

## Leaching techniques on sedimentary and low grade metamorphic rocks: A review, recent results and some perspectives

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### Abstract

The analysis of soluble minerals and residual phases of sedimentary rocks has been used for some time in the obtention of more precise isochron ages. The acid leaching technique has often been applied to Rb-Sr dating, and the problems of selective extraction of radiogenic strontium and of isotopic homogenization between minerals are well known. Even in limestones, selective extraction of Sr and Pb have been recently described, causing distortion of Sr initial ratios or Pb-Pb isochron ages. Although less work has been carried out on the Sm-Nd method, it seems less susceptible to the problems described as a result of the geochemical characteristics of the two elements. Recent analyses performed on leachates and/or residues of clay minerals have provided geologically meaningfull ages. A few experiments have also been done by U-Pb on leachates and residues from limestones. Promising results have been obtained by U-Pb isochrons and the Pb-U concordia diagram.

### Introduction

The first successful acid leaching experiment to obtain an internally precise Rb/Sr isochron age was obtained by Boffinger et al.<sup>1</sup> on middle Ordovician shales. The leaching of radiogenic <sup>87</sup>Sr from Rb-rich minerals was not detected. A series of studies using HCl<sup>2-4</sup> were later reported, together with the results obtained with other reagents, such as anhydrous sodium acetate<sup>5</sup>, HBr<sup>6</sup>, etc. Procedures using ion exchange resins<sup>7-8</sup>, were undertaken for dating rocks or to elucidate the effects of acid leaching on the isotopic compositions of minerals, leachates<sup>6,7,9,10</sup> and residues<sup>11</sup>.

In this presentation, we show that with precise mass spectrometry it is possible to detect selective extraction of radiogenic Sr from carbonate rocks, even by extraction with water. Water extraction may also explain recent U and/or Pb losses in limestones which provide reasonable Pb-Pb isochrons and reliable U-Pb concordia ages. For the Sm-Nd system, the behaviour in limestones and clays is very different. The system can be used to date diagenesis in argillaceous sediments<sup>12</sup> and perhaps also residues extracted from limestones.

### Leaching experiments on the Rb-Sr system

Despite a number of successful applications, there are a number of restrictions when argillaceous or carbonate rocks are studied. The following conclusions are drawn:

Leaching processes using HCl or other reagents which are not particularly effective in dissolving carbonates usually selectively remove radiogenic Sr. In consequence, the isochron parameters derived are false, and various examples show that the interpretation must be undertaken with due caution;

Calcite-free clay fractions ( $< 0.2 \mu\text{m}$ ) from argillaceous sediments or shales (when a fraction  $< 2.0 \mu\text{m}$  is preferable) generally align with their leachates and residues on the isochron diagram, and the ages derived are usually geologically meaningful;

The results obtained for leached fractions from carbonate rocks must be accepted with caution because Sr in the soluble (carbonate) phase may not have equilibrated with Sr in the insoluble phase<sup>5</sup>.

#### **Leaching experiments on the Sm-Nd system in detritic sediments and carbonate rocks**

The application of the Sm-Nd method on sediments is a recent development, and the use of leachates and residues<sup>13</sup> was shown to be a valid approach<sup>14</sup>. A Sm-Nd isochron age of  $3,102 \pm 64$  Ma using clay fractions ( $< 2\mu\text{m}$ ) separated from silicate residues obtained from 0.5-1.5 kg of Fig Tree Group carbonate rocks was shown to be geologically meaningful, representing recrystallization during a thermal event. A study on diagenetic argillaceous sediments demonstrated that complete isotopic homogenization was achieved between diagenetic apatite, Fe oxide/hydroxides and clay fractions ( $< 0.2 \mu\text{m}$ ).

A more recent study<sup>15</sup> on bulk residues extracted with 1N HCl from Bambuí Group limestones and a marble resulted in a well-aligned array of points on a Sm-Nd isochron, yielding an age of  $570 \pm 43$  Ma, in agreement with an approximate chemostratigraphic  $^{87}\text{Sr}/^{87}\text{Sr}$  age of 595 Ma<sup>16</sup>.

The examples quoted show that carbonate depositional environments are well-suited to the formation of clay minerals and to their isotopic equilibration<sup>17</sup>. Furthermore, it is also possible to use silicate fraction separated by weak HCl attack together with the leachates to rapidly obtain ages of carbonate rocks.

#### **Leaching experiments on Pb/Pb and U-Pb systems**

After a pioneer study on Archaean stromatolitic limestones using the Pb-Pb isochron method<sup>9</sup>, this approach was used for dating depositional and metamorphic ages of carbonate rocks. Stepwise leaching experiments using HBr yield consistent Pb/Pb isochron ages<sup>6</sup>. Most of this study used Bambuí Group carbonate rocks and revealed four distinct types of Pb. The ages obtained were 520-680 Ma, and were interpreted as the ages of anchi- and epi-metamorphic episodes which occurred during the Brasiliano orogeny. Despite some successful U-Pb dating of limestones<sup>18</sup>, most samples revealed recent U or Pb losses. Of Bambuí limestone samples (MF-10) lie on two discordias, which suggest that they have lost both U and Pb. The lower concordia intercept of 530 and 560 Ma defined by the two discordias agree with the Pb/Pb isochron age of  $520 \pm 53$  Ma. The upper intercept of  $\sim 2300$  Ma of one discordia could be either fictitious, or could reflect the age either of the lead source or of the basement rocks.

#### **Conclusions**

Stepwise leaching is useful in geochronology, but the interpretation of the data needs caution, especially for the Rb-Sr method. The best prospect for obtaining reliable ages seems to lie with analysis of residues and leachates from carbonate rocks by Sm-Nd, Pb-Pb and U-Pb methods.

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