

Springwater geochemical response to a seismic event

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Temporal variations of groundwater physical parameters, such as piezometric levels or temperature have been used since long in the quest for earthquake precursors. More recently, attention has been focused on the gas content of these waters, as well as on the major anions variations (especially chloride and sulphate) linked to the earthquake (Hauksson, 1981; Tsunogai and Wakita, 1995; Sugisaki *et al.*, 1996). A major elements geochemical study of the Alet springwater on a time series encompassing a $M_j = 5.2$ seismic event occurring in the French Pyrénées on the 18th February 1996, near St Paul de Fenouillet, led to the observation of a chlorine anomaly starting 5 days prior to the seismic event and lasting for slightly less than two weeks (Toutain *et al.*, 1997). We have further expanded this work using trace element and isotope geochemistry and preliminary results are presented here.

Methods

The material used consisted of water samples spanning nearly two years, from the summer 1995 to the winter 1997. In addition to the major anion and cation determination reported elsewhere (Toutain *et al.*, 1997), 0.2 micrometer filtered and HNO_3 -acidified samples were used for trace elements analysis without preconcentration scheme. Water samples were analysed by quadrupole inductively coupled plasma mass spectrometry (Q-ICP-MS; Perkin Elmer Elan 5000) with a cross flow nebulizer in Toulouse. Ultratrace elements were determined using a double focusing inductively coupled plasma mass spectrometer (DF-ICP-MS; Element, Finnigan) attached to an ultrasonic nebulizer with a desolvation unit (USN 6000+, CETAC) in Trondheim. This allowed detection limits to be commonly below the ppt level with RSD of a few percent at the ppt level. ^{206}Pb , ^{207}Pb and ^{208}Pb isotopic compositions were

determined along with the elemental concentrations. These lead ratio were obtained with RSDs usually better than 1% in these waters containing few tens of ppt of lead.

Results

Among all the trace elements analysed across the time series, Zn and Pb showed particularly conspicuous anomalies close to the earthquake. Figure 1 shows preliminary data obtained by Q-ICP-MS. The zinc anomaly is characterized by concentrations up to four times above the baseline values. The earthquake effect is also clearly apparent on Pb, with concentrations being up to 10 times above the background, although the baseline is around the detection limit of the Q-ICP-MS.

To overcome this detection limit problem for lead, the more sensitive DF-ICP-MS technique was used on a time series extending from August 1995 till February 1997. Although a few water samples from the baseline showed spikes due to rain events, the result shown in Fig. 1 was confirmed with more than twenty analyses to establish the baseline.

Furthermore, isotopic analyses showed significant $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ variations on the samples with anomalously high Pb concentrations. These isotopic ratios, which normally display crustal-like signatures in the baseline, point to anthropogenic lead during the anomaly.

An other noticeable feature is that although the Pb anomaly is more intense than the Cl one (the latter showing concentrations only 36% above background values around the earthquake), it occurs over a shorter time span. Whereas the chlorine anomaly lasted for *c.* 12 days, the lead anomaly lasted for one week only. It started three days before the earthquake (that is one day after the Cl anomaly), and ended about 3-4 days after the seismic event, at least two days before the end of the chlorine anomaly.

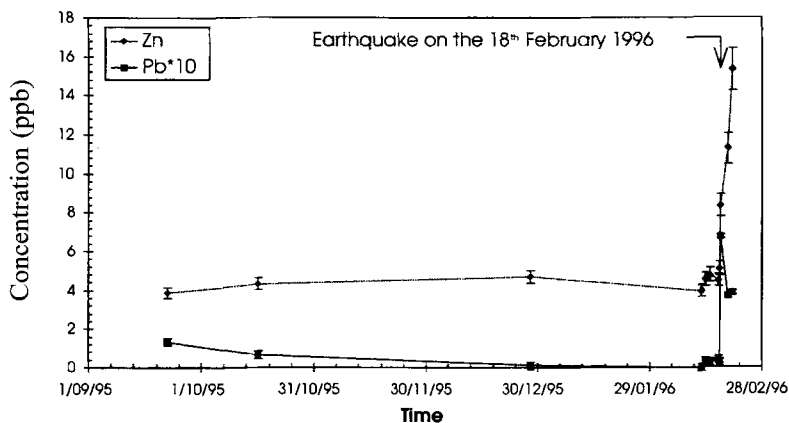


FIG. 1. Quadrupole-ICP-MS time series of the Alet springwater showing Zn and Pb geochemical anomalies starting 3 days prior to the earthquake.

Discussion

The chlorine anomaly was interpreted in terms of pre-seismic strain of the crust which eventually went through a threshold, beyond which mixing of geochemically different aquifers occurred (Toutain *et al.*, 1997). Geological and geochemical arguments indicate that the Rennes les Bains aquifer is a likely candidate as a contaminant for the Alet waters. Both aquifers are hosted by the same geological formation, i.e. Devonian-Carboniferous carbonates, and the Rennes les Bains waters, which rise about 10 km away from the Alet spring, is *c.* 15 times more enriched in chlorine than the latter.

Although the Rennes les Bains waters have a Pb concentration about twenty times higher than those of the Alet baseline, they cannot explain the lead anomaly via the scenario described above. This is because the temporal shift between the two geochemical anomalies cannot be accounted for by a single mixing process of waters from two different aquifers. They are, a priori, no physical process which may explain a difference of mobility of several days between Cl and Pb in water. Furthermore, the Rennes les Bains waters do not have the adequate Pb isotopic composition to give the Alet anomaly.

Instead, a more likely scenario is the involvement of three different aquifers: Alet, Rennes les Bains and an additional one. Although the geochemistry of the springs rising in the vicinity of Alet was surveyed, none of them has the adequate trace element content and Pb isotopic composition. Nevertheless, the shorter response, on a time basis, of the lead signal

compared to the chlorine one, as well as the more anthropogenic Pb isotopic signatures suggest that the third aquifer is probably closer to the Alet spring than the Rennes les Bains one, and is also shallower.

The hydrogeology of the Alet area is now becoming well characterized (Bouchaala, 1991). This, together with the intensities of the geochemical anomalies, the time difference of their occurrence prior to the earthquake, and total duration allow to calculate estimates for the volumes of water masses involved in the mixing, as well as the distance from the Alet spring where the aquifer became connected. This in turn can help to estimate the locations in the crust where the strain was beyond the threshold leading to the mixing of different aquifers. Such geochemical studies of groundwaters can therefore usefully complement geophysical studies of the spatial distribution of strain before a seismic event.

References

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