Origin and significance of mobile trace elements in volcanic lakes – a case study at Poás, Costa Rica

Image: Wendy Sáenz, 25 August 2005

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Abstract

Many active volcanoes host a crater lake that receives input from fluids derived from the underlying magmatic-hydrothermal system. The chemical properties of such a volcanic lake are to a large extent determined by the injection of subaqueous fumaroles and/or the influx of thermal water at the lake bottom. The chemistry of lake water therefore provides insight into the transport of chemical elements from deep sources to the surface. Dynamic changes in subsurface parts of the system are often reflected in changes in the lake-water composition with time. Hence, monitoring the lake-water chemistry can be an important tool in assessing the nature of transient subsurface processes and in predicting future manifestations in the crater area, including upcoming eruptive events.

Interpretations of lake compositions are not straightforward and rely on detailed insights into the processes and conditions that control the presence and concentration of each individual dissolved chemical species of interest. This study focuses on a group of trace elements that are known to be highly mobile in volcanic environments but have rarely been investigated as yet. Based on available analytical data from several decades of monitoring, it uses the active crater lake of Poás volcano in Costa Rica as an example to explore the behavior of B, Zn, As, Mo, Sn, Sb, Tl and Pb and to identify possible sources and sinks in volcanic lake systems.

For all of these elements, concentrations in the lake water show enrichment relative to magnesium and other rock-forming elements, which argues against congruent rock dissolution as main source but is consistent with preferential input via subaqueous fumarolic gas. Time-series trends covering periods with fluctuations in the activity state of the lake (between 1980 and 2009) indicate increased concentrations when the lake system was most active. There is a general correlation between concentration levels and lake temperature, and an inverse correlation with pH. These patterns point to an enhanced input of the elements during intervals of increased activity and phreatic eruptions, in agreement with evidence for a stronger influx of magmatic gas. In contrast, concentration levels were lower during periods of decreased activity when conduits below the lake were presumably blocked. Still, this group of elements remained more enriched relative to elements that predominantly partition into brine water, suggesting that in these intervals gas/vapor transport was less affected by reduced permeability than the input of hydrous fluid.

Though the time-series trends for the investigated elements are roughly parallel, they are not identical for the entire group in detail, which points to differences in behavior and in the underlying controls. Similar trends for lead and tin indicate that the input of this element pair is controlled by the same process, possibly transport by supercritical water as dissolved Pb and Sn-trichloride complexes. A role of sulfides can explain an occasionally deviating behavior of As, Mo and Sb. A sudden depletion was observed during the recent active period, which possibly reflects the uptake of these elements by sulfides that started forming in response to increasing temperatures at depth.

The results of this study demonstrate the potential of monitoring this group of mobile elements in crater lakes and associated surface manifestations. They provide insights into the nature and conditions of processes in magmatic-hydrothermal systems that can be different and complementary to those delivered by the more traditional group of monitored elements.

Origin and significance of mobile trace elements in volcanic lakes – a case study at Poás, Costa Rica

Thesis outline

1 – Introduction

Many volcanoes around the world host lakes in their crater or caldera. Information is available on over 300 volcanic lakes (Rouwet and Chiarini, 2013). These lakes can provide interesting data concerning the activity of the volcanic and hydrothermal systems beneath the lake by water-rock and water-magma interaction. Additionally, a degassing magma body can release its volatiles into the waters of the hydrothermal system, and the lake can act as a buffer for these chemical species.

Lakes on top of volcanic craters or calderas can be very dynamic systems. When such a lake interacts with the magma source underneath it, by means of a hydrothermal system, different gases, vapors and magmatic fluids can be transferred into the lake. As these systems can be indicative of the current activity of the volcano, active monitoring can bring insight into the processes and the development of the system. This development can be physical (temperature, conductivity, color, volume) or chemical (pH, concentration of various elements or element species) in origin.

Even though volcanic lakes can indicate volcanic activity, the regular use of volcanic lake monitoring is not applied very often. This can be because regular sampling of lake waters might be dangerous, expensive or very difficult. For example, when crater walls are very steep, sampling may only be possible by means of a rope stretching from one end of the crater to the other end (Ohsawa et al., 2010).

Volcanic lake monitoring is applied mainly to determine the volcanic activity, to recognize rising magma, and give early warnings for volcanic eruptions. To this end, the main elements analyzed are those that are released from magma in the form of volatiles, sulphur and chlorine being the most common. These serve well to provide a larger scale picture of past, current and future events (Rowe et al., 1992).

However, magmatic volatiles are not limited to elements that are released in large quantities. Many elements are present in relatively low concentrations. Analyzing these trace elements can be useful to determine trends that might be too small to see otherwise. As trace elements only need a little enrichment to show strong changes, certain processes might be identified by means of trace elements and not by trends in main elements. The high mobility of certain trace elements might also contribute to this. The high mobility of trace elements is attributed to their tendency to partition into vapors and brines, which transfer easily from the magmatic source, through the hydrothermal system, and into a crater lake (Heinrich et al., 1999).

In this study we try to discover the origin and significance of these trace elements. To investigate these elements, the active lake of Poás volcano in Costa Rica is selected. Observatory OVSICORI (Observatorio Vulcanológico y Sismológico de Costa Rica) has been conducting regular geophysical and geochemical monitoring of the active lake, Laguna Caliente, since 1978. With measurements stretching over 30 years and with great regularity, a detailed time-series of the lake's activity is available.
Next to the availability of physical characteristics and main element concentrations of the samples (pH, temperature, sulphur, chlorine, etc.) there is also a detailed time series for trace elements available (Martínez, 2008). The good quality of information on Laguna Caliente makes it the best option to conduct a case-study on volcanic lake trace element chemistry.

The elements in this study are: B, Zn, As, Mo, Sn, Sb, Tl and Pb. The main reason for selecting these elements is their mobility and availability in the data (Martínez, 2008).

In this study, first some background information concerning volcanic lakes is provided: how they are formed, what the general processes influencing their behavior are, and to what end the monitoring of these lakes can be used. Next, we explore the mobile trace elements concerned in this study. After that, we look at the geology and processes that formed Laguna Caliente, in the volcano Poás in Costa Rica.

This study was conducted using the data from Martínez (2008) and from A. Huizinga (2013, personal communication). A preliminary overview of the data was compiled, the results of which are presented in detail in chapter 4. Time series of temperature, pH, main- and trace elements were compiled, and the various different elements were plotted against each other. Some trends and correlations were marked to be investigated at a later point, and outliers were identified.

To separate volcanic enrichment from enrichment through other sources (rock dissolution, water evaporation), Element Transfer Ratio analysis has been conducted. The details are mentioned in chapter 5. Carr et al. (2003a,b; 2007) provided rock composition of rocks around Poás. Elemental compositions missing from this data were amended with averages from the USGS Rock Database (2013a,b; chapter 5.2).

Though some trends could be explained by means of Element Transfer Ratio analysis, it did not provide a full picture. A sudden event of arsenic, antimony and molybdenum depletion between November 2007 and June 2008 required a different approach. In chapter 6, the hypothesis that this drop is caused by sulfide precipitation was posed and analyzed.

## 2 – Theoretical background – Volcanic lakes systems and trace elements

2.1 – Volcanic lakes

Volcanic lakes form when water – either meteoric water or ground water – establishes a permanent feature in a volcanic crater or caldera (Pasternack and Varekamp, 1997). Depending on the fumarolic activity, a hydrothermal system can be established, in which the water can interact with magmatic gases.

Volcanic lakes can be classified based on their overall chemistry. Varekamp et al. (2000) made such a classification based on 157 different lakes. At the top level, the difference between pH-neutral and acidic lakes was made. Neutral lakes are either bicarbonate like Lake Nyos in Cameroon (Sigvaldson, 1989) or classified as "dilute", meaning there is no excess carbon dissolved. An example of this is Lake Albano in Italy (Anzidei et al., 2006).

Most of the active volcanic lakes are acidic in nature, while others are pH-neutral. Acidic lakes include: Crater Lake at Mount Ruapehu, New Zealand (Christenson, 2000); Laguna Caliente in Poás Volcano, Costa Rica (Martínez, 2008); Yugama Lake in Kusatsu-Shirane Volcano, Japan (Ohba et al., 2008).

Crater lakes can also be classified based on their geophysical behavior. Classifications based on this, range from very highly active (variable mass, frequent volcanic eruptions, high thermal energy output) to hardly active, where the main hazard is a limnic CO_2 explosion (Pasternack and Varekamp, 1997).
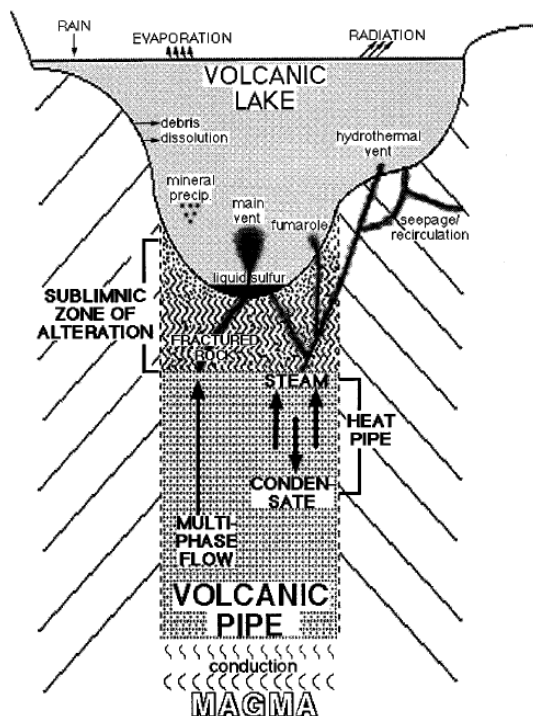
Fig 2.1 Schematic overview of a volcanic lake system. Image from Pasternack and Varekamp, 1997. See text for explanation.

Figure 2.1 shows a schematic overview of a typical acid volcanic lake system, similar to that of Poás. The lake is established in the crater. Water enters the system through hydrothermal venting of groundwater, by H_2O degassing of the magma body or by rain, and leaves the system through evaporation of water, overflow or seepage through the crater walls and into outflow streams (Pasternack and Varekamp, 1997). Percolation of the water through the host rock can form a hydrothermal system between the magma reservoir and the lake. Convection is the main driving force of such a hydrothermal system, as heat and hot gases released from the magma cause the heated waters to rise, while colder water seeps down to replenish this.

Gases released from the magma reach the lake through this hydrothermal system, where the chemical species dissolved in the gases are transferred into the lake. High concentrations of sulphuric species can lead to a layer of liquid sulphur at the bottom of the lake, as pictured in Figure 2.1. Poás has such a layer of liquid sulphur,

indicated by sulphur globules that reach the surface regularly (Martínez, 2008).

Other factors that regulate the lake's chemistry are precipitation of minerals of which the concentration exceeds maximum solubility, dilution by meteoric waters or volatilization of chemical species (well-known examples are HCl, H_2S and other sulphur species), and removal of chemical species through outflow (Rouwet and Tassi, 2011; Martínez, 2008). Concentrations can be increased through dissolution of host rock (both in the crater walls as in the rock surrounding the hydrothermal system) or evaporation of lake waters.

2.2 – Monitoring of volcanic lakes

The use of geophysical parameters in the monitoring of volcanic lakes can be very useful. Values such as temperature, pH and conductivity can provide an indication of the amount of volatiles and thermal energy being injected into the lake. The level of the lake, combined with its bathymetry can provide the volume of the lake. This is mainly useful in lakes with varying volume (Pasternack and Varekamp, 1997), especially so in situations where the lake is prone to overflow, causing lahars.
Observed color changes in the lake might give a preliminary insight into the chemical composition of the lake, and the level of subaqueous fumarolic activity from the hydrothermal system (Ohsawa et al., 2010)

Next to geophysical parameters, the geochemistry of volcanic lakes can be a very useful monitoring tool. As explained earlier, the chemistry of volcanic lakes is regulated by multiple different factors. Increase in concentration might be attributed to enhanced volcanic enrichment, host rock dissolution, evaporation of water or any combination of those factors. Similarly, decrease in concentration might be by decreased volcanic enrichment, precipitation of mineral species, dilution by inflow of meteoric- or groundwater, removal of chemical species from the system by outflow, volatilization of chemical species, or once again any combination of those processes.

When lakes are situated in environments with a clear wet and dry season, the seasons can easily influence absolute concentrations in the lake. Assuming a constant absolute amount of dissolved species, concentrations are expected to decrease during the wet season, and increase during the dry season. Concentrations are expected to increase and decrease by approximately the same amount due to rainfall and evaporation respectively, so concentration ratios between various elements can be used to filter out the effects that evaporation and rain have on the lake's chemistry. A much used concentration ratio is that of Mg/Cl (e.g. Martínez, 2008; Pasternack and Varekamp, 1997). Assuming all magnesium is released via rock dissolution and not directly from magmatic sources, a drop in this concentration ratio might mean increased volcanic activity.

When lake waters drop below the levels of the fumaroles, or when fumarolic activity shifts from subaqueous fumaroles to subaerial fumaroles, enrichment by volcanic gases might reach lake waters in reduced amounts, or not at all. Such shifts in fumarolic activity have been speculated to play a role in the difference between the various phases of Poás development (see chapter 3 and Martínez, 2008).

2.3 – The importance of trace elements

Most of the geochemical monitoring of volcanic lakes focuses on major constituents such as sulphur, chlorine, magnesium and iron (e.g. Martínez, 2008; Ohsawa, 2010) or – for CO_2-saturated neutral lakes – the partial pressure of CO_2 and other dissolved gases (e.g. Kusakabe et al., 2008). Tracking these constituents can provide insight in volcanic activity, and may even indicate future eruptive activity (e.g. Giggenbach and Glover, 1975)

Of the elements with low abundance, the Rare Earth Elements (REE) are often used. Their normal relative abundances are well known and studied, and the distribution of these elements in case studies can reveal mineralogy and formation processes (e.g. Wolkersdorfer, 2002).

This study concentrates on several trace metals and metalloids with high mobility (i.e. elements that move easily from magmatic sources into aqueous solution and magmatic vapors) and relatively low abundance in the lake. There is some, but not much, fundamental information on the behavior of these elements in hydrothermal systems. Johnson et al. (2013) reported on the fundamental behavior during crystallization of a number of low-abundance metals in magmatic systems. A lot of work has been done on arsenic due to its nature as a pollutant (e.g. Wang and Mulligan, 2008; Craw et al., 2003). But in general, the behavior of mobile trace elements in magmatic- or magmatic-hydrothermal systems is not well understood yet.

2.4 – Element mobility

The mobility of elements is determined by the speed at which they pass through a system. In essence, this comes down to the phase where they preferentially partition in to.
Elements that remain locked in minerals can be considered immobile as they do not move much.
Elements that remain in magmatic melts are somewhat more mobile, though the only time where they effectively pass through a system is during an eruption.
Elements that preferentially partition into aqueous solution are able to pass through the system quite easily, and are relatively mobile.
The most mobile type of elements are those that partition into vapors and gases. Vapors and gases have the highest speed of flow through the magmatic and hydrothermal system, and therefore have the lowest residence times.

As a result of this, element mobility can be expressed by means of partitioning coefficients of these elements into brines or vapors. A higher degree of partitioning will mean a higher degree of mobility. Knowledge about element partitioning can therefore provide insight into the relative mobility of different elements.

To determine which elements are gas-mobile and to what extent, condensates from fumaroles can be used (e.g. Zelenski et al., 2013; Gemmell, 1987). Elements that are enriched as compared to the magmatic source can be seen as gas-mobile. A great number of trace metals and metalloids fall in this category (Symonds et al., 1987; Zoller et al., 1983). Table 2.1 lists fumarole condensate concentrations of the main elements and the elements of this study, of Poás and a number of other volcanoes, table 2.2 lists a few more fumarole condensates from Poás, taken over several years (Africano et al., 2007).

When looking at the mobility of elements, the different sources and sinks of these elements must be taken into account as well. While fumarolic gas most likely originates directly from a magmatic source, intermittent deposition or revolatilization of material can alter the composition of these fumarolic gases and thus affect the apparent mobility of the elements dissolved in these gases.

	Poás Costa Rica (ppm) [1]	Cerro Negro Nicaragua (ppm) [1]	Ela Arte Ethiopia (ppm) [2]	Merapi Indonesia (enr.fact) [3]	Colima Mexico (ppb) [4]
Cl	1090	1760	5800	8000	10500 (ppm)
F	2.0	4.7	2300	540	310 (ppm)
B	N/A	N/A	117 (ppb)	N/A	28 (ppm)
Zn	2.7	0.60	2.0	190	5300
As	N/A	0.061	1.2	810	433
Mo	N/A	0.22	36 (ppb)	85	91
Sn	2.5	0.87	0.21	N/A	N/A
Sb	0.005	0.003	4.0 (ppb)	17	42
Tl	N/A	N/A	109 (ppb)	N/A	24
Pb	2.4	N/A	0.49	35	451

Table 2.1 Fumarole condensate values of various volcanoes around the world. Concentrations, unless indicated otherwise are specified in the top row. N/A: not available.
Sources:
[1] Gemmell, 1987.
[2] Zelenski et al., 2013.
[3] Symonds et al., 1987. Values listed are enrichment factors instead of concentrations, compared to Li. See chapter 5 for details on enrichment factors.
[4] Taran et al., 2001

	17-Apr-1997	5-Dec-2002	Jan-2003	17-Jan-2003	Mar-2003
T (°C)	93	122	92	120	97
Cu	22	154	17	82	2.85
Zn	620	349	69	N/A	456
As	1.35	86	N/A	4.9	31
Se	0.62	0.86	N/A	1.69	1.26
Sn	0.78	3.04	1.68	0.75	0.4
Sb	0.49	2.47	0.76	0.41	0.76
Tl	0.08	0.23	0.07	0.08	0.05
Pb	11	100	63	77	0.9
Bi	0.02	0.58	0.02	0.29	0.03

Table 2.2 Fumarole condensate values of Poás, Costa Rica. Concentration values in ppm (Africano et al., 2007)

When a crater lake overlies a fumarolic system, the crater lake can be seen as a condensation vessel for the gases from the fumaroles. Exploring the chemistry of the crater lake means indirectly exploring the fumarolic discharge. Though care should be taken when doing this, as there are many factors determining the chemistry of the lake, such as those described in sections 2.1 and 2.2.

2.5 – Elements in this study

The elements used in this study were selected based on the average element transfer ratios (ETR) as reported by Martínez (2008). The ETR is in essence the volcanic enrichment factor. This is explored in detail in chapter 5.

In this study, we look at boron (B), zinc (Zn), arsenic (As), molybdenum (Mo), tin (Sn), antimony (Sb), thallium, (Tl) and lead (Pb). In the next sections, the important properties and some general information of each of these elements are described. The elements are listed in order of their atomic number in the Periodic Table. Additionally, some information is presented about the concentrations of these elements in other crater lakes, as a comparison. Lakes used for this are:

- Ruapehu, New Zealand (Giggenbach, 1974; Christenson and Wood, 1993; Deely and Sheppard, 1996).
- Two of the three lakes of Keli Mutu, Indonesia, being Tiwu Ata Polo (TAP) and Tiwu Nua Muri Koohi Fah (TiN) (Pasternack and Varekamp, 1994).
- Kawah Ijen, Indonesia (Van Hinsberg et al., 2010).

2.5.1 – Boron (B)

Boron (atomic number 5) is both the lightest and most abundant of the trace elements concerned in this study. Concentrations ranged from 1100 µg/kg on May 25, 2004 to 88900 µg/kg on April 2, 1993 (Martínez, 2008).

In Ruapehu crater lake, New Zealand, the concentrations of boron ranged from 10.6 mg/L to 18.4 mg/L between late 1988 and late 1990 (Christenson and Wood, 1993). In the lakes of Keli Mutu, in TAP, boron was found to be 12.4 ppm in 1989 and from 20.8 to 21.8 ppm in 1992 and in TiN, 135 ppm in 1989 and from 224 to 230 ppm in 1992 (Pasternack and Varekamp, 1994). In Kawah Ijen, boron was found to be between 46 and 52 ppm in 2007 (Van Hinsberg et al., 2010).

In nature, boron is found in low concentrations in a wide variety of rocks and environments. More concentrated deposits are often associated with volcanic and hydrothermal activity. In these environments, boron is often found as borate compounds, most likely by precipitation from dissolved boric acid (Matterson, 1980). In industry, boron is used as an additive in glass making, bleaches and detergents and pesticide (Woods, 1994). Boric compounds generally dissolve well in acidic waters, so we expect this element to have a high overall mobility in the Poás system.

2.5.2 – Zinc (Zn)

The second lightest, and second most abundant trace element in this study is zinc (atomic number 30). Concentrations in the lake ranged from 650 µg/kg on February 22, 2005 to 17200 µg/kg on April 2, 1993. There are no measurements available for zinc after November 2, 2005 (Martínez, 2008).

In the crater lake of Ruapehu, concentrations of zinc ranged from 2.8 to 4.8 mg/L between 1971 and 1973 (Giggenbach, 1974), were found to be 2.16 mg/L in 1990 (Christenson and Wood, 1993) and found to be 1610 µg/L in 1992 (Deely and Sheppard, 1996). In the lakes of Keli Mutu, in TAP, zinc was found to be 1.7 ppm in 1989 and from 1.7 to 2.0 ppm in 1992 and in TiN, 7.5 ppm in 1989 and from 8.8 to 9.6 ppm in 1992 (Pasternack and Varekamp, 1994). In Kawah Ijen, zinc was found to be between 4.9 and 6.2 ppm in 2007 (Van Hinsberg et al., 2010).

In nature, zinc is widely associated with hydrothermal mineral deposits. It is most commonly found as sphalerite ((Zn,Fe)S), which is the primary ore for zinc mining. Sphalerite is often found in conjunction with galena (lead sulfide), and therefore both of these elements have been included in this study to assess the similarity in trends. Applications of zinc range from use in alloys (most commonly used together with copper to form brass) to dietary supplements.

2.5.3 – Arsenic (As)

Arsenic (atomic number 33) is a relatively abundant and enriched element in the lake. Concentrations ranged from 143 µg/kg on June 4, 2008 to 16000 µg/kg on November 19, 1992 (Martínez, 2008).

In the Ruapehu crater lake, arsenic concentrations ranged from 0.2 to 3.3 mg/L between 1971 and 1973 (Giggenbach, 1974) and were found to be 1.6 mg/L in 1990 (Christenson and Wood, 1993). In 1992 they were found to be 672 µg/L (Deely and Sheppard, 1996). In the lakes of Keli Mutu, in TAP, arsenic was found to be 1.3 ppm in 1989 and from 0.6 to 0.9 ppm in 1992 and in TiN, 7.2 ppm in 1989 and from 5.1 to 5.4 ppm in 1992 (Pasternack and Varekamp, 1994). In Kawah Ijen, arsenic was found to be between 1.6 and 2.0 ppm in 2007 (Van Hinsberg et al., 2010).

In hydrothermal systems, arsenic is often associated with sulfide precipitation, most notably for its tendency to be incorporated into arsenopyrite (Craw et al., 2003;) or as a trace element in pyrite, under influence of H_2S (Berner et al., 2013). Arsenic is notorious as a pollutant and byproduct from mining from hydrothermal deposits – most notably gold mining (Johnsen, 2007, pg121).

2.5.4 – Molybdenum (Mo)

Molybdenum (atomic number 42) is the second least abundant of the elements in this study. Its concentration ranged from 1.7 µg/kg on May 25, 2004 to 700 µg/kg on November 19, 1992 (Martínez, 2008).

In Kawah Ijen crater lake, molybdenum was found in concentrations ranging from 0.002 to 0.005 ppm in 2007 (Van Hinsberg et al., 2010).

Molybdenum is often found as molybdenite in high-temperature hydrothermal systems (e.g. Seo et al., 2012). Molybdenite is the primary ore mineral for molybdenum (Johnsen, 2007, pg122). In oxidizing environments, molybdenum binds to lead, forming wulfenite ($PbMoO_4$ – Johnsen, 2007, pg226).

2.5.5 – Tin (Sn)

Tin (atomic number 50) concentrations in Poás ranged from 1.3 µg/kg on January 5, 1996 to 2310 µg/kg on April 2, 1993 (Martínez, 2008).

In Kawah Ijen crater lake, tin was found in concentrations ranging from 0.30 to 0.46 ppm in 2007 (Van Hinsberg et al., 2010).

Tin easily forms structures with chloride, the most notable being stannous chloride ($SnCl_2$). In hydrothermal solutions, tin can also form trichloride complexes, $SnCl_3^-$ (Uchida et al., 2002). In oxidizing environments, tin can occur as cassiterite (SnO_2 – Johnsen, 2007, pg169). Already in historical times, the metallic form of tin has been used in alloy together with copper to form bronze. Today, use in alloys is still tin's main use.

2.5.6 – Antimony (Sb)

Antimony (atomic number 51) is the least abundant of the elements in this study. Its concentration ranged from 0.48 µg/kg on January 5, 1996 to 410 µg/kg on November 19, 1992 (Martínez, 2008).

In the crater lake of Ruapehu, antimony was found to be in concentrations of 0.0045 mg/L in 1990 (Christenson and Wood, 1993). In the lakes of Keli Mutu, in TAP, antimony was found to be 0.07 ppm in 1989 and less than 0.5 ppm in 1992 and in TiN, 0.2 ppm in 1989 and less than 0.5 ppm in 1992 (Pasternack and Varekamp, 1994). In Kawah Ijen, antimony concentrations ranged from 0.03 to 0.06 ppm in 2007 (Van Hinsberg et al., 2010).

Antimony is in the same group in the periodic table as arsenic, and shares it's affinity with sulfide minerals. As with arsenic, when under the influence of H_2S it is easily incorporated into pyrite (Berner et al., 2013). In nature, it is commonly found as stibnite (Sb_2S_3). In contrast with pyrite, stibnite is often associated with low-temperature hydrothermal veins (Johnsen, 2007, pg113). At higher temperatures and under oxidizing conditions, antimony can form valentinite or its less common polymorph senarmonite (Sb_2O_3, Johnsen, 2007, pg157).

2.5.7 – Thallium (Tl)

The abundancy of thallium (atomic number 81) is in the middle of the range of elements in this study. Concentrations ranged from 12 µg/kg on February 22, 2005 to 3160 µg/kg on September 24, 1991. Similar to zinc, there are no thallium measurements after November 2, 2005 (Martínez, 2008).

In Kawah Ijen crater lake, concentrations of thallium were found to be 0.8 ppm in 2007 (Van Hinsberg et al., 2010).

Thallium is not commonly found as a single metal in sulfide minerals, though it is a major constituent in lorandite ($TlAsS_2$) and exists in trace amounts in other sulfide minerals such as pyrite (Shaw, 1952).

