The precise measurement of thallium isotopic compositions by MC-ICPMS: Application to the analysis of geological materials and meteorites

M. Rehkämper — Department of Geological Sciences, The University of Michigan, Ann Arbor, MI 48109-1063, USA,

A. N. Halliday — Department of Geological Sciences, The University of Michigan, Ann Arbor, MI 48109-1063, USA

A number of astrophysical studies have predicted the existence of ^{205}Pb, an s-process nuclide that decays to ^{205}Tl with a half-life of ~15 Myr, in the early Solar System. Recent theoretical calculations suggest an initial $(^{205}Pb/^{204}Pb)_{BSSI}$ abundance ratio for the bulk Solar System of $6.5-11 \times 10^{-4}$ (Wasserburg *et al.*, 1994). At this abundance level, early elemental fractionation processes in the solar nebula or small planetary bodies may lead to the formation of reservoirs with distinct Tl isotopic compositions. Previous Tl isotope studies of terrestrial and lunar samples as well as meteorites, however, have hitherto been unable to provide evidence for the existence of live ^{205}Pb in the early Solar System.

The primary difficulty of Tl isotope studies is the mass spectrometric measurement. The precision of Tl isotope ratio measurements by thermal ionization mass spectrometry (TIMS) is severely limited by the fact that Tl possesses only two naturally occurring isotopes. Therefore, there is no invariant isotope ratio (as in the case of Sr or Nd) that can be used to monitor and correct for mass fractionation. The accuracy of Tl isotope ratio measurements for geological samples is furthermore compromised by the fact that the Tl separated from a natural matrix is assumed to display the same fractionation behaviour during the TIMS measurement as a pure laboratory standard.

We have developed new chemical and mass spectrometric procedures for the determination of Tl isotopic compositions in geological materials and meteorites. High-precision Tl isotope ratio measurements were performed with the new technique of multiple-collector inductively coupled plasma-mass spectrometry (MC-ICPMS). An important consequence of plasma ionization is, that elements of similar mass display identical mass discrimination effects. In our case, this was exploited by admixing Pb, of known isotopic composition, to the sample solutions. By simultaneously monitoring Tl and Pb isotopic compositions during the measurement, we are able to precisely correct for the mass discrimination of Tl. Using these procedures we achieve a precision of 0.01–0.02% for Tl isotope ratio measurements of geological samples. This is at least a factor of 3–4 better than the best previously published results by TIMS (Arden, 1983).

Results and discussion

Our Tl isotope data for terrestrial rock samples (Fig. 1) appear to indicate that variations of Tl isotopic compositions are also caused by natural fractionation processes. Of the three magmatic rock samples analysed in this study, two (rhyolite ATHO from Iceland and USGS standard reference material granite G-2) display Tl isotopic compositions indistinguishable from our laboratory standard, the isotopic reference material NIST-997 Tl. Sample D-174, a gabbro from the Dufek Layered Intrusion, Antarctica, however, is characterized by $\Sigma_{Tl} \approx +2.5 \pm 1.5$, where ε_{Tl} represents the deviation of the $^{205}Tl/^{203}Tl$ isotope ratio of the sample relative to NIST-997 Tl in parts per 10^4. Even larger deviations were identified for the ferromanganese crusts CD29-2 and D11-1 from the Pacific Ocean. These samples display positive ε_{Tl} values of approximately $+5.0 \pm 1.5$ and $+11.7 \pm 1.3$. The large variability of Tl isotopic compositions in Fe-Mn crusts is probably related to low-temperature processes. With respect to the formation of ferromanganese crusts by precipitation from seawater, the two stable valence states of Tl and the different stabilities of Tl^{+} and Tl^{3+} species in seawater may provide suitable mechanisms for the fractionation of Tl isotope ratios by a kinetically controlled fractionation process.

