

## Acid-leaching of clay mineral: a new dating method of fluid-flows?

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Clay minerals were often used as indicator during diagenetic evolution of a sedimentary succession since they could date diagenetic or hydrothermal activities. However, frequent occurrence of detrital material as well as of authigenic soluble mineral phases in the finest separated size fractions modify the K-Ar and Rb-Sr dates which prompted the use of leaching techniques. They are commonly used now to improve the fit of clay fraction data points in isochron diagrams by concentrating adsorbed elements and soluble mineral phases in the leachates. Chemical analysis of the leachates also provides information about the type of the crystalline phases intimately mixed with the clay particles (e.g. carbonates or phosphates).

In this study, the HCl-leaching method was applied to a smectite-rich bentonite layer occurring in a sedimentary claystone succession. Bentonite was known to be detrital material free. A Rb-Sr isochron age based on the leachate and residue data points of the finest size fraction was identical to the K-Ar value of the same fraction (140 Ma), suggesting that: (1) this age corresponds to the crystallization time of the smectite, and (2) the HCl-soluble phase and the smectitic material are contemporaneous. This result allows to constrain an evolution model for the clay minerals of the claystones, despite low burial temperature and systematic occurrence of detrital material in the clay fractions.

The same leaching method was also applied to the  $<0.2\mu\text{m}$  clay fractions of the claystones and the REE patterns suggest the occurrence of apatite-like minerals in the leachates. Use of the Rb-Sr isochron method outlined two types of leachates: those of the smectite-rich illite/smectite mixed-layers (I/S) giving meaningless Rb-Sr dates suggesting a mixture of non-contemporaneous soluble mineral phases, and those of the illite-rich I/S providing a value of 100 Ma, which indicates the crystallisation of authigenic phosphates during late fluid-flows without interactions with the clay particles.

In addition, chemical compositions of Na-saturated fundamental particles from the same samples suggested that the smectite interlayers contributed to the chemical and isotopic characteristics of the leachates. This behaviour might explain the deviation of the  $<0.2\mu\text{m}$  smectite-rich clays from the 100 Ma-isochron line. To validate the 100-Ma age, it is needed to estimate the contribution of the smectite interlayers, in saturating  $<0.2\mu\text{m}$  fractions with a Na-rich solution containing Sr with a known isotopic signature.

This new method may ultimately be used as a tool to date fluid-flow epochs in sedimentary sequences, and contribute to knowledge of fluid circulations leading to permeability decreases in these rocks.

## Abiotic or biotic iron isotope fractionation during oceanic crust alteration ?

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In this study we explore the potential of using Fe isotope signatures to unravel the presence of the deep biosphere associated with the alteration of the oceanic crust. We carried out this investigation using samples from ODP site 801C drilled during Leg 129 and 185 in Jurassic Pacific oceanic crust seaward of the Mariana Trench [1]. The site comprises approximately 450m of sediment overlying a section of 500m of basalt which includes intercalated pelagic and chemical sediments in the upper basaltic units and two low-temperature (10-30°C) ocherous Si-Fe hydrothermal deposits. Thread-like filaments of orange Fe-oxyhydroxide are locally present in the hydrothermal deposits and are similar to those produce by Fe-oxidizing bacteria.

Fe was chemically separated from 70 selected samples and  $^{57}\text{Fe}/^{54}\text{Fe}$  ratios were measured by MC-ICP-MS *Isoprobe*. The results are reported relative to IRMM-14 with an external precision of 0.2‰ (2σ). A detailed investigation of the  $\delta^{57}\text{Fe}$  values and Fe redox state of Fe-bearing phases indicates that the deep-sea sediment section has a restricted range of  $\delta^{57}\text{Fe}$  which is close to the Bulk Earth value. In contrast, large variations are observed in the basaltic section with positive  $\delta^{57}\text{Fe}$  values (up to 1.95‰) for highly altered basalts and negative values (down to -2.47‰) for the associated alteration products. Secondary Fe-minerals, such as Fe-oxyhydroxides or Fe-bearing clays have  $\delta^{57}\text{Fe}$  values highly variable which have been interpreted as resulting from the partial oxidation of  $\text{Fe}^{2+}$  leached during basalts alteration. In contrast, altered basalts display an increase in  $\delta^{57}\text{Fe}$  values relative to fresh values due to the preferential leaching of light iron. The apparent fractionation factor between dissolved  $\text{Fe}^{2+}$  and Fe remaining in the mineral is between 0.5‰ to 1.3‰ and may be consistent with an biotic scenario where Fe isotope fractionation is the result of chelating ligands stripping Fe from the minerals [2].

The Fe-isotope systematics presented in this study suggest that, despite iron behavior during seafloor weathering may be mediated by microbes, such as iron-oxidizers,  $\delta^{57}\text{Fe}$  variations of more than 4‰ may also be explained by abiotic processes. Further laboratory experiments are now required to distinguish between biotic and abiotic Fe isotope fractionation during seafloor weathering.

[1] Plank T., Ludden J. et al. (2000) Proc. ODP, Init Repts. 185.

[2] Brantley S.L., Liermann L. and Bullen T.D., (2001) *Geology* **29**, 535-538.