2.5.8 – Lead (Pb)

Lead (atomic number 82) is the heaviest of the elements in this study, and in moderately high abundance in the lake. Concentrations ranged from 38 µg/kg on February 22, 2005 to 8190 µg/kg on April 2, 1993 (Martínez, 2008).

In Ruapehu crater lake, concentrations of lead ranged from 0.4 to 0.9 mg/L between 1971 and 1973 (Giggenbach, 1974), were reported to be 0.96 mg/L in 1990 (Christenson and Wood, 1992) and were reported to be 303 µg/L in 1992 (Deely and Sheppard, 1996). In the lakes of Keli Mutu, in TAP, lead was found to be less than 0.3 ppm both in 1989 and in 1992, and in TiN, 3.7 ppm in 1989 and from 3.5 to 4.0 ppm in 1992 (Pasternack and Varekamp, 1994). In Kawah Ijen, lead ranged in concentrations from 4.5 to 4.9 ppm (Van Hinsberg et al., 2010).

Lead is in the same group in the periodic table as tin, and shares many of its properties. Like tin, lead forms trichloride complexes ($PbCl_3^-$) in magmatic vapors or brines (Uchida et al., 2002). In hydrothermal systems, lead can precipitate as galena (PbS). Under very acidic conditions, lead remains in solution, complexing with chloride forming $PbCl_{2\,(aq)}$ or $PbCl_4^{2-}{}_{(aq)}$. Rising pH breaks down these complexes, causing galena to precipitate (Reed and Palandri, 2006).

3 – Geological background – Central America, Costa Rica and Poás

3.1 – Central America and Costa Rica

At the western end of Central America, the Cocos-plate subducts below the Caribbean plate and the Panama block, resulting in the Central America Volcanic Arc (CAVA). Costa Rica is located at the southern end of the Caribbean plate, and directly offshore to the west of Costa Rica, the Middle American Trench (MAT) marks the location where this active subduction takes place (Carr et al., 2003a; Husen et al., 2003, Fig. 3.1).
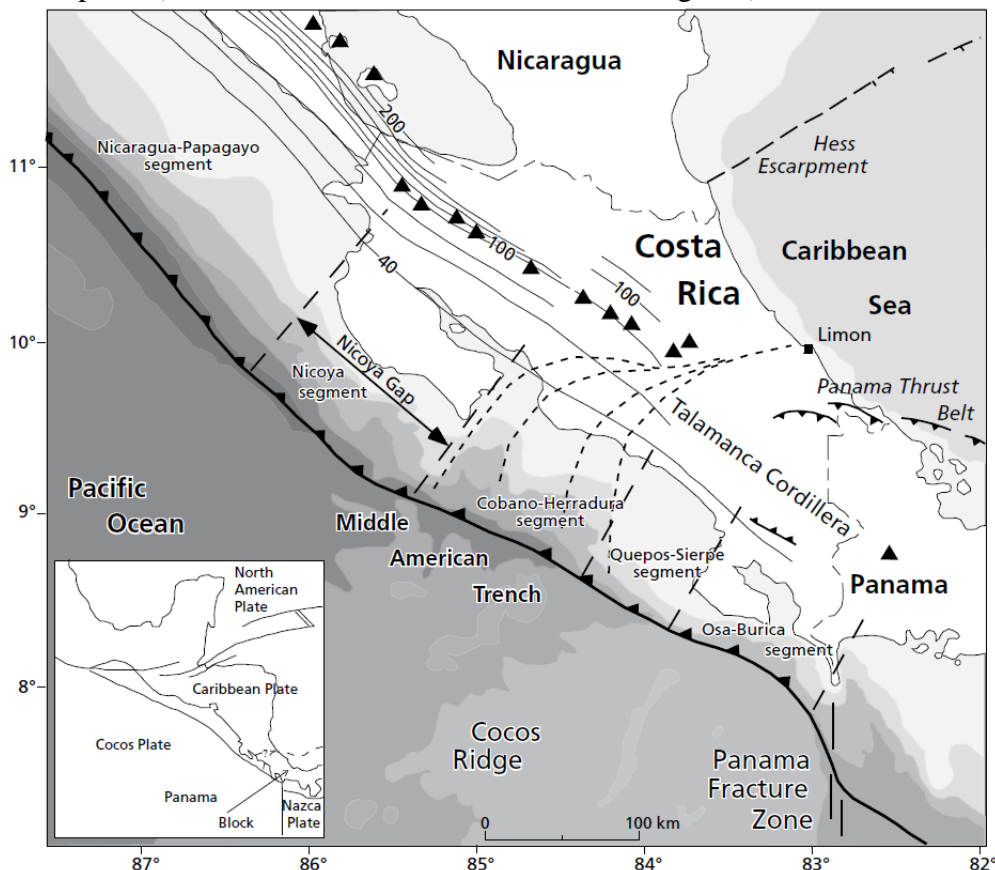
Fig 3.1 Tectonic setting of Costa Rica and the area around it. (adapted from Protti et al., 2001 and Martínez, 2008)

The Costa Rican part of the CAVA consists of at least 290 volcanic centers or apparatuses, of which 8 are currently being monitored or exploited for geothermal products (Alvarado, 2000; Martínez, 2008).

The Costa Rica Volcanic Arc (CRVA) consists of two zones, Cordillera de Guanacaste and Cordillera Central. Cordillera de Guanacaste is the northern part of the CRVA, running from the border between Costa Rica and Nicaragua towards the SE. The geochemical signatures of these volcanoes transition between the volcanoes of Nicaragua, which are characterized by a depleted mantle source and a strong subduction component, and those of the Cordillera Central. Like the Cordillera de Guanacaste, Cordillera Central also runs from NW to SE. The country's capital San Jose is located in close proximity to this mountain belt. One of the more prominent volcanoes of this belt is Poás (Martínez, 2008, and references therein).

3.2 – Poás

The Quaternary volcano Poás lies approximately 35 kilometers to the NW of San Jose, in the Cordillera Central. The volcanic cone is a broad basaltic to andesitic stratovolcano, with a maximum elevation of 2708 meters above sea level. The Poás massif is a complex system with multiple cones and craters. In historical times though, the only active crater was that of the Poás cone, in between the Botos cone to the southeast and the Von Frantzius cone to the north (see Fig 3.2). The Botos cone contains a cold freshwater lake, while the Poás cone contains the hyperacidic hot crater lake Laguna Caliente. The lake is fed and warmed by a shallow hydrothermal system (Martínez, 2008).
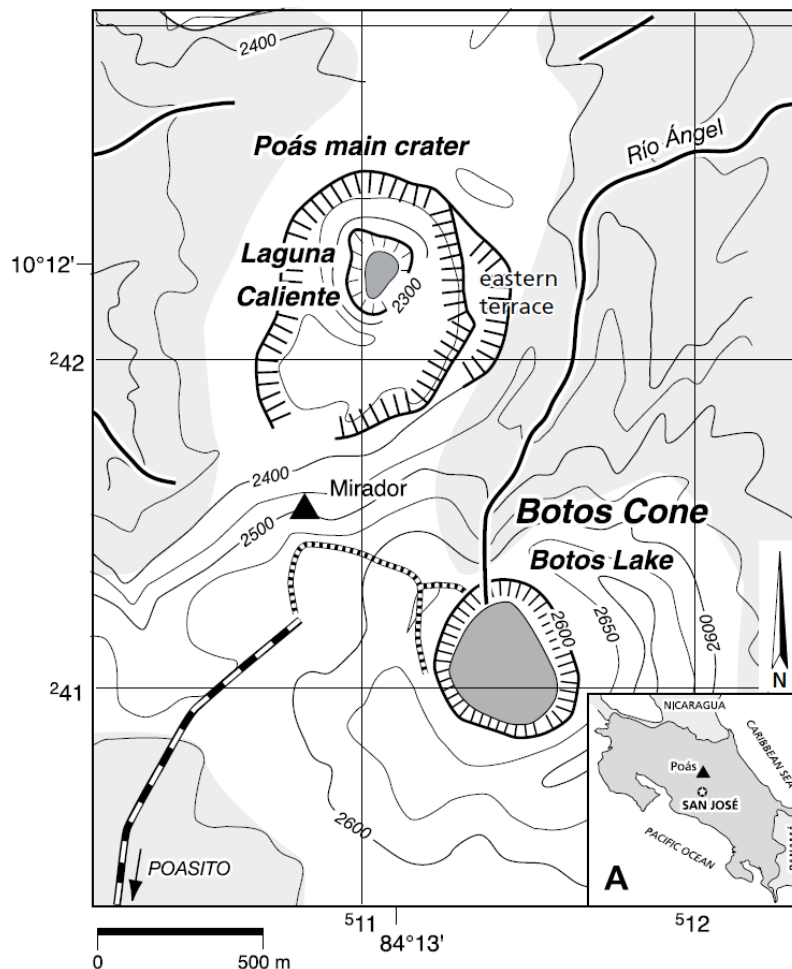
Fig 3.2 Schematic overview of the Poás massif, with the Botos cone and lake, and Laguna Caliente. The Von Frantzius cone is not shown on this image. Image adapted from Martínez, 2008.

3.3 – Long term geochemical evolution of Poás

Active geochemical monitoring of Laguna Caliente started in 1978 by OVSICORI, but records over the past 175 years have over 60 subaqueous eruptions documented (Martínez, 2008).
During the three decades of active monitoring at Laguna Caliente, a broad range of morphological and geochemical changes have been documented. The depth and diameter of the lake at maximum have been 55m and 320m respectively, though the lake has dried out and/or evaporated fully several times. Temperatures ranged from 22 to 95 ℃ and the color of

the lake varied between bluish, greenish, and gray. Geochemically, there have been a number of large fluctuations and variations as well. The pH ranged between -0.87 and 1.75, and various chemical species have had concentration differences of several orders of magnitude (Martínez, 2008).

OVSICORI (the Costa Rican volcanological and seismological observatory) has been sampling Poás lake regularly for the past three decades. Detailed chemical time-series, both of main and trace elements, have been presented by Martínez (2008). Sampling of the lake is done mainly in one spot, but extra sampling from multiple spots and depths have established that the lake is fairly homogeneous. The different measurements of January 2001 show that this is also the case for the trace elements in this study.

The long term evolution of the lake is divided into five distinct stages. Descriptions of these stages are paraphrased from Martínez (2008).

- Stage I (from the beginning of regular monitoring to August 1980) was a rather active stage. pH dropped below 0, temperatures averaged 49 degrees Celsius and the total dissolved solutes (TDS) averaged around 1.5×10^5 mg/kg. A few sporadic phreatic explosions were recorded.
- Stage II (September 1980 – April 1986) was relatively quiescent compared to Stage I. Although the temperature of the lake did not change on average, pH levels were above 0 and TDS was reported at an average 8.7×10^4 mg/kg. No phreatic explosions were reported during this stage.
- Stage III (May 1986 – August 1995) was the most active stage in the past three decades of Poás' evolution. Large degrees of fumarolic degassing regularly evaporated the entire lake, leaving only mud pools on the crater floor. Temperatures averaged 66 degrees Celsius, but peaked 94 degrees at times, the boiling point at the altitude of the lake. TDS was reported around 1.6×10^5 mg/kg, and pH averaged to -0.2. Phreatic eruptions were intense and numerous.
- Of all stages, stage IV (September 1995 – February 2005) was the most quiescent stage in the recorded evolution of the lake. Though fluctuations were large, the average temperature (33 degrees Celsius), TDS (2×10^4 mg/kg) and pH (around 1), combined with no phreatic eruptions, clearly mark this stage as the most quiescent stage.
  Stage 4 is subdivided into five substages, 4a through to 4e. These substages alternate between very quiescent (stages 4a, 4c and 4e) and somewhat more active (4b and 4d). This is possibly due to conduit blockages by mineral precipitation in substages 4a, 4c and 4e. These substages are explored in more detail in chapter 5.
- Stage V (March 2005 – Present) shows clear signs of renewed activity. Phreatic eruptions returned (e.g. Fig 3.3), temperatures rose to around 58 degrees Celsius, and pH dropped to around 0. TDS increased by almost an order of magnitude to over 1.5×10^5 mg/kg in September 2007. This stage is ongoing, and due to the similarity to the transition between stages II and III, phreatic activity is expected to continue.

Fig. 3.3 Stage V phreatic explosion of Poás, February 25, 2014. Image captured on webcam by OVSICORI

4 – Data in this study

4.1 – Poás data

Main- and trace element data up to November 2005 were collected by OVSICORI and presented by Martínez (2008). Further data, up to April 2009, were collected by OVSICORI (A. Huizinga, personal communication 2013). The total number of samples with trace element data per stage is listed in table 4.1.

Stage	Time period	Number of samples	Source
I	Before August 1980	0	[1]
II	Sept. 1980 – Apr. 1986	6	[1]
III	May 1986 – Aug. 1995	10	[1]
IV	Sept. 1995 – Feb. 2005	48	[1]
V	Mar. 2005 - Present	44*	[1], [2]

Table 4.1 Number of samples with trace element data, listed per stage.
*No analytical data is available for zinc and thallium after November 2005.
Sources:
(1) Martínez, 2008. Data up to November 30, 2005
(2) A. Huizinga, personal communication, 2013. Data up to April 3, 2009

The complete data set used is provided in Appendix A. Time series of the elements in this study (B, Zn, As, Mo, Sn, Sb, Tl and Pb) and time series of temperature, pH and total sulphur are provided in figure 4.1. The different stages have been marked, and are easily recognizable by their trends.

As noted, of the trace elements, no data is available on Stage 1. But the temperature graph (Fig 4.1i) shows temperatures ranged from 70 to 30 °C. In temperature, stage 1 is comparable to the latter part of stage 3. The single pH measurement of -0.10 in February 1979 (Fig 4.1j) confirms this.

The beginning of stage 2 is characterized by a short dip in temperature. The temperature does rise somewhat, but drops again. With an average of 48 °C, temperature wise the lake was not much different from stage 1. The first measurements of trace elements are from this stage (Fig 4.1a-h). While there are not a lot of measurements, they do show that in general the concentrations of these elements did not vary by much in this stage, arsenic being the biggest exception.

The onset of stage 3 is marked by higher concentrations of all elements, a higher temperature and a lower pH. Of arsenic, and especially of molybdenum, concentrations varied by large amounts over the course of stage 3, stretching over 2 orders of magnitude for molybdenum. Together with that, the concentration of sulphur (Fig. 4.1k) varied notably as well, especially in the later phase of stage 3.

Stage 4 is clearly recognizable as the least active stage of Poás' evolution with low concentrations of all the trace elements, the lowest temperatures on average, and the highest pH values on record. In all graphs, a repeated up- and downwards trend can be seen. Martínez (2008) explained this by repeated conduit sealing and reopening during this stage; this will be explored further in chapter 5.

In stage 5, the activity of the volcano increased again. Concentrations of the different elements rose, temperatures increased, and pH decreased. Note the anomalous sudden decrease of concentration of arsenic, molybdenum and antimony towards the end of stage 5. Careful examination of this sudden decrease, shows that the drop in molybdenum preceded antimony, which in turn preceded that of arsenic. This will be further explored in chapter 6. A general decrease in concentrations of boron, tin and lead is most likely due to lake dilution. However, during this time the pH still decreased, indicating that the activity of stage 5 is still ongoing.

Figure 4.2 focuses on the behavior of different trends in stages 4 and 5, as data is more complete in this interval.
These images can show us the time delay in element concentrations. Figure 4.2a shows the concentration ratio arsenic-antimony through time, with the concentration of arsenic overlain. At the beginning of stage 5, both increase suddenly. But while arsenic concentrations keep increasing, the ratio arsenic-antimony starts dropping around April 2006, when antimony begins to increase.

A similar behavior is seen in Figure 4.2b, where the concentration ratio arsenic-lead is seen through time, once again, with the arsenic concentration overlain. The onset of stage 5 is marked by an increase in arsenic, and a similar increase in the ratio, after which the ratio drops, but the arsenic concentration keeps rising, indicating the lead concentration starts rising at this point.
Another interesting point to note here is that of June 2002, where the arsenic-lead ratio is at its highest point during these two stages, while the absolute arsenic concentration shows a local lowest point. This is also a point where the concentration of lead is lowest. The concentration decrease of lead is much stronger than that of arsenic, leading to the high concentration ratio. And throughout stage 4, the concentration ratio shows inverse trends as compared to the concentrations themselves.
The concentration drop of arsenic at the latter parts of stage 5 is paired with an equal drop in the concentration ratio. Concentrations of lead did not change much during this stage.

The behavior of the arsenic-boron ratio shows a steadily increasing ratio at the beginning of stage 4, peaking at March 2003. This is somewhat later than the peak at the arsenic-lead ratio. Arsenic concentrations slightly peaked at this time, while the concentrations of boron were slowly rising. The continued rise of boron concentrations lead to the downward trend of the arsenic-boron ratio.
The second notable peak in this concentration ratio is just after the onset of stage 5, when arsenic concentrations rose sharply, to be followed by that of boron somewhat later.
As with lead, the drop of the arsenic-boron ratio follows that of the arsenic concentration at the latter parts of stage 5.
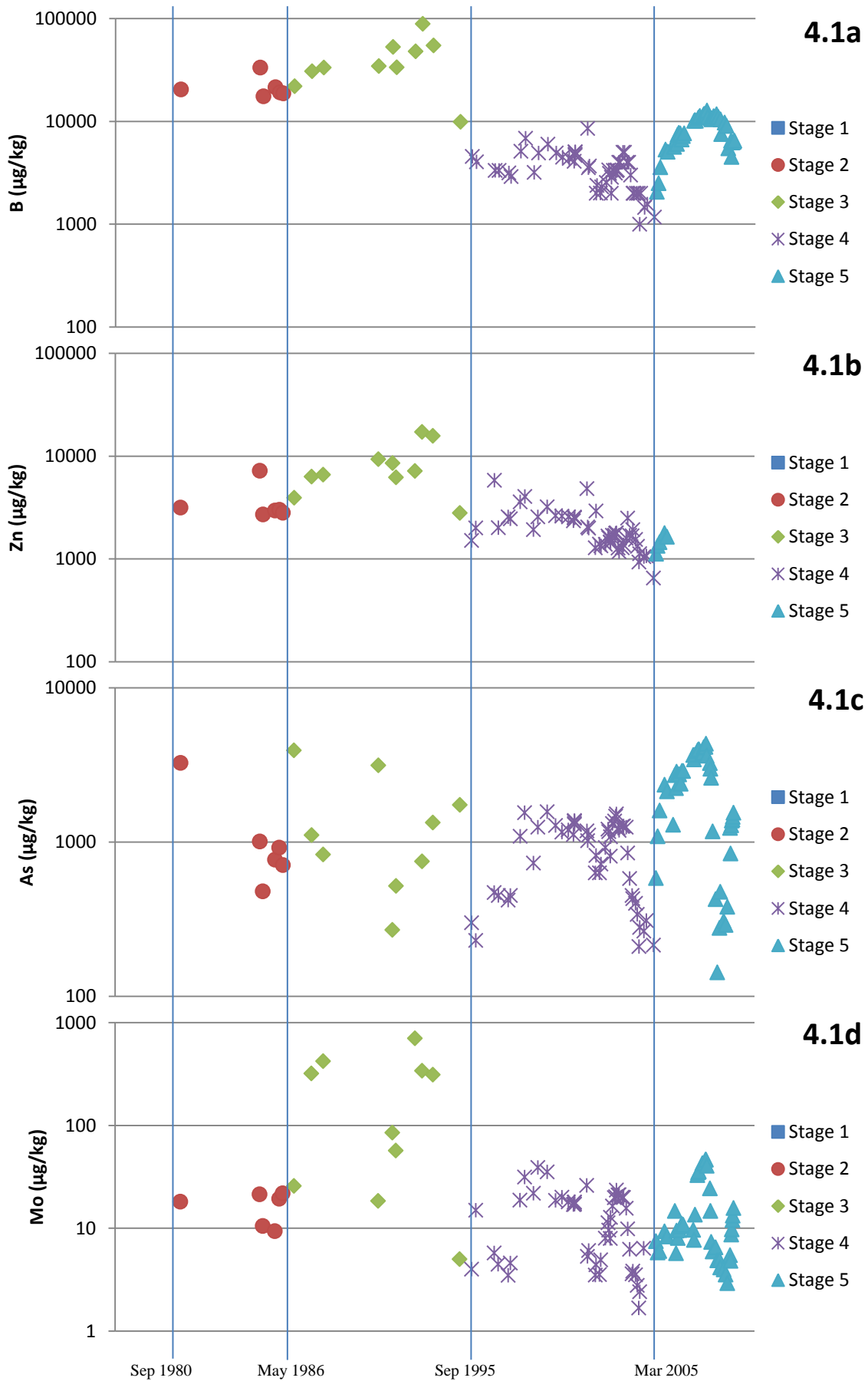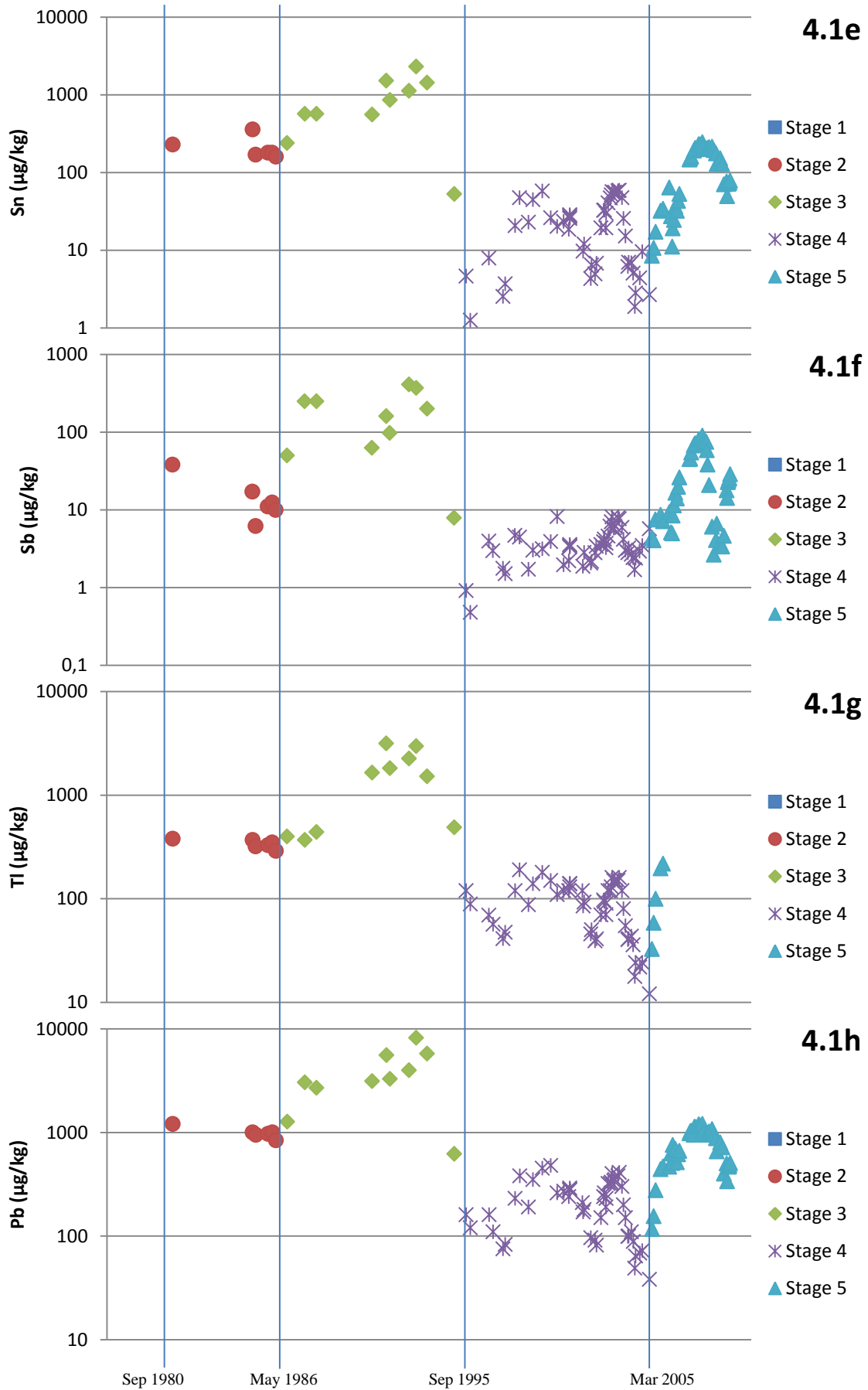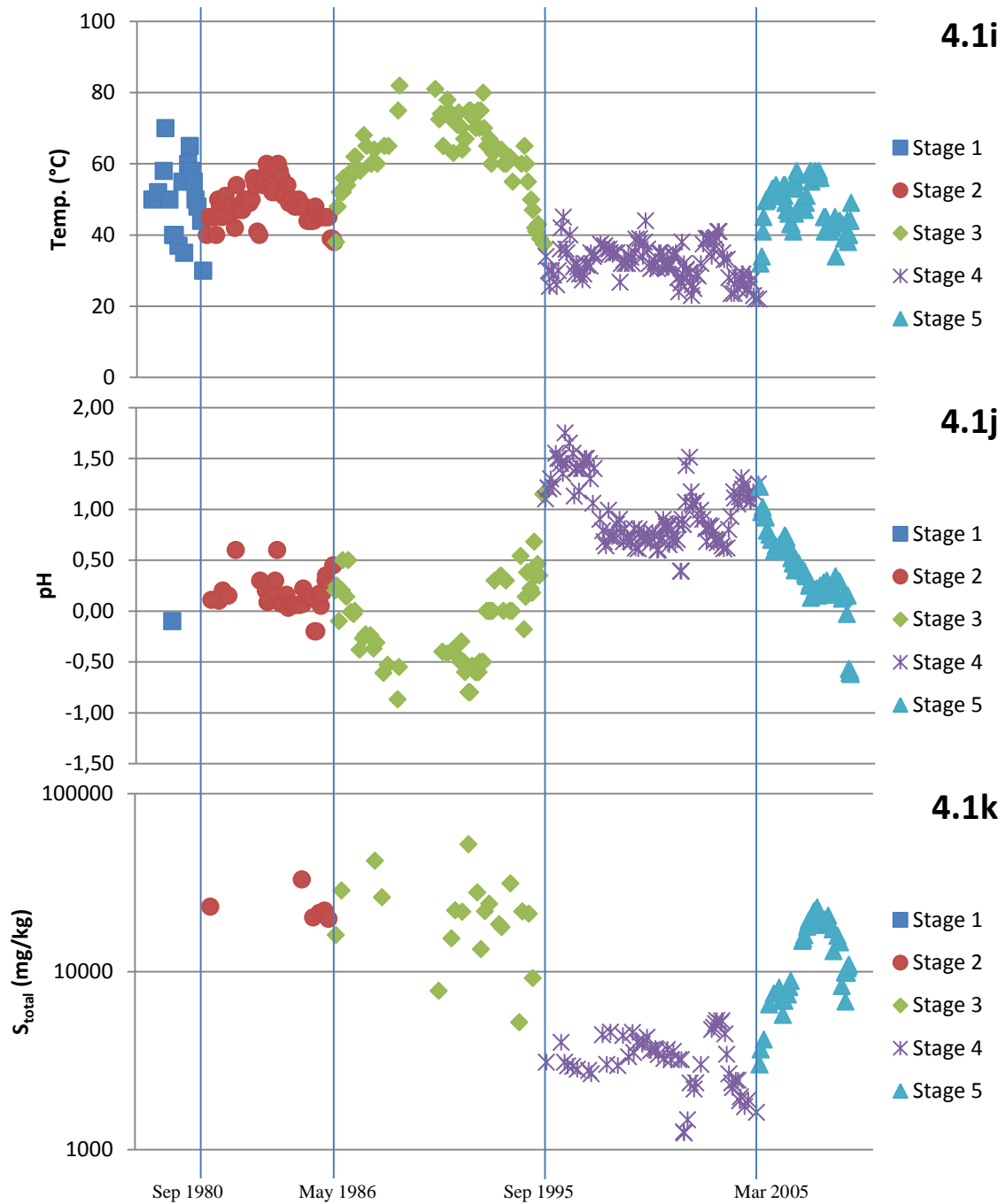
Figure 4.1 Time series of (a) Boron, (b) Zinc, (c) Arsenic, (d) Molybdenum, (e) Tin, (f) Antimony, (g) Thallium, (h) Lead, (i) temperature, (j) pH and (k) total sulphur of Poás evolution between March 1978 and April 2009. The different stages of Poás evolution as explained in chapter 3.3 are marked.
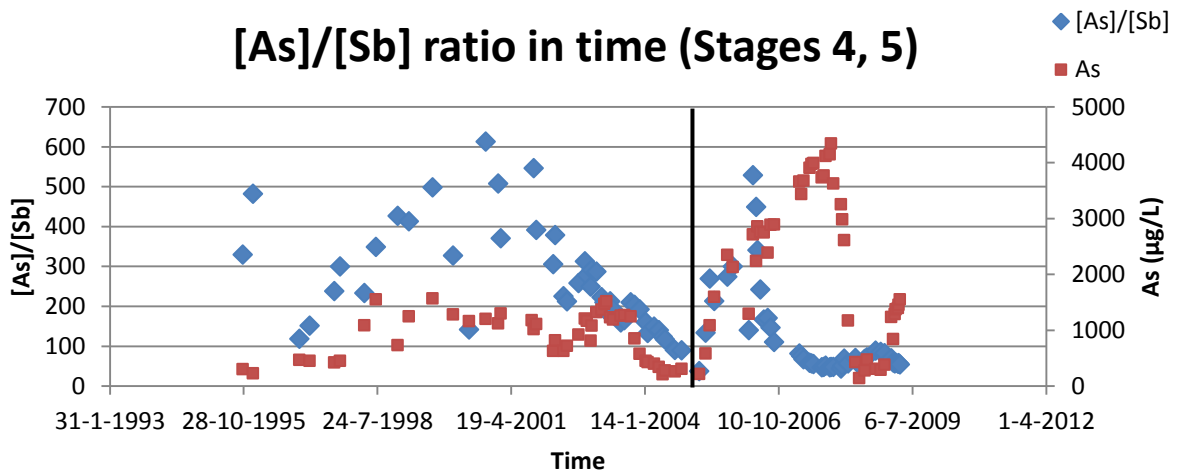
Figure 4.2a In blue (on left axis): concentration ratio arsenic-antimony of stages 4 and 5. In red (on right axis): concentration of arsenic. Black line indicates onset stage 5
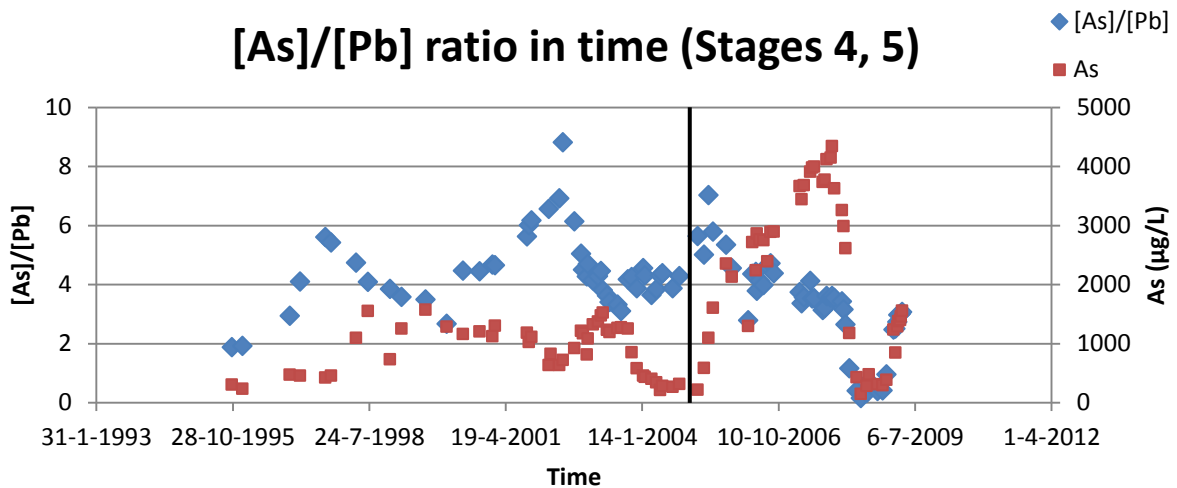
Figure 4.2b In blue (on left axis): concentration ratio arsenic-lead of stages 4 and 5. In red (on right axis) concentration of arsenic. Black line indicates onset stage 5
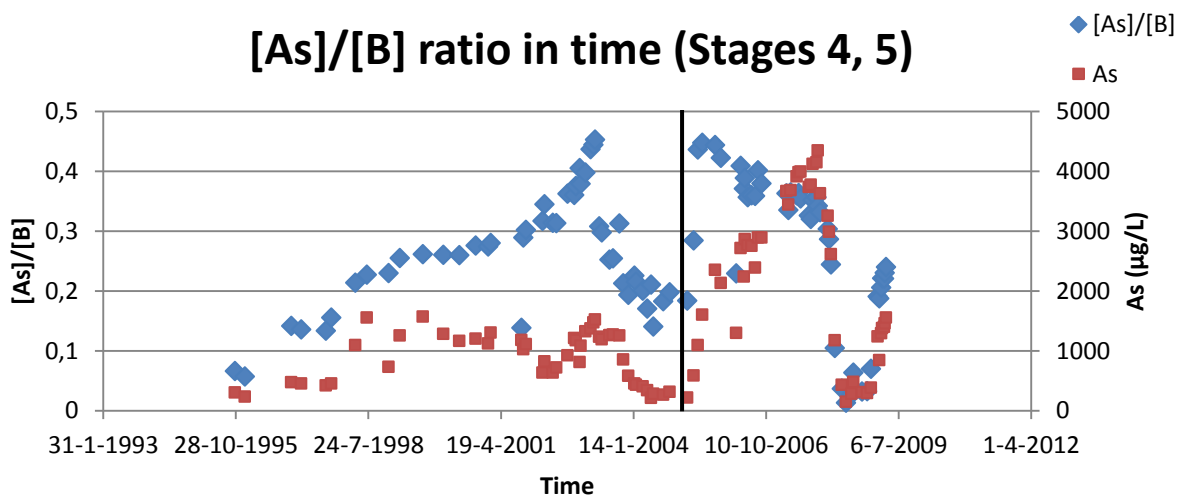
Figure 4.2c In blue (on left axis): concentration ratio arsenic-boron of stages 4 and 5. In red (on right axis) concentration of arsenic. Black line indicates onset stage 5

