

## Water – rock reaction experiments for application to the formation mechanism of Kuroko deposits

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We performed water – rock interaction experiments using the artificial seawater containing no  $\text{SO}_4^{2-}$  and several kinds of rocks to clarify why the Kuroko hydrothermal solution contains high amount of K, Ca and Ba which are enriched in Kuroko deposits and surrounding altered rocks.

Experimental study on the fresh rock (basalt, andesite, rhyolite etc) – artificial seawater interaction indicates that the dissolution rate of K accompanying the interaction with the acidic rock is faster than that accompanying the interaction with other rocks, and consequently K is enriched in the solution reacted with acidic rocks. However, Ca which is the source of anhydrite and gypsum is taken into rocks accompanying the interaction with the fresh acidic rocks.

The experiments using weakly altered dacite containing small amount of smectite from the Kuroko mining area were also performed. The elemental mobility accompanying the interaction with the fresh acidic rocks is quite different from that accompanying the interaction with the altered acidic rocks. Namely, there are two (early and late) stages of the precipitation of smectite accompanying the alteration of acidic rocks. The incorporation of Mg and Ca and dissolution of Na and K occur in the fresh acidic rock experiments corresponding to the early stage of hydrothermal activity, and the ion exchange reactions accompanied by the incorporation of Mg into rocks and dissolution of Ca and K occurs in the weakly altered rock experiment corresponding to the late stage of hydrothermal activity. The dissolution rate of K in the late stage is still large, and Ca which is incorporated into rocks in the early stage dissolves into solution in the late stage. The degree of Ba mobility in the later is larger than that in the early stage. Therefore, the present study suggests that large amounts of barite, anhydrite and gypsum in the Kuroko deposits would have precipitated from the hydrothermal solution generated in the late stage due to the interaction of hydrothermal solution with altered acidic rocks.

## Sources of the dissolved inorganic carbon in shallow coastal waters

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In the present study the sources of dissolved inorganic carbon (DIC) in pore water of surficial carbonate-rich sediments in the coastal marine zone in the Gulf of Trieste (northern Adriatic) were determined using stable carbon isotopes and chemical analyses.

### Discussion of results

The diagenetic model developed by McNichol et al. (1988) was used to understand the observed variations of DIC and corresponding C isotopic composition. In this model major processes affecting the pore water concentration of DIC are considered: oxidation of organic matter, dissolution and precipitation of  $\text{CaCO}_3$ , and irrigation by benthic infauna. The transport of DIC due to biological irrigation was described using the non-local source model (Emerson et al., 1984). Changes in the concentration of DIC by oxidation of organic matter or equilibration with  $\text{CaCO}_3$  were described by the  $\text{CO}_2$ -production rate,  $R_c(z)$ .  $R_c(z)$  is assumed to decrease exponentially with depth and in our model it is described by two exponential functions. The same diagenetic model with the best-fit parameters obtained by fitting the pore water profiles of DIC, was used to describe the profiles of  $^{13}\text{C}$  isotopic composition of DIC. It was found that this model does not reproduce the observed profiles. Data from all the cores showed that the inorganic carbon added to pore water during early diagenesis was enriched in  $^{13}\text{C}$  with respect to  $C_{\text{org}}$ . The possibilities which could be responsible for this enrichment were further examined using the calculated value of  $R_c(z)$  or by C isotope mass balance equation (McNichol et al., 1991).

### Conclusions

Dissolution of carbonates in these sediments appears to be controlled by seasonal processes and contribution to DIC production was estimated to be 57%, 14% and 35% in June 1995, in September 1995 and January 1996, respectively. The enrichment of  $^{13}\text{C}$  observed in DIC could be explained with isotopic exchange with bottom water, or the diffusion of  $^{13}\text{C}$ -depleted  $\text{H}_2\text{CO}_3^*$  from pore water to bottom water.

### References

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