

## Geochemical stratigraphy near the core-mantle boundary: Evidence from Hawaii drilling project results

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The Hawaii Scientific Drilling Project (HSDP) sampled a 3 km section of basalt lava from the Mauna Kea volcano, covering ages of 200–600 ka. When combined with surface and dredge samples, there is a 600 ky record of the lava output from Mauna Kea as well as a 200 ky record from Mauna Loa. The isotopic stratigraphy of the core samples (Gcubed Theme) reflects the geochemical structure of the Hawaiian plume, given a model for the sampling of the plume by melting and melt transport (Bryce et al., 2005). The data show that there is radial geochemical zoning of the plume in terms of He, Pb, Nd, Sr and Hf isotopes. Data from other volcanoes indicate there is also heterogeneity along the axis of the plume, as well as asymmetry (Loa-Kea dichotomy). To first order, the radial geochemical structure of the plume represents the vertical structure at the thermal boundary layer from which the plume originates. Numerical models of plumes show that this vertical structure, which corresponds to potential temperature, is likely to be preserved during passage of the plume through the mantle. In the case of Hawaii, all of the lavas are derived from melting of mantle that originates from within 20–50 km of the base of the mantle, so the inferred radial geochemical structure maps to stratigraphy at the base of the mantle.

HSDP data indicate that the high  $^3\text{He}/^4\text{He}$  anomaly ( $R/R_a > 16$ ) is restricted to the innermost core of the plume and is much larger in amplitude and smaller in diameter than the Nd, Sr or Hf anomalies. The He-3 anomaly must have an origin different from that of other isotopes; the anomalous mantle is restricted to the lowermost 10–20 km of the plume source. This observation accords with along-ridge variations of Nd, Sr, and He near Iceland. The HSDP data are consistent with two models for the configuration of the plume source. If the plume originates from the top of a dense layer separating the main mantle from the outer core, then the high- $^3\text{He}$  signal must be attributed to the dense layer and distinguishes it from the main lower mantle. The dense layer is not significantly different from the rest of the lower mantle in terms of Nd, Sr, or Hf isotopes. If the plume originates directly from the CMB, then probably the  $^3\text{He}$  signal comes from the core. Models for core formation can accommodate this possibility. The dense layer may have distinctive He because it receives He from the outer core, or because it has retained primordial He. Hawaii and Iceland data imply that the lower mantle also has large regions with elevated  $^3\text{He}/^4\text{He}$ , but these typically have  $R/R_a \leq 16$ .

### References

Bryce, J., DePaolo, D.J., Lassiter, J., 2005. *Gcubed* 6 (9). Gcubed Theme "Hawaii Scientific Drilling Project".

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## Pyrite ( $\text{FeS}_2$ ) oxidation as a function of pH: A multitechnique approach

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This work intends to identify the  $\text{FeS}_2$  oxidation mechanism and to evaluate the effects of carbonates during its dissolution. Oxidative dissolution experiments are carried out at several pH associating solution speciation to surface solid analysis (XPS, FTIR, SEM and Nuclear Microprobe Analysis). The influence of carbonates is investigated at several contents in equilibrium with air.

We show that fast  $\text{FeS}_2$  air oxidation explains the disparity of both results and oxidation mechanisms published.

Previous works indicate S at oxidation number 0 ( $\text{FeSSO}$ ) and 2 ( $\text{FeS}_2\text{O}_3$ ) on localized points of  $\text{FeS}_2$  surface (Descostes et al., 2001).  $\text{SO}_4^{2-}$  and  $\text{S}_2\text{O}_3^{2-}$  are the main S aqueous species whatever the pH. Under acidic conditions ( $\text{pH} < 3$ ), a S deficit leads to ratios  $R = [\text{S}]_{\text{tot}}/[\text{Fe}]_{\text{tot}} < 2$  (Descostes et al., 2004). Given a kinetic model  $\text{FeS}_2$  dissolution may be ruled by a localized first solid-state oxidation step followed by  $\text{S}_2\text{O}_3^{2-}$  dissolution. In acidic media,  $\text{S}_2\text{O}_3^{2-}$  dismutation into  $\text{S}^0$  and  $\text{S}_4\text{O}_6^{2-}$  explains the observed uncongruence with a predicted S/Fe ratio:  $R = 1.6$ . This work offers a new sight of the well accepted iron preferential dissolution models.

In buffering conditions,  $\Sigma\text{CO}_2 \geq 10^{-2}$  mol/L 90% of aqueous S is under  $\text{S}_2\text{O}_3^{2-}$  form. The dissolution rate raises with  $\Sigma\text{CO}_2$ . The observed  $\text{FeS}_2 \rightarrow$  siderite  $\text{FeCO}_3 \rightarrow$  goethite  $\alpha\text{-FeO-OH} \rightarrow$  lepidocrocite  $\gamma\text{-FeOOH} \rightarrow$  ferric sulfate transformation cannot be predicted by an equilibrium thermodynamic model. The competition between Fe(II) oxidation and complexation–precipitation explains the raising of the dissolution rate vs  $\Sigma\text{CO}_2$ . Concurrently, a component GR- $\text{SO}_3$  from the green rust compounds family incorporates  $\text{SO}_3^{2-}$ .

### References

Descostes, M., Beaucaire, C., Vitorge, P., 2004. *Geochim. Cosmochim. Acta* **68**, 4559–4569.  
Descostes, M., Mercier, F., Beaucaire, C., Zuddas, P., Trocellier, P., 2001. *Nucl. Instr. Meth. B* **181**, 603–609.

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