4.2 – Comparison with other crater lakes

Comparing the lake of Poás with other crater lakes can give insight in how representative Poás is as a proxy for volcanic lakes in general. Comparison is made with the same volcanic lakes as in chapter 2.5. Unfortunately, there is not much more data available from other volcanic lakes to make this comparison with. Though many lakes are studied, thorough trace element analyses are still relatively rare. This section attempts to draw parallels between the data available, and the various stages of Poás' geochemical evolution.

Trace element geochemistry Ruapehu between 1971 and 1973 closely resembled the end of Stage 2 in Poás. Ruapehu lake had similar concentrations of zinc and arsenic, and slightly lower concentrations of lead (Giggenbach, 1974). Between 1988 and 1990, concentrations of boron and lead in Poás matched those of Ruapehu, but arsenic and antimony were present in much higher concentrations in Poás at that time (Christenson and Wood, 1992). In 1992, Ruapehu closely resembled stage 4D of Poás evolution, once again with elevated arsenic (Deely and Sheppard, 1996).
In 1989, Keli Mutu's Tiwu Ata Polo (TAP) lake was quite similar to Poás in late 2007. Poás had notably higher arsenic and lead, but boron and antimony were similar. In 1992, this lake had more in common with stage 2 of Poás in all elements except zinc, where Poás had a higher concentration. Also in Keli Mutu, Tiwu Nua Muri Koohi Fah (TiN) did not have many similarities with Poás, except in the most extreme points of stage 3 (Pasternack and Varekamp, 1994).
Trace element chemistry of Kawah Ijen in 2007 is very different from that of Poás in all stages (Van Hinsberg et al., 2010). Boron, zinc and thallium values are much higher than those in stage 3 of Poás, while lead, tin, molybdenum, arsenic and antimony in Kawah Ijen are significantly lower compared to all stages of Poás.

5- Element Transfer Ratios (ETR)

5.1 – ETR Introduction

From the time series data described in chapter 4, we can get a grasp on the overall activity of the system. However, to study these trends in detail, we need to distinguish volcanic enrichment from other factors affecting the system, such as meteoric precipitation, evaporation, and similar processes described in chapters 2.1 and 2.2. To this end, the volcanic enrichment factor or Element Transfer Ratio (ETR) can be used (e.g. Martínez, 2008; Pasternack and Varekamp, 1994).

The basis behind an ETR analysis is determining the ratio between the element in question, and a reference element, assuming this reference element originates from dissolved rock only during congruent rock dissolution. Knowing the concentrations of the reference element R and the element in question X in the rock enables us to determine this ratio. The ratio between the element in question and the reference element can be determined both for the rock, $(X/R)_{rock}$, as for the water sample, $(X/R)_{sample}$. The volcanic enrichment factor can then be described by a modified version of the equation of Zoller et al. (1983), Equation 1. EF_X is the enrichment factor of element X.

$$EF_X = \frac{(X/R)_{sample}}{(X/R)_{rock}} \qquad \text{(Eq. 1)}$$

When the concentrations of these elements in the water is due to pure congruent rock dissolution, both ratios $(X/R)_{rock}$ and $(X/R)_{sample}$ will be the same. Equation 1 will then give an enrichment factor of 1: no enrichment.
When X is depleted in the water, for instance by mineral precipitation incorporating X into its crystal structure, $(X/R)_{sample}$ will be less than $(X/R)_{rock}$, this will give an enrichment factor of less than 1: depletion.
When the concentration of X is not only due to congruent rock dissolution, but is increased by volcanic input, $(X/R)_{sample}$ will be greater than $(X/R)_{rock}$. In this case, the enrichment factor will be greater than 1, and will indicate volcanic enrichment. The greater this enrichment factor, the greater the extent of volcanic enrichment.

Because magnesium does not transfer from the magmatic source into the vapors released (Varekamp and Pasternack, 2000), it can be taken as a reference element for pure congruent rock dissolution. Equation 2 describes the formula for the Element Transfer Ratio of element X in a certain measurement. The factors in Equation 1 have been rearranged, the sample concentration is taken as the aquatic (dissolved) concentration of elements X and Mg.

$$ETR_X = \frac{[Mg]_{rock*}\,[X]_{aq}}{[X]_{rock*}\,[Mg]_{aq}} \qquad \text{(Eq. 2)}$$

ETR values higher than 1 indicate enrichment compared to congruent rock dissolution. Processes that could be responsible for the enrichment of an element include the injection of volcanic gas carrying high concentrations of the element into the lake, or dissolution of secondary minerals that do not belong to the original mineral assemblage, but were

precipitated at a later stage. ETR values lower than 1 indicate depletion compared to congruent rock dissolution, which can be due to retention of the element in an insoluble mineral in the rock, or to precipitation of a mineral that became saturated in the lake.

ETR analysis is therefore a useful tool in determining the degree of enrichment or depletion in the lake waters, possibly in respons e to the status of volcanic activity.

5.2 – Assumptions for rock composition – calculating the average andesite rock

To determine element transfer ratios of Poás, the composition of those rocks with which the water interacted should be known. Carr et al. (2003a,b) analyzed lavas from volcanoes throughout Central and South America, including several rocks from Poás lavas and surroundings.

However, this data does not include concentrations for S, F, B, As, Sn and Sb. To carry out ETR analysis on these elements, some information on their relative abundances in rock is needed. For a representative estimate, an average could be taken from rocks that are compositionally very similar to those of Poás. This section describes that process.

Compositionally, Poás lavas can be classified as andesite, with an SiO_2 content of 55.9 wt% on average (Carr et al., 2003a, b).

To calculate the average andesite composition, rock values from the USGS rock database (2013a) were imported into a database. For this, the XML schema of the USGS database (2013b) – the defined data format for the database – was imported and converted to an SQL schema (see Appendix B), using PHP scripting and the SimpleXML library (php.net, 2013). A PHP script was made that analyzed the XML definitions, and selected the elements needed for the SQL schema. The script then outputted this schema as an SQL "create table" query, which was ran to create a database table. The 'PhpMyAdmin' interface was used to run these database queries (PhpMyAdmin, 2012).

All data from rocks marked as being andesite were imported (USGS Rock database, 2013,a). The data was received in a comma-separated-value (.csv) format, and imported into the database via the PhpMyAdmin (PhpMyAdmin, 2012). Further PHP scripting was then applied to select the rocks with a composition close to that of Poás lavas, to count these, and determine their average composition.

All data operations were carried out by means of the WAMP-server package (Windows Apache, MySQL, PHP), version 2.2C (Wampserver, 2012).

Only those rocks with an SiO_2 content of within 5 wt% of the Poás lavas as calculated by Carr et al. (2003b), between 50.9 and 60.9 wt% SiO_2, were selected. 5354 samples matched this criterion. From these samples, a quick inventory was made, the results of which are presented in table 5.1. In this inventory, the samples are classified by the various major analysis techniques, the date at which the sample was submitted to the USGS for analysis, and whether or not the sample was found to be inside or outside of detection limits.

Concerning the date of the samples, an arbitrary cutoff was made at January 1st, 1990, based on the assumption that analytical quality has improved since then. Samples without a clear

date have been classified as before 1990 and have been largely omitted from analysis. Of the selected samples, 1860 samples matched this criterion.

In the USGS Rock database (2013,b), every field of analytical data is accompanied by a qualifier field. This field is only used when the corresponding concentration was found to be outside of detection limits, or not detected at all.

In essence, when the concentration was found to be outside of machine calibration, the concentration cannot be accurately verified. The qualifier field is used to indicate when this is the case. There are three main cases in which this qualifier field is used.

- The element was analyzed but was not detected at all in the analysis.
- The element was detected in analysis, but at a concentration lower than the lowest calibration point of the detector.
- The element was detected in analysis, but at a concentration greater than the highest calibration point of the detector.

In all these cases, the value filled in in the data field is the detection limit value, in essence the lowest calibration value (first two cases) or highest calibration value (third case). In the inventory, the actual content of the qualifier was not taken into account, meaning that no distinction was made between samples that were measured at concentrations below the lower detection limit or not at all, and samples that were measured at concentrations above the upper detection limit.

The information about the qualifiers is useful to take into account when determining the average abundance of an element. When a significant percentage of analyzed rocks were found to have concentrations outside of the detection limits, taking only those analyses within detection limits can affect the average. For instance, when half of the analyses is below detection limit, taking the average of the other half will lead to an overestimation of the relative abundance of that element.

To solve this problem, in case of a large percentage of analyses outside of detection limits, those analyses will have to be taken into account as well. As no information is available other than the value of the detection limit itself, this will most likely still not provide the correct average, but it will be better than before.

To select which samples and methods were to be used to determine the average abundance for the elements not available in the rock analysis of Poás lavas (Carr et al., 2003a,b), the following considerations have been made, based on the inventory of samples presented in table 5.1.

- For **sulphur (S)**, the samples of after 1990, both inside (36%) and outside (64%) of detection limits, which were described as "other" in the database were selected for the average. The field that this selection is based on is described as "*Miscellaneous methods: Total Sulphur (percent) – Concentration of total sulphur (S) in percent, usually determined by a combustion method*" (USGS Rock Database schema, 2013b).

- The **fluorine (F)** samples classified as "other methods" were all analyzed by means of ion selective electrode. Only those samples after 1990 were selected for the average. These were all found to be inside of detection limits.

- For the **boron (B)** average, the samples analyzed by means of emission spectrometry and analyzed in or after 1990 were selected. Due to the large percentage (50%) of samples that were found to be outside of detection limits, the average was determined over both the samples inside as well as outside of detection limits.

- For **arsenic (As)** the choice was made to look at the post-1990 neutron activation analysis results, this produces both the highest amount of samples inside detection limits and the highest proportion of samples inside detection limits. However, approximately one third of the samples analyzed this way still fall outside of detection limits. Additional counting has been executed to see if these numbers change as the samples become more recent.
Looking at only those samples collected and analyzed in or after 1995, 21 samples fall inside detection limits, while 2 samples fall outside of them. Due to the low percentage of samples outside detection limits in this time period, only those inside detection limits were used.

- The samples for **tin (Sn)** marked as method unknown provide both the highest amount and the highest proportion of samples inside detection limits. However, it is unknown which method is used to analyze the samples. Also, all samples in this category are from before 1990. Yet it was the only viable choice for determining the average for tin. In any case, due care should be taken when working with the tin average, as the calculated average might differ substantially from the actual average found in andesite rocks.

- Neutron activation analysis was the prevalent analysis method for **antimony (Sb)**, and seeing the large amount of samples that fall within detection limits and were analyzed in or after 1990, those samples were used to determine the average. As a relatively small proportion of analyses fall outside of detection limits, these are left out of the calculation.

METHOD	XRF				Emission spectrometry				ICP-AES				ICP-MS				Neutron activation analysis				Other				Unknown			
DATE	Before 1/1/1990		After 1/1/1990		Before 1/1/1990		After 1/1/1990		Before 1/1/1990		After 1/1/1990		Before 1/1/1990		After 1/1/1990		Before 1/1/1990		After 1/1/1990		Before 1/1/1990		After 1/1/1990		Before 1/1/1990		After 1/1/1990	
DETECTION	Out	In	Out	In	Out	In	Out	In	Out	In	Out	In	Out	In	Out	In	Out	In	Out	In	Out	In	Out	In	Out	In	Out	In
S	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	60	75	**34**	**19**	0	0	0	0
F	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	35	0	**48**	2	146	0	0
B	0	0	0	0	318	72	**11**	**11**	0	0	0	2	0	0	0	0	0	0	0	0	0	0	0	0	79	95	0	0
As	0	0	174	13	190	1	20	2	245	21	230	17	0	0	0	0	84	58	100	**211***	7	1	0	0	98	4	0	0
Sn	0	1	167	13	385	5	22	0	265	1	243	2	0	0	0	0	0	0	0	0	1	1	0	0	**113**	**23**	0	0
Sb	0	0	177	0	191	0	22	0	0	0	0	0	0	0	0	0	175	464	42	**223**	7	0	0	0	80	4	0	0

Table 5.1: Counts of rock samples in the USGS rock database (2013,a) with information on the following elements. Distinctions are made between the different analysis methods, the date at which the samples are analyzed (pre-1990 is separated from post-1990) and whether or not the samples are found to be inside or outside detection limits. Samples marked bold are those selected for the average rock abundance calculations.

* Of the As samples selected, only those after 1995 were taken into consideration due to analysis accuracy. See text for explanation.

5.3 – ETR values

The average composition of Poás lavas was calculated and can be found in table 5.2 (Carr et al, 2003a,b; USGS rock database, 2013a). The main elements (top part) are noted in Wt%, the trace elements in mg/kg or Wt-ppm.

ELEMENT	Relative abundance (Wt%)	Source	ETR Stage 2	ETR Stage 3	ETR Stage 4	ETR Stage 5
SiO_2	55.9	[1] [2]	0.0053	0.0074	0.014	0.0091
Al_2O_3	17.3	[1] [2]	0.678	0.96	0.43	0.92
MgO	3.62	[1] [2]	1	1	1	1
S	0.40	[3]	1340	1100	300	1100
F	0.087	[3]	17.1	46.3	8.28	19.2

ELEMENT	Relative abundance (ppm)	Source	ETR Stage 2	ETR Stage 3	ETR Stage 4	ETR Stage 5
B	13.6	[3]	75.7	130	20.3	43.5
Zn	79.5	[1] [2]	2.16	4.45	1.99	2.08*
As	1.79	[3]	26.1	90.3	39.3	83.5
Mo	2.42	[2]	0.34	4.54	0.47	0.42
Sn	10.6	[3]	0.93	3.79	0.17	0.76
Sb	0.426	[3]	1.50	20.3	0.75	4.81
Tl	0.055	[2]	291	1270	125	196*
Pb	6.32	[1] [2]	7.33	25.8	3.15	8.10

Table 5.2: Main and trace element average composition of Poás lavas. Main elements are presented in wt%, trace elements are presented in ppm. Next to that, the average ETR as compared to MgO for the last four stages of Poás' evolution.
* No data available after October 2005
Sources:
[1] Poás lavas and lapilli tuff, compiled by Carr et al. (2003a,b).
[2] Poás lavas near Rio Cuarto, compiled by Carr et al. (2007).
[3] Calculated average andesite rock with SiO_2 content within 5 WT% of the average found in Poás lavas. Calculated by means of rock data from the USGS rock database (2013,a). For precise method of calculation, see section 5.2
Analyses have been carried out by M. Carr unless otherwise specified, by means of XRF measurements at Michigan State University (Thomas Vogel lab, SiO_2, Al_2O_3, MgO), dc-plasma emission spectrometer lab at Rutgers during the period 1976-2005 (SiO_2, Al_2O_3, MgO), high resolution ICP-Ms at the Institute of Marine and Coastal Sciences, Rutgers University (Zn, Mo, Tl, Pb) or quadrupole ICPMS Department of Chemistry Rutgers University (Gene Hall Lab, Pb, carried out by L. Patino). Analyses from the USGS rock database (2013,a, source [3]) have been carried out by the USGS.

Table 5.2 also lists the average element transfer ratios for the trace elements during the last four stages of Poás' evolution, using the data collected from OVSICORI-UNA (Martínez, 2008). Detailed time series graphs of these can be found in Figure 5.1a-h. Note that the ETR values presented in table 5.2 are averages only.
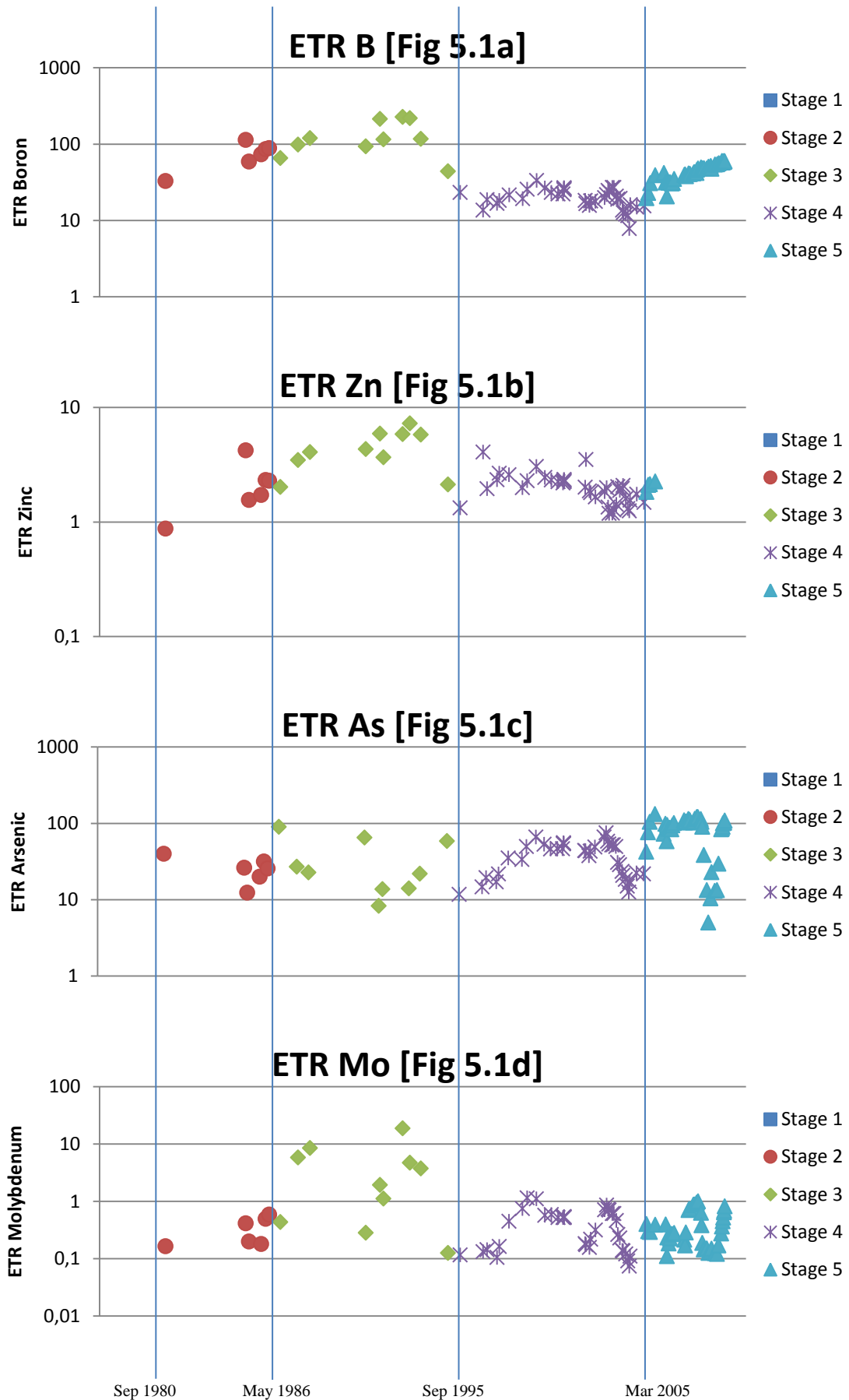
Figure 5.1a,b,c,d – ETR diagrams of (a) boron, (b) zinc, (c) arsenic and (d) molybdenum, plotted against time
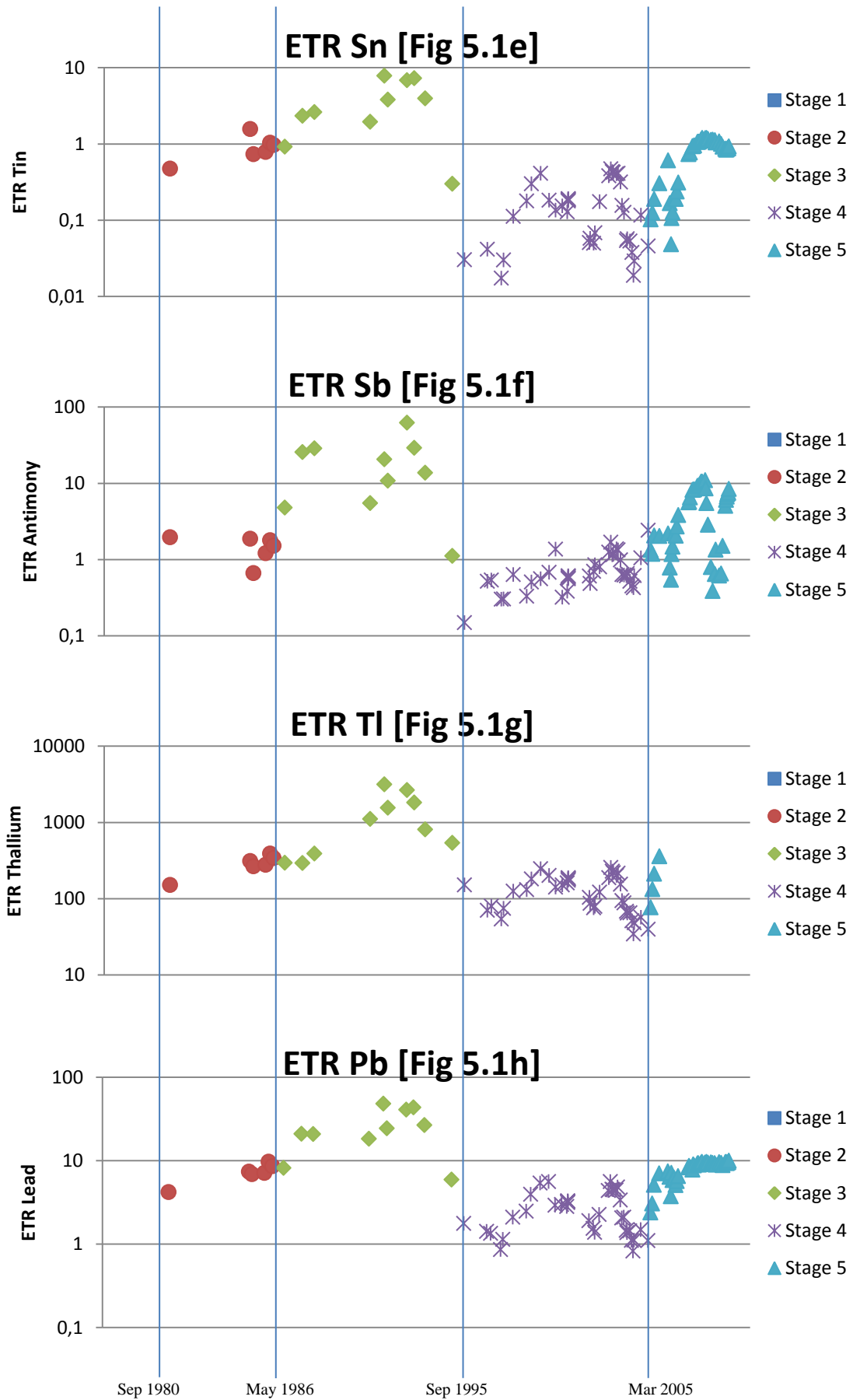
Figure 5.1e,f,g,h ETR diagrams of (e) tin, (f) antimony, (g) thallium and (h) lead, plotted against time.

As shown in figure 5.1, the ETR trends follow those of the absolute concentration. In stage 2, ETR values were moderately high. This increased substantially in stage 3, with arsenic being the only exception. Stage 4, the most quiescent stage, showed the lowest overall ETR values but did indicate a repeated up and down trend, similar to what is seen in the concentration graphs of figure 4.1. The arsenic, antimony and molybdenum decrease towards the latter part of stage 5 is very visible here as well.

5.4 – ETR discussion

The Element Transfer Ratios of zinc, molybdenum, tin, antimony and lead are relatively low. For tin and antimony, this might be due to the error introduced by the calculation of the relative abundance in the average andesite, in chapter 5.2.
As explained in that section, the process of calculating relative abundances introduces an error when not all samples are within detection limits. This is true for antimony to some extent: even though not a large amount of rock analyses indicated that they were outside of detection limits, taking only those analyses that do not, leads to an overestimation of average relative abundance in andesites.
This is even more a problem with tin, as the largest part of the tin analyses provided values outside of detection limits. The calculated relative abundance of 10.6 ppm is most likely an overestimation.
Equation 2 states that the relative abundance of the element in question in the rock is in the denominator of the equation. This means that if the calculated relative abundance is an overestimation, the equation will provide an underestimation of the absolute element transfer ratio value. It is therefore likely that the true volcanic enrichment factor of both antimony and tin (and sulphur, boron and arsenic for that matter) is higher than the values calculated in this study.

When looking at trends, and relations between ETR values, having an ETR value being an underestimation is not a big problem. When looking at absolute numbers, it will be. So when considering absolute ETR values, the lowest reliable ETR values are those of zinc, molybdenum and lead. So initially, it would seem that these elements are the least affected by volcanic activity. But it is possible that some other process affects the apparent mobility of these elements as well.

During the rest of the analysis, trends and relative amounts will mostly be used, so the introduced underestimations of ETR values will not be a problem.

Johnson et al. (2013) found that in the Taupo Volcanic Zone, in New Zealand, zinc, molybdenum and lead fractionate from the melts into the crystallizing minerals in the magma reservoir, zinc being the strongest. If a similar process were to happen at Poás, this could explain why these elements are not degassed as heavily, and do not react to volcanic activity with the same sensitivity as other elements.
However, Johnson et al. (2013) also found that arsenic fractionates into crystallizing minerals as well. Seeing the high ETR values of arsenic at Poás, this seems unlikely to have happened here. Especially as the arsenic ETR, as explained above, might be an underestimation of the actual volcanic enrichment that took place.
Seeing the high ETR values for arsenic, it most likely transfers from the melt to volcanic vapors or gases that are ultimately transferred into the lake.

Another argument against drawing a parallel between the TVZ and Poás, is the behavior of lead, combined with the behavior of tin. Their ETR-time graphs look remarkably similar, and when plotting the previously calculated ETR values of lead against those of tin, as is done in Figure 5.2a, it shows a near perfect straight line.

As well as with arsenic, following the same argumentation, the ETR values of tin are most likely an underestimation. In fact, it is even more likely to be so, as in 83% of the analyses, tin is found to be below the detection limit, and in these cases the value for the detection limit is calculated into the average.

While tin ETRs are most likely to be an underestimation, those of lead are calculated by means of rocks of around Poás (Carr et al., 2003a,b, 2007) are more accurate.

Before we draw any conclusions from this data, we need to consider the effect that stage 3 of Poás' evolution (see chapter 3.3) had on this correlation. In this stage of heightened activity, the lake volume drastically decreased, until almost complete evaporation. Even if the input of tin and lead did not change from earlier stages, their respective concentrations would be much greater, most likely also increasing their ETR values. As these values would increase by approximately the same amount, a linear correlation is easily found.

Figure 5.2b shows the same correlation, but then with phase 3 removed from the system. The lead value of March 13, 2002 was also omitted, as that value was over 10 times higher than the values directly in front (February 27, 2002) and after (May 16, 2002) and was most likely an outlier. The correlation between lead and tin is not as good as with phase 3 included, but still good enough to be able to say that they are in some way connected.

Also note that the underestimation of tin ETR values can be responsible for the nonzero intersection of the calculated linear regression line in these figures.
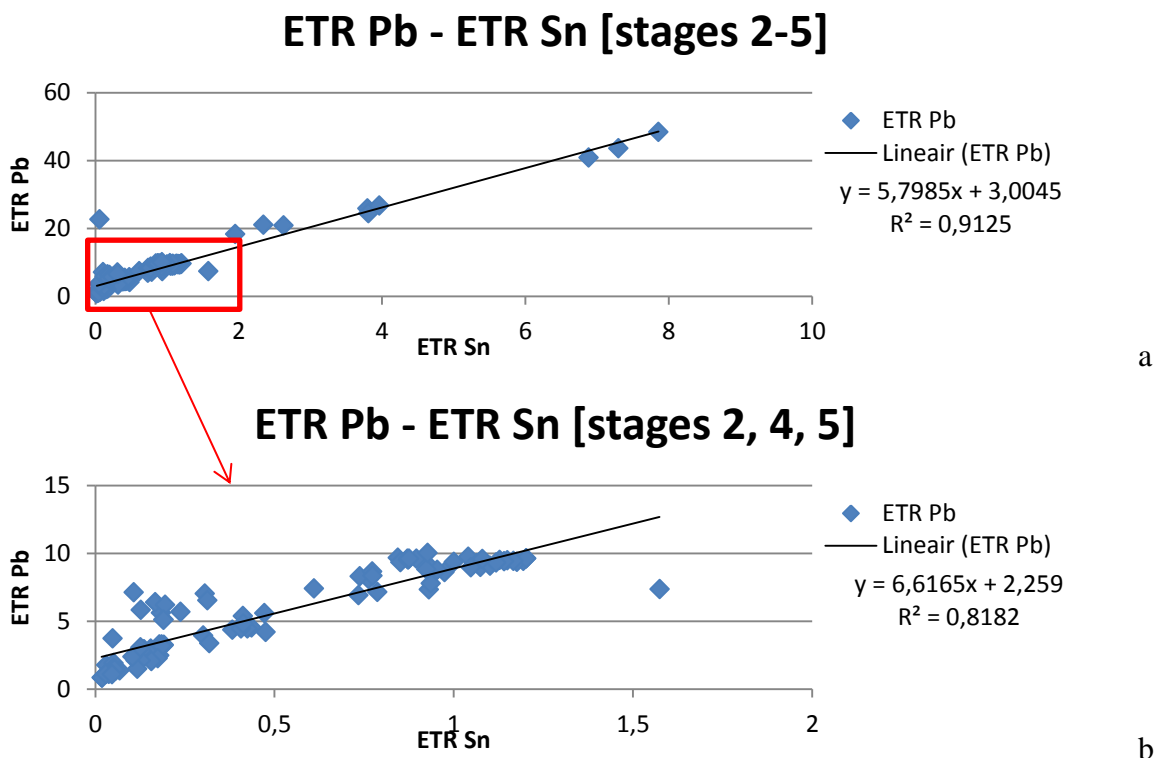
Figure 5.2a,b (a) ETR of tin plotted against ETR of lead, including trend line, trend line equation and R^2 value. (b) ETR of tin plotted against ETR of lead, including trend line, trend line equation and R^2 value, of only samples of stage 2, 4 and 5, omitting stage 3. Axes are zoomed in, and field of view corresponds to the red box in Fig. 5.2a

A possible connection between tin and lead is proposed by Uchida et al. (2002). They found that tin and lead can both be released from the magmatic source by forming $SnCl_3^-{}_{(aq)}$ and $PbCl_3^-{}_{(aq)}$ complexes respectively, dissolved into supercritical water, for transport into the hydrothermal system. However, their geochemical data suggests that zinc would be affected by the same process as well. And as we can see in figure 5.3b, there is no correlation between tin and zinc in the element transfer ratios of Poás. This also demonstrates that the effect of stage 3 is notable, as the R^2 when this stage is included in the analysis (Fig. 5.3a) is 0,63.
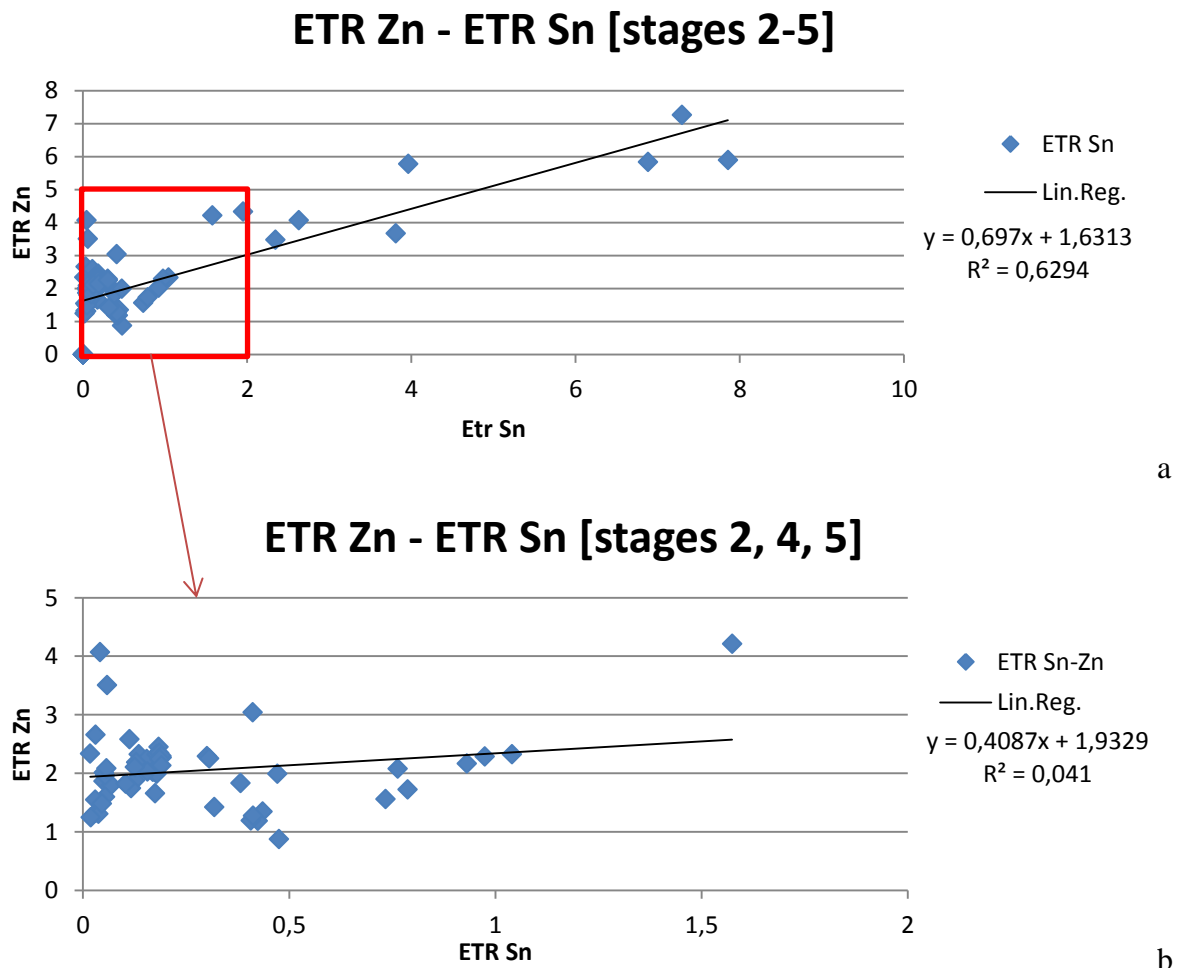
Figure 5.3a,b (a) ETR of tin plotted against ETR of zinc, including trend line, trend line equation and R^2 value. (b) ETR of tin plotted against ETR of zinc, including trend line, trend line equation and R^2 value, of only samples of stage 2, 4 and 5, omitting stage 3. Axes are zoomed in, and field of view corresponds to the red box in Fig. 5.3a

A possible explanation for this, is that the concentration of zinc might not be dominated by injection through trichloride complexes dissolved in supercritical water. It does not exclude this process from happening with zinc, however, the zinc concentration is most likely controlled by a different mechanism.
Further proof that the concentration – or at least the ETR – of zinc is controlled by a different mechanism than lead is in Fig 5.4. From this graph, it can be seen that the ratio of these two ETRs is highest in phase 4, and lowest in phase 3. This appears to be an inverse relationship with the volcanic activity. This possibly indicates that the ETR of zinc is less indicative of volcanic activity than that of lead.
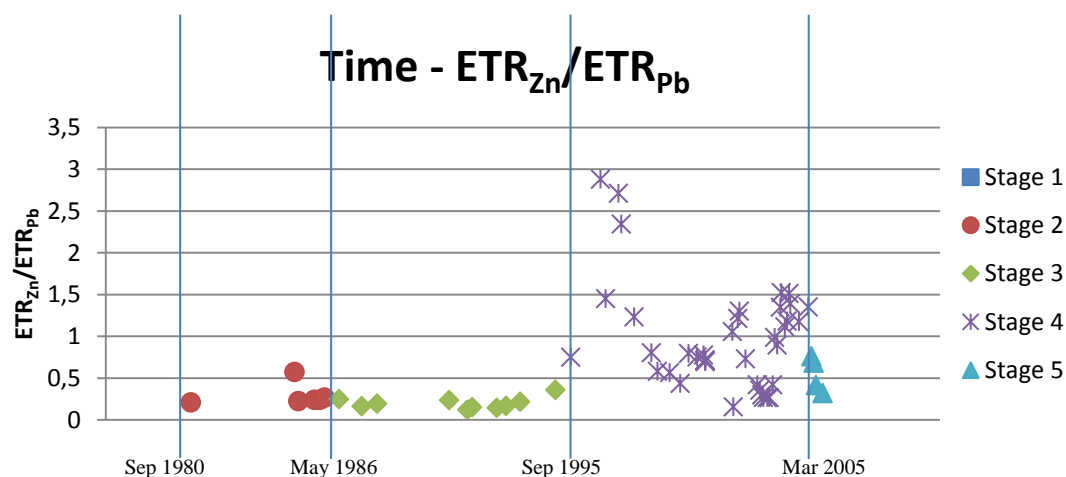
Figure 5.4 ETR of zinc divided by ETR of lead, plotted against time.

When the supercritical fluids cool down, and rise to areas of lower pressure, they will fractionate into vapor and brine. Heinrich et al. (1999) found that – of the trace elements analyzed here – Zn, Sn, Tl and Pb preferably partition into the brine (probably as chloride complexes), while As (probably as HS complex) and B partition into the vapor. No information is available on antimony.

To more thoroughly explore this partitioning, and the processes responsible for that, it's important to look at stage 4 of Poás' evolution. Being the most quiescent stage, it might be easier to work out processes from this stage.
Martínez (2008) concluded from data that the interaction between the lake's hydrothermal system and the magma reservoir appeared to have been blocked multiple times during stage 4, being in stage 4a, 4c and 4e. Such a blockage lead to even more decreased volatile input into the lake, and the subsequent removal of this blockages lead to resumed input.
In the various ETR values, this can be seen. Each of the transfer ratios is lower in stages 4a, 4c and 4e, and higher in stages 4b and 4d, as can be seen in figure 5.1. But there is quite a difference in how much the ratios are affected by the blockages.

To assess what these differences are, we compared each of the ETR ratios with that of lead. Lead is most likely included in the brine (Heinrich et al., 1999), and could serve as a good comparison.

Tin and molybdenum are affected by the blockages to a greater degree than lead. On the other hand, boron, zinc, arsenic and antimony appear to be affected by the blockages to a lesser degree than lead. Thallium appears to be affected by the blockages to approximately the same degree as lead.
Of boron, zinc, arsenic and antimony, zinc is most affected by the blockages.

A possible explanation for this is that the blockages did block the brines, but affected the vapor flow to a much lesser degree. This would explain why boron, arsenic and antimony do not appear to be affected to a very large degree by the blockages, compared to other elements. This also implies that antimony preferentially partitions into the vapor as well. Zinc, thallium, lead, molybdenum and tin most likely partition into brines to a greater degree than boron, arsenic and antimony.

Comparing this with the ETRs in the other stages of Poás' evolution (Fig 5.1), we can see that both the very active stage 3 as well as the current stage, stage 5, are less dominated by vapor

than stage 4. This can be expected, as there is no evidence to a blockage in those stages, leading to a free flow of both vapor and brine. Unfortunately, there is little information available on stage 2, so no accurate assessment can be made concerning this stage. But seeing the general activity, it seems likely that this stage is less vapor-dominated than stage 4 as well.

5.5 – ETR conclusions

Overall, we can say that most of the elements concerned in this study are enriched when compared to congruent rock dissolution. The sub-one values in arsenic and tin are most likely to be an underestimation, though a more thorough analysis of Poás lava chemistry is needed to confirm this.

Stage 4 was more vapor-dominated than any other stage, most likely because of brine-conduits being blocked. Vapors and gases still had some way of reaching the lake water. The elements that preferentially partition into the vapors were affected by the blockages, but to a lesser degree than those elements that preferentially partition into the brine.

The correlation between tin and lead ETRs imply that they might be controlled by the same process. Transport by supercritical fluids is a possibility, but more thorough research needs to be done in order to confirm this.

6 – Mineral precipitation

6.1 – Trace metal depletion

Between November 6, 2007 and June 4, 2008, during the later parts of Stage 5, the concentration of arsenic, antimony and molybdenum in the Poás lake decreased dramatically. Arsenic saw a decrease from 4342 to 143 ppb, antimony from 90.1 to 2.64 ppb, and molybdenum from 46.3 to 4.85 ppb (Fig. 6.1). Molybdenum continued to decrease until December 9, 2008, where the concentration was 2.92 ppb. During this period, the concentrations of tin and lead did not decrease this strongly, and their ratios as compared with chloride remained roughly the same.
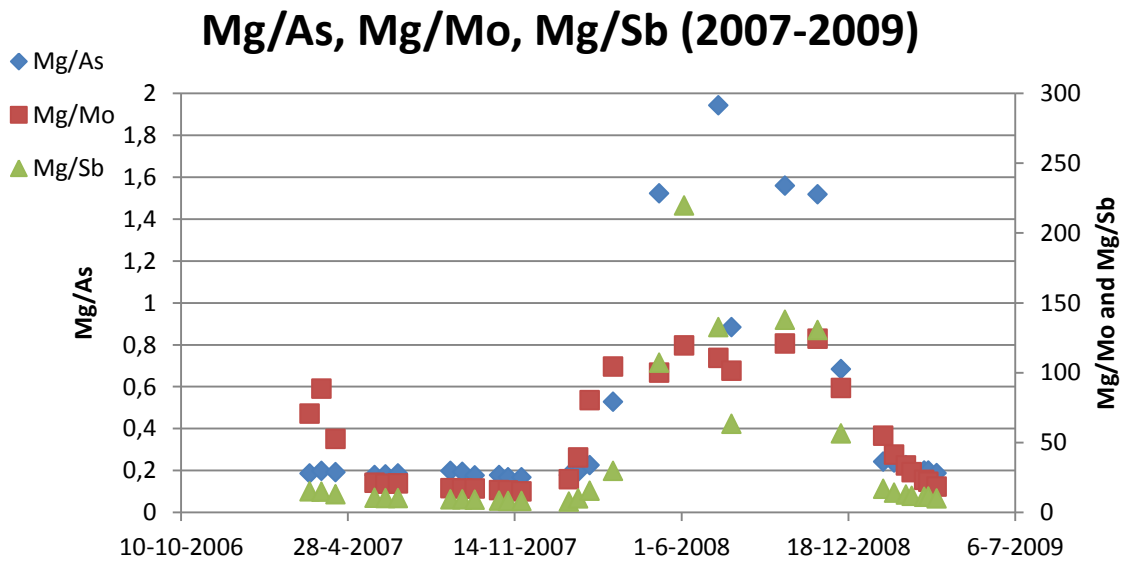
Fig 6.1 Concentration ratios Mg/As (left axis, in blue), Mg/Mo (right axis, in red) and Mg/Sb (right axis, in green) plotted against time in the period from early 2007 to mid-2009. The peak shown is the deficiency of these three elements compared to magnesium in this time period.

While the absolute concentrations of lead and tin did decrease during this period, stable Pb/Cl and Sn/Cl ratios (Fig. 6.2) suggest that this is due to an overall dilution of the lake, which took place during this period as well. Unfortunately, there is no data concerning zinc and thallium in this time period, so little can be said about the effects on those elements.
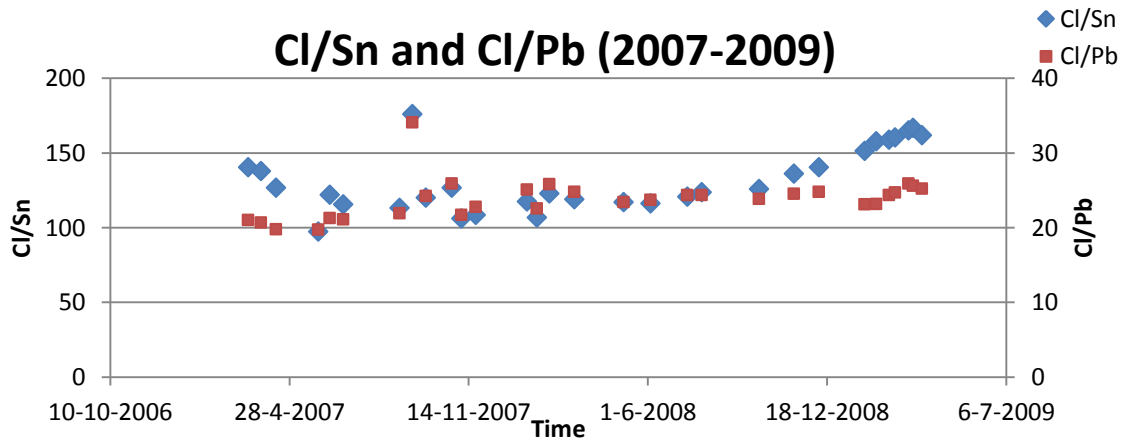
Figure 6.2 Concentration ratios Cl/Sn (left axis, in blue) and Cl/Pb (right axis, in red) plotted against time in the period from early 2007 to mid-2009.

A possible hypothesis for this sudden decrease in molybdenum, arsenic and antimony is that they are incorporated into native sulphur or sulphide precipitate, both of which can incorporate these elements (Africano et al., 2007; Berner et al., 2013). In this chapter, we explore the effects that sulphur and sulphide precipitation might have had on the composition of the lake.

6.2 – Native sulphur, sulphur globules and sulfides as potential sinks

When volcanic gases pass through a layer of molten sulphur at the bottom of a volcanic lake (see Fig 2.1), it is possible that some sulphur is taken along in this stream of gas. As temperatures drop during the ascent through the water, this molten sulphur can solidify and form sulphur globules (e.g. Martínez, 2008; Africano et al., 2007). Chalcophile elements (elements that react with sulphur easily, these include As, Pb, Sb, Sn, Tl, Zn) can be incorporated into these globules.

While these elements can be incorporated in trace amounts into native sulphur, it is also possible that they can be incorporated into sulfide minerals, where they form an essential part of the structure. Alternatively, they can be present in trace amounts, included in other sulfide minerals. These sulfides can also be incorporated into sulphur globules (Takano et al., 1994). Studying the sulphur globules can therefore give a good idea of sulphur and sulfide chemistry in the lake.

Takano et al. (1994) detected inclusions of pyrite (FeS) in native sulphur at Yugama Crater Lake, Kusatsu-Shirane, Japan. Conditions in this lake are similar to that of Poás, with low pH, high temperature, and strong evidence for a subaqueous layer of molten sulphur. Sulphur with around 10% of pyrite or more was found to have a distinct black colour, as compared to the yellow to green colours of sulphur without pyrite.

Strong evidence for molten sulphur at the bottom of Poás lake is present as well. In all stages of Poás' evolution, numerous sulphur globules have been reported to be present at the lake's surface (Martínez, 2008). This indicates continued degassing through this molten sulphur layer.

In mid-2003, the sulphur globules at Poás lake were reported to be darker than usual, and even turning black (Martínez, 2008). This can indicate the presence of pyrite in the sulphur globules. Investigation of Poás' sulphur globules by Africano et al. (2007) indicated the presence of cristobalite, a high temperature SiO_2 polymorph (Handbook of Mineralogy version 1.2), and pyrite.

6.3 – Possible role of arsenic-bearing minerals

As shown in chapter 6.1, the ratio Mg/As and Cl/As increases sharply between November 2007 and June 2008, suggesting precipitation of an arsenic-rich mineral. The most likely minerals to have precipitated during this period is some form of arsenic-sulfide or arsenic-bearing sulfide, due to the high total sulphur concentrations.

Concentrating on arsenic-sulfide minerals, examining the difference between realgar (AsS), orpiment (As_2S_3) and arsenopyrite (FeAsS) can be an important clue in determining the conditions in which this precipitation phase took place.

As demonstrated by Pokrovski et al (2002), realgar and orpimentprecipitate at lower temperatures, and are highly soluble in temperatures above 250 - 300 °C. At these higher temperatures, arsenopyrite can precipitate. The solubility of arsenopyrite is expected to be relatively similar to that of non-arsenic bearing pyrite, which has a solubility peak at around 250 °C, with lower solubilities as temperatures increase (Reed and Palandri, 2006; Zachariáš et al., 2004, Figure 6.3). This means that based on which mineral is precipitating, the temperature at which it happened may be determined. And at higher temperatures, assuming the mineral precipitates from solution instead of sublimating from gas, the pressure and therefore the depth at which it happened may be determined as well.

Unfortunately, based on concentration data from the lake, distinguishing which of the three precipitated is very difficult to do.
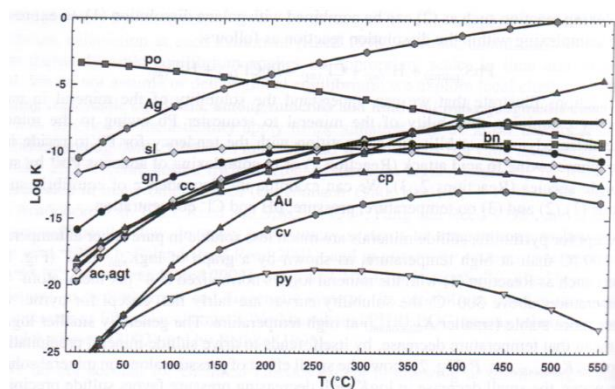
Figure 6.3 Solubility curve at constant pH with varying temperatures of different minerals. Notable is pyrite (denoted with "py") which has a solubility peak at around 250 °C. Image: Reed and Palandri, 2006

Different amounts of arsenic can be incorporated into normal pyrite by means of a solid solution substitution (Zachariáš et al., 2004). The substitution mechanism can be expressed as $Fe(As_xS_{1-x})_2$ with endmembers FeS_2 (normal pyrite) and FeAsS (arsenopyrite). Temperature constraints on this solid solution series have not been found.

An other possibility is that pyrite is incorporated into other sulfide minerals such as bismuthinite (Bi_2S_3) or luzonite (Cu_3AsS_4), which have been found to be stable in the lake of Kawah Ijen, Indonesia (Delmelle and Bernard, 1994; Utrecht University, unpublished)

Inclusions of sulphur globules do indicate the presence of pyrite in the Poás system (Africano et al., 2007; see chapter 6.2), suggesting that the precipitation event took place at high temperatures, and was transported up in suspension together with the cristobalite inclusions that were found. Inclusions of bismuthinite, luzonite and pure arsenopyrite have not been found in the globules of Poás.

6.4 – Mineral precipitation discussion

Assuming all the arsenic deficit (4200 ppb) is converted into arsenopyrite, this would mean a similar reduction of iron. Assuming the water is 1 kg/dm^3 (which it may not be due to the amount of total dissolved solids, but because the calculation goes both ways this doesn't matter), 4200 ppb arsenic is equivalent to 56 µmol/dm^3. This means that to precipitate all the

arsenic deficit to arsenopyrite, iron should be reduced by 56 µmol/dm^3, equivalent to 3130 ppb.

During this period, the absolute reduction in iron is from 1610 to 1250 ppm, a change that could well be due to the overall dilution of the lake, as the Cl/Fe ratio remains roughly the same during this period. Next to that, a 3.1 ppm decrease in iron is well below detection and significance limits of the iron concentration measurements (Martínez, 2008).

As suggested in chapter 6.2 and 6.3, it is possible that the arsenic is not precipitated as pure arsenopyrite, but rather as trace inclusion in normal pyrite or native sulphur. Enrichment factor analyses have been carried out on sulphur globules and sulfide fractions within those globules (Africano et al., 2007 – the same kind of calculations have been carried out in chapter 5 of this thesis). Around the world, sulphur globules and sulfide inclusions have shown arsenic enrichment factors of $10^2 – 10^5$, antimony enrichment factors of $10 – 10^4$, and zinc, tin and lead enrichment factors of up to 10^3. No information was collected on the enrichment factor of molybdenum in sulphur globules. The values found in Poás' sulphur globules appear to be representative of this spectrum.

Reed and Palandri (2006) examined factors that can play a role in the precipitation of sulfide minerals. They found that at temperatures higher than 300 degrees C, pyrite becomes increasingly less soluble and more prone to precipitation. They also found that a rise in pH and non-isothermal dilution (dilution with cold water) in general decrease the solubility of many different sulfide minerals.

During the period November 2007 to June 2008, the temperature of the lake waters is lower than in the period before (Martínez, 2008), while the pH did not much change or differ. This suggests that an increasing pH would not have been a factor in the precipitation of an arsenic bearing pyrite, and that the changes might be attributable to non-isothermal dilution instead. However, this would most likely mean that we would also see precipitating galena (PbS) and sphalerite (ZnS) (Reed and Palandri, 2006). Unfortunately, there are no measurements of zinc of that period, so the presence or absence of precipitating sphalerite cannot be confirmed. We do see very little decrease in the concentration of lead in the lake at this point, so it seems unlikely that galena has precipitated along with arsenic bearing sulfides. This would suggest that pH increase or non-isothermal dilution are not the mechanisms responsible for the precipitation event. Though dilution did take place during this period, it is most likely not the controlling mechanism in the precipitation event.

Another possibility is an increase in temperature. As Reed and Palandri (2006) found, at higher temperatures most sulfide minerals become increasingly soluble, except pyrite which has a solubility peak at around 250 °C, beyond which the effective solubility decreases and pyrite can start to precipitate (Figure 6.3). This would explain why the concentration of arsenic – which is easily bound in pyrite (e.g. Craw et al., 2003) decreases even when other element concentrations do not.

Pyrite precipitation could also be the mechanism removing molybdenum and antimony from the solution. Under reducing conditions and under strong influence of H_2S, precipitating pyrites can incorporate molybdenum, arsenic and antimony quite easily (Berner et al., 2013).

Such a precipitation will have to have occurred at depth, as the temperatures at which this kind of precipitation occurs are too high for water to be liquid at surface pressures. This is

assuming precipitation from waters and not from vapours. Because of the high concentrations and enrichments in fumarole condensates (Africano et al., 2007; Gemmell, 1987; chapter 2.4 of this study), it seems likely that the material used in the precipitation of pyrite will have originated from a magmatic source as opposed to dissolving secondary minerals.

Concentrations in fumarole condensates of these elements might be able to identify the part of the hydrothermal system where the precipitation took place. As can be seen in Figure 2.1, deeper in the system the vapours and brines coexist, and rise in a multi-phase flow. At some point, they separate. If the trace element signature of the fumarole condensates shows this precipitation event in the same way the lake waters do, it is likely that the precipitation itself took place in this multi-phase flow regime.

When this is the case, the temperature of precipitation, and the accompanying pressures needed to keep water liquid could provide some constraints on the depth of the multi-phase flow regime. Unfortunately, no fumarole condensate data was available for this time period, so it was not possible to constrain the depth at which the multi-phase flow separates into brine and vapour.

6.5 – Mineral precipitation conclusions

There is quite strong evidence of pyrite precipitation in the lake of Poás. The blackness of sulphur globules between September and October 2003 (Martínez, 2008) indicates the presence of a significant fraction of pyrite inclusion in these globules (Takano et al., 1994). Additionally, pyrite has been directly observed in sulphur globules from Poás (Africano et al., 2007).

A sudden event of pyrite precipitation could explain the dip in concentration of both arsenic, antimony and molybdenum. Pyrite becomes less soluble at temperatures above 250 degrees Celsius, contrary to galena and other sulfide minerals (Reed and Palandri, 2006). An event of water heating could therefore trigger pyrite precipitation, while keeping other sulfide minerals in solution. The heated water also serves to explain the presence of cristobalite, as this is a SiO_2 polymorph that precipitates under elevated temperatures (Handbook of Mineralogy version 1.2).

Assuming the water is not vaporized at this point, this will have to occur at depth, under larger pressures. The lake is overall well mixed (Martínez, 2008), most likely due to convection. So it is to be expected that this pyrite precipitation takes place in the hydrothermal circulation underneath the lake. The pressures there validate the assumption that the water is in liquid form during the precipitation.

It can be assumed that the waters in the hydrothermal system are anoxic and reducing, as we do not expect them to be under the influence of an oxygen-rich environment. Furthermore, due to the acidity and sulfur content of the lake waters, there is most likely enough H_2S available to facilitate the conditions in which pyrite is able to take in arsenic, antimony and molybdenum easily (Berner et al., 2013).

Now the only thing left to explain is why this sudden pyrite precipitation occurred. As noted above, a sudden event of water heating past 250 degrees Celsius could push the solubility of

pyrite down, leading to precipitation. This event happened in stage 5 of Poás development as defined by Martínez (2008), which is the most recent and one of the more active stages. However, this stage was underway for a few years already when the pyrite precipitation event happened. The overall water temperature of the lake decreased during this period as well. So unfortunately there is no clear signal of a heating of subaqueous fumaroles around the period November 2007 to June 2008.

The decrease in lake temperature might be attributable to overall dilution of the lake, which is seen in (among others) the decreasing concentration of lead, but the lack of change in the Pb/Cl ratio. This means that any signals concerning the heating of subaqueous fumarolic activity might be lost.

Even though the chemistry would suggest increase in temperature of subaqueous fumaroles, the physical characteristics of the lake support nor disprove this hypothesis.

7 – Conclusions and recommendations

Mobile trace elements can indicate or independently verify processes occurring in the magmatic system, in the hydrothermal system, or in the lake. Spikes and dips in trace element trends might indicate sudden enrichment, or depletion by precipitation. The differences in trends between different elements can indicate differences in transport, enrichment or precipitation mechanisms. This study aimed to determine the origin of these trace elements in volcanic lake waters, the significance of their presence, and their significance to the overall activity of the volcanic system. The lake of Poás was used for the analysis, due to the quality of available data.

In this section, the main conclusions of this study and recommendations for further research are listed.

It is found that the lake of Poás, while generally being one of the more active volcanic lakes, is chemically representative of volcanic lake systems. The processes influencing Poás' chemistry are not fundamentally different of those in other volcanic lakes.

Element transfer ratios (ETRs), being a method that describes relative enrichment, can be a very useful tool for exploring and describing processes in the hydrothermal system. For ETRs to work quantitatively, accurate rock compositions are needed. World averages can be used, but only when working in a qualitative sense. For accurate enrichment calculations, we recommend careful compositional analysis of lavas originating from Poás, especially where the elements of study are concerned.

The high to relatively high ETR values of the trace elements in question indicate that they have been significantly enriched in the lake of Poás. They most likely originate from a degassing magma-body, and are therefore volcanic in origin.

The similarity in ETR trend between Sn and Pb indicate that they are most likely controlled by the same process. A suggested possibility for this is transport as trichloride complexes dissolved in supercritical water (as per Uchida et al., 2002). Further research is needed to confirm this hypothesis.
In stage 4 of Poás development, ETR trends independently verified the conduit-blockage hypothesis (Martínez, 2008). Elements partitioning into brines were affected to a larger degree by the conduit-blockages compared to elements partitioning into the vapor. Next to verifying the hypothesis, this indicates that the conduit-blockages did not block vapors as effectively as it did with brines.

In a hot and acid hydrothermal environment, sulfide precipitation can be expected. Trace elements can aid in exploring which sulfide minerals precipitate at what point. Through this and what is known about depositional environments of these minerals, the conditions in the hydrothermal system may be examined.
In stage 5 of Poás development, a sharp decrease in As, Mo and Sb indicated pyrite precipitation in reducing, and anoxic conditions under strong influence of H_2S. As other sulfides as galena did not precipitate, it seems likely that the temperature in the hydrothermal system rose to above 250 degrees Celsius, the region where pyrite becomes increasingly less soluble (Reed and Palandri, 2006).

Further research might be needed to reconfirm the presence of arsenic, molybdenum and antimony bearing pyrite in sulfide precipitates, or to confirm the presence of other precipitating minerals incorporating these elements. Additionally, fumarole condensate data form this time period can aid in understanding the flow regimes in the hydrothermal system of the volcano.

Acknowledgements

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Appendix A – Poás trace element data set

This section lists all data that has been used in this thesis. Only those data entries with information on the elements in this study (B, Zn, As, Mo, Sn, Sb, Tl, Pb) are listed. Fields marked N/A were not available. No data including trace elements was available on Stage 1 of Poás' evolution.
Sources:
[1] Martínez, 2008
[2] A. Huizinga, personal communication, 2013

Date	Temp. (°C)	pH_{lab} 24±2°C	S_{Total} (mg/kg)	F (mg/kg)	Al (mg/kg)	Si (mg/kg)	Cl (mg/kg)	Mg (mg/kg)	B (µg/kg)	Zn (µg/kg)	As (µg/kg)	Mo (µg/kg)	Sn (µg/kg)	Sb (µg/kg)	Tl (µg/kg)	Pb (µg/kg)	Source
Stage 2																	
31-10-1980	45	0,11	23200	1320	6700	130	26900	1650	20400	3160	3260	18	230	38	380	1210	[1]
28-11-1984	48	0,07	33000	1500	1670	N/A	23700	780	33400	7200	1010	21	360	17	370	1000	[1]
24-1-1985	44	0,14	N/A	1660	3000	50	25400	790	17500	2700	480	11	170	6,2	320	950	[1]
10-9-1985	45	0,05	21400	1320	2620	15	28500	780	21500	2950	770	9,3	180	11	330	970	[1]
29-11-1985	45	0,30	22000	1030	2280	N/A	23500	590	19100	3010	920	19	180	12	350	1000	[1]
4-2-1986	39	0,26	19800	1010	1210	17	16500	560	18700	2810	710	22	160	10	290	840	[1]
Stage 3																	
1-9-1986	56	0,50	28600	1310	2670	N/A	24000	890	22000	3940	3940	26	240	50	400	1270	[1]
27-7-1987	68	-0,27	N/A	2110	2370	N/A	44900	830	30700	6320	1110	320	570	250	370	3040	[1]
2-3-1988	60	-0,31	42000	2100	2520	N/A	51300	740	33300	6600	830	420	570	250	440	2690	[1]
1-1-1991	74	N/A	7800	6100	3300	N/A	44000	980	34400	9300	3150	18	560	63	1650	3120	[1]
24-9-1991	71	-0,44	22100	6320	3600	N/A	55800	660	52900	8530	270	85	1520	160	3160	5560	[1]
29-11-1991	70	-0,50	N/A	6790	4200	N/A	61100	770	33500	6190	520	57	860	97	1820	3280	[1]
19-11-1992	80	-0,50	13400	5720	3300	74	73000	560	47900	7170	N/A	700	1130	410	2260	3980	[1]
2-4-1993	60	0,00	24100	7550	7710	N/A	75500	1080	88900	17200	750	340	2310	370	2980	8190	[1]
22-10-1993	60	0,00	17800	5330	5670	N/A	27600	1240	54800	15700	1340	310	1440	200	1520	5760	[1]
10-3-1995	42	0,68	9200	950	1300	20	7780	600	9920	2800	1740	5,0	53	7,9	490	620	[1]

Origin and significance of mobile trace elements in volcanic lakes – a case study at Poás, Costa Rica

Date	Temp. (°C)	pH_{lab} 24±2°C	S_{Total} (mg/kg)	F (mg/kg)	Al (mg/kg)	Si (mg/kg)	Cl (mg/kg)	Mg (mg/kg)	B (µg/kg)	Zn (µg/kg)	As (µg/kg)	Mo (µg/kg)	Sn (µg/kg)	Sb (µg/kg)	Tl (µg/kg)	Pb (µg/kg)	Source
Stage 4A																	
20-10-1995	30	1,21	3100	190	490	45	3800	520	4550	1510	300	4,0	4,6	0,91	120	160	[1]
5-1-1996	29	1,22	N/A	200	N/A	N/A	3590	N/A	4040	2000	230	15	1,3	0,48	89	120	[1]
18-12-1996	29	1,13	2930	260	550	83	3650	650	3330	5800	470	5,7	7,9	4,0	70	160	[1]
3-3-1997	29	1,18	2830	170	540	97	3260	470	3320	2010	450	4,5	N/A	3,0	57	110	[1]
Stage 4B																	
5-9-1997	35	1,30	2790	170	500	120	4330	500	3150	2560	420	3,5	2,5	1,8	41	75,0	[1]
17-10-1997	34	1,06	2670	360	520	96	6520	420	2900	2450	450	4,6	3,7	1,5	48	83,0	[1]
17-4-1998	37	0,68	4430	460	1000	77	8870	630	5110	3570	1090	19	21	4,7	120	230	[1]
13-7-1998	35	0,73	N/A	600	N/A	N/A	11800	N/A	6830	4040	1550	31	47	4,4	190	380	[1]
23-12-1998	27	0,90	2970	600	850	84	7840	440	3180	1920	730	22	23	1,7	88	190	[1]
17-3-1999	32	0,81	4370	720	1210	64	10900	510	4910	2560	1250	39	45	3,0	140	350	[1]
8-9-1999	39	0,62	3510	660	970	89	8120	480	6010	3200	1570	35	58	3,2	180	450	[1]
10-2-2000	44	0,69	4110	830	390	65	10800	490	4920	2630	1280	19	26	3,9	150	480	[1]
9-6-2000	31	0,77	3600	710	1220	81	11900	510	4470	2600	1160	20	20	8,2	110	260	[1]
10-10-2000	35	0,70	3420	580	1200	97	11700	520	4360	2560	1200	18	24	2,0	120	270	[1]
12-1-2001	31	0,86	3250	680	1140	69	11400	490	4090	2350	1120	17	19	2,2	120	240	[1]
31-1-2001	31	0.80	N/A	620	1130	98	10800	490	4650	2500	1300	17	26	3,5	130	280	[1]
21-9-2001	38	0,39	N/A	N/A	N/A	N/A	N/A	N/A	8540	4820	1180	26	N/A	N/A	120	210	[1]
5-10-2001	29	0,90	N/A	N/A	N/A	N/A	N/A	N/A	3530	2040	1020	5,3	9,7	1,9	85	170	[1]
24-10-2001	32	0,85	N/A	N/A	N/A	N/A	N/A	N/A	3680	1990	1110	6,1	12	2,8	93	180	[1]
Stage 4C																	
27-2-2002	23	1,17	N/A	160	590	79	4670	290	1990	1280	630	3,5	4,3	2,1	46	96	[1]
13-3-2002	26	1,06	2370	190	650	100	5760	380	2380	2920	820	4,4	6,5	2,2	50	N/A	[1]
16-5-2002	29	1,08	2190	230	640	110	6260	340	2010	1390	630	3,5	5,0	2,8	39	91	[1]
Stage 4D																	
11-6-2002	29	0,90	2370	130	660	110	5780	340	2300	1340	720	4,9	6,8	3,4	41	82	[1]

Date	Temp. (°C)	pH$_{lab}$ 24±2°C	S$_{Total}$ (mg/kg)	F (mg/kg)	Al (mg/kg)	Si (mg/kg)	Cl (mg/kg)	Mg (mg/kg)	B (µg/kg)	Zn (µg/kg)	As (µg/kg)	Mo (µg/kg)	Sn (µg/kg)	Sb (µg/kg)	Tl (µg/kg)	Pb (µg/kg)	Source
4-9-2002	38	0,90	3010	300	850	130	8720	380	2540	1380	920	8,0	19	3,6	70	150	[1]
23-10-2002	39	0,81	N/A	470	N/A	N/A	12500	N/A	3360	1670	1210	11	33	3,9	97	240	[1]
6-11-2002	39	0,68	N/A	410	N/A	N/A	10400	N/A	3120	1600	1170	9,5	33	4,2	94	260	[1]
5-12-2002	39	0,82	N/A	N/A	N/A	N/A	N/A	N/A	2000	1460	810	7,9	19	3,2	70	190	[1]
11-12-2002	39	0,84	N/A	430	N/A	N/A	10700	N/A	2850	1440	1080	13	30	3,7	91	230	[1]
17-1-2003	34	0,83	N/A	480	N/A	N/A	10500	N/A	3320	1690	1320	16	41	4,6	120	320	[1]
24-2-2003	36	0,77	4730	520	1200	36	10900	420	3140	1690	1370	20	47	6,2	120	320	[1]
18-3-2003	38	0,70	N/A	N/A	N/A	N/A	N/A	N/A	3310	1770	1470	20	52	7,0	130	330	[1]
31-3-2003	39	0,70	4870	580	1220	24	15000	410	3360	1790	1520	24	57	8,1	160	400	[1]
30-4-2003	41	0,67	5100	620	1270	27	16100	430	4000	1270	1230	21	55	5,8	150	340	[1]
20-5-2003	41	0,70	5310	620	1320	36	16200	450	4000	1170	1190	21	56	6,2	150	350	[1]
17-7-2003	35	0,64	5150	650	1360	31	17100	490	5000	1280	1260	20	58	7,9	150	380	[1]
12-8-2003	33	0,61	5290	720	1410	32	18200	490	5000	1370	1270	20	59	7,7	160	410	[1]
30-9-2003	33	0,62	4470	560	1320	43	15300	510	4000	1590	1250	16	48	5,9	120	300	[1]
Stage 4E																	
28-10-2003	28	0,80	3440	320	1080	60	12700	560	4000	2490	850	10	26	4,2	80	200	[1]
5-12-2003	24	0,93	2670	240	820	79	8310	410	3000	1690	580	6,2	15	3,0	55	150	[1]
20-1-2004	24	1,17	2370	180	660	98	6670	390	2000	1680	450	3,6	6,2	2,8	40	99	[1]
3-2-2004	29	1,11	2230	190	720	100	5880	420	2000	1920	430	3,8	7,0	3,2	41	100	[1]
23-3-2004	25	1,05	2450	180	800	110	6530	440	2000	1540	400	3,5	6,9	2,7	44	110	[1]
27-4-2004	28	1,12	2450	160	840	120	6330	460	2000	1320	340	2,8	5,1	2,4	36	89	[1]
25-5-2004	28	1,31	1880	26	680	120	5380	340	1000	930	210	1,7	1,9	1,7	18	49	[1]
11-6-2004	29	1,20	1980	65	680	100	6480	330	2000	1120	280	2,4	2,8	2,4	24	64	[1]
25-8-2004	25	1,15	N/A	N/A	N/A	N/A	N/A	N/A	1450	1050	265	6,4	4,4	2,9	22	68	[1]
13-10-2004	27	1,08	1900	150	740	220	6820	280	1570	1070	310	N/A	10	3,5	24	72	[1]
22-2-2005	22	1,25	1620	92	560	230	3680	200	1170	650	215	N/A	2,7	5,7	12	38	[1]

Origin and significance of mobile trace elements in volcanic lakes – a case study at Poás, Costa Rica