For a bulk sample of the C3V chondrite Allende, we have determined a Tl isotopic composition of ε_{Tl}

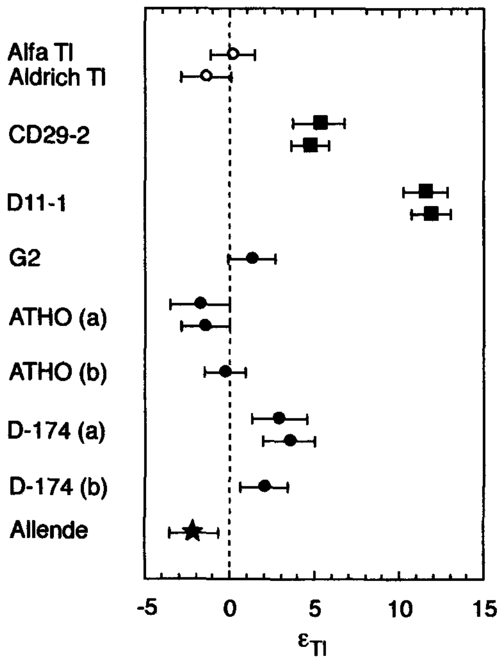

FIG. 1. Tl isotopic compositions measured for two commercial Tl solutions, terrestrial rocks and a bulk sample of the C3V chondrite Allende. All data are shown with $\pm 3\sigma$ errors. ε_{Tl} represents the deviation of the $^{205}Tl/^{203}Tl$ isotope ratio of the sample relative to NIST-997 Tl in parts per 10^4.

= -2.12 $\pm$ 1.43, the lowest value analysed in this study. This result can be combined with previously published Tl isotope data in order to obtain useful limits for the abundance of ^{205}Pb in the early Solar System. In the simplest model, the different Pb/Tl ratios of chondritic meteorites are assumed to be the result of volatile element depletion processes. The combination of our result for Allende with a relatively precise Tl literature value for the L3 chondrite Mezö-Madaras (Huey and Kohman, 1972) places an upper limit on the $^{205}Pb/^{204}Pb$ abundance ratio of the Solar System at the time of volatile depletion (VD): $(^{205}Pb/^{204}Pb)_{VD} = 9.2 \times 10^{-5}$. Recent cosmochemical studies suggest that the chemical depletion of volatile elements probably occurred during the condensation of an initially hot solar nebula (Humayun and Clayton, 1995), such that Pb and Tl were fractionated from one another within a few million years after the formation of the Solar System. This would indicate that the present astrophysical estimates for the initial abundance of ^{205}Pb are significantly too high.

Terrestrial volatile element and Pb isotope systematics indicate that the bulk Earth (BE) is characterized by $(^{204}Pb/^{203}Tl)_{BE} = 12 \pm 8$. By combining this value with the constraints obtained from chondritic meteorites, we can estimate that the BE should have an ε_{Tl}-value of between -3.5 and +4.8. Using numerical techniques we have investigated the effect of accretion and concomitant core formation on Tl isotopic systematics of the bulk silicate earth (BSE). If core formation was late or accretion slow, as indicated by recent W isotopic evidence (Halliday *et al.*, 1996), the Tl isotopic composition of the BSE is expected to be at most 1 ε_{Tl}-unit less radiogenic than the BE.

References

Arden, J. W. (1983) *Anal. Chim. Acta* **148**, 211–23.

Halliday, A.N., Rehkämper, M., Lee, D.-C. and Yi, W. (1996) *Earth Planet. Sci. Lett.*, **142**, 75–89.

Huey, J.M. and Kohman, T.P. (1972) *Earth Planet. Sci. Lett.*, **16**, 401–12.

Humayun, M. and Clayton, R.N. (1995) *Geochim. Cosmochim. Acta*, **59**, 2131–48.

Wasserburg, G.J., Busso, M., Gallino, R. and Raiteri, C.M. (1994) *Astrophys. J.*, **424**, 412–28.