumed to be important globally." We address their comments below.

First, we do not feel that our results contradict "the conclusions of several previous workers," which implies that those works had carefully considered the cation-exchange hypothesis. None of the references cited considered the cation-exchange reaction in global weathering budgets.

Second, Berner et al. rightly point out that comparison of the excess sodium (sodium minus chloride) concentration to the silica concentration

in shale waters could constitute an important test of the source of sodium. Does sodium primarily come from cation exchange (which would result in a large amount of excess sodium) or from plagioclase weathering (in which case the waters presumably would have a [Na–Cl]/SiO_2 ratio similar to that found in waters draining igneous terrains)? The Bighorn Basin, Wyoming, provides a good example for such a comparison because it has rivers and streams draining either Cretaceous shales or igneous rocks; the igneous rocks have considerable plagioclase available for weathering. Table 1 and Figure 1 show that the (Na–Cl)/SiO_2 ratio is much higher for rivers draining shales (4 to 200) than igneous rocks (0.15 to 20). Ground waters from the Pierre Shale in the western United States and from the basalt aquifer of the Snake River Plain (Wood and Low, 1988) show the same results (Fig. 1).

Third, we pointed out that because smectites can be produced in the weathering zone, it is not possible to get a lower limit on the amount of sodium contributed to the global weathering budget (Cerling et al., 1989, p. 554). For that reason we stated that the exchange process could contribute "*up to* 34% of the total dissolved load" (Cerling et al., 1989, p. 552 and 554, italics added). However, oxygen isotope geochemistry can address this problem on a local scale. Studies of soils formed on shales in western North America (Lawrence and Taylor, 1972) and on glacial till containing a lot of shale (Spiers et al., 1985) do not show that smectite is actively forming or dissolving in these soils, so at least for those soils the smectites are available for recycling.

The following is in answer to the specific questions of Berner et al.

1. Most of the dissolved Na derived from shales from western North America is not associated with dissolved silica and may come from the cation exchange process.

2. We examined three shales from road cuts in Wyoming that were out of the active soil zone. They all had cation-exchange capacities between 30 and 50 meq/100 g, and Na was the dominant cation. Therefore, not all Na-rich clays are lost during diagenesis.

3. The ratio of excess sodium to silica in waters draining shales is an average of 50 times higher than the ratio in waters draining igneous rocks in the same drainage basin (Bighorn Basin, Wyoming). Ground waters show the same results.

4. The fourth question simply asks if plagioclase is more important globally than cation exchange. The purpose of our paper was to suggest that the latter is certainly important enough to be seriously considered and therefore should be addressed in future studies.

5. Stable isotope studies (discussion above) of modern soils show that smectites in shales and glacial tills can survive the weathering process and therefore are available for recycling.

We therefore stand by our original conclusions, which were that *up to* 34% of the sodium in the total dissolved stream load may be due to cation exchange, and that this implies that silicate dissolution is less important (in the global sodium budget) than was previously thought, and that future sodium weathering budgets should include the cation-exchange process.

TABLE 1. CHEMISTRY OF STREAM WATERS DRAINING UNIFORM LITHOLOGIES IN THE BIGHORN BASIN, WYOMING, USA

	T(°C)	pH	Na+	K+	Ca+2	Mg+2	Alk	Cl-	SO4-2	F-	SiO2
Cretaceous shales											
2001	22.0	7.6	26.09	0.22	6.33	3.84	4.70	1.29	20.29	0.05	0.28
2008	21.5	7.5	10.30	0.55	2.95	2.08	5.12	3.41	6.14	0.04	0.53
2009	19.0	7.1	3.57	0.08	1.38	0.81	2.63	0.19	2.71	0.02	0.17
2016	19.0	7.9	29.39	0.09	4.48	4.57	4.52	0.68	21.23	0.04	0.12
2018	17.0	7.2	2.26	0.04	1.45	0.50	2.46	0.03	1.77	0.01	0.18
2024	11.0	8.1	1.70	0.13	1.88	1.18	4.00	0.10	2.27	0.04	0.37
84-2	15.0	8.0	7.74	0.13	2.08	2.02	4.09	0.12	5.83	0.03	0.12
84-3	11.0	7.9	5.48	0.13	1.46	0.80	2.72	0.10	3.75	0.03	0.21
Volcanic and plutonic rocks											
2000	8.5	7.1	0.07	0.04	0.12	0.04	0.28	0.01	0.04	<0.01	0.16
2005	15.0	7.2	0.36	0.03	0.40	0.18	1.08	0.01	0.17	<0.01	0.25
2006	13.5	7.8	0.59	0.06	0.38	0.28	1.40	0.01	0.21	0.01	0.30
2023	9.5	7.1	0.09	0.01	0.07	0.04	0.30	<0.01	0.02	<0.01	0.15
84-9	8.5	7.4	0.70	0.01	0.17	0.07	0.94	0.04	0.08	0.01	0.19
84-10	6.0	7.6	1.10	0.01	0.23	0.15	1.54	0.03	0.10	0.02	0.32
84-11	7.0	7.3	0.44	0.02	0.23	0.14	0.91	0.03	0.10	0.01	0.42
84-12	8.0	7.2	0.39	0.01	0.15	0.09	0.70	0.01	0.07	0.01	0.37

Note: values are mmol/l, except alkalinity which is in meq/l.

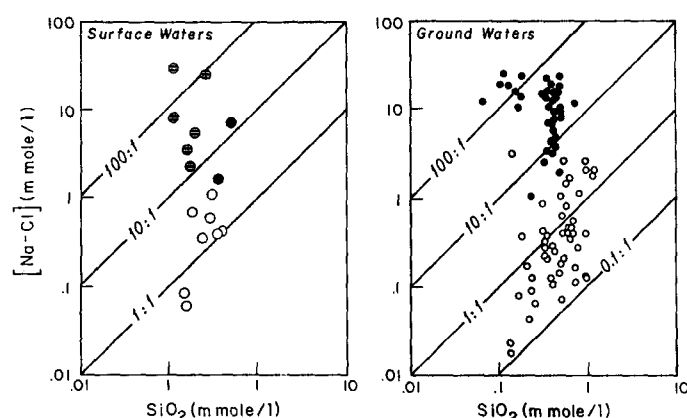Figure 1. Excess sodium (Na–Cl) and silica concentrations from streams in Bighorn Basin, Wyoming, that drain exclusively Cretaceous shales or igneous rocks, and from ground waters in Pierre Shale and in basalt aquifer of Snake River Plain, Idaho. Waters from shales have (Na–Cl)/SiO_2 ratios between 200 and 4, whereas waters from igneous rocks have ratios between 20 and 0.15, with averages of about 50 and 1, respectively.

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