Date	Temp. (°C)	pH_lab 24±2°C	S_Total (mg/kg)	F (mg/kg)	Al (mg/kg)	Si (mg/kg)	Cl (mg/kg)	Mg (mg/kg)	B (µg/kg)	Zn (µg/kg)	As (µg/kg)	Mo (µg/kg)	Sn (µg/kg)	Sb (µg/kg)	Tl (µg/kg)	Pb (µg/kg)	Source
Stage 5																	
12-4-2005	34	0,97	3010	220	820	193	6570	280	2060	1120	585	7,5	8,5	4,4	33	117	[1]
13-5-2005	45	0,98	N/A	300	950	N/A	7140	290	2500	1340	1090	5,8	11	4,0	59	155	[1]
16-6-2005	50	0,92	N/A	420	1150	142	8230	310	3580	1450	1600	6,0	17	7,5	100	277	[1]
20-9-2005	52	0,70	6560	750	1610	122	11100	360	5300	1780	2350	9,3	32	8,6	196	440	[1]
2-11-2005	53	0,59	N/A	N/A	N/A	N/A	N/A	N/A	5050	1640	2130	8,3	34	7,1	218	468	[1]
28-2-2006	51	0,59	8121	990	1490	50	13400	360	5659	N/A	1295	N/A	64,4	9,24	N/A	465	[2]
1-4-2006	54	0,63	6906	1050	2470	52	15700	560	6641	N/A	2714	14,7	27,4	5,13	N/A	624	[2]
25-4-2006	54	0,74	5717	990	2370	67	13000	780	6036	N/A	2237	5,7	11,1	4,98	N/A	506	[2]
3-5-2006	49	0,74	6897	1150	2860	55	15100	610	7371	N/A	2861	9,48	19,1	8,39	N/A	756	[2]
25-5-2006	47	0,72	6869	1130	2890	46	15900	660	7740	N/A	2759	8,02	24,6	11,4	N/A	670	[2]
22-6-2006	46	0,59	7682	1090	2770	63	16300	640	7645	N/A	2748	9,58	36,5	16,5	N/A	691	[2]
20-7-2006	43	0,62	7451	890	2410	57	13400	580	6665	N/A	2388	10,4	32,3	14	N/A	515	[2]
11-8-2006	43	0,52	8205	1100	2540	60	16100	620	7196	N/A	2888	11	43,2	19,7	N/A	613	[2]
5-9-2006	41	0,47	8890	1100	2540	51	17100	580	7622	N/A	2891	10,8	53,1	26,1	N/A	661	[2]
13-3-2007	47	0,39	14869	N/A	3350	36	20645	680	10103	N/A	3664	9,62	147	44,8	N/A	982	[2]
27-3-2007	49	0,36	15263	N/A	3360	35	21211	680	10264	N/A	3439	7,67	154	45,5	N/A	1026	[2]
13-4-2007	51	0,34	16027	1500	3420	34	20400	710	10104	N/A	3681	13,5	161	54,5	N/A	1032	[2]
30-5-2007	57	0,25	17914	1360	3460	32	18700	700	10868	N/A	3908	32,8	192	67,1	N/A	949	[2]
12-6-2007	58	0,28	18610	N/A	3530	32	24022	720	10957	N/A	3979	34,9	197	69,6	N/A	1130	[2]
27-6-2007	55	0,13	19460	1530	3560	30	23900	740	11275	N/A	3992	35,6	207	71,9	N/A	1132	[2]
29-8-2007	58	0,21	21058	1500	3430	31	26162	740	11472	N/A	3736	42,6	231	79,9	N/A	1194	[2]
12-9-2007	56	0,16	21702	1800	3480	31	40300	730	11788	N/A	3771	42,6	229	78,5	N/A	1182	[2]
27-9-2007	56	0,22	21926	1750	3470	31	27632	730	11724	N/A	4118	42,7	230	80,6	N/A	1141	[2]
26-10-2007	58	0,15	22310	1840	3370	30	30280	740	11639	N/A	4146	46,3	239	87,6	N/A	1169	[2]
6-11-2007	57	0,16	22977	1720	3420	30	26100	730	12712	N/A	4342	46,3	246	90,1	N/A	1204	[2]
22-11-2007	56	0,25	19603	1740	2860	34	23307	610	10958	N/A	3628	40,4	215	75,1	N/A	1023	[2]

Origin and significance of mobile trace elements in volcanic lakes – a case study at Poás, Costa Rica

Date	Temp. (°C)	pH$_{lab}$ 24±2°C	S$_{Total}$ (mg/kg)	F (mg/kg)	Al (mg/kg)	Si (mg/kg)	Cl (mg/kg)	Mg (mg/kg)	B (µg/kg)	Zn (µg/kg)	As (µg/kg)	Mo (µg/kg)	Sn (µg/kg)	Sb (µg/kg)	Tl (µg/kg)	Pb (µg/kg)	Source
18-1-2008	45	0,28	18376	1630	2660	35	23870	580	10732	N/A	3254	24,3	203	74,6	N/A	952	[2]
29-1-2008	41	0,26	18311	1540	2610	42	21372	580	10440	N/A	2987	14,7	200	58,4	N/A	947	[2]
12-2-2008	45	0,21	19124	1680	2740	36	25540	590	10704	N/A	2612	7,35	208	38,1	N/A	989	[2]
11-3-2008	42	0,30	19604	1640	2800	35	25240	620	11233	N/A	1174	5,94	212	20,8	N/A	1019	[2]
5-5-2008	41	0,23	20600	1650	2910	34	25184	650	11752	N/A	427	6,49	215	6,06	N/A	1076	[2]
4-6-2008	42	0,16	18461	1450	2620	37	22537	580	11020	N/A	143	4,85	194	2,64	N/A	951	[2]
15-7-2008	45	0,20	17327	1360	2440	39	21363	540	10452	N/A	278	4,88	177	4,07	N/A	877	[2]
31-7-2008	34	0,34	13068	1100	1800	60	15944	420	7504	N/A	475	4,14	129	6,62	N/A	655	[2]
3-10-2008	44	0,29	15906	N/A	2130	45	19112	480	9749	N/A	308	3,97	152	3,48	N/A	801	[2]
11-11-2008	43	0,12	14638	960	1920	57	17570	440	9007	N/A	290	3,54	129	3,37	N/A	717	[2]
9-12-2008	39	0,14	8316	540	1100	60	9881	260	5469	N/A	380	2,92	70,4	4,6	N/A	399	[2]
29-1-2009	44	-0,03	9897	N/A	1320	63	11595	300	6488	N/A	1236	5,45	76,6	17,8	N/A	502	[2]
11-2-2009	38	0,15	6794	N/A	870	81	7806	200	4499	N/A	843	4,82	49,5	14,2	N/A	337	[2]
25-2-2009	40	N/A	9834	N/A	1240	64	11497	290	6262	N/A	1287	8,64	72,4	22,7	N/A	472	[2]
4-3-2009	40	-0,57	9887	N/A	1220	66	11478	280	6240	N/A	1377	9,71	71,6	23,6	N/A	465	[2]
19-3-2009	44	-0,61	10465	N/A	1250	68	12129	280	6338	N/A	1398	12	73,5	25,1	N/A	468	[2]
24-3-2009	44	-0,59	10695	N/A	1270	66	12414	290	6328	N/A	1457	13,2	74,4	25,4	N/A	485	[2]
3-4-2009	49	-0,62	10955	N/A	1290	69	12759	290	6480	N/A	1552	15,7	78,8	28,7	N/A	506	[2]

Appendix B – USGS rock database schema for importing in SQL

Note that in this schema, the comments denominating the type of data stored in the database columns have been omitted. A full schema, including these comments is available upon request.

```
--
-- Tablestructure for table `tblRockGeoData`
--

CREATE TABLE IF NOT EXISTS `tblRockGeoData` (`lab_id` varchar(10) NOT NULL, `job_id`
varchar(10) NOT NULL, `submitter` varchar(75) NOT NULL, `date_sub` int(11) DEFAULT NULL,
`field_id` varchar(16) DEFAULT NULL, `state` varchar(2) DEFAULT NULL, `country` varchar(20)
DEFAULT NULL, `datum` varchar(50) DEFAULT NULL, `spheroid` varchar(25) DEFAULT NULL,
`latitude` double DEFAULT NULL, `longitude` double DEFAULT NULL, `depth` varchar(65) DEFAULT
NULL, `locat_desc` varchar(254) DEFAULT NULL, `datecollct` varchar(25) DEFAULT NULL,
`sample_src` varchar(40) DEFAULT NULL, `methcollct` varchar(15) DEFAULT NULL, `primeclass`
varchar(30) NOT NULL, `xndryclass` varchar(33) DEFAULT NULL, `spec_name` varchar(40) DEFAULT
NULL, `addl_attr` varchar(254) DEFAULT NULL, `geol_age` varchar(60) DEFAULT NULL, `stratgrphy`
varchar(254) DEFAULT NULL, `mineralztn` varchar(35) DEFAULT NULL, `alteration` varchar(50)
DEFAULT NULL, `struct_src` varchar(30) DEFAULT NULL, `dep_envirn` varchar(20) DEFAULT NULL,
`source_rk` varchar(12) DEFAULT NULL, `metamrphsm` varchar(15) DEFAULT NULL, `facies_grd`
varchar(35) DEFAULT NULL, `prep` varchar(254) DEFAULT NULL, `mesh_size` varchar(60) DEFAULT
NULL, PRIMARY KEY (`lab_id`)) ENGINE=InnoDB DEFAULT CHARSET=latin1;

-- --------------------------------------------------------


--
-- Tablestructure for table `xtbEsChem`
--

CREATE TABLE IF NOT EXISTS `xtbEsChem` (`lab_id` varchar(10) NOT NULL, `alpct_s` double
DEFAULT NULL, `alpct_sq` varchar(1) DEFAULT NULL, `capct_s` double DEFAULT NULL, `capct_sq`
varchar(1) DEFAULT NULL, `fepct_s` double DEFAULT NULL, `fepct_sq` varchar(1) DEFAULT NULL,
`kpct_s` double DEFAULT NULL, `kpct_sq` varchar(1) DEFAULT NULL, `mgpct_s` double DEFAULT
NULL, `mgpct_sq` varchar(1) DEFAULT NULL, `napct_s` double DEFAULT NULL, `napct_sq` varchar(1)
DEFAULT NULL, `ppct_s` double DEFAULT NULL, `ppct_sq` varchar(1) DEFAULT NULL, `sipct_s`
double DEFAULT NULL, `sipct_sq` varchar(1) DEFAULT NULL, `tipct_s` double DEFAULT NULL,
`tipct_sq` varchar(1) DEFAULT NULL, `agppm_s` double DEFAULT NULL, `agppm_sq` varchar(1)
DEFAULT NULL, `asppm_s` double DEFAULT NULL, `asppm_sq` varchar(1) DEFAULT NULL, `auppm_s`
double DEFAULT NULL, `auppm_sq` varchar(1) DEFAULT NULL, `bppm_s` double DEFAULT NULL,
`bppm_sq` varchar(1) DEFAULT NULL, `bappm_s` double DEFAULT NULL, `bappm_sq` varchar(1)
DEFAULT NULL, `beppm_s` double DEFAULT NULL, `beppm_sq` varchar(1) DEFAULT NULL, `bippm_s`
double DEFAULT NULL, `bippm_sq` varchar(1) DEFAULT NULL, `cdppm_s` double DEFAULT NULL,
`cdppm_sq` varchar(1) DEFAULT NULL, `ceppm_s` double DEFAULT NULL, `ceppm_sq` varchar(1)
DEFAULT NULL, `coppm_s` double DEFAULT NULL, `coppm_sq` varchar(1) DEFAULT NULL, `crppm_s`
double DEFAULT NULL, `crppm_sq` varchar(1) DEFAULT NULL, `csppm_s` double DEFAULT NULL,
`csppm_sq` varchar(1) DEFAULT NULL, `cuppm_s` double DEFAULT NULL, `cuppm_sq` varchar(1)
DEFAULT NULL, `dyppm_s` double DEFAULT NULL, `dyppm_sq` varchar(1) DEFAULT NULL, `erppm_s`
double DEFAULT NULL, `erppm_sq` varchar(1) DEFAULT NULL, `euppm_s` double DEFAULT NULL,
`euppm_sq` varchar(1) DEFAULT NULL, `gappm_s` double DEFAULT NULL, `gappm_sq` varchar(1)
DEFAULT NULL, `gdppm_s` double DEFAULT NULL, `gdppm_sq` varchar(1) DEFAULT NULL, `geppm_s`
double DEFAULT NULL, `geppm_sq` varchar(1) DEFAULT NULL, `hfppm_s` double DEFAULT NULL,
`hfppm_sq` varchar(1) DEFAULT NULL, `hgppm_s` double DEFAULT NULL, `hgppm_sq` varchar(1)
DEFAULT NULL, `hoppm_s` double DEFAULT NULL, `hoppm_sq` varchar(1) DEFAULT NULL, `inppm_s`
double DEFAULT NULL, `inppm_sq` varchar(1) DEFAULT NULL, `irppm_s` double DEFAULT NULL,
`irppm_sq` varchar(1) DEFAULT NULL, `lappm_s` double DEFAULT NULL, `lappm_sq` varchar(1)
DEFAULT NULL, `lippm_s` double DEFAULT NULL, `lippm_sq` varchar(1) DEFAULT NULL, `luppm_s`
double DEFAULT NULL, `luppm_sq` varchar(1) DEFAULT NULL, `mnppm_s` double DEFAULT NULL,
`mnppm_sq` varchar(1) DEFAULT NULL, `moppm_s` double DEFAULT NULL, `moppm_sq` varchar(1)
DEFAULT NULL, `nbppm_s` double DEFAULT NULL, `nbppm_sq` varchar(1) DEFAULT NULL, `ndppm_s`
double DEFAULT NULL, `ndppm_sq` varchar(1) DEFAULT NULL, `nippm_s` double DEFAULT NULL,
`nippm_sq` varchar(1) DEFAULT NULL, `osppm_s` double DEFAULT NULL, `osppm_sq` varchar(1)
DEFAULT NULL, `pbppm_s` double DEFAULT NULL, `pbppm_sq` varchar(1) DEFAULT NULL, `pdppm_s`
double DEFAULT NULL, `pdppm_sq` varchar(1) DEFAULT NULL, `prppm_s` double DEFAULT NULL,
`prppm_sq` varchar(1) DEFAULT NULL, `ptppm_s` double DEFAULT NULL, `ptppm_sq` varchar(1)
DEFAULT NULL, `rbppm_s` double DEFAULT NULL, `rbppm_sq` varchar(1) DEFAULT NULL, `reppm_s`
double DEFAULT NULL, `reppm_sq` varchar(1) DEFAULT NULL, `rhppm_s` double DEFAULT NULL,
`rhppm_sq` varchar(1) DEFAULT NULL, `ruppm_s` double DEFAULT NULL, `ruppm_sq` varchar(1)
DEFAULT NULL, `sbppm_s` double DEFAULT NULL, `sbppm_sq` varchar(1) DEFAULT NULL, `scppm_s`
double DEFAULT NULL, `scppm_sq` varchar(1) DEFAULT NULL, `seppm_s` double DEFAULT NULL,
`seppm_sq` varchar(1) DEFAULT NULL, `smppm_s` double DEFAULT NULL, `smppm_sq` varchar(1)
DEFAULT NULL, `snppm_s` double DEFAULT NULL, `snppm_sq` varchar(1) DEFAULT NULL, `srppm_s`
```

```
double DEFAULT NULL, `srppm_sq` varchar(1) DEFAULT NULL, `tappm_s` double DEFAULT NULL,
`tappm_sq` varchar(1) DEFAULT NULL, `tbppm_s` double DEFAULT NULL, `tbppm_sq` varchar(1)
DEFAULT NULL, `teppm_s` double DEFAULT NULL, `teppm_sq` varchar(1) DEFAULT NULL, `thppm_s`
double DEFAULT NULL, `thppm_sq` varchar(1) DEFAULT NULL, `tlppm_s` double DEFAULT NULL,
`tlppm_sq` varchar(1) DEFAULT NULL, `tmppm_s` double DEFAULT NULL, `tmppm_sq` varchar(1)
DEFAULT NULL, `uppm_s` double DEFAULT NULL, `uppm_sq` varchar(1) DEFAULT NULL, `vppm_s` double
DEFAULT NULL, `vppm_sq` varchar(1) DEFAULT NULL, `wppm_s` double DEFAULT NULL, `wppm_sq`
varchar(1) DEFAULT NULL, `yppm_s` double DEFAULT NULL, `yppm_sq` varchar(1) DEFAULT NULL,
`ybppm_s` double DEFAULT NULL, `ybppm_sq` varchar(1) DEFAULT NULL, `znppm_s` double DEFAULT
NULL, `znppm_sq` varchar(1) DEFAULT NULL, `zrppm_s` double DEFAULT NULL, `zrppm_sq` varchar(1)
DEFAULT NULL, PRIMARY KEY (`lab_id`)) ENGINE=InnoDB DEFAULT CHARSET=latin1 COMMENT='Major,
minor and trace element by emission spectrometry';


-- --------------------------------------------------------

--
-- Tablestructure for table `xtbIcpaesChem`
--

CREATE TABLE IF NOT EXISTS `xtbIcpaesChem` (`lab_id` varchar(10) NOT NULL, `alpct_aes` double
DEFAULT NULL, `alpct_aesq` varchar(1) DEFAULT NULL, `capct_aes` double DEFAULT NULL,
`capct_aesq` varchar(1) DEFAULT NULL, `fepct_aes` double DEFAULT NULL, `fepct_aesq` varchar(1)
DEFAULT NULL, `kpct_aes` double DEFAULT NULL, `kpct_aesq` varchar(1) DEFAULT NULL, `mgpct_aes`
double DEFAULT NULL, `mgpct_aesq` varchar(1) DEFAULT NULL, `napct_aes` double DEFAULT NULL,
`napct_aesq` varchar(1) DEFAULT NULL, `ppct_aes` double DEFAULT NULL, `ppct_aesq` varchar(1)
DEFAULT NULL, `sipct_aes` double DEFAULT NULL, `sipct_aesq` varchar(1) DEFAULT NULL,
`tipct_aes` double DEFAULT NULL, `tipct_aesq` varchar(1) DEFAULT NULL, `agppm_aes` double
DEFAULT NULL, `agppm_aesq` varchar(1) DEFAULT NULL, `asppm_aes` double DEFAULT NULL,
`asppm_aesq` varchar(1) DEFAULT NULL, `auppm_aes` double DEFAULT NULL, `auppm_aesq` varchar(1)
DEFAULT NULL, `bppm_aes` double DEFAULT NULL, `bppm_aesq` varchar(1) DEFAULT NULL, `bappm_aes`
double DEFAULT NULL, `bappm_aesq` varchar(1) DEFAULT NULL, `beppm_aes` double DEFAULT NULL,
`beppm_aesq` varchar(1) DEFAULT NULL, `bippm_aes` double DEFAULT NULL, `bippm_aesq` varchar(1)
DEFAULT NULL, `cdppm_aes` double DEFAULT NULL, `cdppm_aesq` varchar(1) DEFAULT NULL,
`ceppm_aes` double DEFAULT NULL, `ceppm_aesq` varchar(1) DEFAULT NULL, `coppm_aes` double
DEFAULT NULL, `coppm_aesq` varchar(1) DEFAULT NULL, `crppm_aes` double DEFAULT NULL,
`crppm_aesq` varchar(1) DEFAULT NULL, `cuppm_aes` double DEFAULT NULL, `cuppm_aesq` varchar(1)
DEFAULT NULL, `dyppm_aes` double DEFAULT NULL, `dyppm_aesq` varchar(1) DEFAULT NULL,
`erppm_aes` double DEFAULT NULL, `erppm_aesq` varchar(1) DEFAULT NULL, `euppm_aes` double
DEFAULT NULL, `euppm_aesq` varchar(1) DEFAULT NULL, `gappm_aes` double DEFAULT NULL,
`gappm_aesq` varchar(1) DEFAULT NULL, `gdppm_aes` double DEFAULT NULL, `gdppm_aesq` varchar(1)
DEFAULT NULL, `geppm_aes` double DEFAULT NULL, `geppm_aesq` varchar(1) DEFAULT NULL,
`hgppm_aes` double DEFAULT NULL, `hgppm_aesq` varchar(1) DEFAULT NULL, `hoppm_aes` double
DEFAULT NULL, `hoppm_aesq` varchar(1) DEFAULT NULL, `lappm_aes` double DEFAULT NULL,
`lappm_aesq` varchar(1) DEFAULT NULL, `lippm_aes` double DEFAULT NULL, `lippm_aesq` varchar(1)
DEFAULT NULL, `luppm_aes` double DEFAULT NULL, `luppm_aesq` varchar(1) DEFAULT NULL,
`mnppm_aes` double DEFAULT NULL, `mnppm_aesq` varchar(1) DEFAULT NULL, `moppm_aes` double
DEFAULT NULL, `moppm_aesq` varchar(1) DEFAULT NULL, `nbppm_aes` double DEFAULT NULL,
`nbppm_aesq` varchar(1) DEFAULT NULL, `ndppm_aes` double DEFAULT NULL, `ndppm_aesq` varchar(1)
DEFAULT NULL, `nippm_aes` double DEFAULT NULL, `nippm_aesq` varchar(1) DEFAULT NULL,
`osppm_aes` double DEFAULT NULL, `osppm_aesq` varchar(1) DEFAULT NULL, `pbppm_aes` double
DEFAULT NULL, `pbppm_aesq` varchar(1) DEFAULT NULL, `prppm_aes` double DEFAULT NULL,
`prppm_aesq` varchar(1) DEFAULT NULL, `rbppm_aes` double DEFAULT NULL, `rbppm_aesq` varchar(1)
DEFAULT NULL, `sbppm_aes` double DEFAULT NULL, `sbppm_aesq` varchar(1) DEFAULT NULL,
`scppm_aes` double DEFAULT NULL, `scppm_aesq` varchar(1) DEFAULT NULL, `seppm_aes` double
DEFAULT NULL, `seppm_aesq` varchar(1) DEFAULT NULL, `smppm_aes` double DEFAULT NULL,
`smppm_aesq` varchar(1) DEFAULT NULL, `snppm_aes` double DEFAULT NULL, `snppm_aesq` varchar(1)
DEFAULT NULL, `srppm_aes` double DEFAULT NULL, `srppm_aesq` varchar(1) DEFAULT NULL,
`tappm_aes` double DEFAULT NULL, `tappm_aesq` varchar(1) DEFAULT NULL, `tbppm_aes` double
DEFAULT NULL, `tbppm_aesq` varchar(1) DEFAULT NULL, `thppm_aes` double DEFAULT NULL,
`thppm_aesq` varchar(1) DEFAULT NULL, `tlppm_aes` double DEFAULT NULL, `tlppm_aesq` varchar(1)
DEFAULT NULL, `tmppm_aes` double DEFAULT NULL, `tmppm_aesq` varchar(1) DEFAULT NULL,
`uppm_aes` double DEFAULT NULL, `uppm_aesq` varchar(1) DEFAULT NULL, `vppm_aes` double DEFAULT
NULL, `vppm_aesq` varchar(1) DEFAULT NULL, `wppm_aes` double DEFAULT NULL, `wppm_aesq`
varchar(1) DEFAULT NULL, `yppm_aes` double DEFAULT NULL, `yppm_aesq` varchar(1) DEFAULT NULL,
`ybppm_aes` double DEFAULT NULL, `ybppm_aesq` varchar(1) DEFAULT NULL, `znppm_aes` double
DEFAULT NULL, `znppm_aesq` varchar(1) DEFAULT NULL, `zrppm_aes` double DEFAULT NULL,
`zrppm_aesq` varchar(1) DEFAULT NULL, `agppmaesp` double DEFAULT NULL, `agppmaespq` varchar(1)
DEFAULT NULL, `alppmaesp` double DEFAULT NULL, `alppmaespq` varchar(1) DEFAULT NULL,
`asppmaesp` double DEFAULT NULL, `asppmaespq` varchar(1) DEFAULT NULL, `auppmaesp` double
DEFAULT NULL, `auppmaespq` varchar(1) DEFAULT NULL, `bppmaesp` double DEFAULT NULL,
`bppmaespq` varchar(1) DEFAULT NULL, `bappmaesp` double DEFAULT NULL, `bappmaespq` varchar(1)
DEFAULT NULL, `beppmaesp` double DEFAULT NULL, `beppmaespq` varchar(1) DEFAULT NULL,
`bippmaesp` double DEFAULT NULL, `bippmaespq` varchar(1) DEFAULT NULL, `cappmaesp` double
DEFAULT NULL, `cappmaespq` varchar(1) DEFAULT NULL, `cdppmaesp` double DEFAULT NULL,
`cdppmaespq` varchar(1) DEFAULT NULL, `ceppmaesp` double DEFAULT NULL, `ceppmaespq` varchar(1)
DEFAULT NULL, `coppmaesp` double DEFAULT NULL, `coppmaespq` varchar(1) DEFAULT NULL,
`crppmaesp` double DEFAULT NULL, `crppmaespq` varchar(1) DEFAULT NULL, `cuppmaesp` double
```

```
DEFAULT NULL, `cuppmaespq` varchar(1) DEFAULT NULL, `feppmaesp` double DEFAULT NULL,
`feppmaespq` varchar(1) DEFAULT NULL, `kppmaesp` double DEFAULT NULL, `kppmaespq` varchar(1)
DEFAULT NULL, `lappmaesp` double DEFAULT NULL, `lappmaespq` varchar(1) DEFAULT NULL,
`lippmaesp` double DEFAULT NULL, `lippmaespq` varchar(1) DEFAULT NULL, `mgppmaesp` double
DEFAULT NULL, `mgppmaespq` varchar(1) DEFAULT NULL, `mnppmaesp` double DEFAULT NULL,
`mnppmaespq` varchar(1) DEFAULT NULL, `moppmaesp` double DEFAULT NULL, `moppmaespq` varchar(1)
DEFAULT NULL, `nappmaesp` double DEFAULT NULL, `nappmaespq` varchar(1) DEFAULT NULL,
`nbppmaesp` double DEFAULT NULL, `nbppmaespq` varchar(1) DEFAULT NULL, `nippmaesp` double
DEFAULT NULL, `nippmaespq` varchar(1) DEFAULT NULL, `pppmaesp` double DEFAULT NULL,
`pppmaespq` varchar(1) DEFAULT NULL, `pbppmaesp` double DEFAULT NULL, `pbppmaespq` varchar(1)
DEFAULT NULL, `sbppmaesp` double DEFAULT NULL, `sbppmaespq` varchar(1) DEFAULT NULL,
`seppmaesp` double DEFAULT NULL, `seppmaespq` varchar(1) DEFAULT NULL, `sippmaesp` double
DEFAULT NULL, `sippmaespq` varchar(1) DEFAULT NULL, `snppmaesp` double DEFAULT NULL,
`snppmaespq` varchar(1) DEFAULT NULL, `srppmaesp` double DEFAULT NULL, `srppmaespq` varchar(1)
DEFAULT NULL, `thppmaesp` double DEFAULT NULL, `thppmaespq` varchar(1) DEFAULT NULL,
`tippmaesp` double DEFAULT NULL, `tippmaespq` varchar(1) DEFAULT NULL, `tlppmaesp` double
DEFAULT NULL, `tlppmaespq` varchar(1) DEFAULT NULL, `vppmaesp` double DEFAULT NULL,
`vppmaespq` varchar(1) DEFAULT NULL, `wppmaesp` double DEFAULT NULL, `wppmaespq` varchar(1)
DEFAULT NULL, `yppmaesp` double DEFAULT NULL, `yppmaespq` varchar(1) DEFAULT NULL, `znppmaesp`
double DEFAULT NULL, `znppmaespq` varchar(1) DEFAULT NULL, `zrppmaesp` double DEFAULT NULL,
`zrppmaespq` varchar(1) DEFAULT NULL, PRIMARY KEY (`lab_id`)) ENGINE=InnoDB DEFAULT
CHARSET=latin1 COMMENT='Major, minor and trace element by inductively coupled plasma-atomic
emission spectrometry';

-- --------------------------------------------------------

--
-- Tablestructure for table `xtbIcpmsChem`
--

CREATE TABLE IF NOT EXISTS `xtbIcpmsChem` (`lab_id` varchar(10) NOT NULL, `alpct_ms` double
DEFAULT NULL, `alpct_msq` varchar(1) DEFAULT NULL, `capct_ms` double DEFAULT NULL, `capct_msq`
varchar(1) DEFAULT NULL, `fepct_ms` double DEFAULT NULL, `fepct_msq` varchar(1) DEFAULT NULL,
`kpct_ms` double DEFAULT NULL, `kpct_msq` varchar(1) DEFAULT NULL, `mgpct_ms` double DEFAULT
NULL, `mgpct_msq` varchar(1) DEFAULT NULL, `napct_ms` double DEFAULT NULL, `napct_msq`
varchar(1) DEFAULT NULL, `ppct_ms` double DEFAULT NULL, `ppct_msq` varchar(1) DEFAULT NULL,
`sipct_ms` double DEFAULT NULL, `sipct_msq` varchar(1) DEFAULT NULL, `tipct_ms` double DEFAULT
NULL, `tipct_msq` varchar(1) DEFAULT NULL, `agppm_ms` double DEFAULT NULL, `agppm_msq`
varchar(1) DEFAULT NULL, `asppm_ms` double DEFAULT NULL, `asppm_msq` varchar(1) DEFAULT NULL,
`auppm_ms` double DEFAULT NULL, `auppm_msq` varchar(1) DEFAULT NULL, `bppm_ms` double DEFAULT
NULL, `bppm_msq` varchar(1) DEFAULT NULL, `bappm_ms` double DEFAULT NULL, `bappm_msq`
varchar(1) DEFAULT NULL, `beppm_ms` double DEFAULT NULL, `beppm_msq` varchar(1) DEFAULT NULL,
`bippm_ms` double DEFAULT NULL, `bippm_msq` varchar(1) DEFAULT NULL, `cdppm_ms` double DEFAULT
NULL, `cdppm_msq` varchar(1) DEFAULT NULL, `ceppm_ms` double DEFAULT NULL, `ceppm_msq`
varchar(1) DEFAULT NULL, `coppm_ms` double DEFAULT NULL, `coppm_msq` varchar(1) DEFAULT NULL,
`crppm_ms` double DEFAULT NULL, `crppm_msq` varchar(1) DEFAULT NULL, `csppm_ms` double DEFAULT
NULL, `csppm_msq` varchar(1) DEFAULT NULL, `cuppm_ms` double DEFAULT NULL, `cuppm_msq`
varchar(1) DEFAULT NULL, `dyppm_ms` double DEFAULT NULL, `dyppm_msq` varchar(1) DEFAULT NULL,
`erppm_ms` double DEFAULT NULL, `erppm_msq` varchar(1) DEFAULT NULL, `euppm_ms` double DEFAULT
NULL, `euppm_msq` varchar(1) DEFAULT NULL, `gappm_ms` double DEFAULT NULL, `gappm_msq`
varchar(1) DEFAULT NULL, `gdppm_ms` double DEFAULT NULL, `gdppm_msq` varchar(1) DEFAULT NULL,
`geppm_ms` double DEFAULT NULL, `geppm_msq` varchar(1) DEFAULT NULL, `hfppm_ms` double DEFAULT
NULL, `hfppm_msq` varchar(1) DEFAULT NULL, `hgppm_ms` double DEFAULT NULL, `hgppm_msq`
varchar(1) DEFAULT NULL, `hoppm_ms` double DEFAULT NULL, `hoppm_msq` varchar(1) DEFAULT NULL,
`inppm_ms` double DEFAULT NULL, `inppm_msq` varchar(1) DEFAULT NULL, `lappm_ms` double DEFAULT
NULL, `lappm_msq` varchar(1) DEFAULT NULL, `lippm_ms` double DEFAULT NULL, `lippm_msq`
varchar(1) DEFAULT NULL, `luppm_ms` double DEFAULT NULL, `luppm_msq` varchar(1) DEFAULT NULL,
`mnppm_ms` double DEFAULT NULL, `mnppm_msq` varchar(1) DEFAULT NULL, `moppm_ms` double DEFAULT
NULL, `moppm_msq` varchar(1) DEFAULT NULL, `nbppm_ms` double DEFAULT NULL, `nbppm_msq`
varchar(1) DEFAULT NULL, `ndppm_ms` double DEFAULT NULL, `ndppm_msq` varchar(1) DEFAULT NULL,
`nippm_ms` double DEFAULT NULL, `nippm_msq` varchar(1) DEFAULT NULL, `pbppm_ms` double DEFAULT
NULL, `pbppm_msq` varchar(1) DEFAULT NULL, `prppm_ms` double DEFAULT NULL, `prppm_msq`
varchar(1) DEFAULT NULL, `rbppm_ms` double DEFAULT NULL, `rbppm_msq` varchar(1) DEFAULT NULL,
`reppm_ms` double DEFAULT NULL, `reppm_msq` varchar(1) DEFAULT NULL, `spct_ms` double DEFAULT
NULL, `spct_msq` varchar(1) DEFAULT NULL, `sbppm_ms` double DEFAULT NULL, `sbppm_msq`
varchar(1) DEFAULT NULL, `scppm_ms` double DEFAULT NULL, `scppm_msq` varchar(1) DEFAULT NULL,
`seppm_ms` double DEFAULT NULL, `seppm_msq` varchar(1) DEFAULT NULL, `smppm_ms` double DEFAULT
NULL, `smppm_msq` varchar(1) DEFAULT NULL, `snppm_ms` double DEFAULT NULL, `snppm_msq`
varchar(1) DEFAULT NULL, `srppm_ms` double DEFAULT NULL, `srppm_msq` varchar(1) DEFAULT NULL,
`tappm_ms` double DEFAULT NULL, `tappm_msq` varchar(1) DEFAULT NULL, `tbppm_ms` double DEFAULT
NULL, `tbppm_msq` varchar(1) DEFAULT NULL, `teppm_ms` double DEFAULT NULL, `teppm_msq`
varchar(1) DEFAULT NULL, `thppm_ms` double DEFAULT NULL, `thppm_msq` varchar(1) DEFAULT NULL,
`tlppm_ms` double DEFAULT NULL, `tlppm_msq` varchar(1) DEFAULT NULL, `tmppm_ms` double DEFAULT
NULL, `tmppm_msq` varchar(1) DEFAULT NULL, `uppm_ms` double DEFAULT NULL, `uppm_msq`
varchar(1) DEFAULT NULL, `vppm_ms` double DEFAULT NULL, `vppm_msq` varchar(1) DEFAULT NULL,
`wppm_ms` double DEFAULT NULL, `wppm_msq` varchar(1) DEFAULT NULL, `yppm_ms` double DEFAULT
NULL, `yppm_msq` varchar(1) DEFAULT NULL, `ybppm_ms` double DEFAULT NULL, `ybppm_msq`
```

```
varchar(1) DEFAULT NULL, `znppm_ms` double DEFAULT NULL, `znppm_msq` varchar(1) DEFAULT NULL,
`zrppm_ms` double DEFAULT NULL, `zrppm_msq` varchar(1) DEFAULT NULL, PRIMARY KEY (`lab_id`))
ENGINE=InnoDB DEFAULT CHARSET=latin1 COMMENT='Major, minor and trace element by inductively
coupled-mass spectrometry';

-- --------------------------------------------------------

--
-- Tablestructure for table `xtbMajorChem`
--

CREATE TABLE IF NOT EXISTS `xtbMajorChem` (`lab_id` varchar(10) NOT NULL, `sio2_xrf` double
DEFAULT NULL, `sio2_xrfq` varchar(1) DEFAULT NULL, `sio2_grv` double DEFAULT NULL, `sio2_grvq`
varchar(1) DEFAULT NULL, `sio2_aes` double DEFAULT NULL, `sio2_aesq` varchar(1) DEFAULT NULL,
`sio2_aa` double DEFAULT NULL, `sio2_aaq` varchar(1) DEFAULT NULL, `sio2_clr` double DEFAULT
NULL, `sio2_clrq` varchar(1) DEFAULT NULL, `sio2_unk` double DEFAULT NULL, `sio2_unkq`
varchar(1) DEFAULT NULL, `al2o3_xrf` double DEFAULT NULL, `al2o3_xrfq` varchar(1) DEFAULT
NULL, `al2o3_grv` double DEFAULT NULL, `al2o3_grvq` varchar(1) DEFAULT NULL, `al2o3_aes`
double DEFAULT NULL, `al2o3_aesq` varchar(1) DEFAULT NULL, `al2o3_aa` double DEFAULT NULL,
`al2o3_aaq` varchar(1) DEFAULT NULL, `al2o3_clr` double DEFAULT NULL, `al2o3_clrq` varchar(1)
DEFAULT NULL, `al2o3_unk` double DEFAULT NULL, `al2o3_unkq` varchar(1) DEFAULT NULL,
`fe2o3_xrf` double DEFAULT NULL, `fe2o3_xrfq` varchar(1) DEFAULT NULL, `fe2o3_grv` double
DEFAULT NULL, `fe2o3_grvq` varchar(1) DEFAULT NULL, `fe2o3_aes` double DEFAULT NULL,
`fe2o3_aesq` varchar(1) DEFAULT NULL, `fe2o3_aa` double DEFAULT NULL, `fe2o3_aaq` varchar(1)
DEFAULT NULL, `fe2o3_clr` double DEFAULT NULL, `fe2o3_clrq` varchar(1) DEFAULT NULL,
`fe2o3_unk` double DEFAULT NULL, `fe2o3_unkq` varchar(1) DEFAULT NULL, `feo_aa` double DEFAULT
NULL, `feo_aaq` varchar(1) DEFAULT NULL, `feo_aes` double DEFAULT NULL, `feo_aesq` varchar(1)
DEFAULT NULL, `feo_grv` double DEFAULT NULL, `feo_grvq` varchar(1) DEFAULT NULL, `feo_msc`
double DEFAULT NULL, `feo_mscq` varchar(1) DEFAULT NULL, `feo_ttr` double DEFAULT NULL,
`feo_ttrq` varchar(1) DEFAULT NULL, `feo_unk` double DEFAULT NULL, `feo_unkq` varchar(1)
DEFAULT NULL, `feto3_xrf` double DEFAULT NULL, `feto3_xrfq` varchar(1) DEFAULT NULL,
`feto3_aes` double DEFAULT NULL, `feto3_aesq` varchar(1) DEFAULT NULL, `feto3_clr` double
DEFAULT NULL, `feto3_clrq` varchar(1) DEFAULT NULL, `feto3_msc` double DEFAULT NULL,
`feto3_mscq` varchar(1) DEFAULT NULL, `feto3_unk` double DEFAULT NULL, `feto3_unkq` varchar(1)
DEFAULT NULL, `mgo_xrf` double DEFAULT NULL, `mgo_xrfq` varchar(1) DEFAULT NULL, `mgo_grv`
double DEFAULT NULL, `mgo_grvq` varchar(1) DEFAULT NULL, `mgo_aes` double DEFAULT NULL,
`mgo_aesq` varchar(1) DEFAULT NULL, `mgo_aa` double DEFAULT NULL, `mgo_aaq` varchar(1) DEFAULT
NULL, `mgo_unk` double DEFAULT NULL, `mgo_unkq` varchar(1) DEFAULT NULL, `cao_xrf` double
DEFAULT NULL, `cao_xrfq` varchar(1) DEFAULT NULL, `cao_grv` double DEFAULT NULL, `cao_grvq`
varchar(1) DEFAULT NULL, `cao_aes` double DEFAULT NULL, `cao_aesq` varchar(1) DEFAULT NULL,
`cao_aa` double DEFAULT NULL, `cao_aaq` varchar(1) DEFAULT NULL, `cao_unk` double DEFAULT
NULL, `cao_unkq` varchar(1) DEFAULT NULL, `na2o_xrf` double DEFAULT NULL, `na2o_xrfq`
varchar(1) DEFAULT NULL, `na2o_grv` double DEFAULT NULL, `na2o_grvq` varchar(1) DEFAULT NULL,
`na2o_aes` double DEFAULT NULL, `na2o_aesq` varchar(1) DEFAULT NULL, `na2o_aa` double DEFAULT
NULL, `na2o_aaq` varchar(1) DEFAULT NULL, `na2o_msc` double DEFAULT NULL, `na2o_mscq`
varchar(1) DEFAULT NULL, `na2o_unk` double DEFAULT NULL, `na2o_unkq` varchar(1) DEFAULT NULL,
`k2o_xrf` double DEFAULT NULL, `k2o_xrfq` varchar(1) DEFAULT NULL, `k2o_grv` double DEFAULT
NULL, `k2o_grvq` varchar(1) DEFAULT NULL, `k2o_aes` double DEFAULT NULL, `k2o_aesq` varchar(1)
DEFAULT NULL, `k2o_aa` double DEFAULT NULL, `k2o_aaq` varchar(1) DEFAULT NULL, `k2o_msc`
double DEFAULT NULL, `k2o_mscq` varchar(1) DEFAULT NULL, `k2o_unk` double DEFAULT NULL,
`k2o_unkq` varchar(1) DEFAULT NULL, `tio2_xrf` double DEFAULT NULL, `tio2_xrfq` varchar(1)
DEFAULT NULL, `tio2_grv` double DEFAULT NULL, `tio2_grvq` varchar(1) DEFAULT NULL, `tio2_aes`
double DEFAULT NULL, `tio2_aesq` varchar(1) DEFAULT NULL, `tio2_aa` double DEFAULT NULL,
`tio2_aaq` varchar(1) DEFAULT NULL, `tio2_clr` double DEFAULT NULL, `tio2_clrq` varchar(1)
DEFAULT NULL, `tio2_unk` double DEFAULT NULL, `tio2_unkq` varchar(1) DEFAULT NULL, `p2o5_xrf`
double DEFAULT NULL, `p2o5_xrfq` varchar(1) DEFAULT NULL, `p2o5_grv` double DEFAULT NULL,
`p2o5_grvq` varchar(1) DEFAULT NULL, `p2o5_aes` double DEFAULT NULL, `p2o5_aesq` varchar(1)
DEFAULT NULL, `p2o5_aa` double DEFAULT NULL, `p2o5_aaq` varchar(1) DEFAULT NULL, `p2o5_clr`
double DEFAULT NULL, `p2o5_clrq` varchar(1) DEFAULT NULL, `p2o5_unk` double DEFAULT NULL,
`p2o5_unkq` varchar(1) DEFAULT NULL, `mno_xrf` double DEFAULT NULL, `mno_xrfq` varchar(1)
DEFAULT NULL, `mno_grv` double DEFAULT NULL, `mno_grvq` varchar(1) DEFAULT NULL, `mno_aes`
double DEFAULT NULL, `mno_aesq` varchar(1) DEFAULT NULL, `mno_aa` double DEFAULT NULL,
`mno_aaq` varchar(1) DEFAULT NULL, `mno_clr` double DEFAULT NULL, `mno_clrq` varchar(1)
DEFAULT NULL, `mno_unk` double DEFAULT NULL, `mno_unkq` varchar(1) DEFAULT NULL, `loi_msc`
double DEFAULT NULL, `loi_mscq` varchar(1) DEFAULT NULL, `lof_unk` double DEFAULT NULL,
`lof_unkq` varchar(1) DEFAULT NULL, `h2o_m_msc` double DEFAULT NULL, `h2o_m_mscq` varchar(1)
DEFAULT NULL, `h2o_p_msc` double DEFAULT NULL, `h2o_p_mscq` varchar(1) DEFAULT NULL,
`h2o_t_msc` double DEFAULT NULL, `h2o_t_mscq` varchar(1) DEFAULT NULL, `co2_ttr` double
DEFAULT NULL, `co2_ttrq` varchar(1) DEFAULT NULL, `co2_grv` double DEFAULT NULL, `co2_grvq`
varchar(1) DEFAULT NULL, `co2_msc` double DEFAULT NULL, `co2_mscq` varchar(1) DEFAULT NULL,
`co2_aa` double DEFAULT NULL, `co2_aaq` varchar(1) DEFAULT NULL, `co2_unk` double DEFAULT
NULL, `co2_unkq` varchar(1) DEFAULT NULL, `co2_xrf` double DEFAULT NULL, `co2_xrfq` varchar(1)
DEFAULT NULL, `c_crb_ttr` double DEFAULT NULL, `c_crb_ttrq` varchar(1) DEFAULT NULL,
`c_org_dff` double DEFAULT NULL, `c_org_dffq` varchar(1) DEFAULT NULL, `c_tot_cmb` double
DEFAULT NULL, `c_tot_cmbq` varchar(1) DEFAULT NULL, `s_org_msc` double DEFAULT NULL,
`s_org_mscq` varchar(1) DEFAULT NULL, `s_sfd_msc` double DEFAULT NULL, `s_sfd_mscq` varchar(1)
DEFAULT NULL, `s_so4_msc` double DEFAULT NULL, `s_so4_mscq` varchar(1) DEFAULT NULL,
```

```
`s_tot_msc` double DEFAULT NULL, `s_tot_mscq` varchar(1) DEFAULT NULL, `cl_elctrd` double
DEFAULT NULL, `cl_elctrdq` varchar(1) DEFAULT NULL, `cl_clr` double DEFAULT NULL, `cl_clrq`
varchar(1) DEFAULT NULL, `cl_xrf` double DEFAULT NULL, `cl_xrfq` varchar(1) DEFAULT NULL,
`cl_msc` double DEFAULT NULL, `cl_mscq` varchar(1) DEFAULT NULL, `cl_unk` double DEFAULT NULL,
`cl_unkq` varchar(1) DEFAULT NULL, `f_elctrd` double DEFAULT NULL, `f_elctrdq` varchar(1)
DEFAULT NULL, `f_msc` double DEFAULT NULL, `f_mscq` varchar(1) DEFAULT NULL, `f_unk` double
DEFAULT NULL, `f_unkq` varchar(1) DEFAULT NULL, PRIMARY KEY (`lab_id`)) ENGINE=InnoDB DEFAULT
CHARSET=latin1 COMMENT='Major element oxide analysis, forms of carbon, sulfur, chlorine and
fluorine';

-- --------------------------------------------------------

--
-- Tablestructure for table `xtbNaaChem`
--

CREATE TABLE IF NOT EXISTS `xtbNaaChem` (`lab_id` varchar(10) NOT NULL, `capct_na` double
DEFAULT NULL, `capct_naq` varchar(1) DEFAULT NULL, `fepct_na` double DEFAULT NULL, `fepct_naq`
varchar(1) DEFAULT NULL, `fe_cvpct` double DEFAULT NULL, `kpct_na` double DEFAULT NULL,
`kpct_naq` varchar(1) DEFAULT NULL, `k_cvpct` double DEFAULT NULL, `napct_na` double DEFAULT
NULL, `napct_naq` varchar(1) DEFAULT NULL, `na_cvpct` double DEFAULT NULL, `asppm_na` double
DEFAULT NULL, `asppm_naq` varchar(1) DEFAULT NULL, `as_cvpct` double DEFAULT NULL, `auppb_na`
double DEFAULT NULL, `auppb_naq` varchar(1) DEFAULT NULL, `au_cvpct` double DEFAULT NULL,
`bappm_na` double DEFAULT NULL, `bappm_naq` varchar(1) DEFAULT NULL, `ba_cvpct` double DEFAULT
NULL, `brppm_na` double DEFAULT NULL, `brppm_naq` varchar(1) DEFAULT NULL, `cdppm_na` double
DEFAULT NULL, `cdppm_naq` varchar(1) DEFAULT NULL, `cd_cvpct` double DEFAULT NULL, `ceppm_na`
double DEFAULT NULL, `ceppm_naq` varchar(1) DEFAULT NULL, `ce_cvpct` double DEFAULT NULL,
`coppm_na` double DEFAULT NULL, `coppm_naq` varchar(1) DEFAULT NULL, `co_cvpct` double DEFAULT
NULL, `crppm_na` double DEFAULT NULL, `crppm_naq` varchar(1) DEFAULT NULL, `cr_cvpct` double
DEFAULT NULL, `csppm_na` double DEFAULT NULL, `csppm_naq` varchar(1) DEFAULT NULL, `cs_cvpct`
double DEFAULT NULL, `cuppm_na` double DEFAULT NULL, `cuppm_naq` varchar(1) DEFAULT NULL,
`cu_cvpct` double DEFAULT NULL, `dyppm_na` double DEFAULT NULL, `dyppm_naq` varchar(1) DEFAULT
NULL, `dy_cvpct` double DEFAULT NULL, `euppm_na` double DEFAULT NULL, `euppm_naq` varchar(1)
DEFAULT NULL, `eu_cvpct` double DEFAULT NULL, `gappm_na` double DEFAULT NULL, `gappm_naq`
varchar(1) DEFAULT NULL, `gdppm_na` double DEFAULT NULL, `gdppm_naq` varchar(1) DEFAULT NULL,
`gd_cvpct` double DEFAULT NULL, `hfppm_na` double DEFAULT NULL, `hfppm_naq` varchar(1) DEFAULT
NULL, `hf_cvpct` double DEFAULT NULL, `hgppm_na` double DEFAULT NULL, `hgppm_naq` varchar(1)
DEFAULT NULL, `hg_cvpct` double DEFAULT NULL, `hoppm_na` double DEFAULT NULL, `hoppm_naq`
varchar(1) DEFAULT NULL, `ho_cvpct` double DEFAULT NULL, `irppb_na` double DEFAULT NULL,
`irppb_naq` varchar(1) DEFAULT NULL, `ir_cvpct` double DEFAULT NULL, `lappm_na` double DEFAULT
NULL, `lappm_naq` varchar(1) DEFAULT NULL, `la_cvpct` double DEFAULT NULL, `luppm_na` double
DEFAULT NULL, `luppm_naq` varchar(1) DEFAULT NULL, `lu_cvpct` double DEFAULT NULL, `mnppm_na`
double DEFAULT NULL, `mnppm_naq` varchar(1) DEFAULT NULL, `mn_cvpct` double DEFAULT NULL,
`moppm_na` double DEFAULT NULL, `moppm_naq` varchar(1) DEFAULT NULL, `ndppm_na` double DEFAULT
NULL, `ndppm_naq` varchar(1) DEFAULT NULL, `nd_cvpct` double DEFAULT NULL, `nippm_na` double
DEFAULT NULL, `nippm_naq` varchar(1) DEFAULT NULL, `ni_cvpct` double DEFAULT NULL, `rbppm_na`
double DEFAULT NULL, `rbppm_naq` varchar(1) DEFAULT NULL, `rb_cvpct` double DEFAULT NULL,
`sbppm_na` double DEFAULT NULL, `sbppm_naq` varchar(1) DEFAULT NULL, `sb_cvpct` double DEFAULT
NULL, `scppm_na` double DEFAULT NULL, `scppm_naq` varchar(1) DEFAULT NULL, `sc_cvpct` double
DEFAULT NULL, `seppm_na` double DEFAULT NULL, `seppm_naq` varchar(1) DEFAULT NULL, `se_cvpct`
double DEFAULT NULL, `smppm_na` double DEFAULT NULL, `smppm_naq` varchar(1) DEFAULT NULL,
`sm_cvpct` double DEFAULT NULL, `srppm_na` double DEFAULT NULL, `srppm_naq` varchar(1) DEFAULT
NULL, `sr_cvpct` double DEFAULT NULL, `tappm_na` double DEFAULT NULL, `tappm_naq` varchar(1)
DEFAULT NULL, `ta_cvpct` double DEFAULT NULL, `tbppm_na` double DEFAULT NULL, `tbppm_naq`
varchar(1) DEFAULT NULL, `tb_cvpct` double DEFAULT NULL, `thppm_na` double DEFAULT NULL,
`thppm_naq` varchar(1) DEFAULT NULL, `th_cvpct` double DEFAULT NULL, `tmppm_na` double DEFAULT
NULL, `tmppm_naq` varchar(1) DEFAULT NULL, `tm_cvpct` double DEFAULT NULL, `uppm_na` double
DEFAULT NULL, `uppm_naq` varchar(1) DEFAULT NULL, `u_cvpct` double DEFAULT NULL, `vppm_na`
double DEFAULT NULL, `vppm_naq` varchar(1) DEFAULT NULL, `wppm_na` double DEFAULT NULL,
`wppm_naq` varchar(1) DEFAULT NULL, `w_cvpct` double DEFAULT NULL, `yppm_na` double DEFAULT
NULL, `yppm_naq` varchar(1) DEFAULT NULL, `ybppm_na` double DEFAULT NULL, `ybppm_naq`
varchar(1) DEFAULT NULL, `yb_cvpct` double DEFAULT NULL, `znppm_na` double DEFAULT NULL,
`znppm_naq` varchar(1) DEFAULT NULL, `zn_cvpct` double DEFAULT NULL, `zrppm_na` double DEFAULT
NULL, `zrppm_naq` varchar(1) DEFAULT NULL, `zr_cvpct` double DEFAULT NULL, `thppm_dna` double
DEFAULT NULL, `thppm_dnaq` varchar(1) DEFAULT NULL, `th__cvpct` double DEFAULT NULL,
`uppm_dna` double DEFAULT NULL, `uppm_dnaq` varchar(1) DEFAULT NULL, `u__cvpct` double DEFAULT
NULL, `eq_u_ppm` double DEFAULT NULL, `eq_u_ppmq` varchar(1) DEFAULT NULL, PRIMARY KEY
(`lab_id`)) ENGINE=InnoDB DEFAULT CHARSET=latin1 COMMENT='Major, minor and trace element
neutron activation analysis';

-- --------------------------------------------------------

--
-- Tablestructure for table `xtbOtherChem`
--
```

Origin and significance of mobile trace elements in volcanic lakes – a case study at Poás, Costa Rica

```
CREATE TABLE IF NOT EXISTS `xtbOtherChem` (`lab_id` varchar(10) NOT NULL, `capct_aa` double
DEFAULT NULL, `capct_aaq` varchar(1) DEFAULT NULL, `fepct_aa` double DEFAULT NULL, `fepct_aaq`
varchar(1) DEFAULT NULL, `kpct_aa` double DEFAULT NULL, `kpct_aaq` varchar(1) DEFAULT NULL,
`mgpct_aa` double DEFAULT NULL, `mgpct_aaq` varchar(1) DEFAULT NULL, `napct_aa` double DEFAULT
NULL, `napct_aaq` varchar(1) DEFAULT NULL, `agppm_aa` double DEFAULT NULL, `agppm_aaq`
varchar(1) DEFAULT NULL, `asppm_aa` double DEFAULT NULL, `asppm_aaq` varchar(1) DEFAULT NULL,
`auppm_aa` double DEFAULT NULL, `auppm_aaq` varchar(1) DEFAULT NULL, `au_sw_aa` double DEFAULT
NULL, `bappm_aa` double DEFAULT NULL, `bappm_aaq` varchar(1) DEFAULT NULL, `beppm_aa` double
DEFAULT NULL, `beppm_aaq` varchar(1) DEFAULT NULL, `bippm_aa` double DEFAULT NULL, `bippm_aaq`
varchar(1) DEFAULT NULL, `cdppm_aa` double DEFAULT NULL, `cdppm_aaq` varchar(1) DEFAULT NULL,
`ceppm_aa` double DEFAULT NULL, `ceppm_aaq` varchar(1) DEFAULT NULL, `coppm_aa` double DEFAULT
NULL, `coppm_aaq` varchar(1) DEFAULT NULL, `crppm_aa` double DEFAULT NULL, `crppm_aaq`
varchar(1) DEFAULT NULL, `cuppm_aa` double DEFAULT NULL, `cuppm_aaq` varchar(1) DEFAULT NULL,
`gappm_aa` double DEFAULT NULL, `gappm_aaq` varchar(1) DEFAULT NULL, `gdppm_aa` double DEFAULT
NULL, `gdppm_aaq` varchar(1) DEFAULT NULL, `geppm_aa` double DEFAULT NULL, `geppm_aaq`
varchar(1) DEFAULT NULL, `hgppm_aa` double DEFAULT NULL, `hgppm_aaq` varchar(1) DEFAULT NULL,
`inppm_aa` double DEFAULT NULL, `inppm_aaq` varchar(1) DEFAULT NULL, `lippm_aa` double DEFAULT
NULL, `lippm_aaq` varchar(1) DEFAULT NULL, `moppm_aa` double DEFAULT NULL, `moppm_aaq`
varchar(1) DEFAULT NULL, `nbppm_aa` double DEFAULT NULL, `nbppm_aaq` varchar(1) DEFAULT NULL,
`nippm_aa` double DEFAULT NULL, `nippm_aaq` varchar(1) DEFAULT NULL, `pbppm_aa` double DEFAULT
NULL, `pbppm_aaq` varchar(1) DEFAULT NULL, `pdppm_aa` double DEFAULT NULL, `pdppm_aaq`
varchar(1) DEFAULT NULL, `ptppm_aa` double DEFAULT NULL, `ptppm_aaq` varchar(1) DEFAULT NULL,
`rbppm_aa` double DEFAULT NULL, `rbppm_aaq` varchar(1) DEFAULT NULL, `rhppm_aa` double DEFAULT
NULL, `rhppm_aaq` varchar(1) DEFAULT NULL, `sbppm_aa` double DEFAULT NULL, `sbppm_aaq`
varchar(1) DEFAULT NULL, `seppm_aa` double DEFAULT NULL, `seppm_aaq` varchar(1) DEFAULT NULL,
`snppm_aa` double DEFAULT NULL, `snppm_aaq` varchar(1) DEFAULT NULL, `srppm_aa` double DEFAULT
NULL, `srppm_aaq` varchar(1) DEFAULT NULL, `teppm_aa` double DEFAULT NULL, `teppm_aaq`
varchar(1) DEFAULT NULL, `tlppm_aa` double DEFAULT NULL, `tlppm_aaq` varchar(1) DEFAULT NULL,
`tmppm_aa` double DEFAULT NULL, `tmppm_aaq` varchar(1) DEFAULT NULL, `uppm_aa` double DEFAULT
NULL, `uppm_aaq` varchar(1) DEFAULT NULL, `vppm_aa` double DEFAULT NULL, `vppm_aaq` varchar(1)
DEFAULT NULL, `wppm_aa` double DEFAULT NULL, `wppm_aaq` varchar(1) DEFAULT NULL, `znppm_aa`
double DEFAULT NULL, `znppm_aaq` varchar(1) DEFAULT NULL, `agppmaap` double DEFAULT NULL,
`agppmaapq` varchar(1) DEFAULT NULL, `asppmaap` double DEFAULT NULL, `asppmaapq` varchar(1)
DEFAULT NULL, `auppmaap` double DEFAULT NULL, `auppmaapq` varchar(1) DEFAULT NULL, `bippmaap`
double DEFAULT NULL, `bippmaapq` varchar(1) DEFAULT NULL, `cdppmaap` double DEFAULT NULL,
`cdppmaapq` varchar(1) DEFAULT NULL, `coppmaap` double DEFAULT NULL, `coppmaapq` varchar(1)
DEFAULT NULL, `cuppmaap` double DEFAULT NULL, `cuppmaapq` varchar(1) DEFAULT NULL, `lippmaap`
double DEFAULT NULL, `lippmaapq` varchar(1) DEFAULT NULL, `mgpctaap` double DEFAULT NULL,
`mgpctaapq` varchar(1) DEFAULT NULL, `mnppmaap` double DEFAULT NULL, `mnppmaapq` varchar(1)
DEFAULT NULL, `moppmaap` double DEFAULT NULL, `moppmaapq` varchar(1) DEFAULT NULL, `nippmaap`
double DEFAULT NULL, `nippmaapq` varchar(1) DEFAULT NULL, `pbppmaap` double DEFAULT NULL,
`pbppmaapq` varchar(1) DEFAULT NULL, `sbppmaap` double DEFAULT NULL, `sbppmaapq` varchar(1)
DEFAULT NULL, `teppmaap` double DEFAULT NULL, `teppmaapq` varchar(1) DEFAULT NULL, `znppmaap`
double DEFAULT NULL, `znppmaapq` varchar(1) DEFAULT NULL, `agppm_clr` double DEFAULT NULL,
`agppm_clrq` varchar(1) DEFAULT NULL, `asppm_clr` double DEFAULT NULL, `asppm_clrq` varchar(1)
DEFAULT NULL, `auppm_clr` double DEFAULT NULL, `auppm_clrq` varchar(1) DEFAULT NULL,
`bppm_clr` double DEFAULT NULL, `bppm_clrq` varchar(1) DEFAULT NULL, `bappm_clr` double
DEFAULT NULL, `bappm_clrq` varchar(1) DEFAULT NULL, `coppm_clr` double DEFAULT NULL,
`coppm_clrq` varchar(1) DEFAULT NULL, `crppm_clr` double DEFAULT NULL, `crppm_clrq` varchar(1)
DEFAULT NULL, `fepct_clr` double DEFAULT NULL, `fepct_clrq` varchar(1) DEFAULT NULL,
`moppm_clr` double DEFAULT NULL, `moppm_clrq` varchar(1) DEFAULT NULL, `nbppm_clr` double
DEFAULT NULL, `nbppm_clrq` varchar(1) DEFAULT NULL, `nippm_clr` double DEFAULT NULL,
`nippm_clrq` varchar(1) DEFAULT NULL, `ppct_clr` double DEFAULT NULL, `ppct_clrq` varchar(1)
DEFAULT NULL, `sbppm_clr` double DEFAULT NULL, `sbppm_clrq` varchar(1) DEFAULT NULL,
`teppm_clr` double DEFAULT NULL, `teppm_clrq` varchar(1) DEFAULT NULL, `thppm_clr` double
DEFAULT NULL, `thppm_clrq` varchar(1) DEFAULT NULL, `vppm_clr` double DEFAULT NULL,
`vppm_clrq` varchar(1) DEFAULT NULL, `wppm_clr` double DEFAULT NULL, `wppm_clrq` varchar(1)
DEFAULT NULL, `asppmclrp` double DEFAULT NULL, `asppmclrpq` varchar(1) DEFAULT NULL,
`cuppmclrp` double DEFAULT NULL, `cuppmclrpq` varchar(1) DEFAULT NULL, `nippmclrp` double
DEFAULT NULL, `nippmclrpq` varchar(1) DEFAULT NULL, `pbppmclrp` double DEFAULT NULL,
`pbppmclrpq` varchar(1) DEFAULT NULL, `sbppmclrp` double DEFAULT NULL, `sbppmclrpq` varchar(1)
DEFAULT NULL, `uppmclrp` double DEFAULT NULL, `uppmclrpq` varchar(1) DEFAULT NULL, `wppmclrp`
double DEFAULT NULL, `wppmclrpq` varchar(1) DEFAULT NULL, `znppmclrp` double DEFAULT NULL,
`znppmclrpq` varchar(1) DEFAULT NULL, `brppm_elc` double DEFAULT NULL, `brppm_elcq` varchar(1)
DEFAULT NULL, `brppm_ic` double DEFAULT NULL, `brppm_icq` varchar(1) DEFAULT NULL, `nbppm_msc`
double DEFAULT NULL, `nbppm_mscq` varchar(1) DEFAULT NULL, `rnppm_msc` double DEFAULT NULL,
`rnppm_mscq` varchar(1) DEFAULT NULL, `seppm_flr` double DEFAULT NULL, `seppm_flrq` varchar(1)
DEFAULT NULL, `uppm_flr` double DEFAULT NULL, `uppm_flrq` varchar(1) DEFAULT NULL, `wppm_msc`
double DEFAULT NULL, `wppm_mscq` varchar(1) DEFAULT NULL, `agppm_fa` double DEFAULT NULL,
`agppm_faq` varchar(1) DEFAULT NULL, `auppb_fa` double DEFAULT NULL, `auppb_faq` varchar(1)
DEFAULT NULL, `irppb_fa` double DEFAULT NULL, `irppb_faq` varchar(1) DEFAULT NULL, `pdppb_fa`
double DEFAULT NULL, `pdppb_faq` varchar(1) DEFAULT NULL, `ptppb_fa` double DEFAULT NULL,
`ptppb_faq` varchar(1) DEFAULT NULL, `rhppb_fa` double DEFAULT NULL, `rhppb_faq` varchar(1)
DEFAULT NULL, `ruppb_fa` double DEFAULT NULL, `ruppb_faq` varchar(1) DEFAULT NULL, `smpwt_fa`
double DEFAULT NULL, PRIMARY KEY (`lab_id`)) ENGINE=InnoDB DEFAULT CHARSET=latin1
COMMENT='Major, minor and trace element by other methods';
```

```
-- --------------------------------------------------------

--
-- Tablestructure for table `xtbUnknownChem`
--

CREATE TABLE IF NOT EXISTS `xtbUnknownChem` (`lab_id` varchar(10) NOT NULL, `agpct_unk` double
DEFAULT NULL, `agpct_unkq` varchar(1) DEFAULT NULL, `agppm_unk` double DEFAULT NULL,
`agppm_unkq` varchar(1) DEFAULT NULL, `alpct_unk` double DEFAULT NULL, `alpct_unkq` varchar(1)
DEFAULT NULL, `alppm_unk` double DEFAULT NULL, `alppm_unkq` varchar(1) DEFAULT NULL,
`aspct_unk` double DEFAULT NULL, `aspct_unkq` varchar(1) DEFAULT NULL, `asppm_unk` double
DEFAULT NULL, `asppm_unkq` varchar(1) DEFAULT NULL, `asppmunkp` double DEFAULT NULL,
`asppmunkpq` varchar(1) DEFAULT NULL, `aupct_unk` double DEFAULT NULL, `aupct_unkq` varchar(1)
DEFAULT NULL, `auppm_unk` double DEFAULT NULL, `auppm_unkq` varchar(1) DEFAULT NULL,
`bppm_unk` double DEFAULT NULL, `bppm_unkq` varchar(1) DEFAULT NULL, `bappm_unk` double
DEFAULT NULL, `bappm_unkq` varchar(1) DEFAULT NULL, `bao_unk` double DEFAULT NULL, `bao_unkq`
varchar(1) DEFAULT NULL, `beppm_unk` double DEFAULT NULL, `beppm_unkq` varchar(1) DEFAULT
NULL, `bippm_unk` double DEFAULT NULL, `bippm_unkq` varchar(1) DEFAULT NULL, `bippmunkp`
double DEFAULT NULL, `bippmunkpq` varchar(1) DEFAULT NULL, `brpct_unk` double DEFAULT NULL,
`brpct_unkq` varchar(1) DEFAULT NULL, `brppm_unk` double DEFAULT NULL, `brppm_unkq` varchar(1)
DEFAULT NULL, `capct_unk` double DEFAULT NULL, `capct_unkq` varchar(1) DEFAULT NULL,
`cdpct_unk` double DEFAULT NULL, `cdpct_unkq` varchar(1) DEFAULT NULL, `cdppm_unk` double
DEFAULT NULL, `cdppm_unkq` varchar(1) DEFAULT NULL, `cdppmunkp` double DEFAULT NULL,
`cdppmunkpq` varchar(1) DEFAULT NULL, `ceppm_unk` double DEFAULT NULL, `ceppm_unkq` varchar(1)
DEFAULT NULL, `copct_unk` double DEFAULT NULL, `copct_unkq` varchar(1) DEFAULT NULL,
`coppm_unk` double DEFAULT NULL, `coppm_unkq` varchar(1) DEFAULT NULL, `crppm_unk` double
DEFAULT NULL, `crppm_unkq` varchar(1) DEFAULT NULL, `cr2o3_unk` double DEFAULT NULL,
`cr2o3_unkq` varchar(1) DEFAULT NULL, `csppm_unk` double DEFAULT NULL, `csppm_unkq` varchar(1)
DEFAULT NULL, `cupct_unk` double DEFAULT NULL, `cupct_unkq` varchar(1) DEFAULT NULL,
`cuppm_unk` double DEFAULT NULL, `cuppm_unkq` varchar(1) DEFAULT NULL, `cuo_unk` double
DEFAULT NULL, `cuo_unkq` varchar(1) DEFAULT NULL, `dyppm_unk` double DEFAULT NULL,
`dyppm_unkq` varchar(1) DEFAULT NULL, `erppm_unk` double DEFAULT NULL, `erppm_unkq` varchar(1)
DEFAULT NULL, `euppm_unk` double DEFAULT NULL, `euppm_unkq` varchar(1) DEFAULT NULL,
`fepct_unk` double DEFAULT NULL, `fepct_unkq` varchar(1) DEFAULT NULL, `gappm_unk` double
DEFAULT NULL, `gappm_unkq` varchar(1) DEFAULT NULL, `gdppm_unk` double DEFAULT NULL,
`gdppm_unkq` varchar(1) DEFAULT NULL, `geppm_unk` double DEFAULT NULL, `geppm_unkq` varchar(1)
DEFAULT NULL, `hfppm_unk` double DEFAULT NULL, `hfppm_unkq` varchar(1) DEFAULT NULL,
`hgpct_unk` double DEFAULT NULL, `hgpct_unkq` varchar(1) DEFAULT NULL, `hgppm_unk` double
DEFAULT NULL, `hgppm_unkq` varchar(1) DEFAULT NULL, `hoppm_unk` double DEFAULT NULL,
`hoppm_unkq` varchar(1) DEFAULT NULL, `ipct_unk` double DEFAULT NULL, `ipct_unkq` varchar(1)
DEFAULT NULL, `ippm_unk` double DEFAULT NULL, `ippm_unkq` varchar(1) DEFAULT NULL, `inppm_unk`
double DEFAULT NULL, `inppm_unkq` varchar(1) DEFAULT NULL, `irppm_unk` double DEFAULT NULL,
`irppm_unkq` varchar(1) DEFAULT NULL, `kpct_unk` double DEFAULT NULL, `kpct_unkq` varchar(1)
DEFAULT NULL, `lappm_unk` double DEFAULT NULL, `lappm_unkq` varchar(1) DEFAULT NULL,
`lippm_unk` double DEFAULT NULL, `lippm_unkq` varchar(1) DEFAULT NULL, `luppm_unk` double
DEFAULT NULL, `luppm_unkq` varchar(1) DEFAULT NULL, `mgpct_unk` double DEFAULT NULL,
`mgpct_unkq` varchar(1) DEFAULT NULL, `mnppm_unk` double DEFAULT NULL, `mnppm_unkq` varchar(1)
DEFAULT NULL, `mopct_unk` double DEFAULT NULL, `mopct_unkq` varchar(1) DEFAULT NULL,
`moppm_unk` double DEFAULT NULL, `moppm_unkq` varchar(1) DEFAULT NULL, `napct_unk` double
DEFAULT NULL, `napct_unkq` varchar(1) DEFAULT NULL, `nbppm_unk` double DEFAULT NULL,
`nbppm_unkq` varchar(1) DEFAULT NULL, `ndppm_unk` double DEFAULT NULL, `ndppm_unkq` varchar(1)
DEFAULT NULL, `nipct_unk` double DEFAULT NULL, `nipct_unkq` varchar(1) DEFAULT NULL,
`nippm_unk` double DEFAULT NULL, `nippm_unkq` varchar(1) DEFAULT NULL, `nio_unk` double
DEFAULT NULL, `nio_unkq` varchar(1) DEFAULT NULL, `osppm_unk` double DEFAULT NULL,
`osppm_unkq` varchar(1) DEFAULT NULL, `ppct_unk` double DEFAULT NULL, `ppct_unkq` varchar(254)
DEFAULT NULL, `pbpct_unk` double DEFAULT NULL, `pbpct_unkq` varchar(1) DEFAULT NULL,
`pbppm_unk` double DEFAULT NULL, `pbppm_unkq` varchar(1) DEFAULT NULL, `pdppm_unk` double
DEFAULT NULL, `pdppm_unkq` varchar(1) DEFAULT NULL, `prppm_unk` double DEFAULT NULL,
`prppm_unkq` varchar(1) DEFAULT NULL, `ptppm_unk` double DEFAULT NULL, `ptppm_unkq` varchar(1)
DEFAULT NULL, `rbppm_unk` double DEFAULT NULL, `rbppm_unkq` varchar(1) DEFAULT NULL,
`rb2o_unk` double DEFAULT NULL, `rb2o_unkq` varchar(1) DEFAULT NULL, `reppm_unk` double
DEFAULT NULL, `reppm_unkq` varchar(1) DEFAULT NULL, `rhppm_unk` double DEFAULT NULL,
`rhppm_unkq` varchar(1) DEFAULT NULL, `ruppm_unk` double DEFAULT NULL, `ruppm_unkq` varchar(1)
DEFAULT NULL, `sbppm_unk` double DEFAULT NULL, `sbppm_unkq` varchar(1) DEFAULT NULL,
`sbppmunkp` double DEFAULT NULL, `sbppmunkpq` varchar(1) DEFAULT NULL, `scppm_unk` double
DEFAULT NULL, `scppm_unkq` varchar(1) DEFAULT NULL, `seppm_unk` double DEFAULT NULL,
`seppm_unkq` varchar(1) DEFAULT NULL, `sipct_unk` double DEFAULT NULL, `sipct_unkq` varchar(1)
DEFAULT NULL, `smppm_unk` double DEFAULT NULL, `smppm_unkq` varchar(1) DEFAULT NULL,
`snpct_unk` double DEFAULT NULL, `snpct_unkq` varchar(1) DEFAULT NULL, `snppm_unk` double
DEFAULT NULL, `snppm_unkq` varchar(1) DEFAULT NULL, `srppm_unk` double DEFAULT NULL,
`srppm_unkq` varchar(1) DEFAULT NULL, `sro_unk` double DEFAULT NULL, `sro_unkq` varchar(1)
DEFAULT NULL, `tappm_unk` double DEFAULT NULL, `tappm_unkq` varchar(1) DEFAULT NULL,
`tbppm_unk` double DEFAULT NULL, `tbppm_unkq` varchar(1) DEFAULT NULL, `teppm_unk` double
DEFAULT NULL, `teppm_unkq` varchar(1) DEFAULT NULL, `thppm_unk` double DEFAULT NULL,
`thppm_unkq` varchar(1) DEFAULT NULL, `tipct_unk` double DEFAULT NULL, `tipct_unkq` varchar(1)
DEFAULT NULL, `tippm_unk` double DEFAULT NULL, `tippm_unkq` varchar(1) DEFAULT NULL,
`tippb_unk` double DEFAULT NULL, `tippb_unkq` varchar(1) DEFAULT NULL, `tlppm_unk` double
```

```
DEFAULT NULL, `tlppm_unkq` varchar(1) DEFAULT NULL, `tmppm_unk` double DEFAULT NULL,
`tmppm_unkq` varchar(1) DEFAULT NULL, `uppm_unk` double DEFAULT NULL, `uppm_unkq` varchar(1)
DEFAULT NULL, `vpct_unk` double DEFAULT NULL, `vpct_unkq` varchar(1) DEFAULT NULL, `vppm_unk`
double DEFAULT NULL, `vppm_unkq` varchar(1) DEFAULT NULL, `v2o5_unk` double DEFAULT NULL,
`v2o5_unkq` varchar(1) DEFAULT NULL, `wppm_unk` double DEFAULT NULL, `wppm_unkq` varchar(1)
DEFAULT NULL, `yppm_unk` double DEFAULT NULL, `yppm_unkq` varchar(1) DEFAULT NULL, `ybppm_unk`
double DEFAULT NULL, `ybppm_unkq` varchar(1) DEFAULT NULL, `znpct_unk` double DEFAULT NULL,
`znpct_unkq` varchar(1) DEFAULT NULL, `znppm_unk` double DEFAULT NULL, `znppm_unkq` varchar(1)
DEFAULT NULL, `znppmunkp` double DEFAULT NULL, `znppmunkpq` varchar(1) DEFAULT NULL, `zno_unk`
double DEFAULT NULL, `zno_unkq` varchar(1) DEFAULT NULL, `zrppm_unk` double DEFAULT NULL,
`zrppm_unkq` varchar(1) DEFAULT NULL, `zro2_unk` double DEFAULT NULL, `zro2_unkq` varchar(1)
DEFAULT NULL,PRIMARY KEY (`lab_id`)) ENGINE=InnoDB DEFAULT CHARSET=latin1 COMMENT='Major,
minor and trace element by unspecified methods';


-- --------------------------------------------------------

--
-- Tabelstructuur voor tabel `xtbXrfChem`
--

CREATE TABLE IF NOT EXISTS `xtbXrfChem` ( `lab_id` varchar(10) NOT NULL, `agppm_xrf` double
DEFAULT NULL, `agppm_xrfq` varchar(1) DEFAULT NULL, `asppm_xrf` double DEFAULT NULL,
`asppm_xrfq` varchar(1) DEFAULT NULL, `bappm_xrf` double DEFAULT NULL, `bappm_xrfq` varchar(1)
DEFAULT NULL, `bippm_xrf` double DEFAULT NULL, `bippm_xrfq` varchar(1) DEFAULT NULL,
`brppm_xrf` double DEFAULT NULL, `brppm_xrfq` varchar(1) DEFAULT NULL, `cdppm_xrf` double
DEFAULT NULL, `cdppm_xrfq` varchar(1) DEFAULT NULL, `ceppm_xrf` double DEFAULT NULL,
`ceppm_xrfq` varchar(1) DEFAULT NULL, `crppm_xrf` double DEFAULT NULL, `crppm_xrfq` varchar(1)
DEFAULT NULL, `csppm_xrf` double DEFAULT NULL, `csppm_xrfq` varchar(1) DEFAULT NULL,
`cuppm_xrf` double DEFAULT NULL, `cuppm_xrfq` varchar(1) DEFAULT NULL, `dyppm_xrf` double
DEFAULT NULL, `dyppm_xrfq` varchar(1) DEFAULT NULL, `erppm_xrf` double DEFAULT NULL,
`erppm_xrfq` varchar(1) DEFAULT NULL, `euppm_xrf` double DEFAULT NULL, `euppm_xrfq` varchar(1)
DEFAULT NULL, `gappm_xrf` double DEFAULT NULL, `gappm_xrfq` varchar(1) DEFAULT NULL,
`gdppm_xrf` double DEFAULT NULL, `gdppm_xrfq` varchar(1) DEFAULT NULL, `geppm_xrf` double
DEFAULT NULL, `geppm_xrfq` varchar(1) DEFAULT NULL, `hoppm_xrf` double DEFAULT NULL,
`hoppm_xrfq` varchar(1) DEFAULT NULL, `lappm_xrf` double DEFAULT NULL, `lappm_xrfq` varchar(1)
DEFAULT NULL, `luppm_xrf` double DEFAULT NULL, `luppm_xrfq` varchar(1) DEFAULT NULL,
`moppm_xrf` double DEFAULT NULL, `moppm_xrfq` varchar(1) DEFAULT NULL, `nbppm_xrf` double
DEFAULT NULL, `nbppm_xrfq` varchar(1) DEFAULT NULL, `ndppm_xrf` double DEFAULT NULL,
`ndppm_xrfq` varchar(1) DEFAULT NULL, `nippm_xrf` double DEFAULT NULL, `nippm_xrfq` varchar(1)
DEFAULT NULL, `pbppm_xrf` double DEFAULT NULL, `pbppm_xrfq` varchar(1) DEFAULT NULL,
`prppm_xrf` double DEFAULT NULL, `prppm_xrfq` varchar(1) DEFAULT NULL, `rbppm_xrf` double
DEFAULT NULL, `rbppm_xrfq` varchar(1) DEFAULT NULL, `sbppm_xrf` double DEFAULT NULL,
`sbppm_xrfq` varchar(1) DEFAULT NULL, `seppm_xrf` double DEFAULT NULL, `seppm_xrfq` varchar(1)
DEFAULT NULL, `smppm_xrf` double DEFAULT NULL, `smppm_xrfq` varchar(1) DEFAULT NULL,
`snppm_xrf` double DEFAULT NULL, `snppm_xrfq` varchar(1) DEFAULT NULL, `srppm_xrf` double
DEFAULT NULL, `srppm_xrfq` varchar(1) DEFAULT NULL, `tbppm_xrf` double DEFAULT NULL,
`tbppm_xrfq` varchar(1) DEFAULT NULL, `thppm_xrf` double DEFAULT NULL, `thppm_xrfq` varchar(1)
DEFAULT NULL, `tmppm_xrf` double DEFAULT NULL, `tmppm_xrfq` varchar(1) DEFAULT NULL,
`uppm_xrf` double DEFAULT NULL, `uppm_xrfq` varchar(1) DEFAULT NULL, `vppm_xrf` double DEFAULT
NULL, `vppm_xrfq` varchar(1) DEFAULT NULL, `wppm_xrf` double DEFAULT NULL, `wppm_xrfq`
varchar(1) DEFAULT NULL, `yppm_xrf` double DEFAULT NULL, `yppm_xrfq` varchar(1) DEFAULT NULL,
`ybppm_xrf` double DEFAULT NULL, `ybppm_xrfq` varchar(1) DEFAULT NULL, `znppm_xrf` double
DEFAULT NULL, `znppm_xrfq` varchar(1) DEFAULT NULL, `zrppm_xrf` double DEFAULT NULL,
`zrppm_xrfq` varchar(1) DEFAULT NULL, PRIMARY KEY (`lab_id`)) ENGINE=InnoDB DEFAULT
CHARSET=latin1 COMMENT='Minor and trace element XRF analyses